145. *Antimony Halides as Solvents. Part I. Cryoscopic Data in Antimony Trichloride.*

By G. B. Porter and E. C. Baughan.

Cryoscopic measurements in antimony trichloride (m. p. 73·17°) are presented which extend and confirm Tolloczko's pioneer work.[1] From solutions of fluorene, dibenzyl, benzophenone, and anthracene the cryoscopic constant has been determined and corrected for non-ideality.

Tetramethylammonium and triphenylmethyl chlorides are strong electrolytes, while cæsium and potassium chlorides are completely dissociated only at infinite dilution (cf. the conductivity data of Klemensiewicz *et al.*[2c]). The osmotic coefficients for these electrolytes can be interpreted in terms of solvation and ion-pair formation by comparison with the Debye–Hückel equation.

Stilbene dimerises completely, and the dimer has been isolated.

The study of non-aqueous ionising solvents[3] has produced many important chemical results; work on sulphuric acid and liquid ammonia, for example, has greatly extended our knowledge of proton acids and bases by providing equilibrium data on many systems previously unknown or inferred from kinetic measurements. The extension of such information to ions produced in ways other than by protonation is therefore desirable. The necessary properties of such solvents are (*a*) the ability to promote ionisation by solvation, just as the formation of OH_3^+ in water or of NH_4^+ in ammonia assists the ionisation of proton acids; (*b*) a high dielectric constant, since otherwise conductivities are almost uninterpretable through ion-association; and (*c*) a convenient melting-point, to permit determination of the number of ions formed by a solute molecule, and also of the activity data necessary for thermodynamic studies.

We investigated liquid antimony trichloride (f. p. 73·2°), chosen since pioneer work in Poland on freezing-point depressions[1] and conductivities[2] has shown that it is a good ionising solvent. In particular, Klemensiewicz and Balówna[2c] measured the conductivities at 99° of several halides in dilute solution; their results give linear Kohlrausch plots as can be seen in Fig. 1, which also shows the theoretical Debye–Hückel–Onsager slopes. In calculating these, we assumed that the viscosity and dielectric constant at 99° are 1·84 centipoises and 30·4 respectively. The former was estimated from Klemensiewicz's viscosity–temperature data[2a] by interpolation, by use of Batschinski's equation,[4] and the latter from Schlundt's value[5] of 33·2 at 75°, by using Onsager's equation[6] relating dielectric constant to dipole moment. We see not only that the interionic effects on conductivity are as expected for a solvent of such a dielectric constant (cf. methanol and ethanol[7]), but also that all the limiting conductivities are almost identical. This suggests that chloride and bromide ions have abnormally high mobilities, and agrees with the high transport numbers (about 0·9) obtained for the chloride ion in ammonium and potassium chloride solutions by Tolloczko.[8] Abnormal mobilities imply favourable rates[9] for such processes as

$$OH_3^+ + OH_2 \longrightarrow OH_2 + OH_3^+$$

and therefore (probably)

$$SbCl_4^- + SbCl_3 \longrightarrow SbCl_3 + SbCl_4^-$$

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[1] Tolloczko, (*a*) *Z. phys. Chem.*, 1899, **30**, 705; (*b*) *Bull. int. Acad. Sci. Cracovie*, 1901, **1**, 1.

[2] (*a*) Klemensiewicz, *Bull. int. Acad. Sci. Cracovie*, 1908, **6**, 485; (*b*) *idem, Z. phys. Chem.*, 1924, **113**, 28; (*c*) Klemensiewicz and Balówna, *Roczniki Chem.*, 1930, **10**, 481; (*d*) *idem, ibid.*, 1931, **11**, 683; (*e*) Klemensiewicz and Zebrowska, *ibid.*, 1934, **14**, 14.

[3] Gutmann, *Quart. Rev.*, 1956, **10**, 451.

[4] Batschinski, *Z. phys. Chem.*, 1913, **84**, 643.

[5] Schlundt, *J. Phys. Chem.*, 1901, **5**, 503.

[6] Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

[7] Murray-Rust, Gatty, MacFarlane, and Hartley, *Ann. Reports*, 1930, **27**, 326.

