334. *Antimony Halides as Solvents. Part II.*[1] *Conductance Data on Solutions of Organic Chlorides in Antimony Trichloride at 75°.*

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Conductance data are presented for tetramethylammonium and triphenyl-methyl chloride which are 1-1 strong electrolytes; application of Walden's rule confirms the earlier evidence for abnormal mobility of chloride ion.

Data are also presented for bornyl, n-decyl, 1-ethylcyclohexyl, cyclohexyl, diphenylmethyl, cinnamyl, and benzyl chloride. These are shown to ionise principally in the new mode $2RCl \rightleftharpoons R_2Cl^+ + Cl^-$, though in dilute solution the simple mode $RCl \rightleftharpoons R^+ + Cl^-$ can be detected. Values for these equilibrium constants are worked out and discussed.

PART I of this series[1] gives data on freezing-point depressions in antimony trichloride. Hydrocarbons show a normal depression, except for stilbene which dimerises. The simple salts potassium chloride, cæsium chloride, and tetramethylammonium chloride give two ions each per molecule and the ionic-strength effects are explicable by Debye-Hückel theory.

Triphenylmethyl chloride also was shown to be a 1-1 strong electrolyte in antimony trichloride, as opposed to other solvents where it is only slightly ionised. The present

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[1] Part I, Porter and Baughan, *J.*, 1958, 744.

work is concerned with the electrical conductance of tetramethylammonium and triphenyl-methyl chloride, confirming the freezing-point data, and with the electrical conductance of several aliphatic and phenyl-substituted aliphatic chlorides.

The most precise previous conductance data [2] on antimony trichloride solutions of inorganic chlorides refer to 99°; we have, however, preferred to work at 75° since this is only just above the freezing point (73·17°) so that our activity data [1] can be used without significant corrections, and since the lower temperature diminishes the difficulties caused by solute volatility and the risk of side-reactions. During this work three papers appeared on conductance in antimony trichloride (at 99° mainly) by Jander and Swart; [3] these were more concerned with inorganic solutes, but confirm our work at several points, in particular for triphenylmethyl chloride.

EXPERIMENTAL

Materials.—" AnalaR " antimony trichloride was further purified by repeated distillation under reduced pressure in an atmosphere of dry, oxygen-free nitrogen. The final distillation into the conductivity cell was carried out over highly pure antimony (99·999%) to reduce any remaining antimony pentachloride to the trichloride. Qualitative tests, based on the intense colour given with triphenylamine with antimony pentachloride,[4] showed the latter to be absent from the purified antimony trichloride.

Diphenylmethyl, cinnamyl, benzyl, cyclohexyl, n-decyl, and bornyl chloride were commercial specimens, 1-ethylcyclohexyl chloride was prepared from cyclohexanone, and triphenylmethyl chloride from triphenylmethanol. Triphenylmethyl chloride and bornyl chloride were repeatedly recrystallised, and the latter finally sublimed at 30 mm. The liquid chlorides were, after preliminary drying, fractionated through a Widmer (spiral band) column until constant refractive index was obtained. The physical properties of the samples used were as tabulated. No attempt was made to separate isomers of cinnamyl chloride.

Chloride	B. p./mm.	n_D	Chloride	B. p./mm.	n_D
Triphenylmethyl ...	(113·5—115·5°) *	—	Benzyl	78°/21	1·5383/20·5°
Bornyl	(131°) *	—	Cyclohexyl	142°/760	1·4609/22·5°
Diphenylmethyl	107°/0·1	1·5950/22·5°	1-Ethylcyclohexyl...	83—86°/23	1·4620/22·5°
Cinnamyl	68—71°/0·5	1·5780/26°	n-Decyl	111—112°/19	1·4367/22·5°

* M. p.

Apparatus.—The conductivity-cell resistance was measured at 1000 c.p.s. by a conventional a.c. bridge with grounding system using audio null-point detection *via* an amplifier.

The conductivity cells were made of Pyrex glass with bright platinum electrodes and were of a conventional type modified for work with small volumes. Since antimony trichloride expands on freezing with force enough to break the glass electrode holders (cf. also Klemensiewicz *et al.*[2]), the cells were made in a λ-shape with both cylindrical arms slightly tapered. Solutions were made and cooled in the main arm; the side arm contained the electrodes; the solutions could be well mixed by pouring from arm to arm. The main arm carried a ground-on cell cap designed for simultaneous passage of dry nitrogen, while the solute entered through a smaller cap; the cell-cap could be kept warm to avoid condensation, and all joints were ground externally and lubricated by Teflon sleeves. Measurements were made in a paraffin thermostat bath at 75° in subdued light (some of the deeply coloured solutions appeared to be photosensitive); cell-constants were determined [5] by using potassium chloride solutions in de-ionised water at 25°.

Procedure.—About 25 c.c. of purified solvent were distilled under reduced pressure of dry nitrogen directly into the cell, a small fore-run being rejected. The entire still, when cool, was transferred to a dry-box where, in dry nitrogen, the cell was removed and closed with a ground-on cap. The liquid was then degassed by lowering the pressure, which reduced the specific conductance κ_0 to 4—6 × 10^{-6} ohm^{-1} cm.$^{-1}$; this increased only very slowly when the liquid was kept in the cell at 75°. After degassing, the amount of solvent was found by direct weighing;

[2] Klemensiewicz and Balówna, *Roczniki Chem.*, 1930, **10**, 481; 1931, **11**, 683.
[3] Jander and Swart, *Z. anorg. Chem.*, 1959, **299**, 252; **301**, 54, 80.
[4] Taylor and Baker, " Sidgwick's Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 63.
[5] Lind, Zwolenik, and Fuoss, *J. Amer. Chem. Soc.*, 1959, **81**, 1557.

the cell-cap was fitted in the dry-box, and the whole cell placed in the thermostat. Solutes were added to the cell at time intervals depending on the stability. Benzyl chloride appeared to be the least stable, so additions were made every 15 min.; other solutes were allowed periods up to hours. Solids were weighed in; liquids were added from a micrometer syringe calibrated for each liquid.

The lowest reported value for κ_0 is 0.85×10^{-6} at 99° in an early paper by Klemensiewicz.[6] Klemensiewicz and Balówna [2] combined repeated distillation with fractional freezing *in vacuo* and in general obtained for κ_0 " several units " of 10^{-6}. Jander and Swart,[3] by repeated distillation in dry carbon dioxide, usually obtained 8—12×10^{-6} at 99°, their lowest value being 6.7×10^{-6}.

