

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 $\epsilon_{1,2}^E - \phi_2$ 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 $\epsilon_{1,2}^E - \phi_2$ 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 (δ) 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 $-C^+ \equiv N^-$ 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 $\epsilon_{1,2}^E$ 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: $\epsilon(303.16\text{ K}) = 35.1$ (CH_3CN) and $\epsilon(303.16\text{ K}) = 33.8$ ($C_6H_5NO_2$). Otherwise, an important feature of the benzonitrile + nitrobenzene system is that molecules possess nearly equal volumes and similar shapes: $V_1^\circ(303.16\text{ K}) = 103.51\text{ cm}^3\text{ mol}^{-1}$ (benzonitrile) and $V_2^\circ(303.16\text{ K}) = 103.17\text{ cm}^3\text{ mol}^{-1}$ (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-

Table I. Molar Volumes, V° , Parameters A , B , C and D , and Standard Deviations σ of the Smoothing Equations

T/K	$V_1^\circ/$ ($\text{cm}^3 \text{ mol}^{-1}$)	$V_2^\circ/$ ($\text{cm}^3 \text{ mol}^{-1}$)	A	B	C	D	$\sigma/$ ($\text{cm}^3 \text{ mol}^{-1}$)
Benzonitrile (1) + Nitrobenzene (2)							
293.16	102.610	102.320	-0.372				0.003
313.16	104.460	104.025	-0.372				0.003
Acetonitrile (1) + Nitrobenzene (2)							
293.16	52.487	102.314	-1.712	0.825	-0.250	-0.142	0.008
303.16	53.234	103.168	-1.805	0.706	-0.192	0.292	0.007
313.16	53.989	104.022	-1.907	1.013	-0.013	-0.110	0.006

tonitrile, and nitrobenzene were purified carefully and dried as reported previously (1, 2). Melting points and physical constants of the products (Tables I and IV) were in close agreement with the most reliable literature data (3-5) as well as with our own previous data (1, 2). Solutions were made by weight (reduced to mass) and protected from moisture as far as possible. Measurements of density were carried out at 293.16 and 313.16 K for the benzonitrile + nitrobenzene system and at 293.16, 303.16, and 313.16 K for the acetonitrile + nitrobenzene system, over the entire composition range. The dielectric constants were measured at 293.16, 313.16, and 333.16 K for the benzonitrile + nitrobenzene system and at 293.16, 303.16, 313.16, and 333.16 K for the acetonitrile + nitrobenzene system, over the entire composition range.

The apparatus and procedure were described elsewhere (1); the maximum error in density was estimated to be $3 \times 10^{-5} \text{ g cm}^{-3}$; the maximum error in the dielectric constants was estimated to be 0.04. The nitrile was identified as component 1 and nitrobenzene as component 2.

Results and Discussion

Excess Volumes. In Figure 1 are shown graphically (a) excess volumes of mixing benzonitrile and nitrobenzene (volume ratio $V_2^\circ/V_1^\circ = 0.997$) and (b) excess volumes of mixing acetonitrile + nitrobenzene (volume ratio $V_2^\circ/V_1^\circ = 1.95$), in the temperature range 293.16-313.16 K. Both systems exhibit negative deviations from ideality. In the case of benzonitrile + nitrobenzene, V^E vs. x_2 plots superimpose on one quadratic curve with a very flat minimum (-0.09 cm^3) at $x_2 = 0.5$, insensitive to the temperature. (The same curve represents indeed also excess volume data drawn from density measurements of Miller, Wachter, and Fried (6) at 298.16 K.) The minimum is deeper (-0.5 cm^3) in the case of acetonitrile + nitrobenzene and slightly skewed toward the smaller component (acetonitrile) rich region, as expected; the magnitude of the minimum increases steadily with temperature.

