gewonnenen [6] gegenübergestellt. Unsere q-Werte haben, abgesehen von dem durch die Euckensche Beziehung eingeführten eventuellen systematischen Fehler, einen mittleren Fehler von $\pm 0{,}05$ und zeigen in dem von uns gewählten Temperaturbereich innerhalb der Fehlergrenzen keine Temperaturabhängigkeit. Das vermutlich von den Quanteneffekten herrührende Ansteigen der q-Werte mit sinkender Temperatur, welches beim H_2 in diesem Temperaturbereich zu beobachten ist [7], tritt beim D_2 noch nicht in Erscheinung.

Tab. 2. Empirische Werte der Koeffizienten k_1 und k_2 in Gl. (1), und aus dem Trägheitsmoment von D_2 berechnete Werte der in Gl. (3) vorkommenden Funktion $48\,\sigma^2 \exp(-6\,\sigma)$, für die drei Meßtemperaturen.

T (K)	18,4	19,6	21,0
$k_1 \cdot 10^3$	2,17	2,43	2,97
$k_2 \cdot 10^3$	2,37	2,27	2,24
$48\sigma^2 e^{-6\sigma} \cdot 10^3$	0,17	0,36	0,80

Tab. 3. Empirische relative Stoßquerschnitt-Differenzen [Gl. (2)].

	Aus Leitfähigkeit			Aus Viskosität	
T (K)	18,4	19,6	21,0	16,6	20,3
$q_{po} \cdot 10^3$	1,00	1,04	1,09	2,6	2,0
$q_{pp} \cdot 10^3$	4,37	4,34	4,41	3,2	2,6

Entgegen der Erwartung stimmen die aus den Leitfähigkeits- und Viskositätsmessungen erhaltenen q-Werte, wie Tab. 3 zeigt, nicht überein. Das könnte, wie in der Einleitung ausgeführt wurde, daran liegen, daß die Viskositätsmessungen auf einen zu kleinen Konzentrationsbereich beschränkt waren und deshalb nur ungenaue q-Werte lieferten.

Der Deutschen Forschungsgemeinschaft danken wir für die Unterstützung der Arbeit durch Sachmittel (Wasserstoff-Verflüssigungsanlage).

The Conductance of the Alkali Halides

II. Potassium Chloride in Sulfolane-Water Mixtures, at 35 °C

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(Z. Naturforsch. **26 a**, 1306—1308 [1971]; received 14 April 1971)

The conductometric behaviour of potassium chloride in water-sulfolane mixtures, at 35 °C, was investigated, the concentration of the salt ranging within 2.10^{-3} and 8.10^{-3} moles/l and the dielectric constant, D, of the solvent mixtures within 75 and 47.

Analyzing the data by the Fuoss, Onsager and Skinner treatment, Λ_0, a_L, A, a_A *and* $\Lambda_0 \eta$ values were obtained. A noticeable association can be evidenced only with the solvent mixtures of lower dielectric constants. Ceteris paribus, KCl is less associated then NaCl. A slight dependence of the Walden product upon the solvent composition may be noticed.

In a previous paper [1] a systematic investigation was planned on the conductometric behaviour of electrolytes in sulfolane-water mixtures, mainly for the purpose of furnishing new data to discuss the influence of the solvent structure on conduction mechanism.

The experimental results on NaCl allowed us to conclude that, in comparison with other isodielectric media, the distance of closest approach of ions is reduced and association to ions pairs is more remarkable in sulfolane rich solutions.

Previous literature [2] supports the idea that, in the case of KCl, association would be enhanced.

In the present paper we report a study on KCl, at 35 °C, in the concentration range $2 \cdot 10^{-3} \div 8 \cdot 10^{-3}$ moles/l, in sulfolane-water mixtures, the weight composition of sulfolane w_2 ranging between 0 and 92% (the salt is sparingly soluble in pure sulfolane).

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Experimental

Solvents and *potassium chloride* were carefully purified as previously [1] reported.

