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Niramol Juntarachat

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UNIVERSITÉ DE LORRAINE

École Doctorale Ressources Procédés Produits Environnement
Laboratoire Réaction et Génie des Procédés

THÈSE

Présentée par

Niramol JUNTARACHAT

Pour l'obtention du grade de
Docteur en Sciences
de l'Université de Lorraine
Spécialité : Génie des Procédés et des Produits

**UTILISATION DE MESURES DE POINTS CRITIQUES POUR LA
CARACTÉRISATION DE NOUVEAUX RÉFRIGÉRANTS ET LA
MODÉLISATION D'UN PROCÉDÉ DE SYNTHÈSE DE
BIODIESEL**

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INTRODUCTION

La connaissance précise des propriétés thermodynamiques des corps purs et des mélanges, en particulier les équilibres des phases, dans des intervalles de température et de pression très larges est nécessaire pour optimiser et développer les procédés des industries chimiques. Ces informations peuvent être acquises principalement par des mesures expérimentales ou des estimations à partir de modèles thermodynamiques prédictifs. Les deux sources d'informations sont complémentaires. Cependant, il est évident qu'aucun modèle mathématique n'est susceptible de remplacer les mesures expérimentales précises et les mesures ne peuvent pas être appliquées pour toutes les conditions opératoires. Les données mesurées sont indispensables pour le développement des modèles prédictifs, plus précisément, pour l'ajustement des paramètres de ces modèles dont les valeurs sont déterminées de manière à obtenir une meilleure représentation possible des comportements de phases. La précision des modèles dépend fortement de la quantité et la qualité des données. En revanche, la précision des données dépend des techniques employées qui sont généralement très coûteuses. Pour conclure, les données expérimentales et les modèles thermodynamiques prédictifs doivent nécessairement être utilisés ensemble afin d'accéder aux informations des équilibres de phases les plus précises.

Parmi les données d'équilibres de phases des fluides disponibles dans la littérature, les points critiques liquide – vapeur de mélanges binaires sont relativement peu présents. Ces données sont pourtant à privilégier pour l'ajustement des paramètres de modèles thermodynamiques, en particulier lorsqu'il est attendu des modèles qu'ils représentent à la fois les domaines subcritique, critique et supercritique.

L'objectif de cette thèse est de mesurer les points critiques de mélanges binaires puis de les utiliser dans le but de développer un modèle thermodynamique prédictif utilisable pour deux applications différentes: I) un procédé de fabrication de biodiesel par voie supercritique et II) l'étude du comportement de phases de mélanges de nouveaux réfrigérants utilisés pour la climatisation automobile.

La structure de ce rapport de thèse est divisée en trois grandes parties :

Une première partie est consacrée à une description des comportements de phases des systèmes binaires sous basse et haute pressions et à des études expérimentales et théoriques des points critiques.

Une deuxième partie décrit la mise au point et la validation des protocoles opératoires permettant de mesurer les points critiques de mélanges binaires obtenus en mélangeant à

température ambiante : deux liquides, un liquide et un gaz et deux gaz. Les mesures sont effectuées à l'aide d'un nouvel appareillage de type synthétique – dynamique. La modélisation des résultats expérimentaux fut réalisée à l'aide d'un programme développé en interne de calcul des diagrammes d'équilibre de phases globaux. Au cours de ce travail, nous avons effectué les mesures de points critiques sur de nombreux systèmes binaires. À titre d'exemple, nous avons commencé par étudier le système binaire acétone + chloroforme, en raison de son comportement thermodynamique atypique (présence d'un azéotrope négatif persistant sous haute pression).

Dans une troisième partie, nous montrons l'intérêt que la mesure de points critiques de mélanges binaires peut présenter pour le développement de deux types de procédés :

- Le développement du procédé de production de biodiesel par voie supercritique; nous avons déterminé les points critiques de nombreux mélanges binaires impliqués dans la production de biodiesel. Les premiers résultats expérimentaux obtenus ont été utilisés pour déterminer les paramètres d'interactions entre groupes du modèle thermodynamique prédictif PPR78 (développé au laboratoire) avec des résultats prometteurs.
- L'étude de comportement de phases de nouveaux réfrigérants, mélanges binaires $\text{CO}_2 + \text{R1234yf}$ et $\text{CO}_2 + \text{R1234ze (E)}$ qui, grâce à leurs avantages du point de vue environnemental, sont susceptibles de remplacer les réfrigérants conventionnels dans la climatisation automobile. Nous avons déterminé expérimentalement les équilibres liquide – vapeur et les propriétés critiques de ces mélanges binaires à l'aide d'un appareil statique – analytique et l'appareil synthétique - dynamique respectivement. Le modèle PPR78 fut ensuite utilisé pour corrélérer les résultats expérimentaux obtenus.

POINTS CRITIQUES DES SYSTÈMES BINAIRES

I. Comportements de phases des systèmes binaires

Par définition, un mélange binaire est un système constitué de deux constituants. Les états multiphasiques fluides pouvant alors être rencontrés sont des équilibres liquide - vapeur, liquide - liquide ou liquide - liquide - vapeur. Pour caractériser un système, on distingue les variables extensives qui sont dépendantes de la quantité de la matière et les variables intensives ($h, s, u, g, c_p, c_v, T, P, v, \dots$) qui sont indépendantes de la quantité de matière. Les variables intensives des phases ne sont pas toutes indépendantes les une des autres : elles sont reliées entre elles par l'équation d'état et éventuellement, par des relations d'équilibres de phases dans le cas où le système considéré est le siège d'un équilibre multiphasique. La règle des phases de Gibbs indique le nombre de variables intensives indépendantes dans le système donné. On définit tout d'abord la variance v , aussi appelée nombre de degrés de liberté, qui est le nombre de variables intensives des phases qu'il est nécessaire de fixer pour définir l'état intensif de chacune des phases d'un système, c'est-à-dire pour que toutes les autres variables intensives des phases en équilibre prennent une valeur définie. La règle des phases de Gibbs permet de calculer la variance d'un système en connaissant le nombre de constituants C , le nombre de phases φ et le nombre de relations supplémentaires r auxquelles le nombre de variables sont susceptibles d'être soumises (relations liées à une éventuelle azéotropie, à un état critique, etc.). La règle des phases de Gibbs s'écrit :

$$v = C + 2 - \varphi - r \quad (1)$$

D'après la règle des phases de Gibbs, pour un système binaire ($C = 2$) et lorsque $r = 0$,

- Si $\varphi = 1$: la variance du système est égale à 3 (on parle de système trivariant). Il faut fixer 3 variables intensives indépendantes pour définir l'état intensif du système. Les domaines monophasiques sont représentés par des volumes.
- Si $\varphi = 2$: la variance du système est égale à 2 (système divariant). Il suffit de fixer deux variables intensives pour définir l'état du système. Les domaines diphasiques sont des surfaces.
- Si $\varphi = 3$: la variance du système est égale à 1 (système monovariant). Il faut fixer 1 variable intensive pour définir l'état intensif du système. Les domaines triphasiques sont représentés par des courbes.

La représentation des états intensifs du comportement de phases des mélanges binaires nécessite donc trois dimensions (par exemple la température T , la pression P et la fraction molaire en constituant 1, z_1). On notera que les équilibres tétraphasiques font intervenir au moins une phase solide.

I.1. Comportements de phases des mélanges binaires à basse température et basse pression

A basse température et basse pression, il existe un nombre limité de configurations de diagrammes de phases observées expérimentalement. Pour représenter ces comportements, on utilise principalement deux types de diagrammes : les diagrammes isobares température - composition (Txy) et les diagrammes isothermes pression - composition (Pxy). Par convention, le composé le plus volatil est souvent noté (1) et le moins volatil (2). Dans ce paragraphe, seules des représentations isothermes sont utilisées. Par la suite, les régions monophasique liquide et monophasique vapeur sont repérées, respectivement, par les lettres L et V. Le domaine d'équilibre liquide-vapeur est indiqué par L+V. La courbe de bulle est la frontière entre les régions L et L+V et la courbe de rosée est la frontière entre les régions L+V et V.

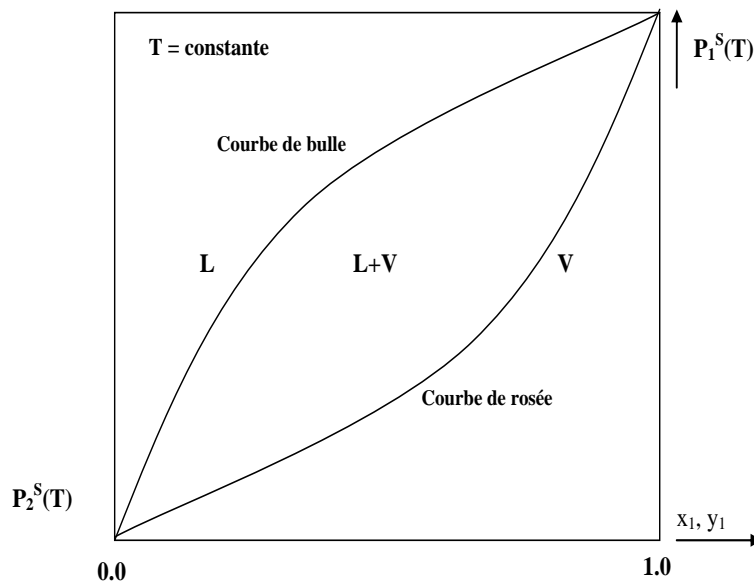


Fig. 3 Exemple de diagramme de phases isotherme sous basse température et basse pression.

En premier lieu, le comportement de phases le plus simple et le plus souvent rencontré montre une évolution monotone des courbes de bulle et de rosée [fig. 3]. Dans les diagrammes isothermes, ces courbes se rejoignent au niveau des pressions de vapeur saturante des deux corps

purs en $x_I = 0$ et $x_I = 1$. Ce type de comportement est toujours observé pour des systèmes binaires constitués des molécules A et B. Lorsque les forces d'interaction entre les molécules A-A et B-B sont identiques à celles entre les molécules A-B. Dans ce cas, la solution A-B est une solution idéale ($g^E = 0$). Elle ne présente pas des déviations à l'idéalité.

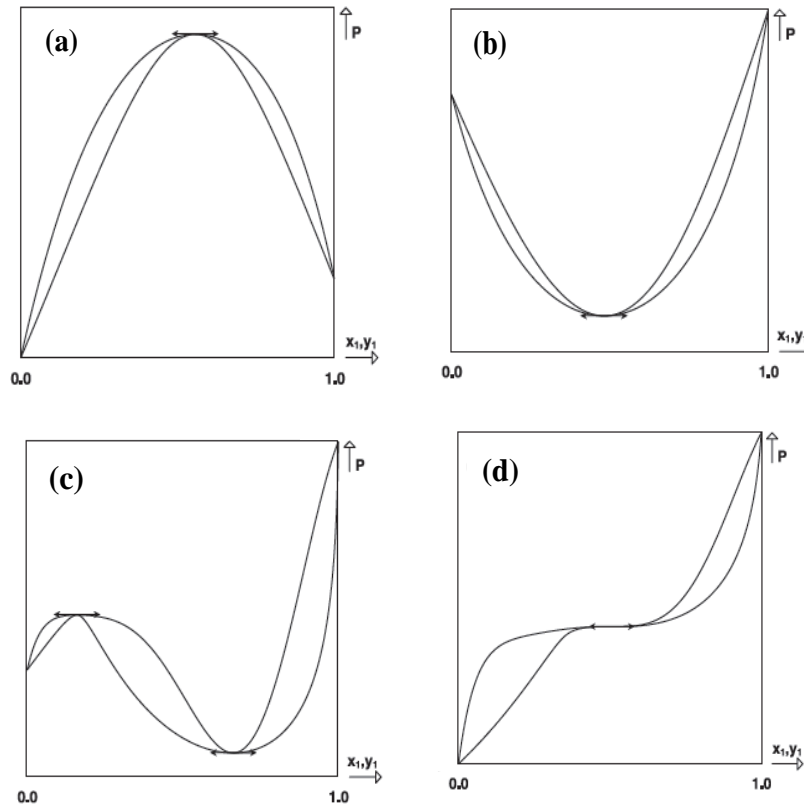


Fig. 4 Différentes configurations du comportement azéotropique de mélanges binaires.

La fig. 4 illustre les phénomènes d'azéotropie sous basse température et pression. Ce comportement est fréquemment observé pour les mélanges binaires dont les constituants ont des volatilités voisines ainsi que pour les mélanges présentant de fortes déviations à l'idéalité. L'azéotrope positif se produit lorsque les courbes de bulle et de rosée isothermes passent simultanément par un maximum en pression [fig. 4a]. Il est observé pour les systèmes binaires présentant des déviations positives à l'idéalité, autrement dit, l'énergie de Gibbs d'excès de la solution A-B est supérieure à celle de la solution idéale ($g^E > 0$). Réciproquement, l'azéotrope négatif se produit lorsque la courbe de bulle et la courbe de rosée passent simultanément par un minimum en pression [fig. 4b]. Ce cas est observé lorsque la solution A-B présente des déviations négatives à l'idéalité ($g^E < 0$). La solution A-B est alors plus stable que la solution idéale. L'azéotrope négatif reste un cas peu répandu expérimentalement. Une coexistence de l'azéotrope positif et de l'azéotrope négatif sur un diagramme isotherme caractérise un

comportement double azéotropique [fig. 4c]. Ce phénomène est extrêmement rare et seule une dizaine de systèmes binaires présentant ce phénomène fut observée expérimentalement [1]. Dans le cas particulier où les azéotropes positif et négatif d'un système double azéotropique fusionnent, on observe l'existence d'un point d'inflexion à tangente horizontale appelé azéotrope point de selle [fig. 4d]. On retrouve bien en ce point la caractéristique des azéotropes : $x_l = y_l$ [2].

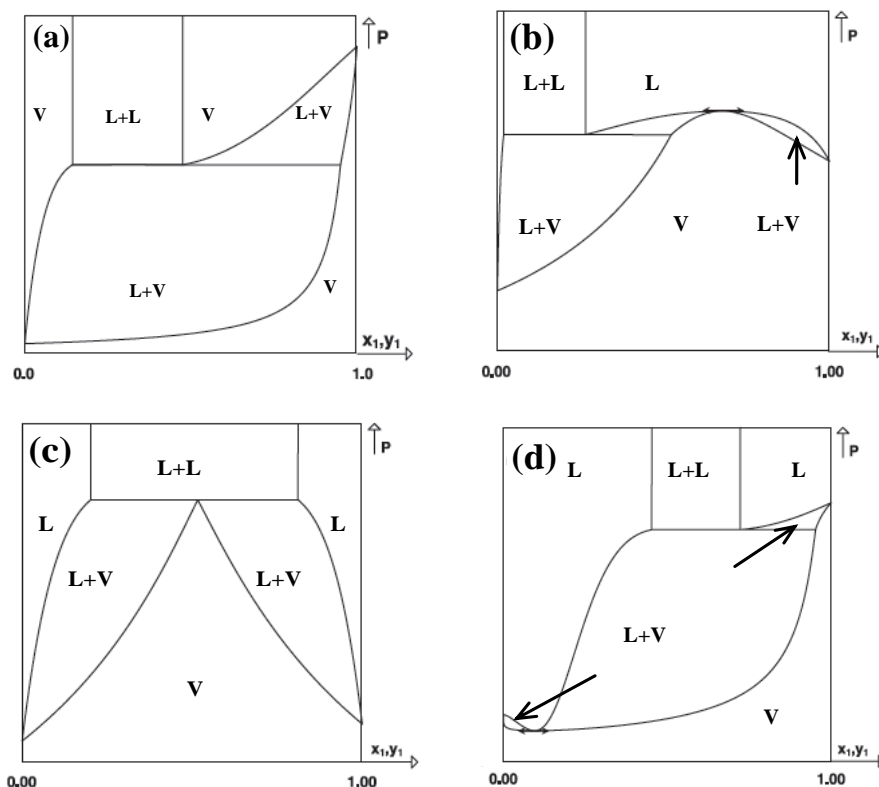


Fig. 5 Différentes configurations de comportements de phases lorsque des domaines d'ELV et d'ELL s'intersectent.

Intéressons-nous à présent à la superposition des régions d'équilibre liquide - liquide et liquide - vapeur dans les diagrammes de phases des mélanges binaires. La fig. 5 montre les différentes combinaisons observées expérimentalement, par exemple, lorsqu'un domaine liquide - liquide intercepte un domaine liquide - vapeur tel que celui décrit par la fig. 3, on observe le diagramme de phases de la fig. 5a. De même, la rencontre d'un diagramme d'équilibre liquide - vapeur présentant un phénomène d'azéotropie positive et d'un diagramme d'équilibre liquide - liquide peut conduire aux configurations 5b et 5c. Enfin, la combinaison d'un comportement azéotropique négatif et d'un équilibre liquide - liquide est illustrée par la fig. 5d. Cette dernière est extrêmement rare. Seulement trois mélanges binaires : acide acétique + triéthylamine, chlorure d'hydrogène + eau et bromure d'hydrogène + eau ont été cités dans la littérature [3]. Il

est à noter que dans la fig. 5, les lignes horizontales représentent l'équilibre triphasique liquide - liquide - vapeur.

I.2. Comportements de phases des mélanges binaires à haute température et haute pression

A haute température et haute pression, le comportement de phases du mélange binaire devient très complexe. Le nombre de configurations et réarrangements des diagrammes de phases augmente considérablement en raison de la présence du phénomène critique.

I.2.1. Point critique

■ Petite histoire de point critique

L'origine du concept de point critique fut mise en évidence pour la première fois en 1822 par le physicien français, le baron Cagnard de la Tour qui a montré qu'il existe nécessairement une limite à la dilatation d'un liquide volatil, au-delà de laquelle il devient vapeur, quelle que soit la pression. En 1823, Michael FARADAY a réalisé pour la première fois une étude systématique sur la liquéfaction de gaz et a revisité toute la signification des résultats expérimentaux de Cagnard de la Tour. L'étude attentive de son journal et de ses correspondances apporte la preuve que le point qu'il appelle *le point de Cagniard de la Tour* n'était pas, pour lui, simplement un point où l'état liquide disparaît, mais bien un point où le liquide et sa vapeur ne font plus qu'une phase, suivant une loi de continuité [4]. En 1860, Dmitri MENDELEEV a réalisé une expérience consistant à chauffer le liquide dans un tube capillaire. Il a observé qu'en chauffant, le niveau du liquide dans le capillaire montait et qu'au-delà d'une certaine température, le niveau du liquide ne montait plus et que le ménisque caractérisant l'interface liquide - vapeur disparaissait. Il a conclu qu'à cette température qu'il appelle *une température d'ébullition absolue*, la phase liquide et la phase gazeuse avaient les mêmes propriétés. Ce fut cependant Thomas ANDREWS qui réussit à démontrer pour la première fois, en 1869, que les états liquide et gazeux sont simplement des stades distincts d'une même condition de la matière et qu'il est possible de passer de l'un à l'autre par un processus de changement continu [4]. A la suite de ce travail, il introduit, notamment, le concept *de point critique, de température critique et de pression critique*.

■ Définition du point critique

a. Point critique des corps purs

Le point critique est un point particulier du diagramme de phases du corps pur où les propriétés intensives du liquide et celles de la vapeur sont exactement identiques (mêmes volumes molaires, mêmes enthalpies molaires, mêmes entropies molaires, etc.). Au niveau du point critique, les phases liquide et vapeur deviennent donc indiscernables et forment une unique phase dite *critique*. Sur une isotherme du corps pur dans le plan P - v , un point critique est un point d'inflexion à tangente horizontale. Il se caractérise mathématiquement par les équations :

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \quad (2)$$

En ce point, la plupart des propriétés physiques prennent des valeurs singulières, comme par exemple la vitesse de propagation du son ($c \rightarrow 0$), les capacités calorifiques ($C_p, C_v \rightarrow \infty$) et le coefficient de compressibilité isotherme ($K_T \rightarrow \infty$) [5].

b. Points critiques des mélanges binaires

Un point critique de système binaire est également caractérisé par l'indiscernabilité des phases liquide et vapeur. Lorsque la température d'un système binaire est égale à la plus petite température critique des deux corps purs ($T = \text{Min} \{T_{c1}, T_{c2}\}$), on observe l'apparition d'un phénomène critique sur les diagrammes de phases binaires. À cette température, les courbes de bulle et de rosée possèdent une tangente commune [fig. 6a] en $x_1 = 0$ si $T = T_{c2}$ ou en $x_1 = 1$ si $T = T_{c1}$. En augmentant légèrement la température, il apparaît un point critique de mélange binaire en $0 < x_1 < 1$. En ce point, les courbes de bulle et de rosée possèdent une tangente horizontale commune [fig. 6b] [6].

Pour chaque température comprise entre T_{c1} et T_{c2} , le système binaire de la fig. 6 possède un point critique de mélange. L'ensemble des points critiques de mélange forme un lieu des points critiques [fig.7]. La forme du lieu des points critiques dépend fortement de la nature, la taille et les forces d'interactions intermoléculaires et intramoléculaires des constituants. Les lieux des points critiques caractérisent donc pleinement les systèmes binaires auxquels ils sont associés [6].

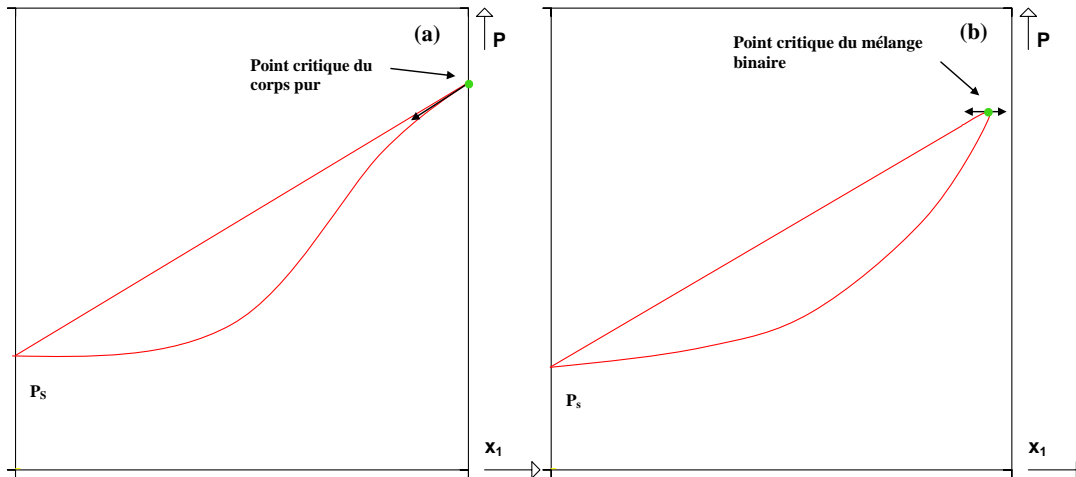


Fig. 6 Apparition du point critique dans un diagramme de phases binaire tel que $T_{cl} = \text{Min} \{T_{c1}, T_{c2}\}$; (a) : $T = T_{cl}$ et (b) : $T = T_{cl} + \varepsilon$

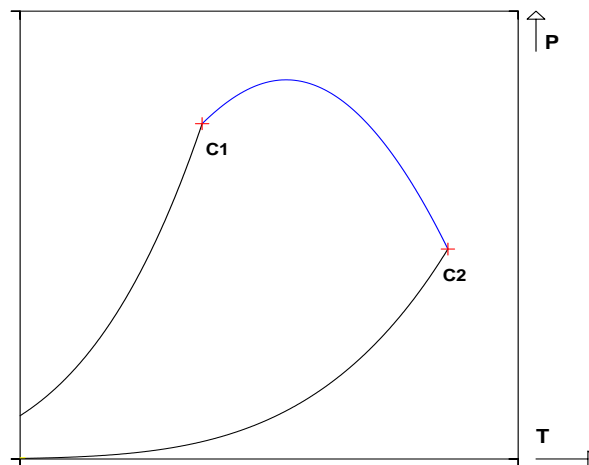


Fig. 7 Lieu des points critiques d'un système binaire dans le plan $P-T$; (ligne bleu) : lieu des points critiques, (ligne noire) : courbe de vaporisation et (+) : point critique des corps purs.

I.2.2. Classification de Van KONYNENBURG et SCOTT

En 1968, P.H. Van Konynenburg et R. Scott étudièrent les comportements de phases fluides de mélanges binaires prédits par l'équation d'état de Van der Waals. Ils portèrent une attention toute particulière aux formes des lieux des points critiques binaires et à leurs interactions avec les lignes triphasiques et azéotropiques. Ils proposèrent ensuite de classer les mélanges binaires suivant leur comportement observé dans le plan $P-T$ en 5 catégories [7].

Bien que la règle des phases de Gibbs impose une représentation de diagrammes de phases des mélanges binaires dans un espace à trois dimensions, Van Konynenburg et Scott prouvent qu'une excellente représentation peut être obtenue dans un espace à deux dimensions. Ils utilisent le plan $P-T$ et n'y représentent que les lieux de variances 0 et 1, qui témoignent de

l'ensemble des caractéristiques du système binaire et qui permettent de se faire une idée très précise sur son comportement. Les éléments qui doivent impérativement être représentés sur ces diagrammes sont les suivants : les lieux des points critiques binaires (liquide – liquide, liquide – vapeur, etc.), les points critiques des corps purs, les lignes triphasiques (liquide – liquide – vapeur), les lignes azéotropiques, l'azéotrope critique, les points critiques terminaux, les courbes de pression de vapeur saturante et le point de Bancroft (ce point matérialise l'intersection entre deux courbes de pression de vapeur saturante dans le plan $P-T$. Il se trouve généralement à très basse température et pression).

Il est à noter que ce type de diagrammes peut être présenté dans n'importe quel plan dont l'abscisse et l'ordonnée sont des variables intensives représentatives des phases. Bien qu'en général, on utilise le plan $P-T$, il est en toute rigueur nécessaire, comme l'indique la règle des phases de Gibbs, d'utiliser deux diagrammes pour accéder à la totalité de l'information : on peut par exemple utiliser conjointement le plan $P-T$ et le plan $P-x$ ou le plan $T-x$. Ces deux plans réunis sont équivalents à l'utilisation de l'espace de représentation $P-T-x$ pour remonter au comportement du système binaire.

■ Diagrammes de type I

Les diagrammes de type I sont les diagrammes les plus simples. Ils sont constitués d'une seule ligne critique liquide-vapeur (LV) qui est continue et bornée par les points critiques des deux corps purs. Les formes des lieux des points critiques peuvent être très variées et dépendent entre autres de la position relative des courbes de pression de vapeur saturante des deux corps purs [6]. Dans la plupart des cas, le lieu des points critiques a la forme d'une fonction monotone croissante ou décroissante. Ils admettent parfois un extremum en pression (souvent un maximum) et parfois un extremum en température (souvent un minimum). Dans certains cas, moins courants, ils peuvent combiner plusieurs de ces caractéristiques en possédant à la fois un maximum et un minimum en pression. Ce type de diagramme est caractéristique du comportement de phases d'un mélange binaire dont les deux constituants sont de même nature chimique et de différence de taille faible à modérée.

De plus, les diagrammes de type I peuvent posséder des comportements azéotropiques. Il existe plusieurs configurations possibles, indépendantes du signe de l'azéotrope (négatif ou positif). On parle d'azéotropie absolue si la ligne azéotropique est présente quelle que soit la température et intercepte le lieu des points critiques en un point de tangence [fig. 9a]. Autrement, on parle d'azéotropie bornée (ou limitée) lorsque la ligne azéotropique débute ou se termine sur l'une des courbes de pression de vapeur saturante.

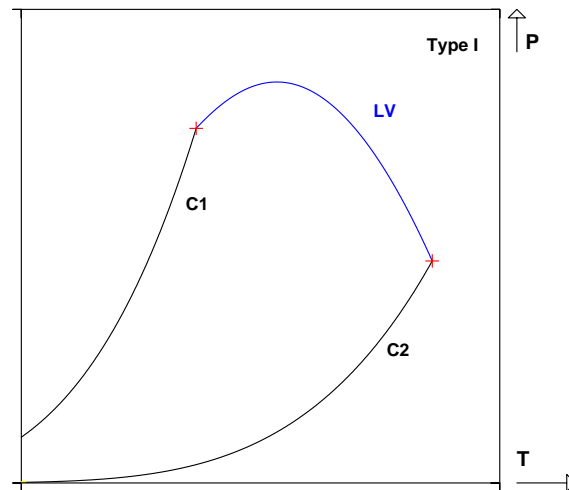


Fig. 8 Diagramme de type I selon la classification de Van Konynenburg et Scott.

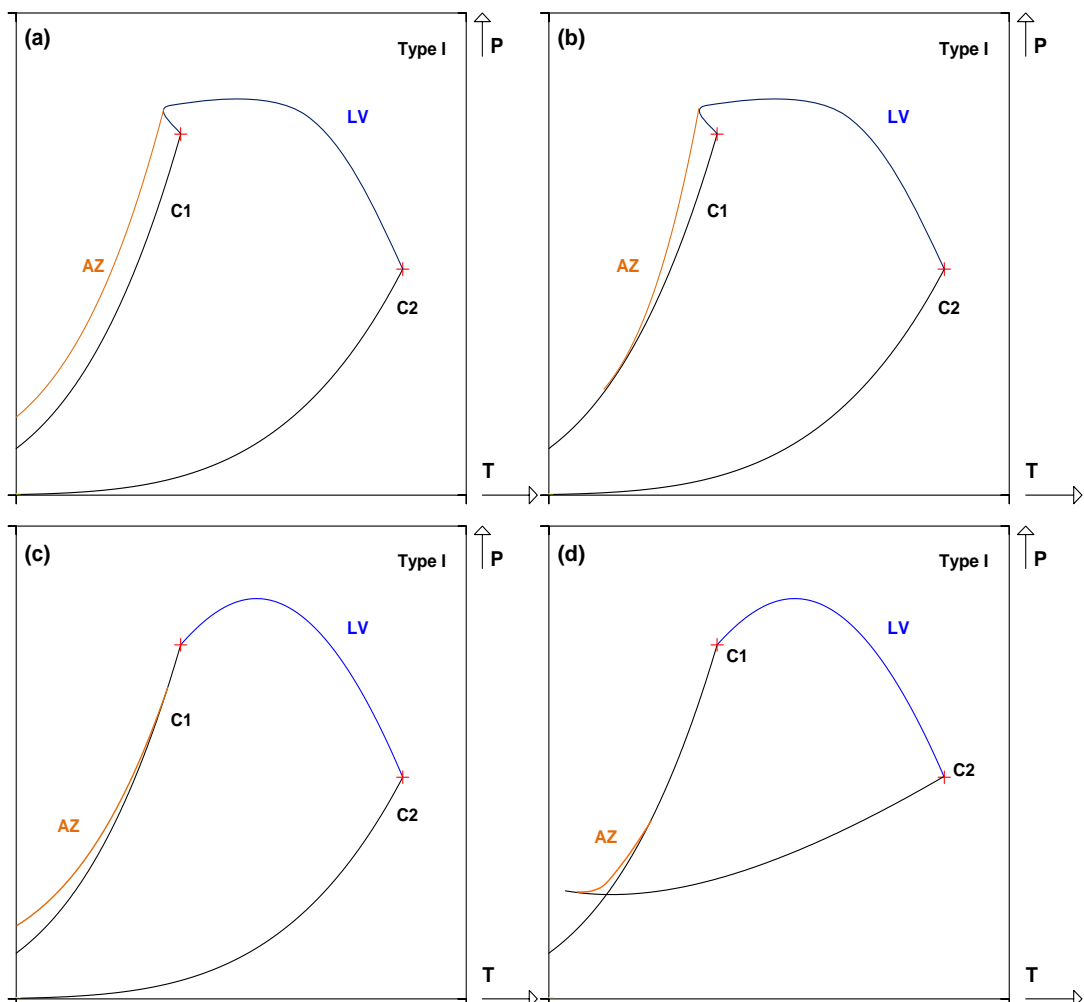


Fig. 9 Différentes configurations de diagramme de type I possédant un azéotrope positif.

L'azéotropie bornée peut être limitée par valeur inférieure si elle démarre sur une courbe de pression de vapeur saturante et se termine sur un lieu des points critiques [fig. 9b]. Elle peut

également être limitée par valeur supérieure si elle est présente aux faibles températures et se termine sur une courbe de pression de vapeur saturante [fig. 9c]. Certains systèmes présentent simultanément des limites inférieures et supérieures [fig. 9d]. L'azéotrope n'existe dans ce dernier cas qu'aux températures et pressions modérées.

Exemples de systèmes zéotropiques de type I : propane + butane, pentane + heptane.

Exemples de systèmes azéotropiques de type I : SO_2 + R227ea, diméthyl ester + décafluorobutane.

■ Diagrammes de type II

Le comportement de type II est similaire à celui de type I. Il est constitué d'un lieu des points critiques liquide-vapeur (LV) continu entre les points critiques des deux corps purs. Cependant, à la différence des diagrammes de type I, les diagrammes de type II possèdent un lieu des points critiques liquide-liquide (LL) et une ligne triphasique liquide-liquide-vapeur (LLV). Le lieu des points critiques liquide-liquide (LL) démarre sur un point critique terminal supérieur (PCTS) et se prolonge à pression infinie. Le PCTS est le point terminal de la ligne triphasique (LLV) qui matérialise un ELLV tel que les deux phases liquides forment une phase critique. La ligne LLV débute à basse température. De nombreuses configurations différentes des lignes critiques et triphasiques sont envisageables dans les diagrammes de type II. Le lieu des points critiques liquide-vapeur (LV) peut montrer des formes aussi variées que celles présentes dans les diagrammes de type I. De plus, le lieu des points critiques liquide-liquide (LL) peut posséder une pente négative, une pente positive et un maximum ou un minimum en température.

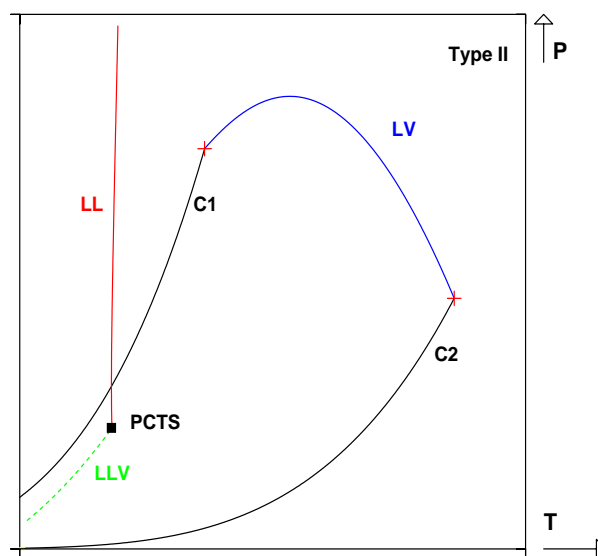


Fig. 10 Diagramme de type II selon la classification de Van Konynenburg et Scott.

Les systèmes binaires de type II peuvent présenter des comportements azéotropiques très similaires à ceux rencontrés dans les diagrammes de type I. De plus, les diagrammes de type II peuvent posséder un biazéotrope Az' (ou azéotrope bigène) qui est le point de rencontre dans le plan $P-T$ de la ligne azéotropique et de la ligne triphasique [fig. 11]. Ce biazéotrope possède la particularité d'être à la fois homogène et hétérogène. Les pressions azéotropiques sont généralement très voisines des pressions triphasiques, par conséquent, le phénomène est très difficile à observer dans le plan $P-T$. En revanche, ils sont bien plus marqués dans le plan $P-x$.

En pratique, il n'est pas simple de déterminer si un système est de type I ou de type II. En effet, si des mesures à basse température n'ont pas été réalisées, l'existence de la ligne triphasique reste incertaine.

Exemples de systèmes de type II : CO_2 + butane, CO_2 + pentane, eau + phénol.

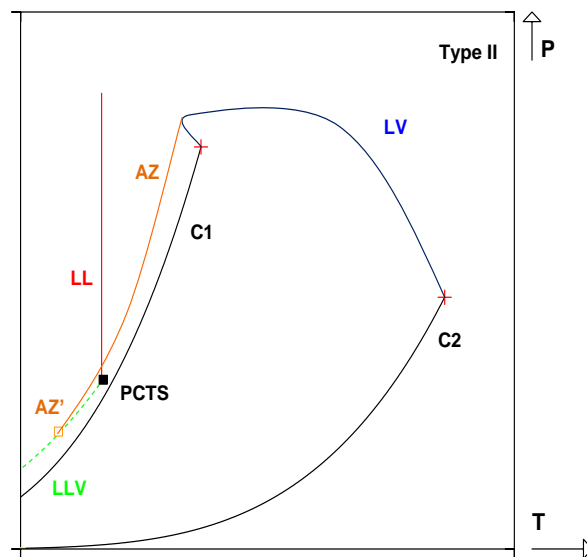


Fig. 11 Existence d'un biazéotrope dans les diagrammes de type II.

■ Diagrammes de type III

Le comportement de type III est caractérisé par deux lieux des points critiques liquide - vapeur discontinus entre les points critiques des deux corps purs et une ligne triphasique liquide - liquide - vapeur. Le premier lieu des points critiques liquide - vapeur (LV1) est attaché au point critique du corps pur le moins volatil (C2), au fur et à mesure que la fraction molaire en composé lourd diminue, la pression tend vers l'infinie. Ce lieu des points critiques peut avoir des formes assez variées. Par exemple, il peut posséder un maximum et un minimum locaux (présence d'une tangence horizontale), un point d'inflexion à tangente horizontale et un extremum en température (présence d'une tangence verticale).

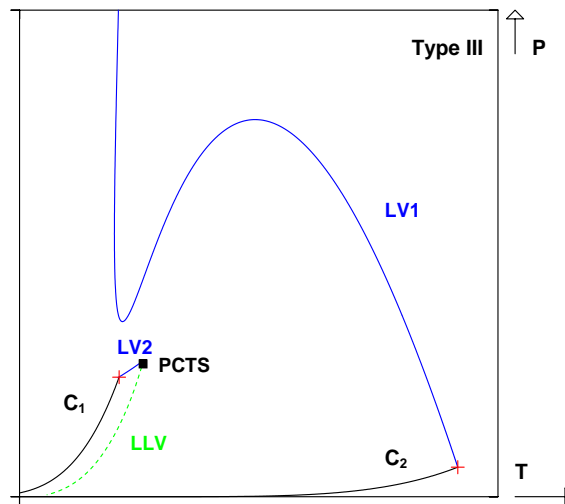


Fig. 12 Diagramme de type III selon la classification de Van Konynenburg et Scott.

Ce lieu des points critiques peut également décrire la pression critique comme une fonction monotone croissante ou décroissante de la température. Le second lieu des points critiques liquide-vapeur (LV2) débute au point critique du corps pur le plus volatil (C_1) et s'achève au point critique terminal supérieur (PCTS). La ligne triphasique (LLV) débute à une très basse température et se termine également sur le PCTS où une phase liquide est en équilibre avec une phase critique liquide-vapeur. La seconde ligne critique est généralement une fonction monotone croissante ou décroissante de la température. Ce type de comportement caractérise généralement les mélanges binaires très dissymétriques en taille.

Exemple de système de type III : éthane + méthanol, CO_2 + tétradécane.

■ Diagrammes de type IV

Les diagrammes de type IV sont caractérisés par trois lieux des points critiques et deux lignes triphasiques liquide-liquide-vapeur. Le premier lieu des points critiques liquide-vapeur (LV1) est relié au point critique du corps pur le plus lourd (C_2) et intercepte la première ligne triphasique (LLV1) au niveau d'un point critique terminal inférieur (PCTI) : une phase gaz en équilibre avec une phase critique liquide-liquide. Cette ligne triphasique, en général très courte, débute en ce PCTI et se termine au point critique terminal supérieur (PCTS1) : une phase liquide en équilibre avec une phase critique liquide-vapeur. Le second lieu des points critiques débute sur le point critique du corps pur le plus léger (C_1) et rejoint le PCTS1. Le troisième lieu des points critiques liquide-liquide (LL) débute sur le PCTS2 : une phase vapeur en équilibre avec une phase critique liquide-liquide et se prolonge à pression infinie. La seconde ligne triphasique (LLV2) démarre à très basse température et se termine au PCTS2.

