in the presence of liquid carbon dioxide at 25 °C. The experimental data in Figure 3 also suggest that solubilities in supercritical carbon dioxide increase as the number of chlorine groups on the solute increases. This is in agreement with the experimental results of Francis and is probably a consequence of the decreased hydrogen bonding in the condensed phase with the addition of chlorine groups.

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Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. Excess Volumes and Dielectric Constants of Benzonitrile–Sulfolane and Acetonitrile–Sulfolane Systems

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Excess volumes and dielectric constants were measured for sulfolane + acetonitrile and sulfolane + benzonitrile mixtures over the entire composition range, $0 \leq x \leq 1$, at several temperatures, ranging between 283.13 and 333.16 K. The observed low deviations from ideality are indicative of only moderate interactions of all kinds; nevertheless the experimental data supply evidence for the supposition that interactions between unlike molecules predominate in acetonitrile–sulfolane mixtures, whereas these interactions are relatively weak if compared with the average of the energies of interaction between benzonitrile pairs of molecules, in benzonitrile–sulfolane mixtures.

Introduction

These measurements were carried out as a part of a long term study (*1*) of the thermodynamic and physical properties of binary mixtures involving sulfolane. The aim of the research was to study the nature and the entity of molecular interactions in these systems and, for this particular work, to provide further experimental data for a comparison of the behavior of the -CN group in aromatic and aliphatic molecules.

In spite of their fairly high dipole moments, ranging between 3.4 and 4.8 D, both nitrile and sulfolane are not good proton acceptors (*2*) even if the negative ends of their dipoles are at the exterior of the molecules; on the other hand, they cannot act as proton donors (*3*) (their donicity numbers range between 11.9 (C_6H_5CN) and 14.8 (CH_3CN) (*4*)). Furthermore the sulfolane, owing to the steric hindrance of its globular molecule, does not easily interact with any kind of ions or molecules.

Therefore the presence of only moderate interactions of all kind is expected in the systems benzonitrile–sulfolane and acetonitrile–sulfolane. A previous study on the nitrobenzene–sulfolane system (nitrobenzene and benzonitrile molecules possess similar shape, quite equal volumes, and dipole moments (*1*)) was consistent with this supposition; the observed very low deviations from ideality were interpreted in terms of moderate interactions between nitrobenzene pairs of molecules, competitive in strength with the interactions between unlike molecules. In the case of acetonitrile (μ = 3.5 D) a reduced self-association is expected because of the lacking of mesomeric forms, which enhance the polarity of molecules; on the contrary they are present in benzonitrile as well as in nitrobenzene.

Therefore the study of acetonitrile–sulfolane and benzonitrile–sulfolane systems should provide a sharper differentiation of the effects, arising from interactions between like and unlike molecules, on excess properties.

Experimental Section

Materials. Sulfolane, kindly supplied by Shell Italia, was purified carefully and dried (*5*); the melting point of the final product was 301.61 K, in close agreement with the most reliable literature data (*6*). Fluka high-purity benzonitrile was fractionally distilled three times through a 60-cm column in accordance with the recommendations of Brown and Ives (*7*) for dielectric constant measurements; bp 464 K. Fluka high-purity acetonitrile was purified in the way reported in ref 8. The specific conductance of the purified sample was less than $2 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$. Solutions were made by weight (reduced to mass) in a drybox and then stored in dark containers and protected from moisture as far as possible. For the sake of uniformity with our previous works (*1*), the sulfolane is identified as component 2 and the other substance as component 1, and compositions are stated as mole fractions, x_2, of sulfolane in the case of volumes and as volume fractions, ϕ_2, in the case of dielectric constants.

Apparatus and Procedure. Measurements of density and dielectric constant were made in the temperature range 283.16–333.16 K and over the entire composition range.

Densities of solutions were measured with an Anton Paar DMA 60 digital density meter thermostated by a Lauda ultrathermostat, which controlled the temperature to within 0.005 K. The density was determined by measuring the period of oscillation of a vibrating U-shaped tube filled with liquid samples. A calibration was made with standard pure liquids for each temperature. The maximum error in density was estimated to be 3×10^{-5} g cm^{-3}.

