Studies on Ionic Solutions in Diethyl Ether

IV. Properties of LiClO₄-Ether Solutions

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In parts I—III of this series [1-3] it has been shown how lithium perchlorate may be used for obtaining solutions in diethyl ether of a constant ionic strength. By the addition of a large and constant amount of $LiClO_4$ to the solutions, the activity factors of various ions such as Ag^+ and halogenide ions may be kept constant so that their concentrations may be measured with emf methods.

The solutions of $LiClO_4$ in diethyl ether are remarkable in many ways. At 25° C, ether dissolves as much as 53.21 per cent by weight of $LiClO_4$, corresponding to a molar fraction of 0.44 (Willard and Smith[4]). The solutions are very viscous especially at the highest concentrations.

On the addition of a small quantity of water to such a solution, one gets immediately a precipitate of $LiClO_4(H_2O)_3$, whose solubility in ether is only 0.196 %[4]. This large difference in solubility would perhaps not have been expected.

A number of other salts, such as lithium chloride and lithium acetate, which are only slightly soluble in pure ether, are considerably soluble in $LiClO_4$-ether solutions. This may be compared with the "neutral salt" effect on the solubility of electrolytes in water. However, the effect seems to be much larger in $LiClO_4$-ether.

To understand better the properties of $LiClO_4$-ether as solvent, it seemed desirable to study the properties of solutions of lithium perchlorate in ether at different concentrations.

From the fall of 1948 to the summer of 1949 we undertook measurements of the vapor pressure and electric conductivity of such solutions. When our experimental work was completed, at the end of September, 1949, one of us had the pleasure of listening to a lecture by Dr. Oliver Johnson at the meeting of the American Chemical Society at Atlantic City [5]. He then learned that Dr. Johnson [6] and another of Professor Fajans's co-workers, Dr. Chu[7,8], had also made a number of measurements on $LiClO_4$-ether solutions, though their approach to the problem was quite different from ours. We exchanged our data and found that they were in many ways complementary. In the

Table 1. Density ϱ of ether (1)-LiClO₄ (2) mixtures of varying mole fraction x_2*, according to Johnson (*p. 39); partial molar volumes* v_1 *and* v_2 *calculated by three methods (see text); molar concentration* c_2.

		Method 1 (from d)		Method 2 (from φ_2)		Method 3 (from v)		
x_2	ϱ	v_1	v_2	v_1	v_2	v_1	v_2	c_2
0	0.70776	104.7	15.2	104.7	14.2	104.7	13.0	0
0.0608	0.76595	104.6	17.5	104.4	19.0	104.3	19.0	0.612
0.0872	0.79265	104.3	19.5	104.3	19.9	104.2	19.9	0.8983
0.1256	0.83301	104.0	22.6	104.1	21.6	104.0	21.7	1.3381
0.1552	0.86661	103.9	23.5	103.8	23.1	103.2	26.0	1.6970
0.2363	0.95999	102.7	28.2	102.3	29.2	101.4	31.6	2.7750
0.2898	1.02559	101.3	31.8	100.7	33.7	99.8	35.2	3.5608
0.3264	1.07330	99.4	36.2	98.9	37.9	98.0	39.2	4.1383
0.4401	1.20807	89.7	52.4	92.0	48.9	94.7	45.6	6.0196

following, with the kind permission of Drs Fajans, Johnson and Chu, we shall compare their measurements with ours and also use some of their data in the discussions.

EXPERIMENTAL

Reagents. Diethyl ether and lithium perchlorate were obtained as described in Part I[1]. The amount of $LiClO_4$ in the ether solutions was determined in principle as described in part II[2] by tipping the ethereal solution into water and evaporating the ether (occasionally by evaporating the ether and dissolving in water), diluting to a defined volume, taking out a sample with a pipet, passing it through a H^+ saturated ion exchanger, and titrating for the liberated hydrogen ions with NaOH.

Temperature. All measurements were carried out in a thermostat room, the temperature of which was kept at $23.5 \pm 0.2°$ C. The choice of this temperature, instead of $25°$ C or $18°$ C which would have been preferable, may be ascribed to the law of mental inertia.

Concentration units, densities, molar volume. In our measurements, the concentration of the solutions was generally obtained as the molar fraction x_2 of lithium perchlorate (1 = ether, 2 = lithium perchlorate). When it was desirable to convert x_2 to the molarity, c_2, we used Johnson's values [6], which are given in Table 1. The density change between $23.5°$ C and $25°$ C was neglected.

From Johnson's figures [6] the partial molar volumes of ether and $LiClO_4$, v_1 and v_2, were calculated by three methods (see *e. g.* Lewis and Randall [11], Ölander [12], Sillén, Lange and Gabrielson [13]): 1) by plotting the "shrinkage" d versus x_2, 2) by plotting the apparent molar volume φ_2 versus log n_2 ([11]method III), 3) by plotting the volume of 1 mole solution, v, versus x_2 ([11]method IV). The results are given in Fig. 3a.

