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Solid–Liquid Phase Diagram for the System Nitrobenzene (1)–Sulfolane (2). An Improved Method for the Calculation of Activity Coefficients of Sulfolane, as Solvent, for Solutions in Equilibrium with Crystal I or Crystal II

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Solid–liquid equilibrium temperatures were measured for the binary system nitrobenzene (1)–sulfolane (2) over the entire composition range. As already reported, in the case of some other binary mixtures involving sulfolane, more than one phase diagram may occur, owing to the occasional formation of different solid and liquid phases, which are sometimes only slightly differentiated thermodynamically. A theoretical treatment of cryoscopic data for solutions in equilibrium with sulfolane rotational solid phase I, on the supposition of no loss of rotational freedom on solidification ($\Delta C_p = 0$), allowed us to derive an equation, $\vartheta = 65m - 17.914m^2 + 5.015m^3 - 1.409m^4$, for the calculation of molal depressions of ideal solutions. It reproduces experimental cryoscopic data for nitrobenzene–sulfolane solutions within the limits of experimental error (±0.02 K). Further development of this equation allows the calculation of the activities of the solvent in any kind of sulfolane solution (ideal or not) in equilibrium with crystal I. The calculated activities of sulfolane, as solvent, in the case of nitrobenzene solutions are coincident with molar fractions, as expected. From cryoscopic data for solutions in equilibrium with crystal II, according to the statement of ideal behavior, the cryoscopic constant, λ_{II}, and ΔC_p on solidification of ordinary crystal II are calculated.

Introduction

Previously (*1*) we carried out some preliminary studies on excess volumes of mixing and dielectric constants for the nitrobenzene–sulfolane binary system over the entire composition range at selected temperatures ranging from 288 to 333 K. Data allowed us to classify this binary system among those which exhibit only slight departures from ideality, interactions between like and unlike molecules being scarcely noticeable.

The two components are indeed both dipolar aprotic substances with low donor numbers (sulfolane DN = 14.8; nitrobenzene DN = 4.4); their molecules possess similar volumes (sulfolane $V^{30°C} = 95.2$ cm^3 mol^{-1}; nitrobenzene $V^{30°C} = 103.2$ cm^3 mol^{-1}) but are different in shape.

A moderate association to molecular pairs, of nitrobenzene molecules flattened by resonance, may not be entirely excluded; sulfolane, because of the steric hindrance of its globular molecule, is a weakly structured substance still below its melting point. This conclusion may be drawn from the insensivity (*2*, *3*) to temperatures of its dipole moment (4.8 D) in the liquid phase and still below the melting point (301.61 K), in the stability range of a mesophase (crystal I) (*4*), in which molecules can freely rotate, until a transition temperature (288.61 K) is gained at which an ordinary nonrotational phase (crystal II) is formed.

The observed strictly regular behavior of this binary system has prompted us to select it as the most likely system to complete the picture of the cryoscopic behavior of sulfolane solutions in equilibrium either with crystal I (initial freezing points of solutions in the temperature range 301.61–288.61 K) or with crystal II (initial freezing points below 288.61 K). We present here the solid–liquid phase diagram for the nitrobenzene–sulfolane system.

Experimental Section

***Materials*.** Sulfolane, kindly supplied by Shell Italia, was carefully purified and dried as reported elsewhere (*4*). Nitrobenzene (Fluka high purity) was dried over P_2O_5 and twice fractionally distilled under vacuum. The melting points of very pure samples of the two substances (28.45 and 5.74 °C, respectively) were in close agreement with literature data (*5*, *6*). The solutions were prepared by weight (reduced to mass), in a drybox.

***Apparatus and Procedure*.** The methods adopted in measuring liquid–solid equilibrium temperatures are described elsewhere (*7*). Temperatures were measured by a Leeds & Northrup G2 Müller bridge, coupled with a NBS-certified platinum resistance thermometer. Cooling curves were preferred to warming curves; the initial freezing temperatures of solutions were determined by extrapolation across the undercooling region. Where undercooling was excessive, warming curves were also taken. Agreement between the two methods was usually within ±0.02 K. The accuracies of the melting temperatures of pure substances and eutectic temperatures are estimated to be 0.02 and 0.1 K, respectively.

