Solid-Liquid Equilibria of Six Binary Mixtures Containing Indole

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Solid-liquid equilibria of the binary mixtures of benzene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, 2-methylindole, and 5-methylindole with indole were determined in the temperature range from 300 to 350 K. Simple eutectic phase diagrams with one eutectic point were observed for these six binary systems. The experimental results have been correlated by using the classical equation for solid solubility in a liquid in conjunction with the activity coefficient calculated with the Wilson equation.

Introduction

Large amounts of heteroaromatic hydrocarbons are contained in coal tar and coal liquids. Since these heteroaromatic hydrocarbons deactivate the catalysis in the hydrocracking process, they are usually decomposed in hydrodenitrogenation and hydrodesulfurization processes. Some of the heteroaromatic hydrocarbons, however, can be used as intermediate materials to synthesize fine chemicals. Therefore, a highly effective separation process is required to separate valuable heteroaromatic hydrocarbons and also to upgrade the coal tar and coal liquids.

Indole is contained in a wash oil fraction of the coal liquid and can be used to synthesize tryptophan. We have studied a high-pressure crystallization technique to separate indole from the wash oil fraction (*1*, *2*). In order to determine optimum separation conditions, the solid-liquid equilibria (SLE) of systems containing indole are required. The purpose of this study is to measure SLE of binary mixtures of benzene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, 2-methylindole, and 5-methylindole with indole. The 1-methylnaphthalene, 2-methylnaphthalene, and biphenyl were selected because they are also contained in wash oil fractions. The 2-methylindole and 5-methylindole can be considered as precursors of indole in coal liquefaction reactions. The SLE data for the 2-methylindole + indole and 5-methylindole + indole systems are important to determine the effect of a methyl group on SLE data. The benzene + indole system was selected in order to compare the present results with those reported by Kravchenko and Pastukhova (*3*). The SLE data for the biphenyl + indole and 2-methylindole + indole systems were reported by Szafranski (*4*). To the best of our knowledge from a literature survey, there have not been any other SLE measurements for the other three systems. The experimental results are compared to those obtained from a solubility equation using the Wilson equation to estimate activity coefficients.

Experimental Section

Materials. The benzene and biphenyl were obtained from Wako Pure Chemical Ind Ltd., and 1-methylnaphthalene, 2-methylnaphthalene, 2-methylindole, 5-methylindole, and indole were from Aldrich Chemical Co., Inc. The purities certified by the manufacturers were as follows: benzene, 99.8%; 1-methylnaphthalene, 98.0%; 2-methylnaphthalene, 98.0%; biphenyl, 98.0%; 2-methylindole, 98.0%; 5-methylindole, 99.0%; and indole, 99.0%. We checked the purities of the samples by gas chromatography and found that the purities were as follows: benzene, 99.9 mol %; 1-methylnaphthalene, 99.9 mol %; 2-methylnaphthalene, 99.8%; biphenyl, 99.8 mol %; 2-methylindole, 99.0 mol %; 5-methylindole, 99.0 mol %; and indole, 99.9 mol %. The benzene and 1-methylnaphthalene were dried by treating for a long time over predried 5-Å molecular sieves, while the other chemicals were used without further purification.

Apparatus and Procedure. SLE were obtained by measuring the temperature at which the last trace of the solid solute melts while slowly heating the solid solute + solvent mixture of a known composition. The temperature obtained represents the liquidus line at the composition of the mixture, and the whole liquidus line is obtained by making measurements at various compositions. The equilibrium cell used was made from a Pyrex glass tube of 6-mm i.d. × 170-mm length and 50 cm^3 volume. A Teflon-coated magnetic bar was used to stir the mixture in the cell, using an external ring magnet. The mouth of the cell was sealed with a screw cap. The experimental procedures of this study were similar to those of McLaughlin and Zainal (*5*, *6*). The sample mixture of a desired composition was prepared by mass in the cell. If a solid exists in the cell, the mixture was heated until the solid melted. Then the cell was immersed in a cooled liquid methanol bath or a liquid nitrogen bath to solidify the mixture completely. Then the cell was immersed in a thermostated bath and heated at a constant rate of 0.05 K min^{-1}. The temperature was recorded at which the last trace of solid disappears.

