Solid–Liquid Phase Equilibria of Ternary Mixtures Containing Polynuclear Aromatic Compounds

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Solid-liquid phase diagrams of two ternary mixtures containing polynuclear aromatic compounds, viz., *cis*-decahydronaphthalene (*cis*-decalin)–naphthalene–biphenyl and 1,2,3,4-tetrahydronaphthalene (tetralin)–biphenyl–dibenzofuran, have been measured at 298 K and 1 atm. These phase diagrams are also predicted using binary interaction parameters obtained from the regression of binary data alone using the UNIQUAC model and regular solution theory. It is observed that, by using binary parameters and UNIQUAC equations for multicomponent mixtures, one can predict the saturation curve for naphthalene within 7% and the saturation curve for biphenyl within 4% for the *cis*-decalin–naphthalene–biphenyl system. For the tetralin–biphenyl–dibenzofuran system, the saturation curve could be predicted within 4% for biphenyl and within 6% for dibenzofuran. Regular solution theory did not predict the saturation curves satisfactorily.

Introduction

The solid–liquid equilibrium phase diagram is useful in a number of chemical engineering processes such as extraction and crystallization. Many researchers have studied solid–liquid phase diagrams for both binary and multicomponent systems consisting of salts and water (*1*), mixtures of light aromatic compounds (*2*), and also systems consisting of mixtures of metals (*3*). However, there are very few data available for binary and ternary systems consisting of polynuclear aromatic compounds. Sediawan et al. (*4*), using a differential scanning calorimeter, studied the solid–liquid phase diagrams of three binary systems of polynuclear aromatic compounds. These compounds are typical constituents of coal liquids (*5, 6*) and heavier feedstocks (*7*), which in the future could be an alternative source for energy production.

In this study we have examined the phase equilibria of two solid aromatic compounds in two solvents: *cis*-decahydronaphthalene (*cis*-decalin) and 1,2,3,4-tetrahydronaphthalene (tetralin). The systems studied were *cis*-decalin–naphthalene–biphenyl and tetralin–biphenyl–dibenzofuran at 298 K and 1 atm. The first component in each of our systems is a liquid, and the other two components are solid at room temperature. We have also predicted the phase diagrams for these systems using parameters obtained from regression of binary data using the UNIQUAC model and using regular solution theory. We hope these data will be useful in industry for design purposes as well as in the development of solid–liquid equilibrium theories.

Experimental Section

The chemicals used were purchased from Aldrich Chemical Co. and were at least 99% pure. Naphthalene, biphenyl, and dibenzofuran were further purified by liquid chromatography on activated alumina using toluene as the eluant. Toluene was removed using a rotary vacuum evaporator. *cis*-Decalin and tetralin were purified further by distillation under vacuum and were stored over molecular sieves to eliminate water. The final purities of the chemicals used were as follows: naphthalene (99.89%, mp 353.3–353.4 K), biphenyl (99.97%, mp 341.8–342.1 K), dibenzofuran (99.78%, mp 355.4–355.5 K), *cis*-decalin (99.72%), and tetralin (99.69%). These percentages represent area percentages as obtained by temperature-programmed gas chromatography.

Unsaturated mixtures with various compositions of solids (solute) in liquid (solvent) were prepared gravimetrically. These samples were then sealed and were allowed to equilibrate in a constant-temperature water bath at 298 K. The temperature of the bath was controlled to within ±0.1 K using an electronic temperature controller supplied by Versa-Therm (model 2149-2). After 1 day in the bath, samples were taken and were visually observed to make sure that no solid phase was present. Thereafer, one of the solids was added to this mixture in excess, such that two phases existed. The samples were sealed again and were left in the constant-temperature water bath for 1 week. Saturated solution was then withdrawn and diluted using a known amount of the same solvent. These samples were analyzed using a gas chromatograph (HP-5890). The gas chromatograph is equipped with a flame ionization detector. A 10-m-length, 50% phenyl methyl silicone glass capillary column with 0.53-mm i.d. and 2-μm coating was used for the analysis. The carrier gas was helium. Temperature programming was used starting at 90 °C and increasing at 20 °C/min to 250 °C. Relative response factors were determined by analyzing known ternary mixtures having compositions similar to those of the unknown samples.