The experimental data, for both binary systems, were fitted, by a least-squares computer program, to smoothing equations of the type

$$V^E = x_1 x_2 [A + B(x_2 - x_1) + C(x_2 - x_1)^2 \dots] \quad (1)$$

which reduced to

$$V^E = Ax_1 x_2 \quad (2)$$

in the case of the benzonitrile + nitrobenzene system. The parameters of eq 1, the volume V° of pure components, and the standard deviations σ of the smoothing equations, at each temperature, are included in Table I; V^E values, as a function of mole fraction, x_2 , of nitrobenzene, are summarized in Tables II and III, as well as deviations δV^E of the smoothing equations, for the two systems.

If eq 1 is differentiated with respect to x_1 and x_2 , relative partial molar volumes of the two components, at each composition and temperature, are obtained.

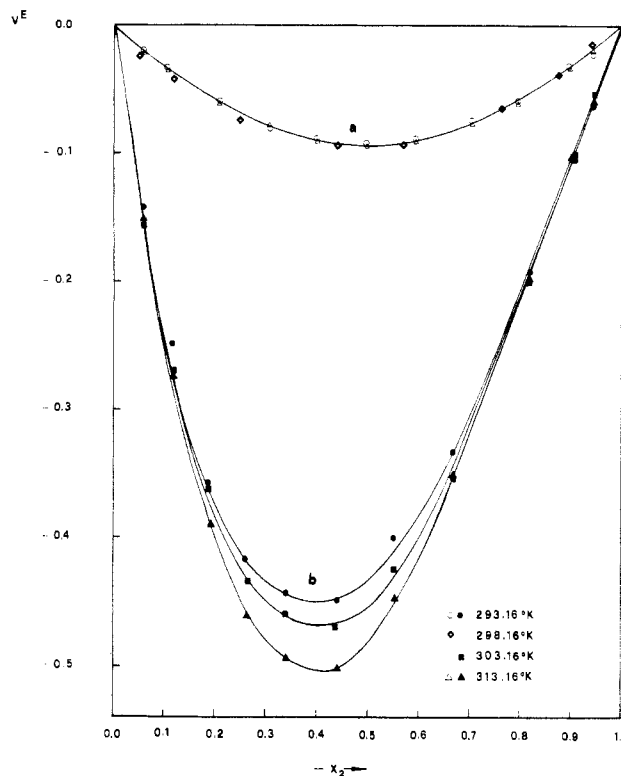


Figure 1. Excess volumes V^E plotted against nitrobenzene mole fraction, x_2 , at several temperatures: (a) benzonitrile (1) + nitrobenzene (2) mixtures, (\diamond) Miller, Wachter, and Fried data (ref 6); (b) acetonitrile (1) + nitrobenzene (2) mixtures.

Table II. Molar Excess Volumes, V^E , of Acetonitrile (1) + Nitrobenzene (2) Mixtures, at Three Temperatures, and Deviations δV^E from the Smoothing Equations

x_2	293.16 K		303.16 K		313.16 K	
	$V^E/$ (cm^3 mol^{-1})	$10^3 \times$ $(\delta V^E)/$ (cm^3 mol^{-1})	$V^E/$ (cm^3 mol^{-1})	$10^3 \times$ $(\delta V^E)/$ (cm^3 mol^{-1})	$V^E/$ (cm^3 mol^{-1})	$10^3 \times$ $(\delta V^E)/$ (cm^3 mol^{-1})
0.0593	-0.142	-1	-0.158	3	-0.151	2
0.1209	-0.248	9	-0.270	-4	-0.274	6
0.1882	-0.358	-8	-0.361	-4	-0.391	-6
0.2591	-0.417	-4	-0.437	10	-0.463	-5
0.3417	-0.443	5	-0.457	-6	-0.495	6
0.4358	-0.450	-2	-0.471	4	-0.501	0
0.5458	-0.399	7	-0.424	-8	-0.446	4
0.6718	-0.333	-10	-0.354	7	-0.353	-8
0.8174	-0.192	6	-0.200	-3	-0.188	6
0.9068	-0.106	2	-0.102	1	-0.096	1
0.9522	-0.064	-6	-0.050	0	-0.054	-5

$\bar{V}_2 - V_2^\circ$ and $\bar{V}_1 - V_1^\circ$ plots vs. x_2 are shown in Figure 2 (benzonitrile + nitrobenzene system) and in Figure 3 (acetonitrile + nitrobenzene system).

