Thermodynamic and Physical Behaviour of Binary Mixtures Involving Sulfolane Viscosity, Dielectric Constant and Solid+Liquid Phase Diagram of Mixtures of Dioxane+Sulfolane

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Excess functions, $H^{\ddagger E}$, $S^{\ddagger E}$, $G^{\ddagger E}$ for activation of viscous flow, as well as the dielectric constants of dioxane (1) – sulfolane (2) mixtures were determined: slight negative deviations from ideality were observed in both cases, with a minimum at $x \approx 0.5$.

Solid-liquid equilibrium temperatures were also measured over the entire composition range. Solid solutions were observed in the region in which mesomorphic sulfolane is in equilibrium with the liquid.

Two phase diagrams may be drawn, in the region $0.33 \leqq x_2 \leqq 0.98$: one is of the simple eutectic type and the other exhibits two eutectics and a flat maximum corresponding to a 1 : 2 molecular compound, the occurrence of which is supposed to be caused by weak electrostatic attractions in a system of favorable crystal geometry rather than by bonding. A lessening of these interactions, with increasing temperature, would result in the liquid solution regular behaviour.

1. Introduction

The volumes of mixing[1] measured on some binary systems involving sulfolane (tetra-hydro-thiophene 1,1-dioxide) seem to point out that dioxane, owing to its molecular geometry, is more apt than carbon tetrachloride and benzene to give "regular" solutions with sulfolane.

To provide further information, solid-liquid equilibrium temperatures, dielectric constants and viscosities were measured on dioxane(1) – sulfolane(2) mixtures over the entire composition range (the latter two at 303.15, 313.15 and 323.15 K).

2. Experimental

Sulfolane, kindly supplied by Shell Co. Industrial Chemical Division, was carefully purified and dried as already reported[2]; dioxane, Fluka high purity, was fractionally distilled, carefully dried over sodium metal and then once more fractionally distilled [$\varepsilon(25\ ^\circ\text{C}) = 2.204$; freezing point $= 11.74\ ^\circ\text{C}$; both in good agreement with previous data[3, 4]].

Solutions were made by weight (corrected to mass) in a dry-box.

The apparatus and procedure, adopted in measuring viscosity, dielectric constant and solid-liquid equilibrium temperatures were described elsewhere[5].

Both cooling and heating curves were taken: the initial freezing temperatures of solutions were obtained by extrapolation across the undercooling region. The accuracy of solid-liquid equilibrium temperatures was estimated to be ±0.04 K for the pure substances and ±0.05 K for the mixtures; the invariant temperatures are to be considered accurate within ±0.06 K.

3. Results

Viscosities

The measured viscosities, $\eta_{1,2}$ (cP) at 303.15 313.15 and 323.15 K are summarized in Table 1. As known[6], transport properties may be correlated to the thermodynamic behaviour of solutions, on the supposition that viscous flow activation parameters: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ are additive functions for ideal solutions. Then the analysis of experimental data by the equation

$$\log \eta_{1,2} V_{1,2} = x_1 \log \eta_1 V_1 + x_2 \log \eta_2 V_2 \qquad (1)$$

shows slight negative deviations from ideality with a minimum at $x \approx 0.5$. Eyring's[7] theory predicts, moreover, linear plots of $\log(\eta_{1,2} V_{1,2})$ vs T^{-1}; from these plots $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated and $\Delta G^{\ddagger}$ derived, at 313.15 K (Table 1), for each composition.

Plots vs x_2 of the excess functions $H^{\ddagger E}$, $TS^{\ddagger E}$ and $G^{\ddagger E}$, are given in Fig. 1; they exhibit a minimum at $x \approx 0.5$.

Even if the low negative $S^{\ddagger E}$ values (never less than $-0.7\ \text{cal}_{\text{th}}/\text{K}$) may be considered as indicative

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Table 1. Viscosity and activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ of viscous flow for dioxane (1) — sulfolane (2) mixtures ($\mathrm{cal_{th}} = 4.184$ J).

