I. A plot of x_H vs. f_H for the hydrogen–α-methylstyrene system is shown in Figure 1.

The Henry's law constant may be expressed as a function of temperature as follows (*1*):

$$\ln H = \Delta \bar{H}_s / RT \qquad (3)$$

where $\Delta \bar{H}_s$ is the molar heat of solution. H is plotted as a function of temperature in Figure 2. The calculated values of $\Delta \bar{H}_s$ from this plot are listed in Table I.

For comparison H values calculated from solubility data published in the literature are also plotted in Figure 2. The agreement with the Berty et al. (*6*) data is excellent. A good agreement with the Herskowitz et al. (*3*) data is observed. On the other hand, the results published by Stefoglo et al. (*4*) for both α-methylstyrene and cumene are considerably lower.

Registry No. Hydrogen, 1333-74-0; α-methylstyrene, 98-83-9; cumene, 98-82-8; cyclohexene, 110-83-8; cyclohexane, 110-82-7; cyclohexanone, 108-94-1.

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Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. 2. Excess Dielectric Constants on Mixing Sulfolane + Propionitrile, + Butyronitrile, + Valeronitrile

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Dielectric constants were measured for three binary systems involving sulfolane + propionitrile, + butyronitrile, and + valeronitrile, over the entire composition range, at selected temperatures ranging between 293.16 and 333.16 K. The behavior of excess dielectric constant vs. composition plots markedly differentiates each system with respect to others; it is however indicative of only moderate interactions of any kind, mainly dipole–dipole interactions, whose importance decreases in a fashion consistent with the diminished role of polarity with lengthening nitrile carbon chain. Data strongly substantiate the supposition that self-association of nitrile to molecular pairs predominates with respect to nitrile–sulfolane interactions with increasing temperature and nitrile chain length, in accord with our previous interpretation of excess volume data.

Introduction

Previous data (*1*) on excess volumes on mixing sulfolane + propionitrile, + butyronitrile, and + valeronitrile were interpreted in terms of moderate competitive interactions between like and unlike molecules, mainly dipole–dipole interactions, whose importance steadily decreases with increasing nitirile chain length (in spite of a dipole moment (μ = 3.57 D) unaffected by molecular size, the polarity indeed plays obviously a reduced role with lengthening nitrile carbon chain). Nevertheless, with increasing temperature self-association of nitrile seems to predominate with respect to interactions with sulfolane according to the observed increased volume contractions on mixing; and this according to the supposition of a more compact structure can be ascribed to the nitrile self-association product rather than to the complex with sulfolane, because of the steric hindrance of its globular molecule.

In order to better substantiate the above interpretation we carried out measurements of dielectric constants of the three binary systems, over the entire composition range, at selected temperatures ranging between 293.16 and 333.16 K.

Table I. Dielectric Constants for Pure Components, ϵ°, Parameters A, B, C, D, and Standard Deviations σ of the Smoothing Equations

T/K	$\epsilon^\circ{}_1$	$\epsilon^\circ{}_2$	A'	B'	C'	D'	σ
		Propionitrile (1) + Sulfolane (2)					
293.16	28.86	[44.62]	2.994	−0.764	0.932		0.02
303.16	27.59	43.38	2.778	−1.084	1.105		0.02
313.16	26.48	42.14	2.632	−1.487	1.229		0.02
		Butyronitrile (1) + Sulfolane (2)					
293.16	24.83	[44.62]	0.692	−0.868	0.721	1.054	0.02
303.16	23.73	43.41	0.467	−0.808	1.072		0.02
313.16	22.79	42.15	0.444	−1.058	1.006		0.02
333.16	20.83	39.83	0.648	−0.841	0.845	−0.634	0.04
		Valeronitrile (1) + Sulfolane (2)					
303.16	19.39	43.38	−2.266	−1.023	0.099		0.02
313.16	18.64	42.14	−2.253	−1.001	0.973		0.03
323.16	17.89	40.94	−2.240	−1.134	1.763		0.04
333.16	17.14	39.84	−1.926	−1.334	2.705		0.04

Experimental Section

Materials, Apparatus, and Procedure. Sulfolane, kindly supplied by Shell Italia, was purified and dried as already reported (*2*); the melting point of the final product was 301.61 K, in close agreement with our own previous data and the most reliable literature data (*3*); BDH nitriles were purified and dried as already (*4*) reported.

