J. Chem. Eng. Data **1980,** *25,* 77–79

Thermodynamic and Physical Behavior of Binary Mixtures Involving Sulfolane. Excess Volumes and Dielectric Constants of Sulfolane–Nitrobenzene Mixtures

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The volumes of mixing and dielectric constants of nitrobenzene–sulfolane mixtures were measured, at several temperatures ranging within 288.16–333.16 K, over the entire composition range. The observed deviations from ideality, decreasing with increasing temperature, are interpreted as not indicative of significant interactions between unlike molecules; autoassociation of nitrobenzene, in a small region close to pure substance, may not be quite excluded.

1. Introduction

Recently, increasing attention has been focused on mixtures of dipolar aprotic solvents, the physical and thermodynamic properties of which are useful for providing a basis for electrochemical studies, mainly in what concerns the interpretation of ion–solvent interactions. We present herewith the volumes on mixing and dielectric constants of nitrobenzene (1) and sulfolane (2) mixtures, over the entire composition range $0 \leq x \leq 1$, at several temperatures. The dielectric constants of the two pure substances are ϵ_1(303.16 K) = 33.8 and ϵ_2(303.16 K) = 43.4.[1] Both components, in spite of their fairly high dipole moments μ_1 = 4.0 D and μ_2 = 4.8 D, are weakly structured liquids with low authoprotolysis constants,[2] rather low donor ability[3] toward Lewis acids and metal ions, and quite negligible tendency to anion solvation.[4] Although their molar volumes do not differ greatly, i.e., $V_1°$(303.16 K) = 103.2 cm^3 mol^{-1} and $V_2°$(303.16 K) = 95.2 cm^3 mol^{-1},[5] their molecules are very different in shape; sulfolane is "globular" whereas nitrobenzene is flattened by resonance.

2. Experimental Section

Materials. Sulfolane, kindly supplied by Shell Italia, was carefully purified and dried as already reported;[6] its melting point was 301.61 K. Nitrobenzene, Fluka high purity, was dried over P_2O_5 and twice fractionally distilled under vacuum, mp 278.84 K, in close agreement with previous data.[7] Solutions were made by weight, with an accuracy of 0.1 mg (corrected to mass), in a drybox and protected from moisture as much as possible.

Apparatus and Procedure. Measurements of density and dielectric constant were made in the temperature range 288.16–333.16 K and over the entire composition range. The densities of solutions were measured by an Anton Paar DMA 60 digital densimeter thermostated by a Lauda ultrathermostat, which controlled the temperature within 0.005 K. The density determination is based on measuring the period of oscillation of a vibrating U-shaped tube which is filled with liquid sample. A calibration was needed with standard pure liquids, at each temperature. The maximum error in density was estimated to be 1×10^{-5} g cm^{-3}.

The dielectric constants were measured, at 2 MHz, by the heterodyne beat method, using a DM01 dipolmeter (Wissenchaftlich technische Werstätten Wilheim, West Germany). The thermostated measuring cells, DFL1/S and DFL2/S, were adequate to cover the dielectric constant range from 1 to 50. The cells were calibrated, at 298.16 K, with standard pure liquids in accordance with ref 8. The maximum error in dielectric constant was estimated to be 0.04.

3. Results and Discussion

Both molar volumes (Table I) and dielectric constants for pure components (Table IV) are in close agreement with the more reliable literature values.[1,5] The values for pure sulfolane, at temperatures lower than 301.61 K, appear in brackets because these are extrapolated values.

Volumes on Mixing. The excess volumes $V_{1,2}^E$ of the binary mixtures, at several temperatures, are plotted in Figure 1 vs. mole fraction of sulfolane, x_2. These excess volumes are all negative, never exceeding 0.26 cm^3 mol^{-1}, with a minimum slightly shifted toward the sulfolane richer region and decreasing in magnitude with increasing temperature. The results for the six sets of experiments were fitted by a least-squares computer program to the expression

$$V^E/\text{cm}^3\ \text{mol}^{-1} = x_1x_2\{A + B(x_2 - x_1) + C(x_2 - x_1)^2 + D(x_2 - x_1)^3\} \quad (1)$$

The parameters (A, B, C, D) listed in Table I are those based on the lowest values of $\sigma = [(\sum \delta V^E)^2/(s - m)]^{1/2}$, in which $\delta V^E = V^E(\text{exptl}) - V^E(\text{calcd})$, s is the number of experimental points, and m is the number of parameters; V^E and δV^E values, at all the measured temperatures and over the entire composition range, are given in Table II.