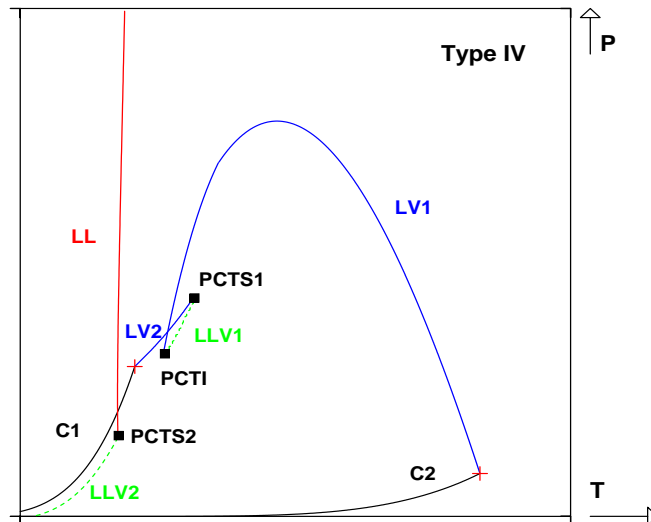


Fig. 13 Diagramme de type IV selon la classification de Van Konynenburg et Scott.

Le comportement de type IV n'a pas été découvert expérimentalement mais par le calcul. Il est en réalité le cas intermédiaire entre le type II et le type III. Il existe quelques légères variantes pour ce type de comportement. Par exemple, la première ligne triphasique (LLV1) peut débuter à une température inférieure ou supérieure à la température critique du corps pur le plus volatil.

Exemples de systèmes de type IV : méthane + hex-1-ène, CO₂ + undécane.

■ Diagrammes de type V

Le comportement de type V a été découvert expérimentalement. Il est identique à celui de type IV, à la différence que le diagramme de type V ne possède pas de lieu des points critiques liquide-liquide (LL).

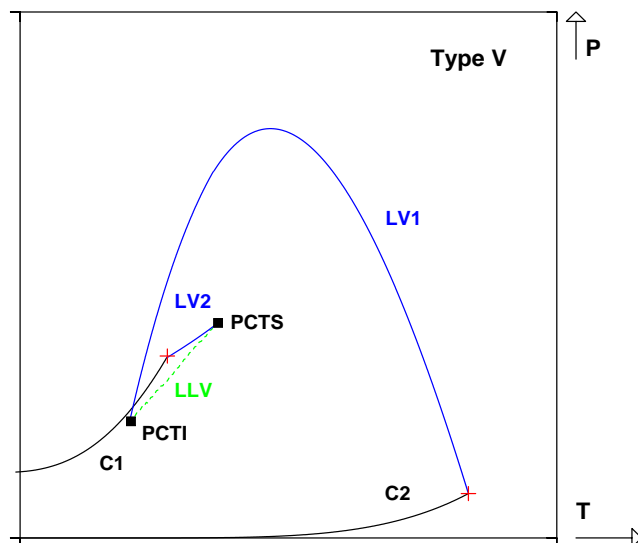


Fig. 14 Diagramme de type V selon la classification de Van Konynenburg et Scott.

Par conséquent, il ne possède pas le point critique terminal supérieur (liquide-liquide) ni de seconde ligne triphasique. Comme pour les diagrammes de type IV, il peut exister quelques légères variantes dans l'allure des diagrammes de type V concernant le point critique terminal inférieur (PCTI) qui se retrouve soit au-dessus ou au-dessous du point critique du corps pur le plus léger.

Exemples de système de type V : méthane + hexane.

■ Extension de la classification : diagramme de type VI

Les diagrammes de type VI ne figurent pas dans la classification initiale proposée par Van Konynenburg et Scott car l'équation de Van der Waals ne permet pas de représenter ce type de comportement. Les diagrammes de type VI sont identiques à ceux de type I concernant le lieu des points critiques liquide - vapeur (LV). Ce dernier est attaché aux points critiques des deux constituants purs. En revanche, les diagrammes de type VI possèdent, à basse température, un lieu des points critiques liquide-liquide (LL) dont la pression ne tend pas vers l'infini : cette ligne critique liquide - liquide débute sur un point critique terminal inférieur (PCTI) et se termine sur un point critique terminal supérieur (PCTS). La zone délimitée par le lieu des points critiques liquide - liquide (LL) forme une boucle d'immiscibilité liquide - liquide. De plus, une ligne triphasique (LLV) relie le PCTI et le PCTS.

Exemples de système de type VI : eau + butoxyéthanol.

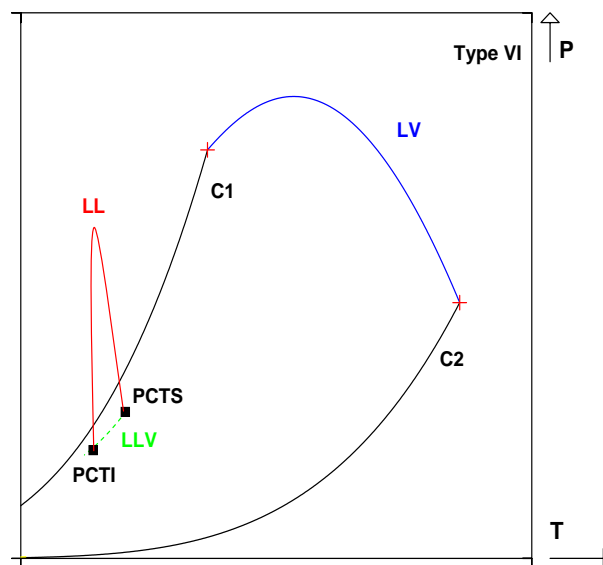


Fig. 15 Diagramme de type VI.

Remarque

Pour étudier les mélanges binaires formés d'un constituant donné et d'une espèce chimique membre d'une série homologue, on peut utiliser le type de représentation de la fig. 16. Cette figure illustre le cas des mélanges binaires $\text{CO}_2 + n$ -alcane. On a tracé la température des points critiques terminaux (T_{PCT}) en fonction du nombre d'atomes de carbone dans le n -alcane (n). Les mélanges $\text{CO}_2 + n$ -alcane sont de type II pour $2 \leq n \leq 9$ (car il n'existe qu'un seul point critique terminal (PCT) pour ces valeurs de n). Le mélange $\text{CO}_2 +$ décane est le type IV (3 PCT : PCTS1, PCTS2 et PCTI pour cette valeur de n) et les mélanges contenant un n -alcane tel que $n \geq 12$ ont un comportement de phases de type III (1 seul PCT pour ces valeurs de n).

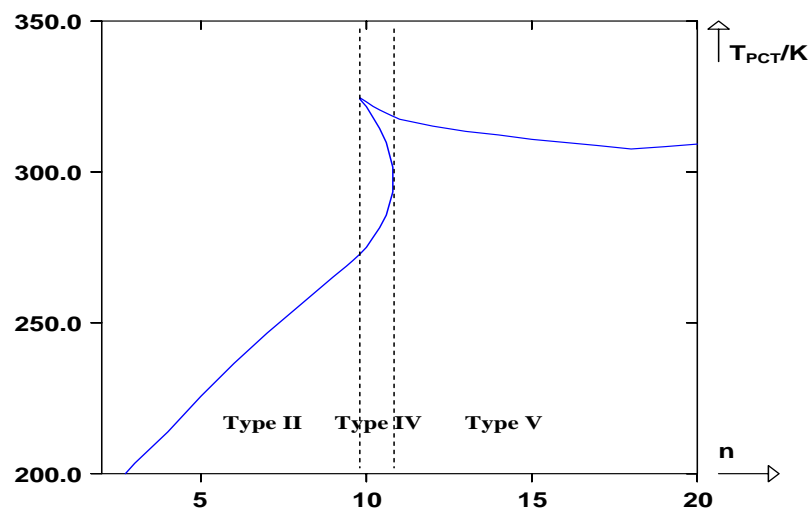


Fig. 16 Evolution des températures critiques terminales (T_{PCT}) en fonction de nombre d'atomes de carbone (n) dans les mélanges binaires $\text{CO}_2 + n$ -alcane (Prédiction par le modèle PPR78).

II. Etudes expérimentales de points critiques

Dans ce paragraphe, nous présentons l'étude expérimentale des comportements de phases. Il existe de nombreux moyens d'accéder aux informations concernant les équilibres de phases des fluides. Nous montrons d'abord des généralités sur des méthodes expérimentales et nous précisons ensuite les principes des méthodes de mesure des points critiques les plus fréquemment employées dans la littérature.

II.1. Généralités sur les méthodes expérimentales

Il est nécessaire de connaître des notions importantes qui permettent de représenter quelques différences entre les méthodes expérimentales permettant de déterminer les équilibres de phases des fluides.

■ Méthodes analytiques / Méthodes synthétiques

Les méthodes analytiques consistent à déterminer des compositions de phases en équilibre des échantillons, portés dans les conditions de mesures souhaitées. Les techniques généralement utilisées pour déterminer les compositions de phases sont la chromatographie, la spectroscopie et l'analyse gravimétrique. La précision des mesures dépend fortement de la manière d'effectuer l'échantillonnage. Il est donc nécessaire de réaliser les prélèvements des échantillons de manière à ne pas perturber les équilibres entre phases. En général, les méthodes analytiques sont peu recommandées dans le cas des études au voisinage des points critiques où la moindre variation de température et de pression peut nuire à la précision.

Les méthodes synthétiques consistent à préparer un mélange d'une composition globale connue puis à observer une transition de phases en faisant varier la pression, la température ou le volume. La composition est simplement déterminée par pesée différentielle des constituants. Ainsi, les problèmes liés au prélèvement des échantillons et aux analyses peuvent être éliminés. On distingue les méthodes synthétiques visuelles (i.e. la détection de changement de phases s'effectue par visualisation au travers d'une cellule) et les méthodes synthétiques non-visuelles (i.e. le changement de phases est détecté au moyen d'une technique intermédiaire non-visuelle telle que la vitesse de son). Les méthodes synthétiques peuvent être mises en œuvre à très haute pression. De plus, elles peuvent être employées lorsque les méthodes analytiques échouent, notamment dans le cas où les phases sont difficilement séparables.

■ Méthodes dynamiques / Méthodes statiques

Les méthodes dynamiques consistent à faire circuler le fluide dans la cellule de mesure (système ouvert). La circulation du mélange est effectuée à l'aide d'une pompe et assure généralement une bonne agitation et une homogénéisation du système étudié. Les méthodes statiques consistent à introduire le mélange étudié dans une cellule fermée puis à l'agiter, à l'aide d'un système d'agitation approprié.

■ Méthodes directes / Méthodes indirectes

Les méthodes directes permettent de mesurer directement les propriétés physiques d'intérêt sans passer par des calculs ou des propriétés intermédiaires. Elles sont applicables seulement aux propriétés pour lesquelles des capteurs spécifiques existent. Les propriétés les plus connues sont la température qui peut être mesurée par sonde de platine ou par thermocouple et la pression qui peut être mesurée, par exemple, par capteur inductif. Cependant, il n'existe pas des capteurs spécifiques pour certaines propriétés. Dans ce cas, les méthodes indirectes sont employées. Elles déterminent les propriétés intermédiaires mesurables pour pouvoir en déduire les propriétés d'intérêt, par exemple, les mesures de la vitesse du son du fluide afin d'identifier le point critique.

II.2. Méthodes expérimentales de mesure de points critiques

Il existe de nombreuses méthodes permettant de déterminer les coordonnées critiques d'un fluide soit pour les substances pures soit pour les mélanges. Dans ce paragraphe, nous présentons les méthodes fréquemment utilisées dans la littérature.

■ Méthode statique

Le principe de cette technique est basé sur l'observation de la disparition et la réapparition de l'interface liquide - vapeur dans un récipient fermé [8-9] de volume fixé. Elle nécessite un chargement d'une masse de fluide telle que la densité soit voisine de sa densité critique ainsi qu'une agitation efficace [10]. Le récipient est chauffé jusqu'à la disparition de l'interface liquide - vapeur puis refroidi jusqu'à la réapparition de cette interface. La disparition et la réapparition du ménisque permettent de cerner le point critique. Dans le cas des substances thermiquement instables, la température critique diminue en fonction du temps de mesure alors que la pression critique augmente (la décomposition thermique provoque la disparition de la substance initiale et produit d'autres composés plus légers). On effectue alors une extrapolation des valeurs mesurées au temps zéro afin d'obtenir les valeurs critiques vraies [11]. Les appareils utilisés dans la méthode statique se différencient selon le type de récipient [12-14], le chargement de l'échantillon [15, 18], la technique de chauffage [13, 16-17] ou encore la détermination de composition [18-19].

■ Méthode dynamique

La méthode dynamique fut proposée par Roess [20] pour déterminer les propriétés critiques des composés thermiquement instables. Le principe de cette méthode repose également sur l'observation de la disparition et la réapparition du ménisque mais cette fois-ci la cellule de mesure est un système ouvert. Le fluide traverse une cellule d'observation avec un débit variable au cours d'une mesure. Cette méthode permet de minimiser le temps de résidence du fluide dans la cellule et donc d'éviter la décomposition à haute température. Cependant, elle consomme une grande quantité du fluide. Teja et al. [21] ont amélioré cette technique par diminution de la taille d'équipement et du temps de résidence. La méthode dynamique fut initialement appliquée aux corps purs tels que les alcanes [22], les acides carboxyliques [23] et d'autres composés [24]. Ensuite, Horstmann et al. [25-28] l'ont développée pour la détermination de points critiques de mélanges multiconstituants. Soo et al. [29] ont couplé la méthode dynamique à la méthode synthétique. Notons de plus que la méthode dynamique fut utilisée pour la mesure de pressions saturantes des substances thermiquement instables à hautes températures [30-32]. En revanche, le désavantage majeur de cette méthode est l'impossibilité de la mesure de la densité critique en raison du volume inconnu.

■ Méthode PvT

La méthode PvT présente l'avantage de pouvoir déterminer toutes les coordonnées critiques (T_c , P_c , v_c) du système étudié. Le principe de cette technique repose sur des mesures de variation de pression en fonction du volume molaire à température donnée. L'isotherme du corps pur qui possède un point d'inflexion à tangente horizontale $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$ est l'isotherme critique T_c . La pression critique et la densité critique correspondent respectivement à la pression et la densité du point d'inflexion à tangente horizontale. L'expérience peut également être réalisée à partir d'isochores. De nombreuses études [33-35] furent réalisées pour développer cette technique de manière à identifier plus précisément les coordonnées critiques. Cho et al. [36] et Lee et al. [37] ont couplé cette méthode à la technique d'observation visuelle pour mesurer les points critiques des mélanges dont la composition est déterminée par méthode synthétique. Yu et al. [38] ont également appliqué cette technique aux mélanges mais ils ont déterminé la composition du mélange par méthode analytique.

■ Méthode acoustique

Le principe de cette méthode non-visuelle repose sur la variation de la vitesse de propagation du son à travers le fluide étudié. L'expression thermodynamique de la vitesse du son d'un composé pur s'exprime selon :

$$c = \sqrt{-\frac{v^2}{M} \left(\frac{\partial P}{\partial v} \right)_s} = \sqrt{-\frac{v^2}{M} \frac{c_p}{c_v} \left(\frac{\partial P}{\partial v} \right)_T} \quad (3)$$

$$\text{Or } c_p = c_v + T \left(\frac{\partial v}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_v \quad (4)$$

L'équation (3) devient alors :

$$c^2 = -\frac{v^2 T}{M c_v} \left(\frac{\partial P}{\partial v} \right)_T \left[\frac{c_v}{T} + \left(\frac{\partial v}{\partial T} \right)_T \left(\frac{\partial P}{\partial T} \right)_v \right] \quad (5)$$

$$c^2 = -\frac{v^2 T}{M C_v} \left[\frac{c_v}{T} \left(\frac{\partial P}{\partial v} \right)_T - \left[\left(\frac{\partial P}{\partial T} \right)_v \right]^2 \right]$$

$$c^2 = \frac{v^2 T}{M c_v} \left[\left(\frac{\partial P}{\partial T} \right)_v \right]^2 \left[1 - \frac{c_v}{T} \frac{\left(\frac{\partial P}{\partial v} \right)_T}{\left[\left(\frac{\partial P}{\partial T} \right)_v \right]^2} \right]$$

Au niveau d'un point critique $c_v \left(\frac{\partial P}{\partial v} \right)_T \rightarrow 0$ de sorte que l'expression de la vitesse du son devient :

$$c = v \sqrt{\frac{T}{M c_v} \left(\frac{\partial P}{\partial T} \right)_v} \quad (6)$$

Dans les expressions précédentes, v le volume molaire, M la masse molaire, c_v la capacité calorifique molaire à volume constant, c_p la capacité calorifique molaire à pression constant T la température et P la pression. Les paramètres critiques sont associés à une vitesse du son minimale [39]. Ce principe peut être appliqué aux mélanges en mesurant la variation du temps de retard (i.e. le temps que met le son pour se progresser depuis l'émetteur et atteindre le récepteur) en fonction de la pression pour chaque isotherme. Le temps de retard maximal correspond à la vitesse minimale. L'isotherme qui possède un maximum absolu de temps de retard est l'isotherme critique T_c . D'après la littérature, cette méthode fut par exemple, appliquée aux corps

purs [40-43], aux mélanges binaires [40, 44-46], aux mélanges ternaires [40, 47] et aux mélanges quaternaires [47]. En revanche, les mesures proches du point critique sont très difficiles à réaliser en raison d'une atténuation importante en vitesse de propagation acoustique. L'utilisation d'une faible fréquence de vibration permet de minimiser l'atténuation [48].

■ Autres méthodes

Au point critique, les propriétés physiques et thermodynamiques prennent des valeurs particulières. Ces propriétés peuvent être utilisées pour identifier ou caractériser le point critique. Nikitin et al. [49] ont utilisé une méthode de chauffage par impulsion de courant électrique pour déterminer les points critiques des substances thermiquement instables. Ils ont appliqué cette méthode aux *n*-alcanes [50-51], *1*-alcènes [52], *1*-alcanols [53], methylphenylsiloxanes [54], peroxyde d'hydrogène [55], acides carboxyliques [56] et d'autres composés. Belyakoy et al. [57] ont utilisé une méthode de diffusion de la lumière. Ils ont mesuré une variation de l'intensité lumineuse en fonction de la température. Wong et al. [58-59] ont mesuré l'indice de réfraction des phases liquide et vapeur d'un fluide à différentes températures. L'indice de réfraction de la phase liquide devient identique à celui de la phase vapeur au point critique. Chester et al. [60-61] ont estimé les températures critiques et les pressions critiques des mélanges binaires à l'aide de mesures chromatographiques en phase supercritique.

III. Etude théorique de points critiques : description du modèle PPR78

III.1. Introduction

En 1873, Johannes Diderik van der Waals [62] propose, pour la première fois, une équation d'état permettant de représenter à la fois la phase vapeur et la phase liquide ainsi que la transition des phases liquide - vapeur. Pour un corps pur, l'équation d'état de Van der Waals s'écrit :

$$P = \frac{RT}{v - b_i} - \frac{a_i}{v^2} \quad (7)$$

a_i et b_i sont les paramètres caractéristiques d'un corps pur i . Le premier terme contenant le paramètre b_i (volume d'exclusion ou covolume) représente l'interaction répulsive et le deuxième

terme contenant le paramètre a_i représente l'interaction attractive entre les molécules. Les valeurs de a_i et b_i peuvent être déterminées par application des spécifications critiques :

$$\left. \begin{array}{l} P_c - P(T_c, v_c) = 0 \\ \left(\frac{\partial P}{\partial v} \right)_{T=v=v_c} \Big|_{T=T_c} = 0 \\ \left(\frac{\partial^2 P}{\partial v^2} \right)_{T=v=v_c} \Big|_{T=T_c} = 0 \end{array} \right\} \Rightarrow \begin{array}{l} a_i = \frac{27}{64} \frac{R^2 T_{c,i}^2}{P_{c,i}} \\ b_i = \frac{1}{8} \frac{R T_{c,i}}{P_{c,i}} \end{array} \quad (8)$$

L'équation de van der Waals fournit une représentation qualitativement correcte du comportement de phases des fluides. Elle n'est cependant pas très performante quantitativement. C'est pourquoi, elle a subi par la suite plusieurs modifications. Dans la plupart des cas, les modifications consistent à améliorer la partie attractive [63-75]. Dans certains cas, les auteurs ont également travaillé sur le terme répulsif [76-81] ou sur les deux termes [82-83]. Parmi les équations d'état modifiées, les équations de Redlich-Kwong-Soave [63] et de Peng-Robinson [65-66] sont les plus connues et largement utilisées dans l'industrie, particulièrement pour le raffinage et la simulation des réservoirs. Leur avantage principal réside dans le fait qu'elles nécessitent la connaissance de peu de données expérimentales pour être appliquées à un corps pur (les propriétés critiques T_c et P_c et le facteur acentrique ω). Cependant, ces équations présentent d'importantes limitations. Par exemple, le calcul des densités liquides n'est généralement pas satisfaisant. De plus, elles s'appliquent plus difficilement aux fluides polaires et associés. Quelles que soient les modifications apportées, il apparaît impossible de représenter de manière satisfaisante la forme de l'enveloppe de phases liquide - vapeur dans le plan P - ρ au voisinage du point critique.

Pour passer des équations d'état des corps purs à celles des mélanges, il est nécessaire d'utiliser des *règles de mélange* qui permettent de calculer les paramètres a et b de mélange à partir des paramètres a_i et b_i des corps purs i . La règle de mélange la plus répandue est celle de Van der Waals décrite par la suite. En 1979, Huron et Vidal [84] ont introduit une nouvelle règle de mélange qui combine une équation d'état avec un modèle de coefficients d'activité (ou modèle d'énergie de Gibbs d'excès g^E). Cette règle de mélange permet de décrire des solutions fortement non idéales. D'autres règles de mélange telles que celles de Michelsen (MHV1, MHV2) [85-86], de Wong et Sandler [87] et de PSRK [88] sont également souvent utilisées.

III.2. Description du modèle PPR78

Le modèle PPR78 (acronyme anglais de Predictive Peng-Robinson 1978) utilise l'équation d'état de Peng-Robinson dans sa version de 1978 [66] et les règles de mélange classique de Van der Waals. Le coefficient d'interactions binaires k_{ij} intervenant dans ces règles de mélange est supposé dépendre uniquement de la température et est calculé par une méthode de contributions de groupes. L'utilisation de la méthode de contributions de groupes rend le modèle prédictif (remarquons toutefois que pour être utilisé, le modèle PPR78 nécessite la connaissance des valeurs expérimentales des paramètres de corps pur (T_c , P_c et ω)).

Le développement du modèle PPR78 a débuté en 2003. Le premier article [89] qui expose les bases du modèle et présente les valeurs des paramètres d'interactions entre groupes pour les systèmes binaires constitués d'alcane linéaires ou ramifiés parut en 2004. Les auteurs proposèrent par la suite l'extension du modèle PPR78 aux systèmes contenant des composés aromatiques [90], aux systèmes contenant des composés naphthéniques [91], aux systèmes contenant des mercaptans [92-93], aux systèmes contenant des gaz : CO₂ [94], N₂ [95], H₂S [96] et H₂ [97], aux systèmes aqueux [98] et aux systèmes contenant les alcènes [99]. Le modèle PPR78 fut récemment appliqué à la pure prédiction du comportement de fluides pétroliers synthétiques [100].

■ Définition du modèle PPR78

L'équation d'état de Peng-Robinson pour un corps pur i [66] s'écrit

$$P(T, v) = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \quad (9)$$

$$\text{Avec} \quad \left\{ \begin{array}{l} R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \\ a_i = 0.457235529 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{T/T_{c,i}} \right) \right]^2 \\ m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad \text{si } \omega_i \leq 0.491 \\ m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3 \quad \text{si } \omega_i > 0.491 \end{array} \right.$$

P est la pression, T la température, R la constante des gaz parfaits et v le volume molaire. $T_{c,i}$, $P_{c,i}$ et ω_i sont respectivement la température critique, la pression critique et le facteur acentrique du

corps pur i . a_i et b_i désignent respectivement les paramètres d'attraction et le covolume du corps pur.

L'application de cette équation d'état à un mélange nécessite l'utilisation de règles de mélange de type Van der Waals.

$$P(T, v, x) = \frac{RT}{v - b_m(x)} - \frac{a_m(T, x)}{v(v + b_m(x)) + b_m(x)(v - b_m(x))} \quad (10)$$

Avec

$$\begin{cases} b_m(x) = \sum_{i=1}^{n_c} x_i b_i \\ a_m(T, x) = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}(T)) \end{cases}$$

Où n_c est le nombre de constituants présents dans le mélange et x le vecteur des fractions molaires des constituants. k_{ij} , le paramètre d'interactions binaires, est calculé à partir de la formule suivante :

$$k_{ij}(T) = \frac{-\frac{1}{2} \sum_{k=1}^{n_g} \sum_{l=1}^{n_g} (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T/K} \right)^{\left(\frac{B_{kl}-1}{A_{kl}} \right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T) a_j(T)}}{b_i b_j}} \quad (11)$$

n_g est le nombre de groupes définis par la méthode de contributions de groupes. k et l sont deux groupes différents. α_{ik} représente la fraction de la molécule i occupée par le groupe k , c'est-à-dire, l'occurrence du groupe k dans la molécule i divisée par le nombre de groupes présents dans la molécule. A_{kl} et B_{kl} sont des paramètres qui quantifient les interactions entre groupes k et l . Ils dépendent uniquement de la nature des groupes k et l . Notons que $A_{kk} = B_{kk} = 0$ et que $A_{kl} = A_{lk}$ et $B_{kl} = B_{lk}$.

■ Estimation des paramètres du modèle PPR78

L'estimation des paramètres A_{kl} et B_{kl} est effectuée à partir des données expérimentales d'équilibre de phases et de points critiques en minimisant l'écart entre les valeurs expérimentales et les valeurs prédites par le modèle PPR78. La fonction objectif à minimiser s'écrit :

$$F_{obj} = \frac{F_{obj,bulle} + F_{obj,rosée} + F_{obj,crit,comp} + F_{obj,crit,presure}}{n_{bulle} + n_{rosée} + n_{crit} + n_{crit}} \quad (9)$$

Avec

$$\begin{aligned}
F_{obj,bulle} &= 100 \sum_{i=1}^{n_{bulle}} 0.5 \left(\frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}} \right)_i & \text{avec } |\Delta x| &= |x_{1,exp} - x_{1,cal}| = |x_{2,exp} - x_{2,cal}| \\
F_{obj,rosée} &= 100 \sum_{i=1}^{n_{rosée}} 0.5 \left(\frac{|\Delta y|}{y_{1,exp}} + \frac{|\Delta y|}{y_{2,exp}} \right)_i & \text{avec } |\Delta y| &= |y_{1,exp} - y_{1,cal}| = |y_{2,exp} - y_{2,cal}| \\
F_{obj,crit.comp} &= 100 \sum_{i=1}^{n_{crit}} 0.5 \left(\frac{|\Delta x_c|}{x_{c1,exp}} + \frac{|\Delta x_c|}{x_{c2,exp}} \right)_i & \text{avec } |\Delta x_c| &= |x_{c1,exp} - x_{c1,cal}| = |x_{c2,exp} - x_{c2,cal}| \\
F_{obj,crit.comp} &= 100 \sum_{i=1}^{n_{crit}} \left(\frac{|P_{cm,exp} - P_{cm,cal}|}{P_{cm,exp}} \right)_i & &
\end{aligned}$$

n_{bulle} , $n_{rosée}$ et n_{crit} sont respectivement le nombre de points de bulle, le nombre de points de rosée et le nombre de points critiques du mélange considéré. x_1 et y_1 sont respectivement la fraction molaire du constituant le plus volatil dans la phase liquide et la fraction molaire du même constituant dans la phase gazeuse. Evidemment, $x_2 = 1 - x_1$ et $y_2 = 1 - y_1$. x_{c1} est la composition critique du constituant le plus volatil et x_{c2} la composition critique du constituant le moins volatil à une température et une pression fixées. P_{cm} est la pression critique du mélange considéré à une température fixée.

Remarque

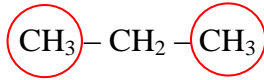
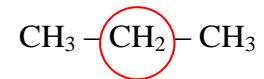
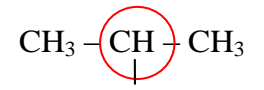
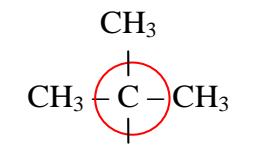
Les points critiques de mélange ont une influence deux fois plus grande que les points de bulle et de rosée sur la fonction objectif car deux écarts interviennent pour un point critique : l'écart à la composition critique et l'écart à la pression critique.

Il est à noter que les écarts en composition sont moyennés sur les deux constituants du mélange de manière à éviter un impact trop important des points expérimentaux dont la composition est très faible ou très élevée sur les paramètres ajustés. Pour certains binaires, les points de bulle expérimentaux ont des compositions très faibles ($x_1 < 0.01$) et les points de rosée expérimentaux ont des compositions très élevées ($y_1 = 0.99$). Si ces points sont majoritaires dans une base de données, la fonction objectif peut alors être assez élevée. Dans ce cas, l'ajustement des paramètres A_{kl} et B_{kl} ne se fait, en réalité que sur ce genre de points puisque l'écart dû aux autres points d'ELV est négligeable. Ce phénomène peut donc entraîner une mauvaise représentation des ELV où $0.01 < x_1$ et $y_1 < 0.99$, et une mauvaise restitution du lieu des points critiques. Pour limiter ce problème, les points dont $x_1 < 0.01$ et $y_1 > 0.99$ qui présentent un écart supérieur à 45% sont automatiquement exclus du calcul de la fonction objectif globale.

III.3. Définition des groupes du modèle PPR78

La définition des groupes repose sur un compromis entre une précision et une capacité de prédiction du modèle PPR78, par exemple si l'on considère le cas limite (1 groupe = 1 molécule), la méthode de contributions de groupes possède une précision maximale mais une capacité de prédiction minimale tandis qu'un grand nombre de groupes définis pour une molécule donnée diminue la précision de la prédiction. Un nombre trop faible ou trop grand de groupes peut impacter significativement la qualité des résultats obtenus par le modèle. A l'heure actuelle, 21 groupes sont définis pour le modèle PPR78 (voir le tableau 1).

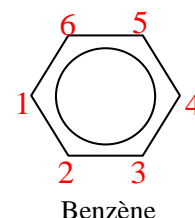
Tableau 1 Définition de groupes dans le modèle PPR78.

N°	Groupe	Description	Exemple
1	CH ₃	C'est le groupement méthyle. Il est présent deux fois dans tous les alcanes linéaires. On le trouve dans les alcanes ramifiés. Il peut également être présent chez les cycloalcanes ou les molécules aromatiques.	 Propane
2	CH ₂	C'est le groupement méthylène. Il est présent dans les alcanes linéaires, ramifiés. Il n'est jamais impliqué dans une insaturation (cycle ou liaison double). Il ne figure donc que dans les groupements alkyles des cycloalcanes et des molécules aromatiques.	 Propane
3	CH	C'est le groupement méthyne. Comme le précédent, ce groupe est rencontré chez les alcanes ramifiés (mais pas linéaires) ou dans les groupements alkyles des molécules. Il n'est jamais impliqué dans une insaturation.	 Isobutane
4	C	Comme les deux précédents groupes, le groupe 4 figure dans les alcanes ramifiés (mais pas linéaires) et les groupements alkyles. Il n'est pas mis en jeu dans une insaturation.	 2,2-diméthylpropane
5	CH ₄	Le groupe méthane est particulier. C'est une molécule qui a été exclue de la série homologue des alcanes linéaires car elle possède un comportement atypique et	

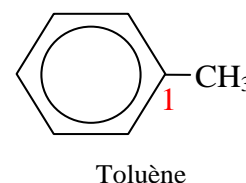
n'est pas représentée correctement lorsqu'elle est incluse avec les autres molécules de la même série. On notera que les premières molécules d'une série homologue doivent souvent faire l'objet d'un traitement spécifique dans la mise en œuvre des méthodes de contributions de groupes.

6 C_2H_6 Le cas de la molécule d'éthane est complètement identique à celui de la molécule de méthane. Sa représentation par deux groupes CH_3 n'est pas réaliste. Elle constitue donc un groupe à elle seule.

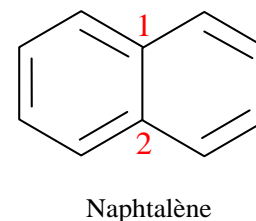
7 CH_{aro} Ce groupe décrit tous les groupes CH impliqués dans un cycle aromatique. Il est différent du groupe CH impliqué dans des chaînes alkyles. On illustre ce groupe par la molécule de benzène qui le contient six fois.



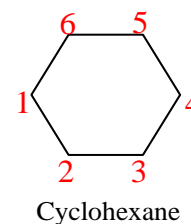
8 C_{aro} De même que le groupe CH_{aro} , ce groupe C_{aro} n'est présent que dans les noyaux aromatiques. A titre d'exemple, on le retrouve une fois dans la molécule de toluène.



9 $C_{\text{poly aro}}$ Ce groupe matérialise les atomes de carbone impliqués simultanément dans deux cycles aromatiques. Dans la plupart des cas, les contributions de ce groupe sont identiques à celles du groupe C_{aro} . Dans certains cas particuliers, on peut être amené à différencier ces deux groupes. On illustre ce groupe par la molécule de naphthalène qui le contient deux fois.

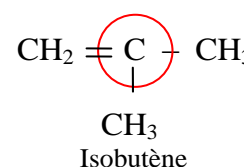
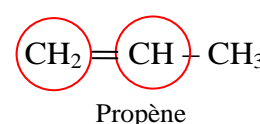
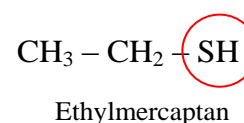
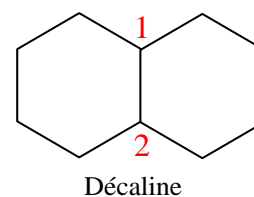


10 $CH_{2, \text{cycl}}$ Ce groupe n'est présent qu'à l'intérieur du cycle d'un cycloalcane. Il ne doit pas être confondu avec le groupe 2. Il est par exemple présent six fois dans la molécule de cyclohexane.

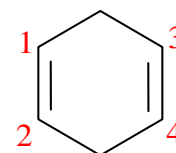


11 $-CH_{\text{cycl}}$ / A l'instar du précédent, ce groupe n'est présent que dans

- C_{cycl} les cycles des cycloalcane. On notera que le modèle PPR78 ne fait pas la distinction entre le groupe CH et le groupe C lorsque ceux-ci sont impliqués dans un cycle. On peut le trouver, par exemple, deux fois dans la molécule de décaline.
- 12 CO₂ La molécule de dioxyde de carbone
- 13 N₂ La molécule de diazote
- 14 H₂S La molécule de sulfure d'hydrogène.
- 15 -SH Ce groupe sulfhydryle caractérise la fonction chimique thiol (équivalent de la fonction alcool dans laquelle l'atome d'oxygène est remplacé par le soufre). Il est impliqué dans toutes les molécules de mercaptans (R-SH, où R désigne un groupement alkyle quelconque). On le trouve, par exemple, une fois dans la molécule d'éthanethiol ou éthylmercaptan.
- 16 H₂O La molécule de l'eau
- 17 C₂H₄ C'est la molécule d'éthylène. Elle est la première molécule dans la série homologue des alcènes linéaires. Comme la molécule de méthane, cette molécule a été exclue des autres composés de la série en raison de son comportement atypique.
- 18 =CH_{2,alcène} / =CH_{alcène-} Ce groupe est présent dans les molécules des alcènes linéaires, ramifiés ou dans les groupements alkyles des molécules (mais jamais des carbones impliqués dans un noyau aromatique ou un cycle). Il ne doit pas être confondu avec les groupes 2, 3, 7, 10 et 11. La molécule de propène contient un groupement CH_{2, alcène} et un groupement CH_{alcène} donc le groupe 18 est présent deux fois.
- 19 =C_{alcène<} A l'instar du précédent, ce groupe n'est présent que dans les alcènes linéaires, ramifiés ou dans les groupements alkyles des molécules. A titre d'exemple, on illustre ci-après ce groupe par la molécule d'isobutène.



- 20 $=\text{CH}_{\text{cyc,alcè}}$ / $=\text{C}_{\text{cyc,alcè}}$ Ce groupe n'est présent que dans les cycles des cycloalcènes, mais pas dans un noyau aromatique ou dans un naphthalène. Il ne doit pas être confondu avec les groupes 3, 4, 7, 8, 9, 11, 18 et 19. Par exemple, le groupe 20 est présent quatre fois dans la molécule de cyclohexa-1, 4-diène.
- 21 H_2 La molécule d'hydrogène



Cyclohexa-1,4-diène

IV. Application

IV.1. Production de biodiesel par voie supercritique

IV.1.1. Procédés de fabrication des biodiesels

Le bioéthanol et le biodiesel sont des biocarburants, c'est-à-dire des carburants non fossiles issus de la biomasse. Par leurs propriétés similaires à celles des carburants conventionnels et leur caractère renouvelable, ils constituent des alternatives prometteuses pour remplacer à court terme l'essence et le gazole (au moins partiellement). Les biocarburants actuellement commercialisés (dits de première génération) sont issus de ressources extraites de la biomasse agricole comestible. Le bioéthanol est obtenu à partir de plantes sucrières (on parle de filière alcool) et est utilisable dans les moteurs à essence, tandis que le biodiesel est obtenu à partir d'oléifères (on parle de filière huile) et est utilisable dans les moteurs diesel. Ces ressources subissent ensuite une conversion en plusieurs étapes reposant sur des transformations mécaniques, chimiques (ou biochimiques) et thermiques.

■ Transformation chimique de l'huile extraite de la biomasse :

Les huiles directement extraites de la biomasse possèdent une viscosité, une densité et une masse molaire très supérieures de celles des carburants commerciaux et ne peuvent pas être utilisées en l'état dans les moteurs classiques. Pour contourner ce problème, les extraits subissent une *transestérification* produisant un biocarburant dont les propriétés physico-chimiques sont semblables à celles des gazoles. Le réactif alcool classiquement utilisé pour réaliser cette réaction est le *méthanol*. L'ester produit est appelé *ester méthylique d'acide gras* (EMAG) [101].

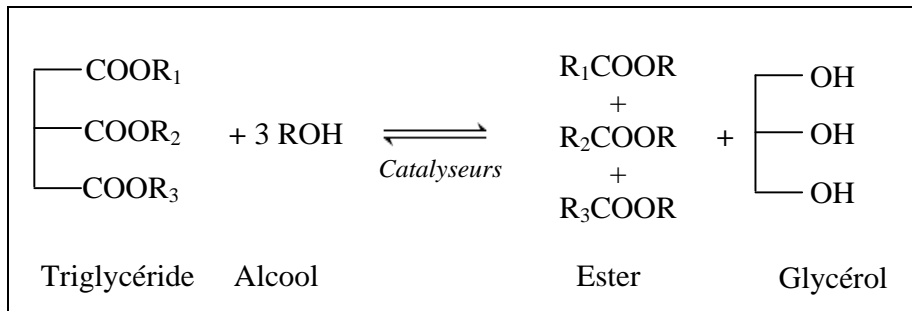


Fig. 17 R\u00e9action de transest\u00e9rification.

■ Caract\u00e9ristiques des proc\u00e9d\u00e9s classiques de fabrication de biodiesel :

- **Sch\u00e9ma r\u00e9actionnel** : la r\u00e9action globale de transest\u00e9rification pr\u00e9sent\u00e9e ci-dessous est la somme de trois r\u00e9actions cons\u00e9cutives :

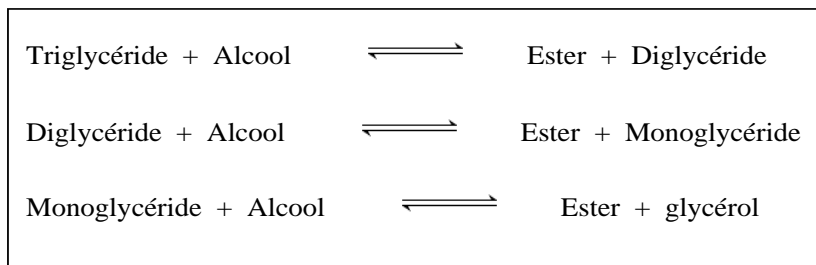


Fig. 18 Trois r\u00e9actions cons\u00e9cutives dans le milieu r\u00e9actionnel de la transest\u00e9rification.

Par cons\u00e9quent, le milieu r\u00e9actionnel contient non seulement le m\u00e9thanol, le glyc\u00e9rol, les triglyc\u00e9rides et les EMAG (biocarburant) mais \u00e9galement des mono- et diglyc\u00e9rides.

- **\u00c9tat physique du milieu r\u00e9actionnel** : la r\u00e9action de transest\u00e9rification ci-dessus produit du biodiesel (EMAG) et du glyc\u00e9rol qui ne sont pas miscibles. Le glyc\u00e9rol est alors \u00e9limin\u00e9 par d\u00e9cantation.