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

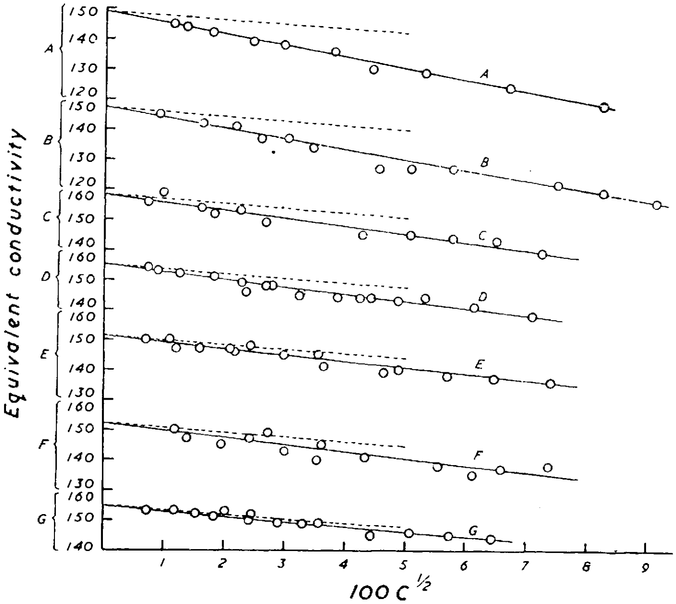
[9] Baughan, quoted in Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 568—575.

with chemical solvation of the ions concerned. A high transport number (0·88—0·97) has also been reported[10] for chloride ions in solutions of tetramethylammonium chloride in arsenic trichloride. This solvent has a lower dielectric constant[5] (12·35 at 21°), and the solubility of alkali-metal chlorides is less than in antimony trichloride, in which only lithium and sodium chlorides are insoluble.[2a]

Antimony trichloride thus seems to fulfil all three of our criteria better than the other metal halides recently investigated.[3] In addition, the chemistry of this solvent is remarkable; it is a " Lewis acid " and therefore a Friedel–Crafts catalyst, and gives colour reactions with conjugated hydrocarbons, such as the standard test for vitamin A, although these appear to be due to traces of antimony pentachloride.[11]

The results reported here show that normal solutes can be found, and that salts show activity effects of the magnitude to be expected; the earlier Polish work is confirmed wherever overlap occurs.

FIG. 1. *Kohlrausch plots of Klemensiewicz's results*[2c] (*C is solute molarity*).



– – – – Limiting Onsager slopes.

A, TlCl; *B*, TlBr; *C*, KCl; *D*, KBr; *E*, NH_4Cl; *F*, NH_4Br; *G*, RbCl.

EXPERIMENTAL

Materials.—" AnalaR " antimony trichloride was repeatedly distilled under reduced pressure in a current of dry, oxygen-free nitrogen. Anthracene (B.D.H. " blue fluorescence ") and the other hydrocarbons were recrystallised; benzophenone was vacuum-distilled. Tetramethylammonium chloride was prepared by neutralisation of the hydroxide (25% aqueous solution), and was recrystallised from ethanol; tetramethylammonium bromide was recrystallised from methanol. Both salts were dried at 120°, and their purity was checked by halide analysis. Potassium and cæsium chlorides (" AnalaR ") were dried at 300°. Triphenylmethyl chloride was recrystallised from light petroleum (b. p. 60—80°) containing 10% of acetyl chloride.

Measurement of Freezing Points.—The apparatus was a conventional Beckmann freezing-point cell, suitably modified to prevent access of moisture, and tapered at the bottom to prevent breakage (since antimony chloride expands considerably on melting). The ground-on head of the cell carried a mercury-sealed stirrer with a Polythene stopper, and three standard ground joints, which accommodated respectively a Beckmann thermometer, a drying-tube containing

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[10] Gutmann, *Svensk Kem. Tidskr.*, 1956, **68**, 1.

[11] Brüggemann, Krauss, and Tiews, *Chem. Ber.*, 1952, **85**, 315.

" Anhydrone " (magnesium perchlorate), and an inlet for nitrogen. The thermometer could be read to ±0·001°, and was calibrated at the National Physical Laboratory. All joints were lubricated with Silicone stop-cock grease. Solutes were introduced, from a device similar to that described by Newman *et al.*,[12] by removing the drying-tube while dry nitrogen was being passed through the apparatus. During measurements the cryoscope was placed in an air jacket in an oil thermostat at 1·5—2·5° below the f. p.

