

## The Conductance of the Alkali Halides

### III. Lithium Chloride in Sulfolane-Water Mixtures at 35 °C

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The conductometric behaviour of lithium chloride in water-sulfolane mixtures, at 35 °C, was investigated within the salt concentration  $2 \times 10^{-4} \div 1.5 \times 10^{-2}$  moles/l, and within the solvent media dielectric constant range 75 (pure water)  $\div$  43 (pure sulfolane). A few solutions of RbCl and CsCl suitable for comparison, were also investigated.

$\Lambda_0$ ,  $\Lambda$ ,  $\alpha_L$ ,  $\alpha_A$  and  $\Lambda_0 \eta$  values, drawn from the experimental data, are discussed and compared with previous results on sodium and potassium chlorides.

The main conclusions which may be drawn from the conductometric behaviour of the alkali halides are: a noticeable association, unusually increasing in the sense  $\text{CsCl} \leq \text{RbCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$ , a dramatically high value of the association constant ( $A=14595$ ) and a noticeable mobility of lithium chloride, in pure sulfolane.

### Introduction

We are engaged in an electrochemical research on the conductance of alkali chlorides in sulfolane-water mixtures<sup>1</sup>.

Previous data on sodium and potassium chlorides allowed us to evidence a noticeable association to ion pairs, unusual in other isodielectric media, while the association order of alkali chlorides was suspected to be reversed in these mixed solvents.

We refer here the results of some conductance measurements on lithium chloride solutions, at 35 °C, where the salt concentration ranged within  $2 \cdot 10^{-4}$  and  $1.5 \cdot 10^{-2}$  moles/liter, and the composition of the solvent covered the whole range  $0 \leq N_2 \leq 1$ .

To provide further informations conductometric data were collected also on RbCl and CsCl, at  $6.5 \cdot 10^{-3} \div 1 \cdot 10^{-3}$  moles/liter, in a  $\sim 92$  weight % sulfolane solution.

The results seem to support our previous assumptions.

### Experimental

Solvent purification was already described<sup>1</sup>.

Lithium chloride (Merck Suprapur) from a freshly opened bottle was fused in a platinum crucible. Then it was poured into a weighing tube and sealed<sup>2</sup>.

Stock solutions were made up by adding to weighted samples of the solvents the weighted samples of the salt. All weighings of the salt were carried out in seal-

ed tubes. The subsequent solutions were prepared from the initial solution by dilution. Large enough samples were used to minimize errors in weighing. All the manipulations were carried out in a dry-box filled with oxygen-free nitrogen to protect the solutions from moisture.

The concentrations  $c$  in moles/liter were calculated from the molal concentration  $m$  (moles/kg solvent) by the equation:  $c/m = \rho - k m$  ( $\rho$  = density g/ml of the solvent mixture at 35 °C) the constant term  $k$  being 0.0135 in the case of LiCl; 0.052 and 0.034 for CsCl and RbCl respectively.

The procedure adopted in measuring density ( $\rho$ ), viscosity ( $\eta$ ), dielectric constant ( $D$ ) and the conductance apparatus were the same as previously described<sup>1</sup>.

### Results

The physical properties of the solvent mixtures,  $\rho$ ,  $\eta$  and  $D$  are summarized in Table 1, where  $w_2$  is the weight % and  $N_2$  the mole fraction of sulfolane.

Conductance data for lithium chloride are summarized in Table 2, whereas in Table 3 the data concerning RbCl and CsCl are reported. The term

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

No.	$w_2$	$N_2$	$\rho$ (gcm <sup>-3</sup> )	$\eta$ (cP)	$D$
1	0	0	0.99406	0.7194	74.64
2	11.44	0.0225	1.02064	0.8225	72.43
3	31.12	0.0633	1.06718	1.093	68.05
4	54.21	0.1522	1.12565	1.620	61.82
5	74.62	0.3115	1.18091	2.574	54.87
6	84.18	0.4445	1.20806	3.398	51.08
7	91.77	0.6259	1.23060	4.543	47.33
8*	91.84	0.6283	1.23083	4.558	47.29
9*	91.91	0.6304	1.23103	4.581	47.26
10	100	1	1.25749	9.033	42.71

\* These two solvents media refer to RbCl and CsCl solutions.

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$\Delta A$  is the difference between the observed conductances and those calculated by the equations:

$$\begin{aligned} \Delta A' &= A + S(c\gamma)^{1/2} - E' c \gamma \ln \tau^2 \gamma \\ &= A_0 + L c \gamma - A c \gamma \Delta \cdot \exp\{-2 \tau \gamma^{1/2}\} \end{aligned} \quad (1)$$

and

$$\Delta A' = A_0 + L c \quad (2)$$

according to the FUOSS, ONSAGER and SKINNER<sup>3</sup> treatment.