The attainment of equilibrium was verified by repetitive measurements after several additional days. The solubility of pure solid in the solvent was determined in the same manner. Finally, the invariant point at constant pressure and at 298 K was obtained by adding both solids in excess and analyzing the saturated solution.

Temperature was measured (±0.1 K) with a mercury thermometer calibrated against the ice point and the boiling point of distilled deionized water. The accuracy of the gas chromatographic composition measurements was ±0.0025 mole fraction verified by analyzing samples of known composition.

Data Analysis

The saturation curves for these two systems were also determined using the extended UNIQUAC equation (*8*). For this purpose, solid–liquid interaction parameters were taken from the literature and solid–solid interaction parameters were either measured or taken from the literature. The activity coefficients obtained were then used in the following

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Table 1. Thermodynamic Properties of the Solute Necessary for Analysis of the Data To Find Activity Coefficients

solute	T_m/K	$\Delta S^f_{i,T_m}$/(J/(mol K))	$\Delta C_{pi,T_m}$/(J/(mol K))
naphthalene	353.45[a]	51.620[b]	8.900[b]
biphenyl	342.60[c]	54.671[d]	36.274[d]
dibenzofuran	355.70[c]	51.59[c]	9.6[c]

[a] According to Gruberski (*10*). [b] According to McCullough et al. (*11*). [c] According to Coon et al. (*12*). [d] According to Spaght et al. (*13*).

equation to predict saturation compositions:

$$-\ln x_i = \frac{\Delta S^f_{i,T_m}}{R}\left[\left(\frac{T_m}{T}\right) - 1\right] - \frac{\Delta C_{pi,T_m}}{R}\left[\left(\frac{T_m}{T}\right) - 1\right] + \frac{\Delta C_{pi,T_m}}{R}\ln\left(\frac{T_m}{T}\right) + \ln \gamma_i + \frac{\Delta v_i}{RT}(P - P_i^{sat}) \quad (1)$$

where Δv_i, ΔC_{pi}, ΔS^f_i, and γ_i are the difference between solid and liquid molar volumes, difference between solid and liquid heat capacities, molar entropy of fusion, and liquid-phase activity coefficient of the solute, respectively. The last term in eq 1 is the Poynting correction factor. This term is usually negligible at low pressure and was therefore neglected in our calculations.

The properties of solutes necessary to calculate the activity coefficients are reported in Table 1.

The saturation curves for these two systems were also predicted using regular solution theory. The following equations were used to determine the activity coefficients for the three components of the ternary mixtures:

$$RT \ln \gamma_i = v_i(\delta_i - \bar{\delta})^2 \quad (2a)$$

where

$$\bar{\delta} = \sum_{j=1}^{m} \phi_j \delta_j \quad (2b)$$

and

$$\phi_j = (x_j v_j)/(\sum_{j=1}^{m} x_j v_j) \quad (2c)$$

The calculated activity coefficients were then used to predict the saturation composition using eq 1. The results of this analysis are given in the next section.

Results and Discussion

Tables 2 and 3 report the results for the *cis*-decalin (1)–naphthalene (2)–biphenyl (3) and tetralin (1)–biphenyl (2)–dibenzofuran (3) systems, respectively. These data are also plotted in Figures 1 and 2. Some of the experimental points for the tetralin–biphenyl–dibenzofuran system were also measured by the method of ref 14 and are plotted in Figure 2.