Dielectric constants were measured, at 2 MHz, with the heterodyne beat method, using a DM 01 dipolmeter (Wissen-

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Table I. Molar Volumes $V°$, 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}
benzonitrile (1)	283.79	101.768	(93.999)	−1.572	−0.111	−0.648	−1.061	0.012
+ sulfolane (2)	293.47	102.639	(94.614)	−1.535	−0.182	−0.504	−0.602	0.008
	303.21	103.529	95.244	−1.549	−0.185	−0.303	−0.459	0.007
	313.11	104.456	95.885	−1.505	−0.210	−0.193	−0.157	0.008
	323.16	105.407	96.564	−1.537	−0.115	−0.125	−0.370	0.008
acetonitrile (1)	293.47	52.520	(94.614)	−2.964	0.755	−0.512	0.608	0.009
+ sulfolane (2)	303.16	53.239	95.245	−2.955	1.062	−0.266	0.641	0.010
	313.16	53.990	95.894	−3.260	1.202	−0.351	0.447	0.011
	323.16	54.761	96.554	−3.442	1.356	−0.161	0.102	0.016

Table II. Molar Excess Volumes V^E at Five Temperatures and Deviations δV^E from Smoothing Equations of Benzonitrile (1) + Sulfolane (2) Mixtures

	283.79 K		293.47 K		303.21 K		313.11 K		323.16 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}
0.0578	−0.070	−2	−0.078	4	−0.073	−2	−0.078	4	−0.070	1
0.1104	−0.131	4	−0.129	−10	−0.126	9	−0.122	−14	−0.126	−6
0.2043	−0.247	−1	−0.242	2	−0.244	−8	−0.239	9	−0.246	12
0.3195	−0.331	9	−0.324	−4	−0.326	0	−0.318	3	−0.325	0
0.4213	−0.382	−1	−0.376	6	−0.370	2	−0.362	2	−0.368	−3
0.5150	−0.395	−1	−0.385	0	−0.382	6	−0.369	−9	−0.371	−14
0.6199	−0.404	−15	−0.391	10	−0.385	−4	−0.371	1	−0.371	0
0.7024	−0.386	−11			−0.363	−7	−0.348	7	−0.347	7
0.7189	−0.376	5	−0.361	5	−0.350	−1	−0.333	0	−0.338	−7
0.8110	−0.320	21	−0.292	−12	−0.280	10	−0.262	−6	−0.264	−4
0.9062	−0.217	10	−0.194	−5	−0.183	−1	−0.160	1	−0.164	1
0.9449	−0.159	−7	−0.135	4	−0.123	−4	−0.102	1	−0.103	−1

Table III. Molar Excess Volumes V^E of Acetonitrile (1) + Sulfolane (2) Mixtures, at Four Temperatures and Deviations δV^E from Smoothing Equations

	293.47 K		303.16 K		313.16 K		323.16 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}
0.0356	−0.158	0	−0.171	−10	−0.173	0	−0.151	18
0.1050	−0.394	−1	−0.396	6	−0.433	4	−0.434	4
0.1945	−0.584	4	−0.602	1	−0.669	−7	−0.708	−26
0.2682	−0.684	0	−0.697	3	−0.763	10	−0.792	16
0.3460	−0.743	−5	−0.759	−6	−0.842	−10	−0.873	4
0.4446	−0.754	0	−0.761	−1	−0.836	3	−0.895	−8
0.5496	−0.714	2	−0.704	2	−0.777	1	−0.812	7
0.6807	−0.587	6	−0.552	8	−0.613	6	−0.647	−2
0.8159	−0.396	−15	−0.351	−16	−0.396	−16	−0.401	−7
0.9080	−0.185	12	−0.148	12	−0.176	14	−0.191	8

chaftlich Techische Werkstätten, 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 9. The maximum error in dielectric constants was estimated to be 0.04.

Results

Both molar volumes (Table I) and dielectric constants for pure components (Table IV) are in close agreement with the most reliable literature values (*1*). The values for pure sulfolane, at temperatures lower than 301.16 K, appear in parentheses because these are extrapolated values.

