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Phase equilibria of phenolic compounds in water or ethanol

Laëtitia CESARI, Sylvain NAMYSL, Laetitia CANABADY-ROCHELLE, Fabrice MUTELET

Université de Lorraine, Ecole Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR CNRS 7274), 1 rue Grandville, 54000 NANCY, France.

Abstract

The mutual solubilities of water and eight phenolic compounds (*i.e.* phenol, guaiacol, syringol, pyrocatechol, o-, m-, p-cresol and vanillin) were investigated between 293.15 and 323.15K. The solubility of the phenolic compounds in water increases as follows: vanillin < syringol < guaiacol < p-cresol < m-cresol < o-cresol < phenol < pyrocatechol. For the molecules presenting liquid-liquid equilibria, the solubility of water into the phenolic phase increases as follows: guaiacol < o-cresol < m-cresol < p-cresol < syringol. The vapor-liquid equilibria of binary mixtures composed of ethanol and phenol or guaiacol or o-cresol were measured in a range of pressure from 0.09 bar to atmospheric pressure. Finally, the mixing enthalpies of the phenolic compounds with ethanol indicate that the reactions are exothermic. It was found that NRTL model is suitable for the representation of phase diagrams of systems containing phenolic compounds and water or ethanol.

Keywords: phase equilibria, phenolic compounds, NRTL, water, ethanol.

24 **1. Introduction**

25

26 Most of the chemicals, such as phenolic compounds, are produced from the petrochemical
27 industry. Yet, with the rise of global warming and the limited stocks of fossil fuels, there is an
28 urgent need to find new ways of production for such compounds. For the last years, lignin has
29 become as interesting tool for the production of monophenols.[1] Indeed, the thermochemical
30 conversion processes of lignin can provide liquid fuels[2] as well as bio-oils rich in valuable
31 chemicals. With specific bioactivities, such as antioxidant or antimicrobial properties,
32 phenolic compounds are used as intermediate or raw material in the food, pharmaceutical and
33 cosmetic industries.[3–6]

34 Bio-oils can be produced by various thermochemical treatments, the famous ones being
35 pyrolysis and liquefaction. Many studies have investigated the influence of solvent on the
36 liquefaction process, including formic acid [7], water [8–10], methanol, 2-propanol [10], or
37 ethanol.[10–13] In order to reduce the CO₂ emission and be more economically competitive,
38 more and more processes are using solvents coming from biomass for liquefaction
39 processes.[14] Besides, biomass pyrolysis also produces aromatic compounds-rich bio-oils.
40 The condensed vapors obtained during a pyrolysis process are generally collected in solvents
41 such as aqueous solution or ethanol. The extraction of high value compounds from this diluted
42 bio-oil is difficult to perform due to its thermal instability and its complex composition. Most
43 of the processes generally start with the recovery of the solvent by distillation. Then, liquid-
44 liquid extraction using water [15], basic aqueous solutions [16–18] or polar organic
45 solvent[19] are predominantly preferred. Although the distillation of ethanol and the liquid-
46 liquid extraction of phenolic compounds with water are regularly used in the extraction
47 process, only few data are available in the literature.[20–39] The method and the range of
48 temperature of the {phenolic compounds-water} systems found in the literature are presented

49 in Table 1. No data has been found for the syringol-water system. The vapor-liquid equilibria
50 (VLE) of the {phenol+ethanol} system were only investigated at atmospheric pressure
51 [40,41], at 288.15K [42] and 293.15 K[43]. Only one isothermal VLE at 290.15 K can be
52 found for the binary {guaiacol + ethanol} [38] and two sets of VLE data for the binary
53 system {o-cresol + ethanol} (0.9576 bar[37] and 291.15K [39]).

54 To date, there is still a huge lack of information about the behavior of phenolic compounds
55 with such solvents, especially for guaiacol and syringol. It is therefore difficult to determine
56 the most adapted solvent for such extraction and to estimate its feasibility and extraction
57 capacity.

58 In this work, we studied the behavior of eight phenolic compounds (*i.e.* phenol, guaiacol,
59 syringol, pyrocatechol, o-cresol, m-cresol, p-cresol and vanillin) with water or ethanol. The
60 mutual solubilities of the compounds with water were investigated as a function of
61 temperature. Bubble curves of phenolic compounds with ethanol as well as their mixing
62 enthalpy were also studied. The phase equilibrium data of the systems were used to regress
63 parameters on the Non-Random Two-Liquids (**NRTL**) [44] thermodynamic models.

64

65 **2. Material and Methods**

66 **2.1. Chemicals**

67 Phenol (CAS 108-95-2), guaiacol (CAS 90-05-1), syringol (CAS 91-10-1), pyrocatechol
68 (CAS 120-80-9), o-cresol (CAS 95-48-7), m-cresol (CAS 108-39-4), p-cresol (CAS 106-44-5)
69 and vanillin (CAS 121-33-5) were supplied by Sigma Aldrich. All chemicals were used as
70 received without any further purification. Deionized water and absolute ethanol were used for
71 all experiments. Table 2 summarizes the parameters of the compounds used in this work.

