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Senior Reporter
G. J. Hills, *Department of Chemistry, University of Southampton*

Reporters
A. Bewick, *University of Southampton*
A. K. Covington, *University of Newcastle upon Tyne*
A. D. Graves, *Imperial College, London*
D. Inman, *Imperial College, London*
T. H. Lilley, *University of Newcastle upon Tyne*
D. Pletcher, *University of Southampton*
D. J. Schiffrin, *University of Southampton*
R. S. Sethi, *Imperial College, London*

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Foreword

This is the first of a series of reports which will attempt to summarise in a comprehensive and authoritative way the progress of research in electrochemistry. Unlike some of the other subjects now being reviewed in this way, electrochemistry is a wide and diverse discipline encompassing a range of different interests, different theoretical treatments and different experimental procedures. It is closely connected to the general study of solutions, to surface chemistry, to reaction kinetics and to biophysics, to name only four other widely ranging subject areas. Inspection of the number of related papers and of the differing degrees of progress within each aspect of electrochemistry suggested that a blanket review, *i.e.* an extension in depth of *Annual Reports on the Progress of Chemistry*, was not desirable and this *Specialist Periodical Report* was conceived as something closer to the *Annual Review of Physical Chemistry*, in which selected areas are chosen for review, at a frequency appropriate to the field and, especially, by known specialists in each of the separate aspects. A number of areas were chosen and six of these are the subject of this first number. More will be added as the initial difficulties of commencing a periodical review are overcome. It is not intended that the articles should reach the depth of comprehension of those periodic reviews in, say, 'Advances in Electrochemistry and Electrochemical Engineering' but they will eventually appear with sufficient frequency to represent a comprehensive survey of the recent literature.

As implied above, the starting up of a *Specialist Periodical Report* is not a particularly easy task. Competent specialist reviewers are busy people and not everyone is able to keep to their promised schedule. Undue delay in awaiting completed articles then jeopardises the timeliness of existing material and the Chemical Society has been more than patient with the problems of this particular report.

All the work reported here covers 1968 and a large part of 1969. All subsequent reviews of these subject areas will be contiguous with the present articles.

G.J.H.

Contents

Chapter 3 The Conductance of Electrolyte Solutions

Chapter 4 Organic Electrochemistry—Synthetic Aspects

Chapter 5 Electrochemistry of Molten Salts

1
Electrolyte Solutions

BY A. K. COVINGTON AND T. H. LILLEY

PART I: Thermodynamic Properties of Electrolyte Solutions

1 Introduction

In the period under review water has remained the most studied solvent system, although more thermodynamic studies are being made using the newer protic and aprotic solvents. A major preoccupation has been with ion-solvent interactions and particularly with 'solvent structure effects', a loose phrase which, as Atkinson has said,[1] may be no more than a collective repository for our ignorance whilst we are still forced to retain a continuum theory of ion–ion interactions. In the following sections it will be noted that tetra-alkylammonium salts have been extensively studied by nearly all available techniques and much discussion has revolved around interactions between large tetra-alkyl ammonium ions and the solvent. Whilst we are still a long way from a complete understanding of the factors involved, progress is being made particularly by modern spectroscopic techniques and for this reason we devote a separate section entirely to discussion of this topic.

In order to improve their knowledge of non-ionic solution interactions a number of 'electrolyte' physical chemists have turned their attention to aqueous *non*-electrolyte solutions.[2—6] Kineticists too, have become more concerned with attempts to understand the effect of environmental factors on ionic reactions. The proceedings of a symposium held in Newcastle in January 1968 which brought together those with a common interest in hydrogen-bonded solvents, have been published,[7] as have lectures presented at an earlier meeting held in Bradford.[8] 'Solute–Solvent Interactions' is the title

[1] G. Atkinson, in 'Hydrogen-Bonded Solvent Systems', ed., A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 269.
[2] R. H. Stokes, *Austral. J. Chem.* 1968, **21**, 1343.
[3] A. Ben-Naim, *J. Phys. Chem.* 1968, **72**, 2998.
[4] H. S. Frank and F. Franks, *J. Chem. Phys.* 1968, **48**, 4746.
[5] C. V. Krishman and H. L. Friedman, *J. Phys. Chem.* 1969, **73**, 1572.
[6] G. Barone, V. Crescenzi, A. M. Liquori, and F. Quadrifoglio, *J. Phys. Chem.* 1967, **71**, 984.
[7] 'Hydrogen-Bonded Solvent Systems', ed., A. K. Covington and P. Jones, Taylor and Francis, London, 1968.
[8] 'Physicochemical Processes in Mixed Aqueous Solvents', ed., F. Franks, Heinemann, London, 1967.

of a collection of essays[9] centred around, rather than on, this theme. A review of hydration effects and the thermodynamic properties of ions has recently appeared.[10] A review[11] essentially complementary to the present one has appeared in Annual Reports on the Progress of Chemistry for 1968.

