Ion Formation from α-Chloroethyl Ethyl Ether and Antimony Pentachloride

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ABSTRACT

The results of electrical conductivity measurements of α-chloroethyl ethyl ether and antimony pentachloride in methylene chloride solution presented previously have been reinterpreted according to the theory of Grattan and Plesch. The results are shown to be more self-consistent and useful than the earlier interpretation.

In an earlier paper [1] the results of electrical conductivity measurements on ethoxymethyl carbenium hexachloroantimonate, $C_2H_5OCH(CH_3) SbCl_6^-$, in methylene chloride were presented and discussed. This stable carboxonium salt was synthesized and studied as a model for the propagating ethyl vinyl ether cation. It is believed that the analysis of the conductivity results contained a number of misinterpretations and inconsistencies. The purpose of this paper is to present in detail the measurements on which the

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TABLE 1. Conductivity Results

$10^3 \underline{c}_0$	$10^6 \kappa$	$10^6 (\kappa - \kappa_x)$	$10^{-2} \underline{c}_0/(\kappa - \kappa_x)$
mol/m^3	S/m	S/m	$S^{-1} \cdot m^2 \cdot mol^{-1}$
0	($\kappa_x = 0.55$)		
1.10	2.1	1.55	7.10
4.44	8.5	7.95	5.59
8.73	17.3	16.75	5.21
13.0	22.0	21.45	6.06
21.3	48.5	47.95	4.44
31.2	66.0	65.45	4.77
45.5	89.0	88.45	5.14
75.5	129.0	128.45	5.88

earlier paper was based and to offer a new, more convincing, self-consistent, and useful interpretation according to the theory developed by one of us [2].

The measurements are shown in Table 1; their interpretation starts from the fact that the electrolyte is of a type which is well known to participate in a neutralization reaction [3, 4], the reverse of which is an ionogenic reaction:

$$C_2H_5OCH(CH_3)Cl + SbCl_5 \overset{K_{11}}{\rightleftharpoons} C_2H_5O\overset{+}{C}H(CH_3) + SbCl_6^- \quad (1)$$
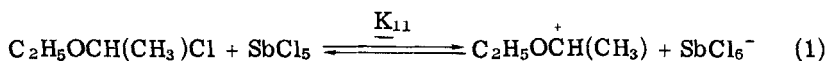
If the original, total concentration of the electrolyte salt is $\underline{c}_0$ and Λ_i is its molar conductivity, the relation between the conductivity κ and the other quantities is

$$\kappa = \underline{c}_0 \Lambda_i \underline{K}_{11}^{1/2}/(1 + \underline{K}_{11}^{1/2}) \quad (2)$$

(Eq. C.2.10 of Ref. 2). (The symbols used here are those of Ref. 2.)

If, as seems likely in CH_2Cl_2, a solvent of moderate polarity, ion-pairs become a substantial part of the solute population at higher concentrations, we have an additional equilibrium involving their formation. For brevity, we write the linked equilibria thus:

$$A + B \overset{K_{F_{11}}}{\rightleftharpoons} R^+Q^- \overset{K_D}{\rightleftharpoons} R^+ + Q^- \quad (3)$$
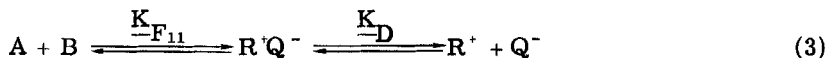
The corresponding equation for κ (Eq. C.2.15 of Ref. 2) is

$$\underline{c}_0/\kappa = (1 + \underline{K}_{F_{11}}^{-1/2}\underline{K}_D^{-1/2})/\Lambda_i + \kappa/\Lambda_i^2\underline{K}_D \qquad (4)$$

It is evident that

$$\underline{K}_{F_{11}} \cdot \underline{K}_D = \underline{K}_{11} \qquad (5)$$

The data of Table 1 have been plotted according to Eqs. (2) and (4) in Figs. 1 and 2. It appears that, as expected, at the lower concentrations ion-pairs are unimportant, whereas above $\underline{c}_0 \approx 2 \times 10^{-2}$ mol/m^3 they predominate. It follows from Eq. (4) that in the lower concentration region the plot in Fig. 2 should become parallel to the κ-axis, as shown by the dotted line.