The temperature of the thermostated bath was measured with an accuracy of ±0.02 K with a quartz thermometer, which was calibrated by means of a Leeds-Northup platinum resistance thermometer. The maximum estimated accuracy of temperature measurements was ±0.05 K. The mass of each component was determined from the mass of the equilibrium cell before and after loading the component. The mass was determined with an analytical balance accurate to ±0.1 mg. The experimental uncertainty of the composition, expressed in mole fraction, was less than ±0.0001.

Results and Discussion

Solid-liquid equilibria were measured over the entire composition range for the six binary systems of benzene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, 2-methylindole, and 5-methylindole with indole. The melting temperature results are compiled in Table I. Table II shows a comparison of the present results and the literature data (*7-24*) for the melting temperature of benzene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, and indole. As can be seen there was a fairly good agreement between them. The melting temperatures of 2-methylindole and 5-methylindole have not been reported yet. The solid-liquid phase diagrams are shown in Figures 1-6. All six systems exhibit a simple eutectic behavior. The eutectic point values determined graphically from the phase diagrams are given in Table III. For comparison, the literature results of Kravchen-

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Table I. Solid–Liquid Equilibrium Data (Mole Fraction of Indole, x, and Temperature, T) for the Six Mixtures Containing Indole

x	T/K	x	T/K
	(1 − x) Benzene + x Indole		
0.0	278.73	0.4010	279.40
0.0521	275.05	0.5010	288.54
0.2000	268.31	0.7150	303.68
0.2510	266.37	0.7920	309.88
0.2810	269.32	0.9020	317.59
0.3490	274.58	1.0	326.26
	(1 − x) 1-Methylnaphthalene + x Indole		
0.0	242.45	0.2560	266.53
0.0340	239.55	0.3020	271.73
0.0414	239.57	0.3952	280.09
0.0692	237.20	0.5952	300.43
0.0912	236.00	0.7982	311.68
0.1027	237.78	0.9227	319.24
0.1708	253.91	1.0	326.26
	(1 − x) 2-Methylnaphthalene + x Indole		
0.0	307.09	0.4976	286.75
0.1434	299.28	0.6036	296.06
0.2179	295.28	0.7038	303.62
0.3168	290.53	0.7970	310.38
0.3849	286.44	0.8993	317.82
0.4426	283.13	1.0	326.26
	(1 − x) Biphenyl + x Indole		
0.0	343.13	0.6538	304.01
0.1436	335.36	0.6826	301.45
0.2864	328.51	0.6995	301.76
0.3709	323.66	0.7530	306.45
0.4637	318.19	0.8002	310.08
0.5565	312.57	0.8978	317.55
0.6098	308.08	1.0	326.26
	(1 − x) 2-Methylindole + x Indole		
0.0	332.77	0.6005	289.52
0.1125	325.03	0.7015	300.39
0.2026	318.87	0.8001	310.05
0.3012	311.01	0.9033	318.18
0.4018	302.02	1.0	326.26
0.4999	292.89		
	(1 − x) 5-Methylindole + x Indole		
0.0	333.74	0.5990	289.20
0.1051	327.70	0.7006	300.78
0.2006	321.45	0.7999	310.37
0.3021	315.52	0.8996	317.99
0.3998	307.85	1.0	326.26
0.5007	298.72		

Table II. Melting Temperatures of Benzene,1-Methylnaphthalene, 2-Methylnaphthalene, Biphenyl, and Indole

substrate	T_m/K	ref	substance	T_m/K	ref
benzene	278.7	3	biphenyl	341.99	4
	278.70	7		344.10	16
	278.65	8		343.30	18
	278.63	9		342.20	19
	278.64	10		342.35	20
	278.73	this work		342.098	21
1-methylnaph-	242.65	11		343.10	this work
thalene	242.67	12	Indole	326.2	3
	242.692	13		324.95	4
	242.45	this work		325.65	22
2-methylnaph-	307.69	4		326.25	23
thalene	307.728	13		327.7	24
	307.45	14		326.26	this work
	307.10	15			
	307.09	this work			

ko and Pastukhova for the benzene + indole system, and those of Szafranski for the 2-methylnaphthalene + indole and biphenyl + indole systems are also plotted in Figures 1, 3, and 4, respectively. It can be seen that fairly good agreement, which is specific about ±0.5 K, was obtained between the present results and those of Szafranski, while a discrepancy between the present results and those of Kravchenko and Pastukhova for the liquidus curve in the region of the liquid + solid indole equilibria is significant.

