12. *The Liquid Hydrogen Chloride Solvent System. Part VI.*[1] *Variation of Molar Conductivities with Concentration.*

By M. E. PEACH and T. C. WADDINGTON.

The variation of molar conductivity with concentration of some electrolytes in liquid hydrogen chloride indicates that the mode of ionisation is complex. The theory of Fuoss and Kraus is applied and it is concluded that strong electrolytes form triple ions in concentrated solutions and single ions only in very dilute solutions.

THE variation of the conductivity of several electrolytes in the liquid hydrogen halides was first studied by Steele, McIntosh, and Archibald.[2] They were unable to draw any definite conclusions from their results, although they suggested that association occurred. When these results are replotted, it is found that the equivalent conductivity is proportional to the square root of the concentration for values greater than *ca.* 0·2 mole l.$^{-1}$ (see Fig. 1). Liquid hydrogen chloride has a dielectric constant of 9·28 at $-95°$, and can be treated as a solvent of low dielectric constant. The variation of the conductivities of salts with concentration in such solvents has been studied by Fuoss and Kraus.[3,4] They found that plots of log Λ against log c (Λ = equivalent conductivity in mho cm.^{2} mole^{-1}, c = concentration in moles/l.) showed a minimum and that this minimum moved to higher concentrations as the dielectric constant of the solvent increased: with aqueous solutions it was at too high concentrations to be observed.

To explain these observations Fuoss and Kraus postulated that a simple salt, A^+B^-, can dissolve to form ion pairs, (A^+B^-), which dissociate into single ions, A^+ and B^-, at low concentrations and triple ions at high concentrations:

$$\begin{aligned} A^+B^- &\rightleftharpoons A^+ + B^-; & K_1 &\simeq c\alpha_1^2 \\ A^+B^- + A^+ &\rightleftharpoons A_2B^+; & K_3 &\simeq \alpha_3/c\alpha, \\ A^+B^- + B^- &\rightleftharpoons AB_2^-; & K_3' &\simeq \alpha_3'/c\alpha_1 \end{aligned}$$

K are the dissociation constants and α the degrees of dissociation. The rather drastic

---

[1] Part V, Peach and and Waddington, *J.*, 1962, 2680.

[2] Steele, McIntosh, and Archibald, *Phil. Trans.*, 1905, **205**, 99

[3] Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21.

[4] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387.

assumption is made, as in Ostwald's dilution law, that $(1 - \alpha)$ can be approximated to unity. The molar conductivity is given by

$$\Lambda = \alpha_1\Lambda_0 + \alpha_3\lambda_0 + \alpha_3'\lambda_0',$$

where Λ_0 is the conductivity of the single ion species and λ_0, λ_0' those of the triple ion species at infinite dilution. This can be rewritten

$$\Lambda = \Lambda_0 K_1^{\frac{1}{2}} c^{-\frac{1}{2}} + K_1^{\frac{1}{2}}(\lambda_0 K_3 + \lambda_0' K_3')c^{\frac{1}{2}},$$

or

$$\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}},$$

and

$$\Lambda c^{\frac{1}{2}} = A + Bc.$$

If the theory is applicable to liquid hydrogen chloride solutions, a plot of $\Lambda c^{\frac{1}{2}}$ against c would be a straight line, the slope and intercept of which would give B and A. There should be minima in the plots of Λ against $c^{\frac{1}{2}}$ and of log Λ against log c, when c_m, the concentration at the minimum, equals A/B. All these values of A/B should be the same.

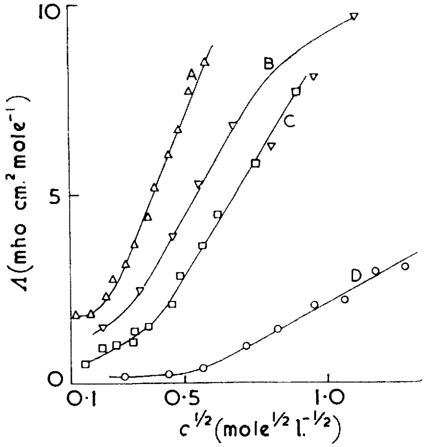

FIG. 1. Steele, McIntosh, and Archibald's results plotted as Λ-$c^{\frac{1}{2}}$ (ref. 2). (A) Et_3NHCl; (B) $MeCN$; (C) HCN; (D) Et_2O.