The derived parameters  $A_0$ ,  $a_L$ ,  $A$ ,  $a_A$  are summarized in Table 4, together with the  $A_0 \eta$  products, the standard deviation of each parameter, and the standard deviations  $\sigma$  of the individual points.

For comparison the corresponding values in pure water<sup>4</sup> are also given.

To analyse the systems 4 ÷ 9 in Table 4 the three parameters Eq. (1), which takes into account association, was used.

Association was undetectable for systems 2 and 3, so the data were reanalysed using the two parameters Equation (2).

In the case of system 10, concerning solutions of lithium chloride in pure sulfolane, owing to the fact that the association term  $A$  becomes of the order of  $10^4$ , the program computation converges slowly or fails to converge and it was preferable to use the method of FUOSS and KRAUS<sup>5</sup> involving the simpler limiting form of Equation (1):

$$A = \gamma (A_0 - S(c\gamma)^{1/2}) \quad (3)$$

which is linearized by the transformation

$$F/A = 1/A_0 + [(c A f^2 A)/F A_0^2],$$

where  $F$  is a tabulated function.

In Fig. 1 the difference  $A' - A_0$  is plotted against the molar concentration  $c$  of the electrolyte, each curve referring to a different solvent composition. No association can be evidenced for dielectric constants  $D > 62$ , in agreement with the linear dependence of the  $A' - A_0$  term on  $c$  in curves 2 and 3.

The linear dependence of  $F/A$  on  $c A f^2/F$  is shown in Fig. 2, the intercept being  $1/A_0$  and the slope  $A/A_0^2$  ( $A = 14595$ ;  $A_0 = 15.919$ ).

Table 2. Equivalent conductance of lithium chloride in sulfolane-water mixtures at 35 °C.

$10^4 c$	$A$	$\Delta A \cdot 10^3$	$10^4 c$	$A$	$\Delta A \cdot 10^3$	$10^4 c$	$A$	$\Delta A \cdot 10^3$
$D = 72.43$			$D = 68.05$			$D = 61.82$		
151.360	112.244	+ 8	113.690	88.494	+ 4	83.182	61.103	- 13
135.237	112.676	- 34	101.371	88.882	+ 21	74.688	61.377	- 4
121.045	113.142	- 23	91.252	89.160	- 30	65.228	61.714	+ 13
106.123	113.698	+ 11	79.064	89.613	- 7	58.132	61.985	+ 25
90.566	114.326	+ 37	56.455	90.555	+ 6	48.629	62.348	+ 6
74.808	115.008	+ 33	45.718	91.085	+ 12	40.837	62.683	- 7
46.159	116.511	- 3	33.828	91.741	- 6	33.051	63.054	- 24
29.421	117.679	- 30				24.388	63.557	- 17
						15.603	64.207	+ 22
$D = 54.87$			$D = 51.08$			$D = 47.33$		
65.435	38.153	+ 5	66.554	27.355	- 1	94.536	18.157	- 13
54.985	38.506	- 4	57.148	27.683	- 1	75.260	18.850	+ 5
45.379	38.879	- 3	45.933	28.120	+ 1	66.128	19.212	-
35.318	39.314	- 11	36.083	28.553	+ 2	56.294	19.656	+ 14
25.490	39.827	- 1	26.036	29.052	- 6	46.772	20.118	+ 6
15.059	40.477	- 11	15.257	29.721	+ 5	37.670	20.607	- 11
10.305	40.907	+ 48	10.265	30.088	- 2	28.647	21.175	- 12
6.381	41.244	+ 12				19.958	21.815	- 11
5.261	41.316	- 40				8.969	22.855	+ 12
			$D = 42.71$					
			$10^4 c$	$A$				
			59.465	1.671				
			50.753	1.831				
			41.276	1.990				
			30.722	2.274				
			21.823	2.677				
			15.308	3.137				
			8.829	3.918				
			4.671	5.078				
			2.952	5.999				