Vapor pressure measurements. Fig. 1 shows the apparatus used. The $LiClO_4$-ether solution to be studied is kept in the bulb A. C is a flask of nearly 1 l volume, intended to act as a buffer volume and thus to eliminate the influence of small unavoidable leaks in the apparatus. The vessel B contains pure diethyl ether, some of which may be let in to build up the ether pressure in C and avoid large evaporation losses in A.

In the beginning of an experiment, the apparatus was mounted and the vessel A, which was closed by means of a stop-cock, dipped into liquid air (about $-190°$ C). The freezing point of diethyl ether is $-116.3°$ C, and at this temperature the vapor pressure is about 0.008 torr [14]. It must therefore be still lower at $-190°$ C.

The whole system was then evacuated by an oil pump, first with closed stopcocks at A and B, then opening the stop-cock at A. The pumping was continued until on closing
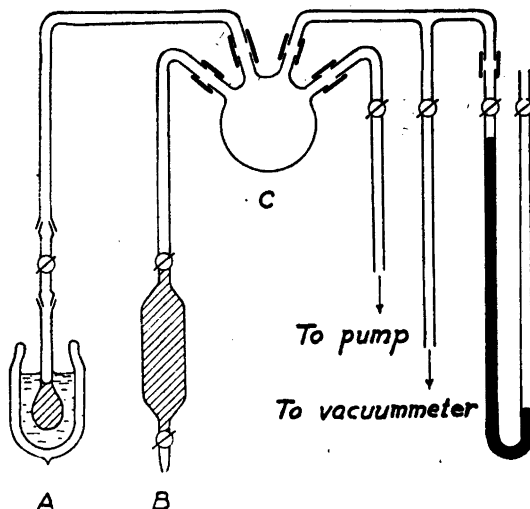
Fig. 1. Apparatus for measuring vapor pressure p_1. *A contains the LiClO$_4$-ether solution,*
B *pure ether.* C = *buffer volume.*

the stop-cock to the oilpump, the pressure given by the vacuummeter was 0.2 torr or
generally less.

Now the stop-cock at A was closed, the liquid air bath taken away, and sufficient
ether let in from B so that the pressure at C, as measured by the manometer, was not far
from the expected equilibrium pressure of the solution at A. Then the stop-cock at A
was opened, and the system allowed to attain equilibrium at the temperature of the
thermostat room, which generally took 4—5 hours.

At the end of the experiment, vessel A was weighed together with its content of solu-
tion, which had been in equilibrium with ether vapor of the measured pressure. Then the
whole solution was tipped into water, and the amount of LiClO$_4$ determined using a
known fraction of the solution, and an ion exchanger as described above.

Table 2. Activity factors f_1 *of ether in LiClO$_4$-ether solutions, calculated from the ether
pressure* p_1 *at 23.5° C (present work), and from the boiling point elevation as measured by
Chu and Fajans* [3] *1949.*

| x_2	p_1	f_1	x_2	p_1	f_1	x_2	ΔT_e	f_1
0	503	1.000	0.241	453	1.187	0.00903	0.142°	1.0043
0.047	489	1.020	0.257	433	1.159	0.02935	0.427°	1.0154
0.059	484	1.023	0.280	426	1.176	0.04542	0.625°	1.0255
0.101	482	1.066	0.280	432	1.193	0.06881	0.880°	1.0422
0.141	470	1.088	0.284	418	1.161	0.08149	0.955°	1.0539
0.177	470	1.135	0.287	398	1.110	0.12859	1.368°	1.0954
0.199	466	1.157	0.317	370	1.077			
0.221	451	1.151	0.319	341	1.019			
0.237	454	1.183	0.321	361	1.057			
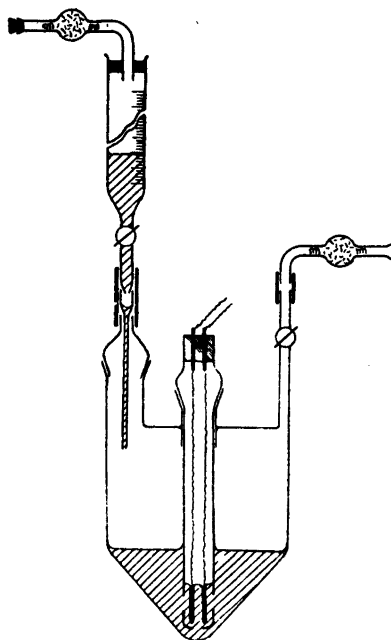
Fig. 2. Cell for measuring conductivity.

