Thermodynamic and Physical Properties of Binary Systems Involving Sulfolane + 2-Methylpropionitrile and Sulfolane + 2,2-Dimethylpropionitrile

Antonio Lopez, Liliana Jannelli,* and Michele Pansini

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

Volumes, dielectric constants, and enthalpies of mixing sulfolane + 2-methylpropionitrile and + 2,2-dimethylpropionitrile were measured over the entire composition range, at selected temperatures, with the aim of studying the influence of nitrile chain branching on the kind and the importance of interactions between like and unlike molecules. The magnitude of the negative excess volumes and the deviations of dielectric constants from ideality, as well as the low positive mixing enthalpies, are consistent with the supposition of only moderate interactions of any kind; nitrile–nitrile interactions seem however to predominate over sulfolane–nitrile interactions with increasing temperature. A review of collected data and results of previous similar measurements on *n*-alkane nitrile + sulfolane mixtures supply evidence for the supposition that the main factor responsible for the behavior of excess properties lies in the steric hindrance of nitrile molecules, the polarity being unaffected by chain lengthening and branching.

Introduction

Previous publications (*1–4*) from our laboratory have described measurements of excess volumes, dielectric constants, and mixing enthalpies of sulfolane + the first four members of the *n*-alkane nitrile series.

The data supply evidence for the supposition of only moderate interactions between like and unlike molecules which decrease in importance with lengthening nitrile carbon chain; however, nitrile self-association seems to predominate with increasing temperature over sulfolane–nitrile interactions.

The studies were continued and extended, in the present paper, by reporting the results of similar investigations on two binary systems involving sulfolane + 2-methylpropionitrile and + 2,2-dimethylpropionitrile and this with the aim of studying the type and importance of the effect of chain branching on interactions of any kind.

Experimental Section

Materials. Primary sources of component liquids as well as adopted purification methods are summarized in Table I together with measured physical properties of purified samples and the most reliable literature data (*5–14*), for the sake of comparison.

A good agreement between our data and literature data is observed in the case of sulfolane and 2,2-dimethylpropionitrile, whereas both the density and the dielectric constant of 2-methylpropionitrile differ markedly from the literature data. However, repeated distillations did not produce changes in the physical properties of the substance. In previous works (*2, 3*) we called attention to the fact that up-to-date measurements of physical properties of nitriles are lacking in the literature and the few reported data exhibit a large variation (*3–10*%).

Apparatus. Densities were measured with a DMA 60 digital precision density meter (Anton Paar, Austria) described previously (*1*). The precision on density was better than 5×10^{-5} g cm^{-3} and the precision on volume was 1×10^{-2} cm^3.

Dielectric constants were measured, at 2 MHz, with a WTW dipolmeter DM01 by using the heterodyne beat method. The apparatus, as well as cell calibration, was described elsewhere (*1, 3*). The precision was estimated to be $\pm 0.04\epsilon$. The excess enthalpies were determined in a LKB microcalorimeter (Model 2107) by using the auxiliary equipment and operating procedures recommended by Benson and Grolier (*15*). The precision of results was 1% or better over most of the mole fraction range.

Solutions for dielectric constants and density measurements were prepared by weight, reduced to mass, and then stored in dark containers and protected from moisture as far as possible.

Density and dielectric constant measurements were carried out at 293.16, 303.16, and 313.16 K.

Enthalpy measurements were carried out at 303.16 ± 0.005 K because below 301.61 K sulfolane is a solid.

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 mole fraction, x, in the case of volumes and mixing enthalpies and as volume fraction, ϕ, in the case of dielectric constants.

Results

Measured excess volumes of mixing sulfolane + 2-methylpropionitrile and + 2,2-dimethylpropionitrile are shown graphically, as a function of composition, in Figure 1. All mixtures exhibit negative excess volumes over the entire composition range with a sharp minimum, in no case exceeding -1.5 cm^3 mol^{-1}; it occurs approximately at $0.5x$. The magnitude of the minimum, more noticeable in the case of the 2,2-dimethylpropionitrile (1) + sulfolane (2) system, increases steadily with temperature.

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

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

The parameters A–D for each temperature, their standard deviations σ, and the standard deviations $\sigma(V^E)$ of the molar excess volumes are given in Table II.