Solutions were made up by weight; the concentration of the salt, c, in moles/l was calculated from the molality, m (in moles/kg of solvent) by means of the equation: $c/m = \varrho - 0.0274\,m$, ($\varrho$ density g/ml of the solvent mixture at 35 °C); the above equation, already applied by HARNED and OWEN [3] to KCl aqueous solutions, has been shown by us to be suitable in recalculating the concentration values of the same electrolyte, in water-sulfolane solutions, within 10^{-7} moles/l.

The density of the mixtures was determined by 20 ml pycnometers at 35 °C ± 0.003 °C; *the viscosity* was measured at 35 °C ± 0.01 by means of four Ubbelohde viscometers, calibrated with pure substances.

The dielectric constant was measured, at 2 MHz, at 35 °C ± 0.05, by a W.T.W. Dipolmeter DMO1 in a cell, suitable for the dielectric constant range 1 ÷ 100, calibrated [4] with standard liquids, according to the N.B.S., Circular 514 (1951).

For the conductance apparatus and procedure compare [1].

Results

Properties of Solvent Mixtures

The physical constants of the solvent mixtures are summarized in Table 1, where ϱ is the density in g/ml; η the viscosity in centipoises and D the dielectric constant. For compactness in later discussion, the solvents are identified with code numbers of the first column in Table 1. Compositions are given in weight percent, w_2, and mole fraction, N_2, of sulfolane in the mixtures.

Table 1. Properties of solvents at 35 °C.

No.	w_2	N_2	ϱ	η	D
1	0	0	0.99406	0.7194	74.64
2	12.0	0.0200	1.02147	0.8271	72.33
3	55.7	0.1584	1.12907	1.665	61.43
4	71.5	0.2735	1.17225	2.428	56.03
5	83.6	0.4335	1.20630	3.347	51.31
6	91.9	0.6282	1.23075	4.543	47.30

Conductance Data for KCl in Sulfolane-Water Mixtures

KCl equivalent conductance data, at 35 °C, are summarized in Table 2, together with the dielectric constants of solvent media and concentrations, c, of the electrolyte.

They were treated according to ONSAGER, FUOSS and SKINNER [5].

The equation:

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

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

10^4 c	Λ $D = 72.33$	$\Delta\Lambda\,10^3$	10^4 c	Λ $D = 61.43$	$\Delta\Lambda\,10^3$	10^4 c	Λ $D = 56.03$	$\Delta\Lambda\,10^3$
82.122	148.755	− 24	83.585	75.353	− 8	74.364	51.052	− 5
65.360	149.691	+ 13	65.628	76.010	+ 5	61.083	51.448	+ 1
49.612	150.687	+ 22	50.400	76.647	+ 12	45.380	51.982	+ 9
36.899	151.624	+ 15	36.973	77.283	− 1	31.494	52.531	+ 2
25.326	152.619	− 30	25.552	77.937	− 8	19.461	53.121	− 6
	$D = 51.31$			$D = 47.30$				
70.130	34.010	—	45.669	24.031	—			
63.784	34.178	—	40.389	24.195	—			
55.975	34.395	− 3	36.649	24.318	—			
51.566	34.533	+ 3	33.585	24.424	—			
44.599	34.758	+ 6	28.047	24.627	—			
38.439	34.697	+ 3	24.699	24.759	− 1			
31.796	35.212	− 1	21.974	24.875	+ 1			
25.968	35.452	− 3	19.091	25.002	—			
21.170	35.660	− 15						
16.494	35.952	+ 12						

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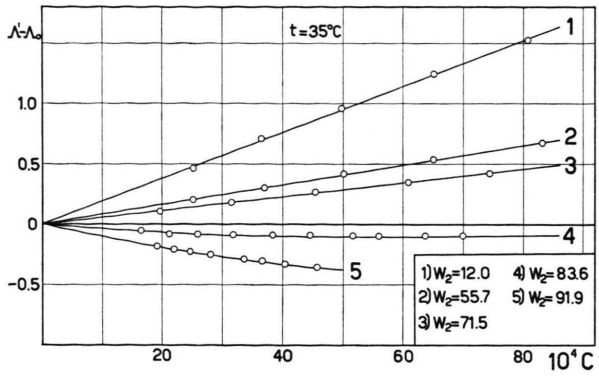

