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Solid−Liquid Equilibria for 4-Methoxyphenol with Catechol, Ethylenediamine, or Piperazine

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Solid−liquid equilibria (SLE) for the binary systems of 4-methoxyphenol + catechol, + ethylenediamine, and + piperazine and the enthalpies of fusion of the pure compounds are reported. The experimental results show that a single eutectic point exists in 4-methoxyphenol + catechol and a 2:1 complex compound is formed in both 4-methoxyphenol + ethylenediamine and 4-methoxyphenol + piperazine. The Wilson model was employed to correlate the SLE data of 4-methoxyphenol + catechol, and the ideal-chemical model (ICM) was used for correlating the equilibrium data of the complex formation systems.

Introduction

Solid−liquid equilibrium measurements have been made previously for the mixtures containing cresols, piperazine, ethylenediamine, and dibutyl ether (Lee and Chi, 1993; Lee et al., 1994; Lee and Lien, 1995). Those experimental results are useful for the feasibility study of adductive crystallization to separate the close-boiling cresol mixtures. The present work focuses on other mixtures of close-boiling compounds: 4-methoxyphenol (normal boiling temperature $T_b = 516.15$ K) and catechol ($T_b = 518.15$ K), which are encountered in the process of producing methoxyphenols. Solid−liquid phase behavior is observed in the present study for 4-methoxyphenol with catechol, ethylenediamine, or piperazine. The empirical equation of Ott and Goates (1983), the Wilson model, and the ideal-chemical model (Stoicos and Eckert, 1987; Feng et al., 1991; Lee et al., 1994) are adopted to correlate these new SLE data.

Experimental Section

4-Methoxyphenol (99+ mass %) and catechol (99+ mass %) were purchased from Merck (Germany). Ethylenediamine (99 mass %) and piperazine (99 mass %) were supplied by Aldrich. Analysis by gas chromatography confirmed the claimed purities of the chemicals (chromatography analysis: 99.8% for 4-methoxyphenol and catechol, 99.6% for ethylenediamine, 99.4% for piperazine). All these substances were used without further purification. The SLE phase behavior was observed in the present study by a solid-disappearance method, which has been verified previously for its reliability by comparison of test data with literature values of the *m*-cresol + *p*-cresol system (Lee and Chi, 1993). The experimental procedure was detailed elsewhere (Lee and Chi, 1993). Each mixture sample (about 3 g) was prepared by weighting pure compounds to ±0.1 mg and sealing then in a tiny glass vial. The solidified sample was then shaken vigorously in a visual thermostated bath (Neslab, TV-4000, stability = ±0.03 K) for observation of the solid disappearance. The bath is connected with an external refrigeration circulator (Neslab, RTE-110, stability = ±0.01 K) for operation at lower temperatures. The visual bath was operable within the temperature range of (274 to 503) K, and the bath temperature was measured by a Hart Scientific Microtherm (Model 1506) with a thermistor probe to ±0.015 K. The accuracy of the reported solid-disappearance temperatures was estimated to be ±0.2 K under normal experimental conditions and to be ±0.5 K around the vicinity of eutectic point.

Table 1. Properties of Pure Compounds

	T_m/K		$\Delta_{fus}H$/kJ·mol^{-1}		V_L/ cm^3·mol^{-1} (at 383.15 K)
substance	this work	lit.^{a}	this work	lit.	
4-methoxyphenol	328.3		18.30		90.66^b
catechol	377.7	376.85^c 377.70^e 377.80^f	22.54	22.75^{a,d}	57.67^b
piperazine	381.8	383.46^g 383.15^i	22.15	22.1^h	
ethylenediamine	284.1	284.29^j	21.08	22.583^{a,j}	

[a] Taken from the TRC Source Database (1996). [b] Estimated from the modified Rackett equation (Spencer and Danner, 1972): $V_L = (RT_c/P_c)Z_{RA}\{1 + [1 - (T/T_c)^{2/7}]\}$, with $Z_{RA} = 0.29056 - 0.08775\omega$, where $T_c = 756.04$ K, $P_c = 51.46$ bar, and $\omega = 0.5874$ for 4-methoxyphenol and $T_c = 764.46$ K, $P_c = 75.61$ bar, and $\omega = 0.6965$ for catechol. The critical properties were estimated from the Joback model (Reid et al., 1987) and the acentric factor ω was computed from the Lee-Kesler equation (Reid et al., 1987). [c] Data source: Bret-Dibat and Lichanot (1989). [d] Average of the values reported by Andrews et al. (1926), Bret-Dibat and Lichanot (1989), and Rai and Mandal (1989). [e] Data source: Rai and Mandal (1989). [f] Data source: Sabbah and Buluku (1991). [g] Data source: Witschonke (1954). The reported purity of the chemical was 98.0 mass%. [h] Taken from Marsh (1995). [i] Data source: Anonymous (1957). The reported purity of the chemical was 98.0 mass %. [j] Data source: Messerly et al. (1975).

