The Thermodynamics of Ion Association in Solution.
I. An Extension of the Denison–Ramsey Equations

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Abstract: The Dension–Ramsey treatment of ion-pair formation has been extended, taking into account in the potential energy term the various possible interactions between ions and their induced dipoles. In addition, orientation entropy effects have been included. Internuclear distances calculated in this way from published ion-pair constants are smaller than those calculated by the Denison–Ramsey or the Bjerrum equation and were only slightly larger (~15%) than the crystallographic radii. Further extension to include higher ionic aggregates was made and the result applied to ion triplet and quadrupole formation. In these ion aggregates the calculated internuclear distances between ions are nearly the same as in ion pairs, in contradistinction to results obtained using earlier treatments. In solvents of dielectric constant less than 7 (benzene, dioxane, anisole, chlorobenzene, and tetrahydrofuran) quaternary ammonium salts do not appear to form solvent-separated ionic aggregates.

The association of ions in solvents of low dielectric constant to form ion pairs, triplet, or higher aggregates is an accepted and well-documented fact. Such ion aggregates are assumed in the quantitative treatment of many properties and reactions of electrolytes in these solvents, *e.g.*, colligative properties, conductance minima, and reaction and polymerization mechanisms. Ion-pair formation in particular has been considered at length in a review by Kraus.[1,2] An essential requirement of all such treatments is a knowledge of the extent of association, *i.e.*, the associated species formed and the association constants. Such constants can often be determined by direct study of the particular systems involved using one or more of the recognized techniques for measuring association constants. Once obtained, these constants are of only limited value in estimating the degree of association in other systems. Attempts have been made to relate association constants to properties of the solvent and solute, but all are limited in their application and can only be used under restricted conditions if the results are to have any meaning. Even it is probable that the results are misleading since they then indicate a physical picture which has much greater interionic separations than expected.

The major equations have been derived by Bjerrum,[3] extended by Fuoss and Kraus[4,5] and Denison and Ramsey,[6a] and improved by Fuoss[6b] and Gilkerson.[7] They have been discussed critically by Flaherty and Stern[8] and by Fuoss.[6b] Internuclear separations for ion pairs calculated by the Bjerrum equation are shown to be surprisingly close to those obtained from the Denison–Ramsey (D.R.) treatment for a range of solvents, but, in every case, the separation is more than one would expect for two ions in contact, strongly suggesting that the ions are somehow solvent separated. Such species have been detected elsewhere,[9] but in solvents of low dielectric constant (D) such as benzene (D = 2.274) solvation energies are very low and contact ion pairs are to be expected. A consideration of the Bjerrum equation immediately indicates that it should not be applied to such solutions at experimentally realizable concentrations. The Bjerrum association constant is expressed in terms of $(1 - \alpha)$, the degree of association, and is derived assuming α to approximate to unity, *i.e.*, in very dilute solution. This situation is unobtainable experimentally. Even in solutions as dilute as 10^{-6} M in benzene, extensive ion-pair formation, together with higher association, is found.[10] The D.R. treatment does not suffer from the same failing but, as Fuoss has pointed out,[6b,11] it does not include any orientation entropy terms. Fuoss and Accascina have made an approximation to allow for this in their revised treatment of ion triplets.[2] These are certainly important. It therefore seems probable that both treatments are limited in accuracy, and the apparent agreement between them is due to a coincidental balance of errors. Theoretically the Bjerrum treatment is less satisfactory, involving as it does an impractical definition of an ion pair. Fuoss has considered the Bjerrum function critically and pointed out its shortcomings.[6b] Further, both treatments consider only ion-pair or triplet formation although the Bjerrum treatment has been extended to cover quadrupoles.[5] We have now extended the D.R. treatment to allow for entropy changes on association and the formation of higher aggregates up to sexapoles.