'Structure and Properties of Water' is the title of a book by Eisenburg and Kauzmann[12] and of a review by Ives and Lemon.[13] Views on this subject remain subjective and often controversial. The translation of the proceedings of a conference held in Tbilisi in 1966 on 'Water in Biological Systems' has been published[14] and contains articles by Gurikov on 'Water Structure' and by Samoilov on the 'Theory of Hydration in Aqueous Solutions'. Franks[15] has reviewed the role of water structure in disperse systems. A computer-compiled bibliography of papers covering the period 1957—68 on water structure and the physical properties of water is available[16] from Bell Telephone Laboratories, Murray Hill, New Jersey. Anomalous, meta or poly-water so-called, has aroused considerable interest even though it was first reported by Deryagin[17,18] in 1962. It is confidently expected to be the subject of a number of papers in 1970 whilst arguments continue about its observed physical properties[18—23] and structure.

The viscosity of (ordinary) water up to 1400 kg cm^{-2} and moderate temperatures (2—30 °C) has been reported.[24] Recent data are considered to be in error.[25] Kay and co-workers[26] have traced discrepancies in reported values for the dielectric constant (ε) of water at various temperatures to a doubtful capacitance correction. The preferred values are given by the equation:

$$\log \varepsilon = 1{\cdot}94409 - 1{\cdot}991 \times 10^{-3} T$$

[9] 'Solute–Solvent Interactions', ed., J. F. Coetzee and C. D. Ritchie, Dekker, Maidenhead, 1969.
[10] J. E. Desnoyers and C. Jolicoeur 'Modern Aspects of Electrochemistry', ed., J. O'M. Bockris and B. E. Conway, Plenum, New York, 1969, vol. 5.
[11] A. D. Pethybridge and J. E. Prue, *Ann. Reports* 1968, **65**, 129.
[12] D. Eisenburg and W. Kauzmann, 'The Structure and Properties of Water', Oxford Univ. Press, 1969.
[13] D. J. G. Ives and T. H. Lemon, *R.I.C. Rev.* 1968, **1**, 62.
[14] 'Water in Biological Systems', ed. L. P. Kayushin, Consultants Bureau, New York, 1969.
[15] F. Franks, *Chem. and Ind.*, 1968, 560.
[16] 'Structure of Water and Physical Properties of Liquid Water (1957–68)', ed. E. S. Turner, Bibliography No. 24, Bell Telephone Labs., Murray Hill, 1969.
[17] B. V. Deryagin, *Discuss Faraday Soc.* 1966, **42**, 109, 321.
[18] B. V. Deryagin, *Bull. U.S.S.R. Chem. Sci.*, 1967, **10**, 2095 (Engl. trans.).
[19] E. Willis, G. K. Rennie, C. Smart, and B. A. Pethica, *Nature* 1969, **222**, 159.
[20] L. J. Bellamy, A. R. Osborne, E. R. Lippincott. and A. R. Bandy, *Chem. and Ind.* 1969, 686.
[21] E. R. Lippincott, R. R. Stromberg, W. H. Grant, and G. L. Cessac, *Science*, 1969, **164**, 1482.
[22] R. W. Bolander, J. L. Kassner, and J. T. Zung, *Nature* 1969, **221**, 1233.
[23] S. R. Erlander, *Phys. Rev. Letters* 1969, **22**, 177.
[24] E. M. Stanley and R. C. Batten, *J. Phys. Chem.* 1969, **73**, 1187.
[25] R. A. Horne and D. S. Johnson, *J. Phys. Chem.* 1966, **70**, 2182.
[26] R. L. Kay, G. A. Vidulich, and K. S. Pribadi, *J. Phys. Chem.* 1969, **73**, 445.