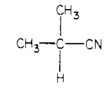
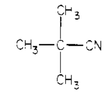
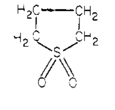
Excess volumes and δV^E, at each composition and temperature, are listed in Table III.

Dielectric Constants. Dielectric constants $\epsilon_{1,2}$ were measured over the entire composition range $0 \leq \phi_2 \leq 1$, at the three temperatures. The results are summarized in Table IV. They exhibit scarcely noticeable deviations from ideal values which can be calculated on the basis of a linear dependence of $\epsilon_{1,2}$ on volume composition, ϕ_2. Deviations are but little influenced by temperature. They are however positive and more remarkable in the nitrile-rich region, at least in the case of the 2,2-dimethylpropionitrile (1) + sulfolane (2) system.

Mixing Enthalpies. Measured $H^E/(\mathrm{J\ mol^{-1}})$ values at 303.16 K are listed in Table V and shown graphically in Figure 2, for

0021-9568/83/1728-0176$01.50/0

Table I. Description and Physical Properties of Component Liquids

component	source	purification ref	T/K	V/(cm^3 mol^{-1}) obsd	V/(cm^3 mol^{-1}) lit.	ϵ obsd	ϵ lit.	mp/K obsd	mp/K lit.
	Aldrich Chemical Co. (analyzed reagent)	*5*	293.16	89.741	89.703 (*6*)	24.42			
			303.16	90.921		23.42			
			313.16	92.084		22.50			
	Aldrich Chemical Co. (analyzed reagent)	*5*	293.16	109.136	109.127 (*8*)	20.93	21.1 (*14*)		
			303.16	110.551	110.542 (*8*)	20.08	20.2 (*14*)		
			313.16	112.000	111.994 (*8*)	19.28	19.4 (*14*)		
	Shell Italia	*9*	293.16	[94.498][a]		[44.61][a]			
			303.16	95.195	95.202 (*10*)	43.38	43.38 (*12*)		
			313.16	95.871	95.894 (*11*)	42.12	42.12 (*12*)	301.61	301.61 (*9*) 301.78 (*13*)

[a] Data for pure sulfolane, at 293.16, appear in brackets because these are extrapolated values.

Table II. Parameters, Their Standard Deviations, σ, in the Smoothing Equation 1, and the Standard Deviations, $\sigma(V^E)$, for the Molar Excess Volumes at Three Temperatures

T/K	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	$\sigma(V^E)$/(cm^3 mol^{-1})
		$C_4H_8O_2S + C_4H_7N$			
293.16	−3.789 ± 0.029	0.385 ± 0.090	−0.117 ± 0.064	0.731 ± 0.142	0.006
303.16	−4.191 ± 0.013	0.707 ± 0.014	−0.522 ± 0.029		0.005
313.16	−4.469 ± 0.021	0.562 ± 0.065	−0.489 ± 0.046	0.426 ± 0.103	0.004
		$C_4H_8O_2S + C_5H_9N$			
293.16	−5.632 ± 0.051	0.327 ± 0.153	0.853 ± 0.121	0.582 ± 0.258	0.012
303.16	−5.884 ± 0.072	0.801 ± 0.208	1.037 ± 0.145	0.359 ± 0.313	0.015
313.16	−6.565 ± 0.036	0.432 ± 0.103	0.547 ± 0.072	2.076 ± 0.155	0.010

Table III. Molar Excess Volumes, V^E, and Deviations, σV^E, from the Smoothing Equation 1 at Three Temperatures