Data supply evidence that benzonitrile + nitrobenzene mixtures may be classified among the so-called "quadratic mixtures" (7) after Rowlinson. (The excess free energy of

Table III. Molar Excess Volumes, V^E , of Benzonitrile (1) + Nitrobenzene (2) Mixtures, at Two Temperatures, and Deviations δV^E from the Smoothing Equation

x_2	293.16 K		313.16 K	
	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \times (\delta V^E)/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \times (\delta V^E)/(\text{cm}^3 \text{ mol}^{-1})$
0.0629	-0.021	1	-0.037	-3
0.1004				
0.1068	-0.035	0		
0.2015			-0.062	-2
0.2061	-0.059	2		
0.3013			-0.080	-2
0.3111	-0.078	2		
0.3990			-0.089	0
0.4064	-0.088	2		
0.5003			-0.092	1
0.5022	-0.088	5		
0.6000			-0.087	2
0.6043	-0.088	1		
0.6962			-0.075	4
0.7032	-0.076	2		
0.8078	-0.060	-2		
0.8512			-0.046	1
0.8990			-0.033	1
0.8993	-0.038	-4		
0.9506	-0.026	-9		

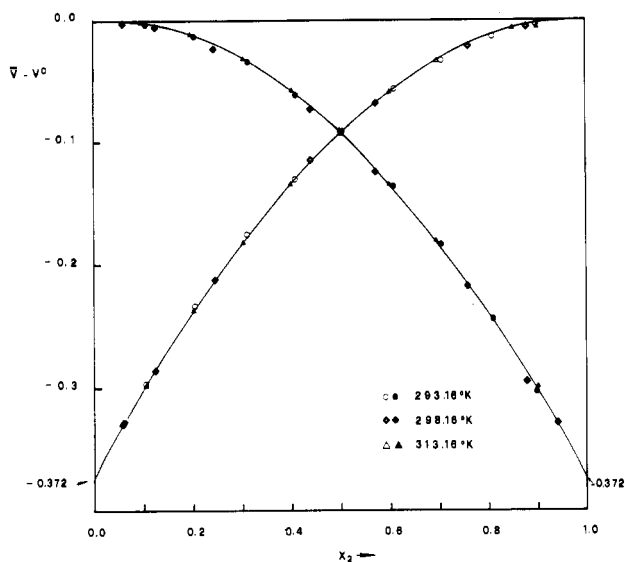


Figure 2. Relative molar partial volumes $\bar{V} - V^0$ of components in benzonitrile (1) + nitrobenzene (2) system, plotted against mole fraction of nitrobenzene, x_2 , at several temperatures: (full symbols) benzonitrile; (hollow symbols) nitrobenzene; (\diamond , \blacklozenge) Miller, Wachter, and Fried data.

quadratic mixtures, g^E , obeys indeed a quadratic equation: $g^E = \xi x_1 x_2$. Then we may derive

$$V^E = (\partial g^E / \partial p)_T = (\partial \xi / \partial p)_T x_1 x_2 = A x_1 x_2$$

If ξ —and hence A —does not vary with temperature, $\partial g^E / \partial T = 0 = -S^E$, which is the Hildebrand criterium for classifying regular mixtures.) Accordingly with eq 2 relative molar volume vs. x_2 plots are symmetric and cross at $0.5x_2$ (Figure 2).