A minimum has been reported[27] in the Kerr constants for H_2O and D_2O near 30 °C, which doubtless is related to structural features. Recalculations of the heat capacity of water at constant volume have been given[28] which are important for testing models of liquid water. Energies of proton solvation have been derived[29] from studies of the generation of protonated water molecules in a high pressure gaseous ion source.

Two other solvents of considerable current interest, dimethyl sulphoxide (DMSO) and dimethylsulphone, have been studied[30] by neutron inelastic scattering and by *X* rays. Similarity of liquid and solid spectra shows a high degree of dipole association. The effect of these solvents on water structure was also studied. *X*-Ray studies are also reported[31] of formamide and of potassium iodide solutions in formamide. It was concluded that concentrated solutions show ion-pair formation and doubly solvated cations.

Physical properties of solvents reviewed, or newly reported, include dimethyl sulphoxide,[32,33] *N*-methyl acetamide and its mixtures with dioxan and benzene (dielectric constants),[34] *N*-methyl propionamide[35] (density and dielectric constants, 20—40 °C) and sulpholan (tetramethyl sulphone) and its mixtures with water and methanol (density, viscosity, and dielectric constant).[36]

Gillespie has reviewed[37] his recent work with the highly acidic solvent, fluorosulphuric acid, in which such interesting ionic species as I_2^+ (red), I_4^{2-}, Se_8^{2+} (green), Se_4^{2+} (yellow) and Te_4^{2+} (red) have been shown to exist. A successful synthesis of perbromates has been reported[38] by electrolytic oxidation of bromate, and rubidium perbromate has been isolated from the chemical oxidation of bromate with xenon difluoride. Zordan and Hepler[39] present a critical Latimer-type compilation of data for manganese and its ions.

2 Single Electrolytes

A. Activity and Osmotic Coefficients.—Cation responsive glass electrodes (see Chapter 2) are now sufficiently well established as reliable electrodes that, with care, they can be used for precise determination of activity coefficients. Such measurements are always made relative to some chosen standard concentration in the same way as determination of activity coefficients from cells

[27] Y. Chen and W. H. Orttung, *J. Phys. Chem.* 1968, **72**, 3069.
[28] N. Dass and N. C. Varshneya, *J. Phys. Soc. Japan* 1968, **25**, 1452.
[29] M. Depas, J. J. Leventhal and L. Friedman, *J. Chem. Phys.* 1968, **49**, 5543.
[30] C. J. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady and E. F. X. Lyden, *J. Chem. Phys.* 1969, **50**, 2140.
[31] R. J. Desandro and G. H. Brown, *J. Phys. Chem.* 1968, **72**, 1088.
[32] J. N. Butler, *J. Electroanalyt. Chem.* 1967, **14**, 89.
[33] A. Collumeau, *Bull Soc. chim. France*, 1968, 4317.
[34] O. D. Bonner, G. B. Woolsey and R. H. Philp, *J. Chem. and Eng. Data* 1968, **13**, 218.
[35] T. B. Hoover, *J. Phys. Chem.* 1969, **73**, 57.
[36] E. Tommila, E. Lindell, M. L. Virtalaine and R. Laakso, *Suomen Kemi* 1969, **42**, 95.
[37] R. J. Gillespie, *Accounts Chem. Res.* 1968, **1**, 202.
[38] E. H. Appleman, *J. Amer. Chem. Soc.* 1968, **90**, 1900.
[39] T. A. Zordan and L. G. Hepler, *Chem. Rev.* 1968, **68**, 737.

with transport and transport numbers. Hostetler, Truesdell, and Christ[40] report activity coefficients for potassium chloride in the range 10—50 °C using potassium-sensitive glass electrodes. A rather complicated graphical method of evaluation was devised to eliminate the effects of e.m.f. drifts with time. Truesdell[41] has reported similar determinations for sodium chloride, where such elaborate analysis is unnecessary because of the better behaviour of the sodium-responsive electrode. Because of interference from hydrogen ions, the pH of the solutions is important. Schindler and Waelti,[42] using a small quantity of added 'tris' to buffer the solution, have confirmed accepted values for sodium chloride activity coefficients in the range 0·13—2·2 molal. A paper by Shatkay and Lerman[43] also reports some measurements on sodium chloride solutions using sodium selective and silver–silver chloride electrodes. Activity coefficients of ammonium nitrate in liquid ammonia at −30 °C were obtained[44] from hydrogen electrode concentration cell measurements and previously determined transport numbers.

