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Solid–Liquid Phase Equilibria of Binary and Ternary Mixtures of Benzene and Polynuclear Aromatic Compounds

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Solid–liquid equilibrium phase diagrams for three binary mixtures of benzene with polynuclear aromatic compounds (fluorene, dibenzofuran, and dibenzothiophene) have been measured by a dynamic method in the temperature range from 0 to 80 °C. These binary data plus previously published data derived from calorimetric studies were used to determine experimental activity coefficients and interaction parameters using the Wilson and UNIQUAC models. The resulting set of interaction parameters gave a good representation of the experimental binary data and ternary data at 50 °C, but were not generally satisfactory for predicting solid–liquid equilibrium in ternary systems at lower temperatures.

Introduction

Separation of organic close-boiling or close-melting components from a mixture is a challenging task in some chemical engineering processes, such as crystallization and extraction. With the present trend in the petroleum industry toward heavier feedstocks and coal-derived liquids, there is a strong need for expansion of the small database of thermodynamic data on heavier compounds that presently exists. The present work is a continuation of systematic studies on solid–liquid equilibrium (SLE) in binary and ternary systems of polynuclear aromatic compounds (*1–7*). There are very few data available for ternary aromatic systems consisting of solvent–solid–solid at different temperatures. Some results of this kind are reported in refs 8–10, for example. In our previous study (*6*), we examined the phase equilibria of two ternary systems containing *cis*-decalin, naphthalene, and biphenyl and tetralin, biphenyl, and dibenzofuran at 25 °C. The first component in each of these systems was a liquid, and the other two components were solids. These ternary systems included three pairs of binary eutectics. The ternary phase diagrams were also predicted using binary parameters obtained from regression of binary data using the UNIQUAC model.

The purpose of the present study was to select systems with a solid solution on one side of the phase diagram. In this paper we present solid–liquid phase equilibria of three ternary systems of this kind: benzene, fluorene, dibenzofuran; benzene, fluorene, dibenzothiophene; and benzene, dibenzothiophene, dibenzofuran, at temperatures from 0 to 80 °C. As indicated by Sediawan et al. (*1*), the fluorene–dibenzofuran system forms a solid solution at any composition, while the fluorene–dibenzothiophene and dibenzothiophene–dibenzofuran systems have solid-phase immiscibility gaps.

New SLE data are also reported for three binary systems: mixtures of benzene with fluorene, dibenzofuran, and dibenzothiophene.

An additional goal of this study is to predict solid–liquid equilibria (SLE) for ternary systems containing such polynuclear aromatic compounds by using binary Wilson or UNIQUAC parameters obtained from the regression of binary SLE data.

The first section is a discussion of the procedure for the solid–liquid equilibrium experiments. This is followed by a brief discussion of the method of determining the Wilson and UNIQUAC constants and correlating results for binary systems. The results of the ternary system analysis are presented in the third section. The last section discusses some of the important conclusions observed in this study. 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 from Aldrich Chemicals, 99% pure grade. The fluorene, dibenzofuran, and dibenzothiophene were recrystallized from toluene. They were analyzed by gas chromatography using a phenyl methyl silicone capillary column and flame ionization detector. Purities (area %) were 99.7% for fluorene, 99.8% for dibenzofuran, and 99.4% for dibenzothiophene. Benzene was purified by fractional distillation and stored over 4A molecular sieves.

Solubilities were determined by a dynamic (synthetic) method described in full by Domanska (*7*). Mixtures of solute and solvent in binary systems and of two solutes and solvent (benzene) in ternary systems, prepared by weighing, were heated very slowly (heating rate did not exceed 2 °C h^{-1} near the equilibrium temperature) with stirring. The temperature at which the last crystals disappeared (decline of solution cloudiness) was taken as the temperature of the solution–crystal equilibrium. Measurements were performed over a wide range of solute concentration and over the temperature range from 0 °C to the boiling temperature of benzene (80.3 °C). The accuracy of temperature measurements was ±0.1 °C. The mixture composition was known within ±0.0003 mole fraction. The saturation temperature for a given mixture was reproducible within ±0.1 °C.

The characteristics of the compounds are collected in Table I. All the direct experimental data are shown in Tables II–V.

Table I. Thermodynamic Properties of Solutes

solute	t_m/ °C	ΔH_m/ (J mol^{-1})	ΔC_p/ (J mol^{-1})	V^{25}/ (cm^3 mol^{-1})	t_{tr}/ °C	ΔH_{tr}/ (J mol^{-1})
benzene	5.50	9 866[a]		89.4		
fluorene	114.75	19 200[b]	1.98[b]	163.7		
dibenzofuran	82.15	18 600[c]	9.60[c]	170.0		
dibenzothiophene	98.80	21 000[d]	31.40[c]	170.1	88.8	1500

[a] Oliver et al. (*11*). [b] Sediawan et al. (*1*). [c] Coon et al. (*4*).

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Table II. Experimental Mole Fraction Solubilities and Activity Coefficients for the Three Solutes in Benzene

fluorene (1)–benzene (2)			dibenzofuran (1)–benzene (2)			dibenzothiophene (1)–benzene (2)		
x_1	t/°C	γ_1	x_1	t/°C	γ_1	x_1	t/°C	γ_1
0.0000	5.5		0.0000	5.5		0.0000	5.5	
0.0202	4.3	1.002[a]	0.0635	2.9	1.027[a]	0.0230	4.8	1.013[a]
0.0407	3.8	1.008[a]	0.0856	0.8	1.017[a]	0.0430	4.0	1.021[a]
0.0535	2.6	1.014[a]	0.0934	0.2	1.015[a]	0.0532	3.4	1.022[a]
0.0631	2.1	1.321	0.1122	−0.8	1.369	0.0598	2.8	1.898
0.0714	4.9	1.314	0.1239	1.6	1.328	0.0663	5.0	1.821
0.0826	9.9	1.306	0.1363	4.7	1.317	0.0784	9.9	1.764
0.0986	15.7	1.294	0.1463	7.0	1.311	0.0867	12.5	1.712
0.1040	17.5	1.290	0.1599	9.6	1.288	0.1010	17.3	1.670
0.1181	21.8	1.279	0.1978	17.1	1.264	0.1152	21.5	1.633
0.1301	25.2	1.271	0.2346	23.1	1.240	0.1330	26.0	1.586
0.1548	31.5	1.242	0.2480	25.1	1.232	0.1429	28.1	1.556
0.1723	35.5	1.221	0.2813	29.3	1.202	0.1573	31.1	1.522
0.2062	42.0	1.189	0.2995	32.1	1.206	0.1699	33.5	1.494
0.2609	51.3	1.160	0.3559	38.8	1.183	0.2066	39.7	1.425
0.3144	58.4	1.140	0.4486	46.8	1.119	0.2516	46.0	1.354
0.3565	64.3	1.113	0.5791	55.9	1.051	0.3038	52.4	1.295
0.3792	66.5	1.110	0.7045	64.5	1.023	0.3601	57.5	1.222
0.4253	71.3	1.099	0.7570	67.7	1.014	0.4131	62.2	1.178
0.4538	74.5	1.094	0.8346	73.2	1.020	0.4733	67.6	1.152
0.4688	76.0	1.000	1.0000	82.1	1.000	0.5351	73.2	1.142
1.0000	114.8					0.5858	77.1	1.129
						0.6423	80.0	1.090
						1.0000	98.8	1.000

[a] Activity coefficients for benzene as a solute.