However, the equations for this type of system give a monotonic dependence of κ on $\underline{c}_0$ and therefore they are not compatible with the present data since the plot in Fig. 1 has an inflection. Whatever may be its cause, it is not due to formation of triple ions since the formation of these leads to a curve with a minimum in $d\kappa/d\underline{c}_0$.

A likely cause of the inflection is that each of the two groups of four points was obtained with a different batch of solvent: the two sets of points would be compatible if either the first four (at $\underline{c}_0 < 2 \times 10^{-2}$ mol/m^3) had larger κ values and thus gave a steeper line, or the other four had κ values ~1×10^{-6} S/m less than was actually recorded. Another possible error which would have the same effect is a hiatus in the scale of the conductivity meter, which would have the effect of making two adjacent ranges not correspond exactly.

The actual scatter of the points is most likely due to the sensitivity of $\kappa - \kappa_x$ and therefore of $\underline{c}_0/(\kappa - \kappa_x)$ to the value of κ_x. The κ_x is the conductivity of the solvent and its impurities, and this is extremely difficult to reproduce from one experiment to another; to appreciate the significance of these variations it must be remembered that the concentrations of ions involved here are substantially less than 10^{-5} mol/dm^3.

DISCUSSION

Despite these uncertainties, an interpretation of the results at low concentration according to Eq. (2) can be attempted. For this we need $\Lambda_i = \Lambda(SbCl_6^-) + \Lambda(C_2H_5O\overset{+}{C}H.CH_3)$. The $\Lambda(SbCl_6^-)$ is known to be 1.052×10^{-2} S$\cdot$m$^2\cdot$mol^{-1} at 298 K in MeCN [5]. By means of Walden's
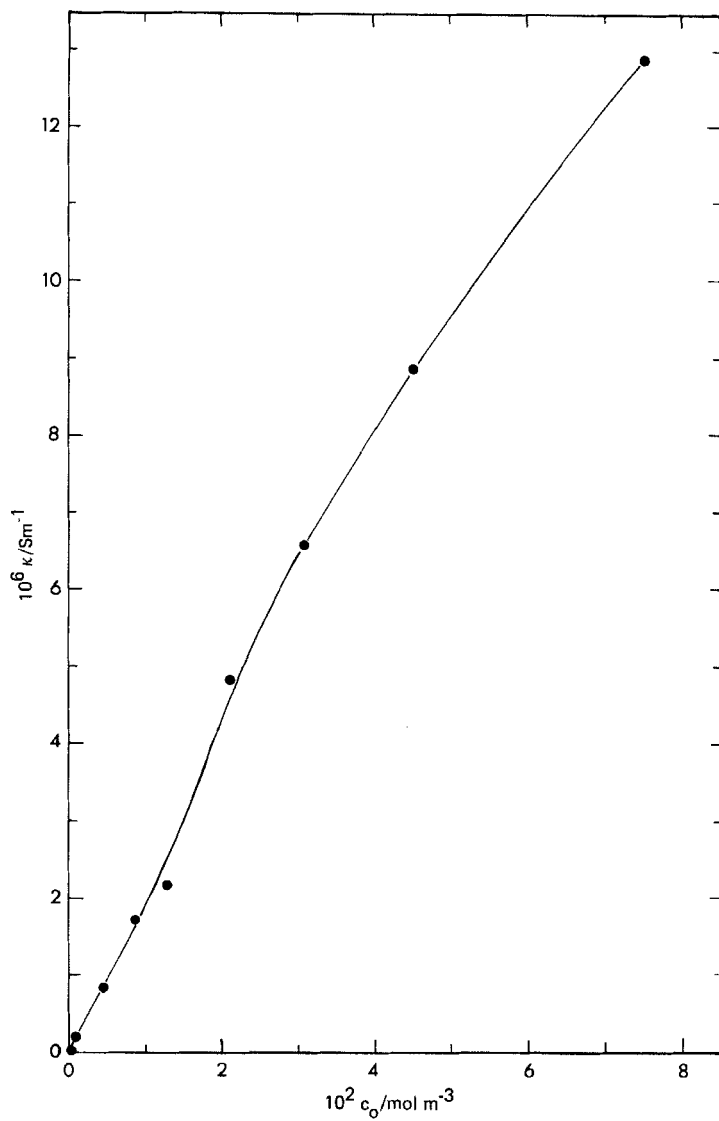
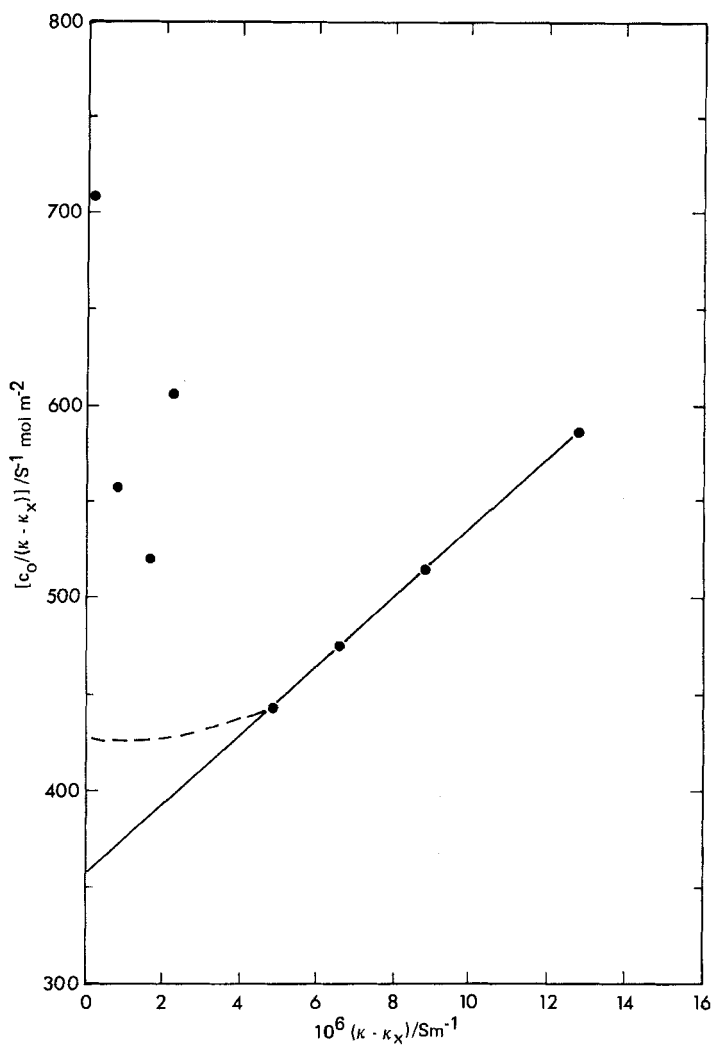FIG. 1. Plot of conductivity versus concentration according to Eq. (2).