Discussion

Denison and Ramsey considered the free-energy changes in the cycle

$$\begin{tikzcd}
\text{ion + ion at infinity in medium} \arrow[r, "\text{IV}"] \arrow[d, "\text{I}"] & \text{ion pair at } r_2 \text{ in medium} \\
\text{ion + ion } \textit{in vacuo} \arrow[r, "\text{II}"] & \text{ion pair } \textit{in vacuo} \arrow[u, "\text{III}"]
\end{tikzcd}$$

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[1] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

[2] See also R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

[3] N. Bjerrum, *Kgl. Danske Videnskab. Selskabs*, 7, No. 9 (1926).

[4] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933).

[5] R. M. Fuoss and C. A. Kraus, *ibid.*, **57**, 1 (1935).

[6] (a) J. T. Denison and J. B. Ramsay, *ibid.*, **77**, 2615 (1955); (b) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

[7] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[8] P. H. Flaherty and K. H. Stern, *J. Am. Chem. Soc.*, **80**, 1034 (1958).

[9] E. F. Caldin, "Fast Reactions in Solution," Blackwell, Oxford, 1964, p 94 ff.

[10] E. D. Hughes, C. K. Ingold, S. Patai, and Y. Packer, *J. Chem. Soc.*, 1206 (1957).

[11] R. M. Fuoss, *J. Am. Chem. Soc.*, 79, 3301 (1957).

and calculated the free-energy change, ΔF_{IV}, from the relationship

$$\Delta F_{IV} = \Delta F_{I} + \Delta F_{II} + \Delta F_{III} \qquad (1)$$

The quantities ΔF_I and ΔF_{III} will include the free-energy changes on solvation of the free ions and the ion pairs, respectively; the solvation energy changes were considered to be approximately the same and therefore were omitted from the calculation. This assumption is reasonable in solvents of low dielectric constant since the absolute magnitude of the solvation energy would normally be small, and the solvation energy of the ion pair, while probably being lower than that of the free ions, would probably approach the latter. Accepting this assumption, the relationship derived by Denison and Ramsey is

$$\Delta F_{IV} = \frac{N\Delta V_2}{D} \qquad (2)$$

where N is the Avogadro number and ΔV_2 the change in potential energy on formation of the ion pair. Inspection of the treatment shows that this relationship is equally applicable to more extensive ion associations and is a general expression irrespective of the degrees of association of steps I and III of the cycle, provided the assumptions concerning changes in solvation energies can still be accepted. Equation 2 will apply rigorously only at absolute zero.

To calculate the free-energy change at temperature T, we use the enthalpy

$$\Delta H^\circ = \Delta F_{IV} + RT^2\left[\frac{\partial \ln Q}{\partial T}\right]_p$$

and entropy

$$\Delta S^\circ = R \ln Q + RT\left[\frac{\partial \ln Q}{\partial T}\right]_p$$

to obtain

$$\Delta G^\circ = \Delta F_{IV} - RT \ln Q$$

where Q is a function of partition functions of the products and reactants. The term $R \ln Q$ ($=\Delta S$) includes the changes in orientational entropy (*i.e.*, changes in vibrational, rotational, and translational entropy associated with the reaction). Thus, eq 2 becomes

$$\Delta G^\circ = \Delta G_{IV} = \frac{N\Delta V_x}{D} - T\Delta S \qquad (3)$$

i.e.

$$-2.303 \log K_x = \frac{N\Delta V_x}{DRT} - \frac{\Delta S}{R} \qquad (4)$$

where both ΔV_x and ΔS will generally be negative. Association constants can therefore be calculated provided ΔV_x and ΔS are known.

Potential energy values for ion aggregates *in vacuo* have been rigorously calculated for the alkali halides. Rittner in 1951 considered ion-pair formation[12] and various other workers have considered quadrupoles[13-15] and sexapoles.[16] For an equation to be of use in calculating potential energy values, all the quantities involved must be available. We therefore set up a potential energy expression for an ion pair (AB), which allowed for all possible interactions between ions and their induced dipoles, but which included the various other forces in a general term B/r^n, where B was obtained by minimizing the expression for the energy as in the Born treatment of ionic lattices, *i.e.*

$$\Delta V_2 = -\left(\frac{e^2}{r} + \frac{\mu_A{}^e}{r^2} + \frac{\mu_B{}^e}{r^2} + \frac{2\mu_A\mu_B}{r^3} - \frac{\mu_A{}^2}{2\alpha_A} - \frac{\mu_B{}^2}{2\alpha_B}\right) + \frac{B}{r^n} \qquad (5)$$

