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On the solubility of phenol in *m*-cresol

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Abstract

The solubility of phenol in *m*-cresol has been measured at four different temperatures, 293, 298, 303 and 308 K, with pressure ranging from 1 to 100 bar. The experimental results have been correlated using a non-cubic equation of state with non-classical mixing rules. The data are well represented using predicted values for most model parameters.

Keywords: Phenol; *m*-Cresol; Solubility; Solid–liquid equilibrium; EOS

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1. Introduction

In a previous study by Di Giacomo et al. [1] the ternary system phenol–*m*-cresol–carbon dioxide was described using the Peng–Robinson cubic equation of state (EOS). This ternary system presents regions where multiple phases are present (SLV) and at the binary solid–liquid interface the predicted solubility of phenol in *m*-cresol appeared to be strongly dependent on pressure in the range 1–100 bar [1]. As typically condensed phases are only slightly influenced by pressure [2] this result seems counter-intuitive and we have decided to investigate more thoroughly the effect of temperature and pressure on the solubility of phenol in *m*-cresol.

2. Experimental

Phenol and *m*-cresol >99% were purchased from Aldrich and used without further purification. ACS grade carbon tetrachloride, used for the quantitative gas chromatographic measurement of phenol and *m*-cresol compositions, was purchased from Fluka.

The system used for the equilibrium measurements is schematically represented in Fig. 1. The pressure is maintained at a set level by a Nova Swiss compressor using nitrogen, IP grade, from Rivoira. A micrometric valve, positioned between the compressor and the equilibrium cell, allows for fine adjustment of the system pressure. The stainless steel cell has a volume of 200 cm^3. The cell temperature is controlled through a thermostatic fluid which flows from a thermostat to a jacket. The pressure at the cell is measured by a Haenni pressure transducer with an accuracy of ±0.5 bar and a J type thermocouple with an accuracy of ±0.05 °C.

The sample from the equilibrium cell is obtained from a connecting pipe positioned at 2/3 of the total height of the cell. The flow of the sample is controlled by a micrometric valve connected to the 1 cm^3 sample collector. The composition is maintained uniform by a magnetic stirrer.

Initially a total of 150 g of phenol and *m*-cresol are introduced in the cell. The pressure is varied introducing nitrogen and the system is maintained under agitation for over 2 h. The stirring is halted and decantation is achieved in approximately 2 h. The liquid solution at equilibrium is collected and carbon tetrachloride is added to maintain a uniform solution for the GC analysis.

The quantitative measurements are obtained using a Supelco GP 10% SP-2100 2 m packed column in a Perkin–Elmer mod. 8310 gas chromatograph.

3. Modelling of high-pressure solid–liquid equilibrium

The description of the solubility of phenol in *m*-cresol as a function of pressure and temperature is of practical relevance in the ternary system that includes CO_2 [1]. Therefore, the modelling approach chosen is aimed at determining the model parameters for an equation of state/mixing rules model that can be extended to describe the ternary system. To describe the liquid-phase fugacity in the pressure range 1–100 bar the non-cubic EOS of Brandani et al. [3] was used:

$$z = 1 + \frac{4\eta - 2\eta^2}{(1-\eta)^3} - \frac{4\varepsilon}{RT}\eta(1 + k_1\eta + k_2\eta^2) \tag{1}$$

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Nomenclature

a_{12}, a_{21}	NRTL binary interaction parameters (K)
b	covolume (m^3)
b_C	covolume at the critical temperature (m^3)
b_0	EOS parameter
f_1^L	liquid-phase fugacity of phenol (Pa)
f_1^S	fugacity of pure solid phenol (Pa)
P	pressure (Pa)
P_1^S	sublimation pressure of phenol (Pa)
P_C	pure component critical pressure (Pa)
R	ideal gas constant (J/(mol K))
T	temperature (K)
T_C	pure component critical temperature (K)
v_1^S	molar volume of solid phenol (m^3)
x_1	liquid-phase mole fraction of phenol
z	compressibility

Greek letters

ε	EOS energy parameter (J/mol)
ε_C	EOS energy parameter at the critical temperature (J/mol)
ε_0, ε_1	temperature dependence of energy parameter
ϕ_1	liquid-phase fugacity coefficient
η	reduced density
ρ	molar density (mol/m^3)

where $k_1 = -1.43279$, $k_2 = 3.97055$ and

$$\eta = \frac{b\rho}{4} \tag{2}$$

Table 1
Pure component parameters

	Phenol	*m*-Cresol
T_C (K)	694.2	705.8
P_C (bar)	61.3	45.6
b_0	0.11513	0.10809
ε_0	−0.19504	−0.23979
ε_1	0.64820	0.74791
Temperature interval (K)	344−455	423−474
AAPD[a], Antoine equation [2]	1.93	0.19
AAPD, this work	1.64	0.22

[a] Average absolute percent deviation (AAPD).