- **D\u00e9placement de l'\u00e9quilibre thermodynamique** : l'\u00e9quilibre chimique \u00e9tant inversible, il peut \u00eatre d\u00e9plac\u00e9 vers la formation des esters en \u00e9liminant le glyc\u00e9rol du milieu r\u00e9actionnel. C'est l'id\u00e9e de base du proc\u00e9d\u00e9 Henkel conduisant la transest\u00e9rification en deux \u00e9tapes avec \u00e9limination interm\u00e9diaire du glyc\u00e9rol.

- **Cin\u00e9tique** : pour acc\u00e9l\u00e9rer la transest\u00e9rification, un catalyseur homog\u00e8ne (acide ou basique) ou h\u00e9t\u00e9rog\u00e8ne est utilis\u00e9. \u00c0 l'heure actuelle, la catalyse homog\u00e8ne basique est pr\u00e9f\u00e9rentiellement utilis\u00e9e car la r\u00e9activit\u00e9 obtenue en milieu basique est meilleure qu'en milieu acide [102]. L'eau est un poison de ces catalyseurs et doit donc \u00eatre \u00e9vit\u00e9e lors de l'\u00e9tape de synth\u00e8se du biodiesel [103]. Dans le cas de la catalyse homog\u00e8ne, le proc\u00e9d\u00e9 n\u00e9cessite une \u00e9tape d'\u00e9limination du catalyseur par lavage \u00e0 l'eau.

- **Prétraitement des ressources lipidiques** : les acides gras libres contenus dans l'huile réagissent avec le catalyseur pour former des savons alcalins [fig. 19] (réaction de saponification, favorisée par la présence d'eau).

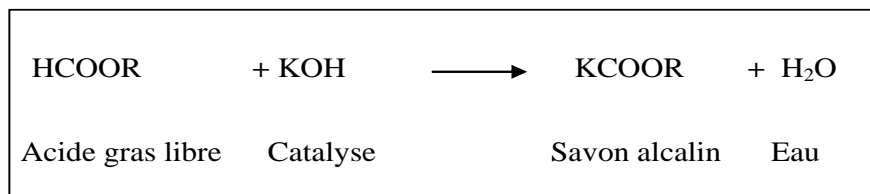


Fig. 19 Réaction de saponification

Ces acides gras libres sont présents dans la majorité des sources lipidiques non alimentaires. Par exemple, la forte acidité libre contenue dans les graisses animales interdit leur utilisation directe dans les unités de fabrication de biodiesel et requiert un prétraitement visant à réduire cette acidité libre par estérification en milieu acide.

■ **Procédé exploratoire de fabrication de biodiesels par voie supercritique :**

De nombreuses études ont démontré la faisabilité et les atouts du procédé de production du biodiesel par voie supercritique comparativement au procédé classique : un temps de réaction plus court, de hauts rendements en biodiesel mais surtout, une absence de catalyseur (et donc une réduction significative des équipements et effluents grâce à la suppression d'unités de prétraitement des ressources et d'élimination du catalyseur) [104]. En outre, la présence d'eau dans le procédé par voie supercritique peut s'avérer bénéfique à la production de biodiesel : alors qu'elle induit des rendements quasi nuls en procédé classique [105]. En effet, en milieu supercritique, l'eau hydrolyse les triglycérides en acides gras libres [fig. 20] qui à leur tour subissent une estérification [fig. 21], celle-ci étant plus rapide que la transestérification des triglycérides.

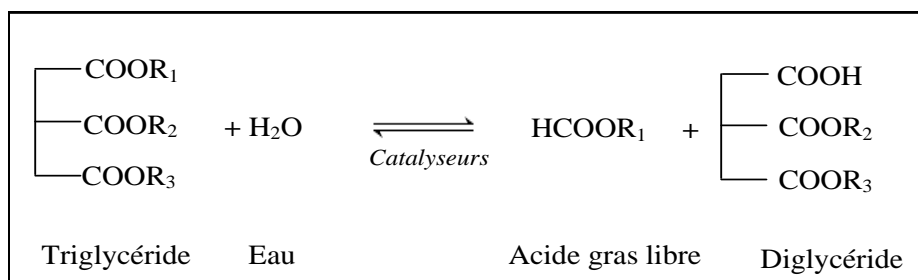


Fig. 20 Réaction de l'hydrolyse

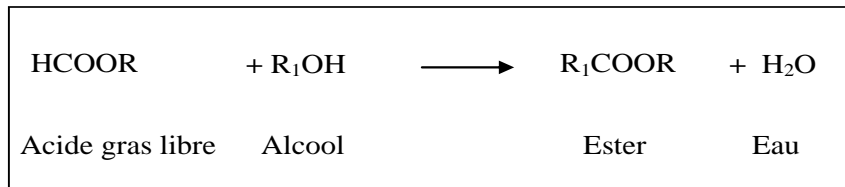


Fig. 21 Réaction de l'estérification

■ Biodiesel méthylique versus biodiesel éthylique :

Dans le cadre du procédé classique (avec catalyseur), alors que le bioéthanol est non-toxique et peut être produit exclusivement par des voies biologiques, le (bio)méthanol reste toutefois l'alcool de prédilection en raison de son coût moindre et des difficultés techniques qu'engendrerait le passage du (bio)méthanol au bioéthanol : temps de réaction légèrement plus long, séparation et purification du biodiesel et du glycérol plus délicates avec formation d'émulsions plus stables et une plus grande solubilité du glycérol dans les esters éthyliques.

Lors du passage à un procédé supercritique sans addition de catalyseur, le problème d'émulsion est évité ; néanmoins subsistent, pour des rendements identiques en esters : un temps de réaction généralement plus long en éthanolyse qu'en méthanolyse, mais qui reste malgré tout acceptable, une plus grande solubilité du glycérol dans les esters éthyliques que méthyliques, qui pourrait cependant être résolue soit par évaporation de l'alcool, soit par addition de glycérol à froid dans le milieu. Enfin, le seul inconvénient majeur du procédé par voie supercritique est sa demande énergétique induite par des conditions opératoires plus sévères qu'avec le procédé classique.

IV.1.2. Apport de la thermodynamique à l'étude d'un procédé de synthèse de biodiesel par voie supercritique : présentation de nos objectifs

L'étude thermodynamique que nous souhaitons mener s'insère dans le cadre d'un projet d'étude et de conception d'un procédé exploratoire de fabrication de biodiesel par éthanolyse supercritique de lipides. Dans le procédé étudié, un cosolvant (le dioxyde de carbone) est ajouté au milieu réactionnel afin de réduire la sévérité des conditions opératoires; de plus, le procédé étudié a recours à une unité de cogénération biodiesel-chaleur-électricité dans le but d'améliorer son bilan exergétique. Afin de dimensionner le procédé, d'en réaliser l'optimisation énergétique, de déterminer les conditions opératoires permettant de satisfaire à la fois aux exigences de débit et de pureté, **l'étude thermodynamique des mélanges impliqués dans le procédé est une étape préliminaire incontournable.**

Si l'on se concentre sur le milieu réactionnel dans lequel la réaction de transestérification s'opère, on recense les catégories de molécules suivantes :

- les triglycérides TG (réactifs de la synthèse présents dans les ressources lipidiques),
- l'éthanol EtOH (réactif de la synthèse),
- les esters éthyliques ou les biodiesels EEAG (produits de la synthèse),
- les monoglycérides MG (produits intermédiaires de la synthèse),
- les diglycérides DG (produits intermédiaires de la synthèse),
- le glycérol G (produit de la synthèse),
- l'eau (présente dans les ressources lipidiques),
- le dioxyde de carbone CO₂ (cosolvant, réactif de la synthèse).

■ Première étape du projet

Le projet de modélisation thermodynamique du milieu réactionnel complexe décrit ci-dessus a débuté en janvier 2013 et s'inscrit nécessairement sur le long terme. Pour découvrir le modèle le mieux adapté à la représentation de ces mélanges, il a été décidé de se concentrer sur la représentation des 28 différentes interactions binaires qu'il est possible de définir à partir des huit différents types de molécules présentes dans le mélange (voir le tableau 2).

Tableau 2 Interactions binaires présentes dans le milieu réactionnel : (X) : interactions binaires étudiées expérimentalement dans ce travail.

	TG	DG	MG	G	EtOH	EEAG	CO ₂	Eau
TG								
DG	X							
MG	X	X						
G	X	X	X					
EtOH	X	X	X	X				
EEAG	X	X	X	X	X			
CO ₂	X	X	X	X	X	X		
Eau	X	X	X	X	X	X	X	

On notera que la quasi-totalité des modèles thermodynamiques utilisent dans leur formulation des paramètres d'interactions binaires dont l'estimation peut être effectuée à partir de données d'équilibre de phases sur les systèmes binaires correspondants. Nous avons décidé de nous intéresser dans un premier temps aux interactions entre les esters éthyliques d'acides gras (EEAG) et le dioxyde de carbone et entre les esters éthyliques d'acides gras et l'éthanol (ces interactions sont matérialisées par une croix rouge dans le tableau 2)

■ Méthodologie de modélisation.

Deux exemples d'EEAG fabriqués à partir des ressources lipidiques concernées par le projet d'étude d'un procédé de synthèse de biocarburant par voie supercritique sont indiqués dans la fig. 22.

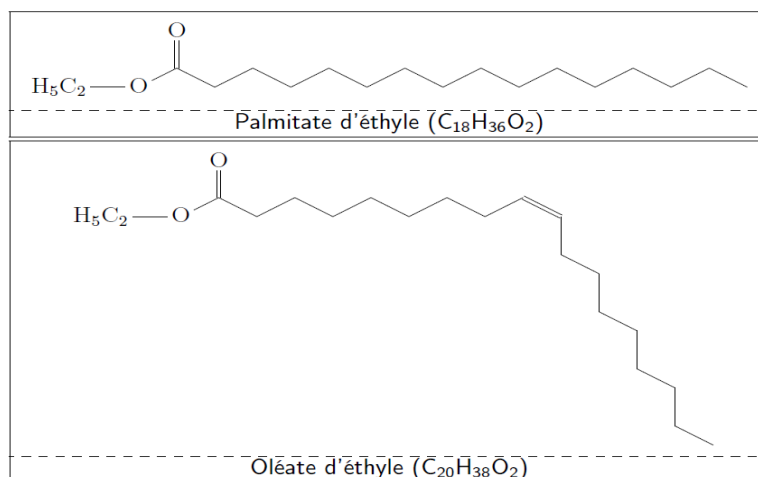


Fig. 22 Représentation d'EEAG présents dans les ressources lipidiques considérées

Puisque la réaction de transestérification s'effectue en milieu supercritique, une équation d'état s'impose pour en effectuer la modélisation. En raison de la grande diversité des molécules d'EEAG susceptibles d'être considérées, il a été décidé d'avoir recours à une équation d'état prédictive dont les paramètres d'interactions binaires seront décrits à partir d'une méthode de contributions de groupes. Le schéma de décomposition en groupes des molécules d'EEAG que nous avons adopté définit quatre groupes élémentaires résumés dans la fig. 23.

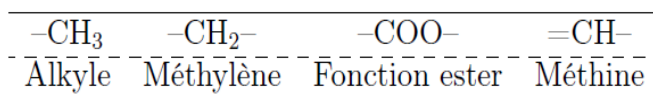


Fig. 23 Groupes élémentaires présents dans les EEAG.

Les molécules de dioxyde de carbone et d'éthanol seront considérées comme deux groupes élémentaires.

En 2003, Polishuk et al. [106] ont montré qu'à partir de la connaissance de quelques données expérimentales bien choisies- les points critiques terminaux (CEP) et les points critiques singuliers du lieu des points critiques dans le plan P - T , il était possible de réaliser une détermination des paramètres de l'équation d'état de grande qualité. À de multiples reprises lors de la mise au point du modèle PPR78, nous avons pu constater la justesse des propos de Polishuk et al. [106]. Ces réflexions peuvent d'ailleurs être étendues aux lieux des points critiques complets qui en pratique, caractérisent pleinement les systèmes binaires auxquels ils sont associés. Par métaphore, le lieu des points critiques est à un système binaire ce que l'ADN est à un individu [5].

De plus, une recherche bibliographique des données d'équilibre entre phases disponibles dans la littérature concernant les systèmes ester éthylique + CO₂ et ester éthylique + éthanol a mis en évidence un nombre de points expérimentaux faible ainsi qu'une importante dispersion expérimentale (ces données bibliographiques sont décrites par la suite). Partant de ce constat, nous avons décidé d'effectuer nos propres mesures d'équilibre de phases sur ces deux types de systèmes afin de développer les méthodes de contributions de groupes.

Finalement, les interactions CO₂ + ester éthylique et éthanol + ester éthylique seront caractérisées expérimentalement par la mesure de lieux des points critiques. À partir de ces résultats expérimentaux, il sera possible de développer des méthodes de contributions de groupes pour l'estimation des paramètres d'interactions binaires d'équations d'état :

- de type Van der Waals (avec des règles de mélange classiques ou sophistiquées),
- dérivant de la théorie d'association moléculaire SAFT.

Le choix de l'équation d'état n'est pas la préoccupation première de ce chapitre qui est consacré à la caractérisation expérimentale d'interactions binaires. Le projet ayant tout récemment débuté, nous avons décidé de recourir dans un premier temps au modèle prédictif PPR78. Bien que l'usage d'une équation d'état cubique avec des règles de mélange de moyenne complexité soit certainement peu approprié pour le type de mélange considéré, il nous paraissait cependant intéressant d'en discuter les capacités et les limitations.

IV.2. Comportement de phases des nouveaux réfrigérants

Aujourd'hui, la production du froid représente une partie considérable de la consommation énergétique dans le monde. Elle couvre un large domaine d'applications : la

réfrigération, la conservation alimentaire et non-alimentaire, la climatisation automobile, etc. Le fonctionnement de la quasi-totalité des systèmes actuels est basé sur le principe thermodynamique qui consiste à utiliser l'énergie thermique produite par le changement d'état (liquide - vapeur) d'un fluide frigorigène. Ce type de fluide doit présenter des caractères spécifiques permettant un bon transfert de chaleur et une bonne efficacité énergétique du système.

IV.2.1. Limitations des réfrigérants conventionnels

Les fluides frigorigènes ont subi quatre évolutions principales liées à quatre générations de fluides :

■ **1^{ère} génération**

Les premiers réfrigérants ou les réfrigérants naturels sont les composés organiques ou inorganiques très présents dans la nature, par exemple, les hydrocarbures, l'ammoniac (NH_3), le dioxyde de soufre (SO_2), le dioxyde de carbone (CO_2), le chlorure de méthyle (CH_3Cl), etc. Les inconvénients principaux de ces fluides sont la toxicité et l'inflammabilité.

■ **2^{ème} génération**

La deuxième génération de fluides est arrivée dans les années 1930 sous la forme de fluides synthétiques, offrant performance, sécurité et durabilité. Ce sont les chlorofluorocarbures (CFC) et les hydrochlorofluorocarbures (HCFC). Ces substances sont très stables, incolores, inodores, non-inflammables, peu toxiques et non-corrosives à l'état gazeux ou liquide. Les CFC se décomposent peu et restent inchangés dans l'atmosphère pendant de nombreuses décennies. Les HCFC sont moins stables et se décomposent dans un laps de temps d'environ 10 ans. En 1974, les fluides de deuxième génération ont été suspectés d'être responsables de la destruction de la couche d'ozone [107]. L'indice d'impact sur la couche d'ozone est l'ODP (Ozone Depletion Potential). La valeur de référence est celle du R12 ($\text{DOP}_{\text{R12}} = 1$). En 1987, le protocole de Montréal qui est un accord international visant à réduire de moitié les substances qui appauvrissent la couche d'ozone, impose la suppression de la production et la consommation des CFC [108]. En 1992, le protocole de Kyoto impose la suppression de l'utilisation des HCFC. De ce fait, l'utilisation des CFC est entièrement supprimée en 1996 dans les pays développés et en 2010 dans les pays en voie de développement. La suppression totale des HCFC est prévue avant 2020.

■ 3^{ème} génération

Les réfrigérants de troisième génération sont les hydrofluorocarbures (HFC) qui ne contiennent pas d'atome de chlore et ne participent donc pas à la destruction de la couche d'ozone. Ces substances sont non toxiques et ininflammables. Elles se décomposent dans l'atmosphère dans un délai variant de 30 à 50 ans. L'avantage de ces fluides est qu'ils peuvent être utilisés dans un grand nombre d'applications et qu'ils présentent des risques minimes même en cas de fuite. De plus, ils sont parfaitement compatibles avec les différentes huiles utilisées pour les compresseurs. Cependant, les HFC sont classés dans la catégorie des gaz à effet de serre selon le protocole de Kyoto [109]. L'effet de serre est le phénomène de réchauffement de l'atmosphère sous l'effet du rayonnement solaire en présence de certains gaz. L'indice d'impact sur le réchauffement global est le GWP (Global Warming Potential). La référence est celle du CO₂, exprimé en kilogramme de CO₂ présent dans l'atmosphère sur une durée de vie de 100 ans.

Tableau 3 Valeurs de DOP et de GWP des certains réfrigérants conventionnels.

génération	Réfrigérant	Formule chimique	DOP	GWP
1 ^{ère} génération	R717	NH ₃	0	0
	R744	CO ₂	0	1
	R290 (propane)	C ₃ H ₈	0	3
	R600a (iso-butane)	C ₄ H ₁₀	0	3
2 ^{ème} génération	CFC-R11	CCl ₃ F	1	1400
	CFC-R12	CCl ₂ F ₂	1	10600
	CFC-R13	CClF ₃	1	11700
	HCFC-R22	CHClF ₂	0.055	1810
3 ^{ème} génération	HFC-R23	CHF ₃	0	14800
	HFC-R32	CH ₂ F ₂	0	675
	HFC-R125	CF ₃ -CHF ₂	0	3500
	HFC-R134a	CH ₂ F-CF ₃	0	1430
	HFC-R152a	CH ₃ -CHF ₂	0	124

En 2006, le parlement européen a voté dans le cadre de la climatisation automobile, secteur dans lequel les taux de fuite sont élevés, l'interdiction d'intégration des réfrigérants ayant un GWP

supérieur à 150 dans les véhicules neufs à partir de 2017 [110]. Le tableau 3 présente les valeurs de DOP et de GWP de certains réfrigérants [111].

IV.2.2. Recherche et développement des nouveaux réfrigérants (4^{ème} génération) : présentation de nos objectifs

Les réfrigérants de quatrième génération sont en cours de recherche et développement. L'objectif principal de la recherche est de trouver des fluides ayant un faible GWP permettant ainsi de réduire l'impact sur le réchauffement de la planète et possédant des propriétés, induisant une performance et une efficacité similaires des HFC. Les chercheurs ont, actuellement, envisagé de synthétiser de nouvelles substances pouvant remplacer les réfrigérants à fort GWP sans modification importante de technologie. Ils ont développé les hydrofluoroléfines (HFO). Certaines HFO et leurs propriétés thermodynamiques [112] sont présentées dans le tableau 4. Parmi les nouveaux réfrigérants, le HFO-R1234yf paraît être le candidat le plus sérieux comme remplaçant du R134a dans la climatisation automobile. Il offre des conditions de fonctionnement et des performances quasi-équivalentes au R134a [113-114], un très faible impact de réchauffement climatique (GWP = 4) [115] et ne détruit pas la couche d'ozone.

Tableau 4 Propriétés thermodynamiques de certaines hydrofluoroléfines (HFO)

réfrigérant	Formule chimique	Tc	Pc	pc	ω
HFO-R1225ye(E)	$\text{CF}_3\text{CF} = \text{CHF}$	386.8	3401	517	0.313
HFO-R1125ye(Z)	$\text{CF}_3\text{CF} = \text{CHF}$	379.3	3335	517	0.305
HFO-R1225zc	$\text{CF}_3\text{CH} = \text{CF}_2$	376.6	3312	517	0.303
HFO-R1234ye(E)	$\text{CHF}_2\text{CF} = \text{CHF}$	379.9	3534	473	0.290
HFO-R1234yf	$\text{CF}_3\text{CF} = \text{CH}_2$	369.3	3435	473	0.280
HFO-R1234ze(E)	$\text{CF}_3\text{CH} = \text{CHF}$	384.4	3576	473	0.295
HFO-R1234ze(Z)	$\text{CF}_3\text{CH} = \text{CHF}$	426.8	3970	473	0.333
HFO-R143zf	$\text{CF}_3\text{CH} = \text{CH}_2$	389.7	3849	423	0.284

Il pose cependant quelques soucis de sécurité au niveau de la limite d'inflammabilité. Cette caractéristique du HFO-1234yf freine l'industrie automobile vis-à-vis de son utilisation dans leurs véhicules. Le CO_2 peut également être un bon candidat de réfrigérant alternatif d'un point de vue environnement. Cependant, il possède une température critique faible et des pressions de vapeur élevées par rapport aux autres réfrigérants. Un petit changement de la température

provoque une grande variation de la pression. L'utilisation de CO₂ comme réfrigérant alternatif nécessite une grande modification des installations.

Pour réduire ces limitations, nous nous sommes intéressés aux mélanges de CO₂ + HFO qui permettent de diminuer la pression de vapeur de CO₂ ainsi que l'inflammabilité des HFO. L'objectif de ce travail est d'étudier le comportement de phases des mélanges binaires CO₂ + R1234yf et CO₂ + R1234ze (E).

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VALIDATION OF THE EXPERIMENTAL
PROCEDURES FOR CRITICAL POINT
MEASUREMENTS

I. Introduction

The critical point specifies the conditions (temperature, pressure, composition) at which a phase boundary ceases to exist. Although multiple types of critical points exist, this work only deals with vapour-liquid critical points. Knowledge of mixture critical data is important for both practical and theoretical reasons as well as for operation conditions of supercritical fluid extraction and for the development of thermodynamic models. As discussed by Privat and Jaubert [1], in order to improve the accuracy of prediction and extend the range of applicability of predictive equations of state, mixture critical data are absolutely necessary. This is the reason why it was decided to acquire a new synthetic - dynamic apparatus capable of determining the critical points of pure substances and multi-component mixtures. In order to obtain accurate experimental data, an apparatus calibration, experimental process and experimental result validations are strictly required.

The measurements of the critical point of pure components; CO₂, *n*-propane, *n*-butane, *n*-pentane, *n*-heptane and *n*-decane, for which literature data are available, were performed in order to check the performance and the reliability of the new apparatus. Firstly, the experimental procedure for determining the critical points of liquid/liquid binary mixtures (i.e. mixtures for which the two components are liquid at standard conditions) were established and validated. The binary systems *n*-pentane + *n*-heptane, *n*-pentane + *n*-decane and *n*-heptane + *n*-decane were studied. These systems were selected owing to their simple behaviour and their lack of critical experimental data in literature since only one publication focuses on their critical properties [2]. Secondly, the experimental method for measuring the critical points of liquid/gas binary mixtures (i.e. mixtures for which one component is liquid and another one is gaseous at standard conditions) are established and validated. The critical properties of the binary systems CO₂ + *n*-pentane, CO₂ + *n*-heptane and CO₂ + *n*-decane are investigated. These binary systems are of the highest interest in enhanced oil recovery processes [3]. They were selected in order to compare our data with those available in the open literature but also to complete the latter. For example, the CO₂ + *n*-pentane system has been studied by Leu and Robinson [4], Chen et al. [5], Gurdial et al. [6], Buechner [7], Cheng et al. [8] and by Poettmann and Katz [9]. The CO₂ + *n*-heptane system has been investigated by Gurdial et al. [6], Choi and Yeo [10], Kalra et al. [11], Chester and Haynes [12] and by Sun et al. [13]. The critical points of the CO₂ + *n*-decane system have been determined by Gurdial et al. [6], Chester and Haynes [12], Nagarajan and Robinson [14], Reamer and Sage [15], and by Polikhronidi et al. [16]. Unfortunately, in most cases, previous

researchers determining critical properties limit their investigations to a small section of the critical curve applicable to their particular research interest thus only investigating a small fraction of the entire critical loci of the mixtures. Thirdly, the establishment and the validation of the experimental method for measuring the critical points of gas/gas binary mixtures (i.e. mixtures for which the two components are gaseous at standard conditions) were performed. The systems $\text{CO}_2 + n$ -propane, $\text{CO}_2 + n$ -butane and n -propane + n -butane are studied. Such systems are of the highest interest in enhanced oil recovery (EoR) processes [17-18]. They were selected to compare our data with those available in the open literature [19-31]. Additionally, all of the experimental critical values measured in this work were compared to those predicted using the PPR78 model [32-39] since such a model is acknowledged to predict with high accuracy the critical locus of binary mixtures containing n -alkanes and $\text{CO}_2 + n$ -alkane up to n -decane.

The established experimental procedure is then applied for determining the critical points of the binary system acetone and chloroform. This system is studied with the aim of understanding the phase behaviour at high temperatures and pressures and checking the presence of a negative critical azeotrope (i.e. an intersection between the critical locus of the mixture and the azeotropic line).

II. Experimental procedure

II.1. Materials

All compounds were purchased from commercial sources and used without any further purification. The purities and the suppliers of the compounds are listed in Table 1.

Table 1 Purity and supplier of the compounds used in this study.

Compound	Purity (%)	Supplier
CO_2	99.998	Messer
n -propane	99.99	Messer
n -butane	100	Messer
n -pentane	99	Fluka
n -heptane	99	Fluka
n -decane	99	Sigma-Aldrich

II.2. Apparatus and procedure

A photo of the apparatus used in this work is presented in Fig. 1 whereas a schematic diagram can be seen in Fig. 2.



Fig. 1 Photo of the apparatus used in this study.

It has been developed by the ARMINES company hosted by the Ecole Nationale Supérieure des Mines de Paris for the measurement of the critical properties (critical temperature and critical pressure) of pure substances and multi-component mixtures with known overall composition. This apparatus can work using two different modes: dynamic or static. Both methods have advantages and limitations. Due to short residence time, the dynamic method enables to determine the critical point of substances likely to thermally decompose but needs a large amount of matter. On the other hand, the static method requires small amounts of substances but is limited to possible thermal decomposition of substances. The temperature and pressure upper limits of application are 673 K and 20 MPa for the dynamic method and 493 K and 20 MPa for the static method. When the dynamic mode is used, the magnetic stirrer is removed from the oven since the circulation of the fluid ensures an efficient stirring. On the other hand, such a magnetic stirrer is absolutely necessary in the static mode explaining why the working temperature is limited at 493 K which is the highest temperature that the stirrer may endure (another type of magnetic stirrer capable of enduring higher temperatures was not found). The experimental setup can be divided into three parts: (1) preparation of sample, (2) loading and (3) measurement.

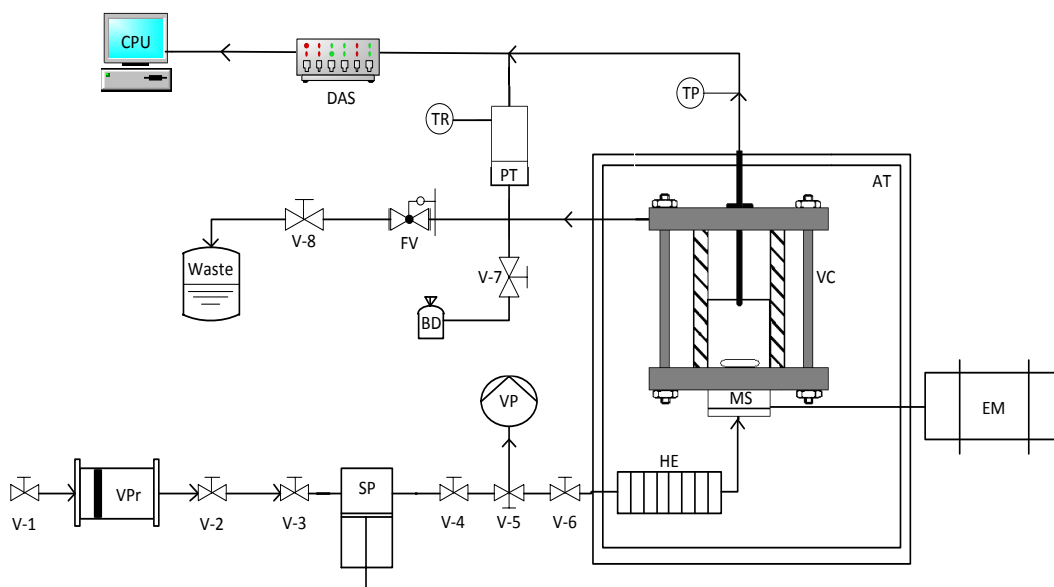


Fig. 2 Schematic diagram of the apparatus; PS: Pressurized source, VPr: Volumetric press, SP: Syringe pump, CB: Cryostat bath, VP: Vacuum pump, HE: Heat exchanger, EM: Electric motor, MS: Magnetic stirrer, VC: View cell, AT: Air thermostat bath (oven), TP: Platinum resistance temperature probe, PT: Pressure transducer, TR: Temperature regulator, BD: Bursting disc, FV: Flow regulation valve, DAS: Data acquisition system, CPU: Central processor unit and V: Valve.

II.2.1. Sample preparation

a. Pure components

The preparation part consists to degas liquid compounds. The liquid compound under consideration is placed in a 150 mL round-bottom flask and then degassed using a vacuum pump (OERLIKON LEYBOLD Model Trivac D2.5). Gas compounds are used without the degassing process.



Fig. 3 Experimental setup for degassing a liquid compound.

b. Liquid/liquid binary mixtures

The preparation part involves preparing a mixture with known overall composition and includes a 150 cm³ volumetric press, in which a homogenous mixture is prepared and also stored. In a first step, the volumetric press is evacuated using the vacuum pump [Fig. 4a] and weighed analytically using a microbalance (SARTORIUS AG Model MSE) having a precision of ± 1 mg. The less volatile compound is placed in the 150 mL round-bottom flask and degassed [Fig. 4b]. This compound is then transferred into the volumetric press [Fig. 4c]. The use of a hair dryer to heat the round-bottom flask and an ice water bath to cool the press aids the transfer process making it faster. The volumetric press and the contents are weighed [Fig. 4d]. In a second step, the same procedure is applied to the more volatile compound. The accurate composition of the mixture can thus be calculated knowing the mass of the two compounds. The volumetric press is finally coupled with flanges for pressurization in the next step [Fig. 4e].

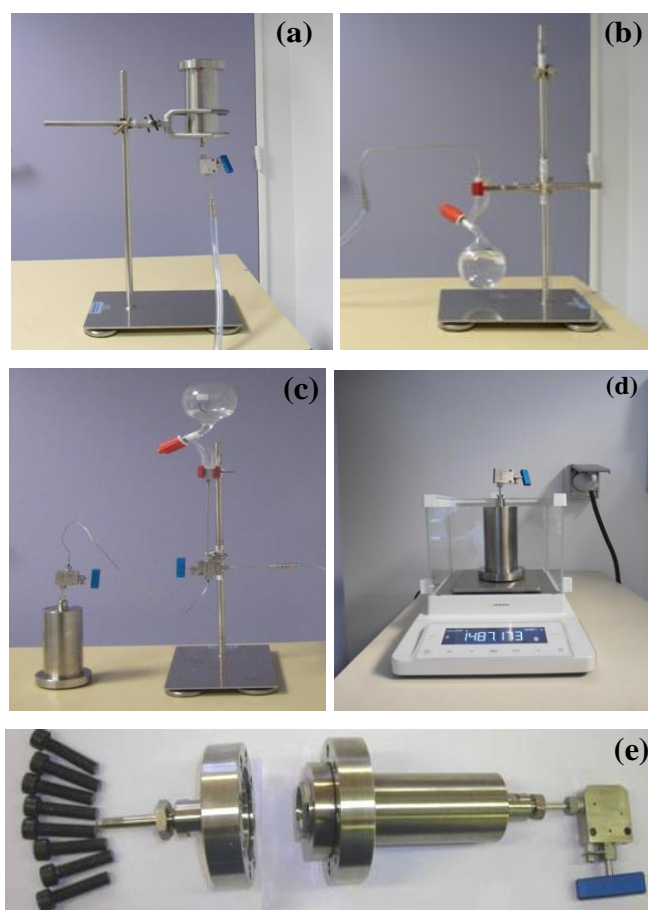


Fig. 4 Experimental setup for the preparation of a liquid/liquid binary mixture.

c. Liquid/gas binary mixtures

For the preparation of the liquid/gas binary mixtures, the liquid compound in the 150 mL round-bottom flask is degassed, transferred into the volumetric press and weighted. The gas compound is transferred directly into the volumetric press using a transfer circuit, until the desired mass is achieved [Fig. 5]. At compositions with high gas mole fraction, the press may be cooled during the transfer process of gas.



Fig. 5 Transfer of a gas compound from a gas cylinder to the volumetric press.

d. Gas/gas binary mixtures

The preparation part of the gas/gas binary mixtures includes a 260 cm³ syringe pump that is used to increase the pressure of pure gas – which is stored at low pressure inside the gas cylinder in which it is commercialized – and to transfer it into the volumetric press [Fig. 6]. Such a procedure which allows increasing the quantity of matter contained in press is used for pure propane and pure butane, which are sold in cylinders, the pressure of which is lower than 6 bar. Gases stored at high pressure inside the gas cylinder in which they are marketed can be directly transferred from this cylinder to the volumetric press (it is the case for pure CO₂).

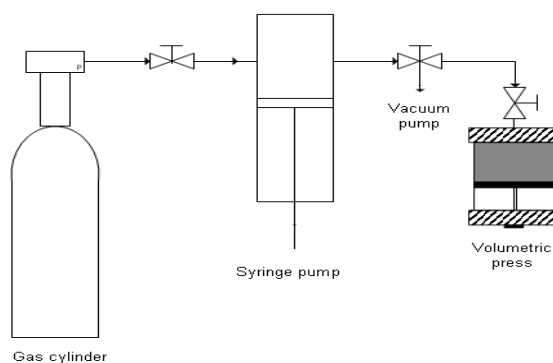


Fig. 6 Schematic diagram of the transfer process - for a gas contained at low pressure inside the gas cylinder – to the volumetric press.

Practically, the heavier gas compound (*n*-propane or *n*-butane) – contained at low pressure in the gas cylinder – is directly filled into the syringe pump and then pumped to the volumetric press that has been evacuated and weighed. The filling and pumping flow rates are regulated by the pump controller. At the end, the volumetric press and its contents are weighed. This procedure may be repeated several times so that the required amount of the first component is acquired. The syringe pump and the transfer circuits are evacuated before each filling procedure. To obtain maximum amount of gas transferable in each procedure, the syringe pump and the press are cooled using a cryostat bath (Fischer Scientific model Poly stat 37+R5) and the ice water bath, respectively. The same procedure is applied to the lighter gas compound if it is available in a low-pressure gas cylinder (this is the case for *n*-propane). It is important to ensure that pressure in the syringe pump is higher than that in the press before opening the valve of the press, causing the first component to enter the pump changing its initial mass. The accurate composition of mixture can thus be calculated using the known mass of the two compounds.

II.2.2. Sample loading

For pure components, the degassed liquid in the round-bottom flask or the gas component in gas cylinder can be directly transferred into the syringe pump using the transfer circuit. For mixtures, the loading part involves the transfer of the mixture contained in the volumetric press to the syringe pump without a change in the initial overall composition of the mixture. Under standard conditions, the mixture usually exists in two phases (liquid and vapour) in the press. The mole fraction of the more volatile component is higher in the vapour phase and lower in the liquid phase compared to the less volatile component and vice-versa. Hence, it is important to pressurize the press in order to obtain a monophasic liquid (i.e. an homogenous mixture) before transferring to the syringe pump avoiding only the liquid phase of the mixture going into the pump and changing the overall composition.

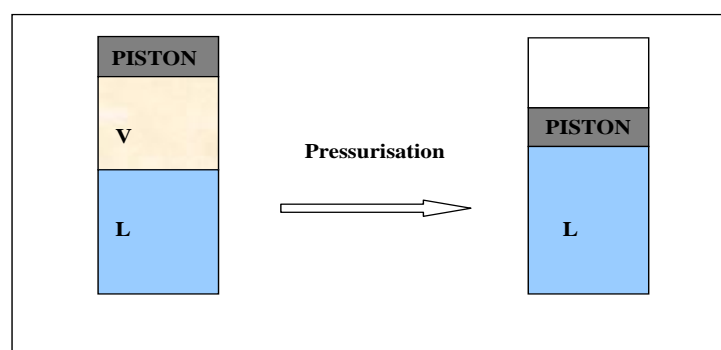


Fig. 7 Schematic diagram of the pressurisation process.

Pressure used in this process thus needs to be higher than the bubble pressure of the mixture studied at the temperature chosen. The volumetric press is connected to a pressurized nitrogen gas cylinder for pressurizing and to the syringe pump for transferring [Fig. 8]. Later on, valve V1 – for the pressurisation of the mixture in the press – is opened and then valves V2 and V3 are opened for the transfer of the mixture to the pump. The transfer process is stopped before pressure dropping in the syringe pump. The pressure in the syringe pump was kept higher than the bubble pressure of the mixture by mean of a pressure constant function of the pump syringe.

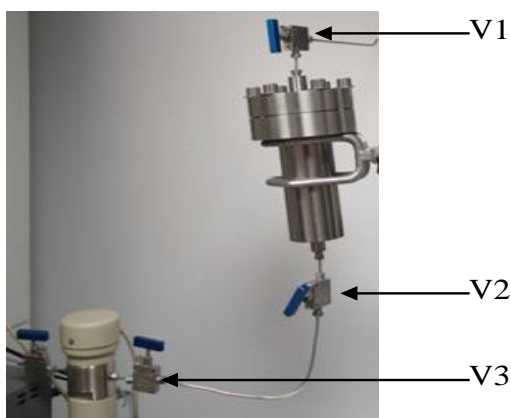


Fig. 8 Mixture transfer from the volumetric press to the syringe pump.

II.2.3. Critical point measurement

The measurement part is similar to the previous works of Soo et al. [40], Horstmann et al. [19, 41-43], Guilbot et al. [44] and Gil et al. [20].

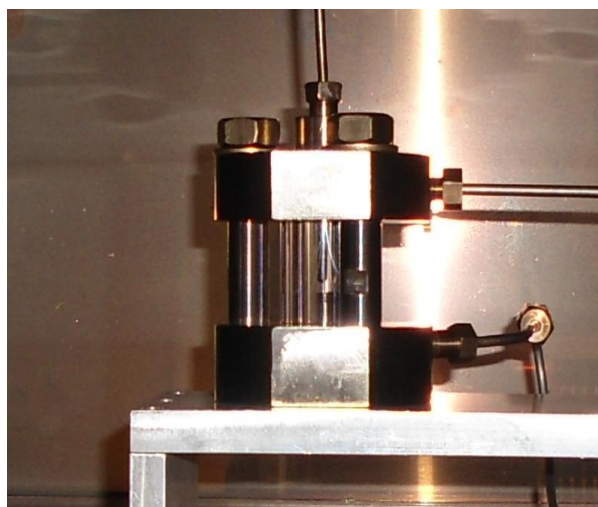


Fig. 9 Photo of the sapphire cell

A 4 cm³ titanium-flanged sapphire cell shown in Fig. 9 is placed in an air thermostat bath. The bottom flange holds a magnetic stirrer which couples with an electric motor (IKA RW 14 basic). The cell operates up to 20 MPa and 673 K. The cell temperature is measured using a Pt100 probe centred in the cell and connected to an electronic display. The cell pressure is measured with a pressure transducer (DRUCK, Model PTX611) which is kept at constant temperature of 100 °C by means of a heating cartridge regulated via a PID regulator (WEST, Model 6100). Experimental setup for calibration of temperature and pressure sensors is described in the appendix 1. Temperature calibration errors are ± 0.02 K and ± 0.15 K for the 323-443 K range and the 443-573 K range, respectively [Fig. 10]. Pressure calibration error is estimated to ± 0.1 kPa for the 0 - 6 MPa range [Fig. 11]. A video acquisition system (PANASONIC Model WV-CP290/G) which consists of an endoscope and a video camera is placed behind a window of the air thermostat bath. It is connected to a monitor for observing the view cell and the critical phenomena.