Salomon reports activity coefficients from e.m.f. work for lithium chloride and bromide in propylene carbonate[45] and lithium bromide in anhydrous DMSO.[46] Lithium metal and amalgamated thallium–thallium halide electrodes were used. Butler and co-workers[47] have determined activity coefficients for lithium chloride in anhydrous DMSO from e.m.f. measurements and also studied the same system by cryoscopy. Their results, however, are at variance with those of Garnsey and Prue,[48] and Dunnett and Gasser.[49] It is suggested[48] that systematic errors are present in the latter two investigations, possibly due to heat transfer effects giving rise to spurious steady temperatures for periods up to thirty minutes. This view is contentious but the differences do not arise from use of the wrong cryoscopic constant. $\lambda_c = 4{\cdot}07$ kg mol^{-1} K was determined[48] from measurements with benzoic acid. Whereas the value used by Dunnett and Gasser[49] was higher (4·36), their raw results of freezing point depression are up to 0·02° higher than those of Garnsey and Prue.[48] The latter workers[48] also report cryoscopic measurements on alkali-metal perchlorates and lithium chloride in sulpholan (tetrahydrothiophene-1,1-dioxide). The advantages of the large cryoscopic constant ($\lambda_c = 64{\cdot}1 \pm 0{\cdot}2$ kg mol^{-1} K) are largely illusory[48] for thermal buffering is poor and differences in the solidus and liquidus slopes are small. DMSO and sulpholan are solvents of different powers of ionic solvation even though they have the same dielectric constant, with the result that the opposite sequence of osmotic coefficients with cationic radius for the alkali-metal perchlorates is observed. These

[40] P. B. Hostetler, A. H. Truesdell and C. L. Christ, *Science* 1967, **155**, 1537.
[41] A. H. Truesdell, *Science* 1968, **161**, 884.
[42] P. Schindler and E. Waelti, *Helv. Chim. Acta* 1968, **51**, 539.
[43] A. Shatkay and A. Lerman, *Analyt. Chem.* 1969, **41**, 514.
[44] J. Baldwin and J. B. Gill, *Chem. Comm.* 1968, 1537.
[45] M. Salomon, *J. Phys. Chem.* 1969, **73**, 3299.
[46] M. Salomon, *J. Electrochem. Soc.* 1969, **116**, 1392.
[47] G. Holleck, D. R. Cogley and J. N. Butler, *J. Electrochem. Soc.* 1969, **116**, 952.
[48] R. Garnsey and J. E. Prue, *Trans. Faraday Soc.* 1968, **64**, 1206.
[49] J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.* 1965, **61**, 622.

perchlorates are incompletely dissociated in sulpholan and there are large differences in the association behaviour of lithium chloride and bromide in this solvent.[48] Another paper[50] reviews the properties of sulpholan as a solvent for cryoscopy.

Russian workers report[51,52] some new determinations and some recalculations of osmotic coefficients from cryoscopic measurements for alkali-metal halides, chlorates, and bromates in aqueous solution. Bonner, Kim, and Torres[53] have carried out cryoscopic studies of various solutes in ethylene carbonate and *N*-methyl acetamide (NMA). They note that the order of osmotic coefficients for the alkali-metal iodides (Li > Na > K > Rb > Cs) is the same for these two solvents as in water at any fixed concentration. Further the osmotic coefficient of bis-trimethylammonium iodide is nearly the same as in water. Since this can be considered as a dimer of tetramethylammonium iodide they conclude there is no structure enforced ion-pairing in aqueous solutions of tetra-alkylammonium salts.[53]

Comparative (isopiestic) vapour pressure measurements are more popular than direct measurements but a few such determinations have been reported. Gardner[54] has revised and extended previous work[55] on the osmotic coefficients of sodium chloride at high temperatures (125—270 °C). Previous data[55] at 1 molal were low by 2% for reasons not ascertained. Using a differential manometric method, Bus, Steinberg, and de Boer[56] have determined vapour pressures in the system D_2SO_4–D_2O, and Campbell and Oliver[57] in the systems lithium or sodium chlorate–dioxan–water. It was concluded[57] that dioxan plays a major role in ionic solvation. By a gas displacement method[58] the partial pressures of hydrogen chloride over saturated lithium chloride (13 molal) containing hydrochloric acid were determined indicating appreciable incomplete dissociation.