Solutions were made by weight (reduced to mass), stored in dark containers, and protected from moisture as far as possible.

The apparatus for measuring dielectric constants was described elsewhere (*5*); the error in the dielectric constants was estimated to be 0.04ϵ.

Dielectric constants were measured over the entire composition range; working temperatures were 293.16, 303.16, and 313.16 K in the case of propionitrile + sulfolane, 293.16, 303.16, 313.16, and 333.16 K in the case of butyronitrile +

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Table II. Measured Dielectric Constants, $\epsilon_{1,2}$(exptl), at Three Temperatures, Calculated Values, $\epsilon_{1,2}$(calcd), and Actual Dielectric Constants, $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, of Components, from Smoothing Equations, for Propionitrile (1) + Sulfolane (2) Mixtures

	293.16 K				303.16 K				313.16 K			
	$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$			
ϕ_2	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$
0.105	30.93	30.91	28.95	47.59	29.68	29.71	27.70	46.32	28.57	28.55	26.60	45.23
0.187	32.37	32.39	29.10	46.68	31.11	31.14	27.87	45.34	30.01	30.02	26.79	44.06
0.270	33.79	33.81	29.29	46.04	32.50	32.54	28.07	44.65	31.38	31.41	27.02	43.29
0.388	35.73	35.74	29.56	45.48	34.43	34.45	28.34	44.07	33.25	33.28	27.31	42.68
0.495	37.43	37.42	29.79	45.19	36.12	36.11	28.55	43.81	34.91	34.90	27.50	42.43
0.576	38.66	38.65	29.96	45.04	37.35	37.33	28.68	43.70	36.11	36.10	27.60	42.35
0.692	40.38	40.36	30.23	44.88	39.07	39.05	28.87	43.59	37.81	37.79	27.71	42.28
0.793	41.82	41.82	30.58	44.77	40.53	40.52	29.12	43.50	39.27	39.27	27.86	42.23
0.894	43.23	43.23	31.11	44.67	41.95	41.95	29.56	43.42	40.68	40.68	28.18	42.17
0.946	43.92	43.93	31.51	44.63	42.66	42.67	29.91	43.39	41.41	41.41	28.46	42.15

Table III. Measured Dielectric Constants, $\epsilon_{1,2}$(exptl), at Four Temperatures, Calculated Values, $\epsilon_{1,2}$(calcd), and Actual Dielectric Constants, $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, of Components, from Smoothing Equations, for Butyronitrile (1) + Sulfolane (2) Mixtures

	293.16 K				303.16 K				313.16 K				333.16 K			
	$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$			
ϕ_2	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$
0.042	25.81	25.81	24.83	45.82	24.75	24.74	23.75	45.07	23.79	23.78	22.81	43.94	21.86	21.81	20.85	41.86
0.091	26.78	26.77	24.84	45.71	25.68	25.69	23.78	44.54	24.71	24.72	22.85	43.38	22.78	22.73	20.90	41.17
0.160	28.18	28.19	24.88	45.43	27.07	27.09	23.87	43.96	26.08	26.10	22.94	42.75	24.09	24.08	21.00	40.47
0.272	30.47	30.48	25.01	44.97	29.30	29.31	24.00	43.45	28.27	22.28	23.09	42.18	26.22	26.21	21.14	39.93
0.366	32.32	32.33	25.13	44.70	31.15	31.13	24.07	43.31	30.06	30.06	23.17	42.00	27.97	27.95	21.20	39.79
0.495	34.86	34.84	25.22	44.58	33.64	33.61	24.05	43.32	32.52	32.48	23.17	41.99	30.34	30.34	21.20	39.78
0.568	36.26	36.26	25.19	44.60	35.04	35.02	23.99	43.37	33.86	33.86	23.11	42.04	31.70	31.70	21.19	39.79
0.689	38.61	38.62	25.04	44.69	37.37	37.38	23.88	43.44	36.15	36.17	22.97	42.13	33.94	33.89	21.17	39.81
0.784	40.47	40.49	24.96	44.72	39.20	39.24	23.84	43.46	38.01	38.00	22.87	42.16	35.73	35.75	21.16	39.81
0.895	42.64	42.65	25.24	44.67	41.40	41.40	23.98	43.43	40.15	40.14	22.89	42.16	37.81	37.84	21.11	39.82
0.945	43.64	43.61	25.65	44.64	42.37	42.36	24.16	43.42	41.10	41.10	22.99	42.16	38.74	38.78	21.02	39.83