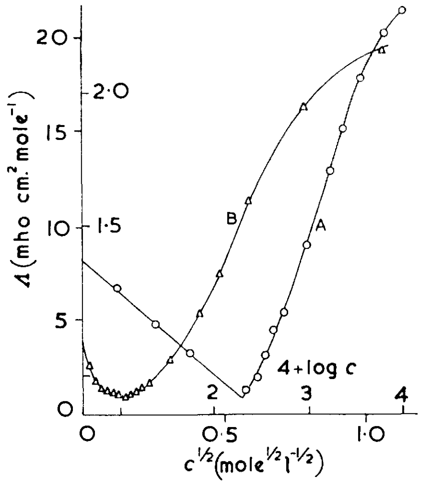

FIG. 2. Plots, for Me_2S, of (A) log Λ against log c and (B) Λ against $c^{\frac{1}{2}}$.

Information of a much more tentative nature can be obtained from the values of Λ_∞ (obtained by extrapolation of the Λ-$c^{\frac{1}{2}}$ plot) and of Λ_m (obtained from the log c-log Λ and Λ-$c^{\frac{1}{2}}$ plots). If is is assumed that $K_3 = K_3'$ and that at the minimum there are equal contributions from single and triple ions, then

$$\Lambda_m = 2\alpha_{1m}\Lambda_0 = 2\alpha_{3m}\lambda_0.$$

Fuoss and Kraus assumed that $\Lambda_\infty = 4\Lambda_0/3$ or $4\lambda_0$, and hence calculated K_1 and K_3:

$$K_1 = c_m(\Lambda_m/\Lambda_\infty)^2/4;$$

$$K_3 = \Lambda_0/\lambda_0 c_m.$$

It will be seen that this treatment involves several very drastic assumptions.

EXPERIMENTAL

The variation of equivalent conductivity with concentration of liquid hydrogen chloride solutions was studied with two strong bases (dimethyl sulphide and trimethylamine), a weak base (acetyl chloride), and a salt (trimethylammonium tetrachloroborate). Dimethyl sulphide and trimethylamine act as strong bases owing to protonation, forming the ions $Me_2SH^+HCl_2^-$ and $Me_3NH^+HCl_2^-$. All the compounds used were very volatile or could be prepared *in situ* from volatile materials (*e.g.*, trimethylammonium tetrachloroborate); thus very small amounts of solute could be added, by determining the pressure change in a small volume (*ca.* 10 mm. in 16 cm.^{3} at room temperature = 0·09 millimole), for the preparation of the very dilute solutions; and the concentrations could be steadily increased, as in an acid–base conductometric titration.[1] The lowest concentration studied was 0·0009M.

The results from these experiments are shown graphically in Figs. 2, 3, and 4.

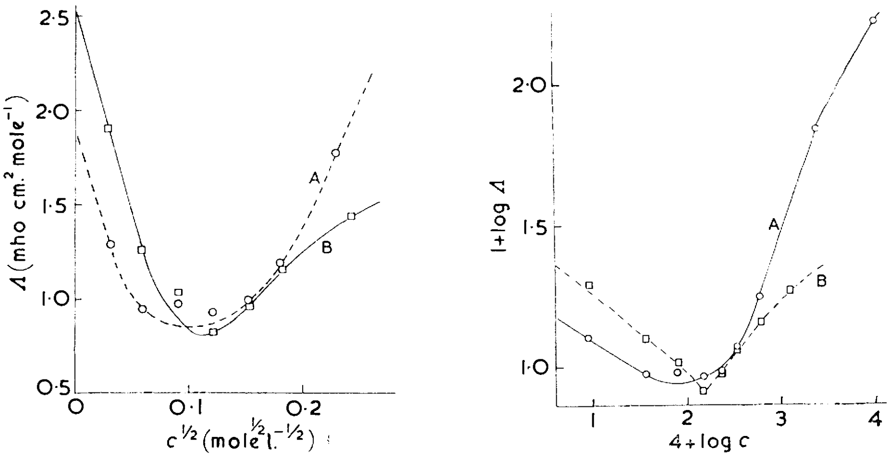

FIG. 3. FIG. 4.

FIGS. 3 and 4. Plots of (Fig. 3) Λ against $c^{\frac{1}{2}}$ and (Fig. 4) log Λ against log *c* for (A) Me_3N and (B) $Me_3NH{\cdot}BCl_4$.

Plots of $\Lambda c^{\frac{1}{2}}$ against *c* are approximately linear at low concentrations for trimethylamine trimethylammonium tetrachloroborate, and dimethyl sulphide. Values derived by Fuoss and Kraus's theory for various quantities are shown in the Table.