Results

Figure 1 shows the solid–liquid phase diagram as taken by thermal analysis for the system nitrobenzene (1)–sulfolane (2). It is rather complex and has features not commonly observed. As already reported, a mesomorphic rotational crystal I is the stable phase of sulfolane in the temperature region 301.61–288.61 K; below this temperature ordinary crystal II becomes the more stable solid phase. That the transition temperature of solutions checks well that of the pure substance (288.61 K) precludes the existence of solid solutions.

On the other hand, nitrobenzene seems to be able to solidify to two crystalline phases with a sluggish transition only 0.29 K below the melting point, as evidenced by the freezing curve in Figure 2. For the sake of uniformity with sulfolane, we indicate as crystal I′ the solid phase which is stable between the melting point (278.90 K) and the transition temperature (278.61 K) and as crystal II′ the solid phase which is stable below the transition temperature; reasonably, these two solid phases possess comparable stability because their freezing points fall within a very narrow temperature range.

Hence, the occurrence of a multiple phase diagram has to be expected. (Multiple phase diagrams have already been observed in some binary systems involving sulfolane, e.g., dioxane–sulfolane (*8*) and 2-methyl-2-propanol–sulfolane (*9*) mixtures, because crystal I seems to have a peculiar ability to reveal latent forms of the other component.)

Sulfolane crystal II and nitrobenzene crystal I′ may indeed form a eutectic-type diagram (solid line with full circles in Figure

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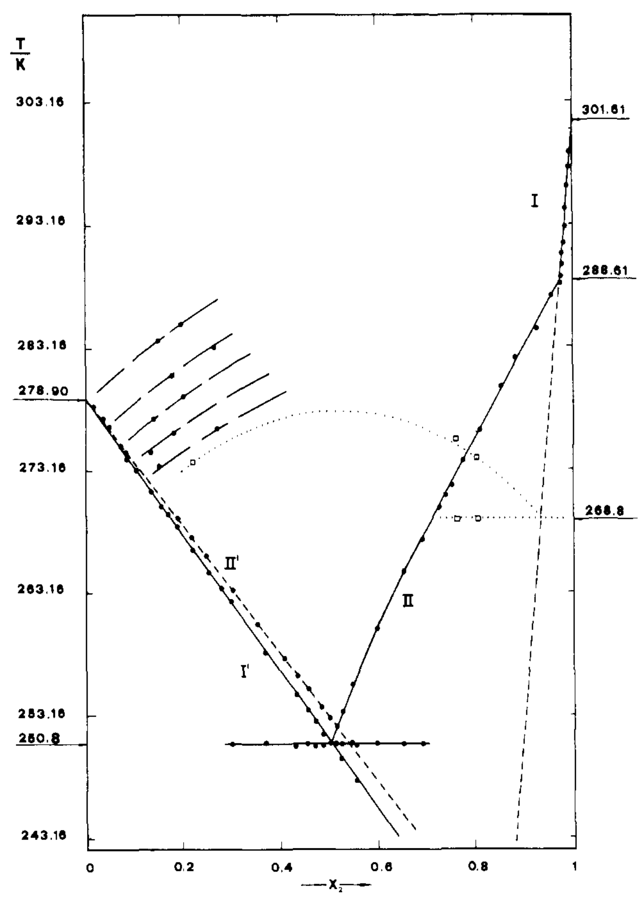

Figure 1. Solid-liquid phase diagram of nitrobenzene (1)-sulfolane (2) system.