A useful discussion of important features for the design of isopiestic apparatus has been given by Luk'yanov,[59] who describes in detail apparatus in which equilibrium attainment is enhanced by the device of rotating the container vessel on a central pivot at an angle of *ca.* 20° to the vertical. A method[60] of double isopiestic measurement where two volatile components are employed, is somewhat restricted in its application because of solubility restrictions.

A modified isopiestic apparatus employing glass flasks instead of the more

[50] M. Della Monica, L. Jannelli and V. Lamanna, *J. Phys. Chem.* 1968, **72**, 1068.
[51] R. I. Mostkova, Yu. M. Kessler and I. V. Safonova, *Soviet Electrochem.* 1967, **3**, 454.
[52] Yu. M. Kessler, L. G. Lozhkina and R. I. Mostkova, *Soviet Electrochem.* 1967, **3**, 209.
[53] O. D. Bonner, S. J. Kim and A. L. Torres, *J. Phys. Chem.* 1969, **73**, 1968.
[54] E. R. Gardner, *Trans. Faraday Soc.* 1969, **65**, 91.
[55] E. R. Gardner, P. J. Jones and H. J. de Nordwall, *Trans. Faraday Soc.* 1963, **59**, 1994.
[56] J. Bus, H. Steinberg and T. J. de Boer, *Rec. Trav. chim.* 1968, **87**, 609.
[57] A. N. Campbell and B. G. Oliver, *Canad. J. Chem.* 1969, **47**, 2671.
[58] D. Glietenburg and M. von Stackelberg, *Ber. Bunsengesellschaft. Phys. Chem.* 1968, **72**, 565.
[59] A. V. Luk'yanov, *Siberian Chem. Journal* 1967, **67**, 707.
[60] S. K. Kharchenko, A. V. Luk'yanov and V. A. Mikhailov, *Russ. J. Phys. Chem.* 1968, **42**, 977.

usual silver or platinum dishes has been described by Wai and Yates[61] and used to determine the water activity of concentrated perchloric acid solutions extending the range of study beyond 16 molal (62—75%).

Two papers report osmotic coefficients for bivalent perchlorates. Libus and Sadowska[62] have studied manganese, cobalt, nickel, and copper perchlorates comparing their results with literature data for zinc and magnesium. Over the range 1·0—3·5 molal the osmotic coefficients of cupric and magnesium perchlorates are slightly lower than those of the other four. Pan and Ni[63] report values for cadmium perchlorate and chloride. Platford[64] has used the isopiestic method to study sodium and potassium tetraborates, sodium metaborate and fluoroborate, and boric acid. The latter behaves like a non-electrolyte up to saturation. An apparatus suitable for studies up to 80 °C has been used[65] to obtain data for potassium chloride and bromide and sodium sulphate, which can be compared with boiling-point elevation studies at reduced pressures (60 °C). Alkylsulphonium salts which are similar in behaviour to alkylammonium salts have been studied by Lindenbaum.[66]

A number of papers report the use of vapour pressure osmometers to determine osmotic coefficients.[67—70] Your reporters share the views of others who consider the accuracy of this method is often exaggerated especially if water is the solvent. Sometimes called the adiabatic isopiestic method, it depends on observation of the condensation of solvent on to droplets of solution and solvent placed separately on two identical thermistors.

Schwabe, Kretschmar, and Gartner[71] report partition measurements of uranyl perchlorate between water and some organic media from which they derive activity coefficients for uranyl perchlorate much lower (3 orders of magnitude) than those determined from isopiestic measurements by Robinson and Lim.[72] The new measurements are also supported by ultracentrifuge studies. Whilst the explanation of the abnormally high values determined isopiestically, may lie in hydrolysis, this also affects the new measurements. Since the actual experimental data are not given, it is not possible to comment further.

From distribution measurements of carboxylic acids and their sodium salts between water and butyl ether, Czeisler and Schrier[73] have derived activity coefficients for the acids and salts in the aqueous phase. Dimer formation of the acids is assumed in the organic phase.