Table III. Equilibrium Data for the Ternary System Benzene (1)–Fluorene (2)–Dibenzofuran (3)[a]

x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C
$x_2^\circ = 0.0866$		$x_2^\circ = 0.1469$		$x_2^\circ = 0.2046$		$x_2^\circ = 0.2437$		$x_2^\circ = 0.2520$	
0.8220	12.0	0.8915	11.0	0.8178	10.4	0.8152	11.9	0.8003	15.2
0.7905	16.8	0.7857	16.9	0.7984	13.8	0.8008	15.0	0.7452	24.5
0.7555	22.0	0.7495	22.4	0.7773	18.1	0.7792	18.9	0.7193	28.6
0.7248	27.4	0.6487	35.8	0.7516	22.2	0.7288	27.5	0.6824	33.6
0.7027	29.8	0.5723	43.1	0.6795	32.1	0.6390	40.0	0.6423	38.8
0.6799	32.7	0.5051	50.0	0.6189	38.9	0.6008	43.4	0.5728	46.8
0.6549	35.6	0.3910	60.0	0.5775	44.1	0.5351	50.0	0.5251	51.7
0.6179	39.6			0.5281	49.4	0.4350	60.0	0.4310	61.2
0.5010	50.0			0.4750	54.6				
0.4351	55.7			0.4080	61.2				
0.3720	60.0								
$x_2^0 = 0.2939$		$x_2^0 = 0.3397$		$x_2^\circ = 0.3736$		$x_2^\circ = 0.3979$		$x_2^\circ = 0.4537$	
0.8198	10.4	0.8042	15.3	0.8158	13.7	0.8311	11.9	0.8172	16.7
0.7652	20.4	0.7849	18.4	0.7943	18.0	0.8124	15.7	0.7825	23.3
0.7168	27.7	0.7384	26.4	0.7621	23.1	0.7940	19.1	0.7604	27.2
0.6972	30.0	0.7164	29.2	0.7306	30.0	0.7786	21.9	0.7092	35.1
0.6345	38.1	0.6676	36.3	0.6781	35.8	0.7612	24.8	0.6663	40.6
0.6050	42.0	0.6294	40.8	0.6368	40.2	0.7357	28.8		
0.5601	47.0	0.5477	50.8			0.6929	34.6		
0.4922	53.9					0.6270	42.8		
0.4220	60.6					0.5710	48.8		
$x_2^\circ = 0.5003$		$x_2^\circ = 0.5566$		$x_2^\circ = 0.6005$		$x_2^\circ = 0.6719$		$x_2^\circ = 0.7262$	
0.8367	14.7	0.8632	11.4	0.8573	14.0	0.8742	13.2	0.8730	15.5
0.8235	17.3	0.8257	19.9	0.8383	18.5	0.8574	18.1	0.8519	20.9
0.8059	21.4	0.8040	24.1	0.8193	22.5	0.8410	21.1	0.8410	23.2
0.7703	27.5	0.7830	27.8	0.7945	27.4	0.8051	27.8	0.8146	29.0
0.7405	32.1	0.7601	31.4	0.7654	32.2	0.7680	34.5	0.7850	35.0
0.6105	49.7	0.7260	36.8	0.7394	36.3	0.7498	37.4	0.7281	43.1
		0.6830	42.6	0.7041	41.5			0.6676	51.0
		0.6118	50.7	0.6494	48.4			0.6003	61.7
				0.5689	57.6			0.4734	80.0
$x_2^\circ = 0.7600$		$x_2^\circ = 0.8086$		$x_2^\circ = 0.8681$		$x_2^\circ = 0.9138$			
0.8784	14.5	0.8808	15.8	0.8821	16.0	0.9113	9.5		
0.8373	24.6	0.8646	20.2	0.8585	24.9	0.8796	20.1		
0.8051	31.1	0.8501	23.8	0.8352	30.3	0.8452	29.1		
0.7654	39.2	0.8372	26.8	0.8271	32.5	0.8121	35.8		
0.7167	46.0	0.8202	30.6	0.8002	37.5	0.7656	44.1		
0.6781	51.2	0.8093	33.0	0.7890	41.5	0.6660	56.2		
0.6314	56.6	0.7775	38.5	0.7631	43.4	0.5871	66.2		
0.5990	61.4	0.7642	41.1	0.6903	53.4	0.4801	79.1		
0.5085	70.9	0.6757	53.3	0.6170	62.5				
		0.5842	64.0						

[a] x_2^0 = mole fraction of the fluorene in the benzene-free binary solid mixtures.

Results and Discussion

The solubility of solid 1 in a liquid may be expressed by (*12*)

$$\ln x_1 = \frac{\Delta H_{\mathrm{m1}}}{R}\left(\frac{1}{T_{\mathrm{t1}}} - \frac{1}{T}\right) - \frac{\Delta C_{p\mathrm{m1}}}{R}\left(\ln \frac{T_{\mathrm{t1}}}{T} - \frac{T_{\mathrm{t1}}}{T} + 1\right) + \frac{\Delta H_{\mathrm{tr1}}}{R}\left(\frac{1}{T_{\mathrm{tr1}}} - \frac{1}{T}\right) - \ln \gamma_1 \quad (1)$$

where x_1, γ_1, ΔH_{m1}, $\Delta C_{p\mathrm{m1}}$, T_{t1}, and T stand for the mole fraction, activity coefficient, enthalpy of fusion, solute heat capacity difference between the solid and the liquid at the melting point, triple point temperature of the solute, and equilibrium temperature, respectively, and ΔH_{tr} and T_{tr1} stand for enthalpy of transition and transition temperature of the solute.

For the organic compounds of this study it is an excellent approximation to substitute the normal melting point temperature for the triple point temperature. The term involving the transition enthalpy and temperature is only needed when the solution temperature is below a solid-phase transition temperature.

In this work the activity coefficient was calculated by eq 1 from the experimentally determined solution composition and temperature. Activity coefficients obtained in this way from binary data were used to determine Wilson (*13*) and UNIQUAC (*14*) interaction parameters. The Wilson and UNIQUAC equations were then used to predict the equilibrium data for the ternary mixtures.