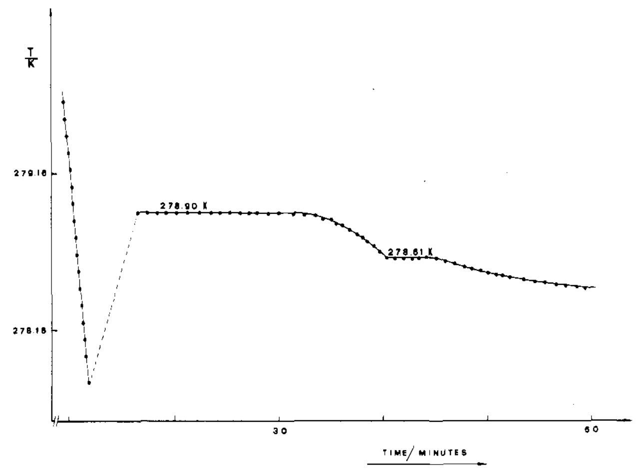

Figure 2. Cooling curve of a highly purified sample of nitrobenzene.

1); the observation of a sharp eutectic halt at 250.8 K for several solutions whose melting points fall in a range of 0.2-10 K above 250.8 K supports this hypothesis. Otherwise, if the transition sulfolane crystal I ⟶ crystal II is avoided by sudden cooling, metastable plastic crystal I may form multiple phase diagrams with both crystalline forms of nitrobenzene.

A eutectic-type diagram may indeed originate with nitrobenzene crystal I′; the occurrence of peritectic points which fall on the extrapolation of the solid line in Figure 1 may be interpreted only by this supposition. We report in Figure 3 the cooling curve of a solution (x_2 = 0.510) whose initial freezing temperature clearly is a peritectic point. Starting from the peritectic point, after a steady decrease with time, the temperature abruptly rises to 250.8 K, where the true equilibrium conditions are attained, implying eutectic deposition.

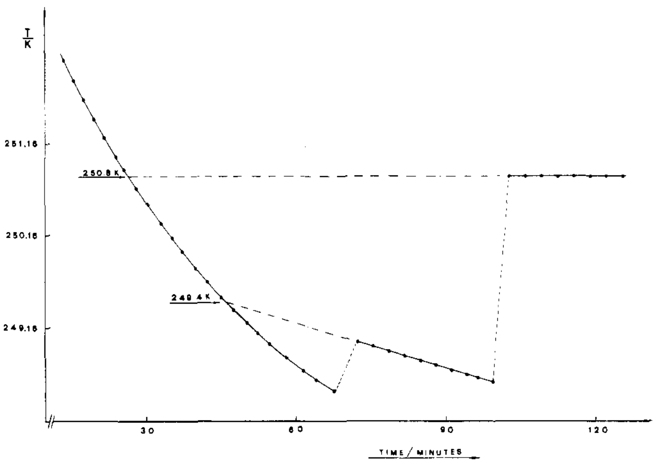

Figure 3. Cooling curve of a solution with x_2 = 0.510 whose initial freezing point is a peritectic point.

Another eutectic-type diagram (dashed line in Figure 1) may originate between sulfolane plastic crystal I and nitrobenzene crystal II′. Both of these diagrams would imply eutectic halts below 250.8 K, but we failed to observe them because of the extreme instability of the system below 250.8 K.

The possibility of weak interactions between the two substances, resulting in a scarcely stable compound, may not be entirely excluded. Some solutions indeed are characterized by initial freezing points which fall on a flat curve (dotted line in Figure 1), and some of them, in the region 0.7-0.8x_2, by a eutectic halt, at 268.8 K. The compound deposition would imply the occurrence of another eutectic halt in the left-hand side of the phase diagram; we failed however to observe this halt because it would occur in a microheterogeneous region, as illustrated below.

Nitrobenzene is suspected of behaving as a mesogenic substance; in fact, several metastable liquid phases of nitrobenzene, separated by well-defined phase transitions (broken lines in Figure 1), may originate, in a narrow region close to the pure substance, by changing the stirring and cooling or warming rate; the formation of each of these phases seems to be quite occasional, and thermodynamic conditions are not reproducible at will. The warming curve of a solution with x_2 = 0.142 in Figure 4 indicates that the system may gain successive metastable equilibrium conditions through abrupt changes in temperature, until a stable solid phase is formed which ends melting at 271.6 K. Similar phase diagrams were observed earlier by Dave et al. (*10-12*) in the case of binary mixtures involving a polymesogenic component exibiting smectic and nematic mesophases.

