The Conductance of the Alkali Halides

IV. Non-Coulomb Variation of Ionic Association in Sulfolane-Methanol Mixtures

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The conductometric behaviour, at 35 °C, of solutions of lithium chloride in sulfolane-methanol mixtures was investigated, the concentration of the salt ranging within 0.8×10^{-3} and 8×10^{-3} moles/l and the dielectric constant of the solvent within 42 and 30.

Using the Fuoss, Onsager and Skinner treatment, the parameters Λ_0, a_L, A and a_A were calculated.

An increase of the Walden products with the sulfolane content of the solution was observed as well as an non-coulomb behaviour of the association constant. Data are discussed and interpreted on the basis of ion transfer energies and the properties of the solute and the solvent mixtures.

Introduction

Recently [1] attention has been called on the possibility of a non-coulomb variation of the ionic association in some binary mixtures involving a protic solvent. The collapse of the structure of the protic solvent on adding the other component has been proposed as the main factor responsible for the anomalous dependence of A on the dielectric constant (D).

It would be desirable indeed to collect data on a more extensive set of electrolytes and of solvent media to furnish further elements to correlate the properties of solvents to ionic association.

We start herewith from the study of the conductometric behaviour of lithium chloride in methanol-sulfolane mixtures, on the basis of the statement that lithium chloride, which is dramatically associated in sulfolane [2] ($D = 42$) is viceversa a strong electrolyte in methanol [3] ($D = 30$), in spite of the limited difference between the dielectric constants of the two media, which otherwise does not influence association in the expected direction.

Experimental

The sulfolane purification has already been described [4]. Methanol (Merck pro analysi) was purified by the method suggested by Beronius, Wikander and Nillsson [5]; it was passed slowly through a molecular sieve (Merck 4 Å) and subsequently distilled through a 50 cm Vigreux column. The middle fraction was refluxed for 10 hours on freshly dried copper sulphate and redistilled through the Vigreux column. The final product had a conductivity lower than 5×10^{-8} Ohm^{-1} cm^{-1}; it's water content (by Fischer titration) was in general close to 0.01 wt %.

Lithium chloride (Merck suprapur) was purified and the solutions prepared as described in [6]. All manipulations were carried out in a dry-box filled with oxygen free nitrogen.

The concentration, c, of the salt in moles/l was calculated from the molality, m (moles/kg solvent), by the equation: $c/m = \varrho - k\,m$ (ϱ density g/ml of the solvent mixtures at 35 °C; $k = 0.0497$, calculated tentatively).

The procedure adopted in measuring the density, viscosity and dielectric constant of the solvents, and the conductivity of the salt solutions, at (35 ± 0.002) °C, was described previously [7].

Results

The physical properties of the solvent mixtures, ϱ (g/ml), η (cP) and D are summarized in Table 1 where w_2 is the wt % and N_2 the mole fraction of sulfolane.

Table 1. Properties of the solvents at 35 °C.

N_0	w_2	N_2	ϱ (g/ml)	η (cP)	D
1	0	0	0.77719	0.4813	30.71
2	14.720	0.0440	0.82871	0.5178	32.37
3	41.050	0.1566	0.93088	0.6832	34.52
4	61.193	0.2960	1.02817	1.010	36.90
5	78.769	0.4973	1.12422	1.790	39.27
6	93.482	0.7927	1.21473	4.408	41.55
7 [14]	100	1	1.25752	9.033	42.71

The conductance data of lithium chloride, in sulfolane-methanol mixtures, are summarized in Table 2 where $\Delta\Lambda$ is the difference between the observed conductances and those calculated by the equations:

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Table 2. Equivalent conductance of lithium chloride in Sulfolane-Methanol mixtures at 35 °C.