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2.2. Solubility of the phenolic compounds in water

Aqueous solubility of the phenolic compounds was determined using the shake-flask method between 293 and 323K. Saturated solutions of each phenolic compound in water were prepared and put in a thermostatic water bath to maintain a constant temperature in the solutions. The temperature was measured with a RTD-126U thermometer ($\pm 0.1\text{K}$). The mixtures were stirred for 48 hours with a coated magnetic stirring bar. Then, the solutions were left for another 48 hours without stirring to allow the phases to settle down. Samples of the aqueous phase were taken with a syringe. In the case of solid-liquid equilibria, a $0.45\text{-}\mu\text{m}$ filter was connected to the syringe. Samples were diluted by factor 10^4 with deionized water before analysis. Quantification of the fraction of the phenolic compound was made using a UV-visible spectrophotometer at the maximum of absorbance for each compound. Maximum wavelengths are provided in **Table S1**. For each studied compounds, a calibration curve was carried out with six known concentrations solutions, comprised within 1 and 10 mg/L. Linear calibration curves (absorbance *A* versus the concentration *C*) provided R^2 correlation coefficients of 0.998 or higher.

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2.3. Solubility of water in the phenolic solution

92 In the case of liquid-liquid equilibria between water and phenolic compound (*i.e.* phenol,
93 guaiacol, o-, m-, p-cresol), the determination of the fraction of water in the phenolic phase
94 was determined by the trouble point method [45] between 293 and 323K. An amount of
95 phenolic compound was put into a jacketed glass cell and connected to a thermostatic bath.
96 The temperature was measured with a RTD-126U thermometer ($\pm 0.1\text{K}$) and maintained

97 constant all over the experiment. Solutions were stirred with a coated magnetic bar and known
98 amounts of water were added stepwise until a second phase appears.

99 **2.4. Vapor-Liquid equilibria of phenolic compound and ethanol**

100 Apparatus used for the VLE measurements was described in our previous work [46]. **Figure 1**
101 presents the device used for the determination of the bubble point of isobaric VLE. A volume
102 of 50 mL of a known mixture of phenolic compound and ethanol was introduced into a round-
103 bottom flask (6). The flask was put into a controlled oil bath (7) and connected to a condenser
104 (3) cooled by a glycol aqueous solution. This condenser was kept at a sufficiently low
105 temperature (267.15 K) to minimize the amount of vapor lost through the vacuum pump
106 section, and hence, to avoid variation of the initial composition of the sample solution. To
107 confirm the measuring accuracy, the seal fittings in the device had to be kept in good
108 connection to avoid air leakage. Then, the pressure was set at the desired value with the pump
109 (11). The temperature was measured by a temperature sensor (T900 series) thermocouple
110 calibrated with high measuring accuracy ($T900 \pm 0.06$ °C) and the pressure was determined
111 by a pressure transducer (Druck-PMP4010) with an accuracy of (± 0.4 mbar). The mixture
112 was stirred by a coated magnetic bar. After 15 min the heating has been turned on, the
113 temperature of the solution was generally stable and the vapor-liquid equilibrium was
114 reached.

115

116 **2.5. Excess enthalpy between phenolic compounds and ethanol**

117 Excess molar enthalpies were measured using a Setaram C80 differential calorimeter
118 (Setaram Instrumentation, France, 2010). The apparatus was calibrated using the Joule effect
119 (electrical calibration) on a vessel containing a platinum resistance. Calibration was
120 performed using several precise heat inputs to simulate experimental samples.[47–49] The
121 phenolic compound and ethanol were initially in two compartments of the cell, separated by a

122 mercury joint. The mixing was obtained by reversing the calorimeter. The calorimeter
 123 principle and the scheme of the cell have been described elsewhere.[50]

124

125 3. Theory/calculation

126 3.1. Thermodynamic correlation

127 The phase equilibrium data of the binary systems were represented using the NRTL [44]
 128 model. This thermodynamic model allows to calculate the activity coefficient γ_i , for any
 129 component i of the binary system using the following expression:

$$130 \ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (2)$$

$$131 \text{ with } G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}, \Delta g_{ij} = a_{ij} + b_{ij}T \text{ and } \alpha_{ji} = \alpha_{ij} = \alpha$$

132 where: g is an energy parameter characterizing the interaction of species i and j , x_i is the mole
 133 fraction of component i , T the temperature and R the ideal gas constant. The value of the non-
 134 randomness parameter α was set to 0.3 according to the literature.[51] The use of NRTL
 135 model requires the knowledge of two sets of parameters a_{ij} and b_{ij} . The parameters were
 136 determined from experimental data, and by minimizing the following objective function:

$$137 F_{obj} = \sum_{k=1}^N \sum_{i=1}^2 \left\{ (x_{i,k}^{I,exp} - x_{i,k}^{I,calc})^2 + (x_{i,k}^{II,exp} - x_{i,k}^{II,calc})^2 \right\} \quad (3)$$

138 Where N is the number of tie lines in the data set, $x_{i,k}^{I,exp}, x_{i,k}^{I,calc}$ are the experimental and
 139 calculated mole fractions of the aqueous phase and $x_{i,k}^{II,exp}, x_{i,k}^{II,calc}$ are the experimental and
 140 calculated mole fractions of the phenolic phase.