Some experiments employing optical and thermal methods to elucidate the mechanism by which different phases of nitrobenzene originate in the presence of sulfolane are in progress in our laboratory. In the meanwhile, we turn our attention to the right-hand side of the phase diagram to complete the picture of the cryoscopic behavior of sulfolane, as planned.

Discussion

As reported elsewhere (*13*, *14*) the activity, a_s, of a solid solvent in equilibrium with a liquid solvent in a solution with solvent molar fraction x_1 may be calculated with the equation

$$\ln a_s = \ln a_1 = \sum_{i=1}^{n} A_i \vartheta^i \qquad (1)$$

where ϑ values are the solvent freezing-point depressions and

$$A_i = \frac{\Delta H_\Theta}{R\Theta^{i+1}} - \frac{i-1}{i}\frac{\Delta C_p}{R\Theta^i}$$

Table I. Cryoscopic Data for Solutions in Equilibrium with Crystal I[a]

x_1	m	T, K	ϑ_{exptl}	$\vartheta_{\text{eq}\,5}$	$\vartheta/m_{\text{exptl}}$	$a_{1\,\text{eq}\,6}$	f_{x_1}
1	0	301.610			(65.00)	1	1
0.9982	0.0149	300.669	0.941	0.965	63.15	0.9983	1.0001
0.9977	0.0191	300.283	1.277	1.235	66.86	0.9976	0.9999
0.9974	0.0220	300.184	1.426	1.421	64.82	0.9974	1.0000
0.9969	0.0255	300.016	1.594	1.646	62.51	0.9970	1.0001
0.9964	0.0301	299.690	1.920	1.940	63.79	0.9964	1.0000
0.9947	0.0439	298.760	2.850	2.819	64.92	0.9947	1.0000
0.9936	0.0538	298.156	3.454	3.446	64.20	0.9936	1.0000
0.9932	0.0574	297.958	3.652	3.673	63.62	0.9932	1.0000
0.9921	0.0662	297.404	4.206	4.226	63.54	0.9921	1.0000
0.9911	0.0747	296.880	4.880	4.758	63.32	0.9912	1.0001
0.9898	0.0857	296.188	5.422	5.442	63.27	0.9898	1.0000
0.9886	0.0960	295.546	6.064	6.079	63.17	0.9886	1.0000
0.9873	0.1070	294.854	6.756	6.756	63.14	0.9873	1.0000
0.9861	0.1176	294.211	7.399	7.404	62.92	0.9861	1.0000
0.9849	0.1279	293.589	8.021	8.031	62.71	0.9849	1.0000
0.9836	0.1388	292.977	8.633	8.690	62.20	0.9837	1.0001
0.9815	0.1569	291.889	9.721	9.776	61.96	0.9816	1.0001
0.9800	0.1696	291.180	10.430	10.530	61.50	0.9802	1.0002
0.9776	0.1909	289.916	11.694	11.789	61.26	0.9777	1.0002
0.9768	0.1980	289.373	12.237	12.204	61.80	0.9767	0.9999
0.9759	0.2051	289.048	12.562	12.619	61.25	0.9760	1.0001

[a] Sulfolane mole fractions, x_1; nitrobenzene molalities, m; initial freezing temperatures, T; experimental and calculated freezing-point depressions, ϑ; molar depressions, ϑ/m; solvent activities, a_1; activity coefficients, f_{x_1}.

Θ is the melting temperature of the solvent; ΔH_Θ is the molar solidification enthalpy of the solvent at Θ; ΔC_p is the difference between solid and liquid molar heat capacities of the solvent; n is the number of significant terms in the series expansion (it needs to be verified numerically every time).