	293.16 K		303.16 K		313.16 K	
x_2	V^E/(cm^3 mol^{-1})	$10^3 \cdot (\delta V^E)$/(cm^3 mol^{-1})	V^E/(cm^3 mol^{-1})	$10^3 \cdot (\sigma V^E)$/(cm^3 mol^{-1})	V^E/(cm^3 mol^{-1})	$10^3 \cdot (\sigma V^E)$/(cm^3 mol^{-1})
			$x_2\ C_4H_8O_2S + (1 - x_2)\ C_4H_7N$			
0.0518	−0.236	−2	−0.258	0	−0.282	−3
0.0980	−0.396	7	−0.449	1	−0.475	8
0.1933	−0.662	−1	−0.756	−4	−0.793	2
0.2908	−0.831	−1	−0.940	4	−0.996	−2
0.3865	−0.926	−3	−1.034	4	−1.100	−3
0.4812	−0.955	−6	−1.050	3	−1.124	−3
0.5879	−0.898	3	−0.992	−3	−1.065	−3
0.6855	−0.777	4	−0.871	−9	−0.926	2
0.7856	−0.578	7	−0.665	2	−0.709	3
0.8907	−0.323	−10	−0.981	4	−0.400	1
0.9393	−0.170	4	−0.228	−1	−0.233	−1
			$x_2\ C_4H_8O_2S + (1 - x_2)\ C_5H_9N$			
0.0462	−0.250	−1	−0.263	3	−0.357	−2
0.1192	−0.558	7	−0.611	−5	−0.745	10
0.2254	−1.005	−7	−1.066	−6	−1.226	−7
0.3386	−1.277	−8	−1.365	−9	−1.519	−15
0.4238	−1.383	0	−1.451	10	−1.612	6
0.5380	−1.377	15	−1.424	22	−1.609	14
0.7288	−1.038	−1	−1.045	−4	−1.200	−3
0.8225	−0.733	−16	−0.703	4	−0.802	1
0.9099	−0.361	6	−0.375	−20	−0.391	−6
0.9558	the solution is solid		−0.162	8	−0.173	2

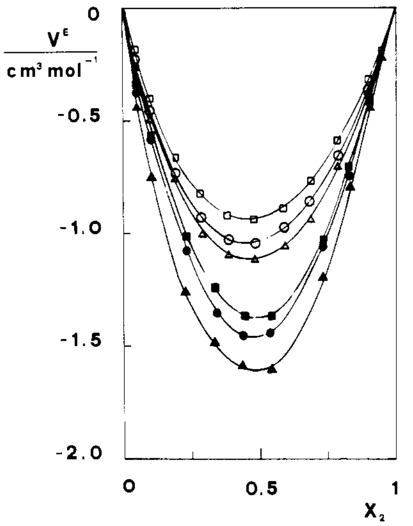


Figure 1. Excess volumes, V^E, plotted against sulfolane molar fraction, x_2, at three temperatures: 293.16 (squares), 303.16 (circles), and 313.16 (triangles) K for the 2-methylpropionitrile (1) + sulfolane (2) system (open symbols) and the 2,2-dimethylpropionitrile sulfolane (2) system (full symbols).

both binary systems. Also data concerning the propionitrile (1) + sulfolane (2) system drawn from a previous work (*4*) are reported in Figure 2, for the sake of comparison. All the systems exhibit positive excess enthalpies over the entire composition range, with a sharp maximum which occurs approximately at 0.5x, its magnitude becoming more noticeable with increasing the number of $-CH_3$ groups in the nitrile molecule.

The data were fitted, by a least-squares computer program, to the smoothed equation

$$H^E/(\mathrm{J\ mol^{-1}}) = x_1x_2\{A' + B'(x_2 - x_1) + C'(x_2 - x_1)^2 + D'(x_2 - x_1)^3\} \quad (2)$$

The parameters A'–D', their standard deviations σ, and the standard deviations $\sigma(H^E)$ of the molar excess enthalpies are given in Table VI.

Discussion

On the whole, the measured volume contractions V^E, never exceeding 2% of the medium molar volume, as well as the deviations from ideality of dielectric constants which only ex-

Table IV. Measured Dielectric Constants, $\epsilon_{1,2}$, and Deviations, ϵ^E, from Ideal Values