The results are given in Table 2 and Fig. 4 (circles). The vapor pressure $p_1^0 = 503$ torr for pure ether, measured with this apparatus, compares very well with the value 503.5 torr at 23.5° C, calculated using the formula of Taylor and Smith [15]. From the p_1 values found, the activity factors $f_1 = p_1/x_1 p_1^0$ were calculated from Chu's and Fajans' boiling point data[8], using the equation $-\log (f_1 x_1) = \triangle T_e \cdot 0.1477_5$ corresponding to a molar heat of evaporation 6.38 kcal mole^{-1}. The results are given as dots in Fig. 5; the range is smaller but the agreement good.

Conductivity measurements. Fig. 2 shows the conductivity cell, its cell constant being 4.77 cm^{-1}. After each experiment it was cleaned with nitric acid and water, and the constant checked using 0.0200 C KCl. A fresh KCl solution was prepared every week. Between measurements, the conductivity cell was stored in ethanol.

As seen from Fig. 2 the vessel was conical, to allow measurements of conductivity over a large range of volumes. The dip cell was inserted into the vessel through a standard ground-glass joint. A burette, containing pure ether, and a calcium chloride tube (for letting out excess air) were connected to the vessel by ground-glass joints with rubber joints as shown in the figure.

At the beginning of an experiment, the vessel was weighed with the dip cell but without burette and calcium chloride tube. A certain amount of concentrated LiClO$_4$-ether was introduced and the vessel weighed again. After waiting for equilibrium, the resistance of the dip cell was measured. Then pure ether was added in portions of 1 — 5 ml from the burette. After each addition of ether, the vessel was shaken, equilibrium waited for and the resistance measured. Finally when about 50 ml had been added, the vessel was weighed again, the apparatus disconnected, and the total amount of LiClO$_4$ present determined as described above. Two different stock solutions of LiClO$_4$-ether were used.

The resistance was measured using a Philoscope. The accuracy was only about 1 %, which was sufficient in our case since the conductivity varied by a factor of more than 10^4 in the concentration range studied and since larger errors came from the concentration calculations.

The primary data $\varkappa$ and x_2 are given in Table 3 (every third one of our points).

Table 3. Conductivity $\varkappa$ and molar conductance Λ of $LiClO_4$ in ether at various concentrations and 23.5° C (present work) or 25° C (Chu [7]).
23.5° C (present work). Every third point is given; (all points are given in Fig. 8.)

x_2	c_2	$\varkappa$	Λ	x_2	c_2	$\varkappa$	Λ
0.00664	0.060	$2.33 \cdot 10^{-8}$	$3.88 \cdot 10^{-4}$	0.113	1.19	$1.87 \cdot 10^{-5}$	$1.57 \cdot 10^{-2}$
0.00896	0.084	3.67	4.37	0.125	1.33	3.10	2.33
0.0141	0.132	6.35	4.81	0.143	1.55	4.99	3.22
0.0174	0.165	8.74	5.30	0.157	1.72	7.59	4.41
0.0284	0.27	$2.05 \cdot 10^{-7}$	7.59	0.174	1.94	$1.13 \cdot 10^{-4}$	5.83
0.0347	0.34	3.27	9.62	0.205	2.35	2.10	8.94
0.0491	0.49	8.93	$1.82 \cdot 10^{-3}$	0.226	2.64	2.56	9.70
0.0583	0.58	$1.55 \cdot 10^{-6}$	2.67	0.249	2.96	3.23	$1.09 \cdot 10^{-1}$
0.0695	0.71	2.62	3.69	0.275	3.34	3.75	1.12
0.0836	0.86	6.16	7.16	0.286	3.50	3.96	1.13
0.0975	1.02	$1.08 \cdot 10^{-5}$	$1.06 \cdot 10^{-2}$	0.307	3.84	4.11	1.07

25° C (Chu)

x_2	c_2	$\varkappa$	Λ
0.0608	0.6120	$9.86 \cdot 10^{-7}$	$1.611 \cdot 10^{-3}$
0.0872	0.8983	$4.659 \cdot 10^{-6}$	$5.186 \cdot 10^{-3}$
0.1256	1.3381	$2.144 \cdot 10^{-5}$	$1.602 \cdot 10^{-2}$
0.1552	1.7101	$5.913 \cdot 10^{-5}$	$3.458 \cdot 10^{-2}$
0.2363	2.7750	$2.552 \cdot 10^{-4}$	$9.196 \cdot 10^{-2}$
0.2898	3.5608	$3.969 \cdot 10^{-4}$	$1.115 \cdot 10^{-1}$
0.3264	4.1383	$4.339 \cdot 10^{-4}$	$1.049 \cdot 10^{-1}$
0.4401	6.0196	$3.111 \cdot 10^{-4}$	$5.169 \cdot 10^{-2}$

In the way our experiments were performed, we immediately obtained the weight percentage, and thus the mole fraction x_2 of $LiClO_4$. Using Johnson's densities [6] (Table 1), x_2 can be converted to give the concentration c_2 in C (moles 1^{-1}), neglecting the difference in density between 23.5° C and 25° C. By means of c_2 we can calculate the molar conductance Λ of $LiClO_4$. In Fig. 8 Λ is given as a function of x_2; our data (circles 23.5° C) are seen to agree well with those of Chu [7] (dots 25° C).

