

Specific Interactions of Tetra-alkylammonium and Alkali Metal Cations with Anions in Aqueous Solutions

By J. E. PRUE, A. J. READ AND G. ROMEO

Dept. of Chemistry, The University, Whiteknights, Reading

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Precise measurements with electrochemical cells give specific interaction coefficients of tetra-alkylammonium ions with hydroxide and acetate ions in aqueous solution. Those with the hydroxide ion are useful in further analysis of specific kinetic salt effects of tetra-alkylammonium ions on the hydroxide-ion-catalyzed depolymerization of diacetone alcohol. Values of the specific interaction coefficients of tetra-alkylammonium cations with anions are tabulated and discussed in relation to corresponding values for alkali metal cations. A qualitative interpretation of trends in the coefficients is given in terms of ion-solvent competition, without invoking so-called "structural" explanations.

The isopiastically determined osmotic coefficients¹ of aqueous tetra-alkylammonium fluoride solutions at a molality of 0.1 and 25°C vary from 0.945 for the tetramethyl salt to 1.04 for the tetrabutyl salt, whilst tetramethylammonium iodide solution has a value of 0.885 and the corresponding tetrapropyl salt one of 0.530. This range of values is much wider than that usually found for 1:1 salts in water.² The value for sodium chloride at this molality is 0.932; the Debye-Hückel equation predicts 0.918 for an electrolyte with an ion-size parameter of 3.0 Å. Large deviations from Debye-Hückel behaviour, specifically dependent on the anion, were first discovered for tetra-alkylammonium salts by cryoscopic measurements.³ A kinetic manifestation of the same phenomenon was studied by Halberstadt and Prue.⁴ For example, although the salt effect of the potassium ion on the rate constant for the reaction of the hydroxide ion with diacetone alcohol is extremely small, the constant is increased by about 10 % in the presence of 0.1 M tetraethylammonium ion. This is presumably due to a difference in the specific interactions of the cation with the hydroxide ion and with the singly-negatively-charged activated complex.

A convenient quantitative description of specific behaviour is provided for both dilute⁵ and more concentrated⁶ solutions by specific interaction coefficients, which are also particularly useful for mixed electrolyte solutions.⁶ Activity coefficients of singly charged ions in mixed solutions are given by equations of the type⁵

$$-\log \gamma_i = AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - \sum_j B_{ij}m_j/2, \quad (1)$$

where I is the ionic strength, A is the Debye-Hückel parameter, and B_{ij} is a specific interaction coefficient. The summation extends over all ions j of the opposite charge to an ion i . These specific interaction coefficients for the alkali metal fluorides, acetates and hydroxides become increasingly positive with increasing cation size, but the reverse is true of the other halides and for oxyanions with a well-dispersed charge.⁶ This inversion of the sequence of activity coefficients is well known, and one qualitative explanation which has been suggested⁷ is based on an ion-solvent competition model.

The range of specific interaction coefficient values so far known⁸ for tetra-alkylammonium salts (+0.7 to -1.6 kg mol^{-1}) is much wider than normal (*ca.*

$0.1 \pm 0.2 \text{ kg mol}^{-1}$).⁶ Within the halides, an inversion of sequence occurs between chloride and bromide. In this paper we report e.m.f. measurements at 25°C on the cells



which are analyzed to give specific interaction coefficients of tetra-alkylammonium ions with hydroxide and acetate ions. Kinetic salt effects are then further discussed, and some comments made on the physical interpretation of specific interaction coefficients.

EXPERIMENTAL

Tetra-alkylammonium chlorides were prepared and purified as follows. Solutions of commercial iodides were shaken with an excess of silver oxide for at least 24 h. The silver oxide was prepared from A.R. silver nitrate and sodium hydroxide and thoroughly washed with hot water. The tetra-alkylammonium hydroxide solutions were filtered free of silver iodide and excess silver oxide and exactly neutralized with bromide-free hydrochloric acid solution. The salts were crystallized, dried and precipitated with ether from solution in chloroform or ethanol. This was repeated at least twice. The concentrations of aqueous stock solutions were determined by titration against standard silver nitrate solution.