RESULTS AND DISCUSSION

(1) *Introductory*; *Results for* 1-1 *Strong Electrolytes.*—Table 1 shows for each run the equivalent conductance Λ derived from the specific conductance κ at concentrations c of solute; no correction is yet made for the specific conductance κ_0 of the solvent sample. For benzyl chloride, where this correction is large, we quote κ itself.

Conductance results of the highest accuracy would require large quantities of solvent; but liquid antimony trichloride is difficult to purify, corrosive, hygroscopic, and poisonous, so large-scale work would involve major difficulties in design. We aimed therefore at a general small-scale survey of this new field of organic ionisations to an accuracy of about

TABLE 1. *Conductance results (uncorrected for κ_0) at 75°. (c throughout in millimoles/l.; Λ in usual units.)*

Triphenylmethyl chloride

Run 1. $\kappa_0 = 6.6 \times 10^{-6}$

c ...	2·21	4·16	5·36	8·83	12·4	14·4	20·0	23·5	29·8	41·3
Λ ...	85·5	84·1	83·4	82·0	81·0	80·2	79·1	78·6	77·7	75·9

Run 2. $\kappa_0 = 5.20 \times 10^{-6}$

c ...	3·12	7·95	12·1	16·5	22·9	30·3	38·5	44·7
Λ ...	85·5	83·5	82·8	81·8	80·8	79·5	78·4	77·5

Run 3. $\kappa_0 = 5.63 \times 10^{-6}$

c ...	1·45	3·86	7·20	12·5	17·7	22·8	29·4	36·5
Λ ...	85·9	82·5	80·8	78·9	77·2	76·3	75·0	73·0

Tetramethylammonium chloride

$\kappa_0 = 6.0 \times 10^{-6}$

c ...	1·56	7·02	10·1	13·9	19·3	26·7	32·9
Λ ...	94·7	90·8	89·1	88·2	87·1	85·8	84·8

Bornyl chloride

Run 1. $\kappa_0 = 5.47 \times 10^{-6}$

c ...	2·37	4·20	7·76	9·95	12·6	16·2	19·5	24·6	32·8	40·5
Λ ...	41·4	40·4	39·0	38·7	38·4	38·2	38·0	37·7	37·9	38·2

Run 2. $\kappa_0 = 4.27 \times 10^{-6}$

c ...	1·54	3·69	5·83	7·85	10·5	12·9	15·5	18·8	24·9	30·5
Λ ...	43·7	40·4	39·3	38·8	38·0	37·6	37·9	37·3	38·1	38·7

n-Decyl chloride

Run 1. $\kappa_0 = 5.54 \times 10^{-6}$

c ...	1·58	3·13	4·69	6·27
Λ ...	37·4	36·2	35·7	35·0

1-Ethylcyclohexyl chloride

Run 1. $\kappa_0 = 4.46 \times 10^{-6}$

c ...	0·82	1·62	3·55	5·35	7·24	9·23	11·2	13·2	16·2	19·3	22·2	26·3
Λ ...	33·2	31·2	28·4	26·5	26·0	25·3	24·9	24·7	24·5	24·3	24·2	24·3

Run 2. $\kappa_0 = 4.06 \times 10^{-6}$

c ...	0·77	1·59	2·40	3·95	5·66	7·37	9·09	10·8	13·4	16·0	18·6	22·2
Λ ...	35·5	31·1	29·5	28·2	26·5	25·6	25·4	24·8	24·4	23·6	23·7	23·2

[6] Klemensiewicz, *Z. phys. Chem.*, 1924, **113**, 28.

TABLE. 1. (*Continued.*)

Cyclohexyl chloride

Run 1. $\kappa_0 = 5.29 \times 10^{-6}$

c	3·65	6·22	8·86	11·5	14·0	16·6	20·6	24·6	30·0
Λ	18·7	18·6	18·5	18·4	18·6	18·6	18·8	19·0	18·8

Run 2. $\kappa_0 = 5.70 \times 10^{-6}$

c	2·12	4·44	6·72	9·06	11·5	13·8	16·3	19·9
Λ	21·80	19·5	18·8	18·5	18·1	18·0	17·8	17·8

Run 3. $\kappa_0 = 5.52 \times 10^{-6}$

c	2·32	4·70	7·02	9·36	11·8	14·1	16·5	20·1
Λ	19·8	19·1	18·9	18·8	18·8	18·9	19·1	19·2

Run 4. $\kappa_0 = 5.33 \times 10^{-6}$

c	1·09	2·34	4·96	7·57	10·24	12·9	15·5	18·1	22·1
Λ	24·8	21·0	19·6	18·8	18·7	18·7	18·7	18·8	19·0

Diphenylmethyl chloride

Run 1. $\kappa_0 = 5.66 \times 10^{-6}$

c	1·85	3·77	5·71	9·50	13·4	17·1	20·8	25·7	31·5
Λ	19·5	17·6	17·0	16·6	16·1	16·1	16·1	16·2	16·4

Run 2. $\kappa_0 = 4.23 \times 10^{-6}$

c	1·00	4·18	7·28	13·0	18·6	24·4	31·3
Λ	22·6	18·4	15·9	15·8	16·5	16·9	17·2

Run 3. $\kappa_0 = 6.66 \times 10^{-6}$

c	1·75	3·57	5·33	8·16	11·9	15·7	19·5
Λ	19·8	17·7	17·1	16·4	16·1	15·7	15·5

Cinnamyl chloride

Run 1. $\kappa_0 = 4.14 \times 10^{-6}$

c	0·77	1·79	3·87	7·01
Λ	16·8	12·4	9·97	8·78

Run 2. $\kappa_0 = 5.35 \times 10^{-6}$

c	1·32	3·22	6·33	9·48	13·54	17·8	22·6	26·3
Λ	12·8	10·2	8·73	8·18	7·93	7·87	7·89	8·18

Run 3. $\kappa_0 = 5.29 \times 10^{-6}$

c	2·06	4·45	7·41	11·4	16·9	22·5	29·2
Λ	12·40	9·88	8·43	7·87	7·72	8·00	8·42

Benzyl chloride (c and κ, the specific conductance)

Run 1. $\kappa_0 = 6.17_3 \times 10^{-6}$

c	2·61	6·33	10·7	15·4	19·8	24·5	29·1	35·3	44·7
$\kappa\ (\times 10^{-6})$	6·96	8·45	10·1	12·3	14·6	17·4	20·6	26·0	47·6

Run 2. $\kappa_0 = 5.19_5 \times 10^{-6}$

c	4·16	10·6	17·2	24·1	31·2	39·7
$\kappa\ (\times 10^{-6})$	6·50	9·02	12·0	16·7	27·6	41·4

Run 3. $\kappa_0 = 4.67_2 \times 10^{-6}$

c	6·81	12·4	18·4	24·3	30·1	36·0	41·8
$\kappa\ (\times 10^{-6})$	8·24	10·5	13·20	16·5	21·4	30·6	42·9

1%; this was almost, but not quite achieved. Even so the interpretation of the results demands the consistent application of ionic-atmosphere (Debye–Hückel) theory, for our results extend up to ionic strengths ($\sim$0·03N) where interionic-force corrections to conductance and to activity amount to tens rather than units %.