About 15 ml. of the purified antimony trichloride were redistilled directly into the lower half of the cryoscope, a small fore-run being rejected. The distillation apparatus was then placed in a glove-box under a positive pressure of dry nitrogen, and the cell detached, sealed with a ground-glass cap, weighed, and replaced in the dry-box, where the solvent was carefully melted and the top of the cell was fitted.

For each determination the apparatus was kept in an auxiliary oil bath at about 95° until the antimony trichloride had melted, and was then transferred to the thermostat. The freezing-point of the pure solvent was recorded at once, but after each addition of solute, the cryoscope was kept in the thermostat for at least 1 hr., to ensure complete solution. It was then reheated for a few minutes in the auxiliary bath (in case crystallisation had occurred), removed, and allowed to cool, with stirring, in the thermostat to not more than 1·5° below the f. p., whereupon a small crystal of pure solvent was introduced through the solute inlet. In many cases spontaneous crystallisation occurred before this point.

The highest observed value for the f. p. of the pure solvent was 73·17°. On any one day, the f. p. of a solution (after correction for supercooling) could be reproduced to within 0·005°, although sometimes a fall of about 0·010° occurred overnight.

The solutes which gave coloured solutions are as follows: anthracene (deep green), fluorene (deep blue), benzophenone (green), triphenylmethyl chloride (orange-red), dibenzyl and stilbene (pale green).

Supercooling Correction.—The true freezing-point depression is given by [13]

$$\theta = \theta_1[1 - (n_1C_p + C_0)S/n_1\Delta H^f]$$

where θ_1 is the observed depression, S the amount of supercooling, n_1 the number of moles of solvent in the solution, ΔH^f the molar heat of fusion of the solvent, C_p the molar heat capacity of liquid solvent, and C_0 the thermal capacity of the cryoscope. The main contribution to the small C_0 term was the heat capacity of the mercury in the thermometer, which was estimated from the dimensions of the thermometer bulb.

This correction was never more than 0·02° for non-electrolytes, and 0·04° for the electrolytes.

Heat Capacity of Solvent.—The heat capacities of fused and solid antimony trichloride were determined by the method of mixtures. The calorimeter was a small Dewar flask containing a constant amount of technical white oil (a convenient non-volatile liquid), and the sample of antimony trichloride was sealed *in vacuo* in a small Pyrex glass ampoule. The calorimeter was calibrated with an ampoule containing mercury (specific heat of Pyrex from de Vries [14]). The resultant mean heat capacities were 33·3 cal. mole^{-1} deg.$^{-1}$ over the range 76—98° for the liquid solvent (mean of six experiments), and 25·8 cal. mole^{-1} deg.$^{-1}$ over the range 28—69° for the solid solvent (three experiments). These values are sufficiently precise for the small correction terms needed in the reduction of the observations; we would draw attention to the unusually large change in specific heat on melting. We have found no previous data except the value 25·1 cal. mole^{-1} deg.$^{-1}$ for the mean heat capacity of the solid between 0° and 33° obtained by Pebal and Jahn [15] with an ice calorimeter.

RESULTS AND DISCUSSION

The cryoscopic equation [16] is, as far as terms in θ^2,

$$\theta(1 + \alpha\theta) = -m_1k_f\ln a_1 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where

$$\alpha = \frac{1}{T_0} - \frac{\Delta C_p}{2\Delta H^f{}_0}; \; k_f = \frac{RT_0{}^2}{m_1\Delta H_0{}^f}$$

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[12] Newman, Kuivila, and Garrett, *J. Amer. Chem. Soc.*, 1945, **67**, 704, Fig. 1*a*.

[13] Gold, Hawes, and Tye, *J.*, 1952, 2170.

[14] de Vries, *Ind. Eng. Chem.*, 1930, **22**, 617.

[15] von Pebal and Jahn, *Wied. Ann.*, 1886, **27**, 584.

[16] Lewis and Randall, " Thermodynamics," McGraw-Hill, New York, 1923, p. 282.

