Association Constants of 1:1 Electrolytes in Water from Conductivity Measurements

By Alan D. Pethybridge and David J. Spiers
(*Department of Chemistry, The University, Reading, Berks* RG6 2AD)

Summary The association constants of most 1:1 salts in water, including those forming so-called outer-sphere complexes, are shown to be principally determined by the combined size of the two ions.

As part of a conductimetric study of association in aqueous solutions of salts of the complex ion *trans*-$[Co(en)_2(NO_2)_2]^+$, we have reanalysed all existing conductance data for 1:1 salts in water at 25 °C in an attempt to establish some pattern in the results. No such pattern can be observed in the published constants because different authors have adopted different theoretical equations, different approximations, and different methods of analysis.

Our method of fitting conductance data in terms of Λ^∞, K_A, and d, the distance of closest approach of free ions, has been described.[1] In this paper we have used the theoretical conductance equation due to Pitts[2] in its full form, but entirely similar results are obtained with the Fuoss–Hsia equation.[3] It is now recognised[1,4] that a wide range of correlated values of K_A and d can give a satisfactory fit and that consideration of only the point of statistical best-fit may make comparison difficult. Our approach overcomes this problem. In Figure 1 we have plotted (circles) actual best-fit K_A and d values obtained by us using the full Pitts equation for all available *precise* (σ_A <0·1%) conductivity results for aqueous KCl solutions.[5–16] The continuous line represents the various K_A–d pairs capable of fitting Chiu and Fuoss's[5] comprehensive results. Some results yield two best-fit points, at d values on either side of data showing

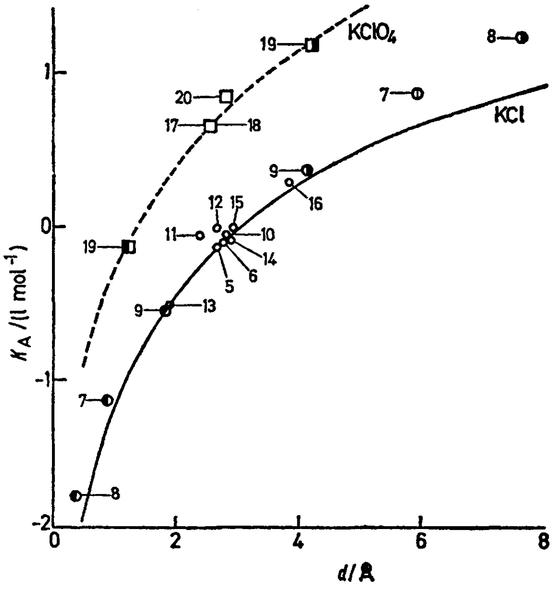

Figure 1

only one minimum. These are represented by half-filled circles. The squares represent the more associated $KClO_4$.[17–20] Consequently, when comparing $K_{\rm A}$ values for different salts in the same solvent it is necessary to do so at the same value of d. The actual value of d chosen is not critical within the range 2—8 Å, but a convenient value is q, the Bjerrum critical distance, which is 3·58 Å in water at 25 °C. We accept that for many salts q is less than the sum of the crystallographic radii. However, when a unique position of best fit was obtained for any salt it occurred at a d value below 3·5 Å for the Pitts equation or 4·5 Å for the Fuoss–Hsia equation, both of which are often significantly less than the sum of the crystallographic radii. Consequently we believe that d cannot be interpreted as a physically meaningful distance, but that it is primarily a property of the charge on the ions and the dielectric constant of the solvent.

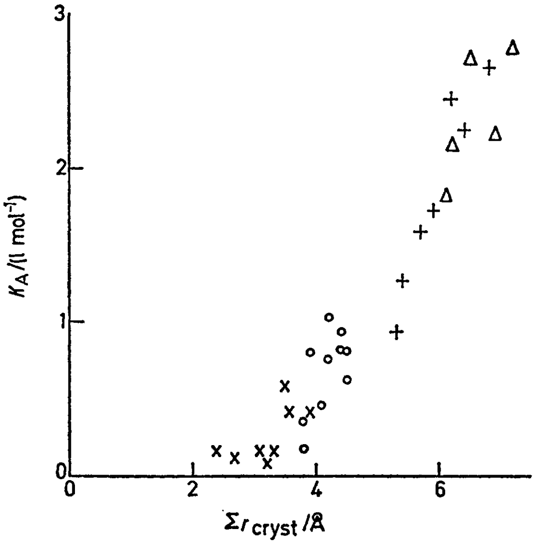

FIGURE 2

In Figure 2 we have plotted $K_{\rm A}$ for various categories of salts at q against the sum of the estimated crystal radii of the constituent ions.[21] Values of $K_{\rm A}$ at $d = 2q$ show the same trend, but are all *ca.* 1·0 l mol^{-1} higher. If d is increased gradually from q for small ions to $2q$ for larger ions the trend demonstrated in Figure 2 is therefore accentuated. Apart from our results for the complexes, only those salts are included where two independent sets of precise results are in good agreement. A more complete examination of all results in the literature will be published later and we are at present studying those salts for which satisfactory data do not exist.