The parameters were fitted to the binary data by an optimization technique. The objective function was as follows:

$$F(A_1,A_2) = \sum_{i=1}^{n} w_i^{-2}[\ln (x_{1i}\gamma_{1i}(T,x_{1i},A_1,A_2)) - \ln a_{1i}(T_i)]^2 \quad (2)$$

where $\ln a_{1i}$ denotes an experimental value of the logarithm of solute activity ($x_1\gamma_1$, from eq 1), w_i is the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the ith experimental point, and n is the number of experimental points. The weights were calculated by means of the error propagation formula:

$$w_i^2 = \left(\frac{\partial \ln x_1\gamma_1 - \partial \ln a_i}{\partial T}\right)^2_{T=T_i} (\Delta T_i)^2 + \left(\frac{\partial \ln x_1\gamma_1}{\partial x_1}\right)^2_{x_1=x_{1i}} (\Delta x_{1i})^2 \quad (3)$$

where ΔT and Δx_1 are the estimated errors of T and x_1, respectively.

According to the above formulation, the objective function is consistent with the maximum likelihood principle, provided that the first-order approximation (eq 3) is valid. Neau and Peneloux (*15*) called this procedure the observed deviation method.

The experimental errors of temperature and solute mole fraction were fixed for all cases and set to ΔT = 0.1 K and Δx_1 = 0.001.

The root mean square deviation of temperature defined by eq 4, where T_i^{calcd} and T_i are, respectively, the calculated and experimental temperatures of the ith point and n is the number of experimental points, was used as a measure of the goodness of fit of the solubility curves. The calculated values

$$\sigma_T = \left[\sum_{i=1}^{n} \frac{(T_i^{\mathrm{calcd}} - T_i)^2}{(n-2)}\right]^{1/2} \quad (4)$$

Table IV. Equilibrium Data for the Ternary System Benzene (1)–Fluorene (2)–Dibenzofuran (3)[a]

x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C
$x_2^\circ = 0.0290$		$x_2^\circ = 0.0829$		$x_2^\circ = 0.1221$		$x_2^\circ = 0.1391$		$x_2^\circ = 0.1743$	
0.9100	13.5	0.9022	14.0	0.8903	16.1	0.9042	11.4	0.9062	9.6
0.8478	29.6	0.8904	17.6	0.8553	24.4	0.8832	17.2	0.8580	22.1
0.7740	42.7	0.8660	23.8	0.8405	27.5	0.8650	21.4	0.8313	27.4
0.7341	48.0	0.8259	32.3	0.7782	38.0	0.8382	27.0	0.7977	33.4
0.6571	57.3	0.7843	39.2	0.7375	43.3	0.8204	30.2	0.7631	42.5
0.5631	67.1	0.7479	44.6	0.6136	56.7	0.7913	35.0	0.6520	52.0
		0.7057	50.3	0.5365	63.3	0.7592	39.7	0.5117	66.8
		0.6364	58.0	0.4642	69.1	0.7180	45.2	0.4118	77.6
		0.5803	62.4			0.6861	48.9		
		0.5002	70.0			0.6029	56.9		
						0.5521	60.8		
$x_2^\circ = 0.2008$		$x_2^\circ = 0.2083$		$x_2^\circ = 0.2838$		$x_2^\circ = 0.3083$		$x_2^\circ = 0.3403$	
0.8906	13.5	0.8815	15.9	0.8725	15.0	0.8831	13.2	0.8861	12.3
0.8341	26.1	0.8587	21.1	0.8623	17.5	0.8359	24.2	0.8456	23.3
0.8201	28.8	0.8329	26.7	0.8461	21.7	0.8023	30.7	0.8165	28.5
0.7821	35.0	0.8065	31.4	0.8285	25.4	0.7444	40.4	0.7489	40.1
0.6724	49.7	0.7733	36.6	0.8210	27.0	0.6987	46.3	0.6906	48.3
0.5824	60.2	0.7450	40.6	0.7900	32.4	0.6355	54.1	0.6379	54.8
0.4614	73.9	0.6784	50.0	0.7740	35.3	0.5331	63.8	0.5432	64.5
		0.6319	56.2	0.5856	59.6	0.4701	70.0	0.4835	69.3
		0.4817	74.2	0.5108	67.0				
$x_2^\circ = 0.3718$		$x_2^\circ = 0.4210$		$x_2^\circ = 0.4938$		$x_2^\circ = 0.5474$		$x_2^0 = 0.6048$	
0.8904	12.0	0.8800	14.5	0.8915	12.5	0.8847	14.9	0.8937	12.8
0.8667	18.3	0.8702	17.1	0.8726	17.6	0.8713	18.0	0.8761	18.1
0.8198	28.1	0.8453	23.2	0.8465	23.9	0.8444	25.4	0.8340	28.1
0.7901	33.5	0.8139	31.0	0.8089	31.6	0.8095	32.2	0.7955	35.5
0.7494	40.3	0.7866	34.5	0.7730	38.1	0.7884	36.2	0.7273	46.5
0.7112	46.0	0.7400	42.1	0.7252	45.2	0.7521	42.2	0.6423	58.4
0.6470	54.1	0.7104	46.1	0.6481	55.9	0.6352	57.5	0.5815	64.7
0.4948	69.2	0.6474	54.1	0.5688	63.7	0.5131	70.0	0.5090	71.5
		0.5799	61.1	0.4976	71.0				
		0.4839	69.5						
$x_2^\circ = 0.6382$		$x_2^\circ = 0.7158$		$x_2^\circ = 0.8370$		$x_2^\circ = 0.8877$		$x_2^\circ = 0.9365$	
0.8929	13.5	0.8910	15.0	0.9026	13.1	0.8977	15.4	0.8965	16.4
0.8702	20.4	0.8691	21.0	0.8654	25.1	0.8816	20.5	0.8757	22.4
0.8439	26.9	0.8498	25.8	0.8474	29.5	0.8535	28.6	0.8572	28.1
0.8086	33.8	0.8315	30.0	0.8307	33.7	0.8343	32.5	0.8390	32.1
0.7776	40.1	0.8039	35.7	0.7945	40.7	0.8057	38.5	0.8028	40.8
0.7463	44.0	0.7749	40.7	0.7678	45.5	0.7537	48.3	0.7690	45.2
0.7087	50.0	0.7255	48.7	0.7421	49.2	0.7005	56.5	0.7443	50.0
0.6571	57.9	0.6730	55.8	0.7228	52.5	0.6296	65.6	0.7162	54.6
0.6041	63.0	0.6073	64.2	0.6798	58.4	0.5444	76.4	0.6733	59.4
0.5426	68.7	0.5495	70.0	0.6347	64.0	0.4797	80.0	0.5857	70.8
0.4828	74.5			0.5371	75.2			0.5384	75.5

[a] x_2° = mole fraction of the fluorene in the benzene-free binary solid mixtures.