$\Delta H_0{}^f$ is the heat of fusion of pure solid solvent at its melting point T_0, ΔC_p the difference between the heat capacities of the liquid and solid solvent, m_1 the molality of the solvent in the solution, k_f the cryoscopic constant, and a_1 the activity of the solvent at the freezing point of the solution.

I. *Non-electrolytes.*—Anthracene, fluorene, benzophenone, and dibenzyl give identical depressions in dilute solution and are therefore normal solutes, although the intense colours of their solutions and the marked negative deviations of the freezing-point depressions from Raoult's law showed that there was some interaction with the solvent. Allowance can be made for this interaction, without specifying its nature, by the following semi-empirical treatment.

For a solution of a non-electrolyte, $a_1 = N_1 f_1$, where N_1 and f_1 are respectively the mole fraction and activity coefficient of the solvent. For many binary systems [17]

$$\ln f_1 = \beta N_2{}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where N_2 is the mole fraction of the solute, and β is a constant at a given temperature. Therefore, since $\ln N_1 \sim -N_2$ for dilute solutions, we can write eqn. (1) as

$$\theta(1 + \alpha\theta) = m_1 k_f (N_2 - \beta N_2{}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $m_1 = 4{\cdot}38$ mole kg.$^{-1}$ for antimony trichloride.

This equation was fitted to our results by the least-squares method (Table 1).

TABLE 1. *Results of least-squares calculations.*

	Fluorene	Anthracene	Benzophenone	Dibenzyl	Stilbene
k_f (deg. mole^{-1} kg.)	16·7	15·5	15·2	15·0	7·89
β	−4·11	−3·20	−4·28	−7·57	−5·43

The mean value of k_f is 15·6 ± 0·2 deg. mole^{-1} kg., which, with $T_0 = 346{\cdot}3°$ K, gives $\Delta H_0{}^f = 3485$ cal. mole^{-1} and $\alpha = 0{\cdot}0018$ deg.$^{-1}$. In Fig. 2 the experimental values of $\theta(1 + 0{\cdot}0018\theta)$ are plotted against N_2, and the curves have been calculated from eqn. (3) with the appropriate values of k_f and β (Table 1). Tolloczko [1a] reported a considerably higher value for k_f (18·4). As can be seen from Fig. 2, his points lie somewhat higher than our own, but show more scatter, and no correction was made for deviation from Raoult's law; a value of 17·9 has been obtained [18] from the difference in heats of solution in hydrochloric acid of the solid and supercooled liquid.

It is evident from Fig. 2 that stilbene is exactly dimerised in this solvent; its value for k_f has therefore been doubled in assessing the mean figure above. The experimental points are from two independent runs. Dimerisation occurred within the time taken for the solvent to melt, as no intermediate depressions were ever observed. The dimer was recovered from solution, and resembled the products obtained from the isomeric stilbenes and sulphuric acid by Brackman and Plesch,[19] who suggested that their dimers were mainly 3-benzyl-1 : 2-diphenylindane.

Isolation of stilbene dimer. The dimer was recovered as a colourless, transparent resin (in almost quantitative yield) by dissolving the solidified melt in benzene, extracting the antimony trichloride with hydrochloric acid, and evaporating the benzene *in vacuo*. It was slowly deposited from alcoholic solution as an amorphous, granular solid, which had a melting transition of 45—70° [Found: C, 93·2; H, 6·7%; *M* (cryoscopic in benzene), 363. $(C_{14}H_{12})_2$ requires C, 93·3; H, 6·7%; *M*, 360]. The substance was unaffected by fractional crystallisation, it would not undergo addition reactions with bromine or potassium permanganate, and the infrared spectrum showed none of the bands characteristic of olefinic double bonds.

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[17] Hildebrand and Scott, "The Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, 1950, p. 35.

[18] Tolloczko and Meyer, *Kosmos*, 1910, **35**, 641; *Chem. Abs.*, 1911, **5**, 1881.

[19] Brackman and Plesch, *J.*, 1953, 1289.