In the case of acetonitrile + nitrobenzene curves, the asymmetry in excess volume vs. x_2 curves may be ascribed mainly to a difference in molar volumes of the two components; excess relative partial molar volume curves cross approximately at $0.4x_2$. A more noticeable effect of dilution on nitrobenzene than on acetonitrile seems to be evidenced by $\bar{V}_1 - V_1^0$ and $\bar{V}_2 - V_2^0$ plots vs. x_2 .

Dielectric Constants. Deviations from ideality for the two systems were calculated on the basis of the supposition of a

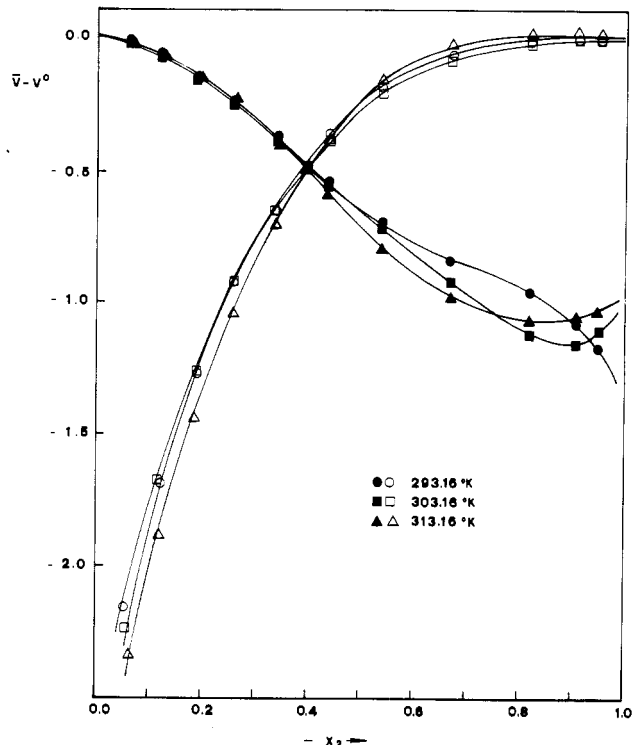


Figure 3. Relative partial molar volumes $\bar{V} - V^0$ of components in acetonitrile (1) + nitrobenzene (2) system, plotted against nitrobenzene mole fraction, x_2 , at several temperatures: (full symbols) acetonitrile; (hollow symbols) nitrobenzene.

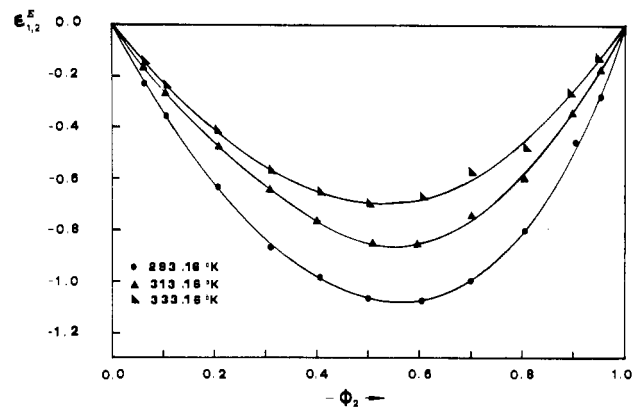


Figure 4. Excess dielectric constants, $\epsilon_{1,2}^E$, of benzonitrile (1) + nitrobenzene (2) mixtures plotted against nitrobenzene volume fraction, ϕ_2 , at several temperatures.

linear dependence of $\epsilon_{1,2}$ values on volume composition, ϕ , for ideal solutions. The equation

$$\epsilon_{1,2} = \bar{\epsilon}_1 \phi_1 + \bar{\epsilon}_2 \phi_2 = \epsilon_{1,2}^E + \epsilon^0_1 \phi_1 + \epsilon^0_2 \phi_2 \quad (3)$$

