Thermochimica Acta, 33 (1979) 19—24
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ACTIVITY COEFFICIENTS OF WATER AND SULFOLANE FROM THE SOLID + LIQUID PHASE DIAGRAM

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(Received 2 October 1978)

ABSTRACT

The solid + liquid phase diagram drawn from thermal analysis is presented. It exhibits a eutectic at $x_2 = 0.303$ and $T = 262.2$ K and precludes the existence of definite compounds between the two components. Mixed crystals are observed in the sulfolane-rich region. The activity coefficients of water, $f_{x,1}$, and of sulfolane, $f_{x,2}$, are calculated from the initial freezing points of water. Log $f_{x,1}$ and log $f_{x,2}$ show a steady dependence on volume composition, providing evidence for the supposition that strongly self-associated water and monomer sulfolane scarcely interact with one another, and that the thermodynamic properties of the mixtures should rather be related to steric factors.

INTRODUCTION

Published thermodynamic data [1—3] on water—sulfolane solutions are consistent with the idea that sulfolane plays the role of an almost inert diluent in spite of a fairly high dipole moment (4.8 D). To provide further information and complete the picture, a study of the solid + liquid phase diagram has been made.

EXPERIMENTAL

Materials

Sulfolane, supplied by the Shell Co. Division of Industrial Chemistry was purified as already described [4,5]; the conductivity of the purified sample did not exceed 10^{-8} Ω^{-1} cm^{-1}; its melting point was 28.45°C.

Twice-distilled water was again distilled in all-Pyrex apparatus over $KMnO_4$ at reduced pressure.

Solutions were made by weighing (corrected to mass) in a dry box. (For the sake of uniformity with previous literature, sulfolane is indicated as substance (2).)

Apparatus and procedure

Cryoscopic apparatus and procedure are described elsewhere [4,5]; solid + liquid equilibrium temperatures were measured by a Leeds and Northrup

Müller Bridge G2 and a NBS-certified platinum resistance thermometer.

Both cooling and heating curves were measured; in the case of cooling curves, the initial freezing points of solutions were obtained by extrapolation across the supercooling 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.

RESULTS

Figure 1 presents the liquid + solid phase diagram drawn from the thermal data summarized in Tables 1 and 2; it precludes the existence of definite compounds and exhibits a eutectic at $x_2 = 0.303$ and $T = 262.2$ K; accordingly a eutectic halt, at this temperature, occurs for solutions represented by a continuous line.

Solid sulfolane shows a transition at 287.09 K; previously [4,5] one of us has demonstrated that pure sulfolane solidifies at 301.68 K as a rotational phase I which undergoes a transition into a non-rotational solid phase II at 288.56 K.

The fact that the measured transition temperature is lower than that of pure sulfolane supports the supposition that water is still present in the solid phase I; furthermore (see Table 1 third column), the molal depressions θ/m_1 of the freezing point of sulfolane are lower than the cryoscopic constant

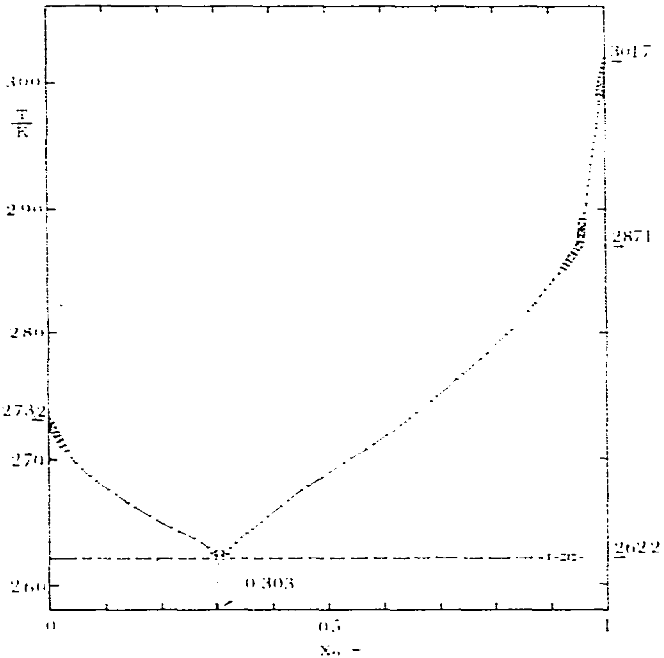

Fig. 1. Initial freezing temperature T (K) versus mole fraction, x_2, plots for water (1) + sulfolane (2) system.