where r is the internuclear separation and μ_A and μ_B are the induced dipole moments. Values for these dipole moments were calculated by the expressions used by Rittner. This expression for V_2 is somewhat simpler than Rittner's and does not require all the experimental quantities necessary in his treatment. Pauling calculated the potential energies of alkali halide ion pairs using a similar term, B/r^n, but n was a variable depending on the ions concerned and polarizabilities were omitted.[17] The value of n in eq 5 was adjusted by us empirically to obtain the best fit with measured potential energies of the alkali halide ion pairs[18] using reported polarizabilities[19] and internuclear separation.[20] It was found that the value of n = 6.9 gave the best agreement, particularly for the larger ions such as rubidium or cesium. For smaller ions smaller n values are required but, since most ions studied in solution are large ions, n = 6.9 was selected as the most generally reliable value. Table I shows a comparison of values for the potential energies at 0°K calculated by eq 5 compared with the values calculated from thermodynamic data,[16] the values shown in parentheses. Considering approximations inherent in the Denison–Ramsey treatment, this agreement is completely adequate for intermolecular separations greater than 2.0 A. Substantial differences are found only in the lithium and sodium fluorides which are much smaller than species encountered in solution studies. This value of n = 6.9 was assumed to apply to ion triplets, quadrupoles, sexapoles, as well as to ion pairs, and was used in all calculations described below.

Table I. Potential Energies of Gaseous Alkali Halide Ion Pairs at 0°K (kcal)

	Li	Na	K	Rb	Cs
F	195.4	159.8	139.1	133.7	129.9
	(178.2)	(144.4)	(136.5)	(131.3)	(127.3)
Cl	152.1	127.7	112.1	107.4	103.5
	(156.8)	(128.2)	(114.9)	(109.9)	(102.3)
Br	143.9	121.5	106.5	101.9	98.0
	(148.0)	(123.1)	(110.9)	(104.6)	(98.7)
I	132.3	113.4	98.9	94.9	91.0
	(138.8)	(116.0)	(103.7)	(98.4)	(89.6)

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(12) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).
(13) C. T. O'Konski and W. Higuchi, *ibid.*, **23**, 1174 (1955).
(14) T. A. Milne and D. Cubicciotti, *ibid.*, **29**, 846 (1958).
(15) J. Berkowitz, *ibid.*, **29**, 1386 (1958).
(16) T. A. Milne and D. Cubicciotti, *ibid.*, **30**, 1625 (1959).
(17) L. Pauling, *Proc. Natl. Acad. Sci.* (India), **A25**, Part I (1956).
(18) D. Morris, *Acta Cryst.*, **9**, 197 (1956); B. Barrow and A. Caunt, *Proc. Roy. Soc.* (London) **A219**, 130 (1953).
(19) J. E. Mayer and M. G. Mayer, *Phys. Rev.*, **43**, 605 (1953).
(20) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1940.