Stock solutions of tetra-alkylammonium hydroxide were alternatively prepared from the solutions of the corresponding recrystallized commercial iodides by passage through a column of De-Acidite FF-IP in the hydroxide form. The concentrations were determined by weight titration against A.R. potassium hydrogen phthalate. Some of the mixed chloride+hydroxide solutions were prepared by partial neutralization of the hydroxide stock solution with hydrochloric acid solution standardized by weight titration against tris(hydroxymethyl)-aminomethane.⁹ Care was taken to exclude carbon dioxide in the preparation of all solutions.

The exclusion of bromide and iodide is always essential in precise measurements with silver/silver chloride electrodes and this is especially so in the presence of tetra-alkylammonium ions. The reason is probably connected with abnormal electrode reactions.¹⁰ One commercial sample of tetraethylammonium chloride was found by radioactivation analysis to contain about 1 % bromide, and simple recrystallization is not a satisfactory method of reducing the bromide content to a tolerable level.

The apparatus and general procedure has already been described.¹¹ The complications encountered with formic acid¹¹ were absent; only platinized electrodes were used, and the flow of hydrogen was stopped before making e.m.f. readings. The experimental procedures were tested by measurements on cells in which sodium ions replaced tetra-alkylammonium ions. Values for the ionic product of water and the acidity constant of acetic acid in accord with the best literature values were obtained from cells A and B respectively. The results with tetra-alkylammonium salts were of inferior quality, but entirely adequate for our purpose. The e.m.f. of cells were reproducible to within $\pm 0.05 \text{ mV}$.

RESULTS AND DISCUSSION

The results of measurements on cell A with $\text{NR}_4 = \text{NMe}_4$ are given in table 1. For cell A

$$\frac{E - E^\ominus}{(RT/F) \ln 10} + \log\left(\frac{b}{a}\right) = -\log K_w + \frac{0.036(a+b)}{\ln 10} - \log\left(\frac{\gamma_{\text{Cl}}}{\gamma_{\text{OH}}}\right), \quad (2)$$

where the term $0.036(a+b)/\ln 10$ takes account of the slight decrease in the water activity as $(a+b)$ increases. We define K'_w by

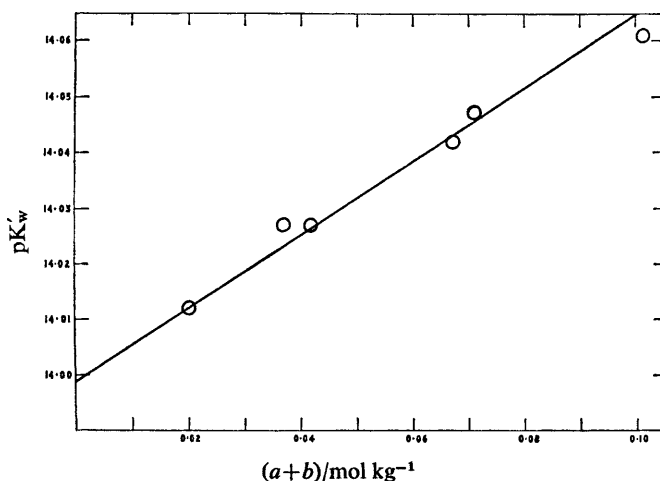
$$\log K'_w = \frac{E - E^\ominus}{(RT/F) \ln 10} + \log\left(\frac{b}{a}\right) \quad (3)$$

TABLE 1.—E.M.F. MEASUREMENTS ON CELL A.