Results and Discussion

Melting temperatures (T_m) of the constituent compounds measured in the present study are compared with literature values in Table 1. Good agreement is shown for catechol and ethylenediamine. The value for piperazine from this work, however, is lower than those of Witschonke (1954) and Anomymous (1957) by about 1.35 K to 1.66 K. To ensure the reliability of the measurements, several repetitions were made for this compound. The observed melting temperature was reproduced to within ±0.2 K.

The experimental SLE data of 4-methoxyphenol + catechol, 4-methoxyphenol + ethylenediamine, and 4-methoxyphenol + piperazine are listed in Table 2. Figure 1 presents the phase diagram of 4-methoxyphenol + catechol in which a eutectic point is shown on the liquidus line. Both 4-methoxyphenol + ethylenediamine and 4-methoxyphenol + piperazine systems exhibit two eutectic points and one congruent point, as shown in Figures 2 and 3, respectively.

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Table 2. Solid−Liquid Equilibria for 4-Methoxyphenol Systems

x_1	T/K	δT/K[a]	x_1	T/K	δT/K
4-Methoxyphenol (1) + Catechol (2)					
0.1003	372.7	−0.02	0.6917	309.7	0.06
0.1994	366.7	0.16	0.7243	311.2	0.53
0.3012	359.0	−0.42	0.7496	313.8	−0.33
0.3981	348.5	0.42	0.7766	315.6	−0.33
0.5005	337.7	−0.09	0.7981	316.3	0.32
0.5824	327.6	0.08	0.8564	319.9	0.03
0.6559	316.5	−0.03			
4-Methoxyphenol (1) + Ethylenediamine (2)					
0.1031	280.2	−0.09	0.7012	344.4	0.69
0.1726	276.4	0.45	0.7697	336.9	0.08
0.2095	275.3	0.16	0.8405	320.4	−0.59
0.2177	277.4	0.02	0.8495	318.5	−0.63
0.2631	287.6	−0.38	0.8604	315.5	0.45
0.4075	316.5	0.52	0.8650	315.2	0.14
0.5518	337.6	−0.55	0.8693	314.6	0.30
0.6309	344.1	−0.21	0.8799	316.3	0.48
0.6606	345.2	0.05	0.9199	323.8	−0.13
0.6694	345.5	−0.05	0.9602	326.8	0.02
4-Methoxyphenol (1) + Piperazine (2)					
0.0958	374.1	−0.10	0.6205	353.3	0.67
0.1949	366.7	−0.04	0.6497	354.4	0.58
0.3506	345.3	−0.59	0.6679	354.7	0.07
0.3691	340.7	0.24	0.7017	353.3	−0.20
0.3821	337.5	0.65	0.7497	348.4	−0.68
0.3895	336.5	0.01	0.7981	339.0	−0.52
0.4130	331.4	−0.33	0.8285	330.0	0.57
0.4205	332.2	0.62	0.8597	320.6	0.14
0.4586	337.8	−0.57	0.8752	314.8	0.06
0.5060	344.2	−0.75	0.8802	316.2	0.23
0.5514	349.2	−0.32	0.8901	318.2	−0.25
0.5594	349.3	0.46	0.9400	324.1	0.00

[a] $\delta T/\mathrm{K} = T_{(\mathrm{calc})} - T_{(\mathrm{expt})}$, where $T_{(\mathrm{calc})}$ is calculated from eq 1.