$10^4 c$	Λ	$\Delta\Lambda \times 10^3$	$10^4 c$	Λ	$\Delta\Lambda \times 10^3$	$10^4 c$	Λ	$\Delta\Lambda \times 10^3$
	$D=30.71$			$D=32.37$			$D=34.52$	
74.675	83.311	11	63.737	80.810	−23	72.051	67.860	1
57.844	85.229	−33	48.697	82.789	25	40.487	71.286	13
42.445	87.588	+33	35.713	84.858	25	28.002	73.254	−16
30.522	89.825	+ 2	25.137	86.927	−17	17.981	75.353	−11
23.397	91.457	−36	20.643	88.006	− 9	13.610	76.529	16
18.844	92.763	+21	15.318	89.485	− 1	10.422	77.496	− 3
			11.352	90.790	1			
	$D=36.90$			$D=39.27$			$D=41.55$	
65.365	52.163	−10	68.924	33.527	− 6	52.762	16.608	9
49.846	53.450	+10	49.205	34.845	+15	42.886	17.307	− 9
36.457	54.856	+19	46.796	35.024	+ 8	33.291	18.148	6
25.182	56.352	+ 3	37.078	35.828	− 9	23.335	19.224	2
20.155	57.166	− 5	19.659	37.727	− 7	18.524	19.864	6
15.848	57.952	−30	15.993	38.238	− 6	13.967	20.559	− 5
11.864	58.834	−13	10.629	39.119	10	9.095	21.470	1
8.235	59.811	30						

$$\Lambda' = \Lambda + S(c\gamma)^{1/2} - E' c\gamma \ln \tau^2 \gamma$$
$$= \Lambda_0 + L c\gamma - A c\gamma \Lambda \exp\{-2\tau\gamma^{1/2}\}, \quad (1)$$
$$\Lambda' = \Lambda_0 + L c \quad (2)$$

according to the Fuoss, Onsager and Skinner treatment, which we usually adopt [8].

The derived parameters Λ_0, a_L, A, a_A (with the corresponding standard deviation) are summarized in Table 3, together with the $\Lambda_0\eta$ products and the standard deviations σ of the individual points. For the sake of comparison, data on pure sulfolane (system 7) from a previous note [9] are also reported; the three parameters Eq. (1), which takes into account the association to ion pairs, was used to analyse the systems 3 ÷ 6, in Table 3. Association is lacking in systems 1 − 2, whose conductance data were analysed by Equation (2).

Discussion

As already observed, in the case of alkali halides water-sulfolane solutions, sulfolane addition results

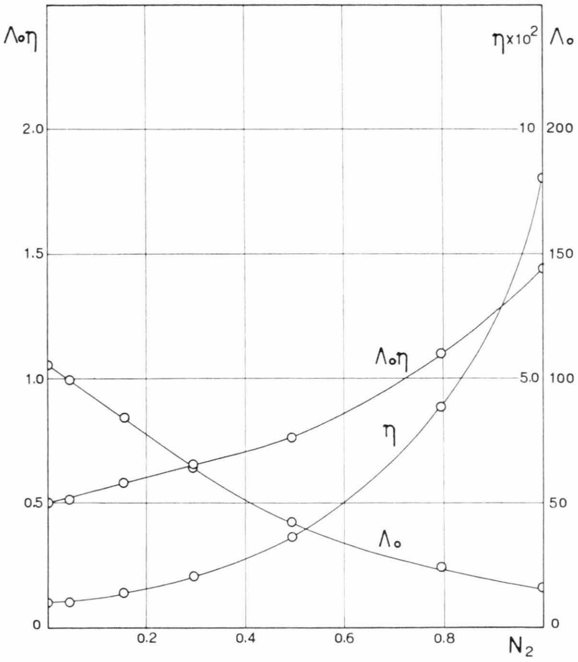

Fig. 1. Viscosity of the solvents limiting conductance and Walden products for lithium chloride vs. sulfolane mole fraction in solvent mixtures at 35 °C.

Table 3. Constants for LiCl in Sulfolane-Methanol mixtures at 35 °C.