TABLE 1

Initial freezing temperatures T (K) of sulfolane for water (1) + sulfolane (2) mixtures up to the eutectic composition

x_1	T (K)	θ/m_1 * (K kg mol^{-1})	x_1	T (K)	x_1	T (K)
0	301.58		0.0455	287.24	0.1537	281.02
0.0034	300.45	39.51	0.0477	287.15	0.1842	279.58
0.0063	299.34	42.18	0.0499	287.01	0.2126	278.34
0.0092	298.44	40.46	0.0520	286.86	0.2391	277.32
0.0121	297.51	39.86	0.0541	286.72	0.2717	276.04
0.0150	296.60	38.31	0.0545	286.66	0.3017	274.99
0.0178	295.67	39.09	0.0573	286.52	0.3359	273.85
0.0207	294.76	38.82	0.0616	286.25	0.3669	272.81
0.0235	293.85	38.61	0.0623	286.13	0.4210	271.13
0.0263	292.89	38.60	0.0668	285.92	0.4666	269.75
0.0319	291.18	37.98	0.0727	285.48	0.5055	268.59
0.0384	289.05	37.69	0.0730	285.44	0.5391	267.55
0.0433	287.74	36.69	0.0791	285.18	0.5818	265.95
0.0438	287.35	36.31	0.0852	284.75	0.6278	264.67
			0.1092	283.35	0.6727	263.10
			0.1320	282.10	0.6951	262.44

* Molal depressions θ/m_1 of freezing temperature of sulfolane on adding water refer to solutions in equilibrium with solid phase I.

$\lambda_I = 65$ (K kg mole^{-1}) [4,6], as expected [*]. Initial freezing points of solutions in equilibrium with solid phase II show a steady dependence on molality and allow us to calculate molal depressions of virtual melting temperature of solid phase II which, at $m_1 = 0$, check well with the cryoscopic constant $\lambda_{II} = 7.5$ (K kg mole^{-1}) [4,5] supporting the supposed absence of solid solutions.

We now turn to the water-rich region of the phase diagram (Table 2); from the depressions θ of the freezing point of water on adding sulfolane, the activities, a_1, of water have been calculated using the equation

$$\log a_1 = -4.2091 \times 10^{-3}\theta - 0.2152 \times 10^{-5}\theta^2 + 0.359 \times 10^{-7}\theta^3$$
$$+ 0.212 \times 10^{-9}\theta^4$$

the coefficients of which have been evaluated from thermal data on water [7]. The rational activity coefficients $f_{x,1} = a_1/x_1$ were then derived.

The molal depressions θ/m_2 are interpolated by the equation

$$\theta/m_2 = 1.8584 - 0.34758m_2 + 0.04335m_2^2 - 0.0024982m_2^3 + 0.0000509 4m_2^4$$

where 1.8584 is the cryoscopic constant λ of water; the osmotic coefficient $j = 1 - (\theta/\lambda m_2)$ can then be evaluated.

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[*] As already pointed out, plastic or liquid mixed crystals final and initial freezing points may not be identified by thermal analysis.

TABLE 2

Depressions θ of freezing temperature of water on adding sulfolane; molal depressions θ/m_2. Rational activity coefficients $f_{x,1}$ and $f_{x,2}$ of water (1) and sulfolane (2)

x_2	θ (K)	θ/m_2 (K kg mol^{-1})	$f_{x,1}$	$f_{x,2}$
0	0	1.8584	1	1
0.0012	0.119	1.82	1.00_0	0.97_8
0.0023	0.224	1.76	1.00_0	0.96_1
0.0061	0.568	1.67	1.00_0	0.90_0
0.0080	0.726	1.63	1.00_1	0.86_0
0.0095	0.846	1.59	1.00_1	0.83_6
0.0110	0.961	1.55	1.00_1	0.81_4
0.0160	1.314	1.45	1.00_2	0.74_6
0.0196	1.606	1.44	1.00_3	0.70_2
0.0203	1.868	1.42	1.00_4	0.66_4
0.0248	1.974	1.40	1.00_5	0.64_6
0.0272	2.142	1.38	1.00_6	0.62_3
0.0297	2.315	1.36	1.00_7	0.60_0
0.0327	2.515	1.34	1.00_8	0.57_4
0.0370	2.778	1.30	1.01_9	0.54_1
0.0402	2.963	1.27	1.01_1	0.51_8
0.0434	3.132	1.24	1.01_2	0.49_6
0.0465	3.295	1.21	1.01_4	0.45_9
0.0501	3.463	1.18	1.01_6	0.45_7
0.0543	3.670	1.15	1.02_8	0.43_5
0.0578	3.835	1.12	1.02_0	0.41_9
0.0619	3.999	1.09	1.02_2	0.40_0
0.0665	4.191	1.06	1.02_5	0.38_2
0.0720	4.395	1.01	1.03_8	0.36_2
0.0783	4.620	0.98	1.03_3	0.34_2
0.0844	4.901	0.96	1.04_8	0.32_5
0.0860	4.904	0.93	1.04_1	0.32_1
0.1005	5.290	0.85	1.05_3	0.29_0
0.1125	5.684	0.80	1.06_6	0.27_5
0.1298	6.215	0.75	1.08_2	0.25_0
0.1562	6.896	0.67	1.10_8	0.21_5
0.1864	7.625	0.60	1.14_1	0.20_1
0.2243	8.594	0.53	1.18_6	0.15_3
0.2684	9.694	0.47	1.24_4	0.12_4
0.2813	9.994	0.46	1.26_2	0.12_2

The equation

$$\log \gamma_2 = -0.4343j - 0.4343 \int_0^{m_2} j/m_2 \, \mathrm{d}m_2 + 0.2389 \times 10^{-3} \int_0^{\theta} \theta/m_2 \, \mathrm{d}\theta -$$

$$0.5976 \times 10^{-5} \int_0^{\theta} \theta^2/m_2 \, \mathrm{d}\theta$$

allows us to evaluate the molal activity coefficients γ_2 of sulfolane in water solutions.