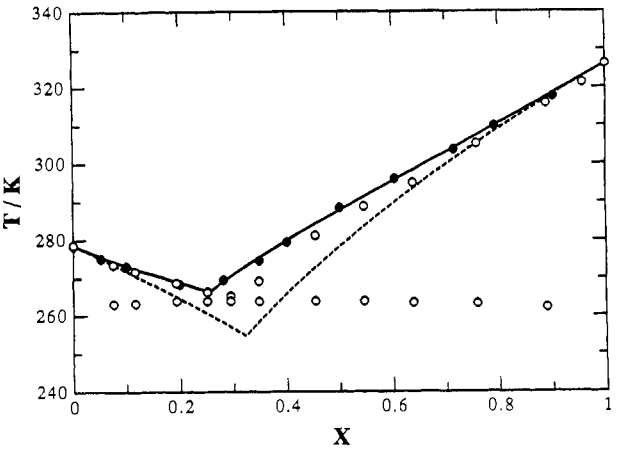

Figure 1. Solid–liquid equilibria for (1 − x) benzene + x indole: (- - -) equation with $\gamma_i = 1$; (—) Wilson equation; (○) Kravchenko and Pastukhova (*3*); (●) this work.

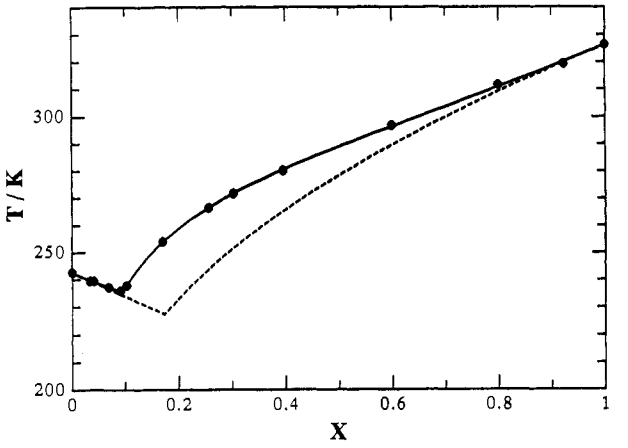

Figure 2. Solid–liquid equilibria for (1 − x) 1-methylnaphthalene + x indole: (- - -) equation with $\gamma_i = 1$; (—) Wilson equation; (●) this work.

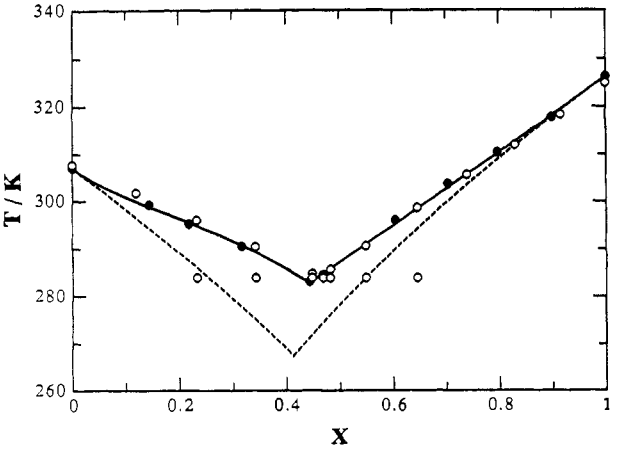

Figure 3. Solid–liquid equilibria for (1 − x) 2-methylnaphthalene + x indole: (- - -) equation with $\gamma_i = 1$; (—) Wilson equation; (○) Szafranski (*4*); (●) this work.