Table V. Equilibrium Data for the Ternary System Benzene (1)–Dibenzothiophene (2)–Dibenzofuran (3)[a]

x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C	x_1	t/°C
$x_2^\circ = 0.0401$		$x_2^\circ = 0.0453$		$x_2^\circ = 0.0830$		$x_2^\circ = 0.0903$		$x_2^\circ = 0.1384$	
0.8403	9.7	0.8070	15.1	0.8184	12.9	0.8229	11.8	0.7995	15.1
0.7827	20.5	0.7379	26.1	0.7260	27.6	0.8075	14.4	0.7158	27.6
0.7305	27.0	0.6372	39.1	0.6495	36.7	0.7527	22.9	0.6125	39.8
0.6790	34.0	0.4593	56.7	0.5501	46.8	0.7019	29.6	0.5761	43.6
0.5882	44.1	0.2429	70.5	0.4463	55.4	0.6551	35.6	0.5032	50.2
0.5148	51.5	0.1925	73.4	0.3604	62.8	0.6128	39.9	0.4240	56.2
0.4100	62.1			0.2683	70.5	0.5471	46.0	0.3424	62.4
						0.4700	53.6	0.2781	70.0
						0.3902	60.0		
$x_2^\circ = 0.1666$		$x_2^\circ = 0.2080$		$x_2^\circ = 0.2822$		$x_2^\circ = 0.3532$		$x_2^\circ = 0.3966$	
0.8160	11.7	0.8025	14.5	0.8097	14.9	0.8262	10.5	0.8192	12.2
0.7801	18.1	0.7586	21.5	0.7706	19.4	0.7318	25.5	0.7374	25.2
0.7374	24.9	0.7136	27.6	0.7118	27.6	0.6800	31.9	0.6883	31.7
0.6711	33.2	0.6695	33.2	0.6738	32.6	0.6049	40.1	0.6424	36.8
0.5770	43.3	0.6310	37.4	0.6383	36.7	0.5458	46.3	0.5970	41.9
0.4951	51.0	0.5612	45.0	0.5473	45.7	0.3990	58.6	0.5481	47.0
0.3975	59.3	0.4806	51.9	0.3610	60.8	0.2190	70.2	0.5170	49.2
0.2923	68.2	0.3946	58.9	0.3120	64.8			0.4158	57.5
		0.3519	62.0	0.2409	70.5			0.3705	60.8
		0.2551	70.1					0.2898	65.8
								0.2231	70.2
$x_2^\circ = 0.4402$		$x_2^\circ = 0.5068$		$x_2^\circ = 0.5485$		$x_2^\circ = 0.5662$		$x_2^\circ = 0.5990$	
0.8161	13.3	0.8076	15.4	0.8201	14.2	0.8437	12.9	0.8364	13.5
0.7338	26.6	0.7648	22.7	0.8070	17.6	0.8163	17.7	0.7973	21.3
0.6672	35.7	0.7161	29.6	0.7601	24.1	0.7731	22.4	0.7222	32.4
0.5742	45.0	0.6563	36.9	0.7110	30.9	0.7212	30.0	0.6570	40.8
0.3848	60.2	0.5510	48.0	0.5838	45.5	0.6769	35.5	0.5851	49.0
0.2855	67.0	0.4584	56.4	0.4874	54.2	0.6121	42.8	0.5260	54.6
		0.3426	65.1	0.3858	62.6	0.5633	47.5	0.4652	59.6
		0.2553	70.5	0.2577	70.6	0.5385	49.7	0.3692	66.0
						0.4900	54.7	0.2871	71.1
						0.4519	57.9		
						0.3931	62.0		
						0.3452	65.1		
$x_2^\circ = 0.6572$		$x_2^\circ = 0.7042$		$x_2^\circ = 0.7623$		$x_2^\circ = 0.8400$		$x_2^\circ = 0.8630$	
0.8531	12.8	0.8574	13.8	0.8775	16.0	0.8928	15.5	0.8980	13.8
0.8173	19.8	0.8453	17.5	0.8378	24.4	0.8600	23.4	0.8601	22.7
0.7703	28.6	0.7961	28.2	0.7967	31.5	0.8156	32.1	0.8261	29.2
0.7104	37.5	0.7432	36.2	0.7368	40.4	0.7430	43.7	0.7881	35.3
0.6593	43.7	0.6753	45.2	0.6248	54.0	0.6796	51.4	0.7328	43.1
0.5732	56.6	0.6027	53.6	0.5041	65.8	0.5779	62.9	0.6610	51.2
0.4903	61.0	0.5251	60.6	0.3353	78.6	0.4489	73.2	0.5919	57.7
0.4122	66.6	0.4552	66.2			0.3463	79.5	0.4348	71.5
0.3230	72.1	0.3851	70.9					0.3252	78.9
$x_2^\circ = 0.9132$		$x_2^\circ = 0.9537$							
0.8835	18.9	0.8986	15.8						
0.8538	25.8	0.8955	16.8						
0.8293	31.0	0.8315	31.5						
0.7836	39.1	0.7594	43.7						
0.7245	47.6	0.7138	48.8						
0.6284	59.8	0.6752	53.7						
0.5469	66.5	0.6460	57.5						
0.3709	80.3	0.5838	63.0						
		0.5596	65.9						
		0.5324	67.5						

[a] x_2° = mole fraction of the dibenzothiophene in the benzene-free binary solid mixtures.

of the equation parameters and corresponding root mean square deviations for both of the liquidus curves of the three measured binary eutectic systems with benzene are presented in Table VI.

It can be noted that a good description has been obtained for every binary system. All deviations are in the range of σ_T from 0.13 to 1.67 °C for the Wilson equation and from 0.09 to 1.78 °C for the UNIQUAC equation. The binary eutectic is the single condition at which a liquid is in equilibrium with two solid phases. Its temperature is a minimum on the liquidus curves of the T-x_i diagram. The invariant eutectic point composition and temperature were $x_1 = 0.063$, $t = 2.1$ °C; $x_1 = 0.112$, $t = -0.8$ °C; and $x_1 = 0.060$, $t = 2.8$ °C for the fluorene–benzene, dibenzofuran–benzene, and dibenzothiophene–benzene systems, respectively, as shown in Figures 1–3. Figures 2 and 3 show the solid–liquid equilibrium data obtained by two different experimental methods—dynamic, used in this work, and static, used in previous work (4), for the same binary systems. It can be noted that only one experimental point for dibenzothiophene–benzene obtained by the static method is far from the liquidus curve (see Figure 3). Generally, the results of the solid solubility correlation, obtained by using the Wilson and the UNIQUAC equations, are comparable with each other and not very far from the ideal solubility, which is shown in Table VII for the dibenzofuran–benzene system as an example. Values presented in this table have to be related to experimental values shown earlier in Table II.