If eq 1 is differentiated with respect to x_1 and x_2, partial molar volumes of both the components may be calculated at each temperature. Relative partial molar volumes $\bar{V} - V°$ are summarized as a function of sulfolane mole fraction, x_2, in Table III. The magnitude of the V^E and the asymmetry of the volume

Table I. Molar Volumes of Nitrobenzene ($V°_1$) and Sulfolane ($V°_2$), Parameters A, B, C, and D, and Standard Deviations σ of the Smoothing Equations

T, K	$V°_1$, cm^3 mol^{-1}	$V°_2$, cm^3 mol^{-1}	A	B	C	D	σ, cm^3 mol^{-1}
288.16	101.902	(94.277)	−0.929	−0.303	−0.533	−0.698	0.008
293.44	102.354	(94.615)	−0.869	−0.293	−0.453	−0.523	0.007
303.12	103.167	95.192	−0.754	−0.234	−0.113		0.002
312.76	103.993	95.832	−0.734	−0.218	−0.075		0.002
323.16	104.891	96.518	−0.720	−0.157	−0.092		0.005
333.16	105.749	97.178	−0.674	−0.170	−0.079		0.003

0021-9568/80/1725-0077$01.00/0

Table II. Molar Excess Volumes V^E at Six Temperatures and Deviations δV^E from Smoothing Equations

	288.16 K		293.44 K		303.12 K		312.76 K		323.16 K		333.16 K	
x_2	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}	V^E, cm^3 mol^{-1}	$10^3\delta V^E$, cm^3 mol^{-1}
0.0560	−0.035	−4	−0.036	−4	−0.033	0	−0.033	−1	−0.032	2	−0.027	4
0.1027	−0.065	−3	−0.063	−3	−0.059	0	−0.057	−1	−0.056	4	−0.051	3
0.2112	−0.130	+2	−0.122	+3	−0.110	−1	−0.105	0	−0.110	0	−0.103	−3
0.3151	−0.179	+5	−0.167	+5	−0.147	0	−0.142	1	−0.154	−8	−0.136	−2
0.4183	−0.216	+1	−0.202	0	−0.175	−1	−0.170	1	−0.168	2	−0.158	0
0.5192	−0.240	−6	−0.226	−6	−0.190	−1	−0.185	1	−0.177	4	−0.168	1
0.6172	−0.251	−6	−0.231	−2	−0.191	−1	−0.186	0	−0.179	1	−0.168	2
0.7098	−0.244	+3	−0.226	+2	−0.178	0	−0.174	−1	−0.164	1	−0.155	1
0.8083	−0.219	+10	−0.200	+8	−0.148	−2	−0.141	−2	−0.137	−5	−0.128	−3
0.9060	−0.158	+4	−0.141	+2	−0.087	−1	−0.081	1	−0.081	−4	−0.074	0
0.9529	−0.119	−22	−0.102	−17	−0.043	+5	−0.038	7	−0.033	9	−0.039	1

Table III. Relative Partial Molar Volumes of Nitrobenzene (1) + Sulfolane (2) Mixtures

	288.16 K		293.44 K		303.12 K		312.76 K		323.16 K		333.16 K	
x_2	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}	$\bar{V}_1 - V_1^\circ$, cm^3 mol^{-1}	$\bar{V}_2 - V_2^\circ$, cm^3 mol^{-1}
0.0560	0.00	−0.58	0.00	−0.58	0.00	−0.57	0.00	−0.53	0.00	−0.58	0.00	−0.52
0.1027	−0.01	−0.61	−0.01	−0.58	−0.01	−0.52	−0.01	−0.50	−0.01	−0.53	−0.01	−0.48
0.2112	−0.01	−0.55	−0.01	−0.51	−0.02	−0.42	−0.02	−0.41	−0.03	−0.42	−0.02	−0.38
0.3151	−0.06	−0.43	−0.05	−0.40	−0.05	−0.34	−0.04	−0.33	−0.05	−0.33	−0.05	−0.31
0.4183	−0.12	−0.33	−0.11	−0.31	−0.09	−0.27	−0.08	−0.26	−0.10	−0.25	−0.10	−0.24
0.5192	−0.16	−0.26	−0.15	−0.24	−0.14	−0.21	−0.14	−0.20	−0.15	−0.19	−0.14	−0.18
0.6172	−0.20	−0.21	−0.20	−0.19	−0.23	−0.14	−0.23	−0.14	−0.23	−0.13	−0.21	−0.12
0.7098	−0.28	−0.17	−0.28	−0.15	−0.34	−0.09	−0.34	−0.09	−0.33	−0.08	−0.31	−0.08
0.8083	−0.53	−0.11	−0.51	−0.09	−0.52	−0.05	−0.51	−0.04	−0.49	−0.04	−0.46	−0.04
0.9060	−1.17	−0.04	−1.06	−0.03	−0.77	−0.01	−0.74	−0.01	−0.70	−0.01	−0.66	−0.01
0.9529	−1.70	−0.01	−1.49	−0.01	−0.92	−0.00	−0.87	−0.00	−0.82	−0.00	−0.78	−0.00