Table 2. Equilibrium Data for the *cis*-Decalin (1)–Naphthalene (2)–Biphenyl (3) System at 298 K[a]

x_2	x_3	x_2	x_3	x_2	x_3
		Naphthalene Saturation Curve			
0.2002	0.0207	0.2264	0.1168	0.2674	0.2112
0.2149	0.0543	0.2361	0.1257	0.2669	0.2221
0.2065	0.0582	0.2302	0.1274	0.2852	0.2299
0.2277	0.0912	0.2369	0.1607	0.2727	0.2508
0.2121	0.1000	0.2602	0.1892		
		Biphenyl Saturation Curve			
0.0095	0.2148	0.1287	0.2750	0.2093	0.2969
0.0172	0.1957	0.1337	0.3000	0.2328	0.3020
0.0427	0.2154	0.1779	0.3022	0.2602	0.3312
0.0805	0.2495	0.1886	0.2955		
0.0887	0.2614	0.2071	0.2910		

[a] Experimental solubility of naphthalene in *cis*-decalin 0.1871 mole fraction. Experimental solubility of biphenyl in *cis*-decalin 0.1940 mole fraction. Invariant point composition of naphthalene 0.3036 mole fraction. Invariant point composition of biphenyl 0.3537 mole fraction.

Table 3. Equilibrium Data for the Tetralin (1)–Biphenyl (2)–Dibenzofuran (3) System at 298 K[a]

x_2	x_3	x_2	x_3	x_2	x_3
		Biphenyl Saturation Curve			
0.3394	0.0339	0.3503	0.0534	0.3403	0.0972
0.3743	0.0325	0.3357	0.0711	0.3415	0.1774
0.3357	0.0511	0.3450	0.0752	0.3486	0.1873
		Dibenzofuran Saturation Curve			
0.0180	0.2647	0.0585	0.2805	0.1082	0.2731
0.0194	0.2342	0.0629	0.2375	0.1158	0.2344
0.0326	0.2763	0.0858	0.2778	0.1717	0.2408
0.0382	0.2776	0.0955	0.2407		

[a] Experimental solubility of biphenyl in tetralin 0.3639 mole fraction. Experimental solubility of dibenzofuran in tetralin 0.2561 mole fraction. Invariant point composition of biphenyl 0.3340 mole fraction. Invariant point composition of dibenzofuran 0.2645 mole fraction.

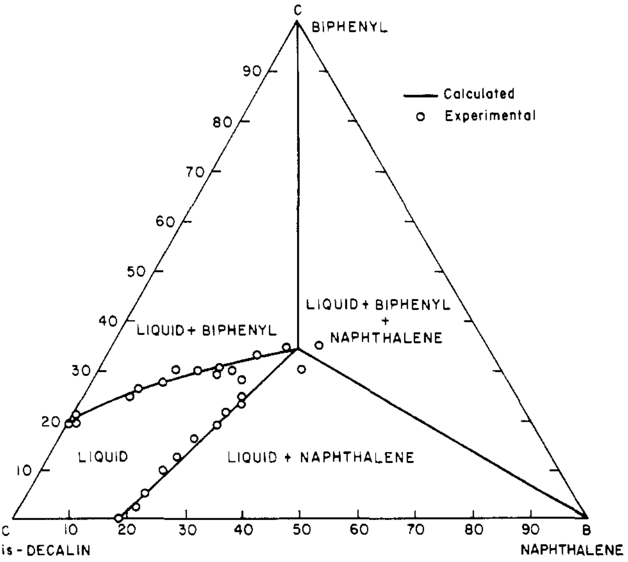

Figure 1. Phase diagram for the *cis*-decalin–naphthalene–biphenyl system at 25 °C.

The data reported in Tables 2 and 3 were also predicted using the extended UNIQUAC equation for multicomponent mixtures (*8*) and regular solution theory. The UNIQUAC equations require interaction parameters for all the binary systems which constitute the ternary system. The binary interaction parameters for the solid–liquid systems were obtained from our previous study (*15*). The solid–solid interaction parameters for the naphthalene–biphenyl system were determined by regression of data available in the literature (*10*) using a linear search method as described in ref 16. Data for the biphenyl–dibenzofuran system were obtained in our laboratory using the method described in ref 14. These data are reported in Table 4 and are also plotted in Figure 3. The solid–liquid equilibrium data for this system were then regressed to obtain UNIQUAC parameters. The values of parameters used in calculations to obtain the activity coefficient in the ternary mixture using the UNIQUAC method are given in Table 5.