Volumes of Mixing. The excess volumes on mixing benzonitrile and sulfolane at 283.79, 293.47, 303.21, and 313.16 K are shown graphically in Figure 1. All mixtures exhibit negative excess volumes over the entire composition range with a minimum (less than −0.4 cm^3) which is slightly shifted toward the sulfolane-rich region and decreases in magnitude with increasing temperature; starting from 40 °C the temperature does not influence the minimum remarkably.

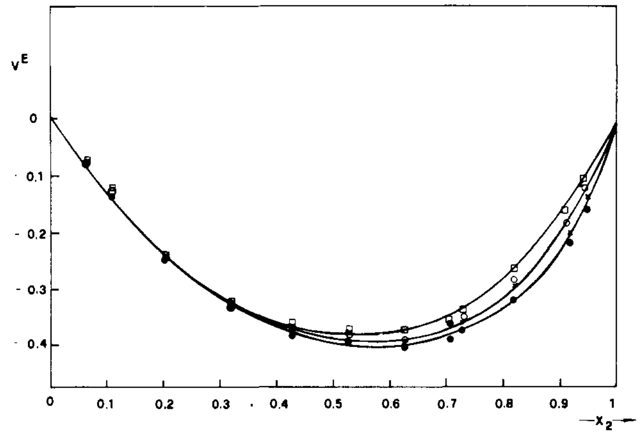


Figure 1. Excess volumes, V^E, for benzonitrile (1) + sulfolane (2) at 283.79 K (●), 293.47 K (○), 303.21 K (◒), 313.11 K (□), and 323.16 K (×).

The excess volumes on mixing acetonitrile and sulfolane at 293.47, 303.16, 313.16, and 323.16 K are shown graphically in Figure 2; all mixtures exhibit negative excess volumes over the entire composition range with a deeper minimum (less than −0.9 cm^3) slightly shifted toward the acetonitrile-rich region; the magnitude of the minimum increases steadily with temperature.

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

	T/K	ϵ_1°	ϵ_2°	A'	B'	C'	D'
benzonitrile (1)	293.47	25.69	(44.50)	−2.305	−1.756	1.735	1.378
+ sulfolane (2)	313.16	23.90	42.08	−2.285	−1.570	0.331	−0.760
	333.16	22.26	39.80	−2.296	−2.106	0.422	1.108
acetonitrile (1)	293.47	36.76	(44.50)	4.319	0.585	−0.075	2.175
+ sulfolane (2)	313.16	33.70	42.06	4.139	1.462	−1.469	−3.328
	333.16	31.10	39.73	3.497	1.204	−0.741	−1.765

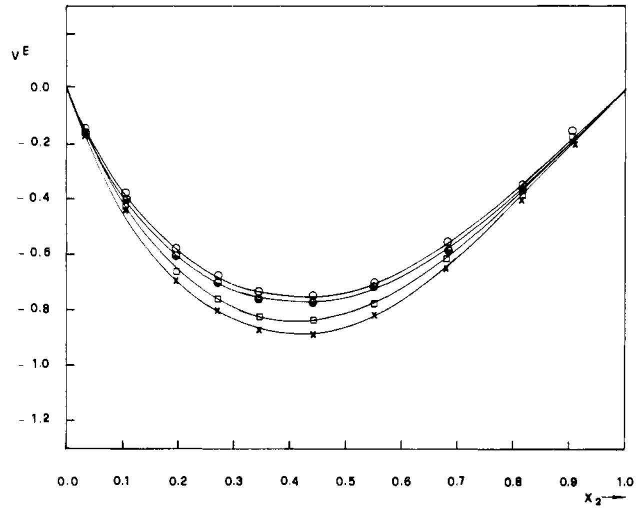


Figure 2. Excess volumes, V^E, for acetonitrile (1) + sulfolane (2) mixtures at 293.47 K (○), 303.16 K (⊖), 313.16 K (□), and 323.16 K (X).