When solid solutions occur, the solubility equation (eq 1 above) must be modified to include activity coefficients in the solid phase and must be applied to both components. The resulting equations, which hold when solid-phase transitions are absent, are

$$x_1^*\gamma_1^* = x_1\gamma_1 \exp\left[\frac{\Delta H_{\mathrm{m}1}}{R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{t}1}}\right) + \frac{\Delta C_{p\mathrm{m}1}}{R}\left(\ln\frac{T_{\mathrm{t}1}}{T}-\frac{T_{\mathrm{t}1}}{T}+1\right)\right] \quad (5)$$

Table VI. Values of the Parameters and of the Root Mean Square Deviations of Temperature Obtained by Wilson and UNIQUAC Equations in Binary Eutectic Systems

system	parameter: Wilson $g_{12}-g_{11}$ $(g_{12}-g_{22})$/(J mol^{-1})	parameter: UNIQUAC ΔU_{12} (ΔU_{21})/(J mol^{-1})	σ_T/°C Wilson	σ_T/°C UNIQUAC
fluorene (1)–benzene (2)	−1264.27 (2210.32)	1462.73 (−738.38)	0.32	0.37
dibenzofuran (1)–benzene (2)	−1373.34 (2354.80)	1640.56 (−852.64)	0.40	0.41
dibenzothiophene (1)–benzene (2)	−1175.65 (2828.56)	1918.68 (−830.52)	1.67	1.78
benzene (1)–fluorene (2)	78 770.36 (3053.71)	5443.90 (−2877.67)	0.35	0.25
benzene (1)–dibenzofuran (2)	−2327.28 (100 837.6)	6112.95 (−2910.86)	0.13	0.09
benzene (1)–dibenzothiophene (2)	8 432 769.6 (5077.38)	1525.97 (2 336 122.1)	0.34	0.41

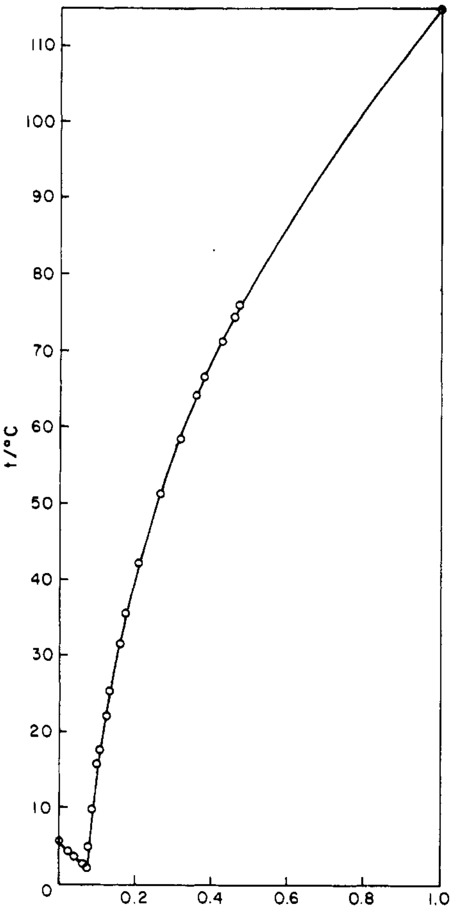

Figure 1. Solid–liquid phase diagram for fluorene (1)–benzene (2). The lines are predicted by the Wilson equation.

$$x_2^*\gamma_2^* = x_2\gamma_2 \exp\left[\frac{\Delta H_{m2}}{R}\left(\frac{1}{T}-\frac{1}{T_{t2}}\right) + \frac{\Delta C_{pm2}}{R}\left(\ln\frac{T_{t2}}{T}-\frac{T_{t2}}{T}+1\right)\right] \quad (6)$$

where the mole fraction and activity coefficient of the solid phase are shown with an asterisk. Summing up the mole fractions leads to the two equations

$$x_1 + x_2 = (\gamma_1^*/\gamma_1)x_1^* \exp\left[\frac{\Delta H_{m1}}{R}\left(\frac{1}{T_{t1}}-\frac{1}{T}\right) - \frac{\Delta C_{pm1}}{R}\left(\ln\frac{T_{t1}}{T}-\frac{T_{t1}}{T}+1\right)\right] + (\gamma_2^*/\gamma_2)x_2^* \times \exp\left[\frac{\Delta H_{m2}}{R}\left(\frac{1}{T_{t2}}-\frac{1}{T}\right) - \frac{\Delta C_{pm2}}{R}\left(\ln\frac{T_{t2}}{T}-\frac{T_{t2}}{T}+1\right)\right] \quad (7)$$

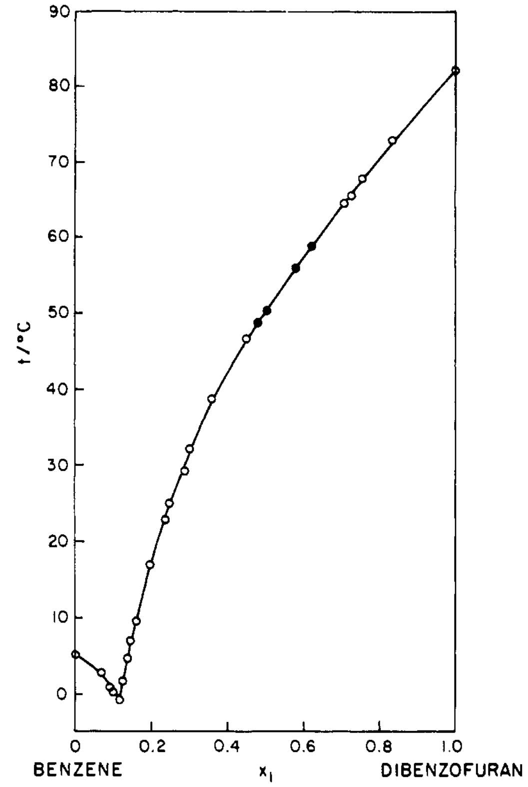

Figure 2. Solid–liquid phase diagram for dibenzofuran (1)–benzene (2). The lines are predicted by the UNIQUAC equation. The solid circles represent experimental points published earlier (*4*).

Table VII. Values of the Calculated Temperatures and Activity Coefficients Obtained by Wilson and UNIQUAC Methods and Ideal Solubilities for the Dibenzofuran (1)–Benzene (2) System

Wilson		UNIQUAC		ideal solubility
t^{calcd}/°C	γ_1^{calcd}	t^{calcd}/°C	γ_1^{calcd}	t/°C
5.5		5.5		5.5[a]
2.8	1.023[a]	2.9	1.025[a]	1.3[a]
0.9	1.019[a]	1.0	1.019[a]	−0.2[a]
0.2	1.016[a]	0.1	1.015[a]	−0.8[a]
−1.4	1.293	−1.5	1.296	−11.3
1.8	1.285	1.7	1.288	−8.1
4.8	1.276	4.8	1.279	−4.9
7.2	1.269	7.1	1.271	−2.5
10.1	1.259	10.1	1.262	0.2
17.3	1.234	17.3	1.236	8.2
23.1	1.211	23.2	1.213	14.6
25.1	1.203	25.2	1.204	16.8
29.5	1.184	29.6	1.185	21.7
31.8	1.174	31.8	1.174	24.3
38.0	1.145	38.0	1.145	31.5
46.6	1.105	46.5	1.103	41.6
56.6	1.060	56.4	1.057	53.6
64.9	1.029	64.7	1.027	63.3
68.1	1.019	68.0	1.018	67.2
72.7	1.009	72.6	1.008	72.2
82.1	1.000	82.1	1.000	82.1