| $10^2 a / \text{mol kg}^{-1}$ | $10^2 b / \text{mol kg}^{-1}$ | $E - E^\ominus \text{ mV}$ | $-\log (K'_w / \text{mol}^2 \text{ kg}^{-2})$ |
|-------------------------------|-------------------------------|----------------------------|---|
| 1.000 | 1.004 | 827.85 | 14.012 |
| 1.016 | 2.699 | 804.70 | 14.027 |
| *1.011 | 3.160 | 800.53 | 14.027 |
| *1.006 | 5.715 | 786.12 | 14.042 |
| *1.038 | 6.074 | 785.65 | 14.047 |
| 1.002 | 9.145 | 775.05 | 14.061 |

* average results for three independent cells in each case.

and from eqn (1) expect a plot of $\log K'_w$ against $(a+b)$ to be linear with an intercept $-\log K_w$ on the ordinate and of slope $B(\text{NR}_4\text{OH}) - B(\text{NR}_4\text{Cl}) + (0.016 \text{ kg mol}^{-1})$. This is shown in fig. 1 for $R = \text{Me}$. The value $(RT/F) \ln 10 = 59.159 \text{ mV}$ was used. The intercept agrees exactly with previous determinations of the ionic product of water and the slope of the line gives a value of $B(\text{NMe}_4\text{OH}) - B(\text{NMe}_4\text{Cl}) = 0.62 \text{ kg mol}^{-1}$.

FIG. 1.—Cell A with $R = \text{Me}$.

Corresponding values for $R = \text{Et}$ and Pr are also given in table 2. The results of measurements on cell B are given in table 3. For cell B,

$$\frac{E - E^\ominus}{(RT/F) \ln 10} + \log \left[\frac{ab(1-\delta)}{c(1+\delta)} \right] = -\log K_a - \log \left(\frac{\gamma_{\text{Cl}} \gamma_{\text{HOAc}}}{\gamma_{\text{OAc}}} \right), \quad (4)$$

where δ is a small correction applied to take account of the fact that the molalities of HOAc and OAc^- are not exactly equal to the stoichiometric molalities owing to

TABLE 2

| cation | $B(\text{NR}_4\text{OH}) - B(\text{NR}_4\text{Cl})$ kg mol^{-1} | $B(\text{NR}_4\text{Cl})$ kg mol^{-1} | $B(\text{NR}_4\text{OH})$ kg mol^{-1} | $B(\text{NR}_4\text{X})$ kg mol^{-1} |
|------------------|---|---|---|--|
| NMe_4^+ | 0.62 | -0.13 ₅ | 0.48 | 0.25 |
| NEt_4^+ | 0.56 | -0.11 | 0.45 | 0.10 |
| NPr_4^+ | 0.63 | -0.11 | 0.52 | 0.07 |

the (slight) ionization of the acetic acid (for this purpose, only an approximate value of K_a is required). We again use eqn (1) for the activity coefficients of singly charged ions in mixed solutions. Although it is common practice to ignore specific interactions between ions and acetic acid molecules, this seems particularly hazardous