Two of the solutes chosen, triphenylmethyl chloride and tetramethylammonium chloride, are typical 1-1 strong electrolytes at 75°. In Fig. 1 we plot Λ against $\sqrt{c}$ for these; Λ approaches Λ_0 with the theoretical Debye–Hückel–Onsager slope X given by

$$X = (0.661\Lambda_0 + 29.74) \qquad \qquad (1)$$

where

$$\Lambda = \Lambda_0 - X\sqrt{c} \qquad \qquad (2)$$

(In calculating X the viscosity coefficient [6] η is taken as 0·0258 c.g.s. unit and the dielectric constant [7] as 33·2.) For more concentrated solutions the results agree with the theoretical first approximation of Falkenhagen, Leist, and Kelbg,[8] *viz.,*

$$\Lambda = \Lambda_0 - X\sqrt{c}/(1 + Y\sqrt{c}) \quad \ldots \quad \ldots \quad (3)$$

the curves drawn in Figs. 1 and 2, the values for Λ_0 (89·4, 96·9) and Y (1·95, 2·4) for triphenylmethyl and tetramethylammonium chloride, respectively, being obtained by successive approximation using the theoretical value for X. While this work was in progress Jander and Swart [3] showed, for more concentrated solutions at 99°, that Λ for triphenylmethyl chloride was only a few units % lower than for potassium, ammonium, or tetramethylammonium chloride; as shown in Part I, the freezing-point data for tetramethylammonium, triphenylmethyl, cæsium, and potassium chloride, and the conductance

Fig. 1. *Plot of equivalent conductance against (concentration)[1] for triphenylmethyl chloride.*

Fig. 2. *Plot of equivalent conductance against (concentration)[1] for tetramethylammonium chloride.*
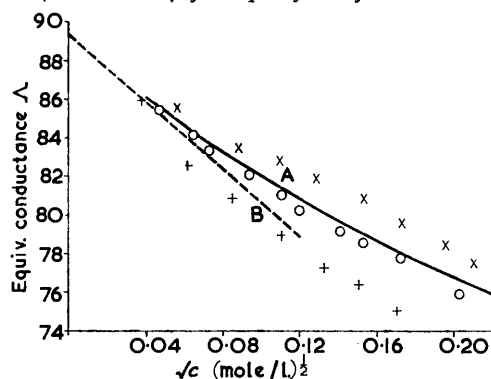
A, line represents eqn. (3). B, *line represents Debye-Hückel–Onsager equation.* O, ×, + *runs* 1, 2, 3.
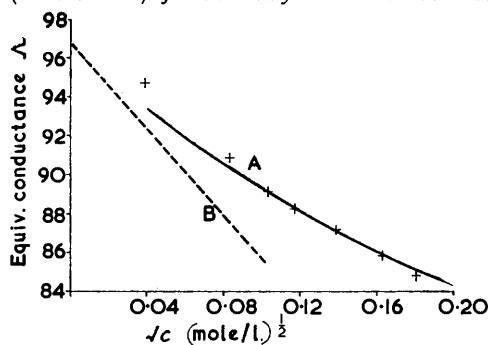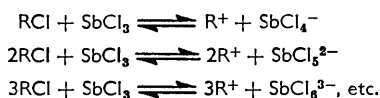
A, B as in Fig. 1.

data of Klemensiewicz and Balówna [2] for potassium, ammonium, rubidium, and thallium chloride at 99° all agree well with the expectations for 1-1 strong electrolytes.

This mass of data shows, therefore, (*a*) that there are 1-1 strong electrolytes in this solvent, and (*b*) that triphenylmethyl chloride is one of them; and it proves the mode of ionisation of the chlorine. In principle RCl could ionise:

$$RCl + SbCl_3 \rightleftharpoons R^+ + SbCl_4^-$$

$$2RCl + SbCl_3 \rightleftharpoons 2R^+ + SbCl_5^{2-}$$

$$3RCl + SbCl_3 \rightleftharpoons 3R^+ + SbCl_6^{3-}, \text{ etc.}$$

and solid addition compounds between alkali chlorides and antimony trichloride are known corresponding to these complex modes. But they are incompatible with either the freezing-point or the conductance data in solution; even the second scheme would imply a limiting van't Hoff factor i of 1·5, and a limiting Onsager slope about three times greater than for a 1-1 electrolyte.

Finally, the results for tetramethylammonium chloride confirm the abnormal mobility of the Cl⁻ (SbCl₄⁻) ion in SbCl₃; Cl⁻ is also abnormally mobile in arsenic trichloride.[9] This point is so important to the further discussion that we repeat here the evidence:

(*a*) the transport number of Cl⁻ in potassium and ammonium chloride solutions at 99°

[7] Schlundt, *J. Phys. Chem.,* 1901, **5,** 503.
[8] Falkenhagen, Leist, and Kelbg, *Ann. Physik,* 1952, **11,** 51.
[9] Gutmann, *Svensk Kem. Tidskr.,* 1956, **68,** 1.

was directly measured at about 0·9 by Frycz and Tolloczko,[10] using Hittorf's method, and in general a high value is suggested by the small variation in Λ from chloride to chloride.[2]

(*b*) Jander and Swart[3] have shown that a conductivity titration curve like that of a strong acid–strong base reaction in water is obtained if triphenylmethyl or potassium chloride in antimony trichloride is titrated with antimony pentachloride at 80°. The explanation is that the reaction is:

$$SbCl_4^- + SbCl_5 \longrightarrow SbCl_3 + SbCl_6^-$$
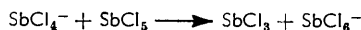
with $SbCl_4^-$ abnormally mobile and $SbCl_6^-$ not. If $SbCl_6^-$ and the cations are about equally mobile, these data imply a transport number 0·86 for Cl^- in triphenylmethyl chloride.