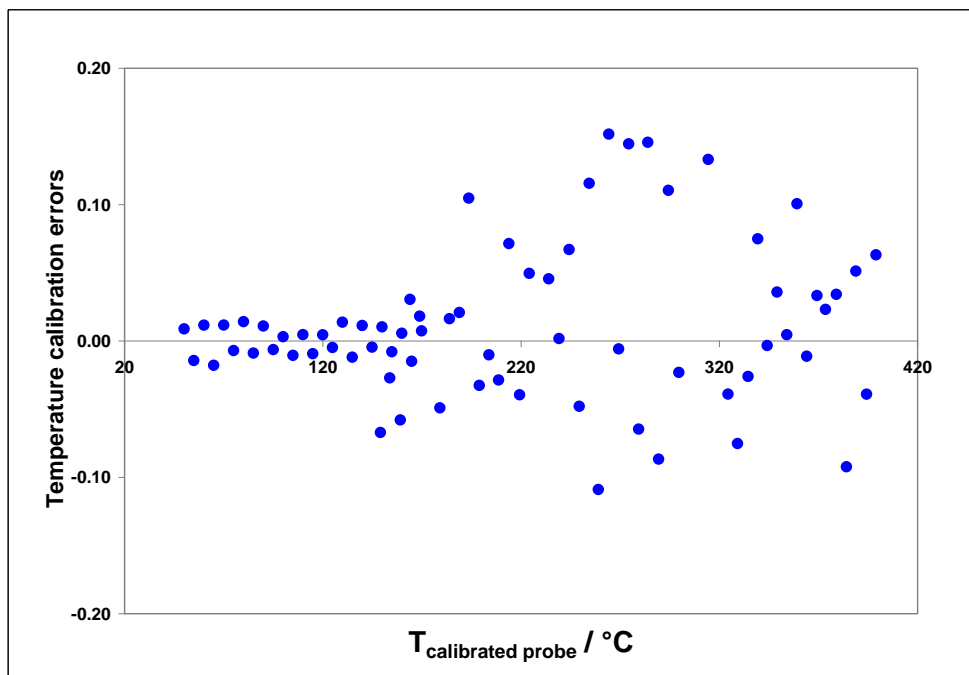


Fig. 10 Temperature calibration errors: the difference between temperatures determined using the calibrated probe and those determined using the Pt100 probe correlated one.

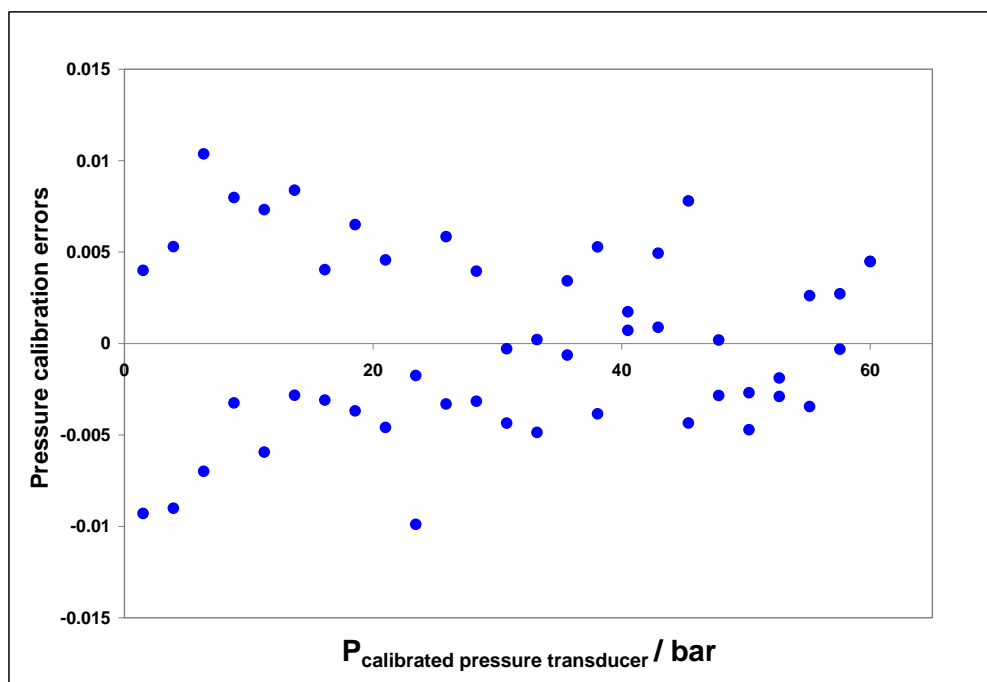


Fig. 11 Pressure calibration errors: the difference between pressures measured using the calibrated pressure transducer and those measured using the pressure transducer (available in our experiments) correlated one.

Before starting a measurement, the view cell and the transfer circuits are cleaned, evacuated and closed. The air thermostat is set below the expected critical temperature of the sample studied. The measurement starts by opening the outlet valve V4 of the pump for filling a half of the view cell with liquid. Liquid is passed through a short heating section before entering into the cell from the bottom. The pump has two control functions: constant flowrate (filling and pumping) and constant pressure, which are regulated by the pump controller. With the constant pressure function, the pressures in the pump and in the cell become equal. At this stage, there is a difference in temperature between the cell and the pump, hence, the presence of liquid-vapour in the cell and monophasic liquid in the pump. The monophasic state of the mixture in the pump ensures that the overall mole fraction remains unchanged when transferred to the cell. Then, the constant-pressure function is changed to constant flowrate.

When the dynamic method (open system) is preferred, a continuous flow through the view cell is necessary along the experiment. The sample in the syringe pump is pumped with a constant flowrate and the regulation valve V8 is opened. The mixture enters from the bottom and exits from the top of the view cell. The pumping flowrate (for fine adjustments) of the inlet and the regulation valves FV and V8 (for coarse adjustments) which control the outlet are adjusted regularly to maintain the halfway liquid level in the cell. The flowrate used varies between 2.5 to 5 mL/min.

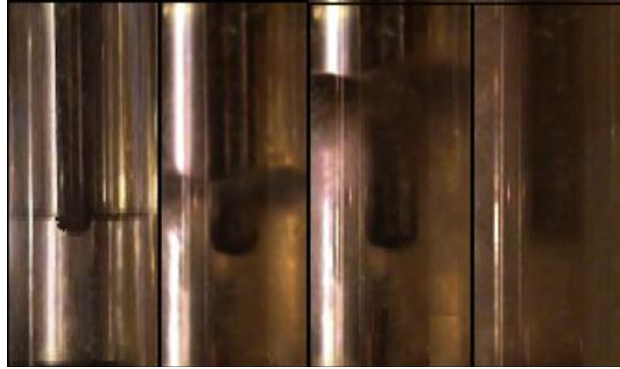


Fig. 12 Transition of a fluid from subcritical state to the critical state on temperature increase. From left to right: classical liquid – vapour mixture (the two phases are perfectly separated by a thin meniscus), cloudy subcritical state (the meniscus is not thin any more, it is coloured in orange which characterizes the critical opalescence), thick and cloudy subcritical state (the meniscus becomes thicker and thicker) and disappearance of the liquid – vapour interface (the meniscus occupies the entire view cell which is orange: we are at the critical point).

When the static method (closed system) is chosen, no inlets and outlets through the cell are needed. After reaching the halfway level liquid in the view cell, the pumping flowrate is stopped and the regulation valve FV is kept closed, except any changes in the level of liquid. This effect is compensated by the pumping flowrate when the liquid level decreases and the opening of regulation valve when liquid level increases. In the case of mixture, it is noticeable that the opening of the exit regulation valve to reduce the level of the liquid makes exit some vapour from the cell and thus makes change the overall composition of the system. Therefore, the static method can be used to determine the critical temperature and pressure but the corresponding overall composition is lost.

Whatever the method (static or dynamic), and as shown in Fig. 12, with increase in temperature at the rate of 0.5 K/min, the pressure increases and the vapour-liquid interface becomes cloudy, thick and then occupies the entire cell at the critical point. At the same time, the cell becomes orange which characterizes the critical opalescence. The temperature increasing and the liquid level maintaining in the cell can be plotted on the phase diagram (P - T) presented in Fig. 13. The critical point determination is indeed performed by following the 50% quality line.

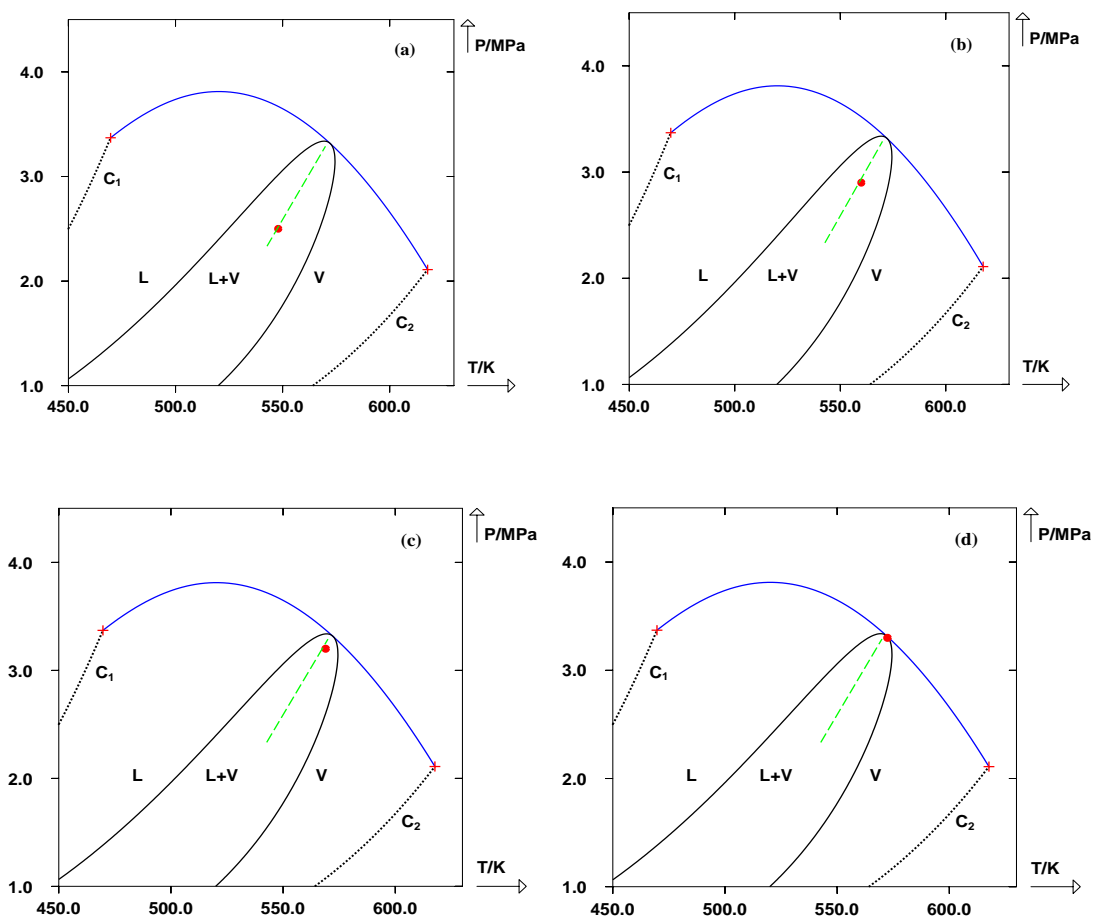


Fig. 13 Determination of the critical point by following the quality line.

After reaching one uncoloured supercritical phase, the temperature of the cell is gradually decreased by opening the ventilator of the air thermostat bath and the pressure of the cell is decreased by slightly opening the regulation valve or decreasing the pumping flowrate. At little above the critical temperature and pressure, the fluid colour changes from colourless to yellow, then from yellow to yellow-red and finally becomes dark-orange. Then the vapour-liquid interface reappears in the middle of the view cell. The critical temperature and pressure are recorded at the point when complete darkness is observed in the cell. For each measurement, the temperature-increasing and decreasing processes are repeated at least eight times and the average of the recorded temperatures and pressures is taken as the critical values reported here. The uncertainty calculation is presented in the Appendix 3.

III. Results and discussion

III.1. Pure components

The critical points of pure components: CO₂, *n*-propane, *n*-butane, *n*-pentane, *n*-heptane and *n*-decane were determined using the dynamic method and then compared to those collected by the DIPPR (Design Institute for Physical Properties) database [45] and the NIST (National Institute of Standard and Technology) database [46]. The comparison between the critical temperatures measured in this work and literature data is given in Table 1 of the Appendix 4, and the comparison between the critical pressures measured in this work and literature data is given in Table 2 of the Appendix 4. The agreement between our critical results and those found in the literature is highly satisfactory.

III.2. Liquid/liquid binary mixtures

The experimental procedure for determining the critical points of the liquid/liquid binary mixtures was established. The critical loci of the three binary systems were measured over the whole composition range, using the dynamic method. The experimental critical values with different mole fractions and their uncertainties for the systems *n*-pentane (1) + *n*-heptane (2), *n*-pentane (1) + *n*-decane (2) and *n*-heptane (1) + *n*-decane (2) are given in Tables 3, 4 and 5 of the Appendix 4, respectively. Experimental data for the *n*-pentane (1) + *n*-decane (2) are available in the open literature and are compared with our data whereas the critical loci of the *n*-pentane (1) + *n*-heptane (2) and *n*-heptane (1) + *n*-decane (2) systems are investigated for the first time in this work. Fig. 14 illustrates a comparison of the experimental critical data in this work with literature data and the predictions given by the PPR78 model. The critical temperatures of the system *n*-pentane (1) + *n*-decane (2) from the collection of Hicks and Young [2] were used as literature data. They show a good correlation with our experimental data as can be seen in Fig. 14c. The discrepancies between the two data set never exceed 2 K.

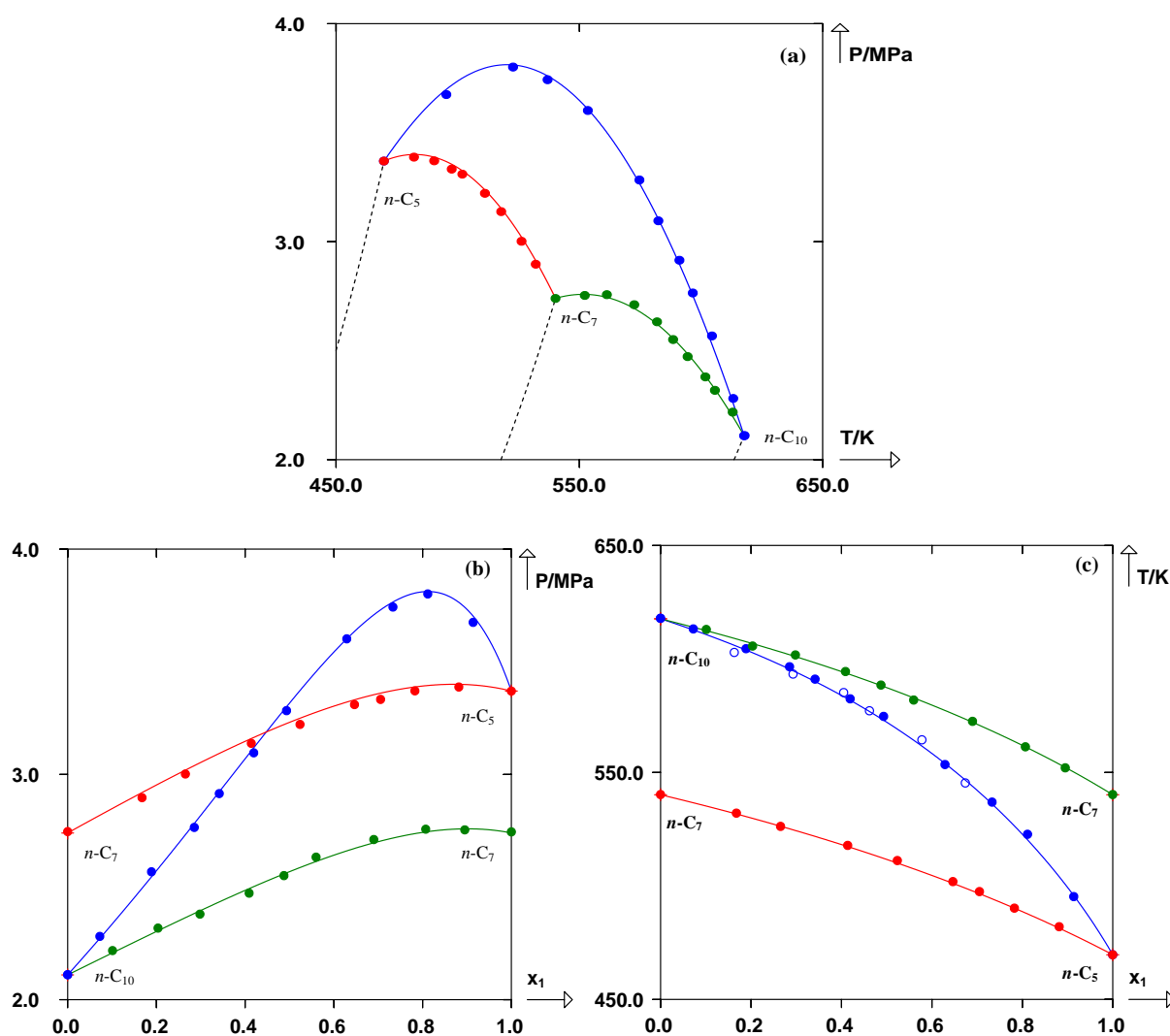


Fig. 14 Critical locus for the systems: *n*-pentane (1) + *n*-heptane (2), *n*-pentane (1) + *n*-decane (2) and *n*-heptane (1) + *n*-decane (2) in (a) *P-T* projection, (b) *P-x* projection and (c) *T-x* projection. (Solid lines): predicted curves with the PPR78 model, (dashed lines): vaporization curves of pure components, Experimental critical points: (●): this work and (○): Hicks and Young [11].

For all three binary systems, the experimental critical points superimpose perfectly on the critical loci predicted by the PPR78 model in pressure-temperature (*P-T*), pressure-composition (*P-x*) and temperature-composition (*T-x*) projections. We know that such a model is able to predict with high accuracy the critical loci of binary mixtures containing alkanes and we thus can be confident in our experimental data. The average discrepancies between the experimental values and the values predicted by the PPR78 model are 0.008 for the critical composition and 0.014 MPa for the critical pressure. These three binary systems show monotonous behaviour of critical temperature vs. composition and a maximum in critical pressures. Therefore, these systems

belong to the type I fluid phase behaviour according to the classification of binary phase diagrams proposed by Van Konynenburg and Scott [47].

III.3. Liquid/gas binary mixtures

In this part, the experimental procedure for determining the critical points of the liquid/gas binary mixtures was established. The critical properties of three binary systems were determined over the entire range of composition using the dynamic method. The experimental critical values with different mole fractions and their uncertainties for the system CO₂ (1) + *n*-pentane (2), CO₂ (1) + *n*-heptane (2) and CO₂ (1) + *n*-decane (2) are presented in Tables 6, 7 and 8 of the Appendix 4, respectively. The critical curves of the above systems were also predicted using the PPR78 thermodynamic model. For heavier *n*-alkanes, the observed type III critical loci – in the classification scheme of Van Konynenburg and Scott [47] – are more difficult to predict. The comparison between the experimental critical data in this work, literature data and the data predictions using the PPR78 model is shown in Figs. 15a, 15b and 15c which correspond to pressure–temperature (P – T), pressure–composition (P – x) and temperature–composition (T – x) projections, respectively. The correlation between the experimental results in this work and those in open literature has been obtained for all systems. At this step, we can however suspect typographical errors in the recent paper by Sun et al. [13]. Indeed the given critical pressure at 373.2 K is totally out of the range of expected values. For the comparison between the experimental values in this work and the critical values predicted by the PPR78 model, Fig. 15a shows the difference and highlights that the variation between the experimental critical points and the predicted critical loci increases as the carbon number in alkanes increases. Figs. 15b and 15c illustrate clearly a perfect superimposition of experimental and predictive values at small and moderate concentrations of carbon dioxide (0 – 0.5) although, at high concentration, experimental critical temperatures are slightly higher than the predicted values and experimental critical pressures are slightly lower. Phase behaviour for the three binary systems CO₂ (1) + *n*-pentane (2), CO₂ (1) + *n*-heptane (2) and CO₂ (1) + *n*-decane (2) belong to type II according to the classification of binary phase diagrams proposed by Van Konynenburg and Scott [47]. The PPR78 model however predicts a type IV for the system CO₂ + *n*-decane explaining the presence of discontinuous vapour - liquid critical loci as can be seen in Figs. 15b and 15c.

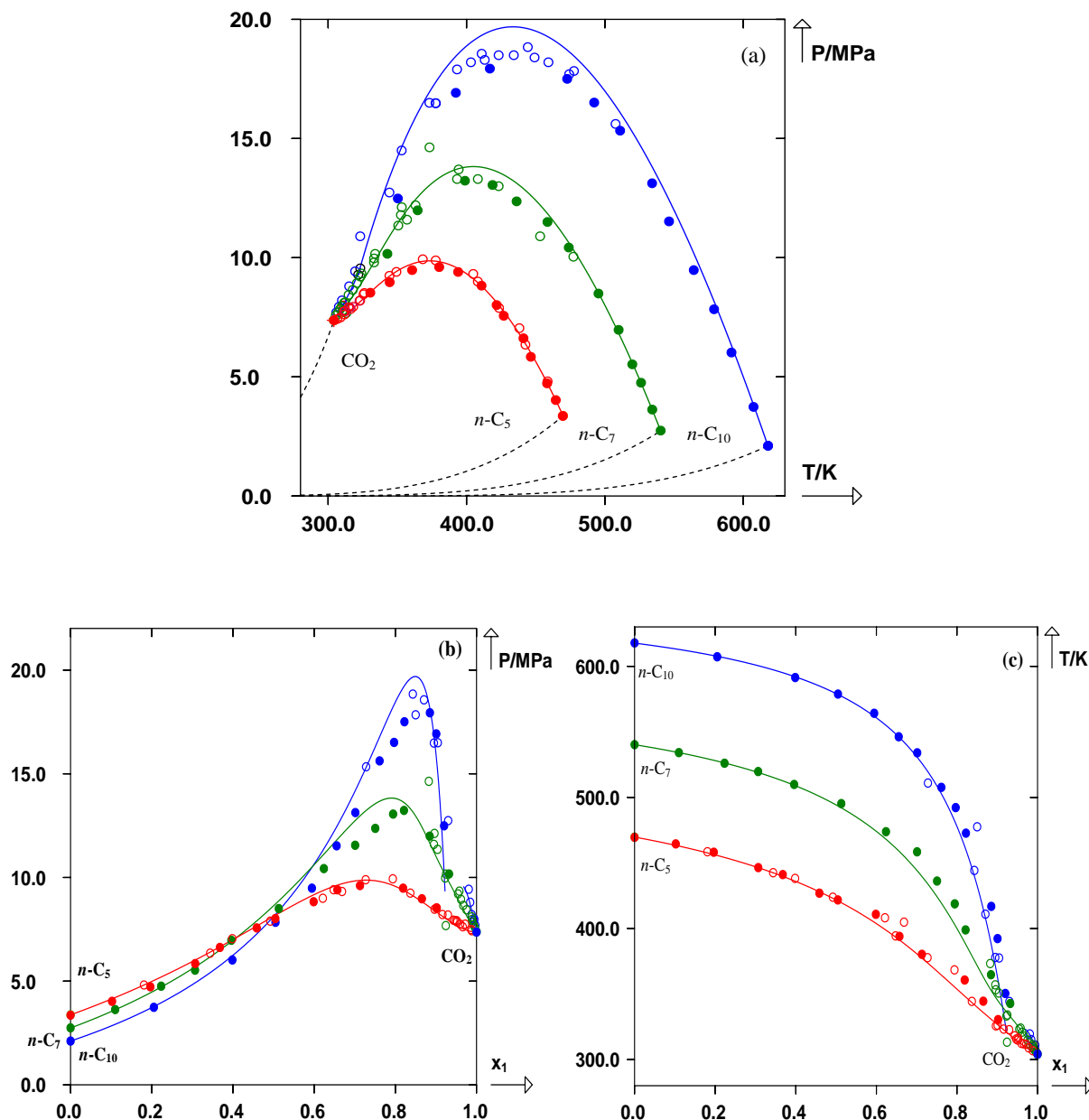


Fig. 15 Critical loci for the systems: **CO₂ (1) + n-pentane (2)**, **CO₂ (1) + n-heptane (2)** and **CO₂ (1) + n-decane (2)** in (a) $P-T$ projection, (b) $P-x$ projection and (c) $T-x$ projection. (Solid lines): predicted curves with the PPR78 model, (dashed lines): vaporization curves of pure compounds, Experimental critical points: (●): this work and (○): literature [4-16].

III.4. Gas/gas binary mixtures

This part focuses on the establishment of the experimental procedure for measuring the critical points of the gas/gas binary mixtures. The critical loci of three binary systems were measured over the whole composition range. The measurements were carried out using the dynamic method. The experimental critical points with different mole fraction and their

uncertainties for the binary systems CO_2 (1) + n -propane (2), CO_2 (1) + n -butane (2) and n -propane (1) + n -butane (2) are listed in, Table 9, 10 and 11 of the Appendix 4, respectively.

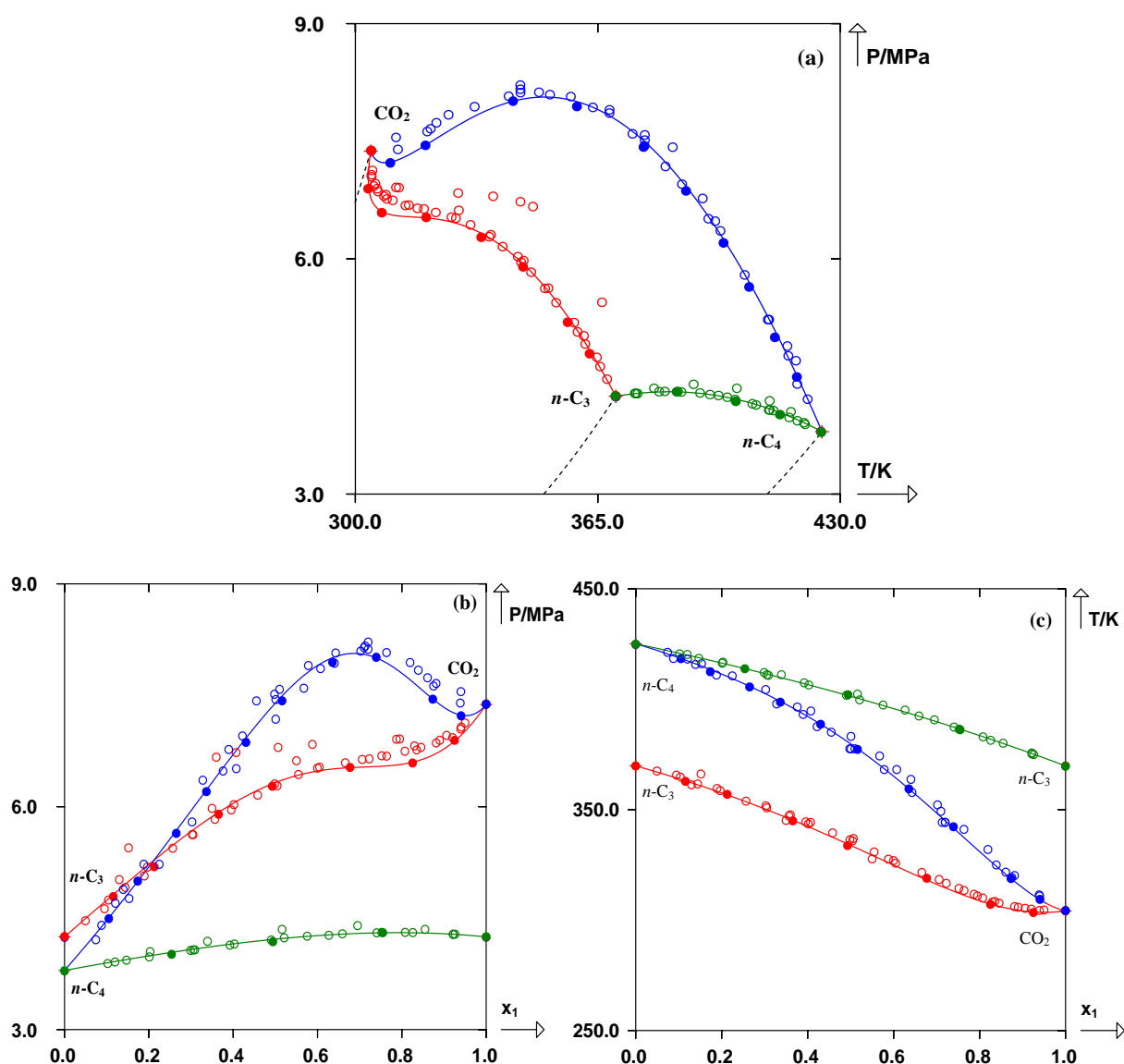


Fig. 16 Critical loci for the systems: CO_2 (1) + n -propane (2), CO_2 (1) + n -butane (2) and n -propane (1) + n -butane (2) in (a) P - T projection, (b) P - x projection and (c) T - x projection. (Solid lines): predicted curves with the PPR78 model, (dashed lines): vaporization curves of pure compounds, Experimental critical points: (●): this work and (○): literature [19-31].

The comparison between the experimental critical data in this work, literature data and the predictions by PPR78 model is shown Fig 16a, 16b and 16c which correspond to pressure – temperature (P - T), pressure – composition (P - x) and temperature – composition (T - x) diagrams, respectively. For the system n -propane (1) + n -butane (2), which belong to the type I fluid phase behaviour according to the classification of binary phase diagrams proposed by Van

Konynenburg and Scott [47], a very strong correlation between our experimental results, the literature data [19], [20], [21-23] and the PPR78 model is obtained in all projections. Only the experimental results from Nysewander et al. [21] are higher compared to the rest. For the systems containing CO₂, which belong to the type II fluid phase behaviour, Fig. 16 shows that the experimental results in this work correlate accurately with the predictions by the PPR78 model. This is not surprising since we know by experience that such a model is able to predict with high accuracy the critical loci of binary mixtures containing a light alkane and CO₂, and we thus can be confident in our experimental data. A small variation with literature data for the system CO₂ + *n*-propane [9, 19, 24-27] and for the system CO₂ + *n*-butane [9, 19, 27-31] is observed at high mole fractions of CO₂ where the critical pressures in this work are slightly lower than those in literatures. However due to the scatter of the experimental data measured by the different authors – especially in the vicinity of pure CO₂ – we can conclude a satisfactory agreement between our new data and those previously published. Fig. 16a, 16b and 16c illustrate that the quality of the data depends strongly on the experimental method. As an example, the critical points of the system CO₂ + *n*-propane from Poettmann and Katz [9] and Reamer et al. [24] are much higher than those collected by other authors. These authors measured the pressure as a function of volume at a given temperature and composition. The bubble and dew pressures were obtained by evaluating the *P-v* curves, and the critical coordinates could be found by an iterative process. This paper allows concluding that such a technique is not accurate enough for the critical point determination. Additionally, the correlation between our experimental data, the literature data and the predictions by the PPR78 model of the critical temperatures is stronger than that of critical pressures as can be seen in the Fig. 16b and 16c.

IV. Conclusion

The performance and the reliability of the new synthetic – dynamic apparatus capable of measuring the critical properties of pure compounds and multi-component mixtures with known overall composition were validated. The experimental procedures of the critical point measurements were established. Our apparatus can work in both the dynamic and the static methods. However, the static method can be used only in the critical point determination of pure substances. In this work, we focus on the binary mixtures so all measurements were carried out using the dynamic method. The experimental results measured in this work were validated by comparing to the literature data and the predictions by the model PPR78 which is acknowledged

to predict with high accuracy the critical locus of binary mixtures containing *n*-alkanes and CO₂ + *n*-alkane up to *n*-decane.

For the liquid/liquid binary mixtures, the critical points of three binary systems: *n*-pentane + *n*-heptane, *n*-pentane + *n*-decane and *n*-heptane + *n*-decane are investigated. The critical temperatures of the system *n*-pentane + *n*-decane show a good agreement with literature data whereas those of the systems *n*-pentane + *n*-heptane and *n*-heptane + *n*-decane were determined for the first time in this work. Moreover, the critical loci of these three systems were predicted with high accuracy with the PPR78 model.

For the liquid/gas binary mixtures, the critical locus of three binary systems: CO₂ + *n*-pentane, CO₂ + *n*-heptane and CO₂ + *n*-decane are studied. The experimental critical points show a good agreement with those found in open literature. The critical loci of these three systems were satisfactorily predicted by the PPR78 model. However, the variation between the experimental critical points and the predicted critical loci increases as the carbon number in alkanes increases.

For the gas/gas binary mixtures, the critical locus of three binary systems: CO₂ + *n*-propane, CO₂ + *n*-butane and *n*-propane + *n*-butane are investigated. For the system *n*-propane + *n*-butane, a good agreement between the experimental data in this work, literature data and predictions by the PPR78 are obtained. For the systems containing CO₂, the critical data in this work perfectly correlates with the critical loci predicted by the PPR78 thermodynamic model although a small variation with the literature critical pressures is observed at high mole fractions of CO₂. Due to the scatter of the many experimental data, such a difference is certainly insignificant. Furthermore, the correlation between all of the data in terms of critical temperatures is better than in terms of critical pressures.

We can thus conclude that our apparatus and our experimental procedures are ready to be used for measuring the critical locus of much more complex binary systems and multicomponent systems.

V. Application: the acetone + chloroform binary system

V.1. Introduction

Knowledge of the presence of an azeotrope is important in the separation and purification operations and has been exploited in a wide range of technological applications. Homogenous azeotropes can be categorized into positive and negative (the isothermal bubble and dew curves pass simultaneously through a maximum and a minimum in pressure, respectively). In the pressure-temperature projection (P - T), an azeotropic line which lies down above vaporisation curves of pure substances for a positive azeotrope and below for a negative azeotrope can disappear either on the vaporisation curve of pure compound (limited azeotropic behaviour) or on the critical locus of the mixture (absolute azeotropic behaviour) and give birth to a critical azeotrope [48]. From an experimental point of view, the negative azeotrope, usually caused by stronger attractive interactions between unlike molecules than those between like molecules, is much less frequently encountered than positive azeotropy, explaining why a negative critical azeotrope, although is thermodynamically possible, was never observed experimentally.

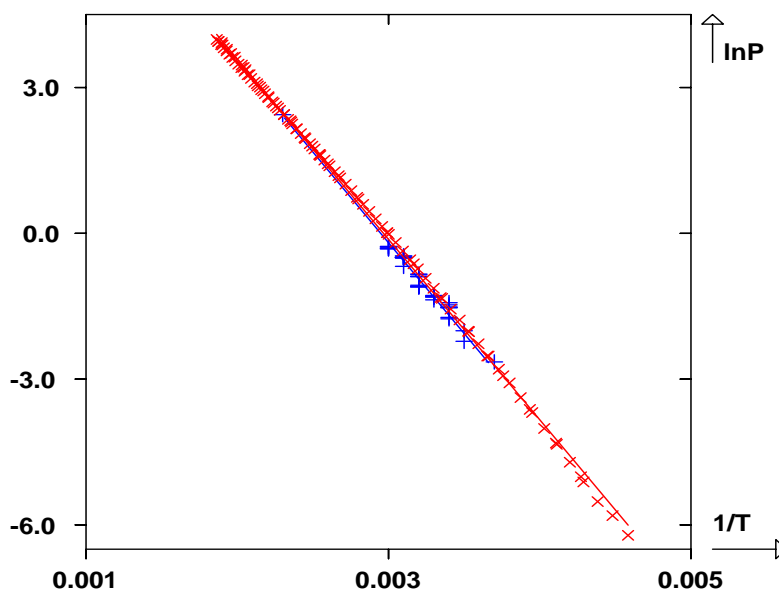


Fig. 17 Vapour pressures and azeotropic pressures available in literature for the binary system acetone (1) + chloroform (2); (x): Vapour pressures [68-70], (+): Azeotropic pressures [49-57, 59-63] and (Solid lines): linear regressions

The acetone (1) + chloroform (2) binary system exhibits a negative azeotrope at low temperatures and pressures according to a large number of experimental and theoretical investigations [49-67]. Fig. 17 highlights a good internal consistency of the azeotropic pressures [49-57, 59-63] and that of the vapour pressures [68-70] at different temperatures. Röch and Schröder [50] and Campbell and Musbally [58] measured the phase equilibrium of this system at temperatures ranging from 15 to 55 °C and from 100 to 180 °C, respectively. Agreeably, they reported that the azeotropic composition shifts towards higher chloroform content as the temperature increases. Moreover, these experimental studies are in a good agreement with the modelisation conducted by Kamath et al. [64]. Although many vapour - liquid equilibrium measurements were performed for the system acetone + chloroform, only few took place at high temperature and pressure and the azeotropic composition was investigated only up to 180°C, by Campbell and Musbally [58]. According to these authors, the azeotrope still exists at this temperature. However, they concluded in their paper that the azeotrope does not carry on up to the critical point by referring to the investigation of Kuenen and Robson [67] who measured the critical points for the acetone + chloroform mixture and the vaporisation curve of each compound. According to Kuenen and Robson [67], there is no maximum critical temperature and that the minimum pressure azeotrope which exists at low temperature and pressure, disappears before becoming critical. Nevertheless, during their critical point measurements, these authors observed a chemical reaction between chloroform and mercury (coming from the apparatus used) at high temperature. The nature of the reaction is such as to generate a gas which reduces the critical temperature and raises the critical pressure. As a consequence, until now, no accurate experimental data at high temperatures and pressures confirms the existence or inexistence of a negative critical azeotrope for the system acetone + chloroform.

In this work, we decided to experimentally study the critical properties of the acetone + chloroform binary system with the aim of understanding the phase behaviour at high temperatures and pressures of this system as well as checking the presence of the negative critical azeotrope (i.e. an intersection between the critical locus of the mixture and the azeotropic line) since we believe that a discovery of such a negative critical azeotrope allows fundamentally understanding the azeotropic behaviour. Additionally, the PPR78 model [32-39] was used for predicting the vapour pressures of the pure components and correlating the critical locus of the mixture under consideration. Then, the experimental results obtained in this work were compared to those available in literature and those modelled by the PPR78 model.

V.2. Experimental procedure

V.2.1. Materials

All compounds used were purchased from commercial sources. The purities and the suppliers of the pure components are listed in Table 2. Acetone was used without any further purification. Chloroform was used after its small quantity of ethanol (about 0.5-0.8%) – added for stabilization – was removed with 5A molecular sieves. Such molecular sieves were activated by heating at 300 °C for 3 hours and then by cooling in a vacuum desiccator. A large quantity of these molecular sieves was added in chloroform, left overnight and finally filtered. The resulting chloroform was degassed using a vacuum pump and stored in a round bottom flask wrapped in aluminium paper in order to avoid a reaction with oxygen when exposed to the air and light. Fresh treatments of chloroform were realized every 3 days. A gas chromatographic analysis indicated that chloroform had a purity of at least 99.9 %.

Table 2 Purity and supplier of the compounds used in this study.

Compound	Purity	Supplier
acetone	$\geq 99.9\%$	Sigma-Aldrich
chloroform	$\geq 99.8\%$	Sigma-Aldrich

V.2.2. Apparatus and procedure

The apparatus and procedure part is identical to that described in Part B, particularly in the section II.2 for the liquid/liquid binary mixtures. The uncertainties on pure components and mixtures critical coordinates at different mole fractions were classically determined by following the statistical method recommended by NIST. Such uncertainties are ≤ 0.11 °C for the critical temperature and ≤ 0.009 MPa for the critical pressure, respectively. Likewise, a mean value uncertainty in the mole fraction, $u(x_i) = \pm 0.00004$ is obtained.

V.3. Database and reduction procedure

The PPR78 model which is described in the Part A, particularly in the section IV.2, is used to correlate the experimental results of the acetone + chloroform binary system. The PPR78 model requires the physical properties of pure components. We used the critical temperature and critical pressure determined in this work and the acentric factor originated from the DIPPR database [45] for both of the compounds under investigation. The temperature – dependant

binary interaction parameters were correlated by considering each molecule as a simple group. We thus need to estimate two constant parameters (A_{12} and B_{12} values) in the following expression:

$$k_{12}(T) = \frac{A_{12} \left(\frac{T_0}{T} \right)^{\left[\frac{B_{12}-1}{A_{12}} \right]} - \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2}{2 \frac{\sqrt{a_1 a_2}}{b_1 b_2}} \quad \text{with} \quad T_0 = 298.15K \quad (1)$$

V.4. Results and discussion

The vapour - liquid critical points for the acetone (1) + chloroform (2) binary system were experimentally determined throughout the entire range of composition. The critical point measurements were carried out using the dynamic-synthetic apparatus in the dynamic method. The experimental critical values with different mole fractions and their uncertainties of are given in Table 12 of the Appendix 4. Then, the PPR78 model was used to predict the vaporisation curve of pure substances and to correlate the critical locus of the system under consideration. The constant parameters are given in Table 3.