TABLE 3.—E.M.F. MEASUREMENTS ON CELL B

| $10^2 a$ mol kg ⁻¹ | $10^2 b$ mol kg ⁻¹ | $10^2 c$ mol kg ⁻¹ | $E - E^\ominus$ mV | $-\log(K'_a/\text{mol kg}^{-1})$ |
|------------------------------------|----------------------------------|----------------------------------|-----------------------|----------------------------------|
| (i) $\text{NR}_4 = \text{NMe}_4$ | | | | |
| 0.2828 | 0.2758 | 0.2662 | 434.50 | 4.7584 |
| 0.5267 | 0.5724 | 0.5825 | 415.58 | 4.7588 |
| 0.9423 | 1.024 | 0.9885 | 400.85 | 4.7635 |
| 1.713 | 2.135 | 2.086 | 385.99 | 4.7676 |
| 2.443 | 3.044 | 2.975 | 377.10 | 4.7704 |
| 3.220 | 3.499 | 3.378 | 369.86 | 4.7735 |
| 4.005 | 4.991 | 4.878 | 364.83 | 4.7774 |
| (ii) $\text{NR}_4 = \text{NEt}_4$ | | | | |
| 0.4221 | 0.4957 | 0.4843 | 421.52 | 4.7574 |
| 0.6597 | 0.7450 | 0.8492 | 414.01 | 4.7588 |
| 0.6814 | 0.7696 | 0.8772 | 413.27 | 4.7605 |
| 1.431 | 1.616 | 1.842 | 394.44 | 4.7649 |
| 1.563 | 1.835 | 1.793 | 388.24 | 4.7652 |
| 2.6819 | 3.158 | 3.086 | 374.64 | 4.7709 |
| 3.515 | 3.970 | 4.526 | 372.00 | 4.7752 |
| 4.190 | 4.920 | 4.507 | 363.66 | 4.7774 |
| (iii) $\text{NR}_4 = \text{NPr}_4$ | | | | |
| 0.2725 | 0.2996 | 0.2916 | 432.91 | 4.7596 |
| 0.5134 | 0.5645 | 0.5494 | 416.70 | 4.7628 |
| 0.9690 | 1.065 | 1.037 | 400.50 | 4.7664 |
| 1.880 | 2.067 | 2.072 | 383.72 | 4.7708 |
| 2.923 | 3.294 | 3.195 | 372.59 | 4.7755 |
| 4.424 | 4.865 | 4.734 | 262.53 | 4.7836 |

when tetra-alkylammonium ions are involved, and in the further analysis of the results we have consistently introduced salting coefficients S_{ij} corresponding to B_{ij} terms to allow for interactions involving neutral molecules. We then obtain for the e.m.f. of cell B,

$$\frac{E - E^\ominus}{(RT/F) \ln 10} + \log \left[\frac{ab(1-\delta)}{c(1+\delta)} \right] + \{B(\text{NaCl}) - B(\text{NaOAc})\}c + \\ \{S(\text{NaCl}, \text{HOAc}) - S(\text{HOAc}, \text{HOAc})\}b(1-\delta) + S(\text{NaOAc}, \text{HOAc})\{c - b(1-\delta)\} = \\ -\log K_a - \{B(\text{NR}_4\text{Cl}) - B(\text{NR}_4\text{OAc}) + S(\text{NR}_4\text{Cl}, \text{HOAc})\}a. \quad (5)$$

A plot of $\log K'_a$ defined by the left-hand side of eqn (5) against a should therefore be linear. The value $B(\text{NaCl}) - B(\text{NaOAc}) = -0.07 \text{ kg mol}^{-1}$ was used and the salting coefficient values used were $S(\text{NaCl}, \text{HOAc}) = 0.06 \text{ kg mol}^{-1}$,¹² $S(\text{HOAc}, \text{HOAc}) = -0.03 \text{ kg mol}^{-1}$,¹³ and $S(\text{NaOAc}, \text{HOAc}) = 0.02 \text{ kg mol}^{-1}$.¹² The last value was determined at 100°C and may be in error, but unless it is seriously so the corresponding term in eqn (5) is in any case within the limits of experimental error. Fig. 2 shows that the plot for $R = \text{Me}$ is linear within the limits of experimental error.

To obtain from the results in the second columns of tables 2 and 4 values for $B(\text{NR}_4\text{OH})$ and $B(\text{NR}_4\text{OAc})$ respectively we first need knowledge of $B(\text{NR}_4\text{Cl})$ values. From measurements on cell A at 25°C with NR_4OH replaced by HCl a value of $B(\text{NMe}_4\text{Cl}) = -0.13_5 \text{ kg mol}^{-1}$ was obtained ($B(\text{HCl})$ is independently