Table IV. Measured Dielectric Constants, $\epsilon_{1,2}$(exptl), at Four Temperatures, Calculated Values, $\epsilon_{1,2}$(calcd), and Actual Dielectric Constants, $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, of Components, from Smoothing Equations, for Valeronitrile (1) + Sulfolane (2) Mixtures

	303.16 K				313.16 K				323.16 K				333.16 K			
	$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$				$\epsilon_{1,2}$			
ϕ_2	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$	exptl	calcd	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$
0.031	20.10	20.09	19.39	42.17	19.37	19.35	18.64	41.55	18.63	18.60	17.90	41.04	17.92	17.89	17.16	41.10
0.088	21.40	21.40	19.40	42.08	20.61	20.64	18.67	41.12	19.86	19.90	17.95	40.26	19.17	19.21	17.24	39.86
0.113	21.95	21.96	19.40	42.06	21.16	21.19	18.69	40.99	20.38	20.44	17.97	40.02	19.70	19.76	17.28	39.46
0.236	24.74	24.75	19.39	42.08	23.86	23.92	18.73	40.73	23.09	23.10	18.08	39.44	22.38	22.39	17.48	38.43
0.317	26.56	26.60	19.35	42.18	25.67	25.70	18.70	40.81	24.78	24.83	18.06	39.48	24.02	24.07	17.50	38.37
0.379	28.01	28.03	19.29	42.29	27.07	27.09	18.62	40.96	26.17	26.17	17.98	39.64	25.37	25.37	17.42	38.51
0.483	30.45	30.44	19.12	42.52	29.46	29.43	18.38	41.27	28.49	28.44	17.68	40.02	27.65	27.59	17.09	38.95
0.577	32.68	32.67	18.86	42.74	31.66	31.62	18.04	41.57	30.60	30.59	17.27	40.39	29.72	29.70	16.61	39.37
0.699	35.67	35.63	18.36	43.02	34.58	35.55	17.48	41.89	33.53	33.48	16.64	40.75	32.57	32.55	15.93	39.77
0.796	38.04	38.03	17.83	43.20	36.95	36.93	17.02	42.05	35.85	35.84	16.19	40.91	34.95	34.89	15.55	39.90
0.902	40.80	40.77	17.06	43.34	39.63	39.62	16.57	42.13	38.49	38.50	15.98	40.95	37.47	37.50	15.65	39.89
0.949	41.98	42.00	16.67	43.37	40.80	40.82	16.44	42.14	39.65	39.66	16.05	40.95	38.63	38.63	15.97	39.87

sulfolane, and 303.16, 313.16, 323.16, and 333.16 K in the case of valeronitrile + sulfolane.

For the sake of uniformity with previous works the sulfolane was identified as component 2 and the other substance as component 1; compositions were stated as volume fractions, ϕ_2.

Results

Pure-sulfolane dielectric constants (Table I) are in close agreement with our own previous data and the most reliable literature data (*3-6*). The values at temperatures below 301.61 K appear in brackets because these are extrapolated values.

Up-to-date data on dielectric constants of nitriles are lacking in the literature. Nevertheless, our measured dielectric constants in the case of propionitrile and butyronitrile are about 3% lower than Dannahuser and Flueckinger's (*7*) data and about the same amount higher than Dereppe and Van Meerssche's (*8*) data; the temperature coefficients are however quite similar to Dannahuser's, whereas the Dereppe values exhibit a less steady dependence on temperature, in the working temperature range.

In the case of valeronitrile a better agreement with literature data (*8*) is observed in the temperature range 303.16–333.16 K, deviations exceeding 1%, only occasionally.

***Dielectric Constants of Mixtures*.** Measured dielectric constants over the entire composition range $0 \leq \phi_2 \leq 1$, at the selected temperatures, are summarized in Table II (propionitrile (1) + sulfolane (2) system), Table III (butyronitrile (1) + sulfolane (2) system), and Table IV (valeronitrile (1) + sulfolane (2) system). All of them exhibit very low deviations from ideal values, which can be calculated on the basis of a linear dependence of $\epsilon_{1,2}$ on volume composition ϕ_2; the magnitude of deviations, $\epsilon^E_{1,2}$, in no case exceeds $\pm 0.8\epsilon$, but the plots $\epsilon^E_{1,2}$ vs. ϕ_2 markedly differentiate each system with respect to others.