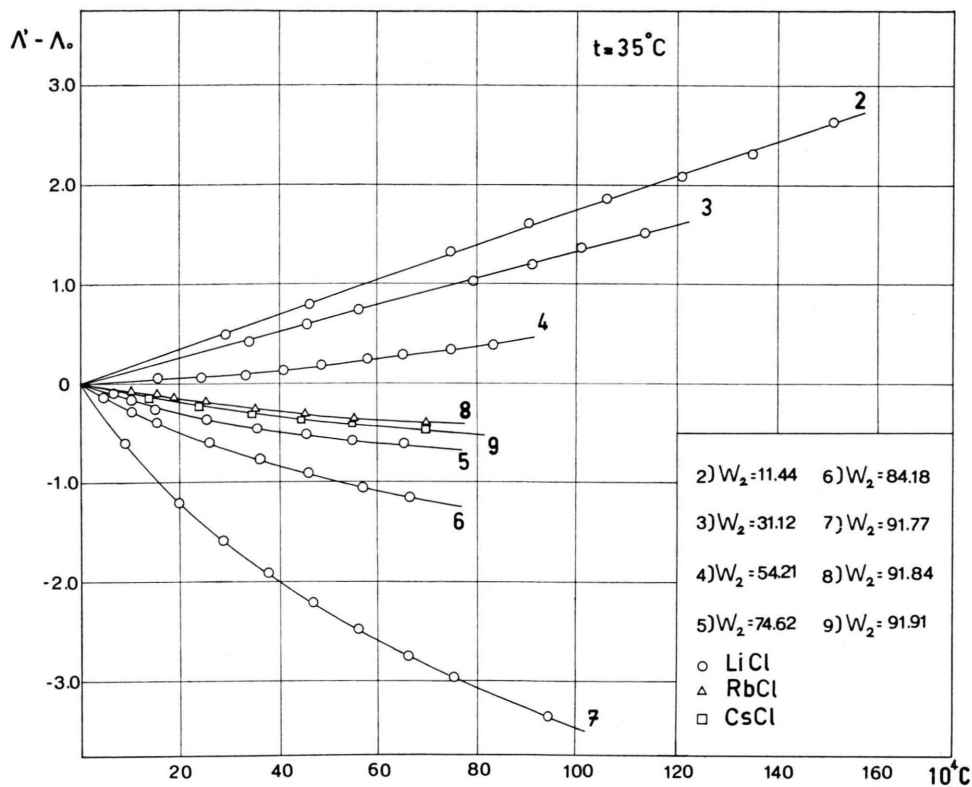
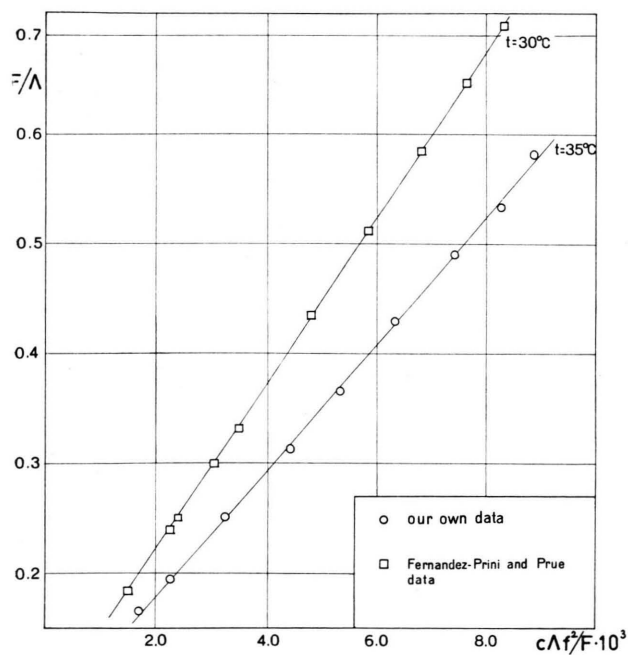
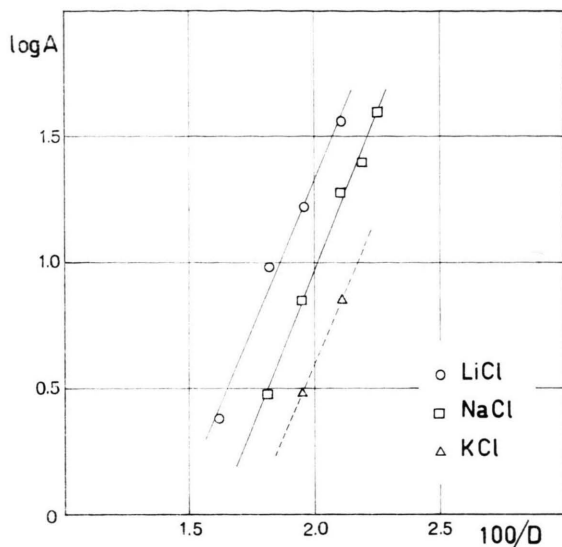
Fig. 1.  $(\Lambda' - \Lambda_0)$  vs.  $c$  plots in several solvent mixtures at 35 °C.Fig. 2.  $F/\Lambda$  vs.  $c \Lambda f^2/F$  for LiCl in pure sulfolane at 30 °C and 35 °C.