Therefore, eq 1 may be written in the form

$$\ln a_1 = A_1 \sum_{i=1}^{n} \frac{i}{\Theta^{i-1}} - \frac{\Delta C_p}{R} \sum_{i=1}^{n} \frac{i-1}{i} \left(\frac{\vartheta}{\Theta}\right)^i \tag{2}$$

Reasonably, in the case of ideal solutions, $\ln a_1 = \ln x_1$. In turn, $\ln x_1$ may be expanded in series as follows:

$$\ln x_1 = \sum_{i=1}^{n} \frac{1}{i} \left(\frac{x_2}{x_1}\right)^i (-1)^i = \sum_{i=1}^{n} \frac{(\alpha m)^i}{i} \tag{3}$$

for

$$x_2/x_1 = mM_1/1000 = -\alpha m$$

where M_1 is the molar weight of the solvent and m the solute molality.

From eq 1 and 3, we derive

$$\vartheta = \sum_{i=1}^{n} \lambda_i m_i \tag{4}$$

The first four coefficients of the series expansion are

$$\lambda_1 = \alpha/A_1$$

$$\lambda_2 = \frac{1}{A_1}\left|\frac{1}{2}\alpha^2 - A_2\lambda_1^2\right|$$

$$\lambda_3 = \frac{1}{A_1}\left|\frac{1}{3}\alpha^3 - 2A_2\lambda_1\lambda_2 - A_3\lambda_1^3\right|$$

$$\lambda_4 = \frac{1}{A_1}\left|\frac{1}{4}\alpha^4 - A_2\lambda_2^2 - 2A_2\lambda_1\lambda_3 - 3A_3\lambda_1^2\lambda_2 - A_4\lambda_1^4\right|$$

It is to be noted that

$$\lambda_1 = \frac{\alpha}{A_1} = \frac{-R\Theta^2}{\Delta H_\Theta}\,\frac{M_1}{1000}$$

is the cryoscopic constant of the solvent.

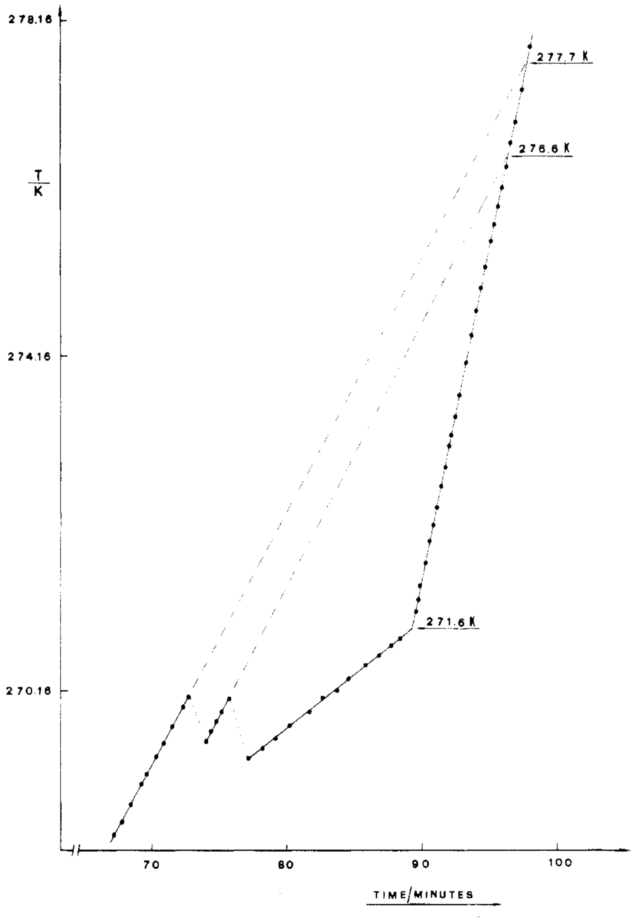

Figure 4. Warming curve of a solution with $x_2 = 0.142$ which evidences successive metastable equilibria.