In the case of the propionitrile + sulfolane system deviations from ideality (Figure 1) are positive over the entire composition

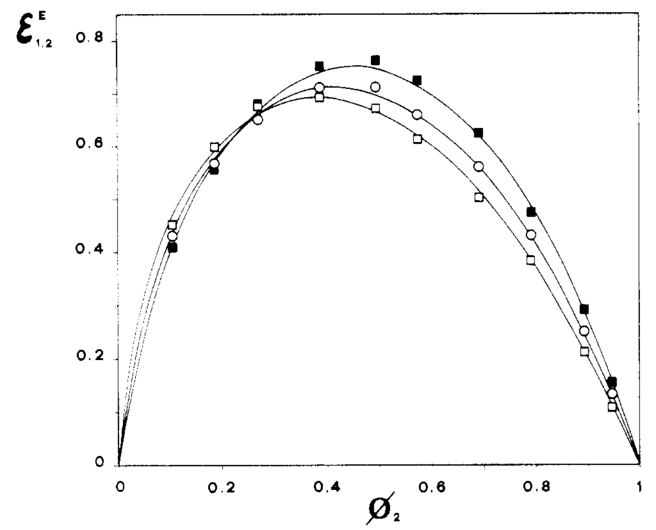

Figure 1. Excess dielectric constants, $\epsilon^E_{1,2}$, plotted against ideal volume fraction, ϕ_2, for propionitrile (1) + sulfolane (2) mixtures: (■) 293.16, (○) 303.16, and (□) 313.16 K.

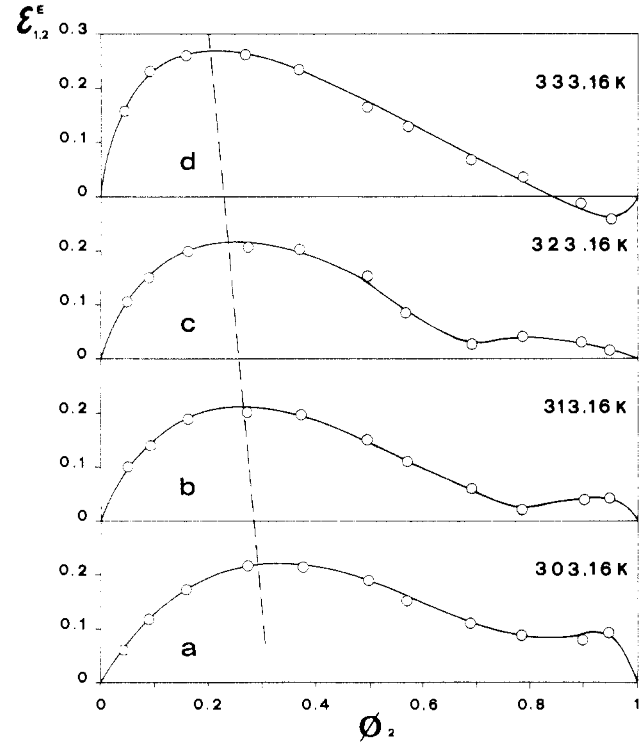

Figure 2. Excess dielectric constants, $\epsilon^E_{1,2}$, at several temperatures, plotted against ideal volume fraction, ϕ_2, for butyronitrile (1) + sulfolane (2) mixtures.

range with a sharp maximum which steadily shifts toward the nitrile-rich region with increasing temperature; the curves intersect at $\sim 0.3\phi_2$; starting from this point the dependence of excess function on temperature is reversed; excess dielectric constants indeed increase with temperature in the region 0–$0.3\phi_2$ and decrease in the region $0.3\phi_2$–$1\phi_2$.

In the case of the butyronitrile (1) + sulfolane (2) system, deviations from ideal values are less noticeable, only occasionally exceeding $0.25\epsilon_{1,2}$; their behavior as a function of volume fraction is represented by S-shaped curves (plots a–d in Figure 2) with an extensive flat maximum in the region 0–$0.6\phi_2$ and another scarcely noticeable maximum in the region 0.9–$1\phi_2$, at least up to 313 K. The effect of increasing temperature results in a steady increase in the magnitude of the maximum in the region 0–$0.6\phi_2$ which, at the same time, shifts toward the nitrile-rich region, and a flattening of the maximum at $0.95\phi_2$, which becomes less and less noticeable, reversing into a minimum at 323.13 K.