Table IV. Measured Dielectric Constants $\epsilon_{1,2}$(exptl) at Five Temperatures and Calculated Values $\epsilon_{1,2}$(eq 2) from Smoothing Equations, Actual Dielectric Constants $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ of Components, and A' and B' Parameters

	293.44 K				303.12 K				312.76 K				322.98 K				333.16 K			
	$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$			
ϕ_2	exptl	eq 2	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	eq 2	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	eq 2	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	eq 2	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	eq 2	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$
0	35.61	35.61	35.61		33.83	33.83	33.83		32.22	32.22	32.22		30.63	30.63	30.63		29.19	29.19	29.19	
0.067	36.23	36.23	35.64	44.36	34.52	34.47	33.90	43.26	32.96	32.88	32.32	42.08	31.41	31.34	30.74	40.80	30.03	29.93	29.34	39.74
0.103	36.52	36.46	35.62	44.29	34.84	34.80	33.97	43.31	33.30	33.23	32.40	42.06	31.77	31.61	30.84	40.86	30.38	30.21	29.42	39.77
0.191	37.22	37.27	35.59	44.14	35.60	35.59	33.83	43.11	34.12	34.06	32.29	41.90	32.65	32.58	30.75	40.69	31.31	31.23	29.35	39.61
0.305	38.08	38.14	35.44	44.07	36.53	36.57	33.68	43.02	35.11	35.09	32.17	41.82	33.69	33.67	30.66	40.61	32.40	32.37	29.28	39.53
0.409	38.80	38.91	35.18	44.03	37.36	37.45	33.47	42.98	35.99	36.03	31.99	41.77	34.60	34.63	30.48	40.56	33.38	33.38	29.15	39.50
0.505	39.52	39.63	34.87	44.09	38.19	38.27	33.27	43.12	36.84	36.89	31.80	41.78	35.48	35.53	30.28	40.58	34.26	34.31	28.94	39.48
0.591	40.12	40.30	34.41	44.07	38.95	39.03	33.01	43.06	37.60	37.69	31.56	41.78	36.26	36.34	30.01	40.58	35.04	35.12	28.67	39.46
0.698	41.17	41.21	33.93	44.31	39.89	40.02	32.54	43.07	38.70	38.71	31.30	41.90	37.40	37.40	29.72	40.72	36.28	36.25	28.46	39.66
0.801	42.21	42.19	33.21	44.44	40.99	41.04	32.59	43.19	39.85	39.76	31.00	42.05	38.56	38.48	29.31	40.86	37.46	37.35	28.10	39.79
0.900	43.37	43.27	32.38	44.50	42.12	42.11	31.58	43.29	40.92	40.83	30.50	42.08	39.72	39.60	28.78	40.94	38.52	38.49	27.48	39.74
0.951	43.94	43.88	31.68	44.50	42.64	42.70	31.14	43.23	41.47	41.41	30.17	42.05	40.28	40.21	28.38	40.89	39.16	39.11	27.19	39.78
1	(44.51)	44.51		44.51	43.30	43.30		43.30	42.00	42.00		42.00	40.83	40.83		40.83	39.73	39.73		39.73
A'		−1.877				−1.356				−1.048				−1.002				−0.789		
B'		2.568				1.633				1.364				1.673				1.603		