Solutions in Equilibrium with Crystal I. In the case of sulfolane solutions in equilibrium with crystal I, no thermal data (ΔH_Θ and ΔC_p), as results of direct measurements concerning the solidification process of crystal I, are reported in the literature. Nevertheless, a reliable ΔH_Θ value ($=-334.21$ cal mol^{-1}) may be derived from the cryoscopic constant, $\lambda_1 = 65$ mol^{-1} kg K, calculated by extrapolation at $m = 0$ (Figure 5) of molar depressions ϑ/m of the freezing point of sulfolane by adding

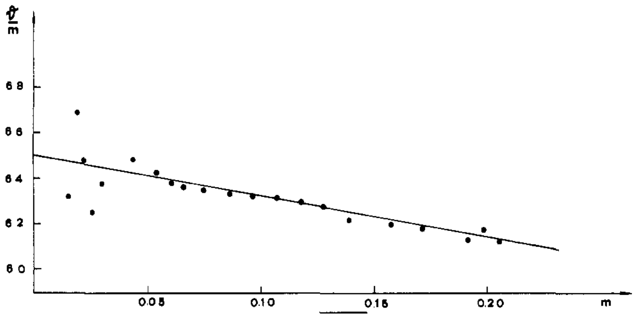

Figure 5. Molar depressions, ϑ/m, as a function of molality, m, of sulfolane (1)–nitrobenzene (2) mixtures in equilibrium with sulfolane crystal I.

Table II. Cryoscopic Data for Solutions in Equilibrium with Crystal II[a]

x_1	m	T, K	ϑ	$10^4 \delta x_{1\,\mathrm{eq}\,7}$
1	0	(290.23)[b]		
0.9678	0.2767	288.121	2.109	3
0.9619	0.3299	287.677	2.553	8
0.9498	0.4402	286.829	3.401	18
0.9329	0.5980	286.050	4.180	−35
0.9163	0.7596	284.582	5.648	14
0.8834	1.0982	282.366	7.864	2
0.8525	1.4396	280.446	9.784	−39
0.7723	2.4532	274.016	16.214	4
0.7603	2.6230	273.241	16.989	−17
0.7486	2.7939	271.876	18.354	35
0.7373	2.9655	271.189	19.041	6
0.7262	3.1374	269.923	20.307	46
0.7157	3.3050	269.492	20.739	−8
0.6856	3.8160	267.236	22.994	−43
0.6577	4.3304	264.777	25.453	−44

[a] Sulfolane mole fractions, x_1; nitrobenzene molalities, m; initial freezing points, T; freezing-point depressions, ϑ; deviations, $10^4 \delta x_1$. [b] The temperature 290.23 appears in brackets because it is an extrapolated value.

nitrobenzene, reported in the sixth column of Table I. This value of λ_{I} is consistent with our own previous data (*7*) on several sulfolane solutions, whose initial freezing points fall in the temperature range 301.61–288.61 K, and with Garney and Prue (*6*) cryoscopic measurements.

Let us introduce into eq 4 the numerical values Θ = 301.61 and $\lambda_{\mathrm{I}} = \alpha/A_1 = 1.8488 \times 10^{-3}$ and let us suppose ΔC_p = 0 according to the supposition of no loss of rotational freedom of sulfolane molecules on solidification. Then eq 5 is derived,

$$\vartheta = 65m - 17.914m^2 + 5.015m^3 - 1.409m^4 \qquad (5)$$

which allows us to calculate the solvent freezing-point depressions of sulfolane solutions as a function of solute molalities, on the supposition of ideal behavior.

In Table II experimental ϑ values for sulfolane solutions of nitrobenzene are compared with those calculated by eq 5. The difference between the two sets of values only exceptionally exceeds experimental error, 0.02ϑ, as expected, affording further evidence for the supposition that nitrobenzene and sulfolane solutions behave ideally.

If numerical values of ϑ and A_1 are introduced into eq 2, the expression

$$\ln a_1 = (-1.8488 \times 10^{-3})[\vartheta + (3.3155 \times 10^{-3})\vartheta^2 + (1.0993 \times 10^{-5})\vartheta^3 + (3.6447 \times 10^{-8})\vartheta^4] \qquad (6)$$

is derived, which enables us to calculate the activities of the solvent as a function of ϑ for any kind of sulfolane solution.