(*c*) Thirdly, our own result for tetramethylammonium chloride confirms these conclusions. For a large number of non-hydroxylic solvents and at many temperatures the Walden product $\lambda_0\eta$ of NMe_4^+ is about 0·3$_4$ (Landolt–Börnstein's tables), the highest recorded value being about 0·45; for these two cases the mobility of NMe_4^+ in antimony trichloride at 75° must be 13 or 18 and the transport number of Cl^- $(97 - 13)/97 = 0·87$ or $(97 - 18)/97 = 0·82$. Since Λ_0 for triphenylmethyl chloride is rather less than for tetramethylammonium chloride, both at 75° and 99°, the transport number for Cl^- in this electrolyte must be yet higher.
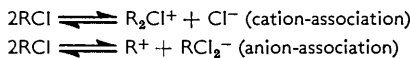
We consider therefore as proved that the Cl^- exists in these solutions as the singly charged species (presumably $SbCl_4^-$) which is abnormally mobile, the transport number in $CPh_3^+Cl^-$ at 75° being about 0·85—0·90. These points will be needed for the later discussion.

(2) *A New Mode of Ionisation.*—The results for the other halides cannot be so simply explained; for Table 1 shows as a general phenomenon that, as the concentration c increases, Λ first falls, then reaches a constant value $\Lambda_{min.}$, and then increases very slightly. Moreover, $\Lambda_{min.}$ varies greatly from case to case, being about 38, 35, 24, 18, 16, 8 for bornyl to cinnamyl chloride in the order of Table 1, and for benzyl chloride about 0·6. Such low values of Λ, varying so much from case to case, can only be due to incomplete ionisation. But incomplete ionisation in the obvious simple mode $RCl \rightleftharpoons R^+ + Cl^-$ would imply that Λ should fall greatly as c increases; this consequence is completely contradicted by the facts. To take but one example: for diphenylmethyl chloride $\Lambda \simeq 19$ at $2 \times 10^{-3}N$; Ostwald's dilution law would predict $\Lambda \simeq 5$ at $30 \times 10^{-3}N$, where in fact $\Lambda \simeq 16$.

Table 1 shows this to be a general phenomenon and it can easily be shown that no reasonable assumption about interionic-force effects could remove so gross a discrepancy.

We must therefore explain how an apparent degree of ionisation, much less than unity and varying from case to case, can yet be almost independent of concentration. The law of mass action, neglecting interionic-force effects, can explain this if, and only if, x covalent solute molecules give an equal number x of ions with the paradoxical consequence that such an electrolyte might be almost completely ionised yet give a normal freezing-point depression; this consequence is supported by some freezing-point data by Dr. G. B. Porter.[11]

There are, of course, various ways in which this could happen. The simplest are the pair–pair ionisations

$$2RCl \rightleftharpoons R_2Cl^+ + Cl^- \text{ (cation-association)}$$

$$2RCl \rightleftharpoons R^+ + RCl_2^- \text{ (anion-association)}$$

If, of course, both these processes occur at once

$$3RCl \rightleftharpoons R_2Cl^+ + RCl_2^- \text{ (bilateral association)}$$

then Λ should increase with increasing c. The small observed increase at higher values of c will be quantitatively explained as an interionic-force effect, so that one or other of the

[10] Frycz and Tolloczko, *Festschrift Univ. Lwów*, 1912, **1**, 1; *Chem. Zentr.*, 1913, I, 91.

[11] Porter, unpublished work in these laboratories.

pair–pair ionisations should be involved. A choice in favour of the first can be made for two reasons: (*a*) *General chemical reasons* (see below). (*b*) *Mobility*. We have shown that Cl^- ($SbCl_4^-$) is abnormally mobile in antimony trichloride. In general, if a foreign molecule has a greater affinity for an abnormally mobile solvent-ion than has the solvent itself, the new complex ion is not abnormally mobile; thus $SbCl_6^-$ and $AlCl_4^-$ are not abnormally mobile [3] in antimony trichloride; nor is OH_3^+ abnormally mobile in methanol or ethanol,[12] nor is NH_4^+ in water. If, therefore, RCl has a greater affinity for Cl^- than has antimony trichloride, the ion RCl_2^- should not be abnormally mobile; if it has not, the ion should not exist significantly, since the trichloride is in enormous excess.

(3) *Strong Electrolytes in this New Mode*: *Bornyl Chloride, Decyl Chloride.*—Now for some of these electrolytes Λ is about half that of the 1-1 electrolytes containing the abnormally mobile Cl^- ion. The explanation is that there are about half as many Cl^- ions (cation-association); alternatively, we would have to suppose a new anion also abnormally mobile but not so much. This is improbable.

TABLE 2. *Comparison of Λ_B for bornyl chloride at concentrations c_B (mmoles/l.)*
with Λ^* for triphenylmethyl chloride.

Run 1.

C_B	2·37	4·20	7·76	9·95	12·63	16·21	19·54	24·59	31·81	40·53
Λ_B	41·4	40·4	39·1	38·7	38·4	38·2	38·0	37·7	37·9	38·2
Λ_B/Λ_0^*	0·463	0·452	0·457	0·434	0·430	0·427	0·425	0·422	0·424	0·427
Λ_B/Λ_C^*	0·479	0·472	0·462	0·461	0·461	0·461	0·462	0·463	0·464	0·472

Run 2.

C_B	1·54	3·69	5·83	7·85	10·52	12·85	15·53	18·82	24·95	30·47
Λ_B	43·7	40·4	39·3	38·8	38·0	37·6	37·9	37·3	38·1	38·7
Λ_B/Λ_0^*	0·489	0·452	0·440	0·434	0·425	0·421	0·424	0·417	0·426	0·433
Λ_B/Λ_C^*	0·502	0·482	0·462	0·459	0·454	0·451	0·457	0·454	0·469	0·480

Considering therefore the cation-association mode, a strong electrolyte in this mode would give exactly half as many chlorine ions as a strong electrolyte such as triphenylmethyl chloride which ionises in the simple mode. As the mobility of the cation is of minor importance, a strong electrolyte in the cation-association mode should give a $\Lambda \approx \frac{1}{2}\Lambda^*$ over the whole concentration range, where Λ^* is the value of Λ for a strong electrolyte in the simple mode (of which we take triphenylmethyl chloride as an example). This simple consequence may easily be compared with fact. Let us consider bornyl chloride, for which Λ is the highest. In Table 2 we show the values of Λ_B, its equivalent conductance at concentration c_B, divided by Λ_0^* for triphenylmethyl chloride (89·4; equation 3). This ratio is rather less than $\frac{1}{2}$ and drifts by only about 10% over a thirty-fold variation in c_B. If, however, this interpretation be correct, the agreement with experiment should be improved if account is taken of interionic-force effects; this can be done approximately by replacing Λ_0^* by Λ_0^*, the value of Λ^* for triphenylmethyl chloride at a concentration one-half of C_B (equation 3). The values of this new ratio are given in the last line of Table 2.