141 The rmsd values, which provide a measure of the accuracy of the correlations, were calculated
 142 according to the following equation:

$$143 \quad rmsd = \left\{ \frac{\sum_{k=1}^N \sum_{i=1}^2 \left\{ (x_{i,k}^{I,exp} - x_{i,k}^{I,calc})^2 + (x_{i,k}^{II,exp} - x_{i,k}^{II,calc})^2 \right\}}{4N} \right\}^{\frac{1}{2}} \quad (4)$$

144

145 3.2. Solid-Liquid Equilibria

146 The solubility of phenolic compounds in water *via* solid-liquid equilibria (*ie* pyrocatechol,
 147 syringol and vanillin) were determined using the simplified thermodynamic equation[52]:

$$148 \quad \ln(x_{PC}\gamma_{PC}) = \frac{\Delta_{fus}H_{PC}}{RT_{fusPC}} \left(1 - \frac{T_{fusPC}}{T} \right) \quad (5)$$

149 where $\Delta_{fus}H_{PC}$ is the melting enthalpy calculated at the melting temperature T_{fusPC} of the
 150 phenolic compound. The objective function and the rmsd definition were similar to the
 151 **equations 3 and 4**. The solid phase was supposed to be pure phenolic component.

152 3.3. Vapor-Liquid equilibria

153 The vapor-liquid equilibria was determined through the following expression:

$$154 \quad P \cdot y_i = P_i^{sat} \cdot x_i \cdot \gamma_i \cdot \mathcal{P} \quad (6)$$

155 where P and P_i^{sat} are respectively the pressure and saturated pressure of compound i, with y
 156 and x the molar fractions in the vapor and liquid phases, respectively. The Poynting
 157 coefficient \mathcal{P} was supposed equal to 1 since the fixed pressure was below the atmospheric
 158 one. The saturated pressures of the components were calculated using the Antoine equation
 159 [53–55] (**Table S2**).

160 The objective function used to regress the a_{ij} and b_{ij} parameter is presented as follows:

161 $F_{obj} = abs(1 - \frac{P_{calculated}}{P_{experimental}})$ (7)

162 The corresponding rmsd was calculated with the expression:

163 $rmsd = \left\{ \frac{\sum_{i=1}^N (P_{i_{experimental}} - P_{i_{calculated}})^2}{N} \right\}^{\frac{1}{2}}$ (8)

164

165 **4. Results and Discussion**

166 **4.1. Solubility of the phenolic compounds in water**

167 For a better display, the solubilities of the phenolic compounds in water were plotted in
168 **Figure 2** with a natural log scale. Experimental data are provided in **Tables 3 and 4**. The
169 solubility of each compounds in water increases with the increasing of temperature.
170 Pyrocatechol, vanillin and syringol present a solid-liquid equilibria while the other
171 compounds are in liquid-liquid equilibria with water. Note that syringol presents also a liquid-
172 liquid equilibria but for a temperature beyond 308.15K. The solubility of pyrocatechol, phenol
173 and vanillin is the most influenced by temperature. At 298.15 K, pyrocatechol presents the
174 highest solubility in water ($x_{pyrocatechol} = 0.123$), followed by phenol ($x_{phenol} = 0.017$). The
175 solubility of the others compounds are in the same range of values, according to the following
176 rank: o-cresol > m-cresol > p-cresol > guaiacol > syringol > vanillin. The pyrocatechol and
177 phenol molecules present respectively two and one hydroxyl groups, which are easily
178 accessible to interact with water. In the case of cresols, the presence of a methyl group hinders
179 the interactions of water with the hydroxyl group and therefore reduces the solubility of the
180 compound. Finally, for guaiacol, syringol and vanillin, the presence of a methoxy group
181 creates an intramolecular hydrogen bond with the hydroxyl group of the phenolic compounds.
182 For these three former molecules, their hydroxyl groups are less available to interact with
183 water. Generally, measurements are in good agreement with those found in literature[20–34].

184 Nevertheless, our experimental data obtained for the vanillin-water system presents some
185 deviation with those measured by Noubigh et al[28]. Indeed, this difference can be explained
186 by the fact these authors waited only 3 hours of stirring and did not reach the equilibria. [56–
187 58] Besides, for the vanillin-water system, the results presented in this work are in good
188 agreement with those from Cartwright[26] and Mange et al[27]. For the solubility of syringol
189 in water, no data have been found in the literature. Plot of the different data are provided in
190 supporting information for comparison (**Figures S1 to S7**).

191

192 **4.2. Solubility of water in the phenolic solution**

193 **Tables 3 and 4** and **Figure 3** gather the results of the solubility of water in the phenolic
194 solutions. Water is more soluble in the phenolic solutions with the rise of temperature. The
195 guaiacol system is the most temperature-dependent. At 300 K, the solubility of water
196 increases in the phenolic compounds as follows: guaiacol < o-cresol < m-cresol < p-cresol <
197 syringol. The solubility of water in guaiacol is very low compared to those obtained in cresols
198 or in syringol. This behavior is mainly due to the fact that guaiacol presents in its structure an
199 intramolecular hydrogen bond between its hydroxyl and methoxy group[59]. Therefore, the
200 hydroxyl group is less accessible to interact with water. In the case of cresols, the solubility of
201 water increases with the increasing distance of the methyl group. The hydroxyl group is less
202 hindered in the para position compared to the ortho position and therefore can interact with
203 water more easily. In the case of syringol, there is an intramolecular hydrogen bond between
204 its hydroxyl and methoxy groups but its second methoxy group remains available to interact
205 with water molecules. Experimental solubility measurements are in good agreements with
206 those found in the literature [21,23–25,35] with a deviation between 0.15 and 1.4%.
207 Comparisons are provided in supporting information (**Figures S4 to S7**).