[a] Activity coefficients and ideal solubilities for benzene as a solute.

$$x_1^* + x_2^* = (\gamma_1/\gamma_1^*)x_1 \exp\left[\frac{\Delta H_{m1}}{R}\left(\frac{1}{T}-\frac{1}{T_{t1}}\right) + \frac{\Delta C_{pm1}}{R}\left(\ln\frac{T_{t1}}{T}-\frac{T_{t1}}{T}+1\right)\right] + (\gamma_2/\gamma_2^*)x_2 \times \exp\left[\frac{\Delta H_{m2}}{R}\left(\frac{1}{T}-\frac{1}{T_{t2}}\right) + \frac{\Delta C_{pm2}}{R}\left(\ln\frac{T_{t2}}{T}-\frac{T_{t2}}{T}+1\right)\right] \quad (8)$$

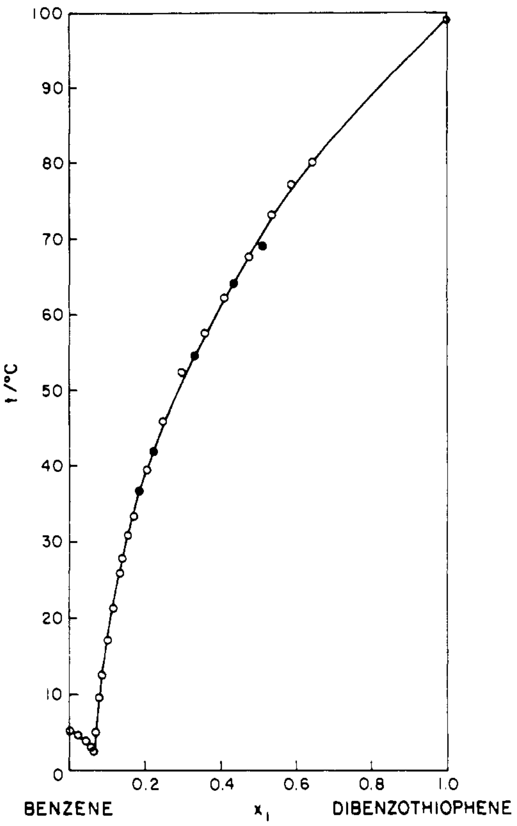

Figure 3. Solid–liquid phase diagram for dibenzothiophene (1)–benzene (2). The lines are predicted by the Wilson equation. The solid circles represent experimental points published earlier (*4*).

Remembering that

$$x_1 + x_2 = 1 \qquad (9)$$

$$x_1^* + x_2^* = 1 \qquad (10)$$

it is possible to minimize the following objective function:

$$\Omega = \sum [x_i^{\text{exptl}} - x_i^{\text{calcd}}(T,A_1,A_2,A_3,A_4)]^2 + [x_i^{*\,\text{exptl}} - x_i^{*\,\text{calcd}}(T,A_1,A_2,A_3,A_4)]^2 \qquad (11)$$

For an ideal solid phase ($\gamma_1^* = \gamma_2^* = 1$) the problem reduces to the minimization of Ω with two parameters (A_1, A_2), using composition data from the liquidus curve. Using the experimental data of Sediawan et al. (*1*), with liquid-phase activity coefficients derived from the UNIQUAC and Wilson equations, the interaction parameters were fitted by this optimization technique. The effect of the α/β phase transition of dibenzothiophene had to be added for the dibenzothiophene–dibenzofuran system. The resulting parameters, calculated from the liquidus curves, are presented in Table VIII.

Table IX shows the experimental data of Sediawan (*1*) in the form of x_1 and x_1^* as functions of temperature for the solid solution region. The table also shows calculated temperatures: T^{calcd} (nonideal solid solution, four UNIQUAC parameters) and $T^{\text{calcd,id}}$ (ideal solid solution, two UNIQUAC parameters). Values of the four parameters and standard deviations of temperature, obtained by th UNIQUAC model in every binary solid–solid system are shown in Table X.

Table VIII. Values of the Parameters and of the Root Mean Square Deviations of Temperature Obtained by Wilson and UNIQUAC Equations in Binary Systems (Liquidus Curves)[a]

system	parameter		σ_T/°C	
	Wilson $g_{12} - g_{11}$ ($g_{12} - g_{22}$)/(J mol^{-1})	UNIQUAC ΔU_{12} (ΔU_{21})/(J mol^{-1})	Wilson	UNIQUAC
fluorene (1)–dibenzofuran (2)	2617.12 (3420.17)	1081.57 (153.70)	1.9	2.2
fluorene (1)–dibenzothiophene (2)	8009.28 (4381.22)	129.57 (1796.20)	1.5	3.0
dibenzothiophene (1)–fluorene (2)	28 721 337.2 (8346.55)	3046.89 (51 075.6)	0.3	0.2
dibenzothiophene (1)–dibenzofuran (2)	65 651.02 (2453.41)	−185.45 (1827.92)	0.7	0.4
dibenzofuran (1)–dibenzothiophene (2)	1 795 145.9 (7693.86)	5683.57 (−2227.56)	2.8	0.1

[a] For $\gamma_1^* = \gamma_2^* = 1$ (ideal solid phase).

Table IX. Equilibrium Data for the Binary System Dibenzothiophene (1)–Dibenzofuran (2) and Temperatures Calculated by the UNIQUAC Equation with Four and Two Parameters (Ideal Solid Phase)

x_1	x_1^*	t/°C	t^{calcd}/°C	$t^{\text{calcd,id}*}$/°C
0.000	0.000	82.1	82.1	82.1
0.395	0.475	81.3	81.4	80.3
0.405	0.499	81.4	81.5	80.4
0.445	0.535	81.8	81.8	80.9
0.499	0.591	82.4	82.3	81.7
0.531	0.625	82.8	82.7	82.3
0.565	0.671	83.3	83.2	83.1
0.600	0.694	83.8	83.8	84.0
0.650	0.751	84.9	84.8	85.4
0.721	0.824	86.8	86.7	87.7
0.751	0.850	87.5	87.7	88.8
0.805	0.882	88.8	89.7	91.0
0.865	0.928	92.7	92.4	93.4
0.880	0.930	93.2	93.1	94.0
0.890	0.940	93.8	93.6	94.4
0.915	0.951	95.1	94.8	95.4
0.929	0.960	95.7	95.5	96.0
0.951	0.972	96.8	96.5	96.8
0.962	0.981	97.3	97.0	97.3
1.000	1.000	98.7	98.7	98.7

Table X. Values of the Parameters and of the Root Mean Square Deviations of Temperature Obtained by the UNIQUAC Equation in Binary Systems (Liquid and Solidus Curves)[a]

system	parameter		σ_T/°C
	ΔU_{12} (ΔU_{21})/(J mol^{-1})	ΔU_{12}^{b} (ΔU_{21}^{b})/(J mol^{-1})	
fluorene (1)–dibenzofuran (2)	2788.68 (−1921.60)	−131.37 (453.08)	0.4
fluorene (1)–dibenzothiophene (2)	−1630.57 (3388.50)	−1516.13 (3567.87)	0.1
dibenzothiophene (1)–dibenzofuran (2)	1208.92 (−1827.76)	3450.25 (−2509.60)	0.3

[a] Standard deviation $\sigma_T = [\sum_{i=1}^{n} [(T_i^{\text{calcd}} - T_i)^2 / n]]^{1/2}$. [b] Solid phase.