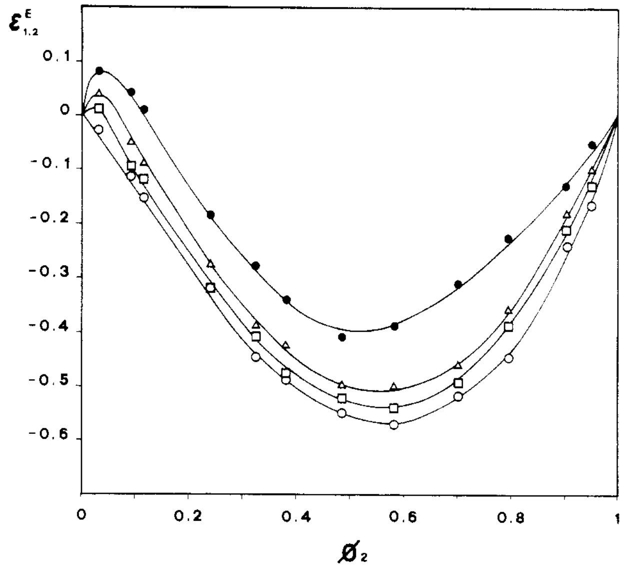

Figure 3. Excess dielectric constants, $\epsilon^E_{1,2}$, plotted against ideal volume fraction, ϕ_2, for valeronitrile (1) + sulfolane (2) mixtures: (○) 303.16, (□) 313.16, (△) 323.16, and (●) 333.16 K.

In the case of the valeronitrile (1) + sulfolane (2) system (Figure 3) scarcely noticeable positive deviations are observed to occur only in a very narrow region 0–$0.1\phi_2$, close to pure nitrile; they are enhanced by temperature; otherwise more remarkable negative deviations are observed, resulting in a minimum at approximately $0.6\phi_2$, decreasing in magnitude with increasing temperature.

The experimental results for the three binary systems were fitted by a least-squares computer program to the expression

$$\epsilon^E_{1,2} = \phi_1\phi_2|A' + B'(\phi_2 - \phi_1) + C'(\phi_2 - \phi_1)^2 + D'(\phi_2 - \phi_1)^3 \ldots|$$

The parameters A', B', C', and D' for each working system, listed in Table I, are those based on the lowest values of $\sigma = |(\sum\delta\epsilon^E)^2/(s - m)|^{1/2}$, in which $\delta\epsilon^E = \epsilon(\text{exptl}) - \epsilon(\text{calcd})$ and s and m have the usual meaning; three-parameter equations were found to be sufficient for the best fit of experimental data, if exception is made for data, at 293.16 and 333.16 K, in the case of the butyronitrile (1) + sulfolane (2) system, where D' parameters were needed.

Experimental results, as well as values calculated by the so-derived equations, are included in Tables II–IV together with actual dielectric constant values, $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, over the entire composition range, at each working temperature.

Discussion

Reasonably the observed behavior of dielectric constant–volume fraction plots may be ascribed to the superimposition and the alternative predominating of two factors, both resulting in enhancing the dielectric constant; their effects on $\epsilon^E_{1,2}$, becoming more negligible the longer the nitrile chain length, appear however to be influenced by temperature in the opposite way.

Let us identify these two factors in nitrile self-association to molecular pairs, whose effect is more remarkable in the nitrile-rich region, and in nitrile–sulfolane interactions, whose effect is more remarkable in the sulfolane-rich region.

Then one may infer that interactions between unlike molecules are lessened by increasing temperature and by lengthening of the nitrile carbon chain (this according to the supposition that, owing to the steric hindrance of the sulfolane globular molecule, the nitrile molecule is needed to check the proper orientation for interacting with the exposed negative end of the sulfolane dipole; hence, only long-range, weak dipole-dipole interactions result, easily disturbed by thermal motions and increasing steric hindrance in nitrile molecules).