	293.16 K		303.16 K		313.16 K	
ϕ_2	$\epsilon_{1,2}$	ϵ^E	$\epsilon_{1,2}$	ϵ^E	$\epsilon_{1,2}$	ϵ^E
	ϕ_2 $C_4H_8O_2S$ + $(1 - \phi_2)$ C_4H_7N					
0.054	25.44	−0.07			23.53	−0.03
0.102	26.39	−0.09			24.56	0.06
0.201	28.53	0.06			26.49	0.06
0.300	30.50	0.01			28.43	0.04
0.397	32.45	0.00			30.29	0.00
0.493	34.37	0.00			32.21	0.05
0.599	36.58	0.06			34.19	−0.05
0.695	38.54	0.07			36.11	−0.02
0.793	40.45	0.01			37.97	−0.07
0.895	42.49	−0.01			39.98	−0.06
0.942	43.45	0.00			40.87	−0.09
	ϕ_2 $C_4H_8O_2S$ + $(1 - \phi_2)$ C_5H_9N					
0.040	21.93	0.05	21.07	0.06	20.27	0.08
0.099	23.38	0.10	22.49	0.11	21.65	0.13
0.200	25.82	0.12	24.88	0.13	23.99	0.16
0.306	28.30	0.10	27.32	0.11	26.38	0.14
0.388	30.20	0.06	29.19	0.07	28.19	0.09
0.501	32.82	0.00	31.77	0.02	30.72	0.04
0.604	35.23	−0.03	34.10	−0.05	33.04	0.00
0.698	37.44	−0.05	36.31	−0.04	35.18	−0.02
0.800	39.84	−0.05	38.67	−0.04	37.50	−0.02
0.897	42.14	−0.04	40.95	−0.03	39.74	−0.01
0.949	the solution is solid		42.18	−0.01	40.95	0.00

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

x_2	H^E/ (J mol^{-1})	x_2	H^E/ (J mol^{-1})	x_2	H^E/ (J mol^{-1})
	x_2 $C_4H_8O_2S$ + $(1 - x_2)$ C_4H_7N				
0.0894	133	0.2542	288	0.7173	262
0.1776	232	0.5553	324	0.8006	205
0.2533	283	0.7116	266	0.9023	110
	x_2 $C_4H_8O_2S$ + $(1 - x_2)$ C_5H_9N				
0.1947	321	0.5560	467	0.7315	371
0.3746	427	0.6386	437	0.7534	347
0.4832	458	0.6853	411	0.7662	332
0.4952	457	0.7080	393		

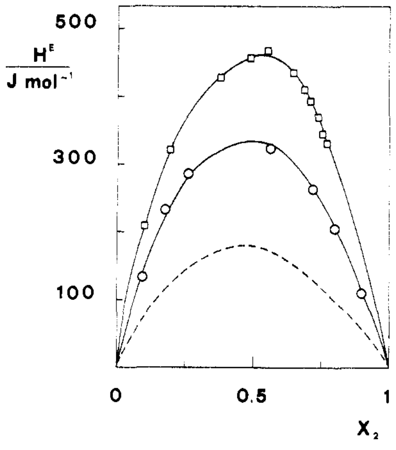


Figure 2. Molar excess enthalpies, H^E, at 303.16 K, plotted against sulfolane molar fraction, x_2, for three nitrile (1) + sulfolane (2) systems: 2,2-dimethylpropionitrile (squares); 2-methylpropionitrile (circles); propionitrile (dashed line).

ceptionally exceed experimental error and the positive low values of mixing enthalpies strongly substantiate the supposition of only moderate interactions of any kind.

Hence, one may infer, as otherwise already pointed out (*1–4*), that steric factors play the most important role in determining the kind and the magnitude of deviations from ideality. And this accords with the statement that the polarity of the molecule is but slightly affected by chain lengthening and branching (*n*-alkane nitriles indeed possess a dipole moment of 3.57 D and branched nitriles a dipole moment of 3.6–3.65 D).

Table VI. Parameters, Their Standard Deviations, σ, in the Smoothing Equation 2, and Standard Deviations, $\sigma(H^E)$, for the Molar Excess Enthalpies at 303.16 K

system	$A' \pm \sigma$	$B' \pm \sigma$	$C' \pm \sigma$	$D' \pm \sigma$	$\sigma(H^E)$/ (J mol^{-1})
$C_4H_8O_2S$					
+ C_4H_7N	1361 ± 11	−234 ± 11	136 ± 29		3
+ C_5H_9N	1845 ± 5	242 ± 28	216 ± 27	−1189 ± 101	3

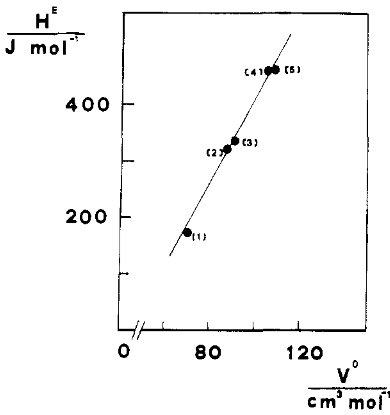


Figure 3. Molar excess enthalpies, H^E, at x = 0.5, for five nitrile + sulfolane mixtures plotted against nitrile molar volume, $V°$, at 303.16 K: (1) propionitrile; (2) butyronitrile; (3) 2-methylpropionitrile; (4) valeronitrile; (5) 2,2-dimethylpropionitrile.