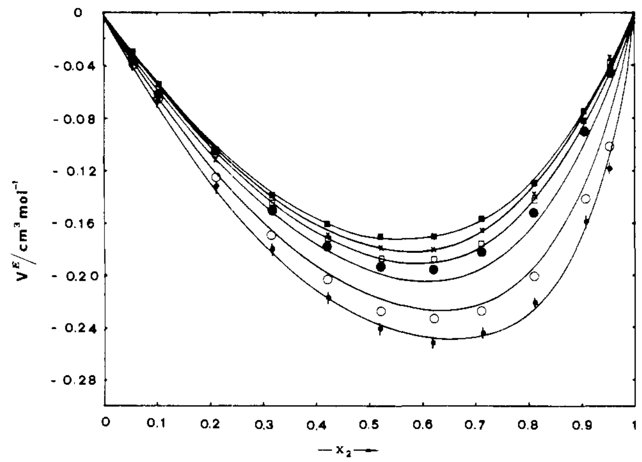

Figure 1. Excess volumes V^E for nitrobenzene (1) + sulfolane (2) at 288.16, 293.44, 303.12, 312.76, 323.16, and 333.16 K: ♦, at 288.16 K; ○, at 293.44 K; ●, at 303.12 K; □, at 312.76 K; ×, at 323.16 K; ■, at 333.16 K.

contractions may be indicative of structural effects rather than specific interactions between unlike molecules.

Dielectric Constants. Measured dielectric constants, $\epsilon_{1,2}$, at the various experimental temperatures show very low deviations, $\epsilon_{1,2}^E$, from the ideal values calculated on the basis of a linear dependence of dielectric constant on ideal volume fraction ϕ.[9] In Figure 2, $\epsilon_{1,2}^E$ values are plotted against ϕ_2. These deviations never exceed 2% of the measured $\epsilon_{1,2}$ values and are always negative, provided an exception is made for a small region close to pure nitrobenzene where positive $\epsilon_{1,2}^E$ values are detected, hardly exceeding experimental error and becoming more significant with increasing temperature. A minimum is observed slightly shifted toward the sulfolane-richer region, decreasing in magnitude with increasing temperature.

The results for the five sets of experiments were fitted by a least-squares computer program to the expression

$$\epsilon_{1,2} = \epsilon_1\phi_1 + \epsilon_2\phi_2 + \phi_1\phi_2\{A' + B'(\phi_1 - \phi_2)\} \qquad (2)$$

which enables the calculation of $\epsilon_{1,2}$ values within 0.1. From eq 2 actual dielectric constants $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ may be derived by the method of intercept, at each temperature, over the entire composition range. These values are summarized in Table IV together with measured and calculated $\epsilon_{1,2}$ values and A' and B' parameters of the smoothed equations. Within the reliability limits of the adopted treatment of experimental data, $\bar{\epsilon}_2$ values are observed which do not differ significantly from the value of the pure substance, over the entire composition range, at each temperature. On the contrary, after a hardly noticeable flat maximum in the region 0–0.2, where positive deviations from ideality are observed, $\bar{\epsilon}_1$ values steadily decrease with increasing sulfolane content in solution. This behavior affords evidence to the supposition that sulfolane, owing to the steric hindrance of its "globular" molecule, plays the role of an almost inert diluent, in spite of its fairly high dipole moment; therefore interactions between unlike molecules are of moderate importance. On the other hand, owing to the fact that nitrobenzene dipole is more exposed, autoassociation to molecular pairs may not be quite excluded, at least at rather low sulfolane concentration. The effects of autoassociation and weak interactions with sulfolane, the former being enhanced by the lessening of the latter, superimpose in determining the behavior of $\bar{\epsilon}_1$. The behavior of $\bar{V} - V^0$ as a function of composition is consistent with the above supposition.

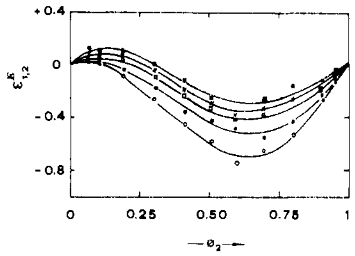

Figure 2. Excess dielectric constants $\epsilon_{1,2}^E$ plotted against ideal volume fraction ϕ_2 for nitrobenzene (1) + sulfolane (2) mixtures: ○, 293.44 K; ●, 303.12 K; □, 312.76 K; ×, 322.98 K; ■, 333.16 K.

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Received for review April 3, 1979. Accepted August 18, 1979.