[61] H. Wai and K. Yates, *Canad. J. Chem.* 1969, **47**, 2326.
[62] Z. Libus and T. Sadowska, *J. Phys. Chem.* 1969, **73**, 3229.
[63] K. Pan and W. Y. Ni, *J. Chim. Chem. Soc. Taipei* 1968, **15**, 69.
[64] R. F. Platford, *Canad. J. Chem.* 1969, **47**, 2271.
[65] W. T. Humphries, C. F. Kohrt and C. S. Patterson, *J. Chem. and Eng. Data* 1968, **13**, 327.
[66] S. Lindenbaum, *J. Phys. Chem.* 1968, **72**, 212.
[67] O. D. Bonner and S. J. Kim, *J. Phys. Chem.* 1969, **73**, 1367.
[68] O. D. Bonner, C. Rushing and A. L. Torres, *J. Phys. Chem.* 1968, **72**, 4290.
[69] S. Amdur, *J. Phys. Chem.* 1969, **73**, 1163.
[70] V. Halaska, L. Lochmann and D. Lim, *Coll. Czech. Chem. Comm.* 1968, **33**, 3245.
[71] K. Schwabe, R. Kretschmar and R. Gartner, *Z. phys. Chem. (Leipzig)* 1968, **238**, 391.
[72] R. A. Robinson and C. K. Lim, *J. Chem. Soc.* 1951, 1840.
[73] J. L. Czeisler and E. E. Schrier, *J. Chem. and Eng. Data* 1969, **14**, 6.

B. Volumes.—Determination of apparent and partial molal volumes from precision density measurements continues to attract considerable attention. In an important series of papers, Dunn[74–76] describes a precise dilatometric technique and reports determinations of densities of sodium chloride, potassium chloride, bromide, and iodide and also tetra-n-butyl ammonium bromide at 25 °C in the range 0·001—1·0M. The third paper[76] extends measurements to seven temperatures in the range 0—65 °C confirming the Debye–Hückel slope for volume at these temperatures for barium and calcium chlorides in addition to the alkali-metal salts mentioned above. It was noted that ϕ_v^0 (apparent molal volume at zero concentration) increases with temperature reaching maximum values at 60 °C for the 1:1 electrolytes, 35 °C for calcium chloride and 45 °C for barium chloride. The effect is attributed to changes in the water structure on temperature increase. Structural effects are often invoked to explain any anomalous behaviour that is encountered. An entertaining paper by Holtzer and Emerson[77] should be compulsory pre-reading for all those tempted to commit their fancies to print. Desnoyers[78] and co-workers, and Millero and Drost-Hansen[79] report precision determinations by float methods for 1:1 electrolytes in water. The latter paper[79] gives data for 0·1 molal solutions at 1° intervals in the range 20—40 °C. A cubic fit to this density data is differentiated[79] to yield apparent molal expansibilities. The same authors with Korson[80] find no evidence for reported anomalies in the temperature dependence of the apparent molal volume (or viscosity) of sodium sulphate near 32·5 °C. Ellis[81] has continued his work on densities of electrolyte solutions at high temperatures (up to 200 °C).

Apparent molal volumes of aqueous solutions of sodium alkyl sulphates (C_{10}—C_{14}) have been reported by Franks and co-workers.[82] ϕ_v exhibits negative deviations from the limiting law, both above and below the c.m.c. at which there is a large positive volume change. Possible explanations of the first have been summarised by Franks and Smith[83] who prefer the 'co-operative hydrophobic hydration effects' explanation. Prue and Pethybridge[11] clearly distinguish the various schools of thought on the topics of 'hydrophobic bonding' and 'hydrophobic interaction' which are current in connection with the many recent studies of tetra-alkylammonium salts over the past few years. Other opinions on these topics can be found in the proceedings of a symposium on 'Hydrogen-Bonded Solvent Systems'.[84] Desnoyers and