Table 6 compares experimental and predicted values of naphthalene and biphenyl solubilities along their respective saturation curves for their solutions in *cis*-decalin. Table 7

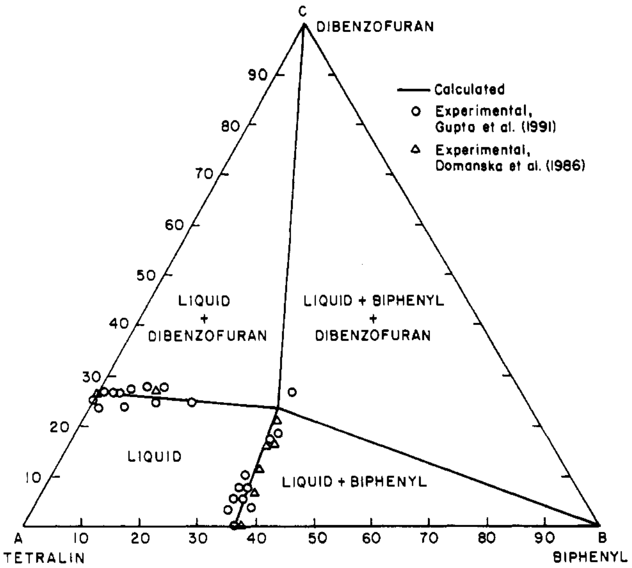

Figure 2. Phase diagram for the tetralin–biphenyl–dibenzofuran system at 25 °C.

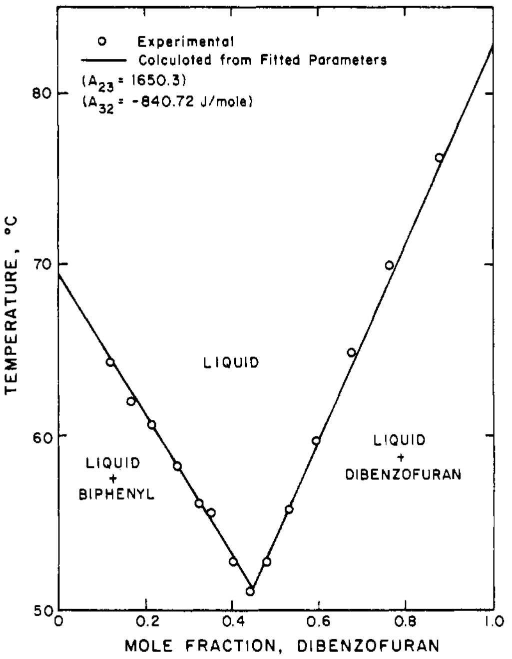

Figure 3. Solid–liquid equilibrium diagram for the biphenyl–dibenzofuran system.

Table 4. Equilibrium Data for the Biphenyl (1)–Dibenzofuran (2) System

x_2	T/K	x_2	T/K
0.8822	349.4	0.4034	325.9
0.7641	343.5	0.3519	328.7
0.6736	338.0	0.3221	329.4
0.5903	332.9	0.2690	331.3
0.5340	329.0	0.2121	333.8
0.4790	326.0	0.1781	335.1
0.4368	324.2	0.1235	337.3

Table 5. Values of Parameters Used in Correlations

UNIQUAC Model

system	A_{12}/(J/mol)	A_{21}/(Jmol)
cis-decalin (1)–naphthalene (2)	1338.51	−586.58
cis-decalin (1)–biphenyl (2)	488.15	118.14
naphthalene (1)–biphenyl (2)	1794.70	−1299.92
tetralin (1)–biphenyl (2)	−917.24	1247.80
tetralin (1)–dibenzofuran (2)	−566.37	736.91
biphenyl (1)–Dibenzofuran (2)	1650.30	−840.72