This EOS is characterised by a volume parameter b and an energy parameter ϵ. These parameters are temperature dependent according to:

$$\frac{b}{b_C} = \left[\frac{1-(1/3)\exp(-b_0(T_C/T))}{1-(1/3)\exp(-b_0)}\right]^3 \tag{3}$$

$$\frac{\varepsilon}{\varepsilon_C} = \frac{1+\varepsilon_T(T_C/T)}{1+\varepsilon_T} \tag{4}$$

$$\varepsilon_T = \varepsilon_0 + \varepsilon_1\frac{T}{T_C} \tag{5}$$

The EOS parameters at the critical point can be evaluated from:

$$\frac{b_C P_C}{RT_C} = 0.16551; \qquad \frac{\varepsilon_C}{RT_C} = 3.10027 \tag{6}$$

The critical constants were obtained from [4]. The pure component constants were obtained from the correlation of experimental vapour pressures [5] and are reported in Table 1.

The phenol–*m*-cresol solution is described using the mixing rules developed by Brandani et al. [3]. These are based on the correct zero pressure limit (second virial coefficient) and the excess Helmholtz energy from the attractive term of the EOS matched at a constant reduced reference density to

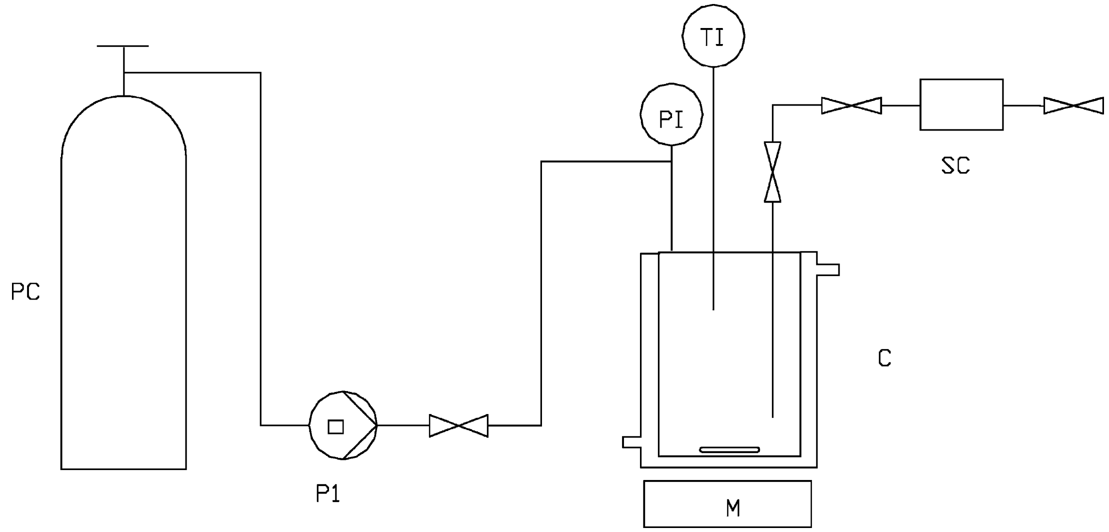

Fig. 1. Simplified flow sheet of apparatus. SC: sample collector; PC: nitrogen cylinder; P1: compressor; C: equilibrium cell; M: magnetic stirrer.

the NRTL activity coefficient model. Therefore, the fugacity of phenol in the liquid mixture is given by:

$$f_1^{\mathrm{L}} = \phi_1 x_1 P \tag{7}$$

where ϕ_1 is the fugacity coefficient and x_1 is the molar fraction of phenol.

The fugacity of pure solid phenol is calculated from

$$f_1^{\mathrm{s}} = P_1^{\mathrm{s}} \exp\left[v_1^{\mathrm{s}} \frac{(P - P_1^{\mathrm{s}})}{RT}\right] \tag{8}$$

where P_1^{S} is the sublimation pressure, v_1^{S} is the molar volume of the solid.