Fig. 1. $(\Lambda' - \Lambda_0)$ vs. c plots in several solvent mixtures at 35 °C. Graphs 1, 2 and 3 show the absence of association. The other plots show a noticeable association.

was used in the simplified form:

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

if no detectable association occurred.

The used program indeed disregards automatically association if the A term in Eq. (1) does not exceed a value of a few units, ($\gamma \cong 1$). Nevertheless, when the choice between the Eq. (1) or (2) was affected by a certain amount of arbitrariness, both of them were applied alternatively to experimental data.

In Fig. 1 the difference $\Lambda' - \Lambda_0$ is plotted vs. the molar concentration, c, of the electrolyte.

Each curve refers to a different solvent composition. No association can be evidenced above $D \cong 52$, accordingly with the linear dependence of the $\Lambda' - \Lambda_0$ terms on c, in the curves, 1, 2 and 3.

As reported above, Eqs. (1) and (2) allow to evaluate the electrolyte constants Λ_0, a_L, A and a_A (a_L being the distance of closest approach of ions calculated from the L term; a_A has the same meaning but is drawn from the A term, which takes into account the association to ion-pairs).

It has been already [1] pointed out that, in the high dielectric constant region, the a_L values obtained from Eq. (2) are more reliable, whereas the a_A terms are more reliable at lower dielectric constants. On this basis, data were summarized in Table 3, where the standard deviation σ and the Walden products $\Lambda_0 \eta$ are also reported.

Discussion

The Λ_0 values steadily decrease with increasing sulfolane content (Table 3). In the high dielectric constant range (starting from $D \cong 61$) the distance of closest approach might be considered as nearly constant ($\cong 2$ Å). Similarly, in the case of NaCl a constant value of 1.5 Å was found, starting from $D \cong 51$. (It may be of some interest to remember that the difference of the crystallographic radii of the two cations is 0.39 Å.) Moreover, both for NaCl and KCl, the a_L and a_A terms are lower than in some other isodielectric media, thus affording further evidence to the supposition of a reduced ion solvation in sulfolane-rich solutions. The $\Lambda_0 \eta$ products may be considered scarcely affected by solvent composition, reasonably owing to a competition between the effects of desolvation and change of physical properties of the solvent mixtures.

In the whole, the conductometric behaviour of KCl may be thought to be similar to that of NaCl, but, ceteris paribus, the association to ion-pairs appears to be reduced in the case of KCl. These preliminary data support therefore the idea that the association order of alkali chlorides, in water-sulfolane mixtures, may be reversed.

Taking into account the circumstance that any system exhibits deviations from conformity to an idealized model, which are characteristic of the particular system, we are waiting for the results of some conductance measurements on LiCl, before advancing any supposition on the influence of properties of solvent mixtures on the conductometric behaviour of alkali chlorides.

Table 3. Constants for Potassium Chloride at 35 °C in the Sulfolane-Water Mixtures listed in Table 1.

No.	Λ_0	a_L	a_A	A	σ	$\Lambda_0 \eta$
1	180.53 ± 0.03 *	3.2 ± 0.05			—	1.30
2	157.93 ± 0.04	2.75 ± 0.08			0.03	1.31
3	81.210 ± 0.013	2.04 ± 0.04			0.01	1.35
4	55.289 ± 0.008	1.97 ± 0.03			0.01	1.34
5	37.578 ± 0.024		2.20 ± 0.50	3 ± 1	0.01	1.26
6	26.561 ± 0.005		1.91 ± 0.04	7 ± 1	0.01	1.21

* R. L. KAY, J. Amer. Chem. Soc. **82**, 2099 [1960].