Table 3. Equivalent conductance data of RbCl and CsCl in sulfolane-water mixtures at 35 °C.

$10^4 c$	$\Lambda$	$\Delta \Lambda \cdot 10^3$	$10^4 c$	$\Lambda$	$\Delta \Lambda \cdot 10^3$
$D = 47.29$			$D = 47.26$		
65.222	23.468	+3	64.730	23.250	-2
55.400	23.723	+2	54.930	23.517	+2
45.152	24.009	-6	44.152	23.836	+2
35.023	24.344	+4	34.542	24.149	-3
24.915	24.714	+1	24.315	24.538	-1
18.579	24.980	-3	14.895	24.967	+1
15.073	25.156	+6			
9.790	25.436	-3			

### Discussion

As observed in the case of (Na, K)Cl water-sulfolane solutions, also for LiCl the addition of sulfolane results in a steady decrease of  $\Lambda_0$ , and in a noticeable association to ion pairs for systems where  $D < 62$ . For the solvent systems 4 ÷ 7,  $\log \Lambda$  exhibits a straightline dependence on  $1/D$  (Fig. 3); however, a dramatic increase of the  $\Lambda$  term occurs in pure sulfolane ( $\Lambda = 14595$  at  $t = 35$  °C; the value

Fig. 3. Log  $A$  vs.  $1/D$  for (Li, Na, K)Cl at 35 °C.

calculated by the same method from PRINI and PRUE's conductance data<sup>6</sup> being 15687 at 30 °C).

The ion distance of closest approach steadily decreases, on adding sulfolane, down to a value of 1.35, scarcely affected by the solvent composition, in the dielectric constant range 55 ÷ 47. (The related values for NaCl and KCl were 1.5 and 2.0 respectively).

The Walden products, ranging within 1.01 ÷ 1.11 in mixed solvents, abruptly rise up to 1.4 in pure sulfolane, affording further evidence to the supposition that the conduction mechanism, in pure sulfolane, might be changed.

A comparison with (Na, K)Cl conductance data, in pure sulfolane, is lacking owing to the poor solubility of these two salts. It may be observed that  $K^+$  and  $Na^+$  are more conducting than  $Li^+$  in water-

sulfolane solutions, just as in pure water. On the contrary,  $Rb^+$  and  $Cs^+$  ions are less conductive than  $K^+$ , at least in the solvent systems taken into account, in agreement with previous conductance data on dioxane-water solutions<sup>7</sup>.

The different ion behaviour is, however, less pronounced in sulfolane richer solutions.

Attention must now be called on the association order of alkali halides:



which appears reversed with respect to the usual order in common solvent media. A similar sequence was already observed in some other aprotic solvents, as acetone and nitrobenzene, in the case of alkali picrates<sup>8</sup>.

A reasonable interpretation of this behaviour might be given on the assumption that competition of sulfolane in ion solvation is nearly lacking. Let us suppose that unsolvated ions are more liable to form stable ion pairs and that the fraction of solvated ions is a smooth function of the properties of the solvent; then the increase of association, on adding sulfolane, may be explained, as well as the linear dependence of  $\log A$  on  $1/D$ , for water-sulfolane solutions.

Ion association is indeed expected to increase with decreasing dielectric constant of the solvent medium and ion size. An easier reduction in the number of solvated ions on adding sulfolane accounts for the higher ability of the lithium ion to form stable ion pairs, even in water-sulfolane solutions; the nearly complete desolvation of ions in pure sulfolane would be responsible for the dramatic increase in the association constant.

The larger mobility of lithium ions in pure sulfolane<sup>9</sup> appears consistent with this assumption, as

Table 4. Constants for (Li, Cs, Rb)Cl in sulfolane-water mixtures at 35 °C.