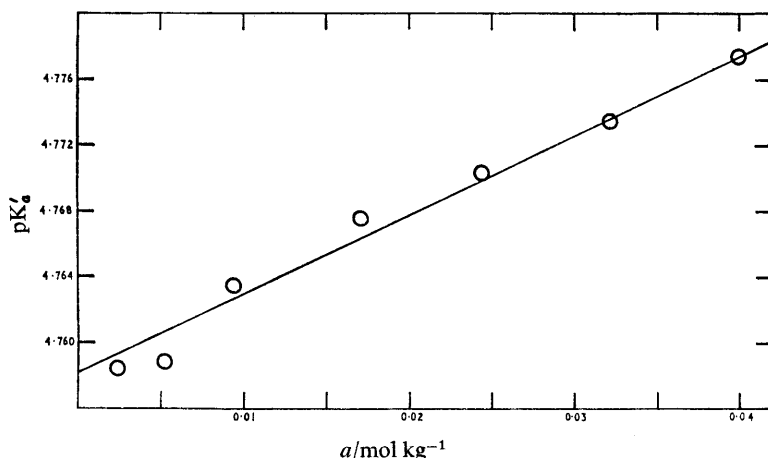


FIG. 2.—Cell B with $\text{R} = \text{Me}$

known). The agreement with a value of $-0.13 \text{ kg mol}^{-1}$ obtained ⁸ from the analysis of cryoscopic data ³ at 0°C suggests that without serious error we can use values of $B(\text{NEt}_4\text{Cl})$ and $B(\text{NPr}_4\text{Cl})$ both equal to $-0.11 \text{ kg mol}^{-1}$ also obtained from cryoscopic data.³ Approximate values of the salting coefficients $S(\text{NR}_4\text{Cl}, \text{HOAc})$ were estimated from measurements on the distribution of acetic acid between benzene and aqueous salt solutions of molalities between 0.5 and 1.0 mol kg^{-1} . The values are given in the fourth column of table 4.

TABLE 4

| cation | $\{B(\text{NR}_4\text{Cl}) - B(\text{NR}_4\text{OAc}) + S(\text{NR}_4\text{Cl}, \text{HOAc})\}$ kg mol^{-1} | $B(\text{NR}_4\text{Cl})$ kg mol^{-1} | $S(\text{NR}_4\text{Cl}, \text{HOAc})$ kg mol^{-1} | $B(\text{NR}_4\text{OAc})$ kg mol^{-1} |
|------------------|---|---|--|--|
| NMe_4^+ | -0.48 | -0.13 ₅ | $+0.12 \pm 0.06$ | 0.46 |
| NEt_4^+ | -0.53 | -0.11 | -0.03 ± 0.01 | 0.39 |
| NPr_4^+ | -0.54 | -0.11 | -0.14 ± 0.03 | 0.29 |

The values of $B(\text{NR}_4\text{OH})$ and $B(\text{NR}_4\text{OAc})$ obtained are given in tables 2 and 4. If all S coefficients are omitted in the analysis of results from cell B, the values in the final column of table 4 would be 0.34, 0.37 and 0.30 kg mol^{-1} respectively. If the possibility of specific interaction with the neutral substrate is ignored, the kinetic results of Halberstadt and Prue ⁴ give values of $B(\text{NR}_4\text{OH}) - B(\text{NR}_4\text{X})$, where X^- is the activated complex of the hydroxide-ion-catalyzed diacetone alcohol depolymerization reaction. The final column of table 2 gives values of $B(\text{NR}_4\text{X})$. The specific acceleration of the rate of reaction by added tetra-alkylammonium salts is caused by more repulsive interaction between these ions and the hydroxide ion than with the activated complex, which is an organic ion presumably with a partly dispersed charge. The difference in the specific interaction increases as the cation size increases.

Although a number of assumptions is made in arriving at our final values of specific interaction coefficients of OH^- and OAc^- with tetra-alkylammonium ions, they are likely to be reliable within $\pm 0.1 \text{ kg mol}^{-1}$, and are compared with values for other anions in table 5. For Cl^- and I^- , values calculated from cryoscopic data ³ have been quoted as they are likely to be more reliable, but they almost invariably agree within 0.1 kg mol^{-1} with values calculated ⁸ from isopiestic data at 25°C .