208 The regression of the parameter a_{ij} and b_{ij} of the NRTL model are listed in **Table 5** for the
209 phenolic compound-water systems. It can be noted that the number of experimental data of
210 the two binary systems {phenol-water} and {syringol-water} does not allow to regress the
211 NRTL parameters. The rmsd values are very low (inferior to 0.3%) for all systems which
212 means that the correlated values fit well with the experimental data (**Figures 2 and 3**).

213

214 **4.3. Vapor-Liquid equilibria of phenolic compound and ethanol**

215 The results of the vapor-liquid equilibria between the phenolic compounds (*i.e.* phenol,
216 guaiacol, o-cresol) and ethanol are summarized hereafter (**Table 6**). The boiling temperature
217 increases with the increase of pressure. Same phenomenon is observed with the increase of
218 the molar fraction of the phenolic compounds. No azeotrope point is observed for the three
219 systems, neither is a demixing of the liquid phase. **Figure 4** presents the plot of the guaiacol-
220 ethanol system as example.

221 The temperature dependency is more important at high fraction of phenolic compounds
222 ($x_{\text{phenolic}} = 0.8-1$). The binary system {guaiacol-ethanol} is less temperature-dependent
223 compared to the phenol or o-cresol systems (**Figures S8 and S9**). Indeed, the slope in the
224 guaiacol system is higher compared to the other systems. Moreover, for the {o-cresol-
225 ethanol} and {phenol-ethanol} systems, the increase of the boiling temperature is more
226 regularly distributed on the range of the molar fraction studied. The final boiling temperature
227 is decreasing depending on the phenolic compounds as follows: guaiacol > o-cresol > phenol.

228 The regression of the parameter a_{ij} and b_{ij} of the NRTL model are listed in **Table 7** for the
229 phenolic compound-ethanol system. The rmsd values are very low (inferior to 0.02 bar) for all
230 systems showing that the correlated values fit well with the experimental data.

231

232 **4.4 Excess enthalpy of the phenolic compound – ethanol systems**

233 Excess properties give information for understanding the origin of the nonideality of mixtures.
234 Molar excess enthalpy (h^E) provides a measure of the intermolecular interactions in the
235 mixture. During mixing, energy is required to break the interactions between the molecules of
236 the pure solvent in order to form new interactions between unlike species releasing energy.
237 The results of the molar excess enthalpy (h^E) for guaiacol, o-cresol and m-cresol and ethanol
238 systems are listed in **Table 8** and plotted in **Figure 6**. The mixing of ethanol and phenolic
239 compounds studied in this work is exothermic and the curves are practically symmetrical
240 towards the molar fraction $x=0.5$. In first approximation, the exothermic effect may be related
241 to stronger interactions between phenolic compounds and ethanol than ethanol-ethanol or
242 phenolic-phenolic compounds interactions. Finally, the mixing enthalpy values decreases as
243 follows: guaiacol > m-cresol > o-cresol. It is worth noting that molar excess enthalpy of
244 {ethanol + guaiacol} is quite small (0 to $-550 \text{ J}\cdot\text{mol}^{-1}$). Replacing the methoxy group of the
245 guaiacol by a methyl group in o-cresol leads to a strong increase of the h^E values.

246

247 **5. Conclusion**

248 The mutual solubilities of water and eight phenolic compounds (*i.e.* phenol, guaiacol,
249 syringol, pyrocatechol, o-, m-, p-cresol and vanillin) were investigated between 293.15 and
250 323.15K. Vapor-liquid equilibria and mixing enthalpy of binary mixtures {phenol or guaiacol
251 or o-cresol + ethanol} were also investigated for different molar compositions. The
252 information provided by this work help to understand the behavior of the phenolic compounds
253 in green solvents. This knowledge is vital for the development of extraction and purification
254 processes of phenolic compounds from bio-oils produced upon biomass thermochemical
255 conversion. Moreover, parameters of the NRTL thermodynamic model were determined and
256 correlate well with the experimental measurements.

257 **Acknowledgment**

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259 research did not receive any other specific grant from funding agencies in the public,
260 commercial, or not-for-profit sectors.

261

262 *List of symbols*

263	α	Non-randomness parameter
264	γ_i	Activity coefficient
265	a_{ij}, b_{ij}	NRTL parameters
266	g	Interaction energy parameter (NRTL)
267	h^E	Molar excess enthalpy
268	$\Delta_{fus}H$	Fusion enthalpy
269	K	Kelvin
270	LLE	Liquid-Liquid Equilibrium
271	N	Number of tie-lines
272	\mathcal{P}	Poynting coefficient
273	P	Pressure
274	P^{sat}	Saturated pressure
275	PC	Phenolic Compound
276	R	Ideal gas constant
277	rmsd	Root mean square deviation
278	SLE	Solid Liquid Equilibrium
279	T	Temperature
280	T_{fus}	Fusion temperature

281 VLE Vapor-Liquid Equilibrium

282 x Molar fractions (liquid phase)