The drift is now almost completely removed except for the most dilute points (where the solvent correction is appreciable), and the mean value

$$\Lambda_B/\Lambda_0^* = 0.467 \pm 0.006 \text{ (median error)} \quad \quad \quad \quad (4)$$

is in excellent agreement with the predictions for complete cation-association ionisation: (*a*) Λ_B/Λ_0^* independent of concentration, (*b*) $\Lambda_B/\Lambda_0^* \approx \frac{1}{2}$. This ratio should not be exactly $\frac{1}{2}$ unless the two cation mobilities were exactly equal; it should not be much different as they are small compared with the anion mobilities; it should even be rather less than $\frac{1}{2}$ as (dibornyl chloride)$^+$ is bigger and presumably slower than (triphenylmethyl)$^+$.

Similarly for the four (Λ_D) points for n-decyl chloride, Λ_D/Λ_0^* is 0·431, 0·420, 0·417,

[12] Goldschmidt and Dahll, *Z. phys. Chem.*, 1924, **108**, 121; 1924, **114**, 1; Murray-Rust and Hartley, *Proc. Roy. Soc.*, 1929, *A*, **126**, 84.

0·413; this solute also must be almost, but perhaps not quite, completely ionised in the cation-association mode. We would emphasise the statistical fact that there exist two clusters of Λ values: (a) at 70—90 for triphenylmethyl, tetramethylammonium, and the alkali chlorides;[6] (b) at 15—40 for bornyl, decyl, the two cyclohexyl, and diphenylmethyl chlorides, with (c) none in between. This is naturally explained if the limiting Λs in these two clusters represent strong electrolytes in different modes.

(4) *Incomplete Ionisation in This Mode* (*Other Chlorides except Benzyl*).—The other solutes show, above a certain concentration, Λ roughly constant which would be expected from incomplete ionisation in the mode $2RCl \rightleftharpoons R_2Cl^+ + Cl^-$. The first approximation is to suppose that this is the only ionisation involved, whence $(R_2Cl^+) = (Cl^-)$, and to

FIG. 3. *Plot of* $\log(\gamma/1 - 2\gamma)$ *against* (*concentration*)$^{\frac{1}{2}}$.
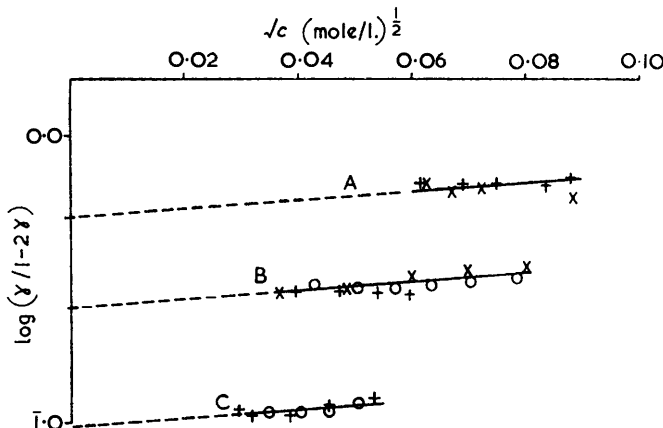
A, 1-*Ethylcyclohexyl*; B, *diphenylmethyl*; C, *cinnamyl*.

obtain (Cl^-) from the observed Λ and that, Λ^*, of the standard electrolyte triphenylmethyl chloride. Let c be the concentration of the chloride considered, and let γc be that of the chlorine anion; then

$$(R_2Cl^+)(Cl^-)/(RCl)^2 = K_0 = \gamma^2/(1 - 2\gamma)^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Identifying the supposedly constant value of γ with $\Lambda_{min.}/\Lambda_0^*$ where $\Lambda_{min.}$ is the value at the shallow minimum in the Λ–c curve, we obtain the following first approximations for K_0: 1-ethylcyclohexyl chloride $0·3_4$, cyclohexyl chloride $0·1_2$, diphenylmethyl chloride $0·07_8$, cinnamyl chloride $0·01_1$.

In this treatment, where the effects of interionic forces are neglected, it is predicted that Λ should be exactly constant; in fact it is only roughly so. For weak electrolytes, Debye–Hückel theory should come in, first, in the effect of ionic strength on mobility, tending to reduce Λ with increasing c (as with bornyl chloride) and, secondly, in the effect on activity coefficients, tending to increase Λ; the second is the larger effect. These corrections are made as follows:

Let the observed value Λ_c of Λ at a given total solute concentration c correspond to an ionic concentration c_i. Let Λ_i^* be the Λ^* for the standard electrolyte triphenylmethyl chloride at the same ionic concentration c_i^*. Since this chloride is a strong electrolyte, for this, $c_i^* = c^*$. We take $\gamma = \Lambda_c/\Lambda_i^*$; Λ_i^* can easily be obtained graphically by successive approximation. Considering the ionic activity coefficients f we have

$$\gamma^2 f^2/(1 - 2\gamma)^2 = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

from the Debye-Hückel limiting law

$$\log_{10} f = -1·46\sqrt{c_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence $\qquad \log_{10}[\gamma/(1 - 2\gamma)] = \frac{1}{2}\log_{10} K + 1·46\sqrt{c_i} \quad . \quad . \quad . \quad . \quad . \quad (8)$

In Fig. 3 we plot for the more concentrated points $\log_{10} [\gamma/(1 - 2\gamma)]$ against $\sqrt{c_i}$, the lines drawn having the theoretical slope. As the points lie fairly well about the theoretical lines, the small rises in Λ in the concentrated solutions have been explained. The values of K so obtained are: 1-ethylcyclohexyl chloride 0·27, cyclohexyl chloride 0·10, diphenyl-methyl chloride 0·063, cinnamyl chloride 0·0093 (10—20% corrections on K_0).