Viscosity measurements. For comparison with the conductance data, we wished to know how the viscosity η varies with the concentration c_2. Since very accurate data were not needed, a Höppler viscosimeter was used. The measurements were made by Miss Christina Mannerskantz, M.Sc. Professor Paul Nylén was kind enough to provide us with a Höppler viscosimeter with calibration tables, the accuracy of which was stated to be $1-3$ %.

What is measured in a Höppler viscosimeter is the time needed by a large steel ball to roll along a tilted tube, filled with the liquid, of only slightly larger diameter than the ball.

No elaborate equipment was used to avoid the evaporation of ether, but the viscosimeter was closed quickly after introducing the solution, and after the measurement of η the solution was quickly transferred to another vessel, where its density was determined by an aerometer. The concentration c_2 was read from a curve (Fig. 3 b) giving c_2 as a function of the density ϱ, as obtained from Johnson's data [6].
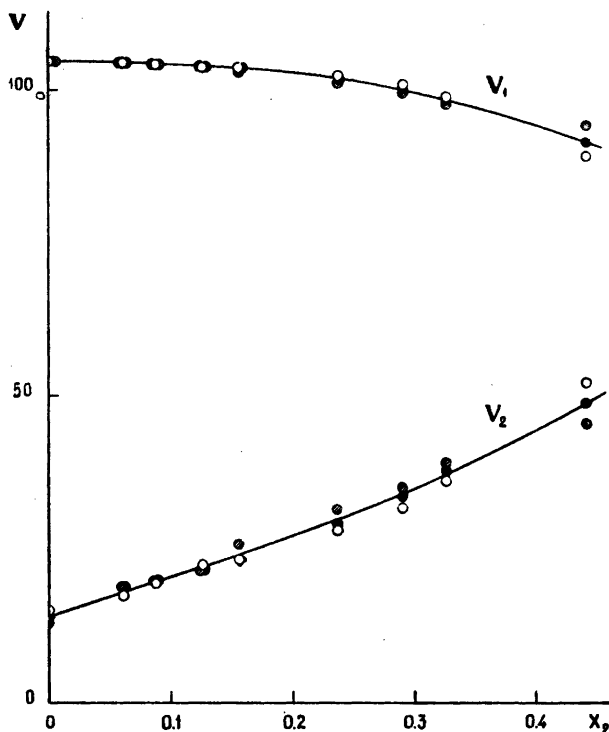
Fig. 3 a) Partial molar volumes v_1 and v_2 (in ml) calculated from Johnson's density values [6]: 1) O Open circles from the shrinkage d, 2) ● black dots from the apparent molar volume φ_2, 3) ⊘ shaded dots from the molar volume v (see text).

This curve was checked using solutions which had been mixed from accurately known amounts of ether and concentrated $LiClO_4$-ether solution. The lithium content of the latter had been determined by the ion exchange method [3]. The agreement was good (see Fig. 3b).

In Fig. 7 η (in cP) is given on a logarithmic scale as a function of x_2 at 20° C and 25° C (see also Table 4). The diagram shows the enormous increase of viscosity with concentration; it was not thought worth while to attempt to increase the accuracy.

<div align="center">DISCUSSION</div>

Association $LiClO_4$-$LiClO_4$ or complexes $LiClO_4$-ether? Chu and Fajans [8] measured the boiling point of $LiClO_4$-ether solutions, and from their data calculated the "apparent molecular weight" of $LiClO_4$ in the solution. They found values between 2 and 3 times the formula weight of $LiClO_4$, but did not consider these figures as exact because the solutions are really non-ideal. The process was described as an "association of $LiClO_4$", and it was pointed out that the conductivity data of Chu [7] indicated the formation of $(LiClO_4)_m Li^+$ and $(LiClO_4)_n ClO_4^-$ with m and n perhaps $= 4$ and 3 ([7] p. 129 and 145).
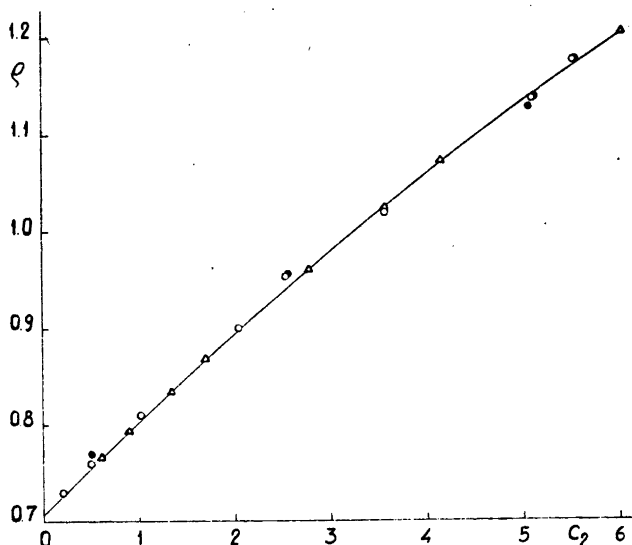
Fig. 3 b) Density ϱ (mg ml^{-1}) as a function of the concentration c_2 (in C). Triangles $\triangle$ and curve from Johnson's density data^6 at 25° C. Dots ● (20° C) and circles ○ (25° C) from direct measurements with an aerometer. (Present work).