T/K x_2	303.15 $\eta_{1,2}$/cP	313.15 $\eta_{1,2}$/cP	323.15 $\eta_{1,2}$/cP	$\Delta H^{\ddagger}$/$\mathrm{cal_{th}\ mol^{-1}}$	$\Delta S^{\ddagger}$/$\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$	$\Delta G^{\ddagger}$ (313.15 K)/$\mathrm{cal_{th}\ mol^{-6}}$
0	1.101	0.9403	0.8147	2707	−1.94	3315
0.0809	1.276	1.086	0.9369	2796	−1.96	3410
0.1742	1.517	1.284	1.104	2900	−1.97	3517
0.2786	1.854	1.558	1.332	3035	−1.94	3643
0.3855	2.293	1.912	1.622	3197	−1.85	3776
0.4739	2.756	2.280	1.922	3340	−1.76	3891
0.5744	3.428	2.809	2.348	3524	−1.61	4028
0.6247	3.841	3.130	2.605	3626	−1.51	4099
0.7169	4.786	3.861	3.182	3826	−1.31	4236
0.8462	6.656	5.275	4.278	4161	−0.88	4437
0.9062	7.852	6.164	4.942	4365	−0.55	4537
1	10.295	8.007	6.346	4640	−0.19	4700

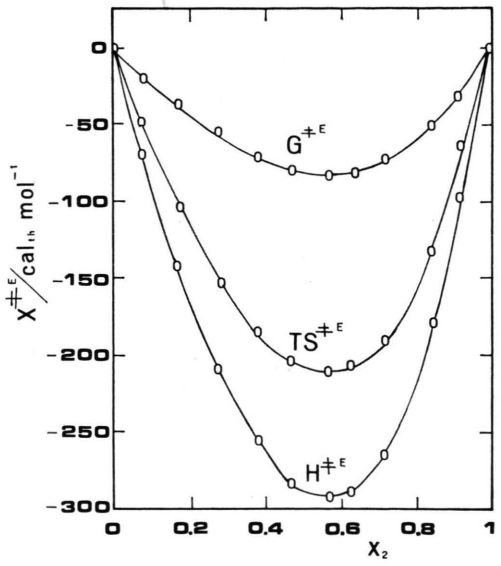

Fig. 1. Excess viscous flow activation functions $X^{\ddagger E}$ plotted against mole fraction X_2 for dioxane (1) + sulfolane (2).

of some local order, the negative values of the function $G^{\ddagger E} = H^{\ddagger E} - TS^{\ddagger E}$ seem rather to preclude[8] strong interactions between unlike molecules, at least in the studied composition and temperature ranges.

Experimental data have also been analysed by the equations[9]:

Dolezalek[9a]

$$\eta_{1,2} = x_1^2\,\eta_1 + x_2^2\,\eta_2 + 2\,x_1\,x_2\,d\,; \tag{2}$$

Ubbelohde et al.[9b]

$$f(\eta_{1,2}) = x_1 f(\eta_1) + x_2 f(\eta_2)\,;\quad f(\eta) = 1/\eta \text{ or } \log\eta\,; \tag{3}$$

Van der Wijk[9c]

$$\ln\eta_{1,2} = x_1^2 \ln\eta_1 + x_2^2 \ln\eta_2 + 2\,x_1\,x_2\,d\,; \tag{4}$$

Grünberg and Nissan[9d]

$$\ln\eta_{1,2} = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1\,x_2\,d\,; \tag{5}$$

Tamura and Kurata[9e]

$$\eta_{1,2} = x_1\,\eta_1\,\varphi_1 + x_2\,\eta_2\,\varphi_2 + 2\,d\,(x_1\,x_2\,\varphi_1\,\varphi_2)^{1/2} \tag{6}$$

but no more significant results have been obtained, with the exception of a steady trend to decrease, with increasing temperature, of the Van der Wijk d term (Fig. 2), which might be related to the "exchange energy" between unlike molecules, by analogy with the second virial coefficient treatment.