The single assumption therefore of a new mode of ionisation $2RCl \rightleftharpoons R_2Cl^+ + Cl^-$ predicts roughly constant values of Λ with an upper limit $\sim\frac{1}{2}\Lambda^*$ to which bornyl and decyl chloride are a good approximation. The same hypothesis, when refined by the Debye–Hückel corrections, explains quantitatively the small decrease of Λ with concentration for bornyl chloride, and the small rise in Λ in the stronger solutions of the weaker electrolytes. Evidently, however, it cannot explain the initial fall in Λ to its minimum value $\Lambda_{min.}$; in dilute solutions of the weaker electrolytes Λ is too high by about 50%.

FIG. 4. *Plot of concentration against conductivities for benzyl chloride.*
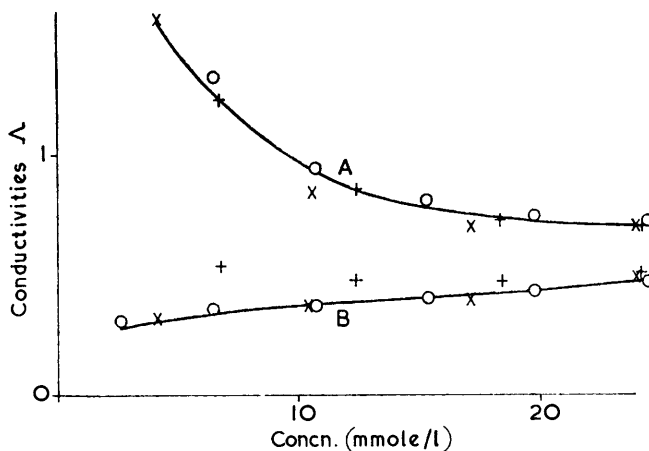
A, $\Lambda_{uncorr.}$. B, $\Lambda_{sub.}$. At $c = 2·6$, $\Lambda_{uncorr.} = 2·68$.

(5) *Effects of Solvent Conductance and of Simple Ionisation (Benzyl Chloride).*—In dilute solutions the self-conductance of the solvent must certainly be of importance, and possibly also the simple mode $RCl \rightleftharpoons R^+ + Cl^-$, which is the principal mode for triphenylmethyl chloride. The results for benzyl chloride provide a convenient case; the degree of ionisation is small ($\sim$1%); hence ionic-strength effects can be neglected and concentration (RCl) of un-ionised chloride equated to c the stoicheiometric concentration, and the self-conductance κ_0 is a major effect (for the four most dilute points $\kappa_0/\kappa = 89$, 80, 75, and 57%, respectively).

The mathematically simplest ways to allow for the solvent conductance are to make no correction at all or to subtract κ_0 from κ in full, thus obtaining two extremes $\Lambda_{uncorr.}$ and $\Lambda_{sub.}$. These are plotted against c in Fig. 4; $\Lambda_{uncorr.}$ falls from about 2·5 to 0·7 whilè $\Lambda_{sub.}$ rises from 0·3 to 0·5, the two estimates approaching a roughly constant value of about 0·55, corresponding to $3·8 \times 10^{-5}$ for the equilibrium constant K_0.

It appears that the full correction is too large for the dilute solutions. To improve it demands an understanding of the cause [13] of κ_0. Simple subtraction implies that the ionisations of the solvent and solute produce no common ion; this seems unlikely here. The facts detailed in the Experimental section suggest strongly that the conductance of antimony trichloride is in fact principally due to impurities (cf. Klemensiewicz and Balówna [2]), some volatile ($AsCl_3$?, an ammonium salt?), and some increasing rapidly at 99° but slowly at 75° and so probably impurity from the glass. These would both probably

[13] Wynne-Jones, *J. Phys. Chem.*, 1927, **31**, 1647.

produce the Cl^- ($SbCl_4^-$) anion, so the most likely hypothesis is that the self-conductance is principally—we assume entirely—due to strong-electrolyte impurities with the Cl^- anion.

This view implies that the self-conductance κ_0 immediately gives the concentration of impurity cation P^+, roughly constant throughout a run.   The conductance κ of the solution at concentration c gives directly the total (Cl^-), as the cation is of minor importance. It can be shown (see Appendix) that in this limiting case

$$[(Cl^-) - (P^+)] (Cl^-)/c = K' + Kc \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where K' and K are the equilibrium constants

$$(R^+)(Cl^-)f^2/(RCl) = K' \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$(R_2Cl^+)(Cl^-)f^2/(RCl)^2 = K \text{ (as before)} \quad . \quad . \quad . \text{ (equiv. to 6)}$$

Fig. 5 shows $[(Cl^-) - (P^+)](Cl^-)/c$ plotted against c for benzyl chloride; the points fall round a straight line giving $K = 3.7 \times 10^{-5}$, $K' \approx 1 \times 10^{-7}$ (the latter uncertain to about

FIG. 5.   *Plot of* $[(Cl^-) - (P^+)](Cl^-)/c$ *against concentration for benzyl chloride.*
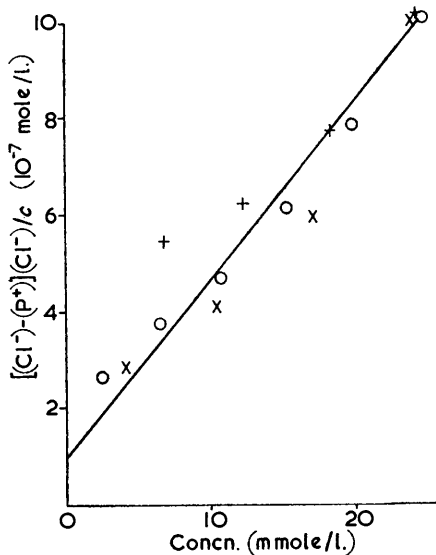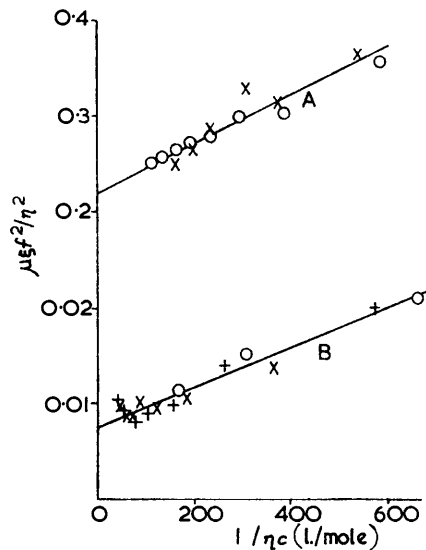
FIG. 6.   *Plot of* $\mu\xi f^2/\eta^2$ *against* $1/\eta c$ *for* (A) 1-*ethylcyclohexyl and* (B) *cinnamyl chloride.*

$\pm 50\%$).   The value of K thus obtained for the whole range agrees with the previous limiting value (Fig. 4), and the non-zero intercept suggests that the simple mode of ionisation is just about detectable.   Essentially the same value of K' is obtained if one assumes the whole of κ_0 to be due to the equilibrium $2SbCl_3 \rightleftharpoons SbCl_2^+ + SbCl_4^-$, but a considerably smaller value if one simply subtracts the solvent correction (*i.e.*, supposes that the anion responsible for κ_0 is not $SbCl_4^-$).

