The Conductance of the Alkali Halides

I. Sodium Chloride in Sulfolane-water Mixtures, at 25 °C and 35 °C

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The electrochemical behaviour of sodium chloride in water-sulfolane mixtures, at 25 °C and 35 °C, was investigated, the concentration of the salt ranging within $(1 \div 7) \cdot 10^{-3}$ moles/liter and the dielectric constant (D) of the solvent mixtures within 78 and 44.

Analyzing the data by the Fuoss, Onsager and Skinner treatment, Λ_0, a_{I}, A, a_{A} and $\Lambda_0 \eta$ values were obtained. At both temperatures, Λ_0 is a smooth function of the solvent compositions; a remarkable association seems evident at $D < 60$; log A vs. $1/D$ plots are linear; the contact distances of the ions are lower than in other isodielectric media.

Except for a limited region close to pure water, the Walden product $\Lambda_0 \eta$ is constant (1.20 at 25 °C and 1.19 at 35 °C) in the whole solvent composition range.

Introduction

Previous data[1] on pure sulfolane $[(CH_2)_4SO_2]$ and on its dilute solutions in inert solvents[2] show that sulfolane is never self-associated, even when its molecules are close-packed in the plastic crystal[3], and this in spite of its high polarity ($\mu = 4.8$ D. u. $D^{30\,°\text{C}} = 43.3$). Furthermore, sulfolane is characterized by a low value of the autoprotolysis constant[4], and by a weak ability to be protonated or to give any kind of ion solvation[5]. Presumably the electrons around the $-SO_2$ group are not easily accessible and the positive charge, which is diffused on the whole ring, can only weakly interact.

Sulfolane-water mixtures behave regularly[6]; water being one of the most strongly self-associated liquids, it might be thought that sulfolane, although polar, plays the role of an inert diluent[7].

The above properties suggested us to carry out measurements on the conductance of electrolytes in water-sulfolane mixtures, to support the idea that only a weak competition[8] in ion solvation may be expected in these binary solvent systems. At the same time the obtained data might be employed to discuss the influence of the solvent structure on the conduction mechanism.

Data are reported on the electrolytic conductance of sodium chloride in the concentration range $(1 \div 7) \cdot 10^{-3}$ moles/liter, in sulfolane-water systems (the weight composition of sulfolane ranging between 0 and 95% at 25 °C; between 0 and 97% at 35 °C). The salt in pure sulfolane is sparingly soluble.

Experimental

Materials

The conductivity water was prepared by passage through a mixed bed ion exchange resin column. The specific conductance of samples, collected and stored in all Pyrex glassware, routinely ranged between $0.4 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ ohm^{-1} cm^{-1}.

Sulfolane, kindly supplied by Shell Co. Industrial Chemical Division, was carefully purified and dehydrated as already reported[9]. The water content (titration by the Fisher method), was 0.007%. The conductivity did not exceed $1 \cdot 10^{-8}$ ohm^{-1} cm^{-1}.

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The Merck certified (Na,K) Cl were carefully purified by recrystallization and then dried in vacuo, at 195 °C, for ~ 4 days.

Apparatus and Procedure

The solutions were made up by weight, and the concentrations, c, in moles/l were calculated from the molal concentration, m, (in mole/kg of solvent) by means of the equation $c/m = \varrho^t + k^t m$ [ϱ: density (g/ml) of the solvent mixture at t °C; k^t: determined empirically]. For NaCl aqueous solutions the k^t values reported by HARNED and OWEN[10] are: -0.0188 at 35 °C, and -0.0183 at 25 °C. Their formulas have been shown by us to be useful in recalculating the concentration values of the same electrolyte, in water-sulfolane solutions, within 10^{-7} moles/l.

Resistance measurements were carried out with a Jones and Joseph bridge (Leeds and Northrup Co.). Oil thermostats, at 25 °C and at 35 °C, were regulated within ±0.005 °C and the temperature checked by means of an NBS certified resistance thermometer in connection with an L & N Mueller Bridge Mod. G 2.

No change in resistance was detected when the frequency ranged between 2.4 and 4 kHz.

Three Jones and Bollinger cells, with unplatinized electrodes (manufactured by L & N), were employed, and carefully calibrated by means of aqueous potassium chloride solutions, as suggested by CHECH CHIU and FUOSS[11]. The values of the cell constants at 25 °C, were 1.0509 ± 0.0002; 0.25305 ± 0.00006; 0.27312 ± 0.00006.

Previous literature[12] indicates that cell constants are not significantly altered within the temperature range of our experiments.

Results

In Figs. 1 and 2, viscosity, dielectric constant and density data of the solvent mixtures are plotted vs. weight % of sulfolane.