Taking into consideration that the results of the solid solubility correlation obtained by using the Wilson and UNIQUAC equations were comparable with each other, calculations of ternary system phase diagrams have been continued with the UNIQUAC equation only. Using the parameters derived from the binary data, it is possible to predict the solidus and liquidus curves in ternary, two-phase mixtures (solid solution–liquid). Taking into account 12 parameters (4 for every binary system), the equilibrium temperature can be predicted by solution of three equations similar to eqs 5 and 6 with $\sum x_i = 1$ and $\sum x_1^* = 1$. In this way it is possible to calculate the temperature and composition of the solid phase for the given composition of the liquid phase. In every ternary system tested in this paper, we have assumed the four solid-phase parameters equal to zero for the two binary eutectic systems. The results of calculation at 50 °C with values of binary eutectic parameters (aromatic compound–benzene liquidus curve) given in Table VI, parameters for solid–solid systems given in Table X, and four

Table XI. Values of the Temperatures Predicted by the UNIQUAC Equation for the System Benzene (1)–Fluorene (2)–Dibenzofuran (3) at 50 °C

x_2	x_3	t^{calcd}/°C	x_2	x_3	t^{calcd}/°C
0.0432	0.4558	51.3	0.1860	0.2239	48.7
0.0727	0.4222	51.4	0.1967	0.1964	48.3
0.0982	0.3817	50.8	0.2127	0.1694	48.5
0.1133	0.3518	50.1	0.2174	0.1446	48.0
0.1154	0.3426	49.7	0.2351	0.1148	48.8
0.1381	0.3319	50.9	0.2382	0.0898	48.5
0.1529	0.2971	50.0	0.2356	0.0744	48.0
0.1642	0.2754	49.7	0.2426	0.0574	48.5
0.1749	0.2646	49.9	0.3253	0.0307	56.2

Table XII. Values of the Temperatures Predicted by the UNIQUAC Equation for the System Benzene (1)–Fluorene (2)–Dibenzothiophene (3) at 50 °C

x_2	x_3	t^{calcd}/°C	x_2	x_3	t^{calcd}/°C
0.0080	0.2671	50.6	0.1186	0.2004	51.4
0.0237	0.2623	50.2	0.1347	0.1853	51.6
0.0391	0.2809	52.3	0.1511	0.1549	51.0
0.0442	0.2738	51.9	0.1631	0.1349	50.7
0.0572	0.2709	52.4	0.1784	0.1166	50.9
0.0663	0.2637	52.3	0.1851	0.1049	50.7
0.0671	0.2549	51.7	0.2033	0.0807	50.7
0.0936	0.2363	51.9	0.2193	0.0427	49.6
0.1025	0.2300	52.2	0.2291	0.0290	49.5
0.1096	0.2124	51.5			

Table XIII. Values of the Temperatures Predicted by the UNIQUAC Equation for the System Benzene (1)–Dibenzothiophene (2)–Dibenzofuran (3) at 50 °C

x_2	x_3	t^{calcd}/°C	x_2	x_3	t^{calcd}/°C
0.0188	0.4500	48.3	0.2113	0.2687	52.2
0.0211	0.4439	48.0	0.2357	0.2294	52.6
0.0407	0.4493	49.3	0.2450	0.2091	53.2
0.0444	0.4477	49.3	0.2604	0.1995	53.4
0.0681	0.4240	49.4	0.2576	0.0803	50.4
0.0825	0.4125	49.7	0.2562	0.0488	49.7
0.1036	0.3944	50.2	0.2831	0.0449	51.7
0.1406	0.3575	50.9	0.2657	0.0252	50.0
0.1752	0.3208	51.7	0.2766	0.0134	50.7
0.1935	0.2945	51.9			

Table XIV. Values of the Standard Deviations of Temperature Obtained by the UNIQUAC Equation for Prediction of Isotherms in Ternary Systems

system	t/°C	σ_T/°C
benzene (1)–fluorene (2)–dibenzofuran (3)	15	17.3
	25	11.3
	40	3.7
	50	1.9
	60	4.2
benzene (1)–fluorene (2)–dibenzothiophene (3)	15	16.2
	25	13.0
	40	5.5
	50	1.5
	60	3.8
	70	5.0
benzene (1)–dibenzothiophene (2)–dibenzofuran (3)	15	18.4
	25	13.3
	40	5.5
	50	1.7
	60	3.3
	70	6.7

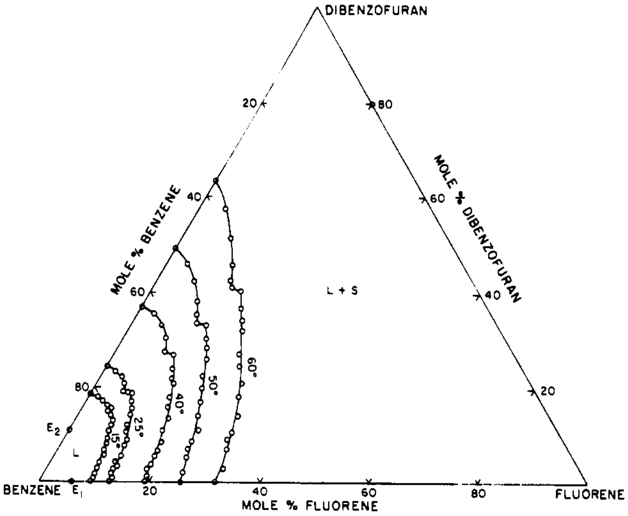

Figure 4. Equilibria for benzene (1)–fluorene (2)–dibenzofuran (3). The second and last of these form solid solutions at any composition with point A characteristic for a rapidly changed liquidus curve and two binary eutectic points E_1 and E_2 for 1–2 and 1–3 systems, respectively.