This is one of the many examples in literature (see also *e.g.* [16]), where measurements of the activity of one component in a mixture have been used for drawing conclusions on the molecular state of the other component. In order to find out how farreaching conclusions can be drawn in this way, Högfeldt [9,10] has recently made a theoretical study of the activity and activity factor curves of binary mixtures A—B under various simple assumptions: formation of compounds A_uB_v, of polymer complexes $(A_uB_v)_n$, association of only A to A_n or of only B to B_n etc.

Högfeldt has assumed that the solutions are ideal as did Fajans and Chu in their rough calculations of "apparent molecular weight". Then all deviations in the activity factors from 1 are caused by the formation of associated groups of like molecules such as A_n or B_n, or of complexes of unlike molecules such as A_uB_v.

Table 4. Viscosity η (cP) of LiClO$_4$-ether solutions at 20° C and 25° C.

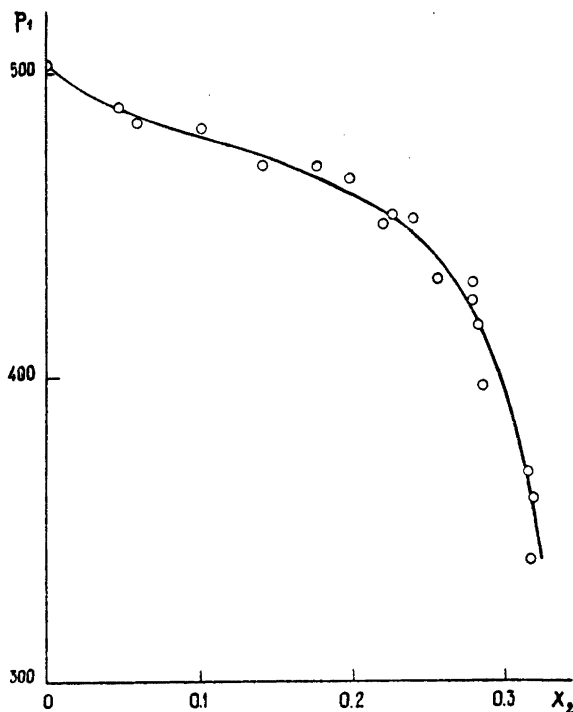| x_2	η_{20}	x_2	η_{20}	x_2	η_{25}	x_2	η_{25}
0.013	0.230	0.232	1.49	0.026	0.220	0.328	11.7
0.015	0.234	0.244	1.95	0.056	0.257	0.345	18.2
0.026	0.242	0.275	3.54	0.104	0.345	0.373	50.1
0.036	0.272	0.285	4.74	0.185	0.815	0.382	63.5
0.066	0.288	0.301	7.02	0.232	1.33	0.417	180
0.075	0.330	0.324	16.3	0.248	2.16		
0.104	0.394	0.349	24.8	0.265	2.51		
0.132	0.475	0.390	91	0.275	3.25		
0.176	0.70	0.417	236	0.285	4.44		
0.210	1.13			0.290	4.87		

Fig. 4. Vapor pressure p_1 *(in torr) at 23.5° C and various* x_2.

One of Högfeldt's results is that the activity factor curves can be used for differentiating between the formation of A_uB_v ($(A_uB_v)_n$) on one hand and the formation of A_u or B_v on the other. If only associates of like molecules are formed, the activity factor curves will continually increase or decrease, and show no maxima or minima. Now, for the system diethyl ether (1)-lithium perchlorate (2), the activity factor of ether, $f_1 = p_1(x_1p_1°)^{-1}$ goes from 1 to a maximum at about $x_2 = 0.25$, and then decreases, passing the value 1 at $x_2 =$ about 0.33 (Fig. 5). The existence of the maximum seems to rule out explanations based on only $LiClO_4$-$LiClO_4$ or ether-ether associates.