TABLE 5.—SPECIFIC INTERACTION COEFFICIENTS (kg mol^{-1})

| cation | OH^- | OAc^- | F^- | Cl^- | Br^- | I^- | X^- |
|------------------|---------------|----------------|--------------|---------------|---------------|--------------|--------------|
| NMe_4^+ | 0.5 | 0.5 | 0.2 | -0.1 | -0.2 | -0.4 | 0.3 |
| NEt_4^+ | 0.5 | 0.4 | 0.5 | -0.1 | -0.2 | -0.5 | 0.1 |
| NPr_4^+ | 0.5 | 0.3 | 0.5 | -0.1 | -0.3 | -0.9 | 0.1 |
| NBu_4^+ | — | — | 0.7 | +0.2 | -0.3 | -1.6 | — |

The magnitude of the interaction coefficients is larger than with the alkali metal salts but the pattern of behaviour is similar. Anions of weak acids which offer a site of high charge density show positive interaction coefficients which tend to increase with increasing cation size. Large anions have negative interaction coefficients which become increasingly so with increasing cation size. The interaction coefficients for anions with an organic component become less positive as the cation size increases.

It is interesting to enquire further into the physical significance of the specific interaction parameters. We recall that negative values of B correspond to attractive cation-anion interaction in excess of the standard Debye-Hückel value, whilst the reverse is true of positive values of B . Fig. 3 shows a plot of specific interaction

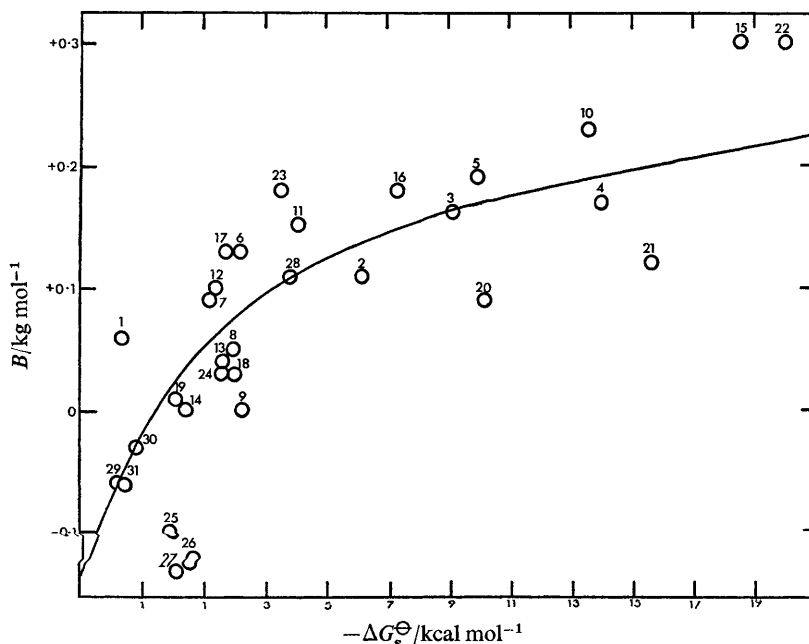


FIG. 3.—Relation between specific interaction coefficients and standard free energies of solution. Salts are NaF(1), KF(2), RbF(3), CsF(4), LiCl(5), NaCl(6), KCl(7), RbCl(8), CsCl(9), LiBr(10), NaBr(11), KBr(12), RbBr(13), CsBr(14), LiI(15), NaI(16), KI(17), RbI(18), CsI(19), NaOH(20), KOH(21), CsOH(22), LiNO₃(23), NaNO₃(24), KNO₃(25), RbNO₃(26), CsNO₃(27), NaClO₄(28), KIO₃(29), KClO₃(30), and KBrO₃(31).