Regular Solution Model

	δ_i/(J/m^3)$^{1/2}$	v_i/(m^3/mol)
cis-decalin	16 360	165.6×10^{-6}
tetralin	18 150	143.0×10^{-6}
naphthalene	19 670	130.9×10^{-6}
biphenyl	19 300	155.2×10^{-6}
dibenzofuran	20 410	152.5×10^{-6}

Table 6. Comparison of Data with Predicted Values for the System *cis*-Decalin (1)–Naphthalene (2)–Biphenyl (3)[a]

	composition (pred)		
	UNIQUAC		
composition (exptl)	A_{23} = 1794.7 A_{32} = −1299.9	A_{23} = 0 A_{32} = 0	regular solution
Mole Fraction of Naphthalene on the Saturation Curve			
0.2015	0.1972	0.1939	0.2210
0.2065	0.2162	0.2071	0.2282
0.2121	0.2367	0.2215	0.2363
0.2149	0.2165	0.2083	0.2291
0.2264	0.2470	0.2305	0.2417
0.2277	0.2362	0.2231	0.2377
0.2302	0.2523	0.2346	0.2441
0.2361	0.2527	0.2356	0.2449
0.2369	0.2671	0.2460	0.2508
0.2602	0.2812	0.2595	0.2595
0.2669	0.2931	0.2696	0.2659
0.2674	0.2897	0.2670	0.2643
0.2727	0.3025	0.2779	0.2713
0.2852	0.2972	0.2753	0.2702
Mole Fraction of Biphenyl on the Saturation Curve			
0.1957	0.2113	0.2095	0.2892
0.2148	0.2143	0.2134	0.2914
0.2155	0.2291	0.2253	0.2987
0.2495	0.2556	0.2499	0.3135
0.2614	0.2623	0.2567	0.3175
0.2750	0.2816	0.2745	0.3283
0.2910	0.3132	0.3041	0.3465
0.2955	0.3079	0.2999	0.3438
0.2969	0.3151	0.3065	0.3479
0.3000	0.2897	0.2843	0.3340
0.3020	0.3235	0.3148	0.3529
0.3022	0.3056	0.2986	0.3429
0.3312	0.3364	0.3303	0.3621

[a] Predicted solubility of naphthalene in *cis*-decalin 0.1832 mole fraction. Predicted solubility of biphenyl in *cis*-decalin 0.2029 mole fraction. Predicted value of the invariant point of naphthalene 0.3271 mole fraction. Predicted value of the invariant point of biphenyl 0.3509 mole fraction.

shows a similar comparison for biphenyl and dibenzofuran in tetralin. The mean absolute percentage deviation is reported in the first column of Table 8. As is clear from this table there is good agreement between experimental and calculated values.

It was realized that the solid–solid interaction in these two systems is small, since the difference in solid solubility parameters is small compared to the difference in solid and solvent liquid solubility parameters at any temperature. We therefore predicted the saturation composition neglecting the solid–solid interaction parameters (A_{23} and A_{32} = 0.0) in the extended UNIQUAC equation for these two systems. The values obtained are reported in the third column of Tables 6 and 7, and the mean absolute percentage deviation is reported in the second column of Table 8. On comparing the second and third columns of Table 8, it can be observed that there is some improvement in the mean absolute difference values by excluding solid–solid interaction parameters for the *cis*-decalin–naphthalene–biphenyl system. The reason for this improvement is probably that the naphthalene–biphenyl system is nearly ideal as reported in ref 17. Measuring solid–liquid equilibrium data and fitting these points to obtain binary parameters using an optimization