Table 3 Group – interaction parameters: ($A_{12} = A_{21}$) / MPa and ($B_{12} = B_{21}$) / MPa.

System	A_{12}	B_{12}
Acetone -Chloroform	-18.98	-27.63

The comparison between the experimental critical data measured in this work, literature data and critical locus correlated using the PPR78 model is graphically presented in Fig 18a, 18b and 18c which correspond to pressure – temperature (P - T), pressure – composition (P - x_1) and temperature – composition (T - x_1) diagrams, respectively. Fig. 18c also shows the azeotropic compositions at high temperature. The acetone + chloroform binary mixture displays a monotonous continuous vapour-liquid critical locus which connects the critical points of the pure components. Such an uninterrupted critical locus indicates that this binary system can belong to the type I or II fluid phase behaviour according to the classification of Van Konynenburg and Scott [47]. When compared to the experimental data available in the literature, Fig. 18a illustrates a large deviation between our critical points and the collection of Kuenen and Robson [67]; the critical temperatures measured in this work are lower whereas the critical pressures are higher. These

differences may come from an insufficiently accurate experimental setup used in Kuenen and Robson's experiment as previously noted. Contrary, Fig. 18c shows a perfect agreement between our experimental results and the data collected by Campbell and Musbally [58] and highlights that the azeotropic composition shifts towards higher chloroform content as temperature increases.

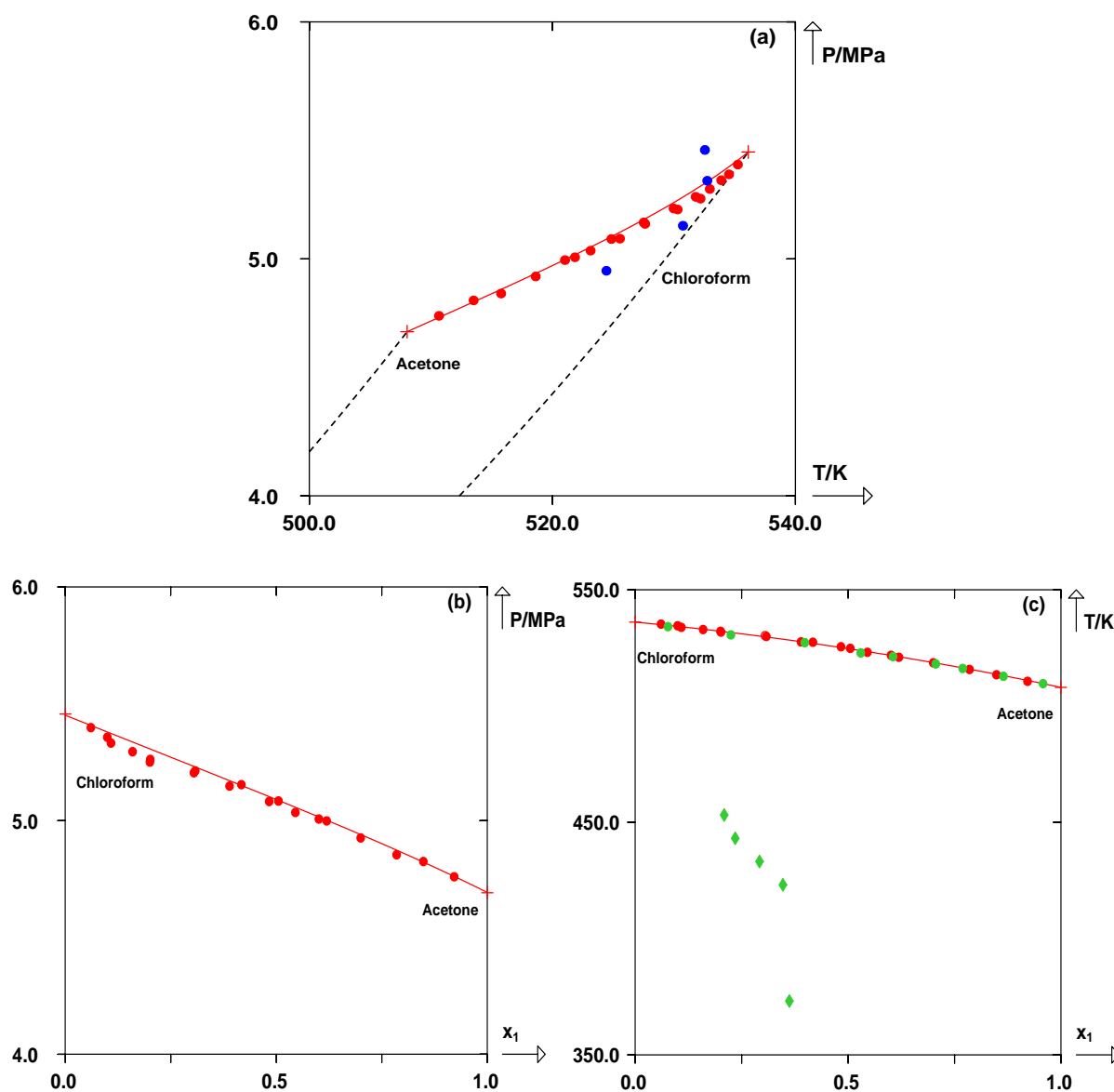


Fig. 18 Critical locus for the system acetone (1) + chloroform (2) in (a): P-T projection, (b) P-x projection and (c): T-x projection. (Solid line): critical locus correlated by the PPR78 model, (Dashed lines): vaporization curves of pure compounds predicted by the PPR78 model, Experimental critical points; (●): this work, (●): Kuenen and Robson [67], (●): Campbell and Musbally [58]. Azeotropic Compositions; (◆): Campbell and Musbally [58].

Unfortunately, these data can not provide information about the existence of a critical azeotrope because the working temperatures are much lower than the acetone critical temperature.

Furthermore, the PPR78 model is able to accurately correlate the critical locus of the binary system acetone and chloroform, except at high chloroform content; the experimental critical pressures are slightly lower than predicted critical values [Fig. 18b]. According to the PPR78 model, the critical locus and the vaporisation curve of pure chloroform do not intersect each other so that a critical azeotrope is not predicted by such a model. Our experimental data highlight that the critical locus of the acetone (1) + chloroform (2) system exhibit neither a minimum in pressure nor a maximum in temperature. Consequently, the unique possibility to obtain a critical azeotrope would be that the critical locus and the vaporisation curve of pure chloroform intersect each other. It is noticeable that the experimentally determined critical points impose on the chloroform vaporisation curve predicted by the PPR78 model. In order to check the prediction accuracy, the chloroform vaporisation curve predicted by the PPR78 model is compared to the experimental values available in literature [68-70]. As can be seen in Fig. 19, the curve predicted by the PPR78 model perfectly agrees with the data reported by Xiang [70] whereas it slightly lies down below data reported by Stull [68] and Campbell and Chatterje [69] at temperature higher 200 °C. As a consequence, the critical locus of the binary system acetone and chloroform intersects with the vaporisation curve of chloroform, thus highlighting the existence of a negative critical azeotrope.

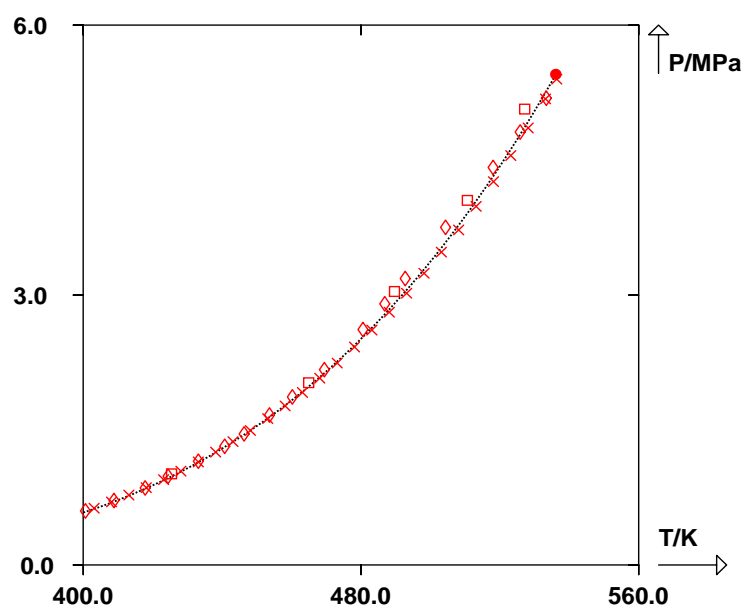


Fig. 19 Vaporisation curve of chloroform; (\square): Stull [68], (\diamond): Campbell and Chatterje [69], (\times): Xiang [70], (Dashed lines): predicted by the PPR78 model and (\bullet): experimental critical points [this work].

However, the existence or inexistence of the negative critical azeotrope strongly depends on the experimental accuracy. Herein, we need additional experimental data such as isothermal vapour-

liquid phase equilibrium at high temperature and pressure to confirm the existence of such a negative critical azeotrope.

V.5. Conclusion

The critical points of the acetone + chloroform binary system were determined experimentally throughout the entire range of composition. The measurements were carried out using the synthetic-dynamic apparatus in the dynamic method. The PPR78 model is able to accurately predict the vapour pressures of the pure components as well as to correlate critical locus of the system under investigation. The experimental critical values obtained in this work are compared to those available in the literature. Large differences were found when compared to the very old literature data collected by Kuenen and Robson. However, a strong agreement was obtained with the data collected by Campell and Musbally. The acetone and chloroform binary system is characterized by the presence of a negative azeotrope at low temperatures and pressures. In this work, it was shown for the first time that the negative azeotrope became critical owing to an intersection between the critical locus and the chloroform's vaporisation curve. However, additional experimental data at high temperatures and pressures are needed to confirm the existence of such a negative critical azeotrope.

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FROM EXPERIMENTAL CRITICAL DATA TO
RESEARCH AND DEVELOPMENT
APPLICATIONS

I. Biodiesel production via the supercritical process

I.1. Introduction

Progressive depletion of world oil resources, combined to increasing energy consumption as well as the negative environmental impact of fossil fuel use, led to a shift toward alternative renewable sources of energy. Biodiesel is among the most viable liquid transportation fuels for the foreseeable future, with the potential of contributing significantly to sustainable development in terms of socioeconomic and environmental concerns [1-5]. Biodiesel is a mixture of alkyl esters obtainable by different processes [6-9]: transesterification (alcoholysis) of triglycerides from vegetable oils or animal fats with short-chain alcohol seems to be the best choice because the physical characteristics of the resulting biodiesel are relatively close to those of diesel fuel. Methanol and ethanol are thus in interest among alcohols employed for the biodiesel production [10-13]. Although methanol is superior owing to its higher production yield and its shorter reaction time [14-15], ethanol becomes more attractive recently, once again, in terms of environmental benefits.

Regarding the ethanolysis reaction, catalysts are necessary to accelerate the reaction rate. Catalysis pathways are usually classified into homogenous, heterogeneous and enzymatic. Homogenous catalysts [16-23] are the most common way. The main drawback of this process is to be water sensitive and to form soapy products between catalysts and free fatty acids contained in oils, preventing the use of non-conventional feedstocks such as waste cooking oils or algal biomass. Moreover, separation and purification steps require a large quantity of water as well as a high energy consumption to treat wastewater generated in downstream processes. Heterogeneous catalysts [24-31], which have higher tolerance toward free fatty acid and simpler separation step, require a long reaction time because of a limited contact surface between liquid reactants and solid catalysts. Enzymatic catalysts [32-38] show many advantages such as moderate reaction conditions, a low alcohol to oil ratio and an easy product recovery. In return, a high cost of resulting biodiesel due to a cost intensive preparation of enzymes prevents its industrial application. Collectively, all weaknesses are linked to the utilisation of catalysts, explaining why many researches recently focus on non-catalytic ethanolysis method based on supercritical ethanol [15, 39-50]. According to current publications, the supercritical method makes increase the phase solubility and the mass transfer, facilitates the separation and purification steps, achieves a significant yield of biodiesel in a short reaction time and can be

applied to a wide range of feedstocks. Nevertheless, their industrial scale application is limited because of the severe operating conditions required (high temperature, high pressure and high alcohol to oil molar ratio). To date, these high conditions can be successfully reduced by addition of a co-solvent. As investigated in the literature [51-54], supercritical CO₂ has been highlighted as a promising co-solvent.

To optimize the non-catalytic supercritical ethanol process with the addition of CO₂, the knowledge of the phase behaviour, especially under high temperatures and pressures for systems containing compounds involved in biodiesel production such as ethanol, ethyl ester and glycerol is an obvious need. Moreover, the knowledge of fluid phase equilibria makes it possible to understand the effect of modifying key operating parameters (e.g. temperature, pressure and ethanol to oil molar ratio) on the reaction rate. Indeed, it is necessary to operate in the one-phase region to obtain a production yield. Regarding the phase behaviour of binary systems containing ethanol and an ethyl ester, the ethanol + ethyl acetate mixture were extensively investigated at low temperatures and pressures [55-74] but briefly studied at high temperatures and pressures [75]. Only few authors focused on binary systems composed of ethanol with other short-chain ethyl esters such as ethyl propanoate [76], ethyl butanoate [77] and ethyl hexanoate [78]. For the phase behaviour of binary systems containing CO₂ and an ethyl ester, some authors investigated vapour-liquid equilibria of mixtures composed of CO₂ with short- and medium-chain ethyl ester such as ethyl acetate [79-86], ethyl propanoate [83, 87], ethyl butanoate [88-89], ethyl hexanoate [90], ethyl octanoate [90] and ethyl decanoate [90]. Few authors [91-94] focused on mixtures involving CO₂ and a long-chain ethyl ester and only two authors [95-96] studied phase equilibria at high temperatures and pressures by determining the critical properties of the system CO₂ + ethyl acetate. Due to expensive high-quality equipments, predictive thermodynamic models are a promising alternative way to access phase behaviour information, for example, a CPA EoS [97] and an artificial neural network model [98] were used to model several CO₂ and ethyl ester binary systems. But due to possible thermal decomposition of some compounds involved in biodiesel synthesis, there is no way to assess their thermodynamic properties except using a predictive model based on the group-contribution (GC) concept. This kind of model offers the great advantage to allow a very quick and quite easy estimation of the thermodynamic properties of nearly any compound without steps of preliminary measurements combined with model-parameter regressions. However, to make the model as accurate as possible, the adjustment of predictive-model parameters requires a high quality of experimental data. Finally, experimental measurements and predictive models are complementary and have to be used together.

The objective of this work is firstly to provide a high-quality experimental data and secondly to develop an accurate predictive model for application in the biodiesel production. In the first part of this work, the critical properties (critical temperatures and critical pressures) of twelve binary mixtures containing ethanol and an ethyl ester (nine saturated ethyl esters in homologous series and three unsaturated ethyl esters) and eleven binary mixtures containing CO₂ and an ethyl ester (nine saturated ethyl esters in homologous series and two unsaturated ethyl esters) are experimentally determined using synthetic-dynamic apparatus in the dynamic mode. The critical points for the CO₂ + ethyl acetate system are compared to those available in literature whereas the critical properties of the other mixtures are investigated for the first time in this study. In the second part, with the experimental values measured in this study and those available in literature, the PPR78 model is extended to ester compounds and an additional group (the ester function) is defined.

I.2. Experimental procedure

I.2.1. Materials

All compounds were purchased from commercial sources and used without any further purification. The purities and the suppliers of the compounds used in this study are listed in Table 1.

Table 1 Purity and supplier of the compounds used in this study.

Compound	Purity	Supplier
Ethyl alcohol	99.9%	Carlo Erba
Carbon dioxide	99.998 vol. %	Messer
Ethyl acetate	≥99.8%	Sigma-Aldrich
Ethyl propionate	99%	Sigma-Aldrich
Ethyl butanoate	99%	Sigma-Aldrich
Ethyl pentanoate	99%	Sigma-Aldrich
Ethyl hexanoate	≥99%	Sigma-Aldrich
Ethyl heptanoate	99%	Sigma-Aldrich
Ethyl octanoate	≥99%	Sigma-Aldrich
Ethyl nonanoate	≥98%	Sigma-Aldrich
Ethyl decanoate	≥99%	Sigma-Aldrich
Ethyl trans-2-butenate	≥96%	Sigma-Aldrich

Ethyl trans-3-hexenoate	≥98%	Sigma-Aldrich
Ethyl trans-2-octenoate	≥98%	Sigma-Aldrich

I.2.1. Apparatus and procedure

The apparatus and procedure part is identical to that described in the part B, particularly the section II.2 for the liquid/liquid binary mixtures and for the liquid/gas binary systems. The uncertainties in the critical coordinates for pure components and mixtures at different mole fractions were classically determined by following the statistical method recommended by NIST. They were found to be ≤ 0.14 °C for the critical temperature and ≤ 0.0135 MPa for the critical pressure, respectively. Likewise, a mean value uncertainty in the mole fraction, $u(x_i) = \pm 0.00006$ is obtained.

I.3. Addition of the ester group to the PPR78 model

Table 2 presents the list of the pure components involved in this study and their physical properties (T_c , P_c and ω). Figs. 1a, 1b and 1c respectively illustrate the evolution of the critical temperatures, critical pressures and acentric factors from different origins [this work, 107-108] with the molecular mass of the saturated ethyl esters. For reason of homogeneity, the critical properties of ethyl nonanoate were obtained by linear regression of the other pure compound properties. The ω of saturated ethyl esters (from ethyl pentanoate to ethyl octanoate) were experimentally determined in this work. The vapour pressures of these components were measured using the synthetic-dynamic type apparatus in the static method. A good agreement between the vapour pressures of ethyl hexanoate measured in this study and literature data [109] allows validating our results. Then, the ω of the components were calculated with the equation:

$$\omega = -\log_{10}\left(\frac{P^s(T=0.7T_c)}{P_c}\right) - 1$$

and using the critical values determined in this study. For the unsaturated ethyl ester, the ω of ethyl trans-3-hexenoate was calculated using the equation of Edminster since its critical point can not be measured in this work. The three parameters of ethyl trans-2-octenoate were determined by the group contribution method developed by Marrero and Gani.

Table 2 List of pure components and their physical properties (T_c , P_c and ω).

Component	Short name	T_c /K	P_c /MPa	ω
Carbon dioxide	CO ₂	304.21 ^b	3.783 ^b	0.223621 ^b
Ethanol	EtOH	514.06 ^a	6.139 ^a	0.643558 ^b
Ethyl acetate	EtC2	523.29 ^a	3.829 ^a	0.366409 ^b
Ethyl propionate	EtC3	546.28 ^a	3.385 ^a	0.394373 ^b
Ethyl butanoate	EtC4	569.98 ^a	2.891 ^a	0.401075 ^b
Ethyl trans-2-butenoate	EtC4D	593.83 ^a	3.670 ^a	0.434 ^c
Ethyl pentanoate	EtC5	594.02 ^a	2.730 ^a	0.4302 ^a
Ethyl hexanoate	EtC6	615.22 ^a	2.531 ^a	0.5117 ^a
Ethyl trans-3-hexenoate	EtC6D	616.00 ^c	2.600 ^c	0.512
Ethyl heptanoate	EtC7	635.12 ^a	2.357 ^a	0.5548 ^a
Ethyl octanoate	EtC8	655.74 ^a	2.1592 ^a	0.5914 ^a
Ethyl trans-2-octenoate	EtC8D	667.23 ^d	2.187 ^d	0.592 ^d
Ethyl nonanoate	EtC9	670.38	1.965	0.639 ^c
Ethyl decanoate	EtC10	688.1 ^b	1.788 ^b	0.625326 ^b
Ethyl laurate	EtC12	716.3 ^b	1.529 ^b	0.699196 ^b
Ethyl myristate	EtC14	738.7 ^b	1.323 ^b	0.764248 ^b
Ethyl palmitate	EtC16	759.4 ^b	1.156 ^b	0.849005 ^b
Ethyl stearate	EtC18	777.9 ^b	1.019 ^b	0.898461 ^b
Ethyl oleate	EtOl	772.1 ^b	1.098 ^b	0.942641 ^b
Ethyl linoleate	EtLin	777.8 ^b	1.127 ^b	0.944319 ^b

^aThis work, ^bDIPPR [107], ^cYaws [108] and ^dGCM of Marrero and Gani.

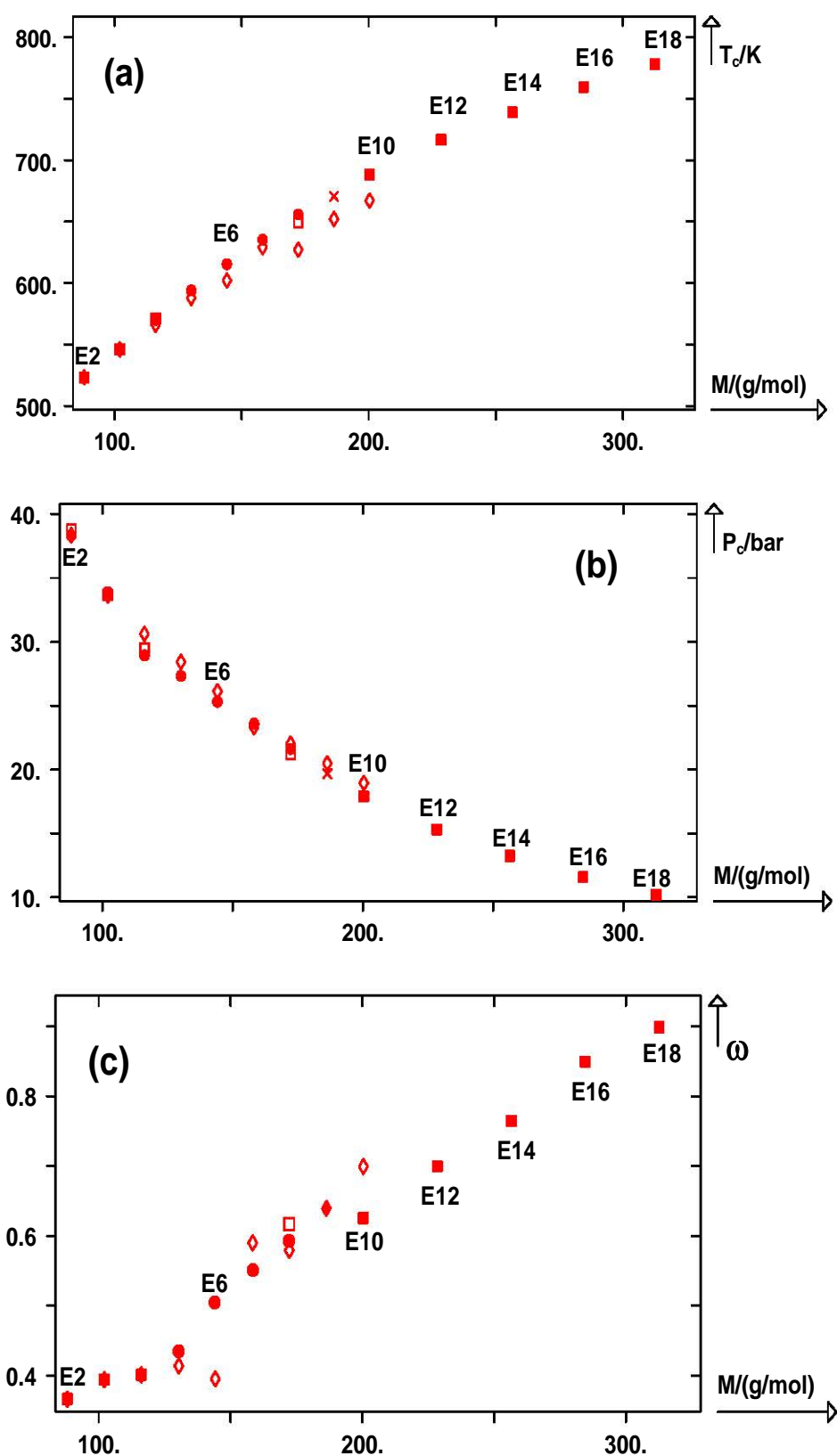


Fig. 1 Evolution of the physical properties of saturated ethyl esters with their molecular mass; (a): critical temperature, (b): critical pressure and (c): acentric factor. (●): this work, (■ and □): DIPPR [65], (◆ and ◇): Yaw [66], (×): linear interpolation and (●, ■, ◆ and ×): values included in our database.

Table 3 details the sources of the binary experimental data used in our evaluations along with the temperature, pressure and composition range for the binary systems containing CO₂ + an ethyl ester. Our databank includes 870 VLE experimental values from literature, 103 experimental critical values from this work and 5 experimental critical values from literature. It finally consists of experimental data on 17 binary systems. Some data available in the literature are not internally consistent and are mutually conflicting for the systems CO₂ + ethyl acetate [80, 83, 85], CO₂ + ethyl propanoate [83, 87] and CO₂ + ethyl butanoate [89], they thus have been removed. To predict the phase behaviour of mixtures involving CO₂ and an ethyl ester, it is necessary to define as a new group the ester function (O – C = O) and to determine the interactions between this new group and the other groups previously defined (CH₃, CH₂, CO₂ and HC=) that are present in the molecules involved in this study. It is well known that the properties of the first molecules of a homologous series generally don't follow the same behaviour as other molecules. For this reason, they are often treated separately in group contribution methods. In this work, the CO₂ + ethyl acetate system was modelled separately without decomposing the ethyl acetate into elementary groups. We thus need to estimate ten constant parameters (5 A_{kl} and 5 B_{kl} values).

Table 4 details the sources of the binary experimental data along with the temperature, pressure and composition range for the binary systems containing ethanol and ethyl ester. Some data available in the literature for the systems ethanol + ethyl acetate [55, 64, 68] have been removed since they are not internally consistent. The study of the thermodynamic behaviour of ethanol and ethyl ester systems is very complex since not only interactions between an oxygen atom of ester function and a hydrogen atom on a hydroxyl group of ethanol but also an ethanol-ethanol hydrogen bonding exist in the systems. As a consequence, the only way to avoid unsatisfactory results is to consider each molecule as one group. It is indeed impossible to find parameters for the O – C = O group which could accurately predict the data available in Table 4. For such systems, the PPR78 model must be regarded as a correlation model rather than a predictive model. We thus need to estimate two constant parameters (1 A_{kl} and 1 B_{kl} value) for each binary system.

Table 3 CO₂ + ester binary systems database

Binary system (first compound- second compound)	Temperature range (K)	Pressure range (MPa)	x_l range (first compound liquid mole fraction)	y_l range (first compound gas mole fraction)	Number of bubble points (P , T , x)	Number of dew points (P , T , y)	Number of binary critical points (P_{cm} , T_{cm} , x_c)	Reference
CO ₂ – EtC2	228.05 - 523.29	0.2942–12.3619	0.0716 - 0.9580	0.7990 – 0.9910	167	37	16	[79, 81-82, 84, 86, 96, this work]
CO ₂ – EtC3	304.30 - 546.28	3.3856–13.3256	0.1446 - 0.9497	-	-	-	10	[this work]
CO ₂ – EtC4	304.30 – 566.98	2.8915–14.7420	0.1457 – 0.9508	0.9940 – 0.9985	22	20	10	[88, this work]
CO ₂ – EtC4D	304.30- 593.94	3.6708-16.6644	0.1593 – 0.9520	-	-	-	10	[this work]
CO ₂ – EtC5	304.30 – 594.02	2.7304–16.0896	0.1489 – 0.9523	-	-	-	11	[this work]
CO ₂ – EtC6	304.30 – 615.22	1.6990–17.5324	0.1916 – 0.9668	0.9963 – 0.9994	30	24	11	[90, this work]
CO ₂ – EtC6D	304.30- 554.05	11.5697-18.0576	0.6118-0.9610	-	-	-	9	[this work]
CO ₂ – EtC7	304.30 – 635.12	2.3569–18.9619	0.2101 – 0.6930	-	-	-	11	[this work]
CO ₂ – EtC8	304.30 – 655.74	1.6990-19.0903	0.2069 – 0.9640	0.9985 – 0.9997	31	31	10	[90, this work]
CO ₂ – EtC9	304.30 – 644.49	7.3669–18.9349	0.4051 – 0.8833	-	-	-	6	[this work]
CO ₂ – EtC10	304.30 – 638.61	1.6650–17.9499	0.2068 – 0.8591	0.9992 – 0.9998	30	30	4	[90, this work]
CO ₂ – EtC12	308.15 – 328.15	1.4800–10.0990	0.1750 – 0.7944	0.9988 – 0.9999	25	25	-	[91]
CO ₂ – EtC14	313.15 – 333.15	1.6500–14.3800	0.305 – 0.9250	0.9630 – 0.9910	65	15	-	[92]
CO ₂ – EtC16	303.15 – 353.15	1.8900–20.3600	0.3250 – 0.9590	0.9590 – 0.9913	88	45	-	[92-93]
CO ₂ – EtC18	313.15 – 333.12	1.4500–19.0800	0.2810 – 0.9550	0.9550 – 1.0000	54	22	-	[92, 94]
CO ₂ - EtOL	313.15 – 333.15	1.1400–18.6200	0.1950 – 0.9260	0.9770 – 1.0000	38	38	-	[94]
CO ₂ - EtLin	313.15 – 333.15	2.0000–16.9700	0.2990 – 0.9470	0.9810 – 1.0000	32	32	-	[94]

Table 4 Ethanol + ester binary systems database

Binary system (first compound- second compound)	Temperature range (K)	Pressure range (MPa)	x_1 range (first compound liquid mole fraction)	y_1 range (first compound gas mole fraction)	Number of bubble points (P , T , x)	Number of dew points (P , T , y)	Number of binary critical points (P_{cm} , T_{cm} , x_c)	Reference
EtOH – EtC2	514.06-521.60	0.0190-5.8200	0.0250-0.9945	0.0314-0.9192	573	289	14	[56-61, 63-67, 69-75, this work]
EtOH – EtC3	514.06-546.28	1.0133-6.1397	0.0497-0.9938	0.1948-0.9903	32	32	9	[76, this work]
EtOH – EtC4	514.06-569.98	1.0133-6.1397	0.0468-0.9771	0.2900-0.9923	31	31	9	[77, this work]
EtOH – EtC5	514.06-585.13	2.7304-6.1397	0.1202-0.9003	-	-	-	9	[this work]
EtOH – EtC6	330.55-615.22	0.4000-6.1397	0.0501-0.9097	-	58	-	9	[78, this work]
EtOH – EtC7	514.06-635.12	2.3569-6.2325	0.1003-0.9008	-	-	-	9	[this work]
EtOH – EtC8	514.06-655.74	2.1592-6.5400	0.1204-0.9544	-	-	-	11	[this work]
EtOH – EtC9	514.06-642.90	4.1062-6.8308	0.4012-0.9494	-	-	-	8	[this work]
EtOH – EtC10	514.06-639.32	5.2829-7.1941	0.6108-0.9494	-	-	-	6	[this work]
EtOH – EtC4D	514.06-593.84	3.6708-6.1397	0.1495-0.9027	-	-	-	8	[this work]
EtOH – EtC6D	514.06-607.23	3.5474-6.1974	0.1980-0.9232	-	-	-	8	[this work]
EtOH – EtC8D	514.06-602.85	6.1397-6.9483	0.6927-0.9499	-	-	-	5	[this work]

I.4. Results and discussion

I.4.1. Binary systems containing CO₂ + ethyl ester

In the first part, the vapour-liquid critical points for eleven binary systems containing CO₂ and an ethyl ester (nine saturated ethyl ester and two unsaturated ethyl ester) were experimentally determined. The measurements were carried out using the synthetic-dynamic apparatus in the dynamic mode. The experimental critical points with different mole fractions and their uncertainties for the binary mixture CO₂ (1) + ethyl acetate (2), CO₂ (1) + ethyl propionate (2), CO₂ (1) + ethyl butanoate (2), CO₂ (1) + ethyl pentanoate (2), CO₂ (1) + ethyl hexanoate (2), CO₂ (1) + ethyl heptanoate (2), CO₂ (1) + ethyl octanoate (2), CO₂ (1) + ethyl nonanoate (2), CO₂ (1) + ethyl decanoate (2), CO₂ (1) + ethyl trans-2-butenoate (2) and CO₂ (1) + ethyl trans-3-hexenoate (2) are given in Tables 13 to 23 of the Appendix 4, respectively. For the binary mixtures involving the saturated ethyl ester, the critical points of the first six systems (i.e. from the CO₂ + ethyl acetate to CO₂ + ethyl heptanoate) could be determined throughout the entire range of composition. Such systems exhibit a continuous vapour-liquid critical locus which connects the critical points of the pure components. Herein, a lack of experimental data at low temperature makes it impossible to know whether liquid-liquid equilibrium exists. We thus cannot exclude that these mixtures belong to the type II fluid phase behaviour according to the classification of Van Konynenburg and Scott [110]. For the three other systems, the temperature and pressure upper limits of the apparatus prevented some critical points from being measured. Moreover, six overall compositions ($0.95 \leq x_1 \leq 1.00$) of the CO₂ (1) + ethyl nonanoate (2) and CO₂ (1) + decanoate (2) systems were prepared and introduced in the view cell but no critical state could be found. As a consequence, these two systems are suspected to exhibit a discontinuous vapour – liquid critical locus which may belong to the type III or IV fluid phase behaviour. Regarding the binary mixtures containing an unsaturated ethyl ester, the critical points of the CO₂ + ethyl trans-2-butenoate system could be measured over the whole composition range and also form an uninterrupted vapour - liquid critical locus. On the other hand, a slightly colour change from colourless to yellowish of the CO₂ + ethyl trans-3-hexenoate mixture was observed practically from the outlet of the view cell at a temperature higher than 330 °C. According to the investigation of Lin et al. [111], such a colour change corresponds to the thermal decomposition which involves a cis/trans isomerisation, polymerisation and a pyrolysis reaction of compounds. Studies of

thermal stability of methyl esters [112-114] and ethyl esters [115-116] show that the degree of thermal decomposition generally increases as temperature increases and that saturated alkyl esters are much thermal resistant than unsaturated ones, explaining that why the colour change phenomenon was not observed for the systems containing the saturated ethyl ester.

In the second part of this work, the PPR78 model was extended to systems containing CO₂ and the ethyl ester. The corresponding A_{kl} and B_{kl} values (expressed in MPa) are summarized in Table 5.

Table 5 Group-interaction parameters: ($A_{kl} = A_{lk}$)/MPa and ($B_{kl} = B_{lk}$)/MPa determined in this study.

	CH ₃	CH ₂	CO ₂	C ₄ H ₈ O ₂	CH=	COO-
CH ₃						
CH ₂	$A_{kl} = 65.50$ $B_{kl} = 105.7$					
CO ₂	$A_{kl} = 144.8$ $B_{kl} = 401.5$	$A_{kl} = 141.4$ $B_{kl} = 237.1$				
C ₄ H ₈ O ₂			$A_{kl} = -6.200$ $B_{kl} = 16.20$			
CH=	$A_{kl} = 48.70$ $B_{kl} = 44.30$	$A_{kl} = 9.600$ $B_{kl} = 50.80$	$A_{kl} = 60.70$ $B_{kl} = 183.9$			
COO-	$A_{kl} = 1034$ $B_{kl} = 342.7$	$A_{kl} = -1346$ $B_{kl} = 168.9$	$A_{kl} = 1062$ $B_{kl} = 21.00$		$A_{kl} = -394.2$ $B_{kl} = -720.1$	

The group ester is defined. For all the data points included in our database, the objective function defined by the Eq. (5) is 12.560%.

The average overall deviation on the liquid phase composition is:

$$\overline{\Delta x_1} = \frac{\sum_{i=1}^{n_{bubble}} (|x_{1,exp} - x_{1,cal}|)_i}{n_{bubble}} = 0.0325 \quad \text{Moreover} \quad \frac{F_{obj,bubble}}{n_{bubble}} = 8.9120$$

The average overall deviation on the gas phase composition is:

$$\overline{\Delta y_1} = \frac{\sum_{i=1}^{n_{dew}} (|y_{1,exp} - y_{1,cal}|)_i}{n_{dew}} = 0.0035 \quad \text{Moreover} \quad \frac{F_{obj,dew}}{n_{dew}} = 20.380$$

The average overall deviation on the critical composition is:

$$\overline{\Delta x_{c1}} = \frac{\sum_{i=1}^{n_{crit}} (x_{c1,exp} - x_{c1,cal})_i}{n_{crit}} = 0.0454 \quad \text{Moreover} \quad \frac{F_{obj,crit.comp}}{n_{crit}} = 17.813$$

The average overall deviation on the binary critical pressure is:

$$\overline{\Delta P_c \%} = \frac{F_{obj,crit.pressure}}{n_{crit}} = \frac{100 \sum_{i=1}^{n_{crit}} \left(\frac{|P_{cm,exp} - P_{cm,cal}|}{P_{cm,exp}} \right)_i}{n_{crit}} = 5.8920\%$$

Two main factors that contribute to increase the objective function are a lack of experimental data, particularly, for the systems CO₂ + ethyl pentanoate, CO₂ + ethyl heptanoate and CO₂ + ethyl nonanoate, CO₂ + ethyl trans-2-butenate and CO₂ + ethyl trans-3-hexenoate and a large immiscibility of CO₂ and ethyl esters at low temperatures. However, the value of the objective function indicates that the PPR78 model remains capable of predicting the phase behaviour of the binary systems under consideration with a satisfactory accuracy. Fig. 2 and fig. 3 show the isothermal phase diagrams for the systems composed of CO₂ and the saturated ethyl ester at different temperatures. Fig. 2a highlights that, for the system CO₂ + ethyl acetate, accurate results were obtained at any temperatures but the critical pressure at intermediate temperature is slightly overestimated. For the system CO₂ + ethyl butanoate, the experimental bubble pressures are significantly overestimated at any temperatures. As can be seen in fig. 2b, the experimental bubble curve at 308.5 K tends to form a three-phase line which appears when the binary mixture belongs to the type IV fluid phase behaviour but the PPR78 model predicts a type I for this system. It is difficult to conclude if this large deviation comes from a poor quality of literature data or incapacity of the model. The binary interaction parameter (k_{ij}) of the mixtures CO₂ + ethyl acetate and CO₂ + ethyl butanoate is negative and decreases as temperature increases. For the others systems, satisfying results were obtained with the prediction of the PPR78 model. The k_{ij} of these mixtures is positive and diminishes with temperature, except for the systems CO₂ + ethyl myristate [fig.3c] and CO₂ + ethyl palmitate [fig. 3d].