Figure 2 shows clearly that $K_{\rm A}$ values at the Bjerrum distance are strongly correlated with the sum of the crystallographic radii of the two ions. A similar correlation is revealed if $K_{\rm A}$ is plotted against the total surface area of the two ions. This correlation holds for such different classes of salts as alkali halides (×), alkali oxy-salts and $AgNO_3$ (○), and tetra-alkylammonium halides (+). Even salts of the complex ion *trans*-$[Co(en)_2(NO_2)_2]^+$ (△) are not associated to an extent greater than that predicted by their size. The only salts that we have found well off the line are TlCl ($\Sigma_{\rm cryst} = 3{\cdot}2$ Å, $K_{\rm A} = 3{\cdot}88$ l mol^{-1}) where a small covalent interaction is suspected, and the higher tetra-alkylammonium iodides, *e.g.* Bu_4NI ($\Sigma_{\rm cryst} = 7{\cdot}1$ Å, $K_{\rm A} = 5{\cdot}21$ l mol^{-1}) where some form of mutual polarization may occur. The trend of $K_{\rm A}$ with ion size shown in Figure 2 is the reverse of that predicted by the Bjerrum theory of association. While this theory is extremely useful for higher valency electrolytes in water and all electrolytes in solvents of lower dielectric constant, Robinson and Stokes[22] have pointed out that this theory can only be expected to be valid when the association sphere is large enough to contain many solvent molecules and can be treated as a continuum. This is not the case with 1:1 electrolytes in water and our calculations indicate that for such systems the association constants, which reflect the breakdown of the continuum model for long-range forces at short interionic distances, may well be simply related to the probability of a collision or near-collision which, in turn, depends on the size of the two ions involved.

One of us (D.J.S.) thanks the S.R.C. and the University of Reading for financial support.

(*Received, 7th February* 1974; *Com.* 169.)

---

[1] E. M. Hanna, A. D. Pethybridge, J. E. Prue, and D. J. Spiers, *J. Solution Chem.*, in the press.
[2] E. Pitts, *Proc. Roy. Soc.*, 1953, *A*, **217**, 43; E. Pitts, B. E. Tabor, and J. Daly, *Trans. Faraday Soc.*, 1969, **65**, 849.
[3] R. M. Fuoss and K.-L. Hsia, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **57**, 1550; 1968, **58**, 1818.
[4] W. C. Duer, R. A. Robinson, and R. G. Bates, *J.C.S. Faraday I*, 1972, **68**, 716.
[5] Y. C. Chiu and R. M. Fuoss, *J. Phys. Chem.*, 1968, **72**, 4123.
[6] T. Shedlovsky, A. S. Brown, and D. A. MacInnes, *Trans. Electrochem. Soc.*, 1935, **66**, 165.
[7] H. E. Gunning and A. R. Gordon, *J. Chem. Phys.*, 1942, **10**, 126.
[8] N. C. C. Li and H. Fang, *J. Amer. Chem. Soc.*, 1942, **64**, 1544.
[9] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, 1945, **13**, 473.
[10] B. B. Owen and H. Zeldes, *J. Chem. Phys.*, 1950, **18**, 1083.
[11] W. P. Smith and C. R. Estes, *Proc. S. Dakota Acad. Sci.*, 1952, **31**, 237.
[12] N. G. Foster and E. S. Amis, *Z. Phys. Chem. Frankfurt*, 1955, **3**, 365.
[13] A. N. Campbell and L. Ross, *Canad. J. Chem.*, 1956, **34**, 566.
[14] J. E. Lind and R. M. Fuoss, *J. Phys. Chem.*, 1961, **65**, 999.
[15] C. G. Swain and D. F. Evans, *J. Amer. Chem. Soc.*, 1966, **88**, 383.
[16] J.-C. Justice, *J. Chim. Phys.*, 1968, **65**, 353.
[17] R. Bury, M.-C. Justice, and J.-C. Justice, *J. Chim. Phys.*, 1970, **67**, 2045.
[18] J. H. Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 855.
[19] Ref. 18, data smoothed to rounded concentrations.
[20] R. Bury and J.-C. Justice, *Compt. rend.*, 1965, **260**, 6089.
[21] R. A. Robinson and R. A. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, 2nd Edn., p. 125, 461; 'Interatomic Distances,' Chemical Society Special Publications, London, No. 11, 1958; No. 18, 1965.
[22] Ref. 21, p. 421.