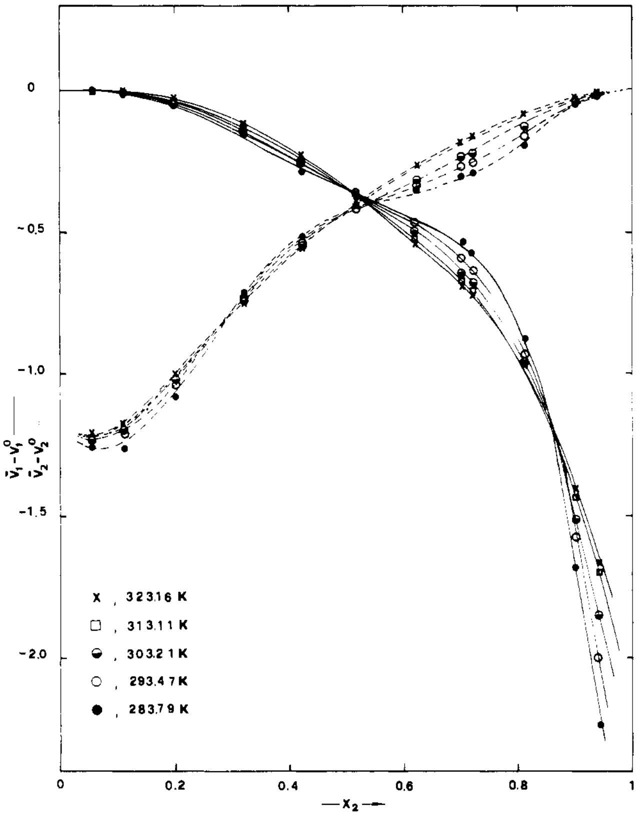


Figure 3. $\bar{V}_1 - V_1^\circ$ and $\bar{V}_2 - V_2^\circ$ plotted against x_2 for benzonitrile (1) + sulfolane (2) mixtures at several temperatures.

The experimental results for the two binary systems are summarized in Tables II and III, where they are compared with the values calculated by smoothing equations of the type

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

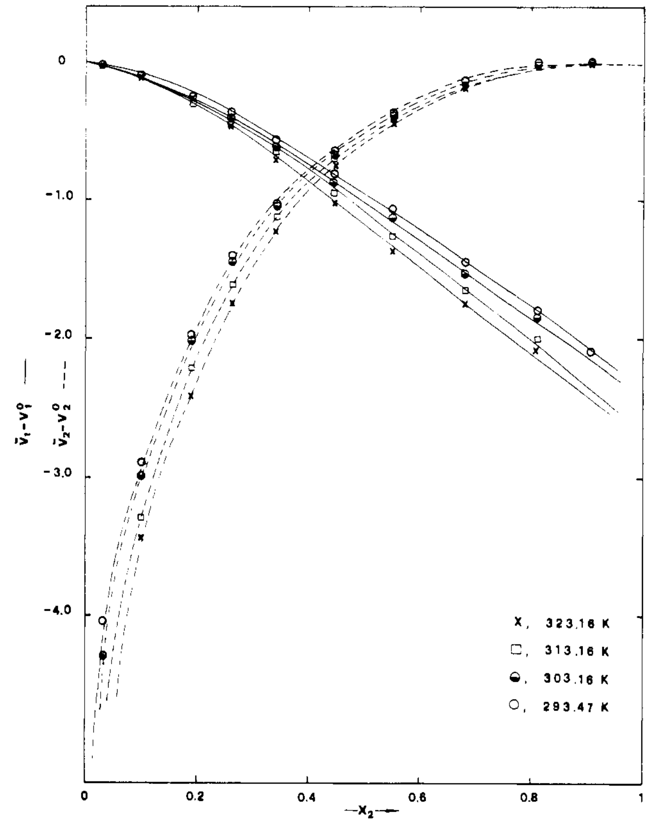


Figure 4. $\bar{V}_1 - V_1^\circ$ and $\bar{V}_2 - V_2^\circ$ plotted against x_2 for acetonitrile (1) + sulfolane (2) mixtures at several temperatures.

The parameters A, B, C, ... of these equations were selected by the method of least squares to obtain the best fit of the experimental results. These parameters and the standard deviations σ, at each temperature, are included in Table I. Deviations $\delta V^E = V^E_{\text{exptl}} - V^E_{\text{calcd}}$, as a function of mole fraction x_2 of sulfolane, at each temperature, are also summarized in Tables II and III. Relative molar partial volumes $\bar{V} - V^\circ$ of both the components of the two binary systems derived from eq 1 are plotted in Figures 3 and 4 against the mole fraction of sulfolane, x_2, for each temperature. Only slight deviations from ideal volumes are observed for both substances, which are scarcely influenced by the temperature.