Table 7. Comparison of Data with Predicted Values for the System Tetralin (1)–Biphenyl (2)–Dibenzofuran (3)[a]

	composition (pred)		
	UNIQUAC		
composition (exptl)	A_{23} = 1650.3 A_{32} = −840.72	A_{23} = 0 A_{32} = 0	regular solution
Mole Fraction of Biphenyl on the Saturation Curve			
0.3394	0.3619	0.3691	0.3866
0.3357	0.3566	0.3716	0.3882
0.3357	0.3595	0.3701	0.3873
0.3403	0.3530	0.3736	0.3893
0.3415	0.3407	0.3780	0.3917
0.3450	0.3564	0.3723	0.3885
0.3486	0.3395	0.3787	0.3920
0.3503	0.3597	0.3711	0.3877
0.3743	0.3638	0.3707	0.3873
Mole Fraction of Dibenzofuran on the Saturation Curve			
0.2342	0.2574	0.2597	0.2692
0.2344	0.2507	0.2652	0.2733
0.2375	0.2548	0.2626	0.2714
0.2407	0.2529	0.2648	0.2730
0.2408	0.2473	0.2691	0.2761
0.2657	0.2612	0.2634	0.2720
0.2731	0.2561	0.2691	0.2763
0.2736	0.2544	0.2705	0.2772
0.2776	0.2616	0.2658	0.2739
0.2805	0.2604	0.2673	0.2749
0.2805	0.2585	0.2688	0.2760

[a] Predicted solubility of biphenyl in tetralin 0.3677 mole fraction. Predicted solubility of dibenzofuran in tetralin 0.2613 mole fraction. Predicted value of the invariant point of biphenyl 0.3261 mole fraction. Predicted value of the invariant point of dibenzofuran 0.2367 mole fraction.

Table 8. Mean Absolute Deviation (%) between Predicted and Experimental Data[a]

	UNIQUAC		
compound	with params	without params	regular solution
cis-Decalin–Naphthalene–Biphenyl			
naphthalene	7.345	2.020	5.165
biphenyl	3.590	2.662	22.467
Tetralin–Biphenyl–Dibenzofuran			
biphenyl	3.920	8.180	12.580
dibenzofuran	6.114	6.452	7.202

[a] Solubility of naphthalene in *cis*-decalin 2.080%. Solubility of biphenyl in *cis*-decalin 4.580%. Solubility of biphenyl in tetralin 1.04%. Solubility of dibenzofuran in tetralin 2.030%. Invariant point prediction: *cis*-decalin–naphthalene–biphenyl, naphthalene, 7.704%; biphenyl, 0.772%; tetralin–biphenyl–dibenzofuran, diphenyl, 2.35%; dibenzofuran, 10.50%. Mean absolute deviation = $(1/N)\sum_{i=1}^{N}|(x_{\mathrm{pred}} - x_{\mathrm{exptl}})/(x_{\mathrm{exptl}})|$.

technique introduces more error. However, for the tetralin–biphenyl–dibenzofuran system solid–solid interactions are significant.

The predicted values of saturated composition using regular solution theory are listed in the fourth column of Tables 6 and 7. Table 8 shows the mean absolute percentage deviation between experimental and predicted values for the two systems. Regular solution theory predicted naphthalene composition within 6% and biphenyl composition within 23% for the system *cis*-decalin (1)–naphthalene (2)–biphenyl (3). For the tetralin (1)–biphenyl (2)–dibenzofuran (3) system, it predicted the biphenyl composition within 13% and dibenzofuran composition within 8%. Therefore, we can say that the regular solution theory was really not very successful in predicting the saturation curve for these two systems.

Glossary

A_{ij}	UNIQUAC binary parameter, J/mol
$\Delta C_{pi,T_m}$	difference in the molar specific heat capacities of the liquid and solid at the melting point, J/(mol K)
m	number of components
N	number of experimental measurements
P	pressure, Pa
P_i^{sat}	vapor pressure, Pa
R	gas constant, 8.314 J/(mol K)
$\Delta S_{i,T_m}^{\mathrm{f}}$	entropy of fusion, *J*/(mol K)
T	temperature, K
T_m	melting point temperature, K
Δv_i	difference in the molar volumes of the liquid and solid, m^3/mol
v_i	molar volume of component *i*, m^3/mol
x_j	mole fraction of *j*

Greek Letters

γ	activity coefficient
δ	solubility parameter, (J/m^3)$^{1/2}$
ϕ	volume fraction
λ	as defined in eq 1

Subscripts

i	component *i*
ij	mixture of *i* and *j*

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