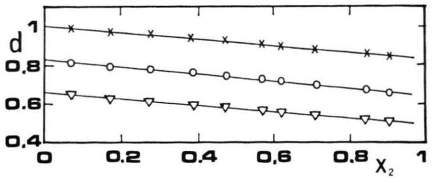

Fig. 2. Van der Wijk parameter **d** plotted against mole fraction X_2 for dioxane (1) + sulfolane (2); ×, 303.15 K; ○, 313.15 K; ▽, 323.15 K.

Dielectric Constants

The dielectric constants, $\varepsilon_{1,2}$, of the mixtures and the apparent dielectric constant of sulfolane [the latter calculated as $\bar{\varepsilon}_2 = (\varepsilon_{1,2} - \varepsilon_1\,\varphi_1)/\varphi_2$ i.e., supposing a linear dependence of $\varepsilon_{1,2}$, on the volume fraction φ_2, for ideal mixtures], are summarized in Table 2. Negative deviations from ideality are observed in Fig. 3, where $\varepsilon_{1,2}$, at 313.15 K is plotted vs φ_2. The quantity $\varepsilon^{E}_{1,2}$ exhibits a minimum at $x_2 \cong 0.5$, scarcely affected by temperature changes.

Table 2. Dielectric constants $\varepsilon_{1,2}$ of dioxane (1) — sulfolane (2) mixtures; apparent dielectric constants $\bar{\varepsilon}_2$ of sulfolane, and correlation parameters g.

T/K	303.15	313.15	323.15	303.15	313.15	323.15	303.15	313.15	323.15
x_2		$\varepsilon_{1,2}$			$\bar{\varepsilon}_2$			$g-1$	
0	2.200	2.185	2.172	—	—	—	0	0	0
0.0874	5.209	5.069	4.936	33.64	32.45	31.30	−0.14	−0.13	−0.13
0.1762	8.582	8.307	8.042	35.58	34.30	33.08	−0.15	−0.15	−0.14
0.2623	12.099	11.688	11.307	37.29	35.97	34.75	−0.14	−0.13	−0.12
0.3630	16.32	15.77	15.26	38.73	37.43	36.22	−0.12	−0.11	−0.11
0.4607	20.53	19.83	19.18	39.95	38.60	37.36	−0.11	−0.10	−0.09
0.5786	25.63	24.80	24.02	41.07	39.76	38.54	−0.09	−0.08	−0.07
0.6877	30.29	29.33	28.43	41.83	40.53	39.31	−0.08	−0.06	−0.06
0.7744	33.99	32.95	31.96	42.37	41.10	39.88	−0.07	−0.06	−0.04
0.9097	39.39	38.60	37.46	42.73	41.88	40.66	−0.06	−0.04	−0.03
1.0	43.38	42.12	40.71	43.38	42.12	40.71	−0.05	−0.04	−0.03

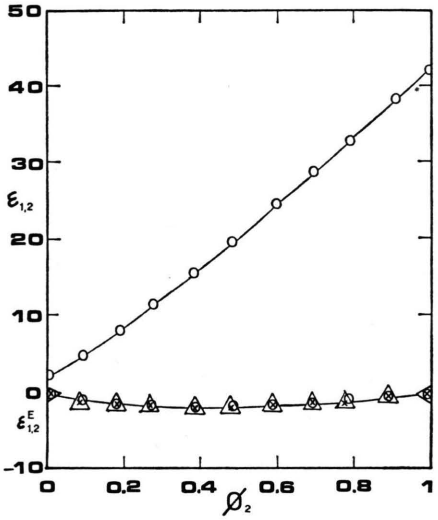

Fig. 3. Dielectric constant $\varepsilon_{1,2}$ and excess function $\varepsilon^E_{1,2}$ plotted against ideal volume fraction Φ_2 for dioxane (1) + sulfolane (2); ×, 303.15 K; ○, 313.15 K; ∇, 323.15 K.