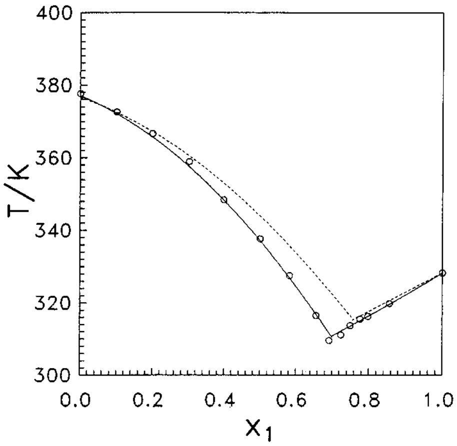

Figure 1. Solid−liquid phase equilibrium diagram for 4-methoxyphenol (1) + catechol (2): (○) experimental values; (- - -) ideal solubilities; (—) calculated from the Wilson model.

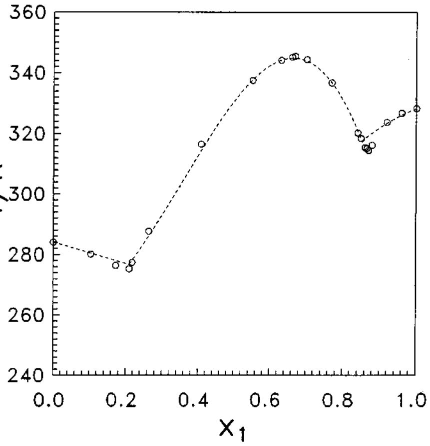

Figure 2. Solid−liquid phase equilibrium diagram for 4-methoxyphenol (2) + ethylenediamine (2): (○), experimental values; (- - -) calculated from the ICM.

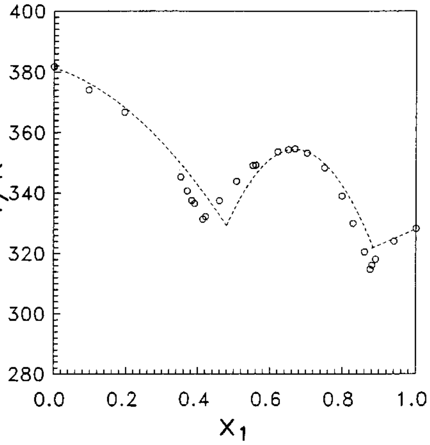

Figure 3. Solid−liquid phase equilibrium diagram for 4-methoxyphenol (1) + piperazine (2): (○) experimental values; (- - -) calculated from the ICM.

Table 3. Locations of Invariant Points

type of invariant point	x_1	T/K
4-methoxyphenol (1) + catechol (2)		
eutectic[a]	0.6925	309.6
4-methoxyphenol (1) + ethylenediamine (2)		
eutectic 1[b]	0.2092	275.3
congruent[c]	0.6667	345.4
eutectic 2[d]	0.8705	314.6
4-methoxyphenol (1) + piperazine (2)		
eutectic 1[e]	0.4133	331.4
congruent[f]	0.6667	354.8
eutectic 2[g]	0.8754	314.9

[a] 4-Methoxyphenol + catechol. [b] Ethylenediamine + (4-methoxyphenol)$_2$−ethylenediamine. [c] (4-Methoxyphenol)$_2$−ethylenediamine. [d] 4-Methoxyphenol + (4-methoxyphenol)$_2$−ethylenediamine. [e] Piperazine + (4-methoxyphenol)$_2$−piperazine. [f] (4-Methoxyphenol)$_2$−piperazine. [g] 4-Methoxyphenol + (4-methoxyphenol)$_2$−piperazine.

The locations of these eutectic and congruent points are compiled in Table 3 and were determined by interpolation from the experimental SLE data. The composition of congruent points is located at the mole fraction of 4-methoxyphenol, about 0.6667 in both systems, implying that a 2:1 complex compound was formed in each binary system.

In addition to the solid-disappearance temperatures, the enthalpies of fusion ($\Delta_{\mathrm{fus}}H$) were determined by a differential scanning calorimeter (DSC-900, DuPont, TA Instrument) for the pure solid compounds. The measured cell was operated at ambient pressure, and the cell factor (K-cell) of the apparatus was calibrated with a standard sample of indium. Liquid nitrogen was used for cooling the sample to about 193 K. The peak area of heat flow during the phase transition was integrated by an on-line computer. The measurements were reproducible to within ±3%. Table 1 reports the experimental results for 4-methoxyphenol, catechol, piperazine, and ethylenediamine. The results of catechol and piperazine agree with the literature values (Andrews et al., 1926; Bret-Dibat and Lichanot, 1989; Rai and Mandal, 1989; Marsh, 1995) to within ±1%, but the value of ethylenediamine is lower than that of Messerly et al. (1975) by 6.6%.