(6) *General Equation.*—Having thus analysed the conductance–composition curve in terms of a complex (R_2Cl^+, Cl^-) and a simple mode (R^+, Cl^-) of ionisation and the effect of strong-electrolyte impurity, it is possible to work out the consequences of these ideas in the general case where interionic-force effects matter and where the degree of ionisation is not small.   This requires no new arguments and is given in an Appendix (cf. Wooster [14]).   In Fig. 6 we show for the two extreme cases of 1-ethylcyclohexyl and cinnamyl chloride the graph of $\mu\xi f^2/\eta^2$ against $1/\eta c$; good straight lines are obtained.

(7) This analysis gives therefore the values of the two dissociation constants K' and K

[14] Wooster, *J. Amer. Chem. Soc.*, 1938, **60**, 1609.

which are shown in Table 3. The errors quoted are random errors; systematic errors of 10% or so may arise through approximations in the treatment, but should affect all solutes alike.

TABLE 3.

Chloride	K	K'
Triphenylmethyl	—	S.E. (>0·2) *
Bornyl (n-decyl)	S.E.	—
1-Ethylcyclohexyl	$2·2 \pm 0·1 \times 10^{-1}$	$2·5 \pm 0·6 \times 10^{-4}$
Cyclohexyl	$9·7 \pm 0·2 \times 10^{-2}$	$4·1 \pm 1·2 \times 10^{-4}$
Triphenylmethyl	$5·8 \pm 0·3 \times 10^{-2}$	$2·6 \pm 1·5 \times 10^{-5}$
Cinnamyl	$7·5 \pm 0·5 \times 10^{-3}$	$2·1 \pm 0·8 \times 10^{-5}$
Benzyl	$3·7 \pm 0·4 \times 10^{-5}$	$1·0 \pm 0·5 \times 10^{-7}$

S.E. = Strong electrolyte.
* The estimate for K' for CPh_3Cl is based on the assumption that 10% of undissociated CPh_3Cl would be just detectable.

(8) In Fig. 7 the rather uncertain values of log K' are plotted against log K. As can be seen, they lie around a straight line of slope unity, whence

$$\log_{10} (K/K') = +2·95 \pm 0·40 \quad \ldots \ldots \ldots (11)$$

The ratio of these two equilibrium constants is, evidently, the equilibrium constant χ given by

$$\chi = (R_2Cl^+)/(RCl)(Cl^-) \quad \ldots \ldots \ldots \ldots (12)$$

This process has, therefore, a standard free energy $\Delta G° = -4·57T \times 2·95 = -4·7 \pm 0·6$ kcal./mole, which is, roughly, independent of the solute. We can thus immediately
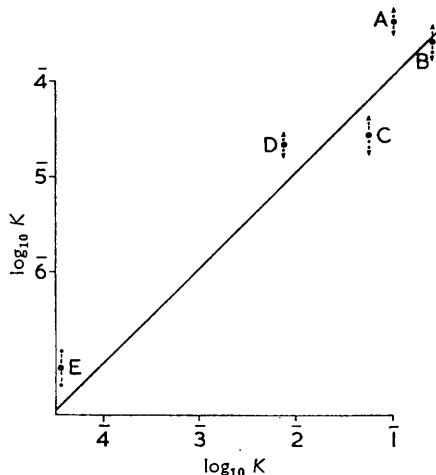

FIG. 7. *Plot of* $\log_{10} K'$ *against* $\log_{10} K$.

A, *Cyclohexyl*; B, *ethylcyclohexyl*; C, *diphenylmethyl*; D, *cinnamyl*; E, *benzyl*.

explain why the complex mode is undetectable for triphenylmethyl chloride; for (Appendix, eqn. A10) the ratio of (R^+) to (R_2Cl^+) is inversely as the proportion of un-ionised RCl which for this solute is very small. It is probable that this effect is enhanced by peculiar repulsion effects.[15]

(9) *Conclusion.*—The results obtained agree to within the limits of their experimental error with the hypothesis of complex and simple ionisation; simple ionisation alone could not represent them to within a factor of 2; and they cannot be explained as due to the obvious side reactions—olefin formation, condensation—since these give hydrogen chloride which in this solvent is effectively a non-conductor.[16]

It is therefore almost certain that carbonium-ion formation has been observed; and such equilibrium ionisations, though not for simple aliphatic systems, have already been

[15] Baughan, *Discuss. Faraday Soc.*, 1947, **2**, 70.
[16] Klemensiewicz and Zebrówska, *Roczniki Chem.*, 1934, **14**, 14.

measured in hydrofluoric [17] and in sulphuric acid.[18] These facts, however, were predictable. For Baughan, Evans, and Polanyi [19] showed that the activation energy of carbonium ionisations (S_N1 reactions in Ingold's terminology [20]) should be for simple cases about equal to the endothermicity of the reaction, and enough is now known about such activation energies, particularly from the work of Ingold, Hughes, and their co-workers,[20] to make it clear that an extra solvation energy of only a few kcal. should make equilibrium ionisation detectable. In theory, antimony trichloride should be a peculiarly favourable solvent, since the dielectric constant is high and the affinity $Cl^- + SbCl_3 \longrightarrow SbCl_4^-$ considerable; in fact, it is peculiarly favourable since triphenylmethyl chloride is a strong electrolyte while even in sulphur dioxide its dissociation constant [21] to R^+ and Cl^- is $10^{-4.4}$ (at $0°$). And these same energetic calculations [19] predict the absence of olefin-formation; for the proton affinity of an olefin is very large (152 kcal./mole for ethylene [22]) so that reactions such as $C_2H_5 + Y \longrightarrow YH^+ + CH_2{:}CH_2$ will not happen unless Y also has a high proton affinity (that of water is 182 kcal./mole; [23] that of alcohols about the same) and there is no reason to suppose this for antimony trichloride.