where $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$ are actual dielectric constants of the two components at each composition, and ϵ^0_1 and ϵ^0_2 are dielectric constants of pure components, was proposed early by Mecke, Reuter, and Schupp (8) for calculating the dielectric constants in the case of mixtures involving one or both highly polar components, where the Clausius-Mossotti treatment falls because it does not take into account the dipole reaction field. Equation 3 was applied successfully by Böttcher (9) in the case of choline + chlorobenzene mixtures and by one of us (1, 2, 10) in the case of several sulfone solutions of scarcely polar solutes as well as of highly polar solutes and finally by Douh ret et al. (11) in the case of acetonitrile + water solutions. In the case of benzonitrile + nitrobenzene mixtures the $\epsilon_{1,2}^E - \phi_2$ plots (Figure 4) exhibit a minimum, slightly skewed toward the nitro-

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

T/K	ϵ°_1	ϵ°_2	A'	B'	σ
Benzonitrile (1) + Nitrobenzene (2)					
293.16	25.66	35.61	-4.469	-1.193	0.02
313.16	23.89	32.14	-3.296	-0.618	0.02
333.16	22.31	29.15	-2.744	-0.158	0.02
Acetonitrile (1) + Nitrobenzene (2)					
293.16	36.60	35.60	1.777		0.04
303.16	35.09	33.80	1.675		0.03
313.16	33.64	32.13	1.566		0.02
333.16	31.04	29.10	1.511		0.02

benzene-rich region; the magnitude of the minimum never exceeding -1.1 decreases sharply with increasing temperature.

In the case of the acetonitrile + nitrobenzene system, deviations from ideality are positive (Figure 5) with a maximum, at $0.66\phi_2$, never exceeding 1% of measured $\epsilon_{1,2}$ and only slightly decreasing by increasing temperature. Taking into account that the dielectric constants of the two components scarcely differ from one another, as already pointed out, whereas the volume ratio is approximately 2, we plotted excess dielectric constants as a function of x_2 and obtained quadratic curves (dotted line in Figure 5 refers to $\epsilon_{1,2}^E$ values vs. x_2 at 293.16 K). Dielectric constant excess data, in the case of benzonitrile + nitrobenzene systems, were fitted, at each temperature, to smoothing equations of the type

$$\epsilon_{1,2}^E = \phi_1\phi_2[A' + B'(\phi_2 - \phi_1)] \quad (4)$$

which allowed us to recalculate excess dielectric constants in the limits of the experimental error, at each composition. In the case of the acetonitrile + nitrobenzene system, equations of the type $\epsilon_{1,2}^E = A'x_1x_2$ were available to obtain the best fit of experimental data. The parameters A' and B' of the smoothing equations, as well as properties of pure components and standard deviations σ of the smoothing equations, for the two systems, are summarized in Table IV. Excess dielectric constants $\epsilon_{1,2}^E$ and deviations $\delta\epsilon_{1,2}^E$, as a function of composition, at each temperature, are summarized in Table V. However, the magnitude of excess properties in both systems supplies evidence for the supposition that interaction energies

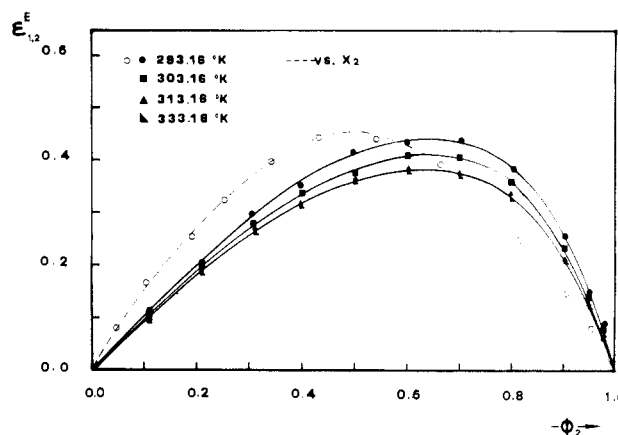


Figure 5. Excess dielectric constants, $\epsilon_{1,2}^E$, of acetonitrile (1) + nitrobenzene (2) mixtures as a function of composition at several temperatures: (solid line) $\epsilon_{1,2}^E$ vs. ϕ_2 plots; (dotted line) $\epsilon_{1,2}^E$ vs. x_2 plot.

