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SOLID–LIQUID PHASE DIAGRAM OF THE BINARY SYSTEM PYRIDINE + SULFOLANE *

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ABSTRACT

Solid–liquid equilibrium temperatures were measured for the binary system pyridine(1) + sulfolane(2) over the entire composition range $0 \leqslant x \leqslant 1$. Solid solutions were observed in the region in which solutions are in equilibrium with mesomorphic sulfolane (crystal I) and a partition coefficient ($K = 0.88$) was calculated. The phase diagram exhibits a eutectic at $T = 216.4$ K and $x_2 = 0.257$. For solutions in equilibrium with sulfolane ordinary crystal II, an equation was elaborated for calculating the activities of sulfolane by a series expansion of initial freezing point depressions ϑ. This equation was found to be capable of reproducing values of x within a few p.p.h. over a very large temperature range: 290.23–216.4 K.

On this basis the binary system pyridine(1) + sulfolane(2) may be classified as a "regular" system, in which low enthalpies of mixing counterbalance excess entropies to minimize the excess free energy. This is also in accordance with our previous measurements of other excess properties (ε^E, V^E, etc.).

INTRODUCTION

Previous measurements of excess properties (enthalpies, volumes and dielectric constants) of the pyridine–sulfolane system [1] over the entire composition range at selected temperatures, indicate the "regular" behavior of these mixtures. Volume contractions do not exceed the values usually found in the literature [2] for solutions of components with similar volumes but different molecular geometry; positive deviations of dielectric constants and negative deviations from ideality of mixing enthalpies exhibit a low maximum (dielectric constants) and a low minimum (enthalpies), roughly at the same composition, in pyridine-rich solutions; the maximum decreases in magnitude with increasing temperature in accordance with the above-mentioned exothermic effect. All available data support the supposition that interactions, presumably dipolar, between unlike molecules are of very

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* Dedicated to Professor E.F. Westrum, Jr., in honour of his contribution to calorimetry and thermal analysis.

limited importance. The steric hindrance of the globular sulfolane molecule prevents strong interactions of any kind, despite the fairly high dipole moment (4.8 D). On the other hand, any self-association by pyridine should be reduced by the moderately high dielectric constant of the medium, ranging from 12 (pyridine) to 43 (sulfolane).

The melting points of the substances (−41.7 °C for pyridine and 28.45 °C for sulfolane) differ markedly from each other (~ 70 °C); hence the system appears particularly suitable for explorations over a large temperature range, over which solutions of pyridine in sulfolane are in equilibrium with the different crystalline forms of sulfolane, corresponding to the different stability domains. As reported in the literature, sulfolane solidifies at 28.45 °C to give a rotational crystal I, which undergoes a transition to the ordinary crystal II at 15.45 C. Literature reports [3] that some changes in the wide line H–NMR spectrum of sulfolane at approximately −63 °C could be indicative of another transition at this temperature have not yet been validated by thermal analysis.

We report herein data concerning solid–liquid equilibrium temperatures for the system pyridine(1) + sulfolane(2) over the entire composition range $0 \leqslant x \leqslant 1$.

EXPERIMENTAL SECTION

Materials, apparatus and procedure

Sulfolane, kindly supplied by Shell Italia, was purified and carefully dried, as previously reported [4]. Properties of the purified sample were found to agree closely with the most reliable literature data and with our own previous data (Table 1).

Pyridine was dried with sodium hydroxide and repeatedly distilled from barium hydroxide. The middle fraction was stored in dark bottles, taking

TABLE 1

Description and physical properties [a] of component liquids

Substance	Source	T (K)	V (cm^3 mol^{-1})		ε		m_p (K)	
			Observed	Literature	Observed	Literature	Observed	Literature
Pyridine	Carlo	293.16	80.4536	80.454	13.621	13.4 [5]	231.46	231.49
	Erba	323.16	83.025	–				231.61
Sulfolane	Shell	303.16	95.215	95.160	43.16	43.30 [4]	301.61	301.61
	Italia	313.16	95.852	95.200	42.10	42.05		
						42.12		

[a] T, Temperature; V, molar volume; ε, dielectric constant; m_p, melting point.

any care to avoid contamination with moisture. In Table 1 the physical properties of the sample are compared with literature data [5].