In the case of nitrobenzene solutions, the calculated activities of the solvent, as a function of molar fraction, are reported in Table I together with the rational activity coefficients $f_{x_1} = a_1/x_1$. They exhibit slight departures from unity, never exceeding 1/10000, as expected.

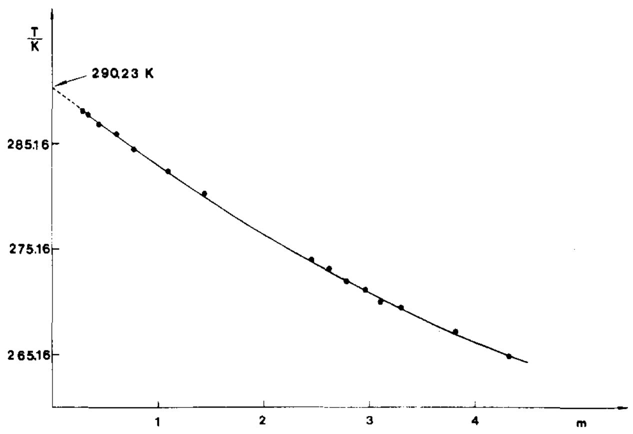

Figure 6. Initial freezing points, T, as a function of molality, m, of sulfolane (1)–nitrobenzene (2) mixtures in equilibrium with sulfolane crystal II.

Solutions in Equilibrium with Crystal II. The handling of cryoscopic data concerning solutions in equilibrium with crystal II (Table II) is more difficult since no thermal data concerning the transition process are reported in the literature; furthermore, in this case, we may not adopt the position ΔC_p = 0 because the transition, at 288.61 K, has to be regarded as an orientational fusion. Therefore, we adopted the following treatment of the experimental data. Let us assume that 290.23 K is the virtual melting temperature of crystal II, as taken from extrapolation, at m = 0, of initial freezing points of sulfolane solutions of nitrobenzene as a function of molality (Figure 6). The choice of this temperature is supported by our previous data (*7*) on selected sulfolane solutions. On the other hand, the statement that sulfolane–nitrobenzene solutions behave ideally supports the position that, in eq 2, $\ln a_1 = \ln x_1$ for solutions in equilibrium with crystal II. Then we introduced into eq 2 the values of Θ = 290.23, the freezing-point depressions ϑ calculated starting from 290.23 K, and the values of molar fractions of the solvent $x_1 = a_1$. From the equation

$$\ln x_1 = A_1'[\vartheta + (3.4455 \times 10^{-3})\vartheta^2 + (1.1872 \times 10^{-5})\vartheta^3 + (4.0905 \times 10^{-8})\vartheta^4] + (\Delta C_p'/R)[(5.9359 \times 10^{-6})\vartheta^2 + (2.7270 \times 10^{-8})\vartheta^3 + (1.05704 \times 10^{-10})\vartheta^4] \qquad (7)$$

the values of $A_1' = -0.015625$ and $\Delta C_p'/R = -5.4715$ are derived by a least-squares computer program. From A' the cryoscopic constant of crystal II, λ_{II} = 7.69 kg mol^{-1} K, is calculated, which agrees well with our previous data on selected sulfolane solutions in equilibrium with crystal II. Similary, the value of $\Delta C_p' = C_p(\text{crystal II}) - C_p(\text{liquid}) = -10.87$ is in good agreement with current values of ΔC_p on melting of complex molecules. Table II illustrates this, as eq 7 reproduces experimental x_1 values with deviations δx_1 never exceeding 6‰.

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Isothermal Vapor–Liquid Equilibria for the Propane–Propylene–Tetralin System

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Total-pressure data are obtained for the binary systems propane–propylene, propane–tetralin, and propylene–tetralin and for the ternary propane–propylene–tetralin system at 273.15 and 293.15 K. Experimental total pressures are compared with calculated values by the NRTL equation ($\alpha = -1$). The root mean square deviations in relative pressures are 0.11–0.95%.

Introduction

Vapor–liquid equilibrium data are useful not only for the design of separation processes but also for the study of the properties of solutions of liquid mixtures. It is also important to know the behavior of solutions for systems which are difficult to separate by distillation.