N_0	Λ_0	a_L	a_A	A	σ	$\Lambda_0\eta$
1	104.63 ± 0.03	3.48 ± 0.02	—	—	0.03	0.504
2	99.16 ± 0.02	3.25 ± 0.01	—	—	0.02	0.513
3	84.19 ± 0.04	—	2.73 ± 0.05	16 ± 1	0.02	0.575
4	64.08 ± 0.04	—	2.11 ± 0.03	25 ± 2	0.02	0.647
5	42.36 ± 0.03	—	1.8 ± 0.02	32 ± 1	0.01	0.758
6	24.30 ± 0.03	—	—	121 ± 3	0.008	1.071
7 [14]	15.919	—	—	14595	—	1.438

in a steady decrease of Λ_0. In Figure 1, Λ_0, η and $\Lambda_0\,\eta$ are plotted versus N_2; it is to be pointed out that the increase of viscosity with N_2 is accompanied by increasing values of Walden products.

This behaviour might be interpreted as caused by the partial cancellation of two opposite effects on Λ_0, since the increasing viscosity plays the role of lowering the conductance, which would be otherwise enhanced by a probably reduced solvation in sulfolane richer solutions.

This idea is supported by the strongly negative values of the transfer enthalpies[10] from sulfolane to methanol of both lithium (−9.1 kcal/mole) and chloride (−4.8 kcal/mole) ions, denoting an enhanced solvating power of methanol.

Table 3 shows the anomalous behaviour of association which appears to be dominated by the extremely high value in pure sulfolane. The association constant falls abruptly on adding small amounts of methanol and then decreases slowly with decreasing dielectric constant of the solvent.

The reversed behaviour of $\log A$ versus $1/D$ is evidenced in Fig. 2 where the analogous plot of $\log A$, calculated by the Fuoss equations

$$\log A = \log A_0 + e^2/a\,k\,T\,D\,,$$

is also reported for comparison ($a = 2.413$ Å being the lithium chloride crystallograph radius).

The failure of the Fuoss equation in reproducing association data reveals that factors other than the dielectric constant influence the association mechanism. These factors have been previously[11] indicated as ion-solvent interactions, solvent-solvent interactions and changes of the structure of the solvent with composition. The overlapping of these effects controles the association to ion pairs.

In the case of LiCl methanol-sulfolane solutions, the interactions might be essentially restricted, to first approximation, to solvation of ions by methanol, the sulfolane-methanol interactions being of limited importance[12]. On the other hand, the dramatically high value of the association constant in pure sulfolane has been explained[13] in terms of a nearly complete desolvation of ions.

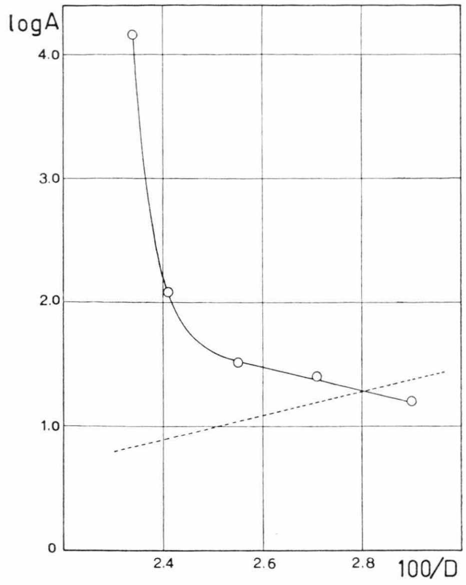

Fig. 2. Dependence of association constants on dielectric constant. Dotted line: association constants calculated from the Fuoss equation (a=2.413 Å).

This mechanism of association to ion pairs reasonably remains the predominating effect so far as the methanol concentration is so small that ion solvation may be neglected, even if in this restricted composition region, the association constant abruptly decreases.

Successively the opposite effects of ion-methanol interactions and of methanol structuration overlap and their partial concellation results in an association constant, scarcely influenced by the composition of the solvent.

The above cited behaviour of Walden products and the values of ion enthalpies of transfer appear to support this interpretation.

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