Empirical Correlation

For interpolation purposes, the liquidus lines were correlated piecewise with the empirical equation of Ott and

Table 4. Correlation of Solid-Disappearance Temperatures with Eq 1

$x_{1,\min}$	$x_{1,\max}$	x_1^*	T^*/K	b_1	b_2	b_3	b_4	b_5	b_6	b_7	AAD/K[a]
				4-Methoxyphenol (1) + Catechol (2)							
0.0	0.6925	0.0	377.7	−0.1528	0.4479	−2.9394	5.2423	−3.2574			0.16
0.6925	1.0	1.0	328.3	0.2758	1.3442	5.7414	7.5647				0.28
				4-Methoxyphenol (1) + Ethylenediamine (2)							
0.0	0.2092	0.0	284.1	−0.1194	−0.1648						0.27
0.2092	0.8705	0.6667	345.4	0.0572	−2.1076	−8.2645	−4.9992	107.274	333.824	290.517	0.32
0.8705	1.0	1.0	328.3	0.1026	0.3634	15.9663					0.21
				4-Methoxyphenol (1) + Piperazine (2)							
0.0	0.4133	0.0	381.8	-0.2830	1.1527	-4.4844	3.5509				0.27
0.4133	0.8754	0.6667	354.8	−0.0643	−2.0307	−1.3034	3.4985	−14.3934			0.43
0.8754	1.0	1.0	328.3	0.1220	−1.5007						0.17

[a] AAD/K = $\sum_{k=1}^{n} |T_{(\mathrm{calc}),k} - T_{(\mathrm{expt}),k}|/n$.

Goates (1983):

$$T/\mathrm{K} = T^*[1 + \sum_{j=1}^{M} b_j(x_1 - x_1^*)^j] \tag{1}$$

where x_1 is the mole fraction of 4-methoxyphenol, T is the solid-disappearance temperature of the sample, and b_j's are the coefficients to be regressed to the experimental data. x_1^* and T^* are the mole fraction of 4-methoxyphenol and the solid-disappearance temperature of the congruently melting compound or the pure substance, respectively. Table 4 presents the best-fitted coefficients and the average absolute deviations (AAD) of the correlation for each mixture. The AAD is defined as

$$\mathrm{AAD/K} = [\sum_{k=1}^{n} |T_{(\mathrm{calc}),k} - T_{(\mathrm{expt}),k}|]/n \tag{2}$$

where n is the number of data points. The subscript (calc) stands for the calculated values, and (expt), for the experimental values. The deviation of the calculated temperature from the experimental value at each measured temperature, δT, is listed in Table 2.

Solid−Liquid Equilibrium Calculation

Theoretical models are also applied to correlate the SLE data. The criterion of SLE for a system without forming a complex compound can be approximately expressed (Stoicos and Eckert, 1987) by

$$\ln a_i = \ln(x_i\gamma_i) = \Delta_{\mathrm{fus}}H_i({T_{\mathrm{m},i}}^{-1} - T^{-1})/R \tag{3}$$

where R is the gas constant. a_i, γ_i, $T_{\mathrm{m},i}$, and $\Delta_{\mathrm{fus}}H_i$ are the activity, activity coefficient, melting temperature, and the molar enthalpy of fusion for compound i, respectively. x_i is the solid solubility (in mole fraction) of compound i at temperature T. If $\gamma_i = 1$, x_i corresponds to the ideal solubility of the solid. The correlated results with eq 3 are shown in Figure 1. The dashed line in the figure illustrates the calculation under the assumption of an ideal liquid phase that appears to be inadequate for 4-methoxyphenol + catechol. To reproduce quantitatively the liquidus line over the entire composition range, nonideality in the liquid phase must be considered. The Wilson model (Wilson, 1964) was thus used in this work for calculating the activity coefficients of the constituents in the liquid phase:

$$\ln \gamma_i = 1 - \ln(\sum_{j=1}^{c} x_j\Lambda_{ij}) - \sum_{k=1}^{c}(x_k\Lambda_{ki}/\sum_{j=1}^{c} x_j\Lambda_{kj}) \tag{4}$$

