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^E_m 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 contradictive behavior of V^E_m and ϵ^E_m 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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Received for review July 1, 1980. Revised manuscript received July 22, 1981. Accepted November 19, 1982.

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

Antonio Lopez, Michele Pansini, and Liliana Jannelli*

Thermodynamic Section, Institute of Chemistry, Faculty of Engineering, University of Naples, Naples, Italy

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 0.5*x*, 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 (μ = 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 Müller bridge Model G2.

Excess enthalpies were determined in an LKB flow microcalorimeter (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-

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Table I. Description and Physical Properties of Component Liquids

component	source	purification ref	$d^{303.16\,\mathrm{K}}/(\mathrm{g\ cm^{-3}})$ obsd	$d^{303.16\,\mathrm{K}}/(\mathrm{g\ cm^{-3}})$ lit.	mp/K obsd	mp/K lit.
acetonitrile	J. T. Baker Chemical Co. (analyzed reagent)	*11*	0.771 11	0.771 20 (*14*)		
propionitrile	J. T. Baker Co. (analyzed reagent)	*11*	0.771 66	0.771 96 (*13*)		
butyronitrile	Aldrich Chemical Co. (analyzed reagent)	*11*	0.781 67	0.781 83 (*13*)		
valeronitrile	Aldrich Chemical Co. (analyzed reagent)	*11*	0.790 27	0.790 32 (*8*)		
sulfolane	Shell Italia	*10*	1.262 35	1.262 30 (*12*)	301.61	301.61 (*10*) 301.78 (*15*)

Table II. Experimental Molar Excess Enthalpies, H^E, at 303.16 K

x_2	$H^E/(\mathrm{J\ mol^{-1}})$	x_2	$H^E/(\mathrm{J\ mol^{-1}})$	x_2	$H^E/(\mathrm{J\ mol^{-1}})$
		$x_2\ C_4H_8O_2S + (1 - x_2)\ CH_3CN$			
0.0533	1.7	0.2135	2.0	0.6128	−17.2
0.0816	2.8	0.3009	−2.7	0.7056	−18.4
0.1086	4.2	0.3987	−9.9	0.8433	−12.6
0.1612	4.0	0.5279	−15.4	0.8700	−11.6
0.1864	2.2	0.5857	−16.5		
		$x_2\ C_4H_8O_2S + (1 - x_2)\ CH_3CH_2CN$			
0.0714	60	0.3284	165	0.5518	166
0.2110	136	0.4157	177	0.7853	105
0.3084	159	0.5302	172	0.8152	88
		$x_2\ C_4H_8O_2S + (1 - x_2)\ CH_3(CH_2)_2CN$			
0.0954	134	0.4649	324	0.6008	304
0.2473	252	0.5098	328	0.8177	189
0.3769	305	0.5778	311	0.8424	159
		$x_2\ C_4H_8O_2S + (1 - x_2)\ CH_3(CH_2)_3CN$			
0.1003	189	0.4213	454	0.6108	427
0.2802	387	0.5063	463	0.8415	256
0.4008	453	0.5485	449	0.8631	221

tyronitrile, and + valeronitrile) and Figure 2 (sulfolane + acetonitrile). The first three systems indeed exhibit positive excess enthalpies over the entire composition range with a sharp maximum which occurs approximately at 0.5x and steadily decreases in importance with decreasing nitrile chain length. In the case of the acetonitrile (1) + sulfolane (2) system, scarcely noticeable positive excess enthalpies occur only in a limited region ($0 \leq x \leq 0.25$) close to pure nitrile; the data indeed lie on an S-shaped curve with a sharp minimum occurring in the sulfolane-rich region.

The experimental results for the four systems were fitted, by a least-squares computer program, to a smoothing function:

$$H^E/(\mathrm{J\ mol^{-1}}) = x_1x_2\{A + B(x_2 - x_1) + C(x_2 - x_1)^2 + ...\} \tag{1}$$

Each point was assigned unit weight.

The parameters A-E, their standard deviations σ, and the standard deviations $\sigma(H^E)$ of the molar excess enthalpies are given in Table III. Excess enthalpies H^E at 0.5x have been reported in Table IV for all investigated systems.