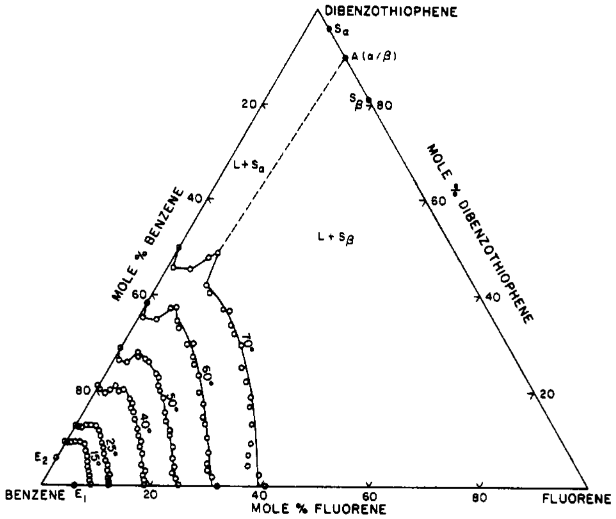

Figure 5. Benzene (1)–fluorene (2)–dibenzothiophene (3). Two different crystal structures α and β and the solid immiscibility gap are present between points S_α and S_β and a minimum on the liquidus curves, changing the α for the β form at point A. The binary eutectics are at points E_1 and E_2 for 1–2 and 1–3, respectively.

parameters equal to zero are shown in Tables XI–XIII. Columns 1 and 2 of Tables XI–XIII list the experimental values of solution composition at 50 °C, and column 3 presents the predicted temperatures. The standard deviation of temperature was from 1.5 to 1.9 °C in these ternary systems at 50 °C. Overly large values of the standard deviation were observed at higher and lower temperatures, especially at 15 °C ($\bar{\sigma}$ = 17.3 °C) as shown in Table XIV. Figures 4–6 show the isothermal lines constructed from data on compositions of mixtures having the same saturation temperature. These diagrams are the contour diagrams of the equilibrium surface of the ternary systems in the triangular prism with temperature as the vertical axis. The isotherms are drawn for 15, 25, 40, 50, 60, and 70 °C. In all the major regions high-temperature isotherms are spread over a large area as compared to low-temperature isotherms, indicating that the slope of the surface at lower temperature is steeper than that at high temperature.

In the first phase diagram (Figure 4) the isotherms represent the varying compositions of the liquid solution in equilibrium with solid solution for the benzene–fluorene–dibenzofuran system at the given temperature. At point A a rapid change in slope of the liquidus curve occurs in the binary system fluorene–dibenzofuran. This may be the reason for existence of the valley on the ternary surface, which is observed as a minimum of the isotherm curve.

Figure 5 shows isotherms for the benzene–fluorene–dibenzothiophene system. Since pure fluorene and diben-

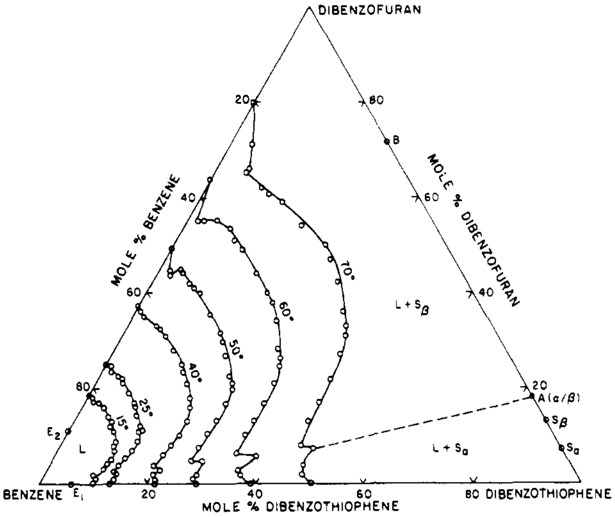

Figure 6. Benzene (1)–dibenzothiophene (2)–dibenzofuran (3). Two different crystal structures α and β and the solid immiscibility gap are present between points S_α and S_β. Point A is characteristic for changing the α form for the β form, and point B is a minimum of the T–x diagram on the liquidus curve. The binary eutectics are at points E_1 and E_2 for 1–2 and 1–3, respectively.

zothiophene have different crystal structures (*16, 17*), it was observed (*1*) that the fluorene–dibenzothiophene system had a solid immiscibility gap between points S_α and S_β on the solidus curve, and point A was observed as a minimum on the liquidus curves, changing α for β crystal structures on the liquidus curve. We observed two minima, connected with the eutectic points of fluorene–benzene and dibenzothiophene–benzene systems and the maximum of the isotherm connected with point A—changing of crystal structure α to β. The same explanation can be applied to the third system, presented in Figure 6, where point A represents the change of solid crystal structure from α to β on the liquidus curve and point B is a minimum of the T–x diagram. The eutectic valleys were found on both sides of the isotherms.

In summary, results of calculation show that the prediction of ternary system isotherms using the UNIQUAC binary system parameters is possible at moderate temperatures (40–60 °C) with average standard deviation $\bar{\sigma}_T = 3.4$ °C. At higher temperatures, the liquidus surfaces of the ternary systems are difficult to describe and the prediction of SLE, especially in the region of the eutectic valleys, is not generally satisfactory. It should be expected that the application of more parameters for two eutectic liquidus lines or two parts of liquidus characteristic for the α/β phase transition of the fluorene–dibenzothiophene system, for example, will make a better description of isotherm curves of such polynuclear aromatic systems possible. Additionally the effect of the immiscibility gap in the solid phase should be added to eqs 5 and 6. At lower temperatures the standard deviation of prediction is unacceptable. Perhaps the ternary systems under study have a tendency to form binary eutectics in equilibrium with solid solution and liquid at lower temperature. Generally, we may expect better predictions for ternary systems which have three pairs of binary eutectics or binary solid solutions.

Glossary

a_1	activity of the solute
A_1,A_2,A_3,A_4	Wilson or UNIQUAC adjustable parameters
ΔC_{pm1}	difference between heat capacities of the solute in the solid and liquid states
F	objective function for optimization
g_{ij}	molar energy of interaction between i and j
ΔH_{m1}	molar enthalpy of fusion of the solute
ΔH_{tr1}	molar enthalpy of transition of the solute
n	number of experimental points
R	universal gas constant
S_α,S_β	points of solid solution crystal structures changing
T/t	experimental equilibrium temperature, K/°C
T_m/t_m	melting point temperature, K/°C
T_t/t_t	triple point temperature, K/°C
T_{tr1}/t_{tr1}	transition point temperature of the pure solute, K/°C
ΔT	estimated error of temperature
T^{calcd}	calculated equilibrium temperature
Δu_{ij}	binary interaction parameter
V	molar volume
x_1	mole fraction of the solute
x_1^{calcd}	calculated equilibrium mole fraction
Δx_1	estimated error of the solute mole fraction
x_i^o	mole fraction of the first named component in the solvent-free binary solid mixture
w	weight of experimental point

Greek Letters

α	crystal structures
β	crystal structures
γ_i	activity coefficient of component i
σ_T	root mean square deviation of temperature
σ_x	mean absolute deviation of composition
Ω	objective function for the least-squares optimization

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