Reasonably the volume contractions, increasing with temperature, might be interpreted in terms of a predominant association product with a more compact structure, presumably a nitrile self-association product, as reported previously for *n*-nitrile + sulfolane binary systems (*2*).

However, owing to the fact that both interactions between like and unlike molecules result in an increase of dielectric constant, the effects of the contemporary strengthening of nitrile self-association and weakening of sulfolane–nitrile association with temperature counterbalance each other in minimizing the influence of the temperature on dielectric constant deviations from ideality.

Attention must be called to the fact that, despite the steady increase of mixing enthalpies, H^E, with the progressive introduction of $-CH_3$ groups in the nitrile molecule (Figure 2), a constant group contribution may not be assigned to the $-CH_3$ group in the C_3–C_5 branched nitrile series. This behavior was otherwise expected, taking into account that chain branching results in an inordinate change in volume and steric hindrance of the molecule. Then the above-reported supposition that thermodynamic excess property behavior with chain lengthening and branching depends mainly on steric hindrance of molecules is consistent with the plot in Figure 3. In it H^E_{303K} values, measured at 0.5x, show a linear variation as a function of molar volume $V°_{303.16K}$ of all studied C_3–C_5 normal and branched nitriles, independently of the geometry of the molecule.

Registry No. Sulfolane, 126-33-0; 2-methylpropionitrile, 78-82-0; 2,2-dimethylpropionitrile, 630-18-2.

Literature Cited

(1) Jannelli, L.; Lopez, A.; Saiello, S. *J. Chem. Eng. Data* **1980**, *25*, 259.
(2) Lopez, A.; Jannelli, L.; Silvestri, L. *J. Chem. Eng. Data* **1982**, *27*, 2, 183–6.
(3) Jannelli, L.; Lopez, A.; Silvestri, L. *J. Chem. Eng. Data*, in this issue.

(4) Lopez, A.; Pansini, M.; Jannelli, L. *J. Chem. Eng. Data*, preceding paper in this issue.
(5) Duncan, N. E.; Janz, G. J. *J. Chem. Phys.* **1955**, *23*, 434.
(6) Hoffman, C.; Barbier, E. *Bull. Soc. Chim. Belg.* **1936**, *45*, 565.
(7) Timmermans, J.; Delcourt, Y. *J. Chim. Phys. Phys.-Chim. Biol.* **1934**, *31*, 85.
(8) Davies, M. *Trans. Faraday Soc.* **1962**, *58*, 1705.
(9) Della Monica, M.; Jannelli, L.; Lamanna, U. *J. Phys. Chem.* **1968**, *72*, 1068.
(10) Fernández-Prini, R.; Prue, J. E. *Trans. Faraday Soc.* **1966**, *62*, 1257.
(11) Sciacovelli, O.; Jannelli, L.; Della Monica, A. *Gazz. Chim. Ital.* **1967**, *97*, 1012.
(12) Jannelli, L.; Sacco, A. *J. Chem. Thermodyn.* **1972**, *4*, 715.
(13) Martinmaa, J. *Suom. Kemistil. B* **1969**, *42*, 33.
(14) Dannhauser, W.; Flueckinger, A. F. *J. Phys. Chem.* **1964**, *68*, 1814.
(15) Kiyohara, O.; Benson, G. C.; Grolier, J. P. E. *J. Chem. Thermodyn.* **1977**, *9*, 315.

Received for review June 15, 1982. Accepted December 2, 1982.