283 y Molar fraction (vapor phase)

284

285

286 Table 1: Temperature range and method of measurements for the {phenolic compounds-
 287 water} systems found in the literature

288

System	Temperature	Method	Reference
Phenol-water	[280-345K]	Conductivity	[31,34]
Phenol-water	[274-338K]	Refractometry	[32]
Phenol-water	[293-339K]	Volumetry	[33]
Pyrocatechol-water	[314-377K]	Visual observation	[29]
Pyrocatechol-water	[295-326K]	/	[30]
Vanillin-water	[273-323K]	Visual observation	[26]
Vanillin-water	[273-303K]	Visual observation	[27]
Vanillin-water	[293-318K]	Shake flask method	[28]
Cresol-water	[273-450K]	Visual observation	[21]
Cresol-water	298K	Shake flask method	[22]
Cresol-water	293K	Turbidity	[23]
Cresol-water	[288;298K]	/	[24]
m-cresol-water	[293-350K]	Chromatography	[25]
Cresol-water	[298-360K]	Turbidity	[36]
Guaiacol-water	298K	Shake flask method	[20]
Guaiacol-water	298K	Density measurements	[35]

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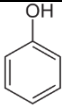
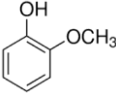
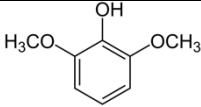
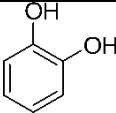
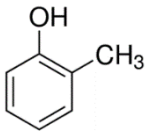
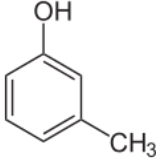
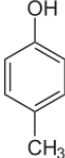
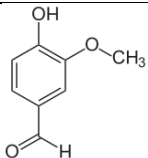
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294 Table 2: Name, CAS number, abbreviation, molar mass, formula, source and purity of the
 295 used compounds

Name and CAS	Abbreviation	Molar mass g.mol ⁻¹	Formula	Source and purity (wt%)
Phenol 108-95-2		94.11		Sigma Aldrich >99.5%
2-methoxyphenol 90-05-1	Guaiacol	124.14		Sigma Aldrich >99%
2,6-dimethoxyphenol 91-10-1	Syringol	154.16		Sigma Aldrich 99%
1,2-benzenediol 120-80-9	Pyrocatechol	110.11		Sigma Aldrich >99%
2-Methylphenol 95-48-7	o-Cresol	108.14		Sigma Aldrich >99%
3-Methylphenol 108-39-4	m-Cresol	108.14		Sigma Aldrich >99%
4-Methylphenol 106-44-5	p-Cresol	108.14		Sigma Aldrich >99%
4-Hydroxy-3-methoxybenzaldehyde 121-33-5	Vanillin	152.15		Sigma Aldrich >99%

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Table 3: Experimental LLE data of the {phenolic compound (PC) - water} systems at atmospheric pressure.

Temperature (K)	Aqueous phase		Phenolic phase	
	x_{PC}	x_{water}	x_{PC}	x_{water}
<i>Phenol-water</i>				
298.15	0.0172	0.9828		
303.15	0.0184	0.9816		
308.15	0.0195	0.9805		
313.15	0.0207	0.9793		
318.15	0.0217	0.9783		
323.15	0.0242	0.9758		
<i>Guaiacol-water</i>				
298.15	0.0036	0.9964	0.2478	0.7522
303.15	0.0037	0.9963	0.2654	0.7346
308.15	0.0038	0.9962	0.2774	0.7226
313.15	0.0039	0.9961	0.3048	0.6952
318.15	0.0039	0.9961	0.3261	0.6739
323.15	0.0041	0.9959	0.3557	0.6443
<i>Syringol-Water</i>				
313.15	0.0041	0.9959	0.6484	0.3516
318.15	0.0044	0.9956	0.6722	0.3278
323.15	0.0048	0.9952	0.6864	0.3136
<i>o-Cresol-water</i>				
298.15	0.0042	0.9958	0.4848	0.5152
303.15	0.0044	0.9956	0.4898	0.5102
308.15	0.0046	0.9954	0.4954	0.5046
313.15	0.0047	0.9953	0.5010	0.4990
318.15	0.0048	0.9952	0.5056	0.4944
323.15	0.0051	0.9949	0.5154	0.4846
<i>m-Cresol-water</i>				
298.15	0.0041	0.9959	0.4791	0.5209
303.15	0.0042	0.9958	0.4913	0.5087
308.15	0.0044	0.9956	0.5002	0.4998
313.15	0.0044	0.9956	0.5141	0.4859
318.15	0.0046	0.9954	0.5308	0.4692
323.15	0.0049	0.9951	0.5427	0.4573
<i>p-Cresol-water</i>				
298.15	0.0036	0.9964	0.5157	0.4843
303.15	0.0037	0.9963	0.5280	0.4720
308.15	0.0038	0.9962	0.5383	0.4617
313.15	0.0039	0.9961	0.5482	0.4518
318.15	0.0040	0.9960	0.5545	0.4455

$u(T) = 0.1K, u(x) < 0.005$

Table 4: Experimental SLE data of the {phenolic compound (PC)-water} systems at atmospheric pressure.