[74] L. A. Dunn, *Trans. Faraday Soc.* 1966, **62**, 2348.
[75] L. A. Dunn, *Trans. Faraday Soc.* 1968, **64**, 1898.
[76] L. A. Dunn, *Trans. Faraday Soc.* 1968, **64**, 2951.
[77] A. Holtzer and M. F. Emerson, *J. Phys. Chem.* 1969, **73**, 26.
[78] J. E. Desnoyers, M. Arel, G. Perron and C. Jolicoeur, *J. Phys. Chem.* 1969, **73**, 3346.
[79] F. J. Millero and W. Drost-Hansen, *J. Chem. and Eng. Data* 1968, **13**, 330.
[80] F. J. Millero, W. Drost-Hansen and L. Korson, *J. Phys. Chem.* 1968, **72**, 2251.
[81] A. J. Ellis, *J. Chem. Soc.* (A), 1968, 1138.
[82] F. Franks, M. J. Quickenden, J. R. Ravenhill and H. T. Smith, *J. Phys. Chem.* 1968, **72**, 2668.
[83] F. Franks and H. T. Smith, *Trans. Faraday Soc.* 1967, **63**, 2586.
[84] B. E. Conway, F. Franks, R. L. Kay, H. G. Hertz and others, 'Hydrogen-Bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor and Francis, London, 1896.

Arel[85] find that plots of $\phi_v - 1{\cdot}86\ c^{\frac{1}{2}}$ versus c are linear for RNH_3Br where R = H to octyl, which they take as evidence that dimerisation cannot explain a minimum and subsequent increase in ϕ_v for $R \geqslant C_7$. Millero and Drost-Hansen[86] report measurements of ϕ_v for R_4HCl where R = H to n-butyl at 1° intervals between 20—40 °C at one concentration only. Broadwater and Evans[87] find that the behaviour of octane-1,8-bi-(tri-n-butylammonium)di-bromide is similar to that of n-butylammonium bromide. The former is considered as a model for a cation–cation pair which is another possible explanation[83] of observed 'hydrophobic hydration' effects. Conway and Laliberté[88] have determined the isotope effect for alkali metal and tetra-alkylammonium salts in light and heavy water. A positive effect $V_2°(D_2O) > V_2°(H_2O)$ is found for structure-making ions (tetra-alkylammonium) and negative for structure breaking ions (sodium fluoride). Since the sizes of H_2O and D_2O are identical it is considered that the differences must reflect the degree to which the solutes affect the structure of the solvent, and therefore D_2O is more structured than H_2O. Darnell and Greyson[89,90] using a dilatometer technique have investigated the effects of solutes on the temperature of maximum density of D_2O (t_{max} 11·17 °C *cf.* 3·98 °C for H_2O). t_{max} is reduced by all salts in both isotopic waters by an extent proportional to the solute concentration. Lithium chloride reduces t_{max} in both solvents and therefore is considered to be a structure breaker at this temperature (but not at 25 °C). With the exception of this salt, lowering is greater in H_2O than in D_2O, which might suggest that more structure is broken in H_2O than D_2O in spite of the fact that the latter is usually considered to be more structured. The preferred explanation for the observations that structure making effects are not found at t_{max} is unconvincing.[90]

Determinations in other media include salts in 6M-urea[91] (where it was noted that $V_2°$ values are greater than in water); tetra-alkylammonium chlorides in ethanol–water mixtures;[92] magnesium and barium perchlorates in dioxan–water;[93] alkali-metal halides in formic acid[94] (where it was noted that $V_2°$ is smaller than in water); tetra-alkylammonium iodides in *N*-methyl acetamide[95] and alkali-metal salts in *N*-methyl propionamide.[96]

Panckhurst[97] reviews the determination and interpretation of absolute

[85] J. E. Desnoyers and M. Arel, *Canad. J. Chem.* 1967, **45**, 359.
[86] F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.* 1968, **71**, 1758.
[87] T. L. Broadwater and D. F. Evans, *J. Phys. Chem.* 1969, **73**, 164.
[88] B. E. Conway and L. H. Laliberté, *J. Phys. Chem.* 1968, **72**, 4317.
[89] A. J. Darnell and J. Greyson, *J. Phys. Chem.* 1968, **72**, 3021.
[90] A. J. Darnell and J. Greyson, *J. Phys. Chem.* 1968, **72**, 3032.
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partial molal ionic volumes. He strongly criticises Zana and Yeager,[98,99] who in their interpretation of ionic vibration potentials define a quantity $\bar{V}_j$ as a partial molal volume whereas it should be an apparent molal volume. He considers that the coincidence of values for V_H^0+ obtained by Zana and Yeager[98] and by Conway, Verrall, and Desnoyers[100] is quite fortuitous. The latter workers extrapolate partial molal volumes for tetra-alkylammonium halides (R_4NX) against molecular weight of the cation linearly to zero (ignoring $R = H^+$) but Panckhurst considers that other abscissa such as number of carbon atoms per chain, sum of atomic numbers per cation would give equally plausible linear plots but *different* intercepts. Whilst the plot against molecular weight requires justification not so far given, the other plots are not equally reasonable as considered by Panckhurst.[101]