Partial Molal Volumes, Expansibilities, and Compressibilities of Aqueous KSCN Solutions from 15 to 35 °C

Harald Hölland* and Ove Jan Kvammen

Department of Chemistry, University of Bergen, N-5014 Bergen U., Norway

The densities and isentropic compressibilities of aqueous solutions of KSCN have been measured from 15 to 35 °C. Partial molal volumes, partial molal expansibilities, and partial molal compressibilities have been calculated. The values at 25 °C are 49.62 $cm^3\ mol^{-1}$, 0.15 $cm^3\ mol^{-1}\ K^{-1}$, and -18.0×10^{-4} $cm^3\ mol^{-1}\ bar^{-1}$, respectively. The partial molal volumes do not agree well with literature values. However, it is strongly believed that the present results are correct.

Introduction

In his review of partial molal volumes of electrolytes in aqueous solution, Millero (*1*) quotes Halasey (*2*) for data on KSCN. Halasey's work appears to be a thorough investigation covering several other electrolytes and a temperature range from 5 to 30 °C. For the other electrolytes there is good agreement between Halasey's values and others workers', but for KSCN the only other value cited is at 25 °C (*3*), and at infinite dilution it is given as 49.0 $cm^3\ mol^{-1}$ compared to Halasey's value of 44.70 $cm^3\ mol^{-1}$.

In connection with other work the partial molal volume of KSCN at infinite dilution was needed. The discrepancies between the two values mentioned above, however, made it necessary to carry out new measurements in order to settle the issue. It was thus found worthwhile to make a thorough investigation and also include the partial molal compressibility and expansibility.

Experimental Section

KSCN was from Merck and was their best quality. It was dried in vacuo at 140 °C for at least 24 h. In order to check the purity, we titrated sample solutions with $AgNO_3$ according to Volhard's method (*4*). The results showed 99.8% KSCN. KSCN of Baker's analyzed quality was also tested. The densities of aqueous solutions were equal irrespective of origin.

The densities were measured by a Paar digital vibrating densitometer, DMA 601. It was calibrated at each temperature by measuring the vibration frequencies when filled with water and air, respectively. The isentropic compressibilities were evaluated from the speed of sound in the solutions as measured by the "singaround" method. The temperature was controlled to better than ±0.004 °C in both cases, as measured with a Hewlett-Packard quartz thermometer.

Results and Discussion

The measured densities and compressibilities are given relative to pure water in Table I.

The apparent molal volumes have been calculated by the usual equation (*5*). They have been plotted in Figure 1 according to the Redlich equation (*6*):

$$V_\varphi = V_\varphi{}^0 + S_v\sqrt{c} + b_v c \qquad (1)$$

Here the molar unit is used. S_v is thus the Debye-Hückel limiting law coefficient and b_v an adjustable parameter providing a measure of deviation from the limiting law.

The partial molal volume of KSCN at infinite dilution and the deviation parameter are presented in Table II. For comparison the data of Halasey (*2*) are also presented; b_v has been calculated from the data given. The discrepancies are large. However, we firmly believe that our data are the correct ones. Our value at 25 °C is in reasonable agreement with that of Fajans and Johnson (*3*). Furthermore, the b_v values calculated on the basis of Halasey's data are extremely large for such a simple 1:1 electrolyte. If we take the b_v values of NaCl, for which Millero (*7*) has provided accurate data, it can be seen that our data on KSCN compare very well with those of NaCl (0.16 and −0.37 at 15 °C, −0.39 and 0.05 at 25 °C, and −0.61 and −0.13 at 35 °C for KSCN and NaCl, respectively). b_v values of simple 1:1 electrolytes should be expected to be of the same order of magnitude. As Millero (*7*) points out, the deviations from the limiting law must arise from cation–cation (or anion–anion) interactions, on one hand, and cation–anion interactions on the other. It appears that positive deviations are due largely to cation–anion interactions and negative deviations due to cation–cation (anion–anion) interactions. Halasey's large and positive b_v values thus suggest a relatively high degree of ion pairing in aqueous KSCN. This does not seem likely. Further, there is no evidence for such ion pairing from, for instance, conductance measurements; see the tabulated values of 1:1 electrolytes given by Parsons (*8*). In fact, by comparison of our b_v data on KSCN with those of NaCl, it appears that KSCN is even less likely than NaCl to form ion

0021-9568/83/1728-0179$01.50/0