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Experimental determination of the critical locus of binary systems containing CO2 and an ethyl ester

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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. Indeed, biodiesel is a mixture of alkyl esters obtained by transesterification (alcoholysis) of triglycerides from vegetable oils or animal fats with an alcohol (methanol or ethanol). The transesterification reaction is commonly carried out in the presence of a catalyst the main drawback of which is to be water sensitive, preventing the use of non-conventional feedstocks (such as waste cooking oils or algal biomass) [1]. Emerging non-catalytic alcoholysis methods based on supercritical fluids allow solving this problem. 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) which can be successfully reduced by addition of a co-solvent, such as CO2 [2-4]. To optimize the supercritical process via simulation, the phase behaviour under high temperatures and pressures for systems containing CO2 and components involved in biodiesel production must be firstly investigated.

In this work, the critical properties of nine binary mixtures containing CO2 and an ethyl ester are investigated. A synthetic-dynamic apparatus capable of measuring the critical points of pure compounds and mixtures is employed using the dynamic method. The critical points can be determined by visually observing the critical opalescence phenomenon in the view cell. Regarding the system CO2 + ethyl acetate, the experimental results in this work are compared to those available in the open literature. Such a comparison is not possible for the eight other systems which are measured for the first time in this study.

2 EXPERIMENTAL

All compounds were purchased from commercial sources and used without any future purification. Their purity and the suppliers are listed in Table 1.

A schematic diagram of the apparatus used in this work is presented in Fig. 1. It has been developed by ARMINES, a company hosted by the Ecole Nationale Supérieure des Mines de Paris, for the measurement of the critical properties of pure substances and multi-component mixtures with known overall composition. This apparatus can work using two different modes: dynamic and static. Due to short residence time, the dynamic method enables to determine the critical points 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 due 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. The temperature upper limits are different owing to the use of a magnetic stirrer, which withstands conditions up to 493 K, in the static method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>99.998%</td>
<td>Messer</td>
</tr>
<tr>
<td>Ethyl acetate (E2)</td>
<td>≥99.8%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl propionate (E3)</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl butanoate (E4)</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl pentanoate (E5)</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl hexanoate (E6)</td>
<td>≥99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl heptanoate (E7)</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl octanoate (E8)</td>
<td>≥99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl nonanoate (E9)</td>
<td>≥98%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethyl decanoate (E10)</td>
<td>≥99%</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
In this work, the measurements were carried out using the dynamic method in which circulation of fluid ensures an efficient stirring.

Figure 1. 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; V: valve.

The state of the art of critical point measurements can be found in the book edited by Weir and de Loos [5] (in particular chapter 16 by Teja and Mendez-Santiago – entitled Critical Parameters - is notably well-documented). It is thus not necessary to recall it in this paper. A critical point can be determined by visually observing the critical opalescence and the simultaneous disappearance and reappearance of the meniscus (i.e. of the liquid-vapour interface from the middle of the view cell).

Fig. 2 illustrates the transition of a fluid from the 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); a thick and cloudy subcritical state (the meniscus becomes thicker and thicker); disappearance of the liquid–vapour interface (the meniscus occupies the entire view cell which is orange: we are at the critical point).

3 RESULTS

In this work, the vapour-liquid critical points for nine binary systems containing CO₂ and an ethyl ester (ethyl acetate, ethyl propionate, ethyl butyrate, ethyl valerate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, ethyl nonanoate and ethyl decanoate) were experimentally determined. The experimental results in this work and literature data are graphically presented in Figs. 3a, 3b and 3c which correspond to pressure – temperature, pressure – composition and temperature – composition diagrams, respectively.

In the open literature. The experimental setup used in this work is the same as that described in one of our previous studies [7]. The uncertainties obtained in the critical temperature and critical pressure for pure compounds and mixtures at different mole fractions were ≤ 0.14 K and ≤ 0.0135 MPa, respectively. Likewise, a mean value uncertainty in the mole fraction, \( u(x_i) = \pm 0.00006 \) was obtained.
4 Conclusions

In this work, the critical properties of nine binary systems containing \( \text{CO}_2 \) and an ethyl ester were studied. The measurements were carried out using a synthetic – dynamic apparatus which was employed in the dynamic mode. For six binary mixtures, the critical loci were experimentally determined over the whole composition range. For the three other systems, the critical loci were only determined in a smaller composition range due to the cell’s capacity. The experimental results were compared to literature data. Some variations were found owing to different experimental methods used.

References

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