Solutions were prepared by weight in a moisture-free environment. The apparatus and procedure adopted in measuring liquid–solid equilibrium temperatures have been described elsewhere [4]. The low temperatures were provided by freezing mixtures of acetone and solid carbon dioxide or, where lower temperatures were needed, by liquid nitrogen. The freezing liquids were circulated in a glass jacket around the cryostat.

Temperatures were measured with a Leeds and Northrup Model G2 Mueller bridge coupled with NBS platinum resistance thermometers. This assembly allowed an accuracy of 0.001 K over most of the temperature range. This accuracy was reduced for the lower temperatures, however, even if frequent calibration of thermometers was performed at fixed points. In evaluating the temperature from the measured resistance the cubic term was disregarded. Both cooling and heating curves were taken for each solution; initial freezing temperatures and final melting temperatures of each solution agreed to within 0.01 K.

For the sake of consistency with previous works, sulfolane is described as component 2, but where needed, in order to avoid misunderstanding between solvent 1 and substance 1 and solute 2 and substance 2, we indicate the mole fraction, activity and rational activity coefficients of sulfolane and pyridine as x_s, a_s and γ_s, and x_p, a_p and γ_p, respectively.

RESULTS AND DISCUSSION

In Tables 2 and 3 cryoscopic data are given for solutions of pyridine in sulfolane in equilibrium with sulfolane crystals I (Table 2) and II (Table 3). Data on solutions of sulfolane in pyridine in equilibrium with solid pyridine are presented in Table 4.

From the data in Tables 2–4, the solid–liquid phase diagram for pyridine(1) + sulfolane(2) was generated (Fig. 1). The diagram is characterized by an eutectic point at 216.4 K and 0.257 x_2. As reported previously, pure sulfolane exhibits a mesomorphic plastic phase in the region 301.6–288.5 K. The transition temperature to the ordinary crystal II is lowered ($T_t = 287.6$) by the presence of pyridine, supporting the supposition that solid solutions are formed. Moreover, the molar freezing point depressions of sulfolane, ϑ_m for pyridine solutions in equilibrium with sulfolane crystal I may be extrapolated, for molarity $m = 0$, to $\vartheta_{m,0} = 56$, lower than the cryoscopic constant ($\lambda_1 = 65$). Hence a value of 0.87 for the partition coefficient of the solute between the liquid and the rotational solid phase may be calculated. In Table 2, the partition coefficients corresponding to each composition are presented. They were calculated from the actual depressions ϑ and from the ideal depressions ϑ_{id} of the solvent freezing

TABLE 2

Cryoscopic behavior of sulfolane solutions of pyridine in equilibrium with crystal I [a]

x_s	m	ϑ	ϑ_m	K
1.0000	0.0000	–		
0.9992	0.0070	0.456	65.143	1.004
0.9983	0.0143	0.842	58.881	0.909
0.9973	0.0223	1.337	59.955	0.928
0.9963	0.0310	1.743	56.226	0.872
0.9948	0.0432	2.456	56.852	0.885
0.9931	0.0432	3.168	55.096	0.861
0.9911	0.0749	4.069	54.328	0.853
0.9901	0.0836	4.613	55.179	0.868
0.9821	0.1518	8.153	53.709	0.861
0.9798	0.1713	9.289	54.227	0.874
0.9770	0.1970	10.602	53.817	0.873
0.9747	0.2158	11.620	53.846	0.878
0.9738	0.2238	11.945	53.374	0.872
0.9730	0.2311	12.439	53.825	0.881
0.9719	0.2402	12.932	53.838	0.883
0.9709	0.2493	13.258	53.181	0.874
0.9698	0.2591	13.860	53.493	0.882
0.9689	0.2671	14.363	53.774	0.888

[a] x_s, sulfolane mole fraction; m, pyridine molarity; ϑ, freezing point depression; ϑ_m, molar freezing point depression; K, partition coefficient.

point calculated using the equation

$$\vartheta_{id} = 65m - 17.914m^2 + 5.015m^3 - 1.409m^4 \qquad (1)$$

The coefficients of eqn. (1) were drawn from thermal data (ΔH, Θ, etc.) for pure sulfolane, disregarding the tiny difference (if any) between the heat capacities of the liquid and the mesomorphic solid phase of sulfolane owing to the molecular disorder of crystal I [6]. The reliability of eqn. (1) in reproducing experimental data for ideal solutions was tested with a set of solutions of nitrobenzene [7] in sulfolane. This binary system behaves regularly, i.e. the excess entropy and the mixing enthalpy [8] counterbalance each other to minimize the excess free energy; hence activities are equivalent to mole fractions.