Glueckauf[102] has modified his previous treatment of the molar volumes of ions valid up to 200 °C to include an additional factor which reduces the local water compressibility as a function of the increase in field strength.

C. Calorimetric Measurements.—Heat measurements continue to be popular following a rebirth of activity in the early 60's. Heats of solution and dilution of adequate precision are still lacking for many common electrolytes, particularly dilution studies at low concentrations. Garrod and Herrington[103] discuss generally the behaviour of partial molal quantities at low concentration and point out that for strong electrolytes both $\partial X_1/\partial_m$ and $\partial X_2/\partial_m \rightarrow \infty$ as $m \rightarrow 0$, where X = V or H. Hence the often suggested practice of plotting an integral heat of solution against m and extrapolating to $m = 0$ with zero slope to find ΔH^∞ is incorrect. Enthalpy measurements are often combined with free energy measurements to yield entropies. Hepler and co-workers[104] report heats of solution for copper, ferrous, zinc, and cadmium sulphates and their hydrates, which they combine with literature data to yield free energies and hence standard potentials for metal–bivalent metal ion couples, which are often difficult to measure electrochemically. For example for the (Stockholm) standard potential $E^0(Fe^{2+}/Fe) = -0{\cdot}47 \pm 0{\cdot}01$ V was obtained, which is more negative than all direct measurements. Enthalpies of solution of hydrates of zinc, nickel, and manganese perchlorates,[105] lanthanide iodates,[106] and ammonium bromide,[107] and of dilution and solution of aqueous solutions of various substituted methylammonium halides[108] have been reported. Tetra-alkylammonium halides have been the subject of heats of solution

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measurements[109] in water and in *NN*-dimethylformamide at 25 °C. Results for a series of salts in anhydrous ethylenediamine[110] have been compared with data obtained by Held and Criss[111] for the same salts in *N*-methylformamide and *NN*-dimethylformamide. Salts having cations which permit ligand formation with ethylenediamine show large heat effects[110] as might be expected.

From integral heat measurements over a temperature range, partial molal heat capacities can be obtained, a method much used by Cobble.[112] His former associate Ahluwahlia and co-workers have used the method to obtain results for tetra-alkylammonium halides[113] and sodium tetraphenylborate.[114] For the latter,[114] values of the change in heat capacity on solution and the partial molal heat capacity at infinite dilution (C_2^0), are positive and larger than those for any other solute so far studied. Deviations from the anticipated linear variation of heat of solution of sodium tetraphenylborate with temperature, lead to discontinuities in the derived functions. Although the deviations are outside the authors' estimated accuracy of their measurements, your Reporters remain unconvinced, particularly as they have experienced difficulty with purification of tetraphenylborates. Cobble and co-workers[115] describe the construction of a pure titanium twin, high pressure, solution calorimeter capable of operation to 200 °C, and report measurements on sodium chloride solutions in the range 100—200 °C. Ackermann and co-workers[116] present apparent molal heat capacity data for various alkali-metal halides and alkylammonium chlorides obtained directly from precise heat capacity measurements, and note that there is generally good agreement between C_2^0 data by the direct method and that based on heats of solution measurements over a small temperature range. There are, however, discrepancies of 4—6 cal mol^{-1} K^{-1} for sodium chloride.[115] Heat capacity measurements for tervalent nitrates have been published by Russian workers.[117] Use of heat capacity data and the results of calorimetric titration studies are discussed in later sections.

D. Solubility.—In a review of the standard free energies of solution of anhydrous salts in water, Johnson[118] suggests that a salt should be very soluble when there is a severe mismatch in cation and anion size; very large ions ensure low lattice energies and the free energy of hydration of a small ion is then nearly enough to bring about solution. This is not so for the larger polyatomic organic cations and presumably anions too. Davies and co-

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