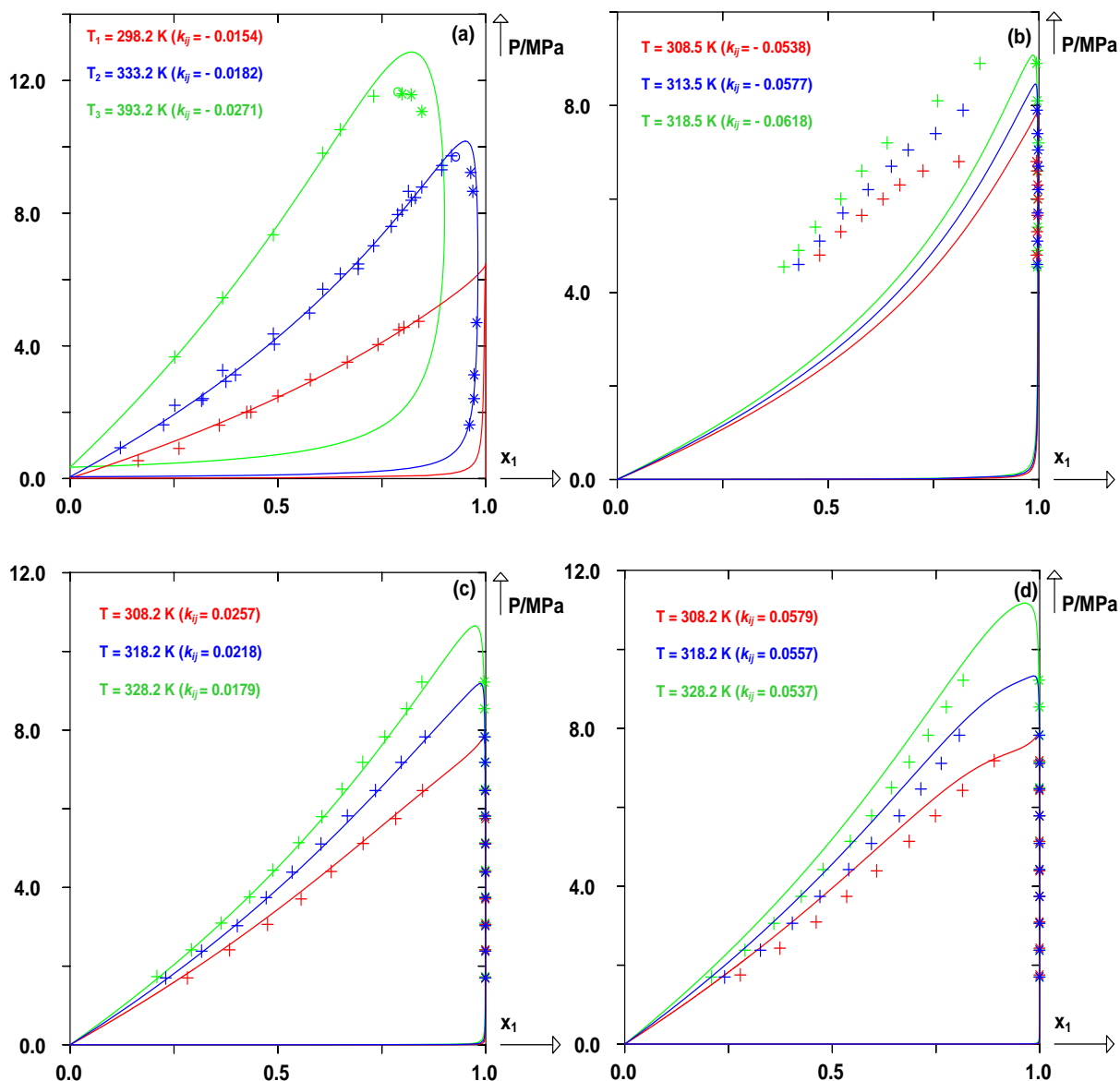


Fig. 2 Prediction of isothermal bubble and dew curves for the binary system containing CO₂ and the saturated ethyl ester; (a): CO₂ (1) + ethyl acetate (2), (b): CO₂ (1) + ethyl butanoate (2), (c): CO₂ (1) + ethyl hexanoate (2) and (d): CO₂ (1) + ethyl octanoate (2). (+): experimental bubble points, (*): experimental dew points, (o): experimental critical points and (Solid lines): predicted curves with the PPR78 model.

Fig. 4 illustrates the isothermal phase diagram of the systems involving C₁₈ ethyl ester. For these systems, the PPR78 model is unable to perfectly reproduce the bubble pressures, particularly at high concentration of CO₂. A significantly under prediction is obtained. The k_{ij} is also positive and slightly varies with the temperature.

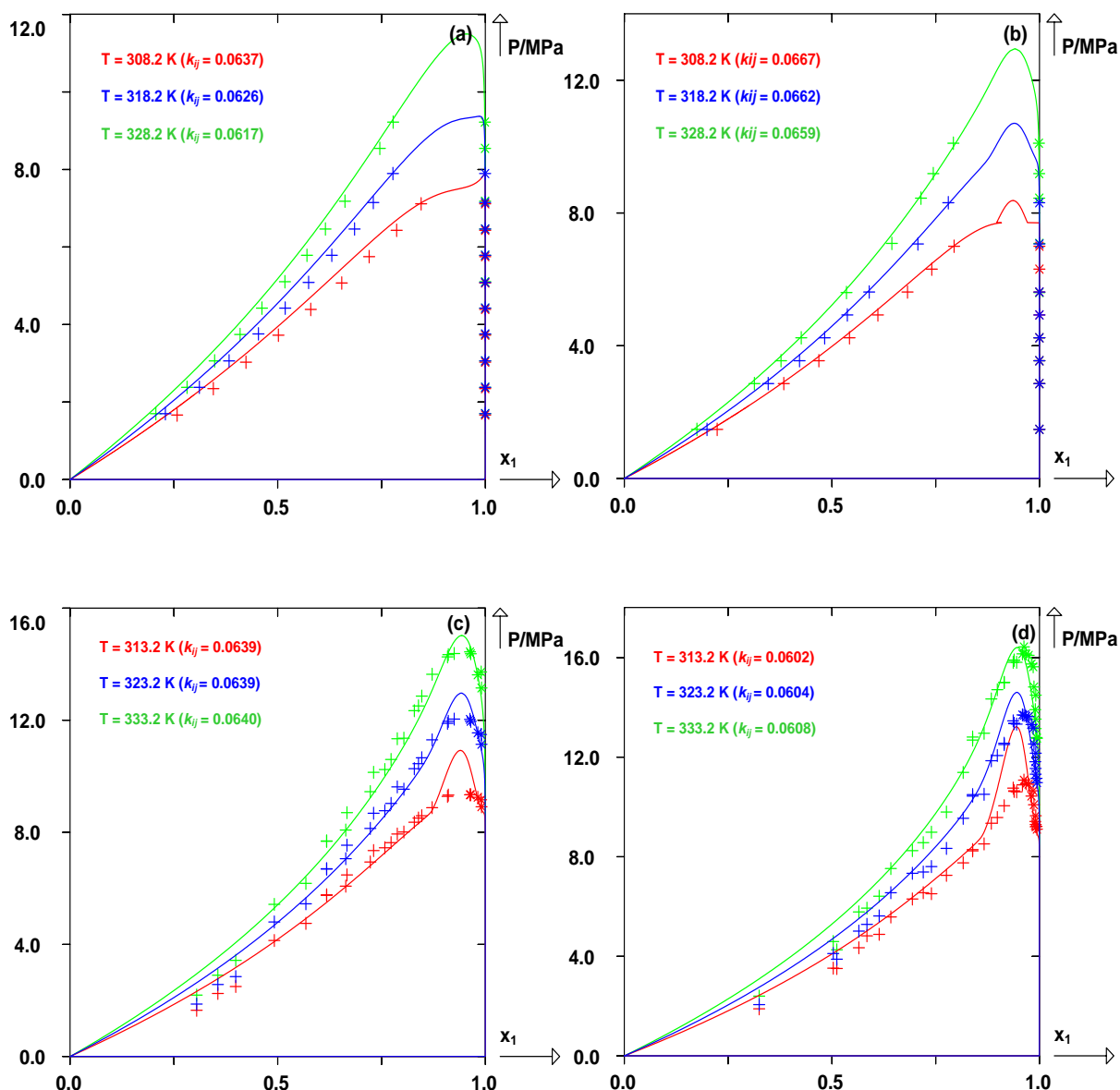


Fig. 3 Prediction of isothermal bubble and dew curves for the binary system containing CO₂ and the saturated ethyl ester; (a): CO₂ (1) + ethyl decanoate (2), (b): CO₂ (1) + ethyl laurate (2), (c): CO₂ (1) + ethyl myristate (2) and (d): CO₂ (1) + ethyl palmitate (2). (+): experimental bubble points, (*): experimental dew points, and (Solid lines): predicted curves with the PPR78 model.

The comparison between our experimental critical points, literature critical data and the critical locus predicted by the PPR78 is graphically presented in Figs. 5a, 5b and 5c which correspond to pressure – temperature (P - T), pressure – composition (P - x) and temperature – composition (T - x) diagrams, respectively. For the system CO₂ and ethyl acetate, a good agreement between the experimental and predictive values is obtained at small and moderate concentration of CO₂ although, at high concentration, the experimental critical temperatures are higher than predicted values and the experimental critical pressures are lower. For the

system CO₂ + ethyl propionate, an opposite situation arises: the critical locus is over predicted at high concentration of CO₂ and under predicted at low concentration.

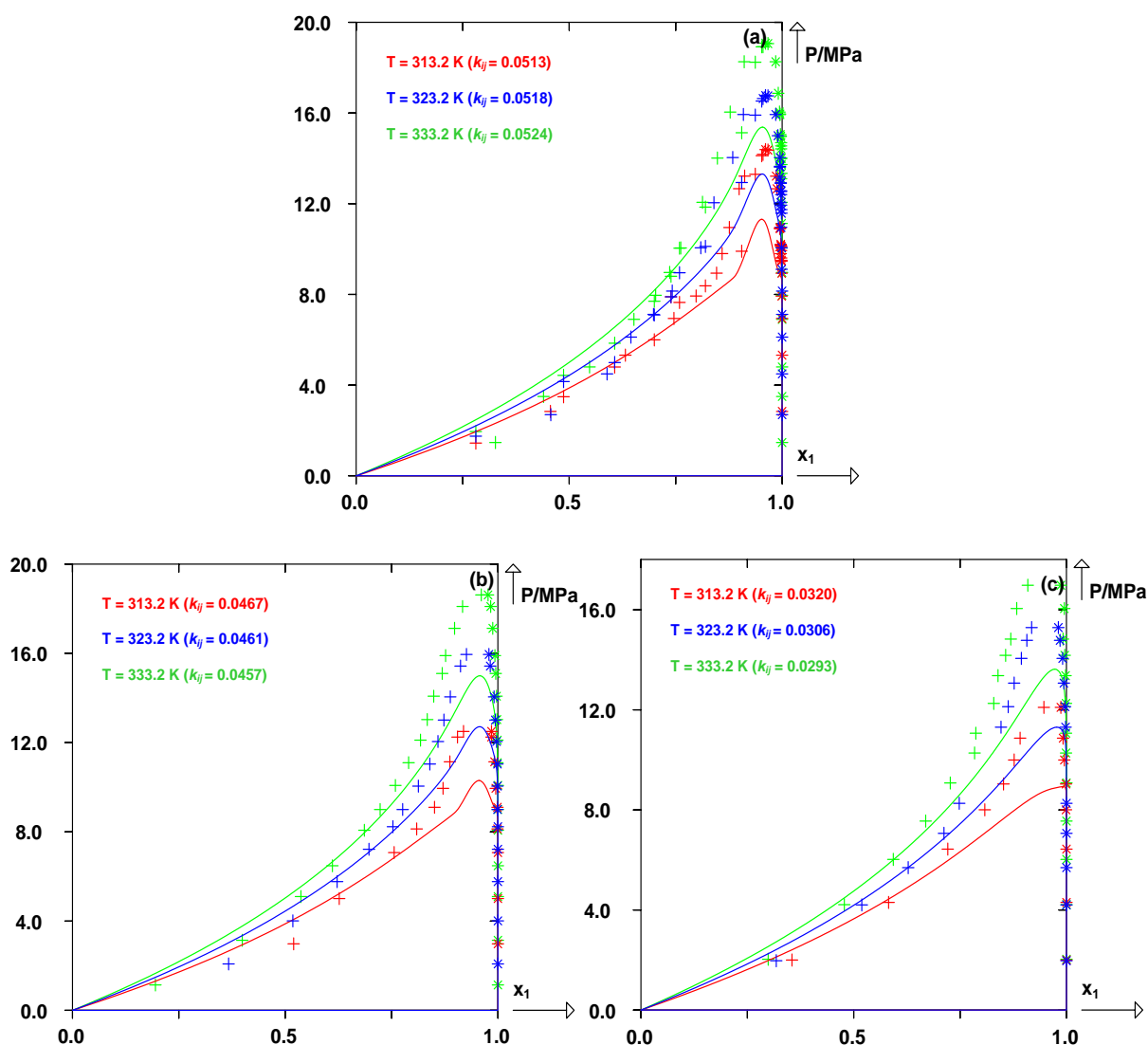


Fig. 4 Prediction of isothermal bubble and dew curves for the binary systems containing CO₂ and the C18 ethyl ester: (a): CO₂ (1) + ethyl stearate (2), (b): CO₂ (1) + ethyl oleate (2) and (c): CO₂ (1) + ethyl linoleate (2). (+): experimental bubble points, (*): experimental dew points and (Solid lines): predicted curves with the PPR78 model.

For the mixtures CO₂ + ethyl butanoate and CO₂ + ethyl pentanoate, a strong deviation between the experimental data and the predicted data are observed. The predicted critical curve is significantly lower than the measured points. For the system CO₂ + ethyl hexanoate, a good agreement between experimental and predictive data is obtained over the whole composition range. The results of the systems composed of CO₂ with ethyl heptanoate, ethyl octanoate and ethyl nonanoate are similar to that of the system CO₂ + ethyl acetate. Lastly, the

critical points of the system CO₂ + ethyl decanoate are slightly higher than the predicted critical locus. Even though, the PPR78 model predicts the critical behaviour of the systems under consideration with some deviations, it remains capable of predicting the global phase behaviour which agrees well with the experimental results for the first seven systems; the type I fluid phase behaviour for the systems CO₂ + ethyl acetate, CO₂ + ethyl propionate and CO₂ + ethyl butanoate and the type II for the rest. However, the model predicts the type II for the systems CO₂ + ethyl nonanoate and CO₂ + ethyl decanoate whereas we experimentally observed the discontinuous critical locus for the both systems. The critical points of ethyl nonanoate and ethyl decanoate could not be measured in this work due to the apparatus limit. The physical properties used in the model are obtained by linear interpolation for ethyl nonanoate and from literature for ethyl decanoate. Additionally, our experimental critical points of the mixture CO₂ + ethyl acetate are compared to the literature data [95-96]. As shown in figs 6a, the critical points measured in this work are a bit higher than those from the collection of Byun et al. [96]. These authors used a static-type experimental apparatus for their critical point measurements. Such an apparatus enables to accurately determine bubble and dew points but is often said not to be accurate enough for critical point measurements due to an iterative process. On the other hand, our critical data are much lower than those from the collection of Chester and Haynes [95]. This deviation is not surprising because it has been found in our previous work [117] that the results reported by Chester and Haynes are always higher than our data and other literature data. These authors estimated pressure – temperature coordinates of the critical points using a peak-shape-sensitive flow-injection procedure. Collectively, the difference found between the three critical data set is a consequence of the different experimental methods used. Regarding the critical behaviour of the mixtures containing CO₂ and the unsaturated ethyl esters, Figs. 6a, 6b and 6c present the comparison between the experimental critical points in this work and the critical locus predicted by the PPR78 model in the P - T , P - x and T - x projections, respectively. The critical locus of the CO₂ + ethyl trans-2-butenoate is overestimated at high concentration of CO₂ and underestimated at low concentration. Beside, the physical properties of ethyl trans-3-hexenoate are available only in the collection of Yaw [108] and the values from this collection always disagree with other sources [fig. 1]. This can partly explain why a large deviation is obtained between the experimental and predictive data for the system CO₂ + ethyl trans-3-hexenoate.

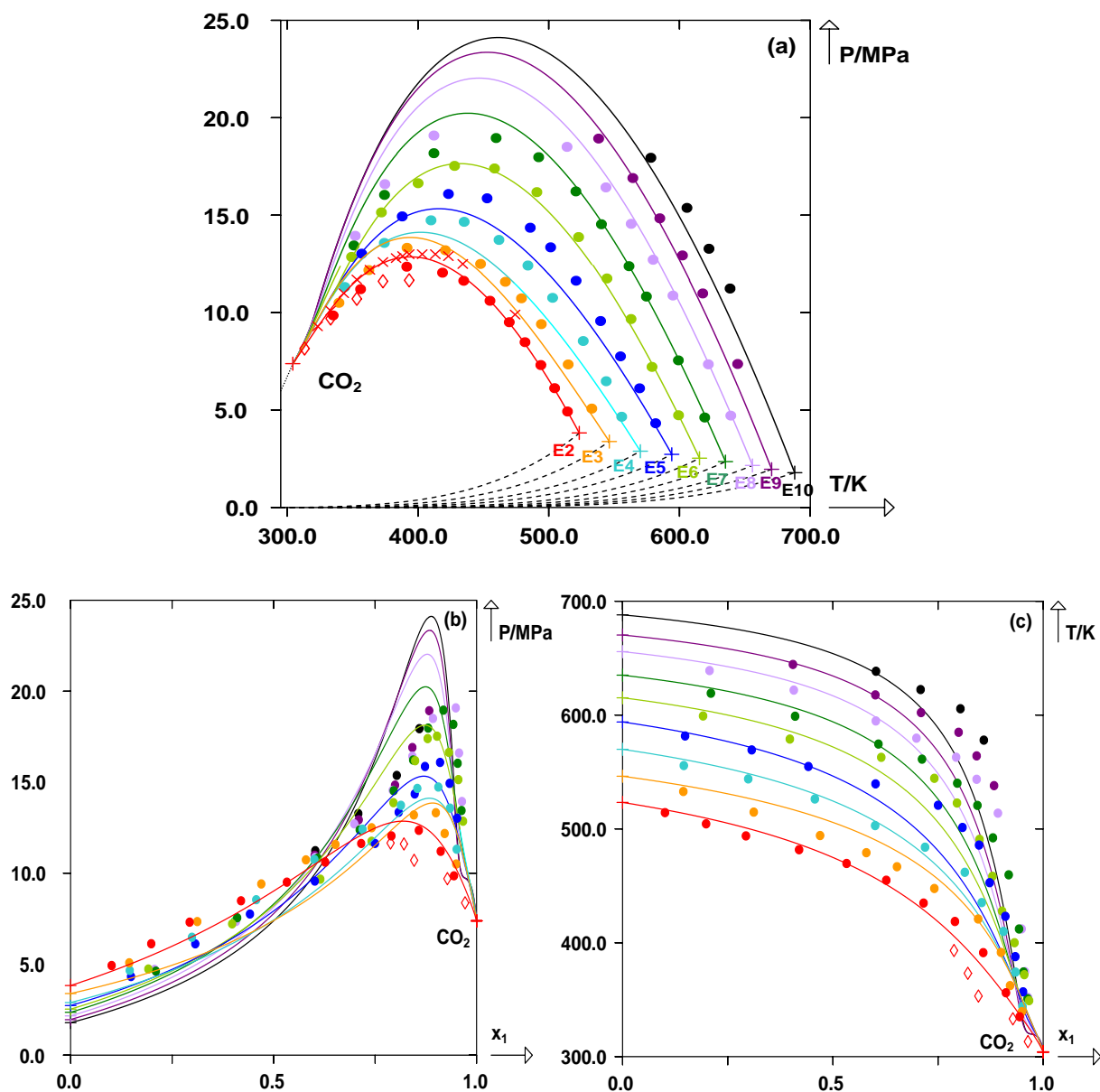


Fig. 5 Critical loci for the systems involving CO₂ and the saturated ethyl ester; CO₂ (1) + ethyl acetate (2), CO₂ (1) + ethyl propionate (2), CO₂ (1) + ethyl butanoate (2), CO₂ (1) + ethyl pentanoate (2), CO₂ (1) + ethyl hexanoate (2), CO₂ (1) + ethyl heptanoate (2), CO₂ (1) + ethyl octanoate (2), CO₂ (1) + ethyl nonanoate (2) and CO₂ (1) + ethyl decanoate (2). Experimental critical data: (Closed symbol): This work, (◇): Byun et al. [96], (×): Chester and Haynes [95], (Solid lines): curves predicted by the PPR78 model, (Dashed lines): vaporisation curves of pure components and (+): critical points of pure components. (a): P-T projection, (b): P-x₁ projection and (c): T-x₁ projection.

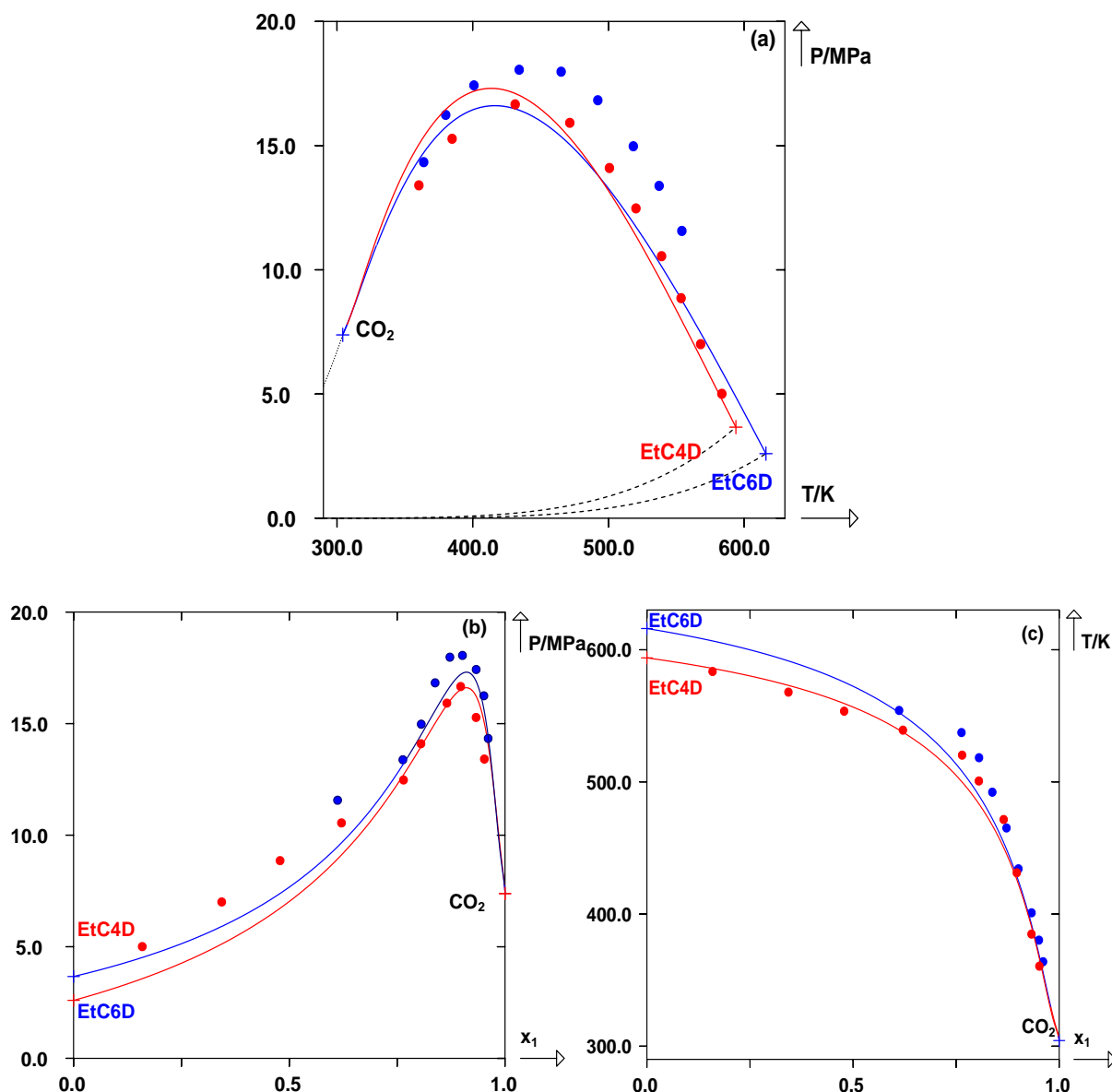


Fig. 6 Critical locus for the systems involving CO₂ and the unsaturated ethyl ester: **CO₂ (1) + ethyl trans-2-butenate (2)**, **CO₂ (1) + ethyl trans-3-hexenoate (2)**. (Closed symbol): experimental critical points in this work, (Solid lines): curves predicted by the PPR78 model. (Dashed lines): vaporisation curves of pure components and (+): critical points of pure components. (a): *P-T* projection, (b): *P-x₁* projection and (c): *T-x₁* projection.

Finally, the evolution in phase behaviour of the homologous series containing CO₂ and a saturated ethyl ester is studied. The PPR78 model is used to predict the global phase behaviour of seventeen binary systems: from CO₂ + ethyl acetate to CO₂ + ethyl stearate. Fig.7 shows the systematic change in the phase behaviour with increasing carbon number in the alkyl chain: from ethyl pentanoate to ethyl stearate. According to the PPR78 model, the systems containing CO₂ and a light ethyl ester (until ethyl butanoate) belong to type I, those

between ethyl pentanoate and ethyl nonanoate belong to type II, ethyl decanoate and ethyl dodecanoate belong to type IV and those beyond ethyl laurate belong to type III. This pattern is similar with the phase behaviour evolution of systems containing CO₂ and a *n*-alkane [118-120]. We recall that, in order to obtain a continuous curve in fig. 7, the physical properties of the pure compounds were obtained by smoothing the values presented in Table 3. For this reason, the PPR78 model predicts the type IV for the system CO₂ + ethyl decanoate. The transition from the type II to the type IV fluid phase behaviour occurs within a small variation of T_c , P_c and ω . This shows, once again, that predictive ability of the PPR78 model strongly depends on the physical properties of the pure components.

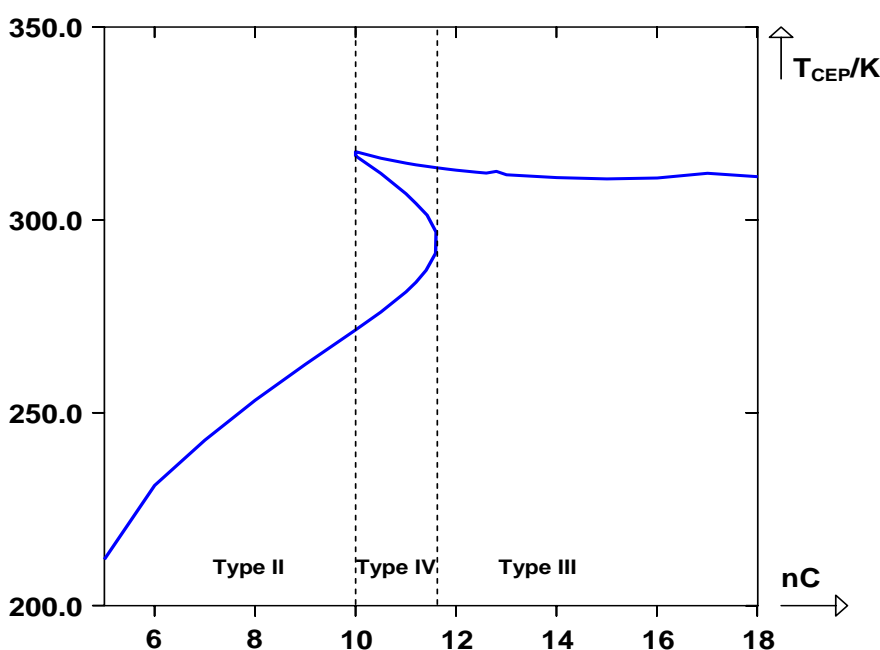


Fig. 7 Evolution of phase behaviour type for the systems involving CO₂ and saturated ethyl ester in the homologous series (from ethyl pentanoate to ethyl stearate)

I.4.2. Binary systems containing ethanol + ethyl ester

The vapour-liquid critical points of twelve binary systems consisting of ethanol and an ethyl ester were experimentally determined. The measurements were carried out using the synthetic-dynamic apparatus in the dynamic method. The experimental critical values with different mole fraction and their uncertainties for the systems ethanol (1) + ethyl acetate (2), ethanol (1) + ethyl propionate (2), ethanol (1) + ethyl butanoate (2), ethanol (1) + ethyl pentanoate (2), ethanol (1) + ethyl hexanoate (2), ethanol (1) + ethyl heptanoate (2), ethanol (1) + ethyl octanoate (2), ethanol (1) + ethyl nonanoate (2), ethanol (1) + ethyl decanoate (2),

ethanol (1) + ethyl trans-2-butenate (2), ethanol (1) + ethyl trans-3-hexenoate (2) and ethanol (1) + ethyl trans-2-octenoate (2) are given in Tables 24 to 35 of the Appendix 4, respectively. For the binary mixtures involving the saturated ethyl ester, the critical points of the first seven systems (i.e. from ethanol + ethyl acetate to ethanol + ethyl octanoate) could be determined throughout the entire range of composition. These mixtures display a continuous vapour – liquid critical locus which connects the critical points of the pure components. Moreover, the system ethanol + ethyl acetate shows a minimum in the critical temperatures. A lack of experimental data at low temperature makes it impossible to know whether liquid-liquid equilibrium exists. We thus cannot exclude that these systems exhibit the type II fluid phase behaviour according to the classification of Van Konynenburg and Scott [110]. However, Hu et al. [75] reported that the system ethanol + ethyl acetate should belong to the type I fluid phase behaviour. On the other hand, the temperature upper limit of the apparatus prevented some critical points of the mixtures ethanol + ethyl nonanoate and ethanol + ethyl decanoate from being measured. For the mixtures containing an unsaturated ethyl ester, the ethanol + ethyl trans-2-butenate system could be investigated over the whole composition range and also shows a continuous critical locus. Slightly colour change from colourless to yellowish for the two other mixtures was observed practically from the outlet of the equilibrium view cell at a temperature higher than 330 °C. According to the investigation of Lin et al. [111], such a colour change corresponds to the thermal decomposition which involves a cis/trans isomerisation, polymerisation and a pyrolysis reaction of compounds contained in biodiesel. The temperature of thermal decomposition of monounsaturated ethyl esters found in this work is much lower than that reported in literature. Vieitez et al. [115-116] studied thermal decomposition of ethyl ester in supercritical ethanol under different operating conditions and reported that the degradation of monounsaturated ethyl ester was not found at 20 MPa, 40:1 ethanol to oil molar ratio and temperatures from 250 °C to 325 °C neither at 20 MPa, 40:3 ethanol to oil molar ratio and temperatures from 250 °C to 375 °C. This difference can be explained by the investigation of Olivares-Carrillo and Quesada-Medina [113] who explained that the high alcohol to oil molar ratio has certain protective effect against the thermal decomposition of the unsaturated ester.

The PPR78 model is used to correlate the experimental data determined in this work and those available in the literature for the systems under consideration. The results are summarized in Table 6.

Table 6 Group-interaction parameters: $(A_{kl} = A_{lk})/\text{MPa}$ and $(B_{kl} = B_{lk})/\text{MPa}$, average overall deviation on the liquid phase composition $(\overline{\Delta x_1})$, the gas phase composition $(\overline{\Delta y_1})$, the critical composition $(\overline{\Delta x_c})$ and the binary critical pressure $(\overline{\Delta P_c \%})$ and the objective function (F_{obj}) determined in this study.

System	A_{kl}	B_{kl}	$(\overline{\Delta x_1})$	$(\overline{\Delta y_1})$	$(\overline{\Delta x_c})$	$(\overline{\Delta P_c \%})$	F_{obj}
EtOH-EtC2	93.33	172.6	43.99	13.37	42.09	9.799	32.89
EtOH-EtC3	110.1	361.7	15.11	12.32	2.097	3.183	11.29
EtOH-EtC4	102.3	293.3	14.32	14.81	4.388	6.911	12.53
EtOH-EtC5	9.800	-1.890	-	-	5.578	5.116	5.347
EtOH-EtC6	85.61	179.1	4.393	-	4.557	6.326	4.642
EtOH-EtC7	16.85	-6.730	-	-	5.997	6.607	6.302
EtOH-EtC8	-0.830	-4.230	-	-	7.056	5.476	6.266
EtOH-EtC9	-0.030	0.310	-	-	8.467	8.084	8.276
EtOH-EtC10	-147.6	-223.0	-	-	8.219	9.135	8.677
EtOH-EtC4D	21.70	51.07	-	-	2.385	1.342	1.864
EtOH-EtC6D	160.8	1198	-	-	4.063	10.29	7.179
EtOH-EtC8D	50.76	147.2	-	-	6.877	8.850	7.866

The system ethanol + ethyl acetate shows the highest objective function value due to the presence of an azeotrope. According to literature investigation [104], the azeotrope artificially increases the objective function.

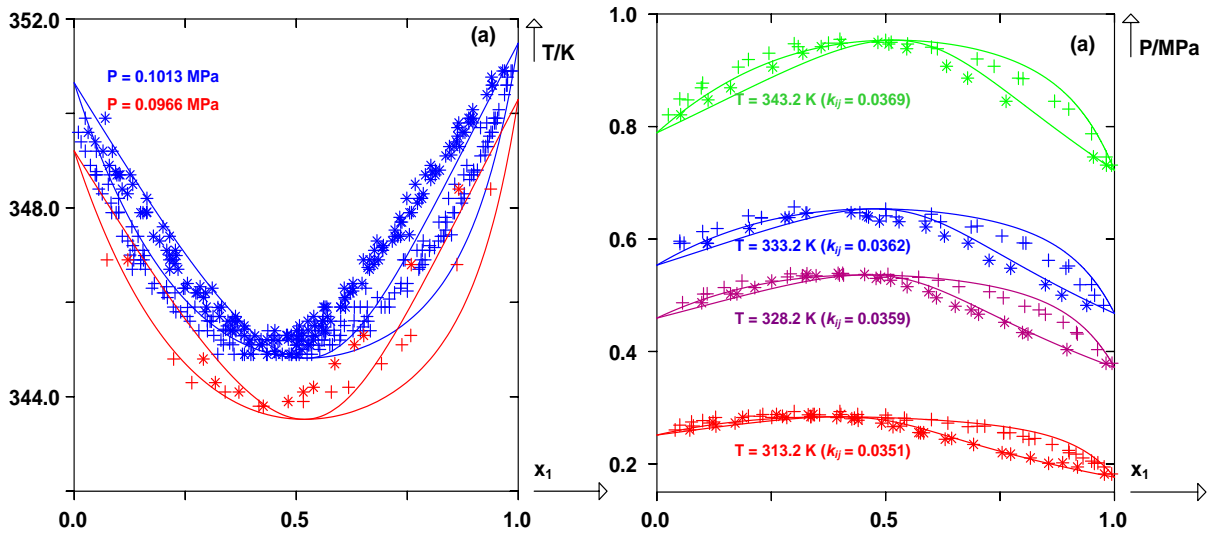


Fig. 8 Prediction of bubble and dew curves of the system ethanol (1) + ethyl acetate (2); (a): isobaric diagram and (b): isothermal diagram. (+): experimental bubble points, (*): experimental dew points and (Solid lines): predicted curves with the PPR78 model.

Fig. 8 shows isothermal and isobaric phase diagrams for the ethanol + ethyl acetate system. This system exhibits a positive azeotrope at low temperatures and pressures. The PPR78 model is able to accurately locate the azeotropic temperature and pressure but a slightly deviation is found in the azeotropic composition. Fig. 8b illustrates that, as temperature increases, the azeotrope composition shifts towards lower ethanol contents.

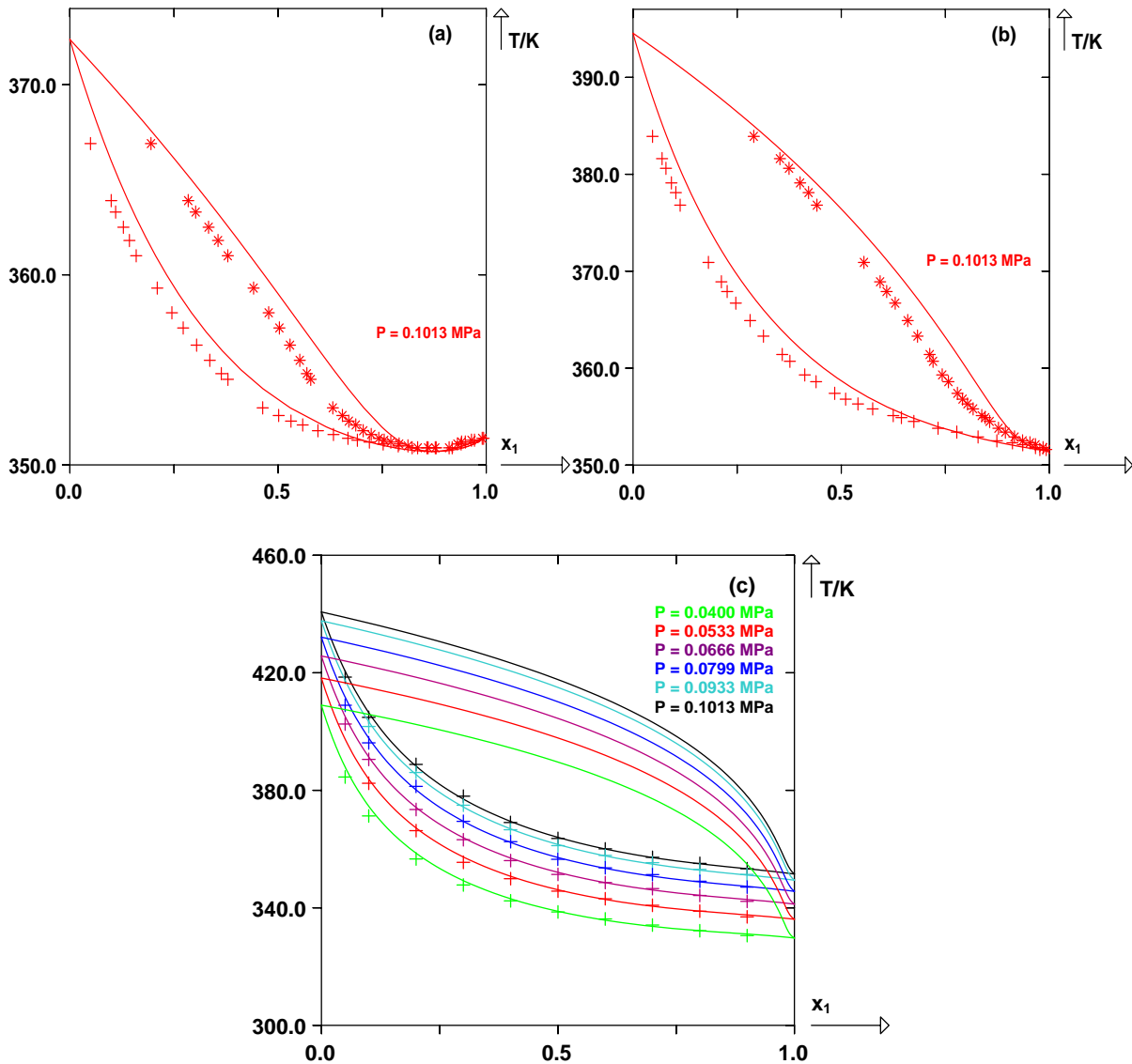


Fig. 9 Prediction of isobaric bubble and dew curves for the binary system containing ethanol and the saturated ethyl ester at different pressures; (a): ethanol (1) + ethyl propionate (2), (b): ethanol (1) + ethyl butanoate (2) and (c): ethanol (1) + ethyl hexanoate (2). (+): experimental bubble points, (*): experimental dew points and (Solid lines): predicted curves with the PPR78 model.

Moreover the deviation between experimental and predicted bubble and dew curves tends to increase. Fig. 9 presents isobaric phase diagrams for the systems containing the short-chain saturated ethyl ester at different pressures. The system ethanol + ethyl propionate also exhibits a positive azeotrope and the PPR78 model perfectly locates this point [fig. 9a]. The bubble and dew curves are slightly overestimated for the systems ethanol + ethyl propionate [fig. 9a] and ethanol + ethyl butanoate [fig. 9b] whereas they are accurately predicted at any pressures for the system ethanol + ethyl hexanoate [fig. 9c]. The comparison between our experimental critical points, literature critical data and the critical locus predicted by the PPR78 model for the systems containing the saturated ethyl ester is graphically presented in figs. 10a and 10b which correspond to pressure – temperature (P - T) and temperature – composition (T - x) diagrams, respectively. Due to the strong molecular polarity and the molecular interactions, the PPR78 model has low capacity for correlating the phase behaviour of these mixtures.

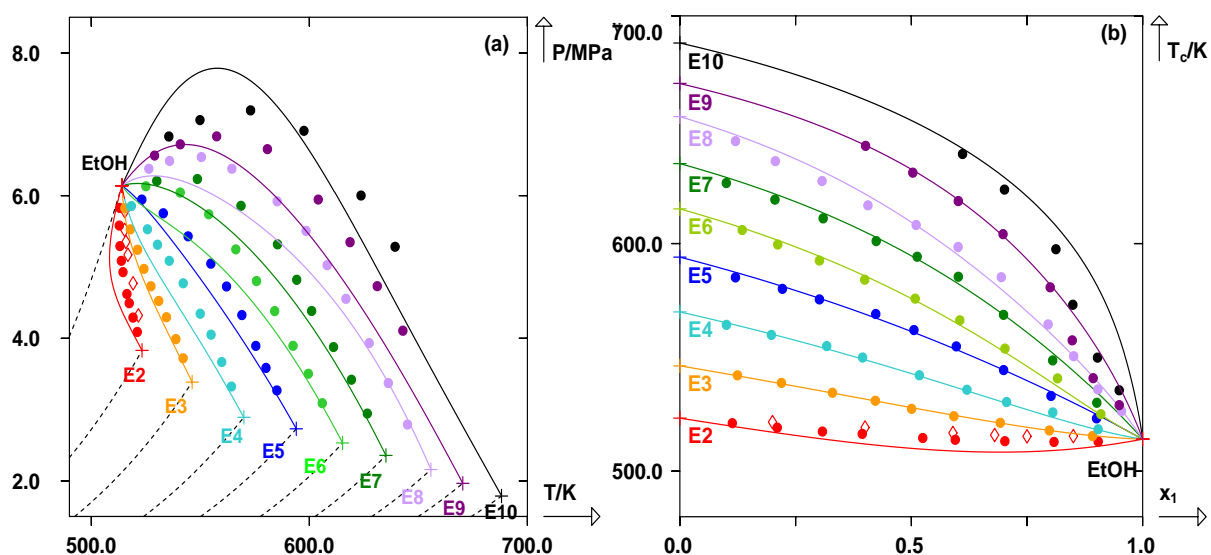


Fig. 10 Critical loci for the systems involving CO_2 and the saturated ethyl ester; CO_2 (1) + ethyl acetate (2), CO_2 (1) + ethyl propionate (2), CO_2 (1) + ethyl butanoate (2), CO_2 (1) + ethyl pentanoate (2), CO_2 (1) + ethyl hexanoate (2), CO_2 (1) + ethyl heptanoate (2), CO_2 (1) + ethyl octanoate (2), CO_2 (1) + ethyl nonanoate (2) and CO_2 (1) + ethyl decanoate (2). Experimental critical data: (Closed symbol): This work, (\diamond): Hu et al. [71], (Solid lines): curves predicted by the PPR78 model, (Dashed lines): vaporisation curves of pure components and (+): critical points of pure components. (a): P - T projection and (b): T - x_1 projection.