For solutions of pyridine in sulfolane in equilibrium with the "ordinary" crystal II, the initial freezing points, as a function of sulfolane mole fraction x_2, lie on a continuous curve, which at $T = 216.4$ K and $x_2 = 0.257$ crosses the line representing the cryoscopic behavior of solutions of sulfolane in pyridine. This continuous curve gives, on extrapolation to $x_2 = 0$, the theoretical melting point of sulfolane crystal II as 290.23 K. Indeed, during some experiments carried out with the aim of demonstrating the transition of sulfolane crystal II to crystal III, liquid sulfolane subjected to rapid

TABLE 3

Cryoscopic behavior of solutions of pyridine in sulfolane in equilibrium with sulfolane crystal II [a]

T_f (K)	ϑ	x_s			Δx_s ($\times 10^4$)
		exp.	calculated		eqn. (4)
			eqn. (3)	eqn. (4)	
290.230	0	1	1	1	
288.184	2.046	0.9677	0.9685	0.9686	−9
288.056	2.184	0.9651	0.9664	0.9665	−14
287.968	2.262	0.9640	0.9652	0.9653	−13
287.840	2.390	0.9622	0.9633	0.9634	−12
287.691	2.539	0.9610	0.9610	0.9611	−1
287.554	2.676	0.9581	0.9589	0.9591	−10
287.120	3.110	0.9527	0.9524	0.9526	1
286.597	3.633	0.9452	0.9446	0.9447	5
286.320	3.910	0.9416	0.9405	0.9406	10
285.542	4.688	0.9304	0.9290	0.9291	13
280.350	9.880	0.8520	0.8553	0.8546	−26
276.837	13.393	0.8131	0.8083	0.8066	65
268.008	22.222	0.6999	0.6994	0.6943	56
262.118	28.112	0.6287	0.6337	0.6257	30
259.094	31.136	0.5866	0.6020	0.5923	−57
255.877	34.353	0.5579	0.5698	0.5582	−3
253.328	36.902	0.5278	0.5452	0.5322	−44
251.425	38.805	0.5095	0.5275	0.5133	−38
241.128	49.102	0.4178	0.4396	0.4184	−6
240.358	49.872	0.4094	0.4336	0.4127	−33
239.458	50.772	0.4011	0.4266	0.4052	−41
238.198	52.032	0.3925	0.4170	0.3948	−23
237.018	53.212	0.3837	0.4081	0.3853	−16
236.068	54.162	0.3743	0.4011	0.3777	−36
234.658	55.572	0.3646	0.3909	0.3667	−21
230.098	60.132	0.3293	0.3593	0.3325	−32
228.128	62.102	0.3171	0.3464	0.3185	−14
226.518	63.712	0.3054	0.3360	0.3074	−20
225.228	65.002	0.2992	0.3280	0.2986	6
223.328	66.902	0.2855	0.3164	0.2861	−6
222.208	68.022	0.2801	0.3097	0.2789	12
221.028	69.202	0.2733	0.3028	0.2714	19

[a] Symbols as in Table 2. T_f, initial freezing point of sulfolane.

cooling solidifies directly to crystal II at 290.23 K. Unfortunately, no real evidence of the transition of crystal II to crystal III could be detected, even from very accurate thermal analysis (using freezing and heating curves of pure sulfolane), presumably because of the very low thermal effect predicted for this transition. Also, the eutectic point at 216.4 K is roughly coincident with the hypothetical transition temperature (~ 210.16 K), making it very