II. *Electrolytes.*—In Fig. 3 we show our results for the electrolytes and those of Tolloczko[1b] for potassium chloride as van't Hoff *i*-factors, calculated (in both cases) from the relation $i = \theta/15{\cdot}6m_2$, where m_2 is the molality of the solute. It is clear that the *i*-factors for the chlorides tend to the obvious value 2 at infinite dilution. Antimony trichloride is however the only solvent yet investigated in which triphenylmethyl chloride is a strong electrolyte. Thus, the ebullioscopic *i*-factor for this solute in liquid sulphur

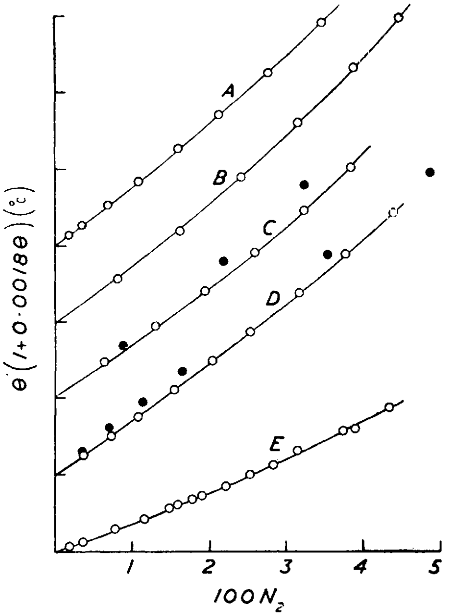

FIG. 2. *Freezing-point depressions produced by non-electrolytes.*

The curves are separated vertically by 1° at their origins.

——— Calculated from eqn. (3).

●, Tolloczko[1a] (*C* and *D*).
○, present investigation.
A, fluorene.
B, dibenzyl.
C, benzophenone.
D, anthracene.
E, stilbene.

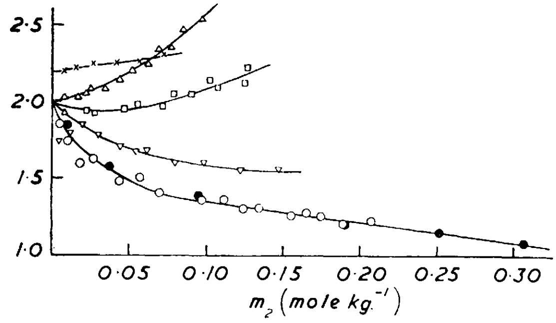

FIG. 3. *i-Factors for electrolytes.*

×, Me_4NBr.
△, Ph_3CCl.
□, Me_4NCl.
▽, CsCl.
○, KCl (present work).
●, KCl (Tolloczko[1b]).

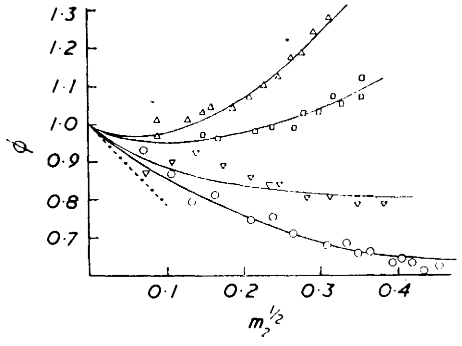

FIG. 4. *Comparison of experimental osmotic coefficients with eqn.* (10).

- - - - Limiting Debye–Hückel slope (eqn. 9).

——— Calc. from eqn. (10) with following values of $\mathring{a}$ and b

	$\mathring{a}$	b
△ Ph_3CCl	15	3·1
□ Me_4NCl	13	1·1
▽ CsCl	4·5	0
○ KCl	2·1	0

dioxide [20] is less than 2 (approaching this value in very dilute solutions), while in nitromethane, it has been shown spectrophotometrically [21] that the chloride exists only as ion-pairs, which dissociate partially when mercuric chloride is added.

The following discussion shows that the general form of the curves in Fig. 3 agrees with the usual extensions to the Debye–Hückel osmotic theory. Tetramethylammonium bromide must be excluded, however, as this solute has a limiting *i*-factor of 2·2, which may be the result of partial halogen exchange, *e.g.*,

$$\mathrm{Me_4NBr + SbCl_3 \rightleftharpoons Me_4N^+ + Cl^- + SbCl_2Br}$$

Such an exchange would not, however, invalidate the conductivity data of Klemensiewicz [2c] on bromides. Similarly, although Gutmann [22] mentions that tetramethylammonium iodide reacts slowly with the solvent arsenic trichloride, he found that the conductivities of " freshly prepared " solutions agreed closely with the Onsager limiting equation for this solvent.