From the $\bar{\varepsilon}_2$ values, the dipole moment μ_2 of sulfolane was calculated by the Mecke and Reuter equation[10], used in the simplified form suitable in the case of strong dipolar solutes in an inert solvent:

$$\mu^2 = (\bar{\varepsilon}_2 - n_2^2)\left(\frac{2+n_2^2}{\varepsilon_{1,2}}\right)\left(\frac{9\,\varepsilon_0\,k\,T\,V_2}{(n_2^2+2)^2\,L}\right) \cdot \left[1 + \frac{(\bar{\varepsilon}_2-\varepsilon_1)\,(n_2^2-\varepsilon_1)\,\varphi_1}{(2\,\varepsilon_{1,2}+\varepsilon_1)\,(\bar{\varepsilon}_2-n_2^2)}\right]$$

where n denotes the refractive index, ε_0 the permittivity in vacuum and $g=\mu_2/\mu_0^2$ is the correlation parameter ($\mu_0 = 4.9$, being the dipole moment[11] of sulfolane at infinite dilution).

The deviations from unity of the correlation parameter g (last three columns of Table 2) may be interpreted in terms of no strong interactions between unlike molecules, with the exception for dipole-dipole interactions.

Phase Diagram

The initial freezing temperatures of the mixtures over the entire composition range are summarized in Table 3 and Figure 4.

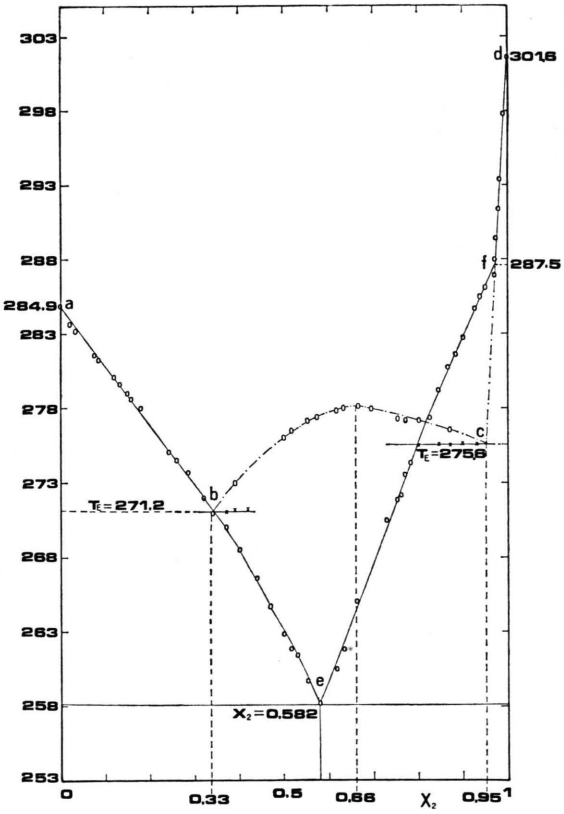

Fig. 4. Phase diagram for dioxane (1) + sulfolane (2).

Table 3. Freezing temperatures T_f of dioxane(1) — sulfolane(2) mixtures.

x_2	T_f/K	T_f/K	T_{Eu}/K
0.0	284.95		
0.0269	283.64		
0.0397	283.11		
0.0759	281.61		
0.0873	281.28		
0.119	280.14		
0.134	279.60		
0.150	279.06		
0.160	278.71		
0.178	278.02		
0.237	275.10		
0.255	274.54		
0.276	273.67		
0.325	271.88		
0.341	—	270.95	
0.369	—	269.97	270.85
0.392	273.06	—	271.15
0.402	—	268.52	
0.421	—	—	271.43
0.441	—	266.64	
0.474	—	264.77	
0.498	276.01	262.91	
0.516	276.53	261.84	
0.530	—	261.46	
0.555	277.19	259.73	
0.576	277.43	—	
0.582	—	258.17	
0.616	**277.88**	**260.47**	
0.634	277.99	261.79	
0.664	—	265.02	
0.666	278.03	—	
0.696	277.98	—	
0.730	—	270.46	
0.754	277.24	271.93	275.32
0.759	—	272.15	—
0.768	—	273.60	—
0.771	277.04	—	—
0.786	—	274.26	—
0.800	277.44	—	—
0.802	277.15	—	275.67
0.810	276.30	—	—
0.827	277.43	—	—
0.847	279.20	—	275.57
0.867	280.78	—	—
0.869	281.00	276.61	275.47
0.880	281.72	—	—
0.897	282.81		275.73
0.921	284.76		—
0.931	285.46		275.67
0.942	286.26		
0.969	287.05		
0.971	288.05		
0.973	289.41		
0.978	291.38		
0.982	293.35		
0.991	297.76		
1.0	301.6		

It is to be noted that a) pure sulfolane exhibits a mesomorphic plastic phase (I) in the region $301.6 + 288.5$ K[12]; b) in binaries involving at least one "globular" substance, able to give plastic crystals, the occurrence of a "double" phase diagram is a frequent feature[13].