of any kind are of moderate importance. Therefore, the conclusion may be drawn that the difference in the properties of the pure components plays the most important role in determining the shape of excess function curves vs. composition. Accordingly, V^E vs. x_2 plots, in the case of mixtures of isocore substances (benzonitrile + nitrobenzene), as well as $\epsilon_{1,2}^E$ vs. x_2 plots, in the case of mixtures of isodielectric substances (acetonitrile + nitrobenzene), are quadratic curves.

The presence of a flat maximum in $\epsilon_{1,2}^E$ vs. ϕ_2 plots is indicative that interactions between unlike molecules presumably of a dipolar kind predominate in the acetonitrile + nitrobenzene system, whereas benzonitrile and nitrobenzene molecules, flattened by resonance, even if moderately, are coupled in more stable molecular pairs and can interact scarcely with one another.

The substitution of $-\text{CH}_3$ in the place of $-\text{C}_6\text{H}_5$ increases indeed the electron density on the $-\text{CN}$ group and steric repulsion of molecules, so that CH_3CN exhibits a higher donor capacity ($\text{DN} = 14.1$) than $\text{C}_6\text{H}_5\text{CN}$ ($\text{DN} = 11.9$), but only a moderate dimerization as evidenced by ^1H NMR chemical shift (12); therefore, the more active monomer molecules may interact with unlike molecules more easily even if weakly.

Table V. Excess Dielectric Constants, $\epsilon_{1,2}^E$, and Deviations $\delta\epsilon_{1,2}^E$ from the Smoothing Equations, at Selected Temperatures

ϕ_2	293.16 K		303.16 K		313.16 K		333.16 K	
	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$
Benzonitrile (1) + Nitrobenzene (2)								
0.0627	-0.21	-0.01			-0.16	0	-0.16	-0.01
0.1064	-0.35	0.01			-0.26	0.01	-0.25	0
0.2054	-0.61	0.01			-0.48	0	-0.41	0.02
0.3104	-0.86	0			-0.64	0.02	-0.56	0.01
0.4054	-0.99	0.03			-0.77	0	-0.65	0
0.5014	-1.09	0.02			-0.85	-0.03	-0.70	-0.01
0.6033	-1.09	0.04			-0.85	-0.03	-0.67	-0.01
0.7024	-1.00	0.02			-0.75	-0.01	-0.57	0.02
0.8072	-0.80	0.01			-0.60	-0.03	-0.48	-0.04
0.8989	-0.48	0.01			-0.34	0	-0.26	0
0.9504	-0.29	-0.03			-0.17	0.01	-0.13	0.01
Acetonitrile (1) + Nitrobenzene (2)								
x_2								
0.0593	0.08	-0.02	0.09	0	0.10	0.01		
0.1209	0.23	0.04	0.24	0.06	0.19	0.02	0.15	-0.01
0.1882	0.32	0.05	0.29	0.03			0.24	0.01
0.2591	0.40	0.06	0.37	0.05	0.30	0	0.28	-0.01
0.3417	0.43	0.03	0.39	0.01	0.37	0.02	0.34	0
0.4358	0.42	-0.02	0.39	-0.02	0.38	-0.01	0.36	-0.01
0.5458	0.40	-0.04	0.39	-0.03	0.37	-0.02	0.37	0
0.6718	0.34	-0.05	0.34	-0.03	0.34	-0.01	0.33	0
0.8184	0.25	-0.02	0.22	-0.03	0.22	-0.01	0.24	0.02
0.9068	0.14	-0.01	0.12	-0.02	0.14	0.01	0.15	0.02
0.9522	0.08	0	0.09	0.01	0.10	0.03	0.12	0.05

A lessening of these interactions with increasing temperature accounts for the decrease of the maximum in $\epsilon_{1,2}$ vs. ϕ_2 curves; however the observed negative V_m^E temperature coefficient seems to contradict this supposition, if negative excess volumes have to be ascribed only to complex formation.