This paper presents the total pressures for the binary systems propane–propylene, propane–tetralin, and propylene–tetralin and for the ternary propane–propylene–tetralin system at 273.15 and 293.15 K. Data for the binary systems are correlated by the NRTL equation, and the predicted values for the ternary system are calculated by using the binary parameters and compared with observed values.

Experimental Section

The total pressures are measured by the static method, and the experimental apparatus and procedure were similar to those of the previous paper (*1*), except for the vapor-phase recirculation by magnetic pump. Pressure measurements were made with a Bourdon pressure gauge which was calibrated with a dead-weight gauge and are reproducible to within ±1 kPa. The equilibrium cell was immersed in a water bath and controlled by a thermostat with a cooling unit. The temperature of the water bath was determined by using a mercury-in-glass thermometer which was calibrated with a standard one in the National Research Laboratory of Metrology, Japan, and maintained within ±0.02 K.

The liquid mole fraction was evaluated from the total (liquid + vapor) weight of each material and their respective material balance in the liquid and vapor phases. The compositions of the vapor phases were first calculated from Raoult's law and then by the iterative calculation procedure discussed later, until successive iterations yielded almost the same values ($\Delta x < 0.0001$). That of tetralin could be neglected because of the very low concentrations in the range of this experiment. The liquid compositions were estimated within ±0.001.

Research-grade propane (99.9 vol %) and propylene (99.7 vol %) purchased by Takachiho Kagaku Kogyo were used without further purification, and commercially available guaranteed-reagent tetralin was used after further purification in a laboratory distillation column where only the middle half of the distillate was recovered. The boiling point of distilled tetralin was 341.05 K at 0.8 kPa and $n^{20}_{\mathrm{D}} = 1.5412$. (The literature values are 0.77 kPa at 341.05 K (*2*) and $n^{20}_{\mathrm{D}} = 1.54135$ (*3*), respectively.)

Results and Discussion

Experimental results for the binary systems are presented in Table I, and those for the ternary system in Table II. The results for the propane–tetralin and propylene–tetralin systems are shown in Figure 1.

The equilibrium equation for each component i containing a vapor phase and a liquid phase, both at the same temperature T and total pressure P, is

$$\phi_i y_i P = \gamma_i x_i \phi_i^{\mathrm{s}} P_i^{\mathrm{s}} \exp\{(P - P_i^{\mathrm{s}}) v_i / RT\} \qquad (1)$$

where ϕ_i is the vapor-phase fugacity coefficient, γ_i is the liquid-phase activity coefficient, P_i^{s} is the pure-component vapor pressure, and v_i is the pure-component saturated liquid volume. The fugacity coefficient ϕ_i is given by

$$\ln \phi_i = \frac{2}{v} \sum_{j=1}^{N} y_j B_{ij} - \ln z \qquad (2)$$

To correlate the vapor–liquid equilibrium data, it is necessary to evaluate the liquid activity coefficients. From the many expressions which have been reported by several investigators (*4–6*), the NRTL equation, where the nonrandomness parameter α is equal to -1 (*7*, *8*), was chosen. The excess Gibbs free energy is given by

$$\frac{g^E}{RT} = \sum_{j=1}^{N} x_j \sum_{i=1}^{N} \frac{x_i w_{ji}}{\sum_{k=1}^{N} A_{ki} x_k} \qquad (3)$$

The liquid activity coefficient is expressed in the form of

$$\ln \gamma_i = \sum_{j=1}^{N} x_j \left[\frac{w_{ji}}{\sum_{k=1}^{N} x_k A_{ki}} + \frac{w_{ij}}{\sum_{k=1}^{N} x_k A_{kj}} - \sum_{l=1}^{N} \frac{x_l w_{jl} A_{il}}{(\sum_{k=1}^{N} x_k A_{kl})^2} \right] \qquad (4)$$

where

$$A_{ij} = \exp(-w_{ij}) \qquad (5)$$

The parameters w_{ij} were determined in such a way that the summation of the difference between calculated and experi-