Osmotic coefficients. The most convenient way of expressing the non-ideality of electrolyte solutions from freezing-point data is in terms of the molal osmotic coefficient, ϕ, defined by eqn. (4), where ν is the number of ions produced by one molecule of solute, and

$$\ln a_1 = -\nu\phi m_2/m_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

m_2 is the molality of the solute. Substituting this expression in equation (1), we obtain eqn. (5) for a solution of an electrolyte.

$$\theta(1 + \alpha\theta) = \nu\phi k_f m_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

If we insert the values $\alpha = 0{\cdot}0018$ deg.$^{-1}$, $k_f = 15{\cdot}6°$ mole^{-1} kg., and $\nu = 2$ (for a symmetrical electrolyte), eqn. (5) becomes eqn. (6).

$$\theta(1 + 0{\cdot}0018\theta) = 31{\cdot}2\phi m_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

In Fig. 4, experimental values of ϕ, calculated from eqn. (6) are plotted against $m_2^{\frac{1}{2}}$. Since ϕ is approximately half the *i*-factor (as defined above) in dilute solutions, Figs. 3 and 4 are similar in form.

Comparison with Debye–Hückel theory. For a uni-univalent electrolyte, the ionic strength in dilute solution is given by $I \sim m_2\rho$, where ρ is the density of the pure solvent, and the Debye–Hückel osmotic equation [23] therefore becomes

$$\phi = 1 - \tfrac{1}{3}Am_2^{\frac{1}{2}}\sigma(x) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where
$$x = B\mathring{a}m_2^{\frac{1}{2}};\; \sigma(x) = \frac{3}{x^3}\left[(1 + x) - 2\ln(1 + x) - \frac{1}{1 + x}\right]$$

$$A = \frac{10^8Be^2}{2\varepsilon kT};\; 10^8B = \left(\frac{8\pi\rho Ne^2}{10^3\varepsilon kT}\right)^{3/2}$$

$\mathring{a}$ is the distance of closest approach of anion and cation in Ångström units, and ε is the dielectric constant of the solvent. Taking the value of ε at the melting point as 33·2, and that of ρ as 2·683 g. cm.$^{-3}$, from Zhuravlev's density data,[24] we have

$$\phi = 1 - 1{\cdot}86m_2^{\frac{1}{2}}\sigma(0{\cdot}768\mathring{a}m_2^{\frac{1}{2}}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

for a uni-univalent electrolyte in antimony trichloride. The corresponding Debye–Hückel limiting law is obtained by putting $\mathring{a} = 0$, when $x = 0$ and $\sigma(x) = 1$ (as can be shown by expanding the σ-function into an infinite series):

$$\phi = 1 - 1{\cdot}86m_2^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

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[20] Jander and Mesech, *Z. phys. Chem.*, 1939, **183**, *A*, 277.

[21] Bayles, Evans, and Jones, *J.*, 1955, 206.

[22] Gutmann, *Monatsh.*, 1954, **85**, 491.

[23] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, p. 233.

[24] Zhuravlev, *J. Phys. Chem., U.S.S.R.*, 1939, **13**, 684.

However, Fig. 4 shows that eqn. (8) is inadequate, because it predicts an osmotic coefficient which is always a decreasing function of concentration, whereas this is not so with triphenylmethyl and tetramethylammonium chlorides. The behaviour of non-associated electrolytes in water is similar, and to fit the results it is customary to add an empirical linear term, which has been interpreted [25] as mainly a correction for ion solvation. In our case, we can write

$$\phi = 1 - 1{\cdot}86 m_2^{\frac{1}{2}} \sigma(0{\cdot}768 \mathring{a} m_2^{\frac{1}{2}}) + b m_2 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where b is a constant. Fig. 4 shows the values of $\mathring{a}$ and b which give reasonable agreement between the curves calculated from eqn. (10) and the experimental results. For cæsium and potassium chlorides, the theoretical curves actually correspond to eqn. (8) ($b = 0$), although a better fit is obtained with negative values of b. Values of $\sigma(x)$ were obtained, by graphical interpolation, from tables [26] (in the range $x = 0$—1) and from further values ($x > 1$) calculated from the definition above.