In order to reduce the number of adjustable parameters that needed to be determined, the following assumptions were made:

- The molar volume of the solid was calculated from the close-packing density and b_{C}, $v_1^{\mathrm{S}} = 55 \times 10^{-6}\,\mathrm{m^3/mol}$.
- The sublimation pressure is calculated using the Clausius–Clapeyron equation, from the literature value the vapour pressure at the triple point [6] and the sublimation enthalpy calculated from the slope of the vapour pressure curve at the triple point and the heat of fusion [6], $\lambda_{\mathrm{S}} = 69290\,\mathrm{J/mol}$.
- As phenol and *m*-cresol are similar components the cross-virial coefficient parameter in the mixing rules is assumed to be $k_{12} = 0$.
- The third parameter in the NRTL equation α_{12} is fixed at 0.3.

With these assumptions, in order to describe the system, it is still necessary to determine the NRTL mixture parameters a_{12} and a_{21} at each temperature, which are left as the only model parameters that need to be fitted to the experimental solubility data.

4. Results and discussion

The solubility of phenol in *m*-cresol at 293, 298, 303 and 308 K as a function of pressure from 1 to 100 bar is reported in Tables 2–5. In order to exclude any effect of nitrogen on the measurements we also determined the solubility of nitrogen in *m*-cresol. At 293 K and 196 bar $x_{\mathrm{N_2}} = 0.0018$ while at 308 K and 187 bar $x_{\mathrm{N_2}} = 0.0011$. These results show that nitrogen can be considered as an inert component in this system and that at the lower pressures investigated any effect would be within the experimental uncertainty. The experimental accuracy on mole fractions is within ±0.001, therefore including the effect of nitrogen at higher pressures the data should be accurate to within ±0.002.

Table 2
Solubility of phenol in *m*-cresol at 20 °C as a function of pressure

P (bar)	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{calc}}$
1	0.644	0.645
21	0.634	0.640
21	0.633	0.640
42.2	0.632	0.635
42.8	0.633	0.635
64	0.632	0.631
65.3	0.631	0.630
78.9	0.629	0.627
79.6	0.628	0.627
101	0.627	0.623
		AAPD = 0.44

Table 3
Solubility of phenol in *m*-cresol at 25 °C as a function of pressure

P (bar)	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{calc}}$
1	0.700	0.705
21.8	0.697	0.701
22.2	0.696	0.701
40.9	0.694	0.697
61.0	0.693	0.693
61.6	0.692	0.693
82.3	0.691	0.689
83.7	0.691	0.688
101	0.689	0.685
102	0.689	0.685
		AAPD = 0.45

Table 4
Solubility of phenol in *m*-cresol at 30 °C as a function of pressure

P (bar)	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{calc}}$
1	0.788	0.772
20.8	0.767	0.768
21.0	0.766	0.768
40.7	0.763	0.764
41.4	0.763	0.764
60.0	0.760	0.760
61.0	0.760	0.760
81.6	0.758	0.756
82.5	0.757	0.756
102	0.755	0.752
		AAPD = 0.33

From the data previously mentioned we determined the following expression for the sublimation pressure of phenol

$$\ln P_1^{\mathrm{s}}(\mathrm{Pa}) = 31.7727 - \frac{8333}{T} \tag{9}$$

Table 5
Solubility of Phenol in *m*-cresol at 35 °C as a function of pressure

P (bar)	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{calc}}$
1	0.886	0.885
21.5	0.882	0.882
40.5	0.880	0.880
61.0	0.878	0.877
61.2	0.877	0.877
80.0	0.875	0.875
80.8	0.876	0.875
100.2	0.871	0.873
101.5	0.871	0.872
102.2	0.870	0.872
		AAPD = 0.11

Table 6
Values of the parameter a_{21} as a function of temperature

T (K)	a_{21} (K)
293.15	−497
298.15	−461
303.15	−575
308.15	−1157

In the correlation of the experimental data the calculated solubility was strongly dependent on the exact value of a_{21}. It was found that a_{12} could be described by the following equation:

$$a_{12} = 23164 - 79T \tag{10}$$

The comparison between the experimental and calculated solubilities is given in Tables 2–5 along with the values of a_{21} reported in Table 6. The EOS mixing rules are capable of accurately representing the solubilities, but the trend of a_{21} with temperature tends to indicate that the simplifying assumptions used are empirically compensated, especially at the lower temperatures as the extrapolated sublimation pressure and liquid-phase pure component properties are less accurate.

5. Conclusions

The experimental results have shown that the solubility of phenol in *m*-cresol is only moderately influenced by pressure. Therefore, the previous predictions of Di Giacomo et al. [1] are not reliable. The EOS/mixing rule approach used is capable of representing the solubility of phenol in *m*-cresol within the experimental accuracy.

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