Temperature (K)	x_{PC}	x_{water}
<i>Syringol+water</i>		
293.15	0.0023	0.9977
298.15	0.0028	0.9972
303.15	0.0034	0.9966
308.15	0.0037	0.9963
<i>Pyrocatechol+water</i>		
293.15	0.0942	0.9058
298.15	0.1229	0.8771
303.15	0.1568	0.8432
308.15	0.1923	0.8077
313.15	0.2477	0.7523
318.15	0.2892	0.7108
323.15	0.3450	0.6550
<i>Vanillin+water</i>		
293.15	0.0010	0.9990
298.15	0.0012	0.9988
303.15	0.0015	0.9985
308.15	0.0019	0.9981
313.15	0.0026	0.9974
318.15	0.0036	0.9964
323.15	0.0051	0.9949

$u(T) = 0.1K$, $u(x) < 0.005$

Table 5: NRTL parameters for the phenolic compound –water (SLE and LLE) systems.

Compounds	a_{12} ($J.mol^{-1}$)	a_{21} ($J.mol^{-1}$)	b_{12} ($J.mol^{-1}.K^{-1}$)	b_{21} ($J.mol^{-1}.K^{-1}$)	rmsd (%)
Guaiacol	-2904.47	14631.14	50.56	-41.82	0.1363
o-Cresol	2238.76	4062.37	36.27	-14.81	0.0403
m-Cresol	-678.03	8057.33	46.23	-27.99	0.0298
p-Cresol	-839.66	6804.87	48.39	-25.14	0.0399
Syringol ^a	-4.48	-4.73	40.04	92.25	0.0041
Pyrocatechol ^a	2049.51	18565.35	182.94	-60.35	0.1488
Vanillin ^a	23464.72	5611.93	-30.50	2754755.83	0.0085

a: solid-liquid equilibrium

Table 6: vapor-liquid equilibrium data of binary mixtures containing phenolic compounds and ethanol.

P (bar)	x_{phenol}	T (K)	P (bar)	x_{guaiacol}	T (K)	P (bar)	$x_{\text{o-cresol}}$	T (K)
0.090	0.100	303.09	0.090	0.109	300.25	0.090	0.097	302.23
	0.198	305.10		0.219	303.33		0.206	305.46
	0.300	310.04		0.322	304.88		0.304	308.67
	0.400	313.16		0.400	307.11		0.390	312.21
	0.495	319.73		0.491	309.40		0.507	319.01
	0.588	325.77		0.592	312.76		0.597	326.79
	0.692	333.65		0.701	316.55		0.699	333.07
	0.794	342.26		0.773	320.29		0.791	342.80
	0.883	353.85		0.889	332.80		0.898	359.99
0.150	0.100	312.58	0.164	0.109	313.11	0.150	0.097	311.87
	0.198	315.16		0.219	315.03		0.206	315.32
	0.300	319.57		0.322	317.28		0.304	319.29
	0.400	323.66		0.400	319.36		0.390	322.19
	0.495	330.26		0.491	321.93		0.507	329.86
	0.588	337.31		0.592	325.08		0.597	336.50
	0.692	345.08		0.701	329.79		0.699	344.12
	0.794	355.05		0.773	333.56		0.791	354.31
	0.883	366.57		0.889	347.75		0.898	373.10
0.330	0.100	328.70	0.333	0.109	328.13	0.351	0.097	329.36
	0.198	331.35		0.219	329.87		0.206	333.25
	0.300	336.15		0.322	332.29		0.304	337.22
	0.400	339.90		0.400	334.17		0.390	340.16
	0.495	347.78		0.491	337.32		0.507	348.90
	0.588	355.56		0.592	340.83		0.597	356.03
	0.692	364.32		0.701	346.20		0.699	363.84
	0.794	376.11		0.773	350.90		0.791	375.90
	0.883	388.50		0.889	368.35	-	-	-
0.550	0.100	340.09	0.500	0.109	337.36	0.551	0.097	339.54
	0.198	342.95		0.219	339.06		0.206	343.48
	0.300	348.05		0.322	341.49		0.304	347.87
	0.400	352.38		0.400	343.46		0.390	350.35
	0.495	360.94		0.491	346.85		0.507	360.29
	0.588	369.17		0.592	350.46		0.597	367.82
	0.692	378.58		0.701	356.72		0.699	376.33
	0.794	389.90		0.773	362.19		0.791	389.39
-	-	-		0.889	381.56	-	-	-
0.750	0.100	347.53	0.700	0.109	345.35	0.750	0.097	346.85
	0.198	350.61		0.219	347.10		0.206	351.09
	0.300	355.78		0.322	349.65		0.304	355.53
	0.400	360.18		0.400	351.60		0.390	357.50
	0.495	369.28		0.491	355.68		0.507	368.40