Discussion

The magnitude of excess enthalpies of mixing sulfolane + acetonitrile, + propionitrile, + butyronitrile, + valeronitrile (H^E_{max} ranging between −18.5 and 480 J mol^{-1}) is indicative of only moderate interactions of any kind. Hence, these mixtures may be classified as not quite athermal (*18*, *19*), this according with the regular behavior arising from our previous measurements of excess volumes of mixing (*6*, *8*) and dielectric constants (*6*, *9*).

The observed behavior of H^E-composition plots may be ascribed to the superimposition and the alternative predominance of the opposite effects of two factors: that is to say, the lessening of interactions between like molecules which result in positive H^E values and interactions between unlike molecules

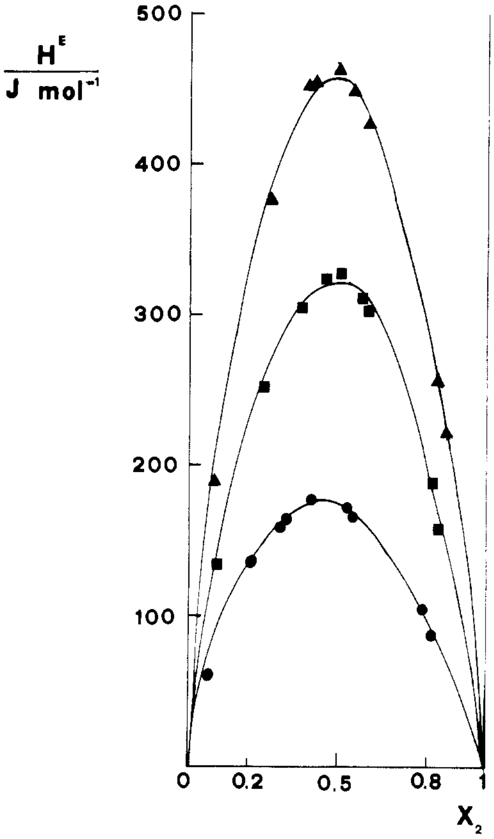

Figure 1. Molar excess enthalpies of nitrile (1) + sulfolane (2) systems at 303.16 K. Experimental results: (●) propionitrile; (■) butyronitrile; (▲) valeronitrile. Curves calculated from eq 1 with coefficients from Table III.

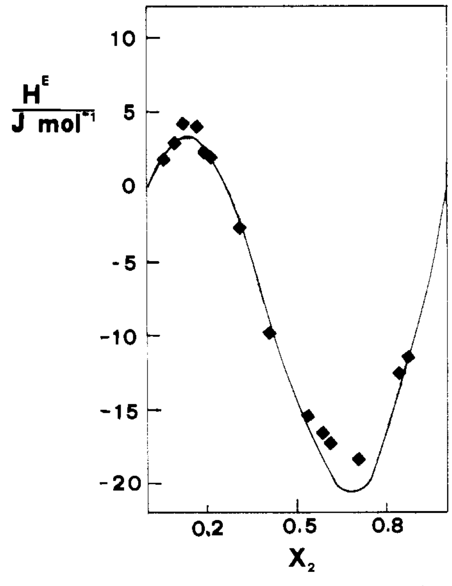

Figure 2. Molar excess enthalpies of acetonitrile (1) + sulfolane (2) system at 303.16 K. Experimental results: (◆) curve calculated from eq 1 with coefficients from Table III.

Table III. Parameters, Their Standard Deviations, σ, in the Smoothing Equation 1, and Standard Deviations, $\sigma(H^E)$, for the Molar Excess Enthalpies at 303.16 K

system	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	$E \pm \sigma$	$\sigma(H^E)$/ (J mol^{-1})
x_2 $C_4H_8O_2S$						
+ $(1 - x_2)$ CH_3CN	−58 ± 4	−117 ± 14	39 ± 12	52 ± 27		1.6
+ $(1 - x_2)$ CH_3CH_2CN	686 ± 6	−67 ± 32	217 ± 74	−324 ± 97	−386 ± 157	2
+ $(1 - x_2)$ $CH_3(CH_2)_2CN$	1289 ± 11	−4 ± 53	105 ± 39	−357 ± 110		5
+ $(1 - x_2)$ $CH_3(CH_2)_3CN$	1834 ± 11	−110 ± 18	269 ± 37			5