Conductance data of sodium chloride, at 25 °C and 35 °C, are summarized in Tables 1 and 2 for different dielectric constants of the solvent. They were treated according to ONSAGER, FUOSS, and SKINNER[13].

The equation

$$\begin{aligned} \Lambda' &= \Lambda + S(c\gamma)^{1/2} - E' c\gamma \ln \tau^2 \gamma \\ &= \Lambda_0 + L c\gamma - A c\gamma \Lambda \cdot \exp\{-2\tau\gamma^{1/2}\} \end{aligned} \tag{1}$$

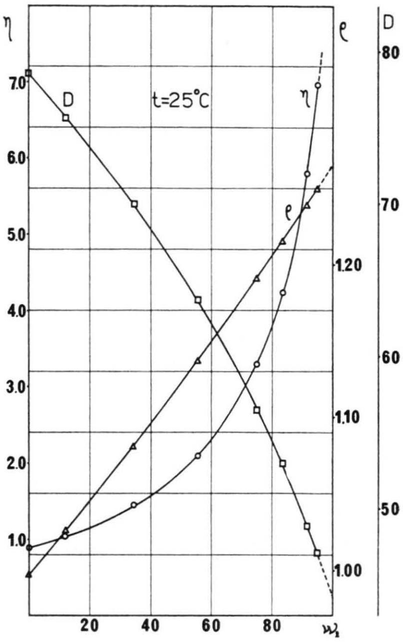

Fig. 1.

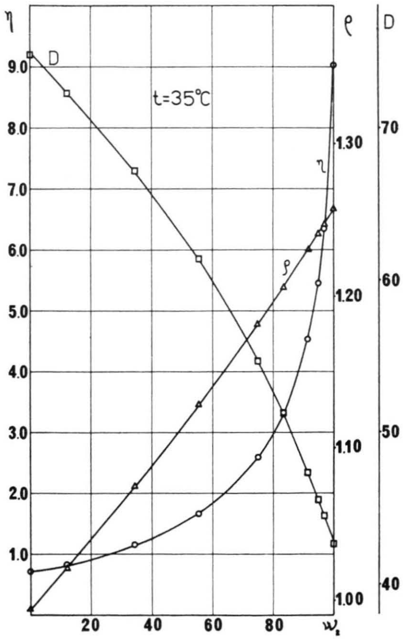

Fig. 2.

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Table 1. Equivalent conductance of Sodium Chloride in Sulfolane-Water Mixtures at 25 °C.

$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$
	$D = 75.65$			$D = 69.97$			$D = 63.68$			$D = 56.51$	
83.913	102.941	− 20	82.613	77.259	− 18	82.805	53.478	− 11	85.268	32.948	− 4
66.907	103.596	+ 18	65.256	77.833	+ 23	65.740	53.949	+ 13	67.802	33.351	+ 6
50.752	104.280	+ 9	49.483	78.377	− 3	50.997	54.384	+ 4	51.762	33.764	+ 7
37.630	104.967	+ 21	35.822	78.991	+ 19	36.699	54.889	+ 3	37.712	34.160	− 18
27.074	105.576	− 27	24.889	79.529	− 21	25.770	55.343	− 9	25.932	34.603	+ 8
	$D = 52.97$			$D = 48.90$			$D = 47.14$				
83.392	24.810	/	53.702	17.862	− 1	57.979	14.369	− 4			
66.855	25.165	− 1	43.852	18.147	− 4	47.950	14.677	+ 5			
50.904	25.559	− 3	34.078	18.477	+ 4	37.393	15.027	− 4			
37.281	25.960	+ 3	23.753	18.866	− 6	25.884	15.481	− 3			
25.437	26.365	− 1	17.767	19.142	+ 2	19.304	15.787	+ 2			

Table 2. Equivalent conductance of Sodium Chloride in Sulfolane-Water Mixtures at 35 °C.

$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$	$10^4 C$	Λ	$10^3 \Delta\Lambda$
	$D = 72.27$			$D = 67.20$			$D = 61.42$			$D = 54.69$	
83.582	125.553	− 37	82.157	95.040	− 19	82.265	66.330	− 7	84.662	41.326	− 6
66.643	126.370	+ 34	64.897	95.771	+ 11	65.311	66.925	+ 4	67.321	41.839	+ 8
50.551	127.207	+ 28	49.210	96.531	+ 26	50.664	67.505	+ 7	51.396	42.369	+ 8
37.481	128.017	+ 13	35.625	97.274	+ 1	36.460	68.155	+ 3	37.444	42.884	− 22
26.968	128.773	− 37	24.752	97.999	− 19	25.602	68.744	− 7	25.748	43.459	+ 10
	$D = 51.34$			$D = 47.34$			$D = 45.60$			$D = 44.54$	
82.796	31.256	− 4	53.318	22.603	+ 3	57.570	18.128	+ 1	51.344	15.699	+ 3
66.377	31.726	+ 5	43.538	22.970	− 7	47.611	18.520	+ 1	43.330	16.062	− 9
50.540	32.238	+ 2	33.834	23.407	+ 10	37.125	18.982	− 1	35.034	16.502	+ 4
37.014	32.742	− 9	23.583	23.913	− 5	25.701	19.570	+ 1	26.885	16.974	− 4
25.255	33.286	+ 4	17.640	24.270	+ 2	19.167	19.959	/	20.197	17.431	+ 7
									15.726	17.759	− 4