Experimental and derived quantities for liquid hydrogen chloride solutions.

Variable		Fuoss & Kraus $\varepsilon = 9{\cdot}0$ *	Me_2S	Me_3N	$Me_3NH{\cdot}BCl_4$	$Me{\cdot}COCl$
c_m	Λ–$c^{\frac{1}{2}}$		0·0196	0·0064	0·01538	0·0625
	$\Lambda c^{\frac{1}{2}}$–c	0·025	0·0197	0·0069	0·0133	0·114
	log Λ–log *c*		0·020	0·0072	0·01514	0·0603
Λ_m	Λ–$c^{\frac{1}{2}}$	5·6	0·85	0·85	0·79	0·00485
	log Λ – log *c*		0·85	0·87	0·80	0·00516
Λ_∞	Λ–$c^{\frac{1}{2}}$	40	3·65	1·90	2·50	0·0151
Initial slope	log Λ–log *c*	−0·5	−0·35	−0·22	−0·23	−0·33
Λ_0		30	2·74	1·43	1·87	0·0113
λ_0		10	0·91	0·475	0·63	0·0038
Λ_m/Λ_∞		0·140	0·233	0·452	0·320	0·341
α_m		0·0933	0·0874	0·169	0·120	0·128
α_{3m}		0·280	0·466	1·004	0·640	0·682
10^3K_1		0·123	0·267	0·353	0·389	1·78
K_3		120	153	435	197	48·8

* From a dioxan–water mixture.

Discussion.—From the Table it will be seen that the value of $c_m(= A/B)$ is the same for a particular strong electrolyte, whichever plot is used to derive it. This is true also of

Λ_m. Fuoss and Kraus's theory of ionisation must apply to liquid hydrogen chloride solutions of strong bases and ionised salts. All the other derived quantities in the Table depend upon the value of Λ_∞. Fuoss and Kraus found, in their experiments, that the initial slope of the plot of log Λ against log c was $-0{\cdot}5$, which would correspond to dissociation according to Ostwald's dilution law; the material used would behave at low concentration as weak electrolytes do in water, and hence extrapolation of a plot of Λ against $c^{\frac{1}{2}}$ would be of limited value, as the conductivity ought to increase rapidly as $c^{\frac{1}{2}}$ approaches zero. The initial slopes of the plots of log Λ against log c for hydrogen chloride solutions were not $-0{\cdot}5$, but did lie on straight lines with negative slope. Plots of log Λ against log c cannot be extrapolated to $c = 0$; so we calculated our value of Λ_∞ from plots of Λ against c_m, and these values must be viewed with scepticism. We then used these values to calculate λ_0 and Λ_0, making Fuoss and Kraus's assumptions; and we used these values to calculate K_1 and K_3. The values obtained for K_1 and K_3 are reasonable, indicating that the triple ions are formed in stronger solutions than single ions.

The values derived for α_{1m} and α_{3m} are not very reliable, though they are of the right order of magnitude. They are, of course, very sensitive to the value of Λ_∞ chosen, and this may well have been too small by a factor of two or more.

If the ionic conductance of the hydrogen dichloride ion were abnormally high, as it might be expected to be since protons can be transferred from one solvent molecule to another, then one could expect to find that Λ_∞ for a base such as trimethylamine would be considerably higher than for the corresponding salt. This is found not to be the case: Λ_∞ for $Me_3N = 1{\cdot}9$, and for $Me_3NH^+BCl_4^- = 2{\cdot}50$; and this suggests that a Grothuss mechanism [5] does not operate.

Acetyl chloride is a weak electrolyte in hydrogen chloride and can ionise in either of two ways:

$$CH_3{\cdot}COCl + HCl \rightleftharpoons CH_3{\cdot}CO^+ + HCl_2^-$$

$$CH_3{\cdot}COCl + 2HCl \rightleftharpoons CH_3{\cdot}COClH^+ + HCl_2^-$$

The latter is probably correct.[1] The conductance minimum occurred at a higher concentration and lower conductivity than for a strong electrolyte. Although the points on the plot of $c^{\frac{1}{2}}\Lambda$ against c lay on a reasonably straight line, the value of c_m so obtained was about twice that from the plots of Λ against $c^{\frac{1}{2}}$ and of log Λ against log c.

One of the authors (M. E. P.) thanks the D.S.I.R. for a maintenance grant.

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

[*Received, June* 25*th*, 1962.]

---

[5] Glasstone, " Textbook of Physical Chemistry," Macmillan and Co., Ltd., London, 2nd edn., 1948, p. 898.