	0.588	378.05		0.592	359.53		0.597	376.10	
	0.692	387.67		0.701	366.51		0.699	385.84	
-	-	-		0.773	372.24	-	-	-	
-	-	-		0.889	394.05	-	-	-	
0.851	0.100	350.58	0.832	0.109	349.63	0.851	0.097	349.95	
	0.198	353.70		0.219	351.45		0.206	354.17	
	0.300	359.06		0.322	354.00		0.304	358.80	
	0.400	363.56		0.400	355.80		0.390	360.75	
	0.495	373.06		0.491	360.20		0.507	371.88	
	0.588	381.78		0.592	364.10		0.597	379.52	
-	-	-		0.701	371.89		0.699	389.62	
-	-	-		0.773	377.68	-	-	-	
-	-	-		0.889	400.47	-	-	-	
0.986	0.100	354.51	0.996	0.109	354.12	0.991	0.097	353.75	
	0.198	357.65	0.961	0.219	354.92	0.977	0.206	357.95	
	0.300	362.97	0.992	0.322	358.70	0.997	0.304	363.05	
	0.400	367.75	0.977	0.400	359.87	0.999	0.390	364.60	
	0.495	376.85	0.990	0.491	365.43	0.991	0.507	374.97	
	0.588	386.30	0.971	0.592	368.80	0.985	0.597	384.56	
-	-	-		0.997	0.701	377.89	0.994	0.699	394.11
-	-	-		0.990	0.773	383.82	-	-	-
-	-	-		0.965	0.889	409.48	-	-	-

$u(T) = 0.06 \text{ K}$, $u(P) = 0.4 \text{ mbar}$, $u(x) < 0.005$

Table 7: NRTL parameters for the phenolic compound – ethanol (VLE) systems.

Compounds	a_{12}	a_{21}	b_{12}	b_{21}	rmsd (bar)
	($\text{J}\cdot\text{mol}^{-1}$)	($\text{J}\cdot\text{mol}^{-1}$)	($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	
Phenol	-0.04	-10.99	0.01	5.47	0.021
Guaiacol	3327.95	-9.21	2215.75	-1.38	0.022
o-Cresol	142951.43	-4.65	-4284.01	5.11	0.025

Table 8: Molar excess enthalpy of the {phenolic compound – ethanol} systems.

x_{Guaiacol}	$h^E (\text{J}\cdot\text{mol}^{-1})$	$x_{\text{o-cresol}}$	$h^E (\text{J}\cdot\text{mol}^{-1})$	$x_{\text{m-cresol}}$	$h^E (\text{J}\cdot\text{mol}^{-1})$
0.0168	-29.95	0.1954	-1112.03	0.2003	-791.99
0.1988	-379.49	0.4127	-1620.73	0.4097	-1227.70
0.3994	-549.10	0.6007	-1652.17	0.5861	-1146.24
0.6080	-505.33	0.8013	-943.58	0.7875	-687.42
0.7783	-237.77	-	-	-	-

$u(T)=0.02\text{K}$; $u(H^E)=5\text{J}\cdot\text{mol}^{-1}$; $u(x) < 0.005$

Figure 3: Water solubility in phenolic phases. Experimental measurements: ● Guaiacol, ○ Syringol, ■ o-Cresol, □ m-Cresol, ▲ p-Cresol. The solid lines have been calculated using NRTL model.

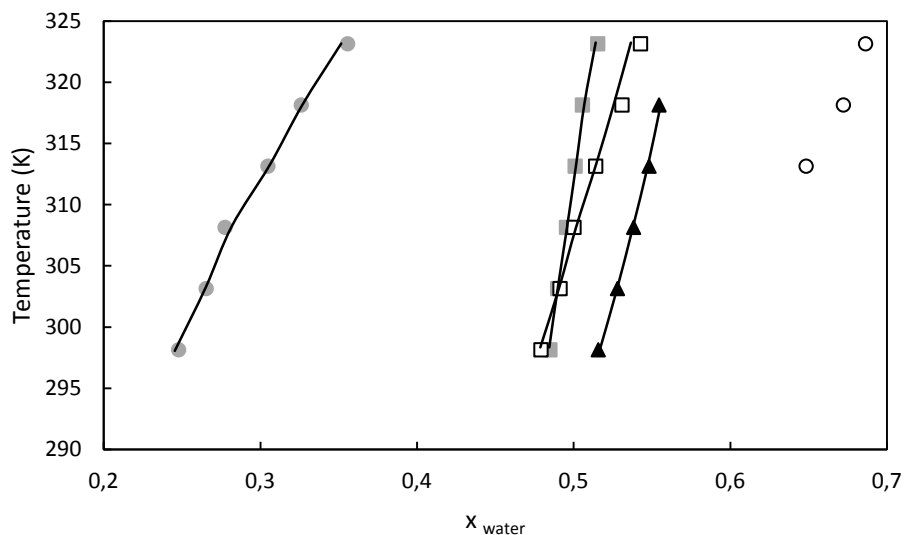


Figure 4: Vapor-Liquid equilibria of the guaiacol-ethanol system in function of the molar fraction of guaiacol at different pressures. Experimental measurements at pressures: ● 0.09 bar, ■ 0.165 bar, ▲ 0.335 bar, ◆ 0.5 bar, ○ 0.7 bar, □ 0.83 bar, △ 0.99 bar. The solid lines have been calculated using NRTL model.