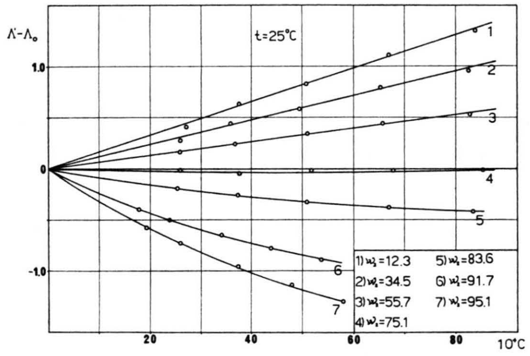

Fig. 3 a.

may be simplified in the form

$$\Lambda' = \Lambda_0 + L c , \qquad (2)$$

if no detectable association occurs.

The symbols in Eqs. (1) and (2) have the same meaning as in [13]. The used program, adapted to an IBM 360 computer, automatically disregards association if the A term in Eq. (1), which is related to the thermodynamic association constant, does not exceed a value of a few units; therefore the dissociation degree γ may be taken as unity.

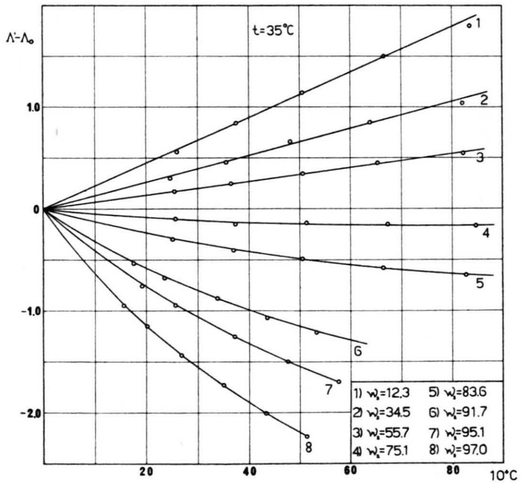

Fig. 3 b.

In Fig. 3 a, b the difference $\Lambda' - \Lambda_0$ is plotted vs. the molar concentration of the electrolyte, at the two temperatures.

Each curve is referred to a different solvent composition. No detectable association is present up to $\omega_2 \cong 50\%$ sulfolane: this explains the linear dependence of $\Lambda' - \Lambda_0$ on c in the curves 1, 2 and 3.

Equations (1) and (2) allowed us to calculate the electrolyte constants Λ_0, a_L, A and a_A, which are summarized in the Tables 3 and 4. a_L is the distance of closest approach of ions as calculated from the L term; a_A has the same meaning but it is drawn from the A term. In the higher dielectric constant region, a_L values may be obtained with better precision from Eq. (2), whereas at lower dielectric constants a_A terms, drawn from A [Eq. (1)], are more reliable.

When the choice between Eqs. (1) and (2) was affected by a certain amount of arbitrariness, both of them have been applied to experimental data.

The accuracy of data may be judged from the standard deviations reported in the sixth column. In the last column, data concerning the Walden product $\Lambda_0 \eta$ are summarized.

Discussion

On adding sulfolane, the Λ_0 values steadily decrease (Tables 3 and 4). The contact distance, a_L, gradually decreases, whereas the a_A terms appear scarcely affected by dielectric constant changes within the range $52 \div 44$.

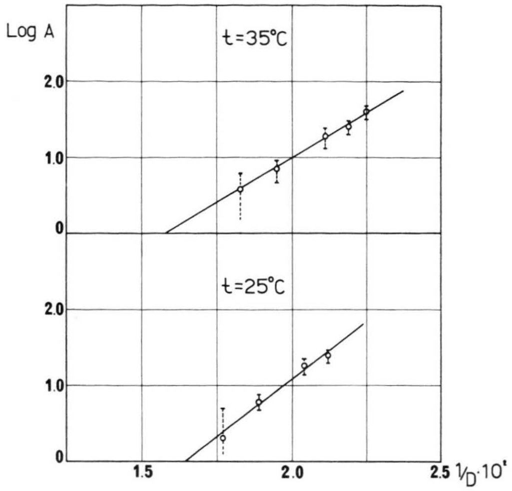

Fig. 4.