We conclude that *lithium perchlorate - ether complexes* must also be formed. The simple assumption, that only one complex namely (ether)$_u$ $(LiClO_4)_v$ is formed, was first tried. Then, according to Högfeldt,

$$x_{2(f_1=1)} = \frac{v-1}{u+v-1} \qquad\qquad x_{2(f_1=\text{max})} = \frac{1}{u+v}\left[v - \sqrt{\frac{uv}{u+v-1}} \ \right]$$

We made a diagram (Fig. 6) of v versus u, treating them as continuous variables, although of course they have a meaning only for integer values. In this diagram were drawn lines (broken) connecting points that would make $f_1 = 1$ at x_2
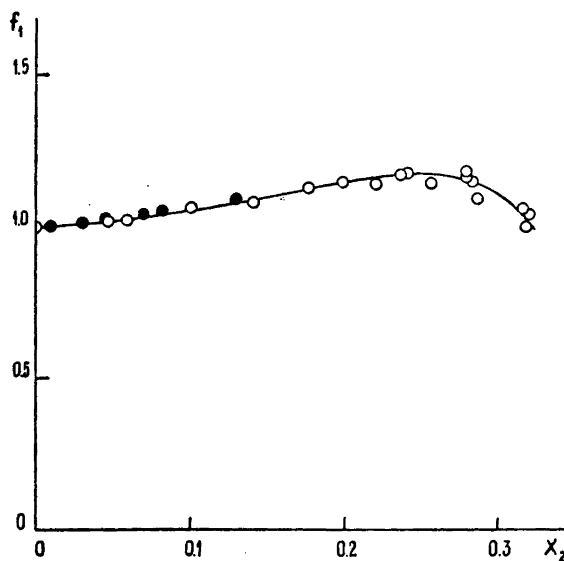
Fig. 5. Activity factor f_1 of ether at various x_2: Circles ◯: f_1 calculated from vapor pressure p_1 (present work); dots ●: f_1 calculated from the boiling point data of Chu and Fajans [3].

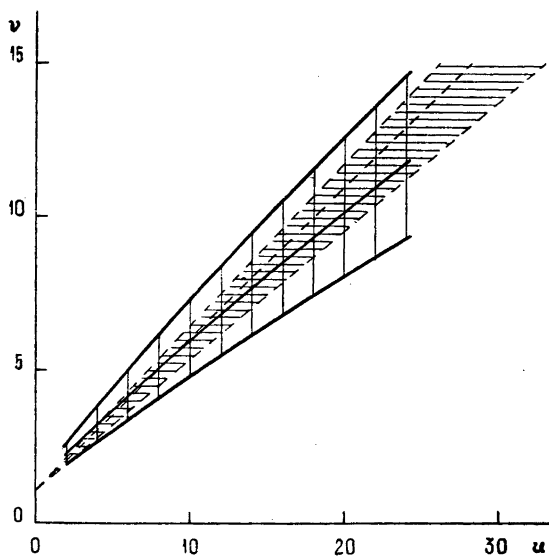
Fig. 6. Diagram for determining u and v, assuming the complex formed to be exclusively
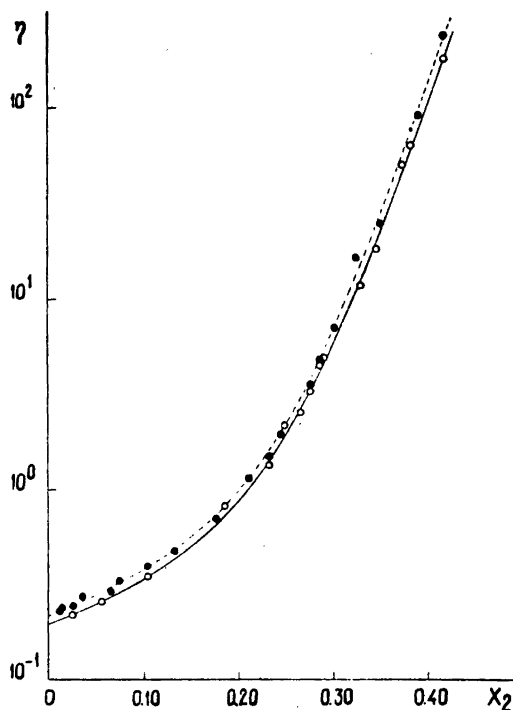$(ether)_u (LiClO_4)_v$ (see text).

Fig. 7. Viscosity η in cP (logarithmic scale) at 25° C (circles) and 20° C (dots) at various x_2.

$= 0.30$, 0.333, and 0.35, which was the widest range we thought possible. Curves were also constructed for the points that would give f_1 a maximum at 0.20, 0.25, or 0.30 (full drawn). If only one complex $(ether)_u(LiClO_4)_v$ is formed, its (u, v) should be in the area where the two bundles overlap (shaded in Fig. 6). Since the angle between the bundles of curves is small, the overlapping area is rather extended. Even if one might pick out some composition such as $(ether)_{10}(LiClO_4)_6$, and work it into a geometrical model, one might object that it is neither proved, nor very likely that only this complex is formed and no other.