To obtain theoretical values of $\mathring{a}$ for comparison with our results, we will assume that only the chloride ion is chemically solvated, and that it forms the anion $[SbCl_4]^-$, by analogy with Gutmann's suggestion [27] that the solvates $Me_4NCl,AsCl_3$ and $KCl,AsCl_3$ contain the anion $[AsCl_4]^-$. (We have not yet, however, succeeded in isolating similar compounds from antimony trichloride solutions.) Then $\mathring{a} = r^+ + r^-$ where r^+ is the radius of the cation, and r^- is that of the $[SbCl_4]^-$ ion. Since the Sb–Cl bond length [28] is 2·4 Å, and the ionic radius of chlorine [29] is 1·8 Å, $r^- \sim 4{\cdot}2$ Å. The corresponding theoretical values of $\mathring{a}$ are compared with the experimental values in Table 2.

TABLE 2.

			$\mathring{a}$ (Å)	
Electrolyte	r^+ (Å)	r^- (Å)	theor.	exp.
KCl	1·3 [a]	4·2	5·5	2·1
CsCl	1·7 [a]	,,	5·9	4·5
Me_4NCl	3·5 [b]	,,	7·7	13
Ph_3CCl	*ca.* 5 [c]	,,	between 7 and 9	15
	(half-thickness *ca.* 2·5)			

[a] Ref. 29. [b] Ref. 23, p. 119. [c] Hughes, Ingold, *et al.*, *J.*, 1957, 1276.

The triphenylmethyl cation is non-spherical, and hence only the upper and lower limits of $\mathring{a}_{\text{theor}}$ can be calculated.

For potassium and cæsium chlorides, the experimental $\mathring{a}$ parameters have obviously been forced to include the effects of association (Fig. 3) and have no geometrical significance, the apparent value for potassium chloride being too small even for completely unsolvated ions ($\mathring{a}_{\text{theor}} = 3{\cdot}1$). The Bjerrum critical distance for a uni-univalent electrolyte in antimony trichloride at its melting-point T_0 is

$$q = e^2/2\varepsilon k T_0 = 7{\cdot}3 \text{ Å}$$

Since the theoretical $\mathring{a}$ values for cæsium and potassium chlorides are less than this, ion-pair formation would be expected. It would also be expected for the chlorides of thallium ($r^+ = 1{\cdot}4$ Å), ammonium, and rubidium (both 1·5 Å); Fig. 1, indeed, shows that the limiting slopes of equivalent conductivity, Λ, against $C^{\frac{1}{2}}$ for NH_4Cl and TlCl are considerably greater than the theoretical values, which would suggest incomplete dissociation; for RbCl, however, the discrepancy is quite small.

For the strong electrolytes, tetramethylammonium chloride and triphenylmethyl chloride, on the other hand, the observed distances of closest approach exceed not only the

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[25] Gillespie and Oubridge, *J.*, 1956, 80.

[26] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1950, p. 597.

[27] Gutmann, *Z. anorg. Chem.*, 1951, **266**, 331.

[28] Lindqvist and Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

[29] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 1945.

critical distance, as expected, but also the theoretical values. In aqueous[30] and in sulphuric acid[25] solutions, the differences between the observed and crystallographic values of $\mathring{a}$ for non-associated electrolytes have been interpreted quantitatively in terms of solvation shells around the ions. In antimony trichloride solutions, one complete solvation shell around the Ph_3C^+ or Me_4N^+ cation would increase $\mathring{a}_{\text{theor}}$ (Table 2) to the observed order of magnitude, the molecular diameter of the solvent being about 6 Å. It is possible to estimate[25] a " solvation number " from the value of the parameter b, but the theoretical basis of such calculations is doubtful.

It is hoped to publish further results, concerning organic solutes which undergo reaction after initial ionisation.

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CHEMISTRY DEPARTMENT, ROYAL MILITARY COLLEGE OF SCIENCE,
SHRIVENHAM, WILTS. [*Received, August* 28*th*, 1957.]

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[30] Stokes and Robinson, *J. Amer. Chem. Soc.*, 1948, **70**, 1870.