Table IV. H^E at $x = 0.5$ at 303.16 K

system	$H^E(x{=}0.5)$/(J mol^{-1})
x_2 $C_4H_8O_2S$	
+ $(1 - x_2)$ CH_3CN	−15
+ $(1 - x_2)$ CH_3CH_2CN	172
+ $(1 - x_2)$ $CH_3(CH_2)_2CN$	322
+ $(1 - x_2)$ $CH_3(CH_2)_3CN$	459

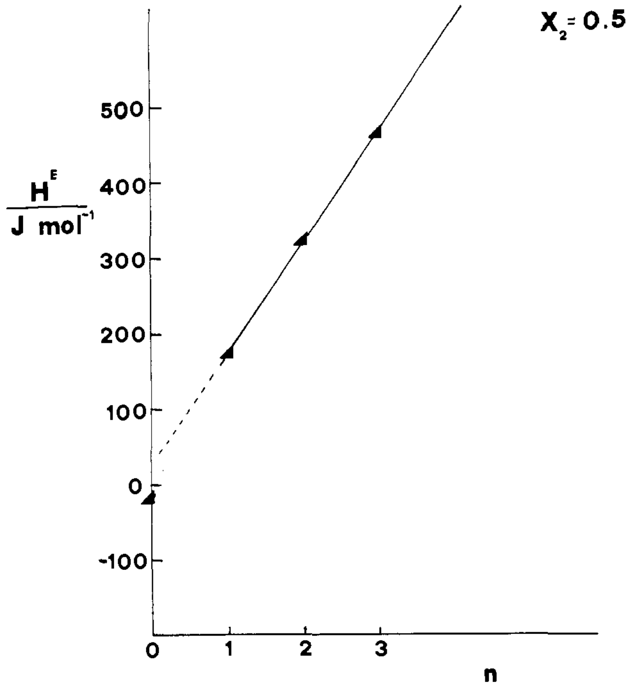

Figure 3. Molar excess enthalpies at $x = 0.5$ vs. n, the number of CH_2 groups in $CH_3(CH_2)_nCN$, at 303.16 K.

which result in negative H^E values.

As already pointed out (*3*, *5*, *6*, *8*), the sulfolane, because of the steric hindrance of its globular molecule, may play the role of an almost inert diluent and limit its action to a disturbing effect on the structure of the other component. This accounts for the positive excess enthalpies which may be ascribed mainly to a reduction of nitrile self-association in the presence of sulfolane. That H^E terms steadily decrease from valeronitrile to propionitrile is indicative that the effect of weak interactions with sulfolane becomes more noticeable with decreasing steric hindrance of nitrile carbon chain. Finally, in the case of acetonitrile the more active monomer molecules, arising from destruction of self-association, may check more easily the proper orientation for interacting, though weakly, with the negative exposed end of the sulfolane dipole. Hence, the S-shaped H^E vs. x_2 curve is consistent with a progressive predominance of nitrile–sulfolane interactions (negative H^E values) over self-association with increasing sulfolane content in solutions.

In Figure 3 one may observe that the magnitude of the excess function H^E, at 0.5x, shows a linear trend to increase with increasing the number, n, of $>CH_2$ groups in the nitrile molecule. This agrees with the supposition that the main factor responsible for determining the importance of interactions of all kinds lies in the geometry of the molecule, the polarity of the molecule being unaffected by chain length (μ = 3.57 D). The point concerning the acetonitrile + sulfolane system deviates from the straight line as otherwise expected. The transmission of the inductive effect of $-CH_3$ to the $-C^+{=}N^-$ group indeed results in a lower dipole moment (μ = 3.44 D) for acetonitrile and reflects in a modified partition of acetonitrile molecules between self-association and interaction with sulfolane. A similar deviation was evidenced by plots of the maximum volume contraction as a function of the number of $>CH_2$ groups, as already reported (*8*). The above interpretation is strongly substantiated by conclusions drawn from dielectric constant measurements.

Acknowledgment

We are indebted to Prof. V. Elia for some helpful technical recommendations.

Registry No. Sulfolane, 126-33-0; acetonitrile, 75-05-8; propionitrile, 107-12-0; butyronitrile, 109-74-0; valeronitrile, 110-59-8.

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Received for review May 4, 1982. Accepted November 22, 1982.