Dielectric Constants. The dielectric constants, $\epsilon_{1,2}^E$, of the benzonitrile-sulfolane system exhibit low deviations (not exceeding 2% of the measured values) from the ideal values which can be calculated on the basis of a linear dependence of $\epsilon_{1,2}$ on volume composition, ϕ_2. These deviations (Figure 5) fall on an S-shaped curve with a shoulder in the benzonitrile-rich region and a sharper minimum which does not exceed 0.6ϵ in the sulfolane-rich region. The magnitude and the position of the minimum are slightly affected by temperature in the explored temperature range.

On the contrary, the dielectric constants of acetonitrile-sulfolane system exhibit positive deviations (~3% of the measured $\epsilon_{1,2}$) from ideality with a sharp maximum at 0.55ϕ_2 (Figure 6); the magnitude of the maximum steadily decreases with increasing temperature.

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

	293.47 K				313.16 K				333.16 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	$\bar{\epsilon}_1$	$\bar{\epsilon}_2$
Benzonitrile (1) + Sulfolane (2)												
0.085	27.29	27.26	25.71	43.88	25.39	25.42	23.95	41.29	23.68	23.68	22.26	38.98
0.132	28.09	28.10	25.74	43.62	26.22	26.22	23.99	40.94	24.47	24.46	22.27	38.89
0.218	29.62	29.61	25.82	43.25	27.68	27.66	24.04	40.66	25.87	25.88	22.32	38.68
0.321	31.38	31.40	25.88	43.07	29.38	29.38	24.02	40.70	27.54	27.55	22.37	38.50
0.409	32.92	32.92	25.81	43.18	30.86	30.86	23.92	40.88	28.99	28.98	22.37	38.52
0.548	35.40	35.38	25.33	43.68	33.25	33.25	23.58	41.24	31.28	31.25	22.05	38.84
0.606	36.48	36.46	24.98	43.94	34.28	34.29	23.39	41.39	32.26	32.24	21.78	39.04
0.698	38.30	38.22	24.32	44.29	35.98	35.98	22.97	41.60	33.87	33.88	21.17	39.37
0.799	40.31	40.33	23.67	44.52	37.96	37.90	22.32	41.82	35.79	35.77	20.34	39.64
0.898	42.40	42.39	23.55	44.54	39.85	39.88	21.32	41.99	37.67	37.71	19.61	39.78
0.948	43.45	43.45	23.91	44.52	40.93	40.93	20.60	42.05	38.76	38.73	19.40	39.80
Acetonitrile (1) + Sulfolane (2)												
0.062	33.37	33.37	36.73	47.13	34.43	34.44	33.74	45.16	31.80	31.81	31.12	42.26
0.172	38.57	38.57	36.69	47.58	35.66	35.64	33.85	44.24	33.02	33.00	31.19	41.68
0.300	39.95	39.91	36.90	46.92	37.01	36.95	33.89	44.10	34.36	34.32	31.25	41.48
0.394	40.72	40.81	37.24	46.29	37.86	37.90	33.98	43.93	35.27	35.27	31.36	41.28
0.484	41.58	41.58	37.63	45.80	38.77	38.77	34.29	43.54	36.10	36.15	31.61	40.97
0.586	42.41	42.37	38.07	45.41	39.56	39.65	35.00	42.93	37.03	37.05	32.14	40.52
0.684	43.03	43.06	38.51	45.16	40.29	40.35	36.01	42.36	37.79	37.82	32.87	40.10
0.791	43.68	43.72	39.22	44.91	41.02	40.95	37.05	41.98	38.52	38.52	33.73	39.79
0.887	44.20	44.20	40.50	44.67	41.40	41.40	37.15	41.94	39.15	39.07	34.15	39.70
0.946	44.43	44.41	41.88	44.55	41.76	41.71	36.29	42.02	39.38	39.40	33.96	39.71
0.974	44.46	44.47	42.76	44.51	41.84	41.88	35.51	42.05	39.57	39.57	33.69	39.73