No.	$A_0$	$a_L$	$a_A$	$A$	$\sigma$	$A_0 \eta$
1	$140.22 \pm 0.01^*$	$3.19 \pm 0.02$	—	—	—	1.01
2	$122.83 \pm 0.03$	$2.97 \pm 0.04$	—	—	0.03	1.01
3	$96.193 \pm 0.020$	$2.80 \pm 0.04$	—	$(0.5 \pm 1)$	0.02	1.05
4	$66.605 \pm 0.047$	—	$1.63 \pm 0.44$	$2 \pm 1$	0.02	1.08
5	$42.448 \pm 0.030$	—	$1.34 \pm 0.09$	$10 \pm 3$	0.03	1.09
6	$31.505 \pm 0.009$	—	$1.40 \pm 0.02$	$13 \pm 1$	0.04	1.07
7	$24.329 \pm 0.021$	—	$1.31 \pm 0.01$	$36 \pm 1$	0.01	1.11
10	15.919	—	—	14595	—	1.44
8	$26.490 \pm 0.010^{**}$	—	$2.12 \pm 0.16$	$5 \pm 1$	0.01	1.21
9	$26.300 \pm 0.008^{***}$	—	$2.18 \pm 0.13$	$5 \pm 1$	0.01	1.21

\* R. L. KAY, J. Amer. Chem. Soc. **82**, 2099 [1960]. \*\* Constants for RbCl. \*\*\* Constants for CsCl.

well as the low ionic radius; to this purpose a more complete interpretation of the distances of closest approach, lower than crystallographic radii, for several salts in pure sulfolane, was given by PRINI and PRUE<sup>10</sup> in terms of dielectric saturation.

In Fig. 4 the Walden products  $\Lambda_0 \eta$  vs.  $N_2$  are plotted. Apart from the above mentioned mobility order ( $K^+ > Na^+ > Li^+$ ), the three salts show a similar dependence on medium composition of the Walden product which appears, however, to tend to a common value at  $N_2 = 0.6 \div 0.7$ .

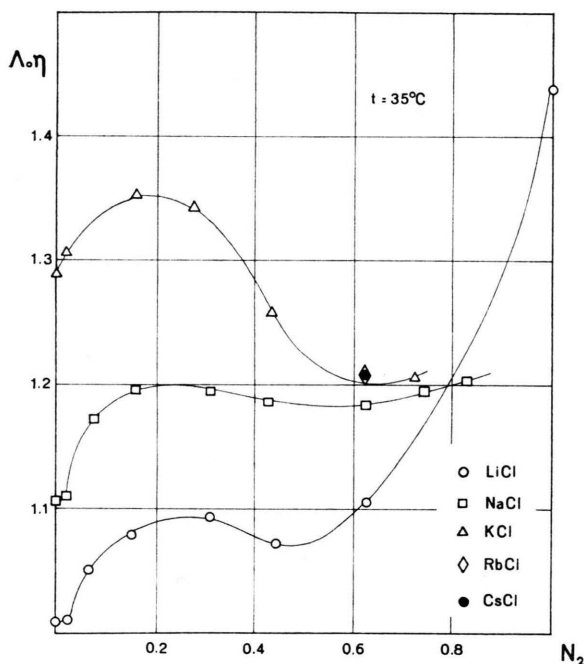


Fig. 4. Walden products for alkali chlorides, at 35 °C, vs. sulfolane mole fraction in solvent mixtures.

The behaviour of the  $\Lambda_0 \eta$  terms can be reasonably referred to the overlap of several effects on ionic mobilities: the gradual collapse of water structure on adding sulfolane, the local change of viscosity in the proximity of ions and the probable desolvation, which predominates in sulfolane rich solutions<sup>11</sup>.

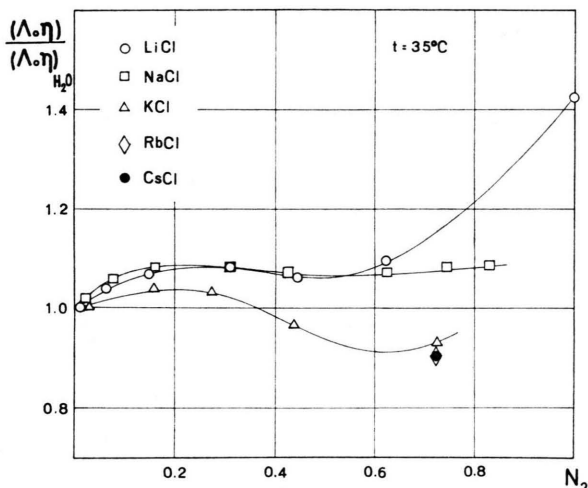


Fig. 5. Walden products, normalized to water, for alkali chlorides, at 35 °C, vs. sulfolane mole fraction in solvent mixtures.

The curves of Fig. 5, where the Walden products (normalized to water) are plotted vs. composition, support the idea that a careful consideration of specific ionic influences on solvent structure<sup>12</sup> is a prerequisite for a meaningful discussion.

These plots appear suitable to differentiate the behaviour of structure maker ions, such as  $Li^+$  and  $Na^+$ , from that of larger ions ( $K^+$ ,  $Rb^+$  and  $Cs^+$ ), which are certainly structure breakers.

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