The solid–liquid equilibrium for a simple eutectic system, in which the solid phase can be approximated to consist of a single pure component *i*, can be expressed as (*25–27*)

$$\ln(x_i\gamma_i) = -\frac{\Delta_{fus}H_M}{RT_{i,m}}\left(\frac{T_{i,m}}{T} - 1\right) - \frac{\Delta C_p}{R}\left(\ln\frac{T_{i,m}}{T} - \frac{T_{i,m}}{T} + 1\right) \quad (1)$$

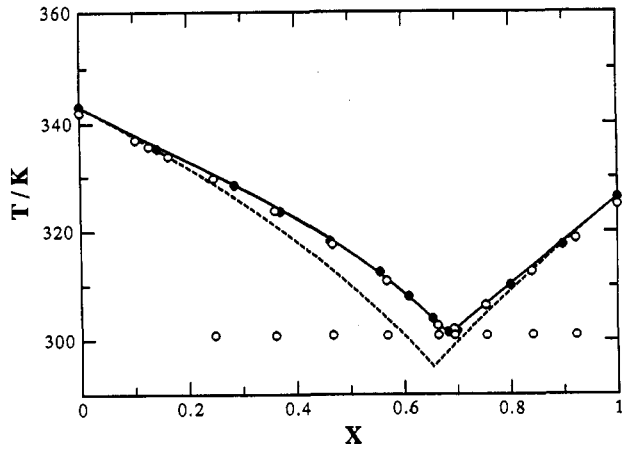

Figure 4. Solid–liquid equilibria for $(1 - x)$ diphenyl + x indole: symbols are the same as in Figure 3.

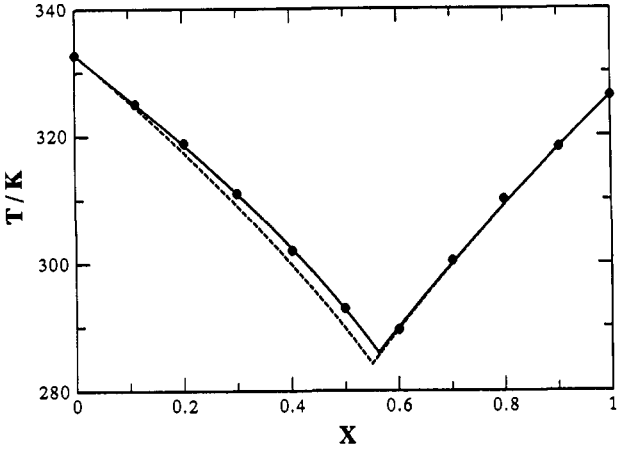

Figure 5. Solid–liquid equilibria for $(1 - x)$ 2-methylindole + x indole: symbols are the same as in Figure 2.

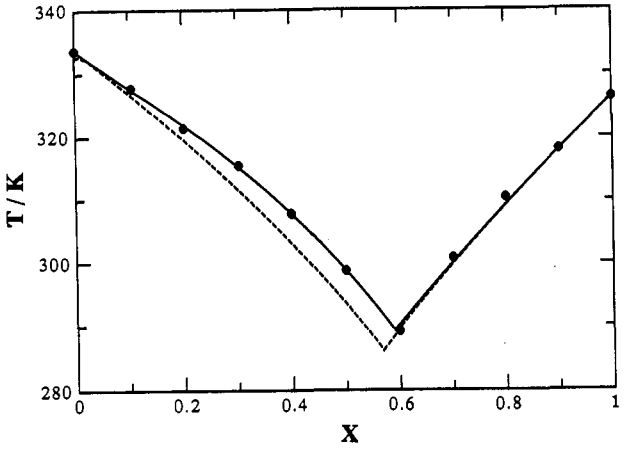

Figure 6. Solid–liquid equilibria for $(1 - x)$ 5-methylindole + x indole: symbols are the same as in Figure 2.

where x_i and γ_i are, respectively, the mole fraction and the activity coefficient of component i in the liquid phase. $\Delta_{fus}H_M$ and $T_{i,m}$ are, respectively, the enthalpy of fusion and the melting temperature of pure substance i, ΔC_p is the heat capacity difference between the liquid and solid, T is the temperature of the system, and R is the gas constant. In this study, we neglect the second term on the right-hand side of eq 1, because the required ΔC_p data are usually not available. The values of $\Delta_{fus}H_M$ and $T_{i,m}$ are taken from our previous studies (*28*, *29*), and are listed in Table IV. The activity coefficient, γ_i, was calculated with the Wilson equation (*30*). The activity coefficient of component i can be expressed as