In the present case the branches a – b and f – d (see Table 3 and Fig. 4) are common to both diagrams, whereas between b and f two sets of freezing points could be observed, mainly in dependence on the fact that the transition, sulfolane plastic phase I into crystalline non rotational phase II, occurs or otherwise is avoided by sudden cooling. In the former case (dashed line $\overline{\text{bcf}}$) two eutectics, at 271.2 K and $x_2 = 0.33$ and at 275.6 K and $x_2 = 0.95$, and a flat maximum in the region $0.61 \leqq x_2 \leqq 0.68$ could be evidenced, denoting the formation of a solid molecular compound (1:2 dioxane-sulfolane) which largely decomposes on melting. In the latter case (solid line $\overline{\text{bef}}$) a single eutectic, at 258.15 K and $x_2 = 0.582$, was observed.

The fact that the phase I → phase II transition temperature, 287.5 K, is lower than that of pure sulfolane supports the supposition that solid solutions are formed. Moreover, a plot (Fig. 5) of the sulfolane freezing point molar depression (ϑ/m) vs molality, for the solutions in equilibrium with sulfolane phase I, emphasizes that $(\vartheta/m)_0 = 54$, lower than the cryoscopic constant of sulfolane, 65[12], as expected.

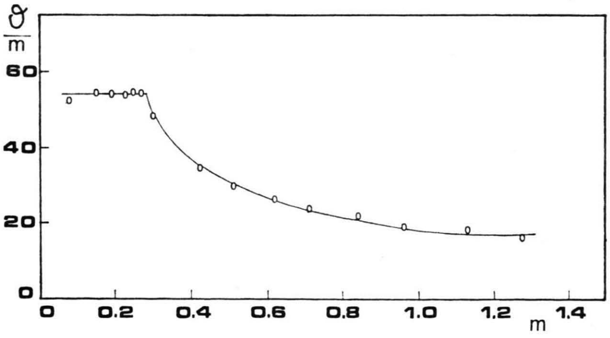

Fig. 5. Sulfolane freezing point molar depression vs dioxane molality.

4. Discussion

All collected data appear consistent with the supposition that the occurrence of a dioxane + sulfolane 1 : 2 compound results from a combination of a favourable packing geometry and weak electrostatic interactions. The fact that the compound separates from metastable liquid solutions where the transition "plastic crystals → ordinary crystals" is avoided by sudden cooling and the ability of dioxane to give mixed crystals with plastic sulfolane provide evidence to the above assumption.

The regular behaviour of liquid solutions, as well as the steady decrease of the Wijk "exchange energy" term with increasing temperature, could indicate a lessened tendency of molecules to interact[15].

It may be of some interest to call the attention on the fact that also in the case of dioxane – chloroform and dioxane – carbon tetrachloride systems two different phase diagrams were obtained and one of them, in both cases, revealed the presence of an AB_2 compound (A = dioxane).

In the case of the dioxane – chloroform system, the heats of mixing have been interpreted by McGlashan and Rastogi[16] in terms of H bonding involving the hydrogen of chloroform and the oxygens of dioxane, whereas in the case of the dioxane + carbon tetrachloride compound, the electronic character of the dioxane oxygens has been indicated by Goates etc.[17] as responsible for the compound formation.

The same authors have recently[18] studied the solid-liquid phase diagram of C_6F_6 + some cyclic mono- and di-ethers, as well as + 1,2-dimethoxyethane, attaining the conclusion that weak electrostatic attractions in a system of favorable packing geometry are a more likely explanation for compound formation.

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