TABLE 4

Cryoscopic behavior of solutions of sulfolane in pyridine [a]

m_s	T_f (K)		T_E (K)	x_s
	Obs.	Calc. (eqn. (5))		
0	231.46	231.46		0
0.0478	231.36	231.36		0.00377
0.1078	230.96	230.96		0.00845
0.1237	230.87	230.89		0.01008
0.2583	230.30	230.30		0.02002
0.3689	229.94	229.85		0.02835
0.4437	229.34	229.35		0.03391
0.4968	229.43	229.34		0.03781
0.5347	229.30	229.20		0.04058
0.8037	228.18	228.25		0.05978
1.0846	228.77	227.37		0.07901
1.2448	227.17	226.93		0.08960
1.4266	226.36	226.49	216.5	0.1014
1.7724	224.98	225.79	216.2	0.1229
2.1355	224.41	225.27	216.3	0.1445
2.8452	221.41	224.89	216.5	0.1837

[a] m_s, molality of sulfolane; T_f, initial freezing point of sulfolane; T_E, eutectic temperature; x_s, mole fraction of sulfolane.

difficult to differentiate between the position of the eutectic and that of the presumed solidification of sulfolane to crystal III. In either case the temperature is likely to remain constant owing to the simultaneous presence of three different phases, liquid + sulfolane, crystal III + solid pyridine or liquid + crystal II + crystal III.

However, pyridine solutions in sulfolane with freezing points ranging between the transition temperature and the eutectic temperature may reasonably be supposed to be in equilibrium with the "ordinary" sulfolane crystal II. Their initial freezing points T, which are included in Table 3 give, on extrapolation to $m = 0$, the theoretical melting point of sulfolane crystal II (290.23 K). From this temperature the freezing point depressions ϑ (Table 3) and the molar freezing point depressions ϑ_m were calculated for each composition.

An analytical treatment of cryoscopic data was adopted for the calculation of solvent activities, by means of an equation which was modified previously by one of the authors for nitrobenzene–sulfolane solutions.

As is well known, the activities of a solvent (or the mole fractions, in the case of ideal solutions) may be calculated by means of a series expansion of freezing point depressions ϑ of the kind

$$\ln a_1 = \sum_{i=1}^{n} A_i \vartheta_i \qquad (2)$$

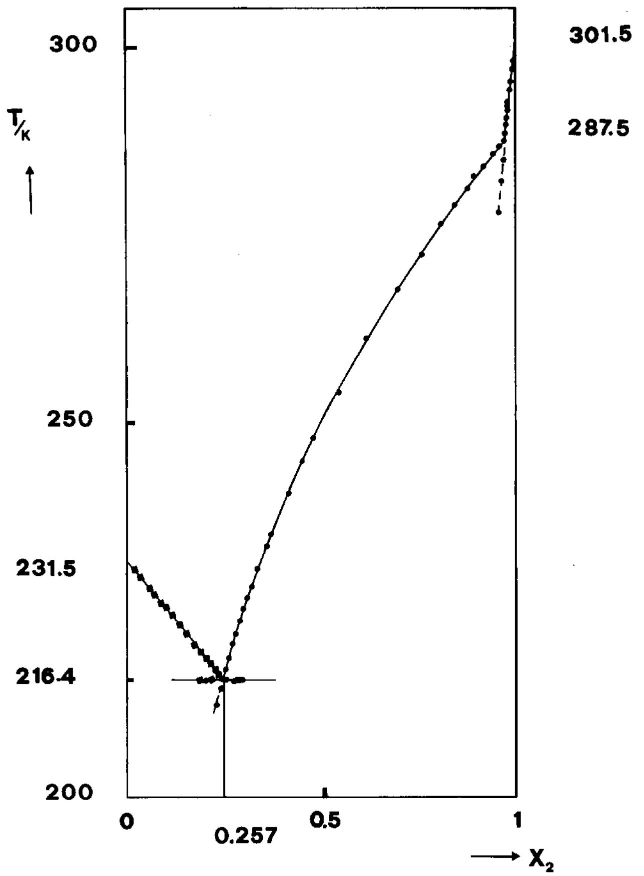

Fig. 1. Phase diagram for pyridine + sulfolane. ●, equilibrium temperatures liquid–solid sulfolane (crystal I or crystal II); ■, equilibrium temperatures liquid–solid pyridine; - - - - - -, metastable equilibria.

where

$$A_i = \frac{i \Delta H \Theta}{R \Theta^{i+1}} - \frac{i-1}{i} \frac{\Delta C_p}{R \Theta^2} \tag{2a}$$

The coefficients of eqns. (2) and (2a) may be drawn from thermal data concerning the solvent, but in the case of sulfolane no data are reported in the literature for ΔC_p ($= C_{p,\text{solid}} - C_{p,\text{liquid}}$).