For all the systems, the predicted critical locus displays an uninterrupted curve which agrees well with the experimental work. The experimental critical pressures are underestimated by the model and the longer the ester-chain length the larger the deviations are. Otherwise, fig.

10b highlights a good agreement between the experimental critical temperatures and the predicted values, except at high concentrations of ethanol for the systems containing ethyl nonanoate and ethyl decanoate where the critical temperatures are overestimated. Furthermore, as previously discussed, the system ethanol + ethyl acetate exhibits a positive azeotrope at low temperatures and pressures and a minimum in the critical temperature vs composition curve. This system may exhibit a critical azeotrope which is an intersection between the critical locus and the azeotropic line. In order to check the existence of such a critical azeotrope, the experimental saturated vapour pressures of ethanol available in literature [121-124] are plotted in fig. 11 which shows the global P - T phase diagram of the mixture ethanol + ethyl acetate. The experimental saturated vapour pressures agree very well with the vaporisation curve predicted by the PPR78 model. The vaporization curve of ethanol does not intersect the critical locus. Consequently, the azeotrope does not persist up to the critical locus for the system ethanol + ethyl acetate (the azeotropic line is located above the vaporisation curve of pure ethanol). It is sometimes said in the open literature that a minimum in the critical temperature is always associated with the positive critical azeotrope. Herein, we prove that this is obvious wrong. Moreover, our experimental critical values for the mixture ethanol + ethyl acetate are compared to those found in literature.

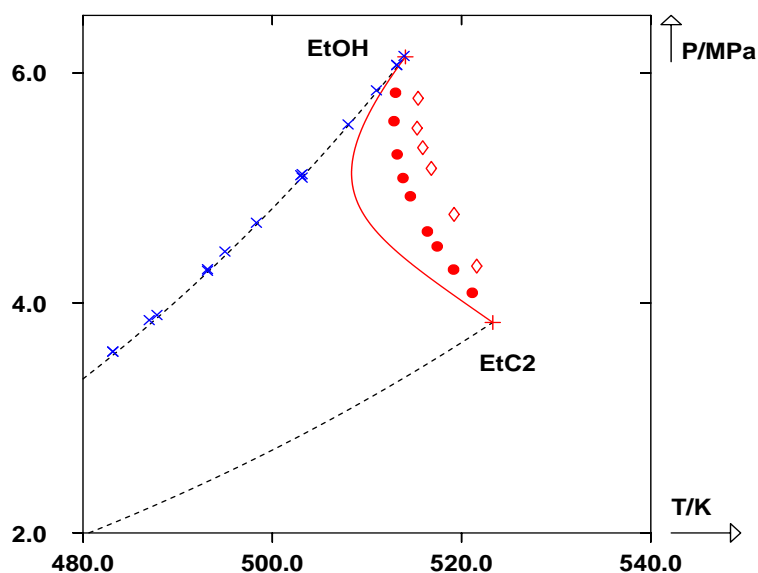


Fig. 11 Global phase diagram of the system ethanol (1) + ethyl acetate (2) in the P - T projection. Experimental critical points: (●): this work, (◊): Hu et al. [75], (x): saturated vapour pressures of ethanol, (+): critical points of pure components, (Solid lines): critical curve predicted by the PPR78 model and (Dashed lines): vaporisation curves predicted by the PPR78 model.

As can be seen in fig. 11, the critical points measured in this work are a bit lower than those collected by Hu et al. [75]. The discrepancies between the two data set are ≤ 3 K for the critical temperatures and ≤ 1.7 MPa for the critical pressures. The difference is probably the consequence of the different experimental techniques used. Hu et al. [75] used the static method for determining the critical properties. Such a method requires information about critical density of mixtures which is a priori unknown. The comparison between the critical point of ethanol and ethyl acetate determined in this work with those measured by Hu et al. [75] and those available in the DIPPR database [107] were performed. Our critical values for pure compounds agree better with those of the DIPPR than those of Hu et al. Finally, fig. 12a and 12b illustrate the comparison between the experimental critical points in this work and the critical locus predicted by the PPR78 model for the systems consisting of the unsaturated ethyl ester in the T - P and T - x projections, respectively. The PPR78 model correlates well the critical locus of the system ethanol + ethyl trans-2-butenoate but poorly reproduces that of the system ethanol + ethyl trans-3-hexenoate and ethanol + ethyl trans-2-octenoate.

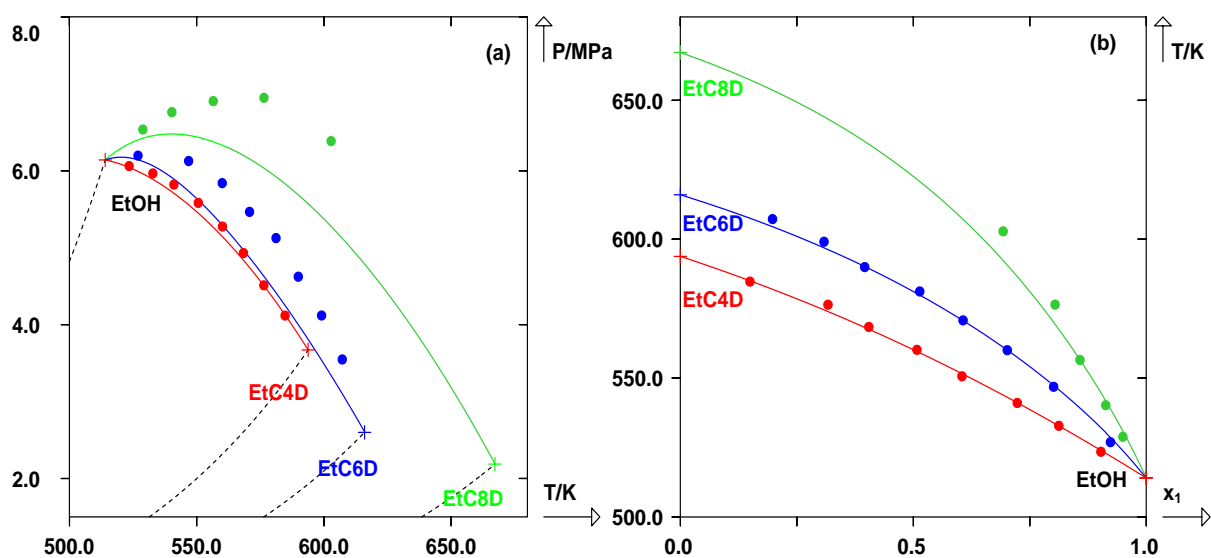


Fig. 12 Critical locus for the systems involving ethanol and the unsaturated ethyl ester; **ethanol (1) + ethyl trans-2-butenoate (2)**, **ethanol (1) + ethyl trans-3-hexenoate (2)** and **ethanol (1) + ethyl trans-2-octenoate (2)**. (Closed symbol): Experimental critical data in this work, (+): critical points of pure components. (Solid lines): critical loci predicted by the PPR78 model and (Dashed lines): vaporisation curves predicted by the PPR78 model. (a): P - T projection and (b): T - x_1 projection.

I.5. Conclusion

For the binary systems containing CO₂ and an ethyl ester, the critical points for the seven systems could be measured over the whole composition range whereas some critical points for the four other systems were prevented from being measured by the cell capacity and the thermal decomposition of compound. Among these binary mixtures, only the systems CO₂ + ethyl nonanoate and CO₂ + ethyl decanoate were found experimentally to exhibit a discontinuous critical locus. The PPR78 model was extended to the systems containing CO₂ and an ethyl ester by defining the ester group. The PPR78 model is capable to accurately predict the subcritical behaviour of all the systems under consideration, except the systems involving C4 and C18 ethyl esters. In the other hand, the PPR78 predicts less accurately the critical behaviour for the systems experimentally studied in this work. The type of binary mixture phase behaviour found by experimental work agrees well with that predicted using the PPR78 except for the systems CO₂ + ethyl nonanoate and CO₂ + ethyl decanoate. In addition, the experimental results for the system CO₂ + ethyl acetate in this work are compared to literature data. Some variations are found owing to different experimental techniques used. Finally, the evolution in phase behaviour of the systems containing CO₂ and saturated ethyl ester was studied using the PPR78 model. The evolution pattern is similar with the systems consisting of CO₂ and a *n*-alkane in the homologous series.

For the binary systems involving ethanol and an ethyl ester, ten systems could be measured over the entire range of composition. The temperature upper limit of the apparatus and the thermal decomposition of unsaturated compounds prevented some critical points of four other systems from being measured. All these mixtures exhibit a continuous critical locus. The PPR78 model is used for correlating the experimental results determined in this work and those found in literature for all systems under consideration. This model is capable of reproducing the subcritical behaviour but poorly estimates the critical phase behaviour due to the strong molecular polarity and the molecular interaction in these systems. For the system ethanol + ethyl acetate, the critical points are compared to those available in literature. The observed difference was assumed to come from the different techniques used. Moreover, the intersection between the vaporisation curve of ethanol and the critical locus was not found. Therefore, a critical azeotrope does not exist.

The experimental data determined in this work could probably correlated using other predictive thermodynamic models which are able to estimate the molecular polarity.

II. Phase behaviour of alternative refrigerants

II.1. Introduction

Due to a high ozone depletion potential (DOP) value of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) and a high global warming potential (GWP) value of Hydrofluorocarbons (HFCs), refrigeration and air-conditioning industries have been carried out extensive researches and development activities to find highly efficient alternative refrigerants under conditions of zero DOP according to the Montreal Protocol and GWP lower than 150 according to the European Union's F gas regulation. Natural refrigerants particularly carbon dioxide was expected as the conventional refrigerant replacement owing to its environmental benefits: zero DOP, low GWP, no toxicity and no flammability. However, CO₂ has some drawbacks including significantly higher pressure and lower thermodynamic cycle efficiency, hence, the use of CO₂ as the alternative refrigerant may require a total redesign of several system components. Recently, hydrofluoro-olefines (HFOs) especially R1234yf (2,3,3,3-tetrafluoropropane) and R1234ze (E) (trans-1,3,3,3-tetrafluoropropane), newly synthesized refrigerants that have zero DOP, low GWP in the range of less than 10 relative to CO₂ for a 100 years time horizon [125-126] and extremely short atmospheric lifetime, have been proposed as a next generation candidate, particularly, to replace HFC-134a in the automobile air conditioning system [127-130].

During the past few years, various thermophysical properties of the R1234yf and R1234ze (E) such as vapour pressures [131-136], critical properties [137-138], PvT and $P\rho T$ behaviours [135-136, 139], specific heat capacities [140-141] densities [135, 142-143] and viscosities [144] were actively investigated. Moreover, some predictive methods were developed for predicting their properties [145-146]. However, one of the main drawbacks of these HFOs is their mildly flammability, linked to a small gap between lower and upper flammability limits. As a consequence, many researchers believe that the combination of refrigerants may offer a good potential as alternative, which can meet the requirements of both utilisable performance and environmental performance, to pure substances. From 2012, phase behaviour of binary systems containing the HFO and another refrigerant were increasingly studied, for example, mixtures composed of R1234yf with HFC refrigerant [147-148] and with natural refrigerant [149] and those composed of R1234ze (E) with HFC refrigerant [150-151] and with natural refrigerant [152-154]. Even through some binary

mixtures were found to exhibit an interesting behaviour such as an azeotrope, they are still responsible for some negative environmental impacts.

In this work, we focus on behaviour of the binary mixtures containing the environmentally friendly natural refrigerant CO₂ and the new possible replacement refrigerants R1234yf or R1234ze (E). Such refrigerant mixtures allow reducing the high saturation pressures of CO₂ as well as the flammability of R1234yf and R1234ze (E). Isothermal measurements of liquid-vapour equilibrium (P - T - x - y) data for the system CO₂ + R1234yf were undertaken at temperatures 283.15 K and 293.15 K with pressures ranging from 0 to 7 MPa. The measurements were carried out using a static-analytic type apparatus coupled with two electromagnetic capillary ROLSITM samplers, with phase analysis via a gas chromatography. Furthermore, the vapour - liquid critical properties (critical temperatures and critical pressures) of binary systems containing CO₂ and R1234yf and CO₂ + R1234ze (E) were experimentally determined over the entire range of composition. The critical point measurements were performed using a synthetic-dynamic apparatus in a dynamic method. The critical points can be determined by visually observing the critical opalescence phenomenon in a high-pressure equilibrium cell. The experimental VLE data are compared to those available in literature whereas the experimental critical data are reported for the first time in this study. Additionally, the PPR78 model is used to correlate all the experimental results obtained in this work.

II.2. Experimental procedure

II.2.1. Materials

All compounds were purchased from commercial sources and used without any further purification. The purities and the suppliers of compounds are listed in Table 7.

Table 7 Purity and supplier of compounds used in this study.

Compound	Purity	Supplier
Carbon dioxide	99.995vol%	Air Liquide
R1234yf	≥99vol%	Honeywell
R1234ze (E)	≥99vol%	Honeywell

II.2.2. Isothermal vapour – liquid equilibrium measurements

A schematic diagram of the static-analytic apparatus used in this work is presented in fig.13. The apparatus has been developed by the ARMINES company hosted by the Ecole Nationale Supérieure des Mines de Paris for measurement of vapour-liquid phase equilibrium of pure compounds and mixtures.

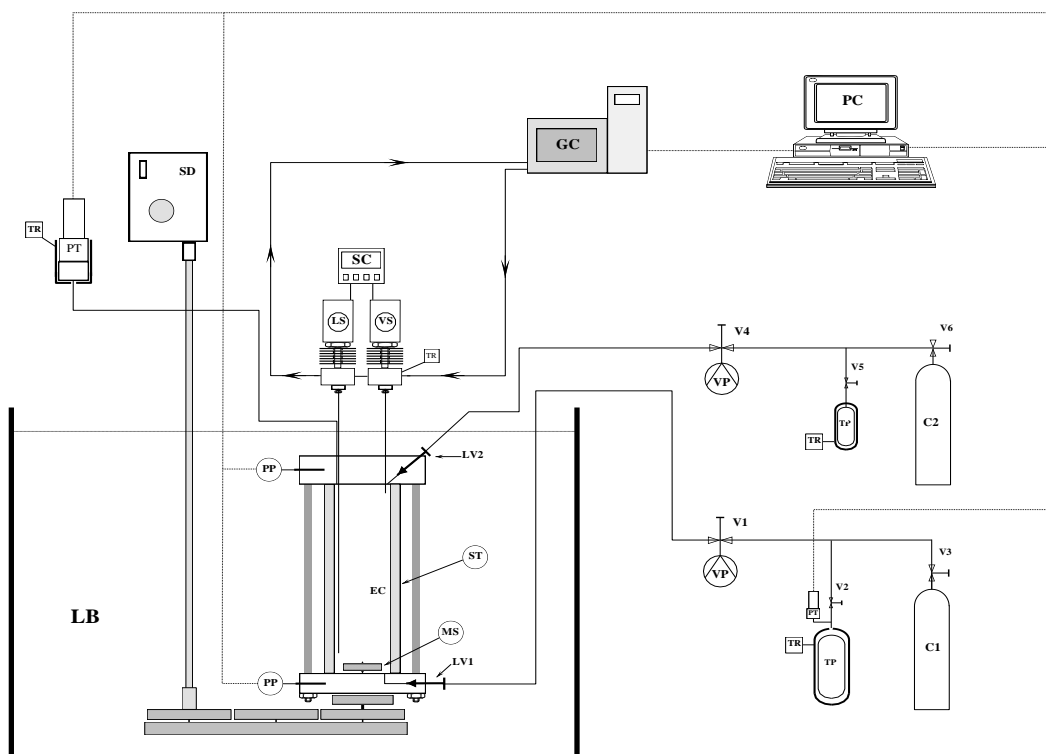


Fig. 13 Schematic diagram of the ELV measurement apparatus. EC: Equilibrium cell; LV: Loading valve; MS: Magnetic stirrer; PP: Platinum resistance thermometer probe; PT: Pressure transducer; RT: Temperature regulator; LB: liquid bath; TP: Thermal press (reservoir press); C1: more volatile compound; C2: less volatile compound; V: Valve; GC: Gas chromatograph; LS: liquid sampler; VS: Vapour sampler, SC: Sample controlling; PC: Personal computer; VP: Vacuum pump.

The apparatus used in this work is similar in concept to that of Laugier and Richon [155], Valtz et al. [156-157] and Coquelet et al. [158-159]. It consists of a 30 cm³ titanium equilibrium cell coupled with electromagnetic capillary samplers ROLSITM (rapid Online Sampling Injection) capable of taking a small quantity of sample in the equilibrium cell and sending to a gas chromatograph (PERICHRON, model PR2100) for determining phase compositions. The equilibrium cell withstands operation conditions up to 543.15 K and 10 MPa and holds between two titanium flanges. The top flange is connected to a 100 Ω platinum resistance thermometer probe (Pt100), a pressure transducer, two ROLSITM samplers

and two inlet valves. The bottom flange is connected to a Pt100 probe and two outlet valves and holds a magnetic stirrer coupled with an electric motor (HEIDOLPH, model RZR2020). The equilibrium cell is immersed in a water thermostat bath (ULTRA KRYOMAT LAUDA) that controls and maintains a desired operating temperature within ± 0.01 K. The cell temperature is measured using two Pt100 probes, at two locations corresponding to the vapour and liquid phases. Experimental setup for calibration of temperature and pressure sensors is described in the appendix 1. The Pt100 probes were calibrated against a Pt25 probe (TINSLEY Precision Instruments) which had been calibrated by the Laboratoire National d'Essais (Paris) based on the 1990 International Temperature Scale (ITS 90). Temperature calibration error is estimated to be ± 0.04 K in the 293.15 – 553.15 K temperature range [fig. 14].

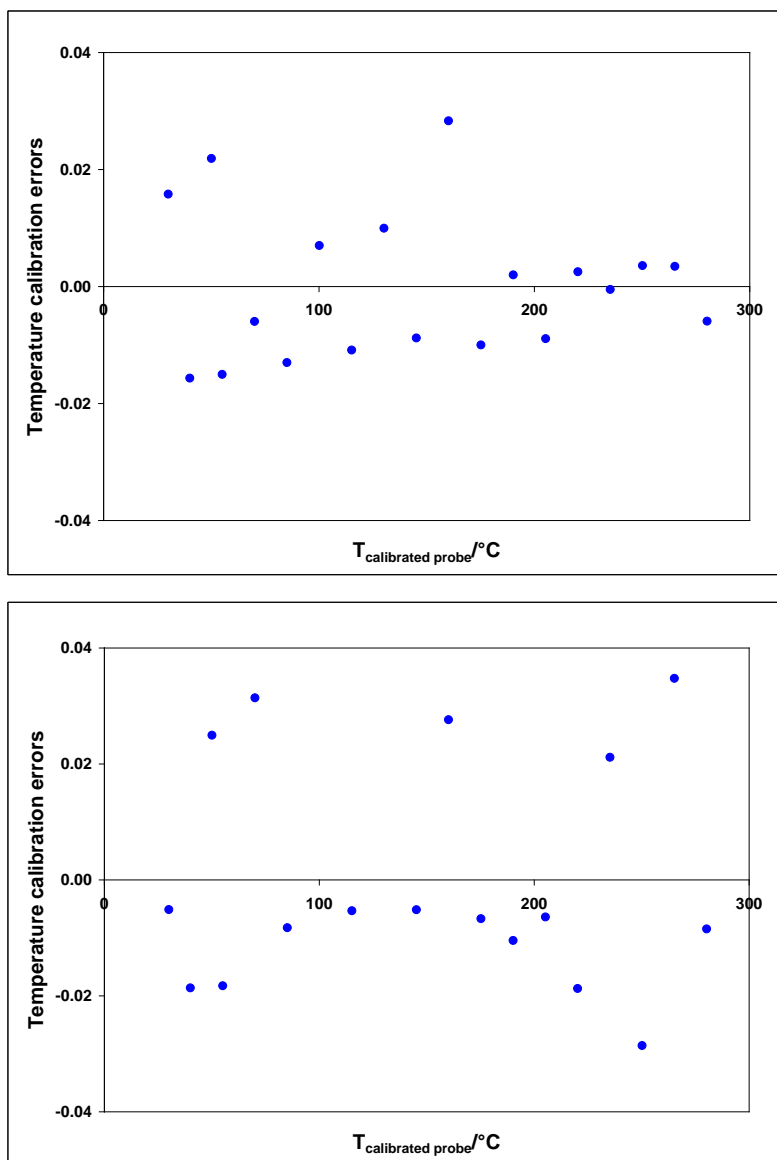


Fig. 14 Temperature calibration errors: the difference between temperatures determined using the calibrated probe and those determined using the Pt100 probe correlated one.

The cell pressure is measured using the pressure transducer (DRUCK, Model PTX6100) which is kept at constant temperature of 353.15 K by means of a heating cartridge regulated via a PID regulator (WEST, model 6100). The pressure transducer was calibrated against a dead-weight balance (DESGRANGES&HUOT, model 5202S). Pressure calibration error is estimated to be ± 0.003 MPa in the 0.1 – 7 MPa pressure range [fig. 15]. The two 100 Ω platinum resistance thermometer devices and the pressure transducer are connected to an online data acquisition unit (HP34970A) which is connected to a personal computer through one RS-232 interface. This system ensures real time reading and saving of temperatures and pressures during acquisition.

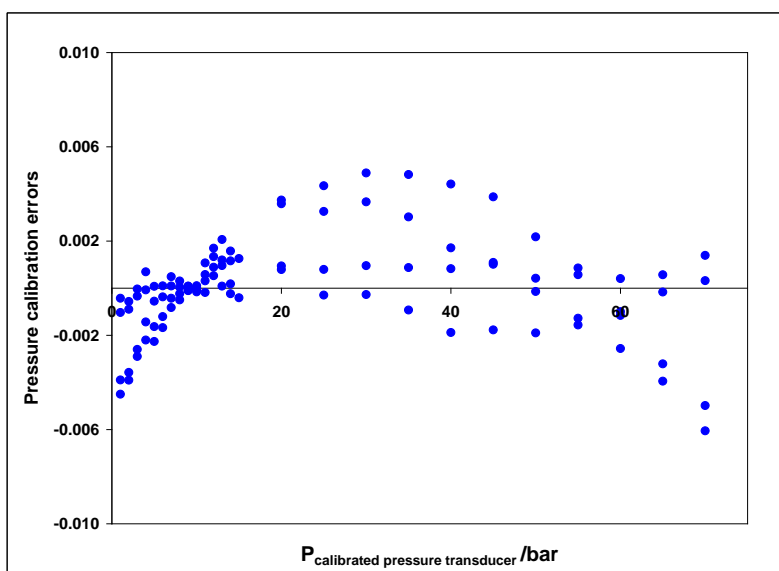


Fig. 15 Pressure calibration errors: the difference between pressures measured using the calibrated pressure transducer and those measured using the pressure transducer (available in our experiments) correlated one.

The loading of gases into the equilibrium cell is carried out through 10 cm³ and 100 cm³ reservoir presses coupled with a temperature regulator system which allows transferring a larger amount of sample. The equilibrium cell and transfer circuits are evacuated using a vacuum pump (OERLIKON LEYBOLD Model Trivac D2.5). In the first step, the less volatile compound is transferred from a gas cylinder to the 10 cm³ reservoir press and then to the equilibrium cell by cooling and heating the reservoir press, respectively. The equilibrium cell is then placed in the water thermostated bath which is set to the desired operating temperature. In a second step, the same procedure is applied to the more volatile compound via the 100 cm³ reservoir press until achieving a desired operating pressure. After reaching an

equilibrium condition (i.e. temperature and pressure inside the cell remain unchanged within their uncertainties during at least 10 min under an efficient stirrer), the electromagnetic ROLSI™ samplers are repeatedly purged with the equilibrium cell content. Then, they are used for withdrawing a sample from the equilibrium cell and sending it to the gas chromatography (GC) for analysis. The GC operating conditions for composition analysis are given in Table 8.

Table 8 GC operating conditions for composition analysis.

Injector temperature	120°C
Carrier gas	Hydrogen
Column	RESTEK, 1% RT-1000 on carboblack B, 60/80 mesh (2 m x 2 mm ID Silcosteel)
Flow rate	110 kPa
Oven temperature	50°C
Detector type	Thermal Conductivity Detector (TCD)
Detector temperature	180°C

The response of the TCD was calibrated for each pure compound using an automatic syringe which ensures a highly accurate injection volume. The mole numbers of compound contained inside the syringe is calculated using the ideal gas equation with the room temperature and pressure measured before each injection. For each component, multiple injections of various volumes were performed and a calibration graph (peak area versus number of moles) was established. The calibration data are fitted to second order polynomials. The correlation error on the mole number is estimated as $\pm 2\%$ for CO₂ [fig. 16] and $\pm 3.5\%$ for R1234yf [fig. 17]. Then, a new equilibrium condition at higher pressure is studied by adding the more volatile compound in the equilibrium cell. It is necessary to maintain the pressure inside the 100 cm³ reservoir press higher than that inside the equilibrium cell. This procedure is repeated until the whole composition range is covered for an isotherm. For each equilibrium condition, the composition analysis of each phase sample was repeated at least six times in order to check the measurement reliability. The cell temperature and pressure of each composition analysis were recorded. The average of the recorded temperatures, pressures and compositions (x and y) were taken as the vapour-liquid phase equilibrium data reported in this work. The uncertainties, classically determined by following the statistical method recommended by

NIST, were estimated ≤ 0.04 for the equilibrium temperature, ≤ 0.0010 for the equilibrium pressure and ≤ 0.0012 for the vapour mole fraction and ≤ 0.0005 for the liquid mole fraction.

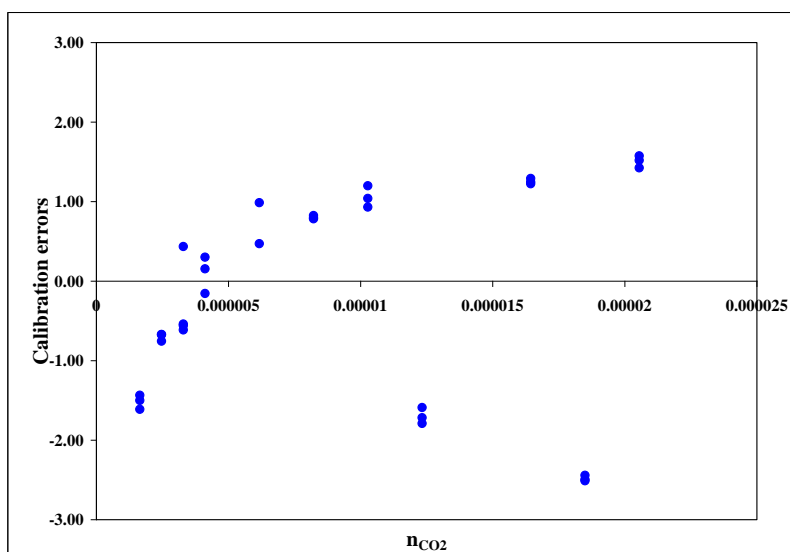


Fig. 16 Calibration errors of the number of mole of CO₂

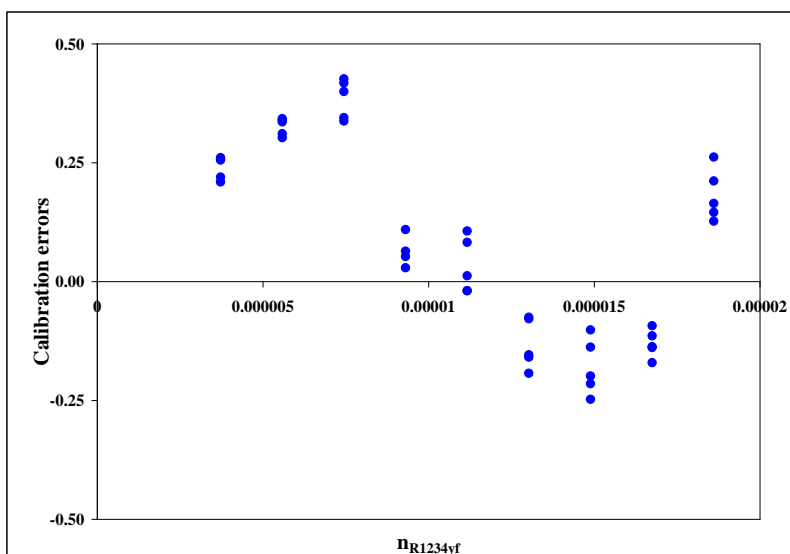


Fig. 17 Calibration errors of the number of mole of R1234yf

II.2.2. Critical point measurements

The critical point measurement is identical to that described in the part B, particularly in the section II.2 for the gas/gas binary systems. The uncertainties on pure component and mixtures critical coordinates, classically determined by following the statistical method recommended by NIST, are $\leq 0.05^{\circ}\text{C}$ for the critical temperature and ≤ 0.0076 MPa for the

critical pressure, respectively. Likewise, a mean value uncertainty in the mole fraction, $u(x_i) = \pm 0.00003$ is obtained.

II.3. Data correlation with the PPR78 model

The PPR78 model which is described in the Part A, particularly in the section IV.2, is used to correlate the experimental results of the binary systems containing CO₂ and the HFO. We used the critical temperature and critical pressure determined in this work and the factor acentric originated from Tanaka and Higashi [137] for R1234yf and from Higashi et al. [138] for R1234ze (E). Since each molecule is considered as one group, we need to estimate two constant parameters (A_{12} and B_{12}) for each system. Such parameters were determined in order to minimize the deviations between calculated and experimental critical data. The experimental data taken into account are those measured in this work. The corresponding values are given in Table 9.

Table 9 Constant parameters: ($A_{kl} = A_{lk}$)/MPa and ($B_{kl} = B_{lk}$)/MPa determined by the PPR78 model.

System	A_{kl}	B_{kl}
CO ₂ (1) + R1234yf (2)	26.28	402.2
CO ₂ (1) + R1234ze (E) (2)	-4.14	12.33

II.4. Results and discussion

In this work, the isothermal (P - x - y) vapour – liquid equilibrium data of the binary system CO₂ (1) + R1234yf (2) were measured at temperatures 283.15 K and 293.15 K using the static - analytic type apparatus. The liquid and gas phase composition, the temperature and the pressure with their standard uncertainties are presented in Table 36 of the Appendix 4. Furthermore, the critical points of two binary systems containing CO₂ and a HFO were experimentally determined over the entire range of composition. The critical point measurements were carried out using the synthetic – dynamic type apparatus in the dynamic mode. The experimental critical values at different mole fractions and their standard uncertainties for the systems CO₂ (1) + R1234yf (2) and CO₂ (1) + R1234ze (E) (2) are given in Table 37 and 38 of the Appendix 6. The experimental VLE data of the system CO₂ (1) + R1234yf (2) are compared to those found in the open literature [154] whereas the

experimental critical data of the systems CO_2 (1) + R1234yf (1) and CO_2 (1) + R1234ze (E) (2) are investigated for the first time in this work. Fig. 16 shows the comparison between the experimental VLE values determined in this work, literature data [154] and values predicted by the PPR78 model. A good agreement is obtained between our experimental data and those collected by Di Nicola [154]. These authors measured the PVT_x properties of the system CO_2 (1) + R1234yf (2) at low concentration of CO_2 using an isochoric apparatus. Moreover, the PPR78 is able to accurately correlate the experimental dew points at all temperatures studied whereas it slightly underestimates the experimental bubble pressures.

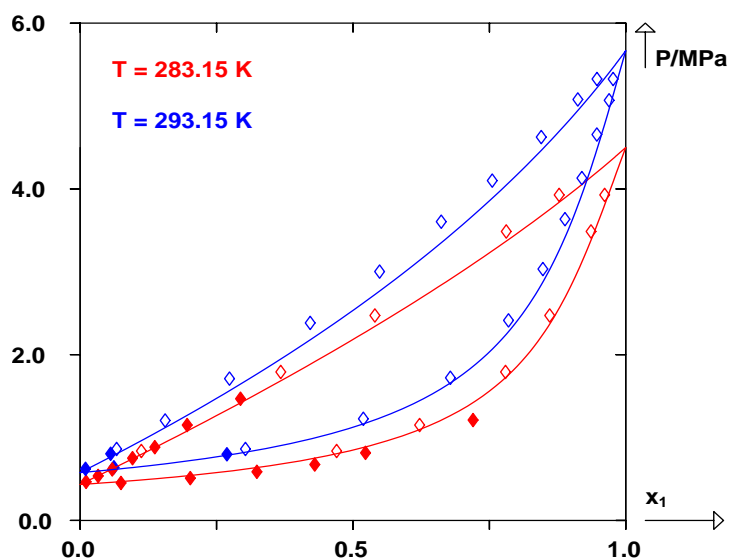


Fig. 16 Isothermal bubble and dew curves for the system CO_2 (1) + R1234yf (2) at two temperatures; Experimental bubble and dew points at 283.15 K : (◇): This work, (◆): Di Nicola et al. [153], Experimental bubble and dew points at 293.15 K: (◇): This work, (◆): Di Nicola et al. [153] and (Solid line): bubble and dew curves correlated by the PPR78 model.

The comparison between the experimental critical values and the critical data predicted using the PPR78 model is presented in Fig. 17a, 17b and 17c which correspond to the pressure – temperature (P - T), pressure – composition (P - x) and temperature – composition (T - x) projections. As can be seen in Fig. 17a, the systems CO_2 (1) + R1234yf (2) and CO_2 (1) + R1234ze (E) display a continuous liquid – vapour critical locus which connects the critical points of the pure substances. Therefore, these systems may belong to the type I or II according to the classification of Van Konynenburg and Scott [110]. As can be seen in fig. 17b and 17c, the PPR78 accurately correlates the critical temperatures but slightly underestimates the critical pressures for all the systems under consideration.

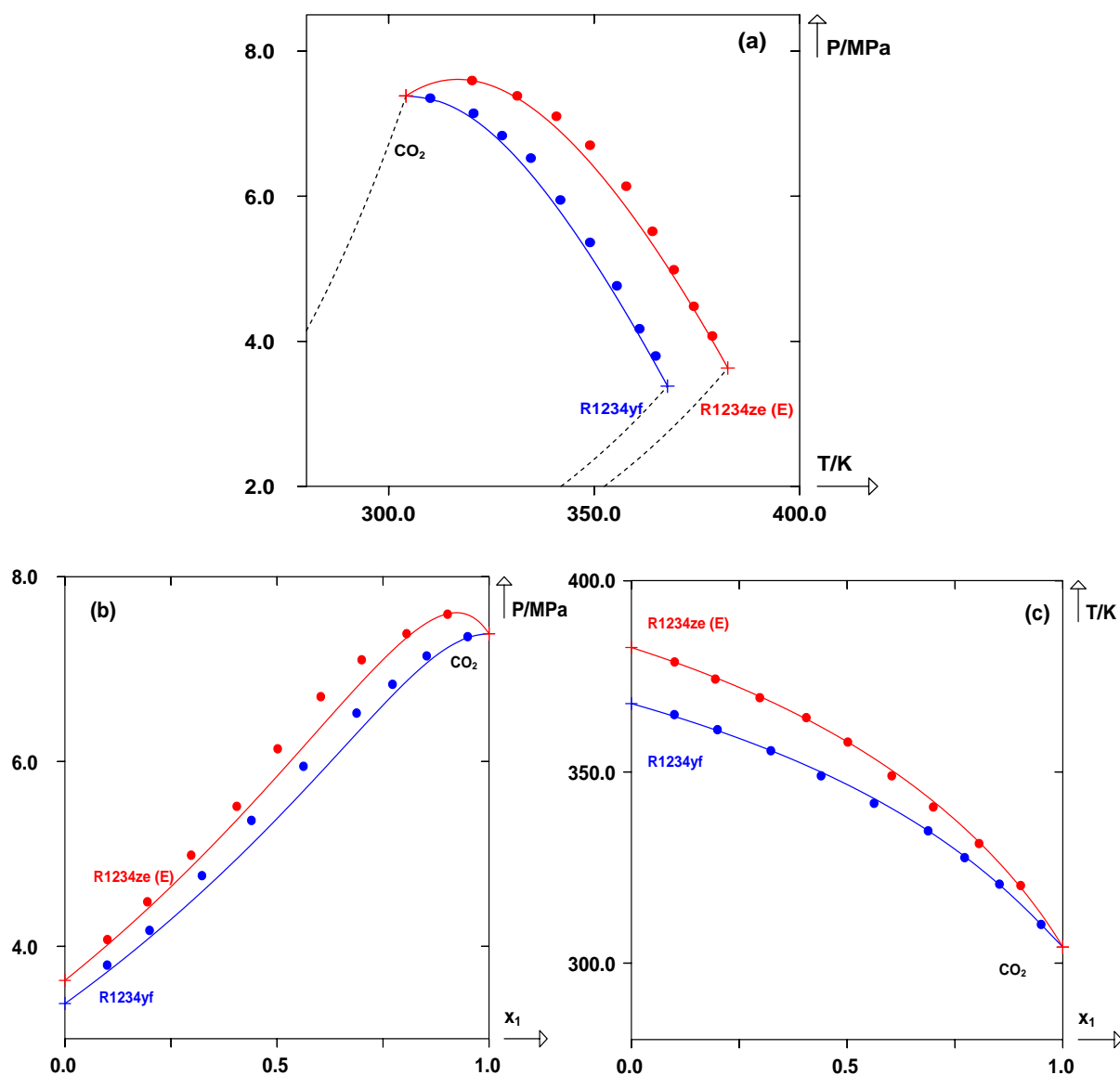


Fig. 17 Critical loci for the systems CO_2 (1) + R1234yf (2) and CO_2 (1) + R1234ze (E) (2) shown in (a): P - T diagram, (b): P - x diagram and (c): T - x diagram. (Closed symbol): experimental critical points, (+): critical points of the pure substances, (Solid line): correlated results by the PPR78 model and (Dashed line): vaporisation curves of pure components.

II.5. Conclusion

Isothermal (P - x - y) vapour-liquid equilibrium data of the system CO_2 + R1234yf are determined at temperatures 283.15 K and 293.15 K using the static – analytic type apparatus. The critical locus of the systems CO_2 + R1234yf and CO_2 + R1234ze (E) were measured over the whole composition range using the synthetic – dynamic type apparatus in the dynamic mode. The experimental VLE data of the system CO_2 + R1234yf are compared to data available in literature. A good agreement is obtained. Additionally, the PPR78 model is used

to correlate the VLE and critical results obtained in this work. The model is able to accurately correlate the VLE data and the critical data. Although small underestimations of the bubble curve at 293.15 K and the critical pressures are observed.

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CONCLUSION AND PERSPECTIVES

During this work, the performance and the reliability of a new apparatus capable of measuring the critical properties of pure components and multi component mixtures were studied. The important advantage of this apparatus is its possible use in both static and dynamic modes. Experimental procedures to measure critical points were developed and the critical loci of the binary systems which are liquid/liquid, liquid/gas and gas/gas at ambient conditions were measured. The experimental results were compared to literature data in order to validate the performance and the reliability of the new apparatus as well as the experimental procedures. The good agreement confirms that the new apparatus and the established experimental methods can be used to measure the critical points of any desired mixture.