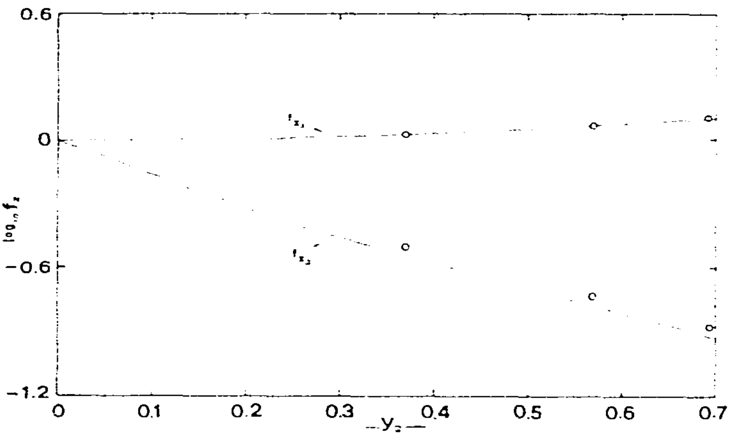

Fig. 2. Logarithms of rational activity coefficients, $f_{x,1}$ and $f_{x,2}$, versus volume fraction, y_2, plots, for water (1) + sulfolane (2) system. ———, this work; ○, Benoit and Choux.

From these values, the rational activity coefficients $f_{x,2}$ of sulfolane in water solutions have been derived. Both log $f_{x,1}$ and log $f_{x,2}$ versus volume composition, y_2, plots appear in Fig. 2 (continuous line). In the same figure activity coefficients drawn from vapor-pressure data [2] are also presented (open circles).

For the sake of comparison a standardisation of reference state was necessary because the reference state is pure sulfolane in the case of activity coefficients drawn from vapor pressures and an infinitely dilute solution in the case of cryoscopic data. The agreement between the two sets of data is satisfactory and provides evidence to support the supposition that solid solutions are absent in the water-rich region; at the same time, an appreciable uniformity of behavior in water—sulfolane solutions over a wide temperature range (263.16—353.16 K) may be claimed.

DISCUSSION

Previous data [8—10] on pure sulfolane and on its dilute solutions in mixed solvents show that sulfolane is never self associated even when its molecules are close-packed in the plastic crystals and this in spite of its high polarity. Furthermore sulfolane is characterized by a low autoprotolysis constant [11] and shows only a weak ability to be protonated or to give any kind of ion solvation. Evidently, owing to the steric hindrance of the globular molecule, the electrons around the $>SO_2$ group, which is the exposed negative end of the dipole, are not easily accessible to protons or to positive ions, whereas the positive charge, diffused over the whole ring, can only interact weakly.

On the other hand water is a strongly self-associated liquid in which each molecule is hydrogen-bonded to four neighbours; accordingly with this model Kirkwood and Oster calculated a dipole moment $\mu = 3.1$ D [12].

Strongly self-associated water has been demonstrated to predominate with respect to monomer molecules in water—sulfolane solutions which behave "regularly" over a wide temperature range (263.16 — 353.16 K).

Excess volumes of mixing [1], measured over the entire composition range, do not exceed 0.1 cm^3; on the other hand the occurrence of mixed crystals in the sulfolane rich region of the solid + liquid phase diagram is indicative of the similar shape and volume of molecules. Similarly, dielectric constants versus volume composition plots show positive deviations from linearity which only occasionally amount to 3% of the measured value and the water dipole moments in sulfolane solutions (3.0 D) which have been calculated by one of us [1] using an unproved method from dielectric constant data, do not differ noticeably from the Oster and Kirkwood value (3.1 D).

The low mixing enthalpies [3] counter-balance the ΔG^E terms drawn from vapor pressures when minimizing $T\Delta S^E$ terms. Therefore, water sulfolane solutions are regarded as microregions of strongly self-associated water dispersed in monomer sulfolane.

Within this general picture falls the behaviour of activity coefficients $f_{x,1}$ and $f_{x,2}$ drawn from cryoscopic measurements whose logarithms are smooth functions of volume composition, still affording evidence to the supposition that short range interactions between unlike molecules are of limited importance and deviations from ideality are to be ascribed essentially to steric factors and constraints on molecular shape.

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