with

$$\Lambda_{ij} = (V_{\mathrm{L},j}/V_{\mathrm{L},i}) \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{5}$$

where c is the number of components and $V_{\mathrm{L},i}$ the liquid molar volume of component i. The molar volumes, as reported in Table 1, were estimated from the modified Rackett model (Spencer and Danner, 1972). Upon the parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{21} - \lambda_{22})$ being specified, the equilibrium temperature T at a given x_i can be solved from eq 3 by an iterative procedure. The optimal values of the model parameters were determined by minimizing the objective function π over the entire composition range:

$$\pi = \sum_{k=1}^{n} [|T_{(\mathrm{calc}),k} - T_{(\mathrm{expt}),k}|/T_{(\mathrm{expt}),k}]/n \tag{6}$$

The parameters as determined for 4-methoxyphenol + catechol are $\lambda_{12} - \lambda_{11} = -1.7027$ kJ·mol^{-1} and $\lambda_{21} - \lambda_{22} = 0.1194$ kJ·mol^{-1} with $\pi = 0.22\%$. The solid line in Figure 1 represents the calculated solid−liquid phase boundary from the Wilson model. Apparently, this model describes the nonideality of the liquid phases satisfactorily.

As mentioned earlier, a congruently melting compound was formed in both 4-methoxyphenol + ethylenediamine and 4-methoxyphenol + piperazine. For these two systems, the SLE calculations should take the chemical effects into account. By consideration of chemical reactions in the systems, eq 3 becomes (Stoicos and Eckert, 1987)

$$\ln a_i = \ln(z_i\alpha_i) = \Delta_{\mathrm{fus}}H_i({T_{\mathrm{m},i}}^{-1} - T^{-1})/R \tag{7}$$

where z_i and α_i are the "true" mole fraction and "true" activity coefficient of species i in the liquid-phase, respectively. The ideal-chemical model (ICM) was employed in this work by assuming that the "true" activity coefficient α_i is unity; that is, only the chemical effects were considered. The "true" mole fractions can be obtained by solving the chemical equilibrium and the material balance equations simultaneously. In this study, the mechanism for the complex A_2B formation in the liquid phase is assumed as

$$\mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{AB} \tag{8}$$

$$\mathrm{AB} + \mathrm{A} \Leftrightarrow \mathrm{A_2B} \tag{9}$$

where AB is an intermediate species involved in the equilibrium reactions. These chemical reactions occur in the entire range of compositions. The temperature dependence of the chemical equilibrium constants, K_{AB} and $K_{\mathrm{A_2B}}$, is expressed by the van't Hoff relationship by assuming that the enthalpy change of complex formation is independent of temperature, i.e.,

$$\ln K_i = (-\Delta_{\mathrm{cp}}H_i/RT) + (\Delta_{\mathrm{cp}}S_i/R) \tag{10}$$

Table 5. Results of SLE Calculation with the ICM

mixture (A) + (B)	complex compound i	$-\Delta_{cp}H_i$/kJ mol^{-1}	$-\Delta_{cp}S_i$/kJ mol^{-1}·K^{-1}	10^2AAD[a]
4-methoxyphenol +	AB	12.65	0.0229	
ethylenediamine	A_2B	13.86	0.0258	0.3
4-methoxyphenol +	AB	11.91	0.0116	
piperazine	A_2B	19.81	0.0486	1.4

[a] AAD $= \sum_{k=1}^{n}[|T_{(calc),k} - T_{(expt),k}|/T_{(expt),k}|/n$.

where $\Delta_{cp}H_i$ and $\Delta_{cp}S_i$ stand for the molar enthalpy and the molar entropy changes of the complex i formation, respectively. The quantities of $\Delta_{cp}H_{AB}$, $\Delta_{cp}S_{AB}$, $\Delta_{cp}H_{A_2B}$, and $\Delta_{cp}S_{A_2B}$ are unknowns. They were obtained in this work from the SLE calculations by minimizing the objective function defined as eq 6. The detailed treatment is similar to that was described by Lee et al. (1994). The calculated results from the ICM are tabulated in Table 5 and also illustrated, as the dashed lines, in Figures 2 and 3. The ICM appears to correlate well for 4-methoxyphenol + ethylenediamine, except for the region near the second eutectic point, and fairly for 4-methoxyphenol + piperazine.

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