coefficients for alkali metal salts against the corresponding standard free energies of solution at 25°C,¹⁴ which are an expression of the thermodynamic solubility. There is a rough but nevertheless striking parallelism. This implies that it is the competition for an ion between the solvent on the one hand and the oppositely charged ion on the other that determines the magnitude of both solubility and specific interaction coefficients. An ion-solvent competition model was discussed previously⁷ for alkali metal and alkaline earth metal salts. The competition principle has a long history and Morris¹⁵ notes that it was first due to Fajans. Fig. 9 of Morris' paper shows how the standard free energy of solution of alkali halides is a maximum (minimum solubility) when the difference between the (conventionally assigned) free energies of hydration of the cation and anion is zero. Basolo¹⁶ notes that solid salts separate from aqueous solutions most easily for combinations of either small cation-small anion or large cation-large anion. An important paper by Onsager¹⁷ points out that the fraction of the self energy of an assembly of ions released by formation of an ionic lattice is a maximum when the surface field intensities of the ions are equal, i.e., equal ionic radii of symmetrical salts. He stresses the importance of "matching" of surface fields of ion and solvent molecules in characterizing liquids which are good

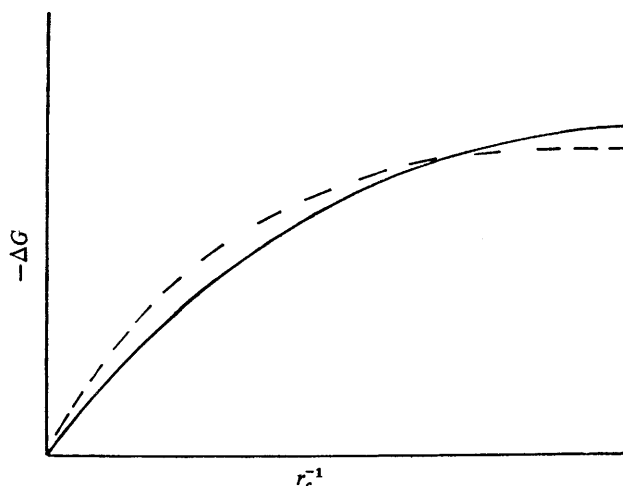


FIG. 4.—Free energies of solvent binding (—) and ligand binding (---) as a function of cation radius.

solvents for electrolytes. Large negative specific interaction coefficients (alternatively described by introducing ion association) are therefore to be expected for interactions between ions of similar surface field intensities. Turning to the trends in the specific interaction coefficients of a given anion with a series of cations, if the anion is large the change in the cation-solvent free energy of interaction as the cation size varies will be greater than the change in the free energy of interaction of the cation-anion pair. If the anion is small, the reverse will be true. The two situations will produce opposing sequences of specific interaction coefficients with ion size, and in this way one can understand how, e.g., the 11 sequences of cation preferences in glasses arise for the alkali metal cations.¹⁸ The same point has been made by Eigen and his associates¹⁹ in a discussion of binding of polydentate ligands by alkali metal cations. They point out that with the help of a schematic diagram such as fig. 4, one can see how with a free energy of ligand binding comparable with that of the solvent, the stability constant, which is given by the difference between the free energies of solvent and ligand binding, may go through a maximum at an appropriate cation size.

A qualitative interpretation of the trends of specific interaction coefficients for both alkali metal and quaternary ammonium salts can therefore be given a common explanation without the "curiously assured, yet essentially sterile, invocations of water structure that seem to be proliferating so needlessly in the literature",²⁰ This is not to deny the interesting problems concerning ion-solvent interaction posed, e.g., by the transport properties of tetralkylammonium salts (for references, see a recent review²¹), but merely in interpreting our data to adhere to the principle of introducing the minimum number of special hypotheses. We have therefore eschewed the introduction of both "icebergs" and cation-cation interactions. We suggest that the phenomena we have been discussing derive simply from the strongly dipolar character of the solvent, not from its "structure" or even its hydrogen-bonding facility.²² Comparative measurements of osmotic coefficients of alkali metal salts in dimethyl sulphoxide and in sulpholane show a change-over from an "abnormal" sequence in the former to a normal sequence in the more weakly solvating sulpholane.²³

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