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Phase equilibria of phenolic compounds in water or ethanol

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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.

1. Introduction

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

Bio-oils can be produced by various thermochemical treatments, the famous ones being pyrolysis and liquefaction. Many studies have investigated the influence of solvent on the liquefaction process, including formic acid [7], water [8–10], methanol, 2-propanol [10], or ethanol [10–13]. In order to reduce the CO_2 emission and be more economically competitive, more and more processes are using solvents coming from biomass for liquefaction processes [14]. Besides, biomass pyrolysis also produces aromatic compounds-rich bio-oils. The condensed vapors obtained during a pyrolysis process are generally collected in solvents such as aqueous solution or ethanol. The extraction of high value compounds from this diluted bio-oil is difficult to perform due to its thermal instability and its complex composition. Most of the processes generally start with the recovery of the solvent by distillation. Then, liquid-liquid extraction using water [15], basic aqueous solutions [16–18] or polar organic solvent [19] are predominantly preferred. Although the distillation of ethanol and the liquid-liquid extraction of phenolic compounds with water are regularly used in the extraction process, only few data are available in the literature [20–39]. The method and the range of temperature of the {phenolic compounds-water} systems found in the literature are presented in Table 1. No data has been found for the syringol-water system. The vapor-liquid equilibria (VLE) of the {phenol + ethanol} system were only investigated at atmospheric pressure [40,41], at 288.15K [42] and 293.15 K [43]. Only one isothermal VLE at 290.15 K can be found for the binary {guaiacol + ethanol} [38] and two sets of VLE data for the binary system {o-cresol + ethanol} (0.9576 bar [37] and 291.15K [39]).

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

In this work, we studied the behavior of eight phenolic compounds (*i.e.* phenol, guaiacol, syringol, pyrocatechol, o-cresol, m-cresol, p-cresol and vanillin) with water or ethanol. The mutual solubilities of the compounds with water were investigated as a

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

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]

function of temperature. Bubble curves of phenolic compounds with ethanol as well as their mixing enthalpy were also studied. The phase equilibrium data of the systems were used to regress parameters on the Non-Random Two-Liquids (**NRTL**) [44] thermodynamic models.

2. Material and methods

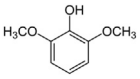
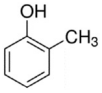
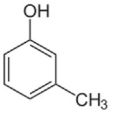
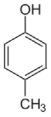
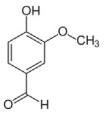
2.1. Chemicals

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

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 (±0.1K). The mixtures were stirred for 48 h with a coated magnetic stirring bar. Then, the solutions were left for another 48 h 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-μm filter was connected to the syringe. Samples were diluted by factor 10^4 with deionized water

Table 2
Name, CAS number, abbreviation, molar mass, formula, source and purity of the 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%
Ethanol 64-17-5		46.07		Carlo Erba absolute anhydrous