Table II. Ion-Pair Formation at 25°

					r_2, A			
Solute	Solvent	D	Log K_2	Ref	Bjerrum[a]	D.R.	Eq 4[b]	ΔS, eu
$Bu_4N \cdot Cl$	Benzene	2.27	17.00	7	5.8	6.2	4.6	−13.6
$Bu_4N \cdot ClO_4$	Benzene	2.27	16.66	7	5.8	6.3	4.6	−15.4
$Bu_4N \cdot Br$	Benzene	2.27	16.85	*c*	5.9	6.3	4.6	−15.0
$NaClO_4$	HAc	6.13	5.48	*d*	6.4	7.2	3.7	−17.4
$HClO_4$	HAc	6.13	4.87	*d*	7.6	8.1	3.8	−18.7
KCl	HAc	6.13	6.88	*d*	4.9	5.8	3.2	−16.8
$Bu_4N \cdot (C_6H_5)_4B$	THF	7.38	4.37	*e*	7.0	7.5	3.4	−17.5
$Na \cdot (C_6H_5)B$	THF	7.38	4.07	*e*	8.0	8.1	3.7	−15.4
$K \cdot (C_6H_5)_4B$	THF	7.38	4.50	*e*	6.6	7.5	3.5	−16.0
$Cs \cdot (C_6H_5)_4B$	THF	7.38	5.72	*e*	4.9	5.8	3.1	−16.1
$(Isoamyl)_4N \cdot NO_3$	Dioxane–water	2.38	15.70	11	6.0	6.5	4.5	−16.5
		2.56	14.00	11	6.2	6.8	4.6	−16.5
		2.90	12.00	11	6.4	7.0	4.6	−16.5
		3.48	9.60	11	6.6	7.3	4.5	−16.5
		4.42	7.50	11	6.7	7.4	4.2	−16.5
		5.80	5.80	11	6.5	7.3	3.8	−16.5
$Bu_4N \cdot$picrate	Anisole	4.34	8.90	7	4.9	6.3	3.7	−18.1
	m-$C_6H_4Cl_2$	5.04	8.60	7	4.9	5.6	3.3	−18.1
	C_6H_5Cl	5.63	7.70	7	4.8	5.6	3.2	−18.1

[a] As pointed out by Fuoss[6b] the Bjerrum function from which these values are calculated is not entirely satisfactory. Values are included here for comparison since this function has been used by many other workers in this field.

[b] In general, internuclear distances in ion pairs are about 15% more than separations in crystals (*cf.* alkali halides). Estimated contact internuclear distances (A) are: KCl = 2.7, $NaClO_4$ = 3.8, $Bu_4N \cdot Cl$ = 4.1, $Bu_4N \cdot ClO_4$ = 4.5, and $Bu_4N \cdot$picrate = 3.7 A (ref 7).

[c] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

[d] S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

[e] D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

Ion-Pair Formation in Solution. Using eq 5 in the way outlined above, potential energy values for ion pairs may be calculated. Where polarizability values are not available, the volume of the ion, in cubic angstroms, will be satisfactory, since the induced dipole interactions contribute only a minor part of the total energy which is therefore not very sensitive to small errors in polarizability values. As the interionic separation increases, the influence of polarization terms decreases so that, in some cases, they can be neglected altogether. The expression for the potential energy of ion pairs then reduces to $\Delta V_2 = -[1 - (1/n)] \cdot (e^2/r)$. Accurate values for the entropy change accompanying stage II of the D.R. cycle for ion-pair formation can be calculated, provided the vibrational frequency of the ion pair is known, using the standard equations of statistical thermodynamics. Assuming the interaction between the ions to be purely Coulombic the force constant, k, and hence the frequency, ω, may be expressed in terms of the second differential of the potential energy expression, *i.e.*

$$k = \mathrm{d}^2V/\mathrm{d}r^2 \tag{6}$$

when $r = r_e$

$$\omega = \frac{1}{2\pi c}\frac{k}{\mu}$$

where μ is the reduced mass.

Having obtained a value for the frequency, ω, the translational, rotational, and vibrational entropies of an ion pair (S_T, S_R, and S_V, respectively) may be evaluated by eq 7, 8, and 9 where M is the molecular weight and I the

$$S_\mathrm{T} = R\left[\frac{5}{2} + \ln\,(2\pi MkT)^{3/2}V/h^3N\right] \tag{7}$$

$$S_\mathrm{R} = R[1 + \ln\,8\pi^2I\,kT/h^2] \tag{8}$$

$$S_\mathrm{V} = R\left[\frac{hc\omega}{kT}\left(\frac{1}{e^{hc\omega/kT} - 1}\right) - \ln\,(1 - e^{-hc\omega/kT})\right] \tag{9}$$