The above-reported supposition accounts for the increase and the steady shifting of the maximum toward the nitrile-rich region with increasing temperature in the case of the propionitrile (1) + sulfolane (2) system according to a slight predominating with temperature of nitrile self-association with respect to interactions with sulfolane, even if interactions of any kind appear competitive in strength.

In the case of the butyronitrile (1) + sulfolane (2) systems, interactions with sulfolane are suspected to be negligible if compared with energies of nitrile association to molecular pairs, as indicated by the relative magnitude of the two maxima in the $\epsilon^E_{1,2}$–ϕ_2 plots in Figure 2. The steady shifting (dashed line in Figure 2) toward the nitrile-rich region of the flat maximum which otherwise increases with temperature may be indicative of a strengthening of self-association with lessening of the scarcely noticeable interactions with sulfolane; these indeed are lacking at 333.16 K (minimum in $\epsilon^E_{1,2}$–ϕ_2 plot d in Figure 2).

In the case of the valeronitrile (1) + sulfolane (2) system, plots in Figure 3 are indicative of very low interactions of any kind; nevertheless, self-association of nitrile may not be quite excluded in a very narrow region close to pure nitrile, where positive deviations, increasing obviously with temperature, are observed.

According to the observed regular behavior of the nitrile series, previous dielectric constant data (*6*) of acetonitrile (1) + sulfolane (2) systems evidence more intensive interactions of any kind, even if the lack of $>CH_2$ groups in the acetonitrile molecule and the consequent transmission to the $-C^+{=}N^-$ group of the inductive effect of $-CH_3$ results in a modified partition equilibrium of nitrile between self-association and interactions with sulfolane.

The above-reported interpretation of $\epsilon^E_{1,2}$ vs. ϕ_2 plots is strongly supported by our own previous data on excess volumes of mixing (*1*). The supposition of a more compact structure to be ascribed to nitrile self-association product, rather than to sulfolane–nitrile complex, accounts indeed for the observed volume contractions increasing with temperature and shortening nitrile chain length, as expected.

Registry No. Propionitrile, 107-12-0; butyronitrile, 109-74-0; valeronitrile, 110-59-8; sulfolane, 126-33-0.

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Excess Volumes and Dielectric Constants of Benzonitrile + Nitrobenzene and Acetonitrile + Nitrobenzene Systems

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Excess volumes and dielectric constants were measured for benzonitrile + nitrobenzene and acetonitrile + nitrobenzene mixtures over the entire composition range, at selected temperatures ranging between 293.16 and 333.16 K. Benzonitrile and nitrobenzene molecules possess quite similar volumes and shapes; acetonitrile and nitrobenzene are isodielectric media; excess volumes are "quadratic" functions of composition in the former system and excess dielectric constants are "quadratic" functions of composition in the latter. On the whole, both systems exhibit only slight departures from ideality which may be interpreted in terms of moderate interactions of any kind; nevertheless, the presence of a flat maximum in excess dielectric constant vs. composition curves is indicative that interactions between unlike molecules predominate in the acetonitrile + nitrobenzene system. These interactions are relatively weak if compared with the average of interactions between pairs of like molecules in benzonitrile + nitrobenzene systems, which have to be regarded as "regular" mixtures of self-associated substances.

Introduction

As part of a long-term study on binary mixtures, which exhibit only slight departures from ideality, we present herewith excess properties of acetonitrile + nitrobenzene and benzonitrile + nitrobenzene mixtures, over the entire composition range, at several temperatures. All these substances may be classified among dipolar aprotic solvents with moderately high dielectric constants. Attention must be called to the fact that acetonitrile and nitrobenzene are isodielectric media: $\epsilon(303.16\ K) = 35.1$ (CH_3CN) and $\epsilon(303.16\ K) = 33.8$ ($C_6H_5NO_2$). Otherwise, an important feature of the benzonitrile + nitrobenzene system is that molecules possess nearly equal volumes and similar shapes: $V_1°(303.16\ K) = 103.51\ cm^3\ mol^{-1}$ (benzonitrile) and $V_2°(303.16\ K) = 103.17\ cm^3\ mol^{-1}$ (nitrobenzene). Previously (*1*, *2*) we studied thermodynamic properties of each of these three substances mixed with sulfolane; on the basis of these results more intensive interactions between acetonitrile and nitrobenzene are expected than between benzonitrile and nitrobenzene.

Experimental Section

Materials, Apparatus, and Procedure. Benzonitrile, ace-