Nevertheless, we can calculate values of activities for ideal solutions, where they are exactly coincident with mole fractions, (e.g. nitrobenzene(1) + sulfolane(2)) by using $\Delta C_p = 0$ in eqns. (2) and (2a) for solutions in equilibrium with crystal I, and $\Delta C_p = -10.87$ for solutions in equilibrium with crystal II. In the latter case the equation

$$\begin{aligned} \ln a_1 = {} & -0.01551[\vartheta + 3.4455 \times 10^{-3}\vartheta^2 + 1.1872 \times 10^{-5}\vartheta^3 \\ & + 4.0905 \times 10^{-8}\vartheta^4] + 5.472[5.936 \times 10^{-6}\vartheta^2 + 2.727 \times 10^{-8}\vartheta^3 \\ & + 1.057 \times 10^{-10}\vartheta^4] \end{aligned} \tag{3}$$

was proposed for the calculation of activities of the solvent from cryoscopic data. This equation was also utilized successfully with dimethyl sulfoxide(1) + sulfolane(2) mixtures [9].

In the case of pyridine solutions in sulfolane, activities, calculated by eqn. (3) (Table 3) differ more and more from mole fractions x_s with increasing ϑ. Positive deviations $a_s - x_s$ exceeding 10% might be ascribed to a departure from ideality of the system as well as to the inadequacy of eqn. (3) in reproducing experimental data, owing to the large temperature range between the theoretical melting point of crystal II (290.23 K) and the eutectic temperature (216.4 K). Over such a range the dependence of ΔC_p on temperature as well as the contribution of terms in the series expansion involving powers of $\vartheta > 4$ may no longer be disregarded. For these reasons eqn. 3 was modified to give

$$\begin{aligned}\ln a_1 = \ln x_1 = {} & -1.5511 \times 10^{-2}(\vartheta + 3.4455 \times 10^{-3}\vartheta^2 + 1.1872 \times 10^{-5}\vartheta^3 \\ & + 4.0905 \times 10^{-8}\vartheta^4 + 1.4094 \times 10^{-10}\vartheta^5 + 4.8561 \times 10^{-13}\vartheta^6) \\ & + 2.5857(5.9359 \times 10^{-6}\vartheta^2 + 2.7270 \times 10^{-8}\vartheta^3 \\ & + 1.0570 \times 10^{-10}\vartheta^4 + 3.8849 \times 10^{-13}\vartheta^5 \\ & + 1.3943 \times 10^{-15}\vartheta^6) \end{aligned} \qquad (4)$$

Taking account of the expected decrease in ΔC_p with decreasing temperature, the value of ΔC_p in eqn. (4) which best fits the experimental data is

$$C_{p,\,\text{solid}} - C_{p,\,\text{liquid}} = -2.5857 \times 1.986 = -5.135$$

Experimental values of x_s and those calculated using both eqns. (3) and (4) are recorded in Table 3, for ease of comparison.

These results are consistent with the classification of the system as being a "regular" mixture, as well as with the assumption that there are only very moderate interactions between the components.

Now we turn our attention to the left-hand side of the phase diagram (Fig. 1), where liquid solutions, with composition ranging from 0 to 0.257 x_s, are in equilibrium with solid pyridine. Related cryoscopic data are summarized in Table 4.

The initial freezing points of solutions in equilibrium with solid pyridine may be reproduced, within a few p.p.h., by

$$T_f = 231.46 - 4.67\, m + 0.831\, m^2 \qquad (5)$$

where 231.46 K and 4.67 are the melting point and cryoscopic constant of pyridine respectively. Both these values are in good agreement with values in the literature [5] ($T_f = 231.49-231.61$ K, $\lambda = 4.75$). On the whole, literature data on solid–liquid phase diagram pyridine(1) + sulfolane(2) give evidence for only slight deviations from ideality of the system, in spite of the fairly high polarity of the two components. This conclusion is consistent with the results of our own measurements of dielectric constants, volumes and enthalpies of mixing.

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