Table III. Eutectic Temperature, T_E, and Mole Fraction of Indole at the Eutectic Temperature, x_E

system	T_E/K	x_E
benzene + indole	265.90	0.2552
1-methylnaphthalene + indole	235.31	0.0946
2-methylnaphthalene + indole	282.77	0.4373
biphenyl + indole	300.71	0.6815
2-methylindole + indole	286.24	0.5621
5-methylindole + indole	289.63	0.5915

Table IV. Heat of Fusion, $\Delta_{fus}H_m$, Melting Temperature, T_m, and Liquid Molar Volume, V_l

compound	$\Delta_{fus}H_m$/(kJ/mol)	T_m/K	V_l/(cm³/mol)
benzene	9.56	278.73	94.30
1-methylnaphthalene	5.76	242.45	143.76
2-methylnaphthalene	9.20	307.09	145.71
biphenyl	18.6	343.13	153.98
2-methylindole	12.9	332.77	125.39
5-methylindole	14.0	333.74	124.63
indole	10.9	326.26	109.65

Table V. Wilson Parameters and Correlation Results

system	$(\lambda_{12} - \lambda_{11})$/(J/mol)	$(\lambda_{21} - \lambda_{22})$/(J/mol)	N[a]	deviation[b] AAD/K	deviation[b] MAX/K
benzene (1) + indole (2)	78.25	576.14	14	0.36	0.92
1-methylnaphthalene (1) + indole (2)	−7.02	520.96	13	0.35	0.92
2-methylnaphthalene (2) + indole (2)	−133.34	1011.09	12	0.35	0.64
biphenyl (1) + indole (2)	−110.70	410.90	14	0.30	0.58
2-methylindole (1) + indole (2)	−417.10	703.50	11	0.30	0.84
5-methylindole (1) + indole (2)	−451.13	956.55	11	0.42	0.76

[a] N = number of data. [b] Deviation: AAD = $\Sigma|T_{exp} - T_{cal}|/N$; MAX = maximum of $|T_{exp} - T_{cal}|$.

follows:

$$\ln \gamma_1 = 1 - \ln[\sum x_j \Lambda_{1j}] - \sum (x_1 \Lambda_{i1} / \sum x_j \Lambda_{ij}) \quad (2)$$

where

$$\Lambda_{ij} = (V_i/V_j) \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \quad (3)$$

and where V_i is the molar volume of pure component i in the liquid phase and λ_{ij} is the molar energy of interaction between components i and j. Since the melting temperatures of some of the substances used in this study are above 300 K, we used the V_i at 333.15 K measured with a Pyrex glass piezometer. The details of the piezometer were described elsewhere (*31*, *32*). As for the 5-methylindole, the V_i at 333.15 K can be measured using a subcooled liquid. The values of the V_i are listed in Table IV. A least-squares fit of the SLE curve using eqs 1–3 generates values of the Wilson parameters $\lambda_{12} - \gamma_{11}$ and $\lambda_{22} - \lambda_{21}$. The obtained values of the Wilson parameters and the deviations between observed and calculated melting temperatures are given in Table V. The solid lines in Figures 1–6 indicate the values calculated with the Wilson equation. The dashed lines indicate calculated values assuming an ideal solution and eq 1. The six binary systems show positive deviations ($\gamma > 1$) from Raoult's law in the liquid phase. The liquid phase of the 2-methylindole + indole and the 5-methylindole + indole systems can be assumed as an ideal solution. It can be seen that the calculated results with the Wilson equation agree well with experiment within ±0.65 K in most cases.

Conclusion

Solid–liquid equilibria have been measured for six binary systems containing indole. The results were correlated with

the use of the Wilson equation for the activity coefficient. The results can be used to design a high-pressure crystallization process to separate indole from the wash oil fraction of coal liquid.

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