The optimisation of the non – catalytic biodiesel synthesis process using supercritical ethanol with the addition of CO₂ was studied by developing a thermodynamic model capable of predicting the phase behaviour of mixtures containing compounds involved in biodiesel production. The binary systems CO₂ + ethyl ester and ethanol + ethyl ester were investigated. A bibliographic review of vapour – liquid equilibrium data for these binary systems shown a lack of data, especially at high temperatures and pressures explaining why the critical points measurements of these systems were conducted using the synthetic – dynamic apparatus in the dynamic method. The applicability range of the PPR78 thermodynamic model (predictive 1978, Peng Robinson Egos) which combines the widely used Peng – Robinson equation of state with a group contribution method aimed at estimating the temperature – dependant binary interaction parameters $k_{ij}(T)$ was extended to ester containing systems by defining the ester function (O-C=O) as a new group. Such a model was able to predict the phase behaviour of the systems involving CO₂ + and ethyl ester with high accuracy. Nevertheless, due to molecular polarity and interactions, the phase behaviour of the systems containing ethanol + ethyl ester was simply correlated by considering each molecule as one group. In the future, the measurement of VLE data for the CO₂ + biodiesel system would make possible to test the predictive ability of the PPR78 model. Other predictive thermodynamic models capable of estimating the molecular polarity such as SAFT (Statistical Associating Fluid Theory) and CPA (Cubic Plus Association) should be tested to determine their accuracy to correlate the experimental data acquired in this study.

Research and development of new alternative refrigerants suitable in the car air – conditioning system was performed by experimentally studying the subcritical behaviour and the critical behaviour of binary systems containing CO₂ and two new synthetic refrigerants (R1234fy and R1234ze (E)). The static – analytic and synthetic – dynamic type apparatus were used for measuring the VLE points and the critical points, respectively. The determined experimental values were correlated with high accuracy by the PPR78. This work will be continued in near future by determining the VLE at other temperature. Moreover, the PPR78 model will be extended for predicting the phase behaviour of other refrigerant compounds.

APPENDIX

Annexe 1: Etalonnage des capteurs de pressions et des sondes de température

a. Etalonnage des sondes de température

Les sondes de température 100 Ω (Pt 100) utilisées sont étalonnées par rapport à une sonde de platine étalon 25 Ω de très grande précision qui est étalonnée par le laboratoire national d'essais (LNE, Paris) en se basant sur l'International Temperature Scale de 1990 (ITS 90)). Les sondes à étalonner sont disposées autour de la sonde de référence dans un bloc en laiton. Ce bloc joue le rôle de conducteur thermique et permet ainsi de garantir que les sondes en périphérie sont à la même température que la sonde de référence. Un ohmmètre lié à la sonde de référence permet de mesurer la résistance de cette dernière. Les sondes à étalonner et la sonde de référence sont reliées à l'unité d'acquisition. Des mesures de température sont effectuées en montée et en descente de température de façon à détecter un éventuel phénomène d'hystérésis. A chaque température de consigne est enregistrée une valeur de résistance de la sonde étalon ainsi qu'une température « lue », notée T_{lue} , sur chacune des sondes à étalonner. Ensuite, nous calculons la température « vraie », notée T_{vraie} , donnée par la sonde étalon en utilisant un polynôme qui relie la température à la valeur de résistance mesurée. Les coefficients de ce polynôme sont fournis par le LNE (ITS 90 : référence internationale). Dans un deuxième temps, nous corrélons T_{vraie} en fonction de T_{lue} avec une expression du type : $T_{vraie} = A (T_{lue}^2) + B (T_{lue}) + C$. (on effectue une régression polynomiale afin de déterminer les coefficients d'ajustement : A, B et C). Finalement, on calcule T à partir du polynôme de régression : $T_{vraie\ cal} = A (T_{lue}^2) + B (T_{lue}) + C$ et on trace les écarts ($T_{vraie} - T_{vraie\ cal}$) en fonction de T_{vraie} afin de déterminer la précision avec laquelle la température est mesurée.

b. Etalonnage des capteurs de pression

Les capteurs de pression sont étalonnés à l'aide d'un étalon numérique (PACE 5000). Comme la réponse de capteur peut varier en fonction de la température, il est préférable d'effectuer un étalonnage à une température constante. L'étalon numérique est connecté au capteur de pression et à une source d'étalon (une bouteille d'azote). Une pression est imposée

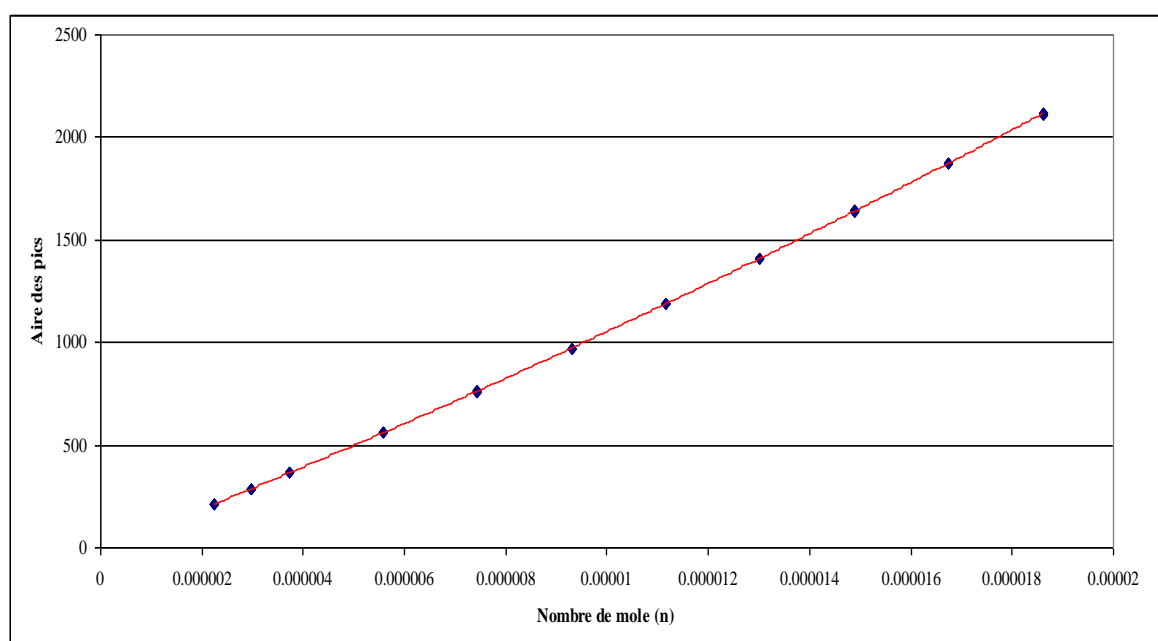
dans le système. Lorsque cette pression est stabilisée, la pression « lue », notée P_{lue} , (le capteur de pression que l'on cherche à étalonner) et la pression « vraie », notée P_{vraie} , (les valeurs imposées par l'appareil d'étalonnage) sont enregistrées. L'opération est répétée pour différentes pressions en montée et descente de pression de façon à vérifier la présence d'hystérésis. Ensuite, nous corrélons P_{vraie} en fonction de P_{lue} avec une expression du type : $P_{vraie} = A (P_{lue}^2) + B (P_{lue}) + C$. Finalement, on calcule P à partir du polynôme de régression : $P_{vraie\ cal} = A (P_{lue}^2) + B (P_{lue}) + C$ et on trace les écarts ($P_{vraie} - P_{vraie\ cal}$) en fonction de P_{vraie} afin de déterminer la précision avec la quelle la pression est mesurée.

Annexe 2 : Etalonnage des détecteurs chromatographiques

L'étalonnage de la réponse d'un détecteur TCD (Thermal Conductivity Detector) est effectué à l'aide d'une seringue automatique, pour chaque composé pur. Il consiste à injecter des volumes connus d'un composé pur dans la colonne, sous des conditions standard de température et de pression. La quantité des gaz injecté est déterminée par la loi des gaz parfaits :

$$Pv = nRT$$

v est le volume injecté (cm^3), T la température ambiante (K), P la pression atmosphérique (Pa) et R la constante des gaz parfait ($\text{Pa}\cdot\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Cette quantité injectée correspond à une aire du pic chromatographiques. L'expérience est recommencée pour différents volumes de composé pur. Nous établissons alors une relation qui corréle l'aire des pics aux quantités de composés injectés (voir la figure ci-dessous).



Nous obtenons ainsi une courbe d'étalonnage qui permet, ensuite, de déterminer la quantité de composé pur à partir de l'aire du pic et donc de calculer la composition des échantillons. En règle générale, un polynôme de second degré est utilisé pour corrélérer la réponse du détecteur TCD aux différentes quantités de composé pur injecté. L'écart entre les quantités de composé pur déterminées par l'injection des volumes connus et celles déterminées à partir de la corrélation de la réponse du détecteur et des aires des pics chromatographiques mesurées est tracé pour chaque composé pur.

Annexe 3 : Calculs d'incertitudes

Les formules données dans cette partie sont conformes aux recommandations du NIST (National Institute of Standards and Technology).

a. Incertitudes sur l'estimation de la température et la pression

On appelle X , la grandeur mesurée et on note n , le nombre d'expériences répétées dans les mêmes conditions (on dispose donc de n valeurs de X). L'estimation de X est sa valeur moyenne \bar{X} . L'incertitude sur l'estimation de X , notée $u(X)$, est donnée par :

$$u(X) = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (X_i - \bar{X})^2}$$

b. Incertitudes sur l'estimation de la fraction molaire en constituant 1

La fraction molaire en constituant 1 est donnée par :

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{m_1 M_2}{m_1 M_2 + m_2 M_1}$$

Où n_i désigne la quantité de matière de constituant i , m_i , la masse de i et M_i , la masse molaire de i . L'incertitude $u(x_1)$ sur l'estimation de x_1 est fonction des incertitudes $u(m_i)$ sur la mesure des masses des corps purs i et des incertitudes $u(M_i)$ sur la connaissance des masses molaires des corps purs i . La valeur de $u(x_1)$ est déduite de la formule de propagation des incertitudes :

$$u^2(x_1) = \left[\left(\frac{\partial x_1}{\partial m_1} \right)_{m_2, M_1, M_2} \right]^2 \cdot [u(m_1)]^2 + \left[\left(\frac{\partial x_1}{\partial m_2} \right)_{m_1, M_1, M_2} \right]^2 \cdot [u(m_2)]^2 \\ + \left[\left(\frac{\partial x_1}{\partial M_1} \right)_{m_1, M_2, M_2} \right]^2 \cdot [u(M_1)]^2 + \left[\left(\frac{\partial x_1}{\partial M_2} \right)_{m_1, M_2, M_1} \right]^2 \cdot [u(M_2)]^2$$

$$\begin{aligned}
 u^2(x_1) = & \left[\frac{m_2 M_1 M_2}{(m_1 M_2 + m_2 M_1)^2} \right]^2 \cdot [u(m_1)]^2 + \left[\frac{-m_1 M_1 M_2}{(m_1 M_2 + m_2 M_1)^2} \right]^2 \cdot [u(m_2)]^2 \\
 & + \left[\frac{-m_1 m_2 M_2}{(m_1 M_2 + m_2 M_1)^2} \right]^2 \cdot [u(M_1)]^2 + \left[\frac{m_1 m_2 M_1}{(m_1 M_2 + m_2 M_1)^2} \right]^2 \cdot [u(M_2)]^2
 \end{aligned}$$

La fraction molaire globale de chaque constituant est estimée indirectement par pesée à partir d'une microbalance précise à $u(m_1) = u(m_2) = u(m) = 10^{-4}$ g

Au final, en négligeant les incertitudes $u(M_1)$ et $u(M_2)$ sur l'estimation des masses molaires, on aboutit à l'expression :

$$u(x_1) = \frac{M_1 M_2 u(m)}{(m_1 M_2 + m_2 M_1)^2} \sqrt{m_1^2 + m_2^2}$$

Annexe 4 : Résultats expérimentaux

Table 1

Comparison between critical temperatures measured in this work (T_c/K) and literature data.

Compound	This work	DIPPR [45]	NIST [46]
CO ₂	304.30±0.03	304.21±0.61	304.18±0.04
<i>n</i> -propane	369.84±0.03	369.83±0.74	369.9±0.2
<i>n</i> -butane	424.82±0.03	425.12±0.85	425±1
<i>n</i> -pentane	469.70±0.05	469.70±0.90	469.80±0.5
<i>n</i> -heptane	540.28±0.02	540.20±1.28	540.00±2.0
<i>n</i> -decane	617.92±0.01	617.70±1.23	617.80±0.7

Table 2

Comparison between critical pressures measured in this work (P_c/MPa) and literature data.

Compound	This work	DIPPR [45]	NIST [46]
CO ₂	7.3798±0.0029	7.383±0.220	7.38±0.02
<i>n</i> -propane	4.2426±0.0029	4.248±0.008	4.25±0.10
<i>n</i> -butane	3.7983±0.0023	3.796±0.007	3.8±0.1
<i>n</i> -pentane	3.3696±0.0088	3.37±0.03	3.36±0.06
<i>n</i> -heptane	2.7475±0.0011	2.74±0.01	2.74±0.03
<i>n</i> -decane	2.1105±0.0066	2.11±0.06	2.11±0.08

Table 3

Experimental critical temperatures (T_c) and pressures (P_c) for the system *n*-pentane (1) + *n*-heptane (2) at different mole fractions and their standard uncertainties (u) with $u(x_1) < 0.0001$.

x_1	T_c/K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	540.28	0.02	2.7457	0.0011
0.1676	532.07	0.02	2.8974	0.0006
0.2654	526.25	0.06	3.0024	0.0025
0.4139	517.90	0.03	3.1379	0.0013
0.5236	511.20	0.05	3.2215	0.0021
0.6465	501.92	0.03	3.3100	0.0014
0.7053	497.54	0.04	3.3334	0.0045
0.7826	490.35	0.22	3.3707	0.0048
0.8814	482.05	0.04	3.3881	0.0015
1.0000	469.70	0.05	3.3696	0.0088

Table 4

Experimental critical temperatures (T_c) and pressures (P_c) for the system *n*-pentane (1) + *n*-decane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00005$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	617.92	0.01	2.1105	0.0006
0.0726	613.25	0.05	2.2808	0.0013
0.1889	604.52	0.09	2.5680	0.0027
0.2853	596.60	0.19	2.7650	0.0066
0.3416	591.11	0.16	2.9149	0.0014
0.4194	582.46	0.19	3.0965	0.0036
0.4933	574.69	0.13	3.2827	0.0011
0.6290	553.52	0.12	3.6018	0.0059
0.7331	536.93	0.18	3.7433	0.0068
0.8116	522.78	0.14	3.8006	0.0017
0.9138	495.32	0.18	3.6755	0.0033
1.0000	469.70	0.05	3.3696	0.0088

Table 5

Experimental critical temperatures (T_c) and pressures (P_c) for the system *n*-heptane (1) + *n*-decane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00005$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	617.92	0.01	2.1105	0.0006
0.1011	613.04	0.03	2.2184	0.0058
0.2036	605.72	0.17	2.3184	0.0143
0.2983	601.82	0.11	2.3800	0.0027
0.4091	594.49	0.10	2.4731	0.0018
0.4875	588.53	0.15	2.5511	0.0039
0.5598	581.93	0.11	2.6327	0.0078
0.6899	572.54	0.07	2.7108	0.0156
0.8070	561.29	0.07	2.7573	0.0082
0.8950	552.21	0.09	2.7538	0.0072
1.0000	540.28	0.02	2.7457	0.0011

Table 6

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + *n*-pentane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00015$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	469.70	0.05	3.3696	0.0088
0.1023	464.47	0.01	4.0274	0.0160
0.1966	458.16	0.09	4.7254	0.0216
0.3071	446.48	0.17	5.8447	0.0111
0.3679	441.12	0.10	6.6237	0.0065
0.4587	426.91	0.01	7.5645	0.0000
0.5045	421.73	0.25	8.0152	0.0119
0.5989	410.81	0.14	8.8288	0.0080
0.6572	393.97	0.16	9.4015	0.0171
0.7130	380.20	0.09	9.6075	0.0151
0.8192	360.66	0.06	9.4810	0.0412
0.8654	344.49	0.07	8.9730	0.0208
0.9020	330.50	0.05	8.5308	0.0030
1.0000	304.30	0.03	7.3798	0.0029

Table 7

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + *n*-heptane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00017$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	540.28	0.02	2.7457	0.0011
0.1101	534.16	0.10	3.6283	0.0094
0.2233	526.07	0.15	4.7557	0.0214
0.3068	519.76	0.21	5.5263	0.0277
0.3961	509.88	0.15	6.9719	0.0165
0.5131	495.28	0.25	8.4976	0.0207
0.6240	473.83	0.37	10.4275	0.0142
0.7009	458.50	0.06	11.5030	0.0044
0.7506	436.17	0.22	12.3655	0.0141
0.7945	418.76	0.12	13.0537	0.0159
0.8212	398.85	0.30	13.2310	0.0104
0.8846	364.69	0.55	11.9903	0.0381
0.9323	342.75	0.04	10.1656	0.0145
1.0000	304.30	0.03	7.3798	0.0029

Table 8

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + *n*-decane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00010$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	617.92	0.01	2.1105	0.0006
0.2051	607.32	0.07	3.7393	0.0032
0.3987	591.43	0.17	6.0210	0.0136
0.5048	578.84	0.02	7.8360	0.0038
0.5946	564.13	0.14	9.4826	0.0156
0.6555	546.30	0.04	11.5237	0.0042
0.7016	534.04	0.07	13.1230	0.0105
0.7613	507.65	0.06	15.6152	0.0115
0.7970	492.23	0.32	16.5093	0.0134
0.8223	472.75	0.40	17.5015	0.0249
0.8852	416.86	0.07	18.3364	0.0111
0.9008	385.23	0.31	16.9220	0.0350
0.9201	345.41	0.23	12.4852	0.0422
1.0000	304.30	0.03	7.3798	0.0029

Table 9

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + *n*-propane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) < 0.00009$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	369.84	0.03	4.2426	0.0027
0.1156	362.84	0.06	4.7906	0.0049
0.2128	356.93	0.07	5.1928	0.0095
0.3653	344.98	0.09	5.8991	0.0030
0.4928	333.78	0.04	6.2759	0.0092
0.6772	319.00	0.13	6.5287	0.0096
0.8253	307.12	0.06	6.5897	0.0009
0.9251	303.46	0.01	6.8938	0.0014
1.0000	304.30	0.03	7.3798	0.0029

Table 10

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + *n*-butane (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) \leq 0.00003$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	424.82	0.03	3.7983	0.0023
0.1052	418.38	0.04	4.4940	0.0034
0.1736	412.48	0.03	4.9997	0.0032
0.2651	405.58	0.04	5.6419	0.0058
0.3365	398.71	0.11	6.2036	0.0095
0.4302	388.66	0.02	6.8676	0.0026
0.5159	377.29	0.07	7.4263	0.0037
0.6355	359.42	0.04	7.9441	0.0045
0.7394	342.29	0.08	8.0122	0.0107
0.8732	318.81	0.12	7.4485	0.0114
0.9402	309.41	0.03	7.2242	0.0058
1.0000	304.30	0.03	7.3798	0.0029

Table 11

Experimental critical temperatures (T_c) and pressures (P_c) for the system *n*-propane (1) + *n*-butane (2) at different mole fractions and their standard uncertainties (u) with $u(x_1) < 0.00004$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
0.0000	424.82	0.03	3.7983	0.0023
0.2540	413.84	0.04	4.0140	0.0006
0.4940	402.02	0.03	4.1837	0.0051
0.7521	386.48	0.03	4.3091	0.0011
1.0000	369.84	0.03	4.2426	0.0027

Table 12

Experimental critical temperatures (T_c) and pressures (P_c) for the system acetone (1) + chloroform (2) at different mole fractions (x_1) and their standard uncertainties with $u(x_1) \leq 0.00004$.

x_1	T_c / K	$u(T_c) / K$	P_c / MPa	$u(P_c) / MPa$
1.0000	508.05	0.06	4.693	0.003
0.9215	510.68	0.03	4.760	0.003
0.8486	513.52	0.03	4.825	0.001
0.7852	515.78	0.07	4.854	0.005
0.7001	518.63	0.07	4.926	0.005
0.6195	521.04	0.07	4.999	0.004
0.6009	521.86	0.07	5.007	0.008
0.5455	523.15	0.04	5.035	0.009
0.5053	524.86	0.04	5.084	0.002
0.4834	525.56	0.04	5.082	0.003
0.4174	527.52	0.05	5.154	0.003
0.3895	527.64	0.10	5.148	0.003
0.3082	529.98	0.11	5.213	0.005
0.3050	530.31	0.04	5.205	0.003
0.2015	531.80	0.05	5.262	0.001
0.2006	532.19	0.03	5.251	0.002
0.1597	532.96	0.04	5.295	0.004
0.1086	533.90	0.06	5.332	0.006
0.0998	534.54	0.03	5.357	0.007
0.0608	535.26	0.03	5.398	0.007
0.0000	536.12	0.05	5.451	0.005

Table 13

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl acetate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	523.29	0.08	3.8289	0.0017
0.1011	514.36	0.02	4.9326	0.0026
0.1988	504.49	0.02	6.1300	0.0034
0.2934	493.95	0.02	7.3116	0.0028
0.4198	481.81	0.06	8.4875	0.0018
0.5328	469.78	0.02	9.5135	0.0036
0.6271	455.01	0.06	10.6103	0.0067
0.7158	434.98	0.06	11.6361	0.0040
0.7902	418.78	0.08	12.0544	0.0090
0.8577	391.38	0.04	12.3619	0.0072
0.9115	356.13	0.02	11.2078	0.0023
0.9443	335.14	0.03	9.8585	0.0050
1.0000	304.30	0.03	7.3798	0.0029

Table 14

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl propionate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	546.28	0.02	3.3856	0.0022
0.1446	532.94	0.06	5.0796	0.0039
0.3120	514.86	0.03	7.3450	0.0032
0.4697	494.30	0.03	9.4133	0.0104
0.5797	479.18	0.05	10.7383	0.0058
0.6525	466.83	0.02	11.5854	0.0042
0.7414	447.82	0.03	12.5015	0.0067
0.8454	420.94	0.10	13.2020	0.0104
0.8997	391.61	0.07	13.3256	0.0063
0.9212	362.40	0.01	12.1841	0.0020
0.9497	339.59	0.01	10.5102	0.0033
1.0000	304.30	0.03	7.3798	0.0029

Table 15

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl butanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	569.98	0.09	2.8915	0.0037
0.1457	555.76	0.07	4.6570	0.0077
0.2989	543.98	0.08	6.4831	0.0082
0.4572	526.35	0.05	8.5480	0.0039
0.6005	502.97	0.02	10.7626	0.0054
0.7192	484.05	0.05	12.4202	0.0083
0.8137	461.92	0.07	13.7322	0.0075
0.8540	435.35	0.04	14.6634	0.0091
0.9057	409.98	0.04	14.7420	0.0068
0.9344	374.30	0.04	13.5798	0.0096
0.9508	344.08	0.05	11.3206	0.0090
1.0000	304.30	0.03	7.3798	0.0029

Table 16

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl pentanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	594.02	0.02	2.7304	0.0011
0.1489	581.75	0.04	4.3256	0.0019
0.3071	569.48	0.01	6.1212	0.0023
0.4418	554.91	0.07	7.7603	0.0082
0.6015	539.64	0.06	9.5720	0.0068
0.7502	520.89	0.04	11.6385	0.0038
0.8082	501.41	0.14	13.3512	0.0071
0.8476	485.89	0.06	14.3590	0.0082
0.8729	452.88	0.07	15.8682	0.0082
0.9100	423.30	0.02	16.0896	0.0118
0.9336	387.94	0.04	14.9415	0.0075
0.9523	356.95	0.04	13.0283	0.0032
1.0000	304.30	0.03	7.3798	0.0029

Table 17

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl hexanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	615.22	0.02	2.5313	0.0011
0.1916	599.29	0.03	4.7372	0.0025
0.3978	578.97	0.02	7.2190	0.0045
0.6151	562.93	0.04	9.6722	0.0112
0.7413	544.52	0.03	11.7575	0.0062
0.7952	522.82	0.05	13.8779	0.0038
0.8487	490.90	0.03	16.1830	0.0039
0.8795	458.46	0.03	17.4004	0.0050
0.9024	427.93	0.02	17.5324	0.0052
0.9319	400.07	0.07	16.6448	0.0135
0.9552	372.03	0.05	15.1488	0.0042
0.9668	349.22	0.08	12.8591	0.0083
1.0000	304.30	0.03	7.3798	0.0029

Table 18

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl heptanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	635.12	0.03	2.3569	0.0036
0.2101	619.26	0.05	4.6230	0.0077
0.4103	599.07	0.03	7.5557	0.0054
0.6085	574.67	0.05	10.8314	0.0045
0.7120	561.36	0.07	12.3863	0.0067
0.7957	540.26	0.02	14.5392	0.0089
0.8437	520.77	0.04	16.2261	0.0037
0.8806	492.29	0.04	17.9783	0.0053
0.9181	459.77	0.02	18.9619	0.0038
0.9427	412.15	0.02	18.1837	0.0033
0.9533	374.42	0.03	16.0419	0.0059
0.9630	351.02	0.06	13.4468	0.0020
1.0000	304.30	0.03	7.3798	0.0029

Table 19

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl octanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00006$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	655.74	0.03	2.1592	0.0032
0.2069	639.13	0.04	4.7187	0.0036
0.4072	622.01	0.04	7.3532	0.0064
0.6023	594.98	0.05	10.8779	0.0034
0.6988	579.77	0.04	12.7159	0.0031
0.7932	563.03	0.03	14.5630	0.0049
0.8419	543.69	0.02	16.4303	0.0044
0.8924	513.96	0.03	18.5094	0.0014
0.9487	412.18	0.03	19.0903	0.0034
0.9568	374.71	0.05	16.6083	0.0047
0.9640	352.06	0.03	13.9403	0.0086
1.0000	304.30	0.03	7.3798	0.0029

Table 20

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl nonanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.4051	644.49	0.02	7.3669	0.0066
0.6011	617.76	0.01	10.9862	0.0044
0.7097	602.22	0.04	12.9387	0.0040
0.7991	584.93	0.02	14.8422	0.0042
0.8418	564.27	0.03	16.9072	0.0020
0.8833	538.10	0.02	18.9349	0.0033
1.0000	304.30	0.03	7.3798	0.0029

Table 21

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl decanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)$	P_c/MPa	$u(P_c)/MPa$
0.4957	651.03	0.02	9.4174	0.0040
0.6026	638.61	0.03	11.2417	0.0014
0.7088	622.49	0.03	13.2829	0.0092
0.8033	605.65	0.03	15.3805	0.0043
0.8591	578.03	0.03	17.9499	0.0030
1.0000	304.30	0.03	7.3798	0.0029

Table 22

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl trans-2-butenoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00006$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	593.84	0.02	3.6708	0.0012
0.1593	583.54	0.02	5.0111	0.0005
0.3433	567.92	0.01	7.0112	0.0047
0.4786	553.50	0.03	8.8625	0.0014
0.6210	539.12	0.02	10.5264	0.0031
0.7647	520.27	0.03	12.4764	0.0033
0.8051	500.72	0.03	14.1015	0.0016
0.8653	471.56	0.02	15.9195	0.0055
0.8972	431.26	0.03	16.6644	0.0015
0.9329	384.81	0.07	15.2777	0.0037
0.9520	360.58	0.03	13.4133	0.0023
1.0000	304.30	0.03	7.3798	0.0029

Table 23

Experimental critical temperatures (T_c) and pressures (P_c) for the system CO₂ (1) + ethyl trans-3-hexenoate (2) at different mole fractions (x_1) and their standard uncertainties (u) $u(x_1) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.6118	554.05	0.07	11.5697	0.0045
0.7632	537.30	0.03	13.3850	0.0079
0.8058	518.31	0.04	14.9781	0.0020
0.8379	492.19	0.04	16.8297	0.0053
0.8721	465.16	0.02	17.9807	0.0059
0.9013	434.25	0.02	18.0576	0.0039
0.9331	400.97	0.02	17.4287	0.0050
0.9508	380.28	0.04	16.2493	0.0069
0.9610	363.93	0.05	14.3384	0.0073
1.0000	304.30	0.03	7.3798	0.0029

Table 24

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl acetate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	523.29	0.08	3.8289	0.0017
0.1134	521.14	0.01	4.0888	0.0023
0.2103	519.16	0.01	4.2903	0.0012
0.3082	517.43	0.01	4.4915	0.0012
0.3941	516.39	0.02	4.6215	0.0037
0.5249	514.59	0.01	4.9278	0.0020
0.5952	513.81	0.03	5.0864	0.0029
0.7022	513.19	0.01	5.2923	0.0018
0.8084	512.86	0.01	5.5808	0.0003
0.9039	513.02	0.01	5.8280	0.0026
1.0000	514.06	0.01	6.1397	0.0008

Table 25

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl propionate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	546.28	0.02	3.3856	0.0022
0.1246	542.14	0.02	3.7198	0.0029
0.2197	538.83	0.04	3.9880	0.0031
0.3298	534.49	0.01	4.2948	0.0018
0.4224	530.94	0.01	4.5233	0.0010
0.5007	527.42	0.02	4.7292	0.0018
0.5920	524.18	0.01	4.9721	0.0012
0.6923	521.25	0.01	5.2403	0.0029
0.7983	517.91	0.01	5.5267	0.0009
0.8917	515.44	0.02	5.8243	0.0023
1.0000	514.06	0.01	6.1397	0.0008

Table 26

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl butanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	569.98	0.09	2.8915	0.0037
0.1007	564.31	0.02	3.3235	0.0010
0.1978	559.86	0.01	3.6667	0.0018
0.3173	554.97	0.02	4.0503	0.0024
0.3950	549.96	0.01	4.3439	0.0009
0.5176	542.18	0.02	4.7702	0.0014
0.6202	535.78	0.01	5.0861	0.0013
0.7059	530.41	0.02	5.3117	0.0028
0.8059	525.81	0.01	5.5281	0.0013
0.9036	518.44	0.01	5.8546	0.0014
1.0000	514.06	0.01	6.1397	0.0008

Table 27

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl pentanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	594.02	0.02	2.7304	0.0011
0.1202	585.13	0.02	3.2690	0.0035
0.2216	580.13	0.02	3.5850	0.0021
0.3015	575.46	0.02	3.8929	0.0025
0.4232	569.08	0.02	4.3257	0.0020
0.5057	562.04	0.01	4.7258	0.0022
0.5972	554.85	0.02	5.0469	0.0012
0.6995	544.44	0.01	5.4292	0.0019
0.8020	533.05	0.02	5.7521	0.0026
0.9003	523.22	0.01	5.9441	0.0023
1.0000	514.06	0.01	6.1397	0.0008

Table 28

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl hexanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00006$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	615.22	0.02	2.5313	0.0011
0.1347	605.97	0.02	3.0893	0.0019
0.2116	599.57	0.02	3.5021	0.0018
0.3016	592.55	0.01	3.8936	0.0015
0.3995	584.14	0.02	4.3813	0.0028
0.5085	575.81	0.01	4.8024	0.0027
0.6048	566.32	0.01	5.2456	0.0038
0.7025	553.90	0.01	5.7378	0.0019
0.8160	540.78	0.10	6.0434	0.0025
0.9097	525.06	0.01	6.1310	0.0008
1.0000	514.06	0.01	6.1397	0.0008

Table 29

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl heptanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00006$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	635.12	0.03	2.3569	0.0036
0.1003	626.60	0.01	2.9447	0.0017
0.2055	619.31	0.01	3.4185	0.0020
0.3097	611.10	0.02	3.8766	0.0019
0.4243	601.08	0.02	4.3832	0.0009
0.5128	594.24	0.02	4.8195	0.0032
0.6016	585.43	0.02	5.3172	0.0056
0.6994	568.70	0.03	5.8572	0.0040
0.8055	548.69	0.08	6.2325	0.0031
0.9008	530.07	0.02	6.2051	0.0030
1.0000	514.06	0.01	6.1397	0.0008

Table 30

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl octanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00007$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	655.74	0.03	2.1592	0.0032
0.1204	645.00	0.01	2.7896	0.0020
0.2063	636.22	0.01	3.3713	0.0030
0.3072	627.47	0.01	3.9329	0.0038
0.4064	616.79	0.01	4.5533	0.0029
0.5105	608.19	0.02	5.0245	0.0036
0.6011	598.52	0.01	5.5048	0.0010
0.6945	585.27	0.02	5.9198	0.0029
0.7956	564.49	0.01	6.3767	0.0026
0.8509	550.50	0.02	6.5400	0.0017
0.9032	535.94	0.02	6.4867	0.0028
0.9544	526.42	0.01	6.3768	0.0012
1.0000	514.06	0.01	6.1397	0.0008

Table 31

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl nonanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00005$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.4012	642.90	0.01	4.1062	0.0031
0.5033	631.16	0.02	4.7310	0.0022
0.6015	618.68	0.02	5.3469	0.0035
0.6983	604.12	0.03	5.9453	0.0030
0.8001	580.78	0.02	6.6517	0.0024
0.8477	557.52	0.03	6.8308	0.0032
0.8931	540.85	0.02	6.7188	0.0037
0.9494	529.03	0.02	6.5610	0.0040
1.0000	514.06	0.01	6.1397	0.0008

Table 32

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl decanoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.6108	639.32	0.01	5.2829	0.0034
0.7014	623.73	0.03	6.0009	0.0036
0.8126	597.54	0.02	6.9088	0.0026
0.8491	573.09	0.02	7.1941	0.0028
0.9024	549.88	0.02	7.0592	0.0012
0.9494	535.58	0.02	6.8291	0.0027
1.0000	514.06	0.01	6.1397	0.0008

Table 33

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl trans-2-butenoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00004$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	593.84	0.02	3.6708	0.0012
0.1495	584.76	0.03	4.1176	0.0023
0.3169	576.42	0.01	4.5738	0.0027
0.4047	568.42	0.02	4.9314	0.0020
0.5080	560.17	0.02	5.2745	0.0032
0.6045	550.66	0.01	5.5825	0.0041
0.7232	541.07	0.02	5.8206	0.0022
0.8123	532.81	0.02	5.9652	0.0020
0.9027	523.48	0.02	6.0611	0.0016
1.0000	514.06	0.01	6.1397	0.0008

Table 34

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl trans-3-hexenoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00008$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.1980	607.23	0.05	3.5474	0.0028
0.3084	599.13	0.03	4.1188	0.0035
0.3957	589.97	0.04	4.6231	0.0041
0.5139	581.21	0.01	5.1249	0.0014
0.6068	570.80	0.04	5.4659	0.0011
0.7017	560.07	0.02	5.8392	0.0017
0.8012	546.88	0.03	6.1257	0.0008
0.9232	526.97	0.04	6.1974	0.0025
1.0000	514.06	0.01	6.1397	0.0008

Table 35

Experimental critical temperatures (T_c) and pressures (P_c) for the system ethanol (1) + ethyl trans-2-octenoate (2) at different mole fractions (x_1) and their standard uncertainties (u) with $u(x_1) \leq 0.00006$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.6927	602.85	0.02	6.3851	0.0029
0.8042	576.47	0.02	6.9483	0.0025
0.8579	556.53	0.02	6.9047	0.0030
0.9131	540.25	0.01	6.7619	0.0001
0.9499	528.87	0.02	6.5370	0.0044
1.0000	514.06	0.01	6.1397	0.0008

Table 36

Experimental VLE data of the system CO₂ (1) + R1234yf (2) and their standard uncertainties (*u*).

x_1	$u(x_1)$	y_1	$u(y_1)$	P_{liq}/MPa	$u(P_{liq})$	P_{vap}/MPa	$u(P_{vap})$
T = 283.21±0.01K							
0,1123	0,0008	0.4701	0.0004	0.8385	0.0004	0.8388	0.0001
0,1963	0,0005	0.6223	0.0003	1.1501	0.0001	1.1520	0.0004
0,3678	0,0009	0.7796	0.0002	1.7913	0.0002	1.7931	0.0003
0,5402	0,0006	0.8606	0.0003	2.4720	0.0001	2.4739	0.0003
0,7809	0,0004	0.9362	0.0001	3.4861	0.0001	3.4869	0.0002
0,8779	0,0004	0.9614	0.0003	3.9281	0.0001	3.9285	0.0001
T = 292.69±0.04 K							
0.0670	0.0002	0.2979	0.0002	0.8648	0.0002	0.8609	0.0001
0.1524	0.0006	0.5143	0.0004	1.2292	0.0000	1.2247	0.0005
0.2688	0.0006	0.6734	0.0002	1.7411	0.0004	1.7439	0.0002
0.4165	0.0002	0.7800	0.0005	2.4107	0.0004	2.4172	0.0008
0.5438	0.0003	0.8429	0.0002	3.0435	0.0010	3.0239	0.0004
0.6567	0.0003	0.8834	0.0004	3.6350	0.0001	3.6358	0.0001
0.7486	0.0004	0.9145	0.0003	4.1301	0.0000	4.1304	0.0001
0.8401	0.0006	0.9418	0.0003	4.6560	0.0001	4.6566	0.0002
0.9087	0.0012	0.9643	0.0002	5.0994	0.0004	5.0994	0.0001

Table 37

Experimental critical temperatures (T_c/K) and pressures (P_c/MPa) of the system CO₂ (1) + R1234yf (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	368.75	0.04	3.3829	0.0012
0.0996	364.98	0.01	3.7985	0.0020
0.1996	361.04	0.04	4.1734	0.0027
0.3232	355.52	0.02	4.7657	0.0018
0.4398	348.99	0.04	5.2936	0.0026
0.5625	341.78	0.03	5.9488	0.0021
0.6879	334.59	0.05	6.5253	0.0016
0.7737	327.28	0.03	6.8664	0.0012
0.8531	320.65	0.01	7.1434	0.0030
0.9496	310.11	0.02	7.3517	0.0017
1.0000	304.20	0.02	7.3798	0.0029

Table 38

Experimental critical temperatures (T_c/K) and pressures (P_c/MPa) of the system CO₂ (1) + R1234ze (E) (2) at different mole fractions and their standard uncertainties (u) with $u(x_i) \leq 0.00003$.

x_1	T_c/K	$u(T_c)/K$	P_c/MPa	$u(P_c)/MPa$
0.0000	382.39	0.01	3.6728	0.0002
0.1002	378.76	0.03	4.0734	0.0021
0.1946	374.25	0.03	4.4834	0.0024
0.2977	369.40	0.01	4.9870	0.0018
0.4053	364.19	0.02	5.5163	0.0076
0.5016	357.79	0.01	6.1381	0.0021
0.6033	348.99	0.02	6.7026	0.0022
0.6997	340.82	0.02	7.1020	0.0017
0.8057	331.27	0.01	7.3836	0.0019
0.9024	320.28	0.02	7.6027	0.0022
1.0000	304.20	0.02	7.3798	0.0029

ABSTRACT

Abstract

Knowledge of mixture critical data is not only important for the design and the improvement of chemical processes but also to extend the range of applicability of predictive equations of state. However, mixture critical data comprise only a small percentage of the fluid phase equilibria data available in the open literature. This is the reason why it was decided to acquire a new synthetic-dynamic apparatus capable of determining the critical points of pure substances and multi-component mixtures. In a first step, the validation of the experimental procedure for critical point measurements was performed by comparing the experimental results obtained in this work with literature data. In a second step, the application of mixture critical data to the development of two types of process: i) biodiesel production via supercritical process and ii) phase behaviour of new refrigerants is presented. The experimental critical points measured in this work were also used for determining new group interaction parameters of the PPR78 model.

Keywords: critical point, refrigerants, biofuels, process, measurements, equation of state.

Résumé

La connaissance des propriétés critiques des mélanges binaires est importante pour la conception et le développement des procédés des industries chimiques, mais également, pour l'amélioration et l'extension des modèles thermodynamiques prédictifs. Cependant, des données expérimentales critiques liquide – vapeur de mélanges binaires sont relativement rare dans la littérature. C'est la raison pour laquelle, nous avons acquis un nouvel appareil permettant de mesurer les points critiques de corps purs et de mélanges. Dans une première étape, nous avons mis au point et validé le protocole expérimental, en comparant les résultats de nos mesures aux données de la littérature. Dans une deuxième étape, nous montrons l'intérêt que la mesure de points critiques de mélanges binaires peut présenter pour le développement de deux types de procédés : i) la production de biodiesel par voie supercritique et ii) l'étude de comportement de phases de nouveaux réfrigérants. Les résultats expérimentaux obtenus ont été également utilisés pour déterminer les paramètres d'interactions entre groupes du modèle PPR78.

Mots-clés : point critique, réfrigérants, biodiesel, procédé, mesures, équation d'état.