Table 3. Constants for Sodium Chloride in Sulfolane-Water Mixtures at 25 °C.

D	Λ_0	a_L	a_A	A	σ	$\Lambda_0\,\eta$
78,54	126.60[a] ± 0.02	3.38 ± 0.04	—	—	0.02	1.12_7
75.65	109.58 ± 0.03	3.29 ± 0.11	—	—	0.03	1.14_2
69.97	82.612 ± 0.029	2.88 ± 0.11	—	—	0.02	1.19_5
63.68	57.796 ± 0.015	2.17 ± 0.06	—	—	0.01	1.21_5
56.51	36.507 ± 0.079	1.89 ± 1.87	—	2 ± 3	0.02	1.20_9
52.97	28.118 ± 0.016		1.68 ± 0.07	6 ± 1	0.01	1.19_3
48.90	20.557 ± 0.036		1.49 ± 0.07	18 ± 4	0.01	1.19_3
47.14	17.290 ± 0.035		1.49 ± 0.05	25 ± 4	0.01	1.20_5

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Table 4. Constants for Sodium Chloride in Sulfolane-Water Mixtures at 35 °C.

D	Λ_0	a_L	a_A	A	σ	$\Lambda_0\,\eta$
74.82	153.84[b] ± 0.03	3.61 ± 0.07	—	—	0.04	1.10_7
72.27	133.76 ± 0.05	3.54 ± 0.13	—	—	0.04	1.11_1
67.20	101.90 ± 0.03	2.56 ± 0.08	—	—	0.02	1.17_1
61.42	71.851 ± 0.010	1.91 ± 0.03	—	—	0.01	1.19_7
54.69	45.928 ± 0.099		1.84 ± 0.77	3 ± 3	0.02	1.19_6
51.34	35.534 ± 0.044		1.62 ± 0.12	7 ± 2	0.01	1.18_6
47.34	26.098 ± 0.059		1.48 ± 0.08	19 ± 5	0.01	1.18_8
45.60	21.885 ± 0.008		1.49 ± 0.01	25 ± 1	0.01	1.19_6
44.54	19.665 ± 0.042		1.41 ± 0.03	40 ± 5	0.01	1.20_3

[b] M. GOFFREDI and T. SHEDLOVSKY, J. Phys. Chem. **71**, 2176 [1967].

Attention may be paid to the fact that both a_L and a_A are lower than in other isodielectric media[14]. [On the other hand, these results agree with data supplied by FERNANDEZ PRINI and PRUE[15] on several electrolytes in pure sulfolane.] Correspondingly a remarkable association to ion pairs may be observed.

Thus, further evidence is given to the supposition that sulfolane shows only a weak capacity to give rise to an ion solvation; hence the association to ion pairs would be enhanced.

The plots of $\log A$ vs. $1/D$ are linear (Fig. 4) within the reliability limits of the calculated A values. (The uncertainty on the first A value is as large as A itself.)

The Walden products appear but little affected by solvent composition, except for a small region close to pure water. Accordingly, with the above mentioned steady decrease of ionic contact distances, the initial increase in the Walden product may be related to a gradual desolvation of ions.

The conclusion may be also drawn from experimental data that, as expected, the sulfolane-water mixtures behave as an ideal conducting medium.

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Spectral Investigations of Some Rare Earth β-Diketonates in the Region 750—250 cm^{-1}

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The infrared absorption spectra of fifteen La^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+} β-diketonates have been studied in the spectral region 750—250 cm^{-1}. The existence of three metal-oxygen vibration modes suggests D_3 symmetry for the chelates under study. The stretching force constants, f_{MO}, of the MO bonds have been computed from the observed infrared M–O vibrations using the method of Müller. The value of f_{MO} is nearly constant ($\sim 2.7 \times 10^5$ dynes/cm) in all the chelates suggesting similar bond strengths.

Introduction

Rare earth β-diketonates are becoming important laser materials due to narrow line width of the internal 4 f transitions and weak crystal field interactions[1]. Though Slater-Condon, Racah, Lande, nephelauxetic and intensity parameters for many of these complexes have been reported[2–6], very little information regarding their structure and strength of various bonds are available. The potential energy and hence the force constant provides valuable information about the nature of interatomic forces[7]. With this in view the present investigation of infrared absorption was undertaken.

The present paper reports the infrared spectra of fifteen La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} complexes of acetylacetone (A), benzoylacetone (BA), dibenzoylmethide (DBM) and thenoyltrifluoroacetone (TFA), in the spectral region 750 – 250 cm^{-1}. The metal-oxygen force constants from the infrared active modes of vibration of these complexes have been computed using the method of MÜLLER[8].

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