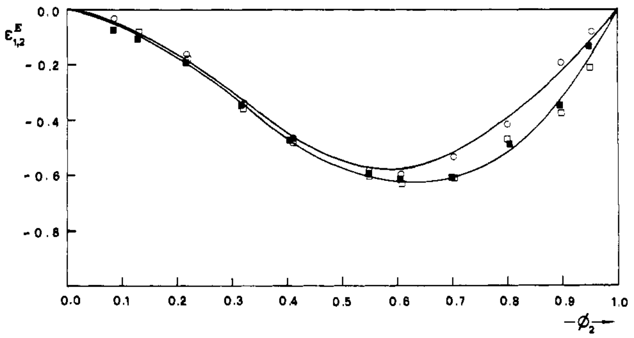


Figure 5. Excess dielectric constants, $\epsilon_{1,2}{}^E$, plotted against ideal volume fraction, ϕ_2, for benzonitrile (1) + sulfolane (2) mixtures at 333.16 K (■), 313.16 K (□), and 293.47 K (○).

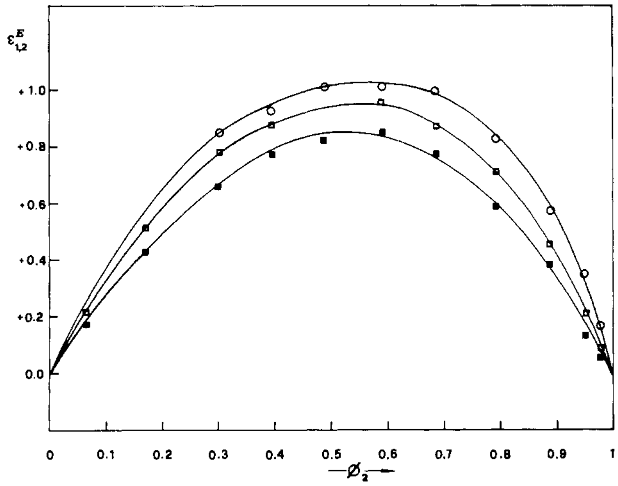
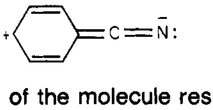


Figure 6. Excess dielectric constants, $\epsilon_{1,2}{}^E$, plotted against ideal volume fraction, ϕ_2, for acetonitrile (1) + sulfolane (2) mixtures at 293.47 (○), 313.16 K (□), and 333.16 K (■).

Discussion

The magnitude of the measured excess functions in the two systems is indicative of only moderate interactions of all kinds. Therefore the asymmetry in the excess volume curves vs. x_2 may be ascribed mainly to a difference in molar volumes of the two components (see Table I); such an effect results indeed in a characteristic skewing of the minimum in the direction of the smaller component (sulfolane in the case of the benzonitrile-sulfolane system and acetonitrile in the case of the acetonitrile-sulfolane system). On the contrary the magnitude of the minimum depends on the superimposition of the opposite effects arising from steric factors and the alternatively predominating of self-association of nitriles or interactions between unlike molecules, the latter being strengthened by the lessening of the former. In the case of the benzonitrile-sulfolane system the presence of mesomeric forms of the type