moment of inertia of the ion pair. Equation 4 may now be used to obtain a value for log K_2. Alternatively, from experimental association constants the value of r_2, the interionic separation in an ion pair, may be derived for comparison with the values calculated by the Bjerrum and original D.R. equations. Such a calculation is possible since, although both ΔS and ΔV are functions of r, the influence of small changes of r on the total entropy change is small, allowing an approximate value to be used in a the calculation of ΔS which can then be used to calculate a more accurate value for r from eq 4. This assumption is acceptable at room temperatures since eq 7 is independent of r, eq 8 is dependent on r only in that it will influence the moment of inertia, and eq 9, while being strongly dependent on ω and hence r, contributes only 1 or 2% toward the total entropy at room temperature. Equation 4 has been used to calculate r_2 from reported association constants for a number of different ion pairs in solution. The results for a representative selection of the data available are shown in Table II where they are compared with results from other treatments. Internuclear distances likely to be found in contact ion pairs are given in the footnote of Table II. Entropy values are estimated to be within ±2 eu, which corresponds to an error of ±0.4 log unit in the value of K_2.

In general, ions which are approximately spherical have been chosen. It will be noticed that, in all cases, the distances are shorter than previously calculated values and correspond closely to the separations expected from two ions in contact. This result indicated that there is no solvent separation as had been previously thought, and many problems in interpreting these r values have been removed since more consistent values are obtained. Perchloric acid appears to have a larger ionic separation than sodium perchlorate indicating that the solvated proton (in acetic acid) is slightly larger than the sodium ion. This result is in full agreement with the crystallographic study of hydroxonium perchlorate carried out by Truter[21] who reported a unit cell for $HClO_4 \cdot H_2O$ of volume 93 A^3, compared with volumes of 81 A^3 for $NaClO_4$ and 100 A^3 for NH_4ClO_4,[22] suggesting that, in acetic acid, the solvated protons should certainly be larger than the sodium ion. In calculating the entropy change on ion-pair formation the species is assumed to be $(H \cdot HAc)^+ ClO_4^-$. Results in tetrahydrofuran ($D = 7.38$) indicate definite solvation (*e.g.*, $Na^+ > Cs^+$).

Specific solvation invalidates assumptions made in the original Dension–Ramsey cycle and, in general, this treatment should be restricted to solvents of lower dielectric constant (*i.e.*, <7). In any case, dielectric saturation becomes appreciable above this value so that macroscopic dielectric constants are inappropriate.

Ion-Triplet Formation. Association constants for the reaction

$$AB + A = ABA \qquad (10)$$

may be calculated from conductivity measurements. Two main approaches have been made to the theoretical treatment of symmetrical ion-triplet formation. In 1933, Fuoss and Kraus extended the Bjerrum treatment of ion pairs,[4] and more recently Fuoss and Accascina[2] considered triple ion formation by the statistical approach suggested by Fuoss.[6b] In the latter treatment an approximation to the translational and rotational entropy changes accompanying association is included ($RT/2$ for each degree of freedom); by this means they obtained a value of 10.7 A for the distance parameter in the tetraisoamylammonium nitrate ion triplet in dioxane–water mixtures. The magnitude of this distance parameter is only slightly larger than that calculated from the ion-pair distance parameter ($1.5 \times 6.8 = 10.2$ A^2). Values of r_3 according to the earlier theory are given for historical interest in Table III, along with values of r_3 calculated from an extended form of the D.R. treatment as described below. It is apparent that the more recent approach of Fuoss and Accascina is a substantial improvement over the earlier F.K. theory. If the simple D.R. treatment is applied to the experimental values of K_3, even larger r_3 values than those obtained by the original F.K. method (in the region of 12–13 A) are found. The extended D.R. treatment, including improved potential energy expressions similar to that used in eq 5 and including polarization terms and a repulsion term of the form $B/r_3^{6,9}$ for each interionic repulsion, was therefore applied to ion triplets in solution. The value for B, obtained by minimizing the potential energy of an ion pair, was used and a new r value (r_3) calculated by minimizing the expression for r_3 with respect to r. This technique gives ion-triplet separations (r_3) slightly greater than the corresponding ion-pair separations (r_2) but considerably less than the increased values predicted by the Fuoss–Kraus treatment. Typical values for the alkali halides are given in Table IV.

Table III. Ion-Triplet Formation

Solute	Solvent	D	Log β_3	Ref	r_3, A F.K.	r_3, A Eq 4	$-\Delta S$/1.5 mole, eu
$Bu_4N \cdot Cl$