· If there be a mechanism which can form a complex out of a certain number of ether molecules, Li^+ ions, and ClO_4^- ions, it seems likely that the same mechanism can build up still larger complexes, so that an infinite series of complexes are formed, perhaps of approximate formula $(A_uB_v)_n$.

Högfeldt has treated this general case too but, unfortunately, the calculations have so far given no explicit equation for calculating u and v from the $f_1(x_2)$ curve. However, it can be concluded that u is in this case greater than v and probably somewhat smaller than $2 v$.
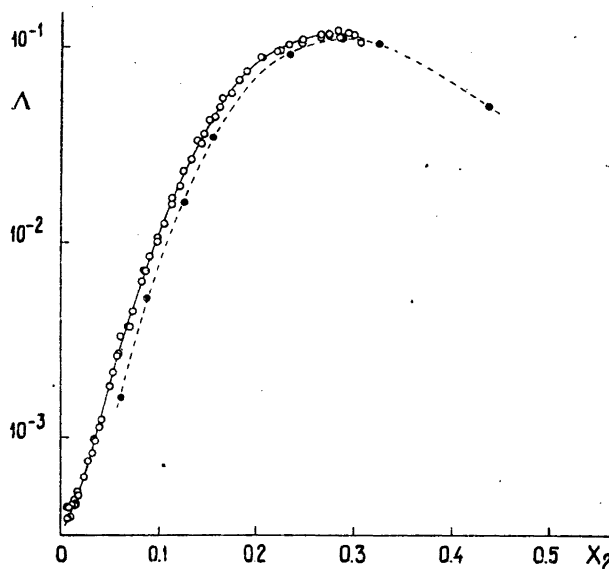
Fig. 8. Molar conductance Λ (logarithmic scale) of LiClO₄ at 23.5° C (circles, present work) and 25° C (dots, Chu⁷).

We thus conclude that ether-LiClO₄ complexes are formed, probably an infinite series of them, and that the ratio ether/LiClO₄ in the complexes is certainly greater than 1 and probably somewhat less than 2.

Conductivity and viscosity. Fig. 8 gives, for varying x_2, log Λ where Λ is the molar conductance of LiClO₄ at 25° C (circles, Chu[7]) and at 23.5° C (our data). The agreement is as good as can be expected; the temperature coefficient is negative, as has been observed in stray experiments by both Chu and ourselves.

It may seem surprising to some that Λ increases by a factor of several hundred with increasing concentration; for aqueous solutions a decrease by a few tenths of the value is the rule. However, as pointed out by Kraus[16], the increase of Λ with c (sometimes to a maximum) is the rule for electrolytes in solvents of low dielectric constant. A factor of increase as large as 10^4 has been observed. According to Kraus, no explanation of this behavior had been given in 1949; as for the views of Strong and Kraus (1950)[17], see below.

The increase in the molar conductance is still more surprising when one observes that for our solutions the viscosity, too, increases by several powers of ten; the most concentrated LiClO₄-ether solutions are as viscous as syrup.

One may well ask what the mechanism of conduction is. The ether-LiClO₄ complexes may well be charged, some containing excess of Li⁺ and others excess of ClO₄⁻. However, it seems extremely unlikely that electrical current is transported only by the movement of whole complexes. With increasing concentration, the contribution to the conductance from this mechanism must decrease since the complexes get bulkier and the solution more viscous.

It seems to us that the easier transport of current at high concentrations can only be explained by the *transport of single ions within the framework of the complexes*. This mechanism, of course, is favored by increased concentration; the complexes get larger and come closer together, and at the highest concentrations the complexes may have grown together throughout the solution, almost to a lattice, so that there are paths along which ions may move from one end to the other.

Fig. 9 gives a very schematic picture of the growth of the complexes with concentration. Of course, the figure is not intended to describe the geometrical arrangement of Li^+, ClO_4^-, and $(C_2H_5)_2O$ molecules in the complexes. In very dilute solutions, Li^+ may have as many as $4(C_2H_5)_2O$ molecules as closest neighbours, completely surrounding it. At the highest concentrations and especially in the complexes with less than $2(C_2H_5)_2O$ per $Li^+ClO_4^-$, the ether molecules can hardly suffice for shielding the ions from each other.

It seems likely that one kind of ion contributes more than the other to the conductivity, and one might imagine the small Li^+ jumping in the lattice of the ether and ClO_4^-. However, this is only a guess.

The mechanism proposed here resembles somewhat the "proton-jump" mechanism responsible for the high ionic conductance of H^+ in aqueous solutions according to Bernal and Fowler [18].

The negative T factor of Λ may be due to the breakdown of the complexes with increasing temperature.

Two liquid phases. Transition to fused salt. In some systems the attraction salt-solvent may cause the complexes to separate as a new liquid phase. For instance, in the system ether-$MgBr_2$ two separate liquid layers are formed, one of ether poor in $MgBr_2$, and one of composition around $MgBr_2(ether)_{2-4}$ (Doering and Noller [19]).