Attention must be called to the fact that this contradictory behavior of V_m^E and ϵ_m^E with temperature is a common feature of some other complex-forming mixtures involving acetonitrile (13-16), sulfolane + acetonitrile mixtures (2) included. In the case of the last system we furnished an interpretation based on an expanded structure to be ascribed to the complex, as a consequence of steric hindrance.

Registry No. Benzonitrile, 100-47-0; acetonitrile, 75-05-8; nitrobenzene, 98-95-3.

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Excess Enthalpies of Mixing Sulfolane + Acetonitrile, + Propionitrile, + Butyronitrile, + Valeronitrile at 303.16 K

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Flow calorimetric measurements, at 303.16 K, of molar excess enthalpy, H^E , of four binary systems involving sulfolane and each member of the n -nitrile series from acetonitrile to valeronitrile are reported. H^E values are positive over the entire composition range for the three higher members of the series with a maximum, at approximately 0.5x, which increases steadily with increasing nitrile chain length. In the case of the acetonitrile + sulfolane system, H^E values lie on an S-shaped curve, with a shoulder in the nitrile-rich region and a sharper minimum in the sulfolane-rich region. The data supply evidence for the supposition of the presence of only moderate interactions of any kind; interactions between unlike molecules seem to predominate only in the case of the acetonitrile + sulfolane system, even if a moderate self-association of nitrile may not be quite excluded in a small region close to pure nitrile; interactions with sulfolane become relatively weak if compared with the average of the energies of interactions between molecular pairs, with increasing nitrile chain length. The data strongly support the conclusions drawn from our previous determinations of excess volumes and dielectric constants.

Introduction

As a part of a long-term study (1-7) of the thermodynamic and physical properties of binary systems involving sulfolane, the present investigation was undertaken with the aim of studying the effect of chain length on the excess enthalpies, H^E , of binary mixtures of sulfolane and each of the first four members of the n -nitrile series.

As previously stated (8), our choice of nitrile series has been guided by a regular varying molecular size of selected nitriles without inordinate alteration in molecular structure and effective

polarity of nitrile ($\mu = 3.57$ D).

Previous data on excess volumes (6, 8) and dielectric constants (6, 9) measured over the entire composition range, at four temperatures ranging between 293.1 and 323.1 K, were indicative of only moderate competitive interactions of any kind, decreasing in importance with lengthening of the nitrile chain; however, interactions between unlike molecules seemed to predominate in the case of acetonitrile + sulfolane mixtures.

Experimental Section

Materials, Apparatus, and Procedure. Sulfolane and nitriles were carefully purified and dried, as already reported (10, 11). The primary sources of component substances as well as the physical properties of purified materials are summarized in Table I and compared with the most reliable literature data (12-15).

Densities, at 303.16 K, were measured with a DMA 60 digital precision density meter (Anton Paar, Austria).

Temperatures were measured with a platinum resistance thermometer, calibrated by the NBS (U.S.A.), and coupled with a Leeds and Northrup M ller bridge Model G2.

Excess enthalpies were determined in an LKB flow micro-calorimeter (Model 2107-121) using the auxiliary equipment and operating procedures described by Benson and Groller (16, 17); studies of test systems indicate that the precision of the results is 1% or better over most of the mole fraction range. A calibration was carried out after each run. All measurements were carried out at a temperature of 303.16 ± 0.005 K because at temperatures below 301.61 K sulfolane is a solid.

For the sake of uniformity with previous works, nitrile was indicated as component 1 and sulfolane as component 2.

Results

Experimental data, H^E (J mol⁻¹), are listed in Table II and shown graphically in Figure 1 (sulfolane + propionitrile, + bu-