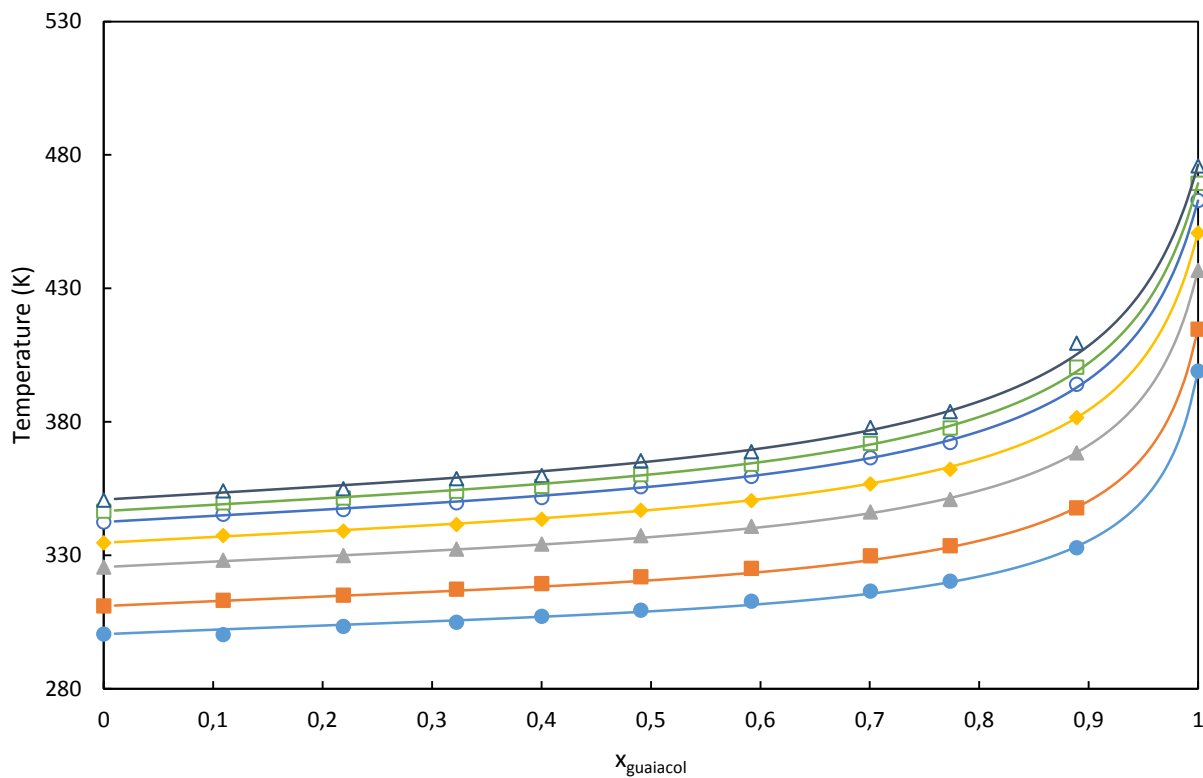
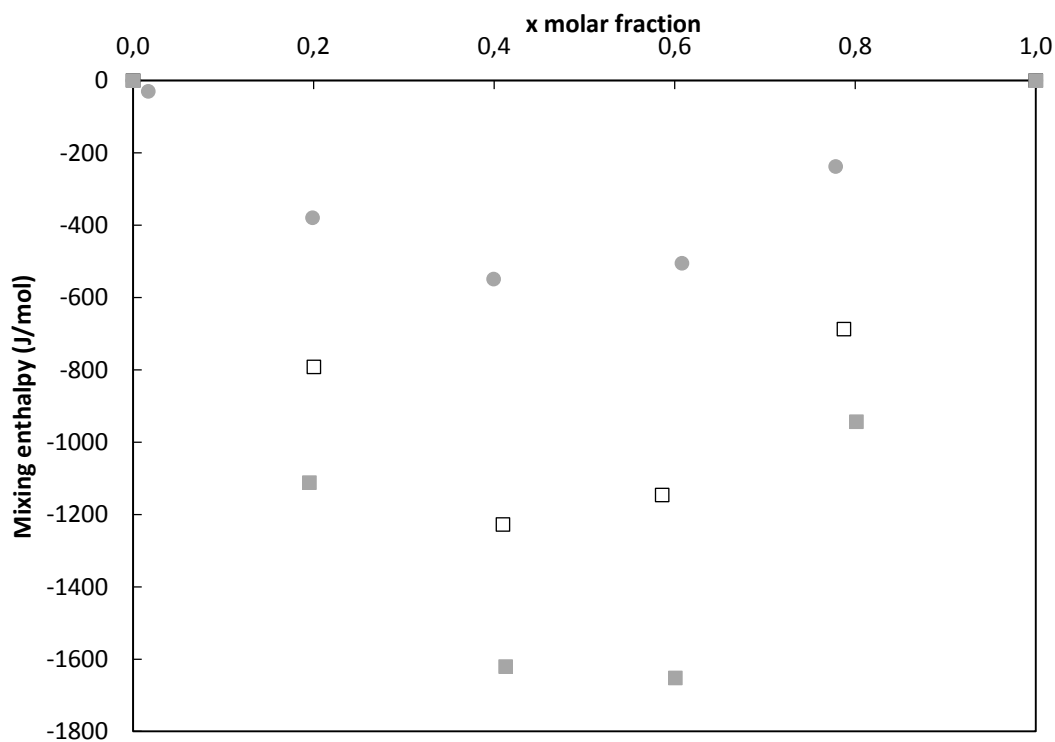


Figure 5: Mixing enthalpy of the phenolic compound - ethanol systems. ● Guaiacol, ■ o-Cresol, □ m-Cresol.



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