For some salt-solvent pairs the salt concentration may be raised beyond the point where the complexes coalesce and one may even have a gradual transition from concentrated solution to fused salt. It would be interesting to know whether in this concentration range the solvent molecules and ions are distributed completely at random in the liquid or whether there are solvent-rich and solvent-poor domains in this range too (cf Fig. 9 b and c).

Strong and Kraus [17] have suggested that concentrated solutions of salts in media of low dielectric constant (*e.g.* benzene) are best regarded as the fused salt, diluted with so much solvent. Whereas their general view is related to ours, we should like to object to some details of the mechanism proposed.

Strong and Kraus assume that the ions aggregate to ion pairs and larger complexes in an intermediate concentration range but are free at very low and very high concentrations. The main support for this assumption seems to be the "association numbers" which Kraus and coworkers have calculated from the freezing points of solutions of salts in benzene, assuming that the main process in the solution is the formation of (salt)$_n$ associates. These "association numbers" at first increase with increasing concentration, as could be expected. For salt of sufficient solubility, however, the "association number" goes through a maximum and then decreases with increasing salt concentration. This behavior seems hard to understand.
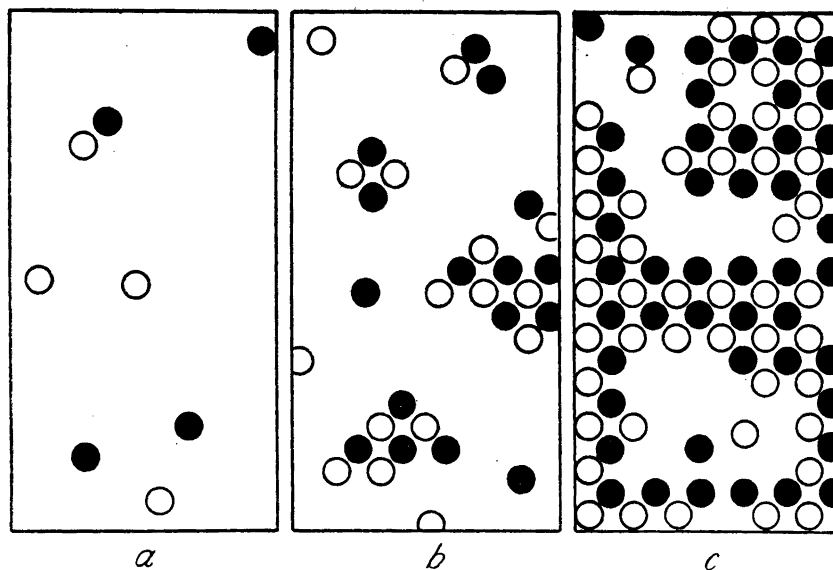
Fig. 9. Schematic picture of the proposed behavior of ions in $LiClO_4$-ether solutions of vary-
ing concentrations. The ions of opposite charges are pictured as circles and dots. The ether
molecules, which are not shown here, should be figured as filling up the "empty" space between
the ions and complexes and being intermixed with the ions in the complexes. a) In very
dilute solutions, the ions occur separately or occasionally in pairs. b) In solutions of inter-
mediate concentration, the ions form separate complexes of varying size. c) In solutions of
high concentration, the complexes come closer together almost to a coherent lattice though the
orderliness of the array is certainly less than drawn in the figure.

Let us, however, assume that solvent-salt complexes are formed — say,
(solvent)$_u$ (salt)$_v$ and that "association numbers" are calculated with the
incorrect assumption of solvent-free complexes. This "association number"
will then be lower than the true average v, and the deviation will increase
with increasing salt concentration (assuming ideal laws, as Kraus has done).
One can see already intuitively that a maximum "association number" might
arise by the combined effect of an increase in the true association number v
and an increasing negative error. The question will be treated more fully
by Högfeldt [10].

SUMMARY

$LiClO_4$ (2) is very soluble in ether (1). The vapor pressure, conductance
and viscosity of $LiClO_4$-ether solutions have been studied at 23.5° C and for
molar fractions x_2 up to about 0.35. The data are compared with densities
and conductances determined by Johnson [6] and Chu [7,8].

The vapor pressure curves cannot be explained only by the formation of
$(LiClO_4)_n$ associates; there must also be $LiClO_4$-ether complexes. Probably
these complexes can form clusters of varying size with an average ether/$LiClO_4$
ratio certainly greater than 1 and probably somewhat smaller than 2.

With increasing concentration, both the molecular conductance and the viscosity increase by several powers of ten. It is concluded that the main mechanism of conduction must be the *transport of single ions within the complexes* and not the movement of the clusters as whole units.

The same explanation may hold true for other electrolyte solutions in media of low dielectric constant.

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