FIG. 2. Plot of $c_0/(\kappa - \kappa_x)$ versus $\kappa - \kappa_x$ according to Eq. (4).

rule and the viscosities of the two solvents at the relevant tempera-
tures, we can calculate $\Lambda(SbCl_6^-)$ in CH_2Cl_2 at 267 K to be 1.71×10^{-2}
$S \cdot m^2 \cdot mol^{-1}$. The dimensions of the cation could be calculated, but
since its charge is concentrated at one end, its "effective radius"
cannot be estimated even approximately, and indeed it seems very
likely that for such an ion the dimension determining the electrostatic
interaction in the ion-pair and that which determines the hydro-
dynamic behavior during transport are quite different. It is, however,
very likely that in both respects it is much smaller than the anion,
so that its Λ will be correspondingly greater. As a guess we take
$\Lambda(EtO\dot{C}HCH_3) = 3.3 \times 10^{-2}$ so that we get $\Lambda_i = 5 \times 10^{-2}$ $S \cdot m^2 \cdot mol^{-1}$.
The slope of the plot according to Eq. (2) (Fig. 1) is $\underline{S_1} = 1.83 \times 10^{-4}$
$S \cdot m^2 \cdot mol^{-1}$. Since $\underline{K_{11}}$ is given by

$$\underline{K_{11}}^{1/2} = (\underline{S_1}/\Lambda_i)/(1 - \underline{S_1}/\Lambda_i)$$

Therefore $\underline{K_{11}} = 1.34 \times 10^{-5}$. In view of the very small "effective radius"
of the "sharp end" of the cation and the resulting high charge density,
this rather low value seems not unreasonable.

As for the four points at higher concentration, the uncertainties
discussed above make an interpretation not worthwhile. It is, however,
worth emphasizing that a self-consistent set of measurements cover-
ing the low range of concentrations in which the unpaired ions are
dominant, and also the higher range in which the ion-pairs are im-
portant, can yield all the constants of the system.

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