The discovery of equilibrium carbonium ionisations in this solvent was in effect the verification of order-of-magnitude predictions already made. The strange feature is that the ionisation by the simple mode is so enhanced by the reaction

$$R^+ + RCl \longrightarrow R_2Cl^+ (\Delta G° \approx -5 \text{ kcal./mole});$$
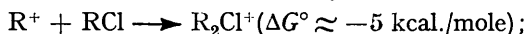
of this various explanations are possible: (*a*) As the charge-bearing radius of the simple carbonium ion is effectively very small since the ion is planar, the association may be a simple ion-dipole effect. (*b*) The carbonium ion is an electron-deficient structure like BH_3 and evidence has been accumulating [24,25] to suggest addition reactions from this cause. (*c*) The ion R_2Cl^+ might be analogous to the diaryliodonium ions. The distinction between these, and other, views might be solved by infrared measurements for which antimony trichloride is very suitable,[26] or in other ways.

One might perhaps expect the equilibrium constants obtained to correlate with the known rates of S_N1 reactions.[20,27] The order benzyl < diphenylmethyl < tertiary aliphatic ≪ triphenylmethyl is what might be expected; the high ionisations of the primary and secondary aliphatic chlorides are, however, surprising. But activation energies measure the maximum energy in the reaction path, and any rearrangement of bonds in, or solvent around, the ion would make this differ from the endothermicity; even for covalent bond-fission the activation energy of the dissociation of hexaphenylethane in solution is about 7 kcal./mole more than the endothermicity. The short-chain primary aliphatic halides, whose difference in reactivity has been so instructive,[20] are inconveniently volatile for our solvent; in any case, their differences will probably be " levelled " off in Hantzsch's sense by their being strong electrolytes.

We conclude by emphasising the main result of this work. We have, following an approximate theory, obtained simple carbonium ions in bulk where their equilibrium properties can be studied; previous knowledge of these interesting species has depended on indirect inferences from reaction kinetics.

[17] Kilpatrick and Luborsky, *J. Amer. Chem. Soc.*, 1953, **75**, 577.
[18] Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.
[19] Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377.
[20] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953.
[21] Pocker, *Proc. Chem. Soc.*, 1959, 386.
[22] Calculations as by Baughan, Evans, and Polanyi (ref. 19), but with the ionization potential of C_2H_5 taken as 200 kcal./mole (Stevenson, *Trans. Faraday Soc.*, 1953, **49**, 867).
[23] Sherman, *Chem. Rev.*, 1932, **11**, 93.
[24] Dewar, *Ann. Reports*, 1951, **48**, 122.
[25] Pauling, " The Nature of the Chemical Bond," Oxford Univ. Press, 1960, p. 383.
[26] Lacher, Croy, Kianpour, and Park, *J. Chem. Phys.*, 1954, **58**, 206.
[27] Streitwieser, *Chem. Rev.*, 1956, **56**, 571.

Appendix: Solution of the general problem.

(*a*) The first stage is to obtain for each point the chloride-ion concentration (Cl^-) from graphical solution of equation (3) and from this the activity coefficient f from equation (7). Equally the chloride-ion concentration in the pure solvent is obtained and put equal to (P^+), the concentration of impurity cation.

(*b*) The following relations hold between the concentrations:

$$(Cl^-) = (P^+) + (R_2Cl^+) + (R^+) \text{ (electrical neutrality)} \quad . \quad . \quad . \quad (A1)$$

$$c = (RCl) + (R^+) + 2(R_2Cl^+) \text{ (stoicheiometry of RCl)} \quad . \quad . \quad (A2)$$

where c is the total concentration of RCl solute; and we have the two equations of thermodynamic equilibrium:

$$(R_2Cl^+)(Cl^-)f^2/(RCl)^2 = K \quad . \quad . \quad . \quad . \quad . \quad . \quad (A3)$$

$$(R^+)(Cl^-)f^2/(RCl) = K' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A4)$$

(*c*) It is throughout assumed that Λ gives (Cl^-) directly, since the cation mobilities are small; it is therefore convenient to express our quantities in terms of (Cl^-), thus:

$$(Cl^-) - (P^+) = (R_2Cl^+) + (R^+) = K(RCl)^2/(Cl^-)f^2 + K'(RCl)/(Cl^-)f^2$$

or

$$[(Cl^-) - (P^+)](Cl^-)f^2 = K(RCl)^2 + K'(RCl) \quad . \quad . \quad . \quad . \quad (A5)$$

the fundamental equation.

(*d*) For benzyl chloride, which is very slightly ionised, $(RCl) \approx c$, $f \approx 1$, whence (A5) becomes

$$[(Cl^-) - (P^+)](Cl^-)/c = K' + Kc \quad . \quad . \quad . \quad . \quad . \quad (A6)$$

This is equation (9) in this paper (Fig. 5).

(*e*) The more general case can be successively approximated as follows:
Define dimensionless ratios:

$$\left.\begin{array}{l} (Cl^-)/c \equiv \xi; \; [(Cl^-) - (P^+)]/c \equiv \mu; \text{ these are easily evaluated} \\ (R^+)/c \equiv \alpha; \; (R_2Cl^+)/c \equiv \gamma; \; (RCl)/c \equiv \eta \\ (R^+)/(R_2Cl^+) = \alpha/\gamma \equiv \psi \end{array}\right\} \quad . \quad . \quad (A7)$$

(A5) now becomes

$$\mu\xi f^2/\eta^2 = K'/\eta c + K \text{ (cf. Fig. 6)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (A8)$$

and

$$\eta = 1 - \mu(\psi + 2)/(\psi + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (A9)$$

Evidently at $\psi = 0$ (no R^+), $\eta = 1 - 2\mu$, and at $\psi = \infty$ (no R_2Cl^+) $\eta = 1 - \mu$. As most of the organic cation in the stronger solutions appears to be (R_2Cl^+), and as μ in the extreme is only about 0·3, η is not very sensitive to ψ. We obtain therefore first approximations K' and K_1 by (A8) with $\eta = (1 - 2\mu)$. This can then be refined as follows:
From (A3) and (A4)

$$\eta = K'/Kc\psi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A10)$$

whence from (A9)

$$K'/Kc = \psi [1 - \mu(\psi + 2)/(\psi + 1)] \quad . \quad . \quad . \quad . \quad . \quad (A11)$$

This quadratic in ψ can be solved for each point by using the first approximation for K_1'/K_1, thus obtaining η for each point. (A8) can then be replotted by using these new values of η and K_2', K_2 obtained, and the whole, if necessary, repeated. Three approximations were needed for 1-ethylcyclohexyl chloride, two for the other solutes (see Fig. 6).

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