enhancing the polarity of the molecule results in a moderate, but more stable, self-association; therefore the system may be regarded as a regular mixture of scarcely self-associated benzonitrile and monomer sulfolane which plays the role of an almost inert diluent; in a small region close to pure benzonitrile, however, a structure-breaking effect, by the addition of sulfolane, may be evidenced by the presence of the shoulder in the dielectric constant curve vs. volume fraction ϕ_2. The scarcely noticeable influence of composition and temperature on both molar volumes and actual dielectric constants (Figure 3 and Table V) of components provides further evidence for the supposition of very low interactions of any kind. Self-association forces should be less intensive in the case of acetonitrile owing to its aliphatic character and the cylindrical symmetry of its molecules, and they should be even more lessened by the presence of sulfolane, which interacts, though weakly, with the more active monomer molecules. The positive deviations from ideality of dielectric constants and the presence of a sharp maximum in $\epsilon_{1,2}{}^E/\phi_2$ plots provide evidence for the supposition of a complex formation presumably arising from dipole interactions; the magnitude of the maximum in $\epsilon_{1,2}{}^E/\phi_2$ curves decreases with temperature, as expected, according to the decrease in complex formation. If the negative excess volumes were ascribed only to complex formation, one would expect, however, a positive $\delta V_m^E/dT$ term, whereas the observed V_m^E temperature coefficient is negative and this is a common feature of other complex forming mixtures involving acetonitrile (*10*). (Interpretation of this anomalous behavior has been given in terms of the volume of the complex decreasing with temperature, whose effect more than compensates the decrease in complex formation.) In the case of acetonitrile–sulfolane mixtures one may rather suppose that, owing to the steric hindrance of its globular molecule, only the exposed negative end of sulfolane dipole is involved in complex formation; this implies that the CH_3CN molecules check the proper orientation for interacting; presumalby a parallel alignment of dipoles is needed resulting in the observed increase in the dielectric constant. On complex decomposition, the monomer acetonitrile may accommodate interstitially in the free volumes or cavities of sulfolane, even if weakly structured, and the related volume contraction superimposes to the steric effects in reducing volume on mixing; reasonably this effect would be enhanced by the temperature.

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Thermal Conductivity of Aqueous Sodium Chloride Solutions from 20 to 330 °C

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Selected thermal conductivity data reported in the literature for aqueous sodium chloride solutions are tabulated for geothermal energy applications. Experimental values were converted where necessary to a set of consistent units of degree Celsius, molal concentration and watts per meter Celsius. A selected empirical equation is given to reproduce the data over the temperature range 20–330 °C, concentrations between 0 and 5 *m*, and at saturation pressures. A table of smoothed values is generated by using the correlation which reproduces the experimental data to ±2% up to 80 °C. Between 100 and 150 °C, the percent deviation is +17% to +31% for the one set of available experimental values. Recommendations for additional data needs are given.

An important facet in the development and utilization of geothermal energy is the thermodynamic and transport data for the hot brines which transport heat and the vapors which drive turbines to produce electricity. While geothermal brines contain a large number of dissolved electrolytes and gases, the main constituent is sodium chloride. Consequently, modeling and other studies which require basic data on geothermal brines are generally based on those of aqueous NaCl solutions (*1*, *2*). While data on many basic properties are needed, this report covers a survey of the available data on the thermal conductivity of aqueous NaCl solutions for regions of geothermal interest: temperatures to 350 °C, pressures to 500 bar (50 MPa), and concentrations up to saturation.

The current published literature on the thermal conductivity of sodium chloride solutions to high temperatures is not extensive; this is especially true for work at temperatures exceeding 80 °C. Only one series of measurements are available to 150 °C: these are the data published by Korosi and Fabuss for application to sea water desalination (*3*, *4*). By far, the most extensive data are contained in graphical form in the publication by Yusufova, Pepinov, Nikolaev, and Guseinov with over 50 data points between 100 and 330 °C (*5*). However, accurate values cannot be read from the graphs.

Unless otherwise noted, the data were compiled from the original publications. Numerical values were converted where necessary to units of degree Celsius, molal concentration, and watts per meter degree Celsius. The density data needed to convert molar to molal concentrations were obtained from the paper by Rowe and Chou (*6*). Data on the thermal conductivity of water and the corresponding correlation equation are contained in publications of ref 7 and 8.

Additional information on the theory and instrumentation is obtained from ref 9; theory and correlations are from the publications by Kestin and Whitelaw (*8*), Riedel (*10*), Korosi and Fabuss (*3*, *4*) and Yusufova, Pepinov, Nikolaev, and Guseinov (*5*). Tabulated data for sodium chloride solutions are given in Table I. Of special interest are the survey by Jamieson, Irving, and Tudhope (*11*) and the correlation developed for sea water by Jamieson and Tudhope (*12*).

Scope of Compilation

The time span covered is mainly from 1929 to December 1979; earlier data are found in ref 13. Besides data on the thermal conductivity of aqueous sodium chloride solutions, selected portions of the available literature are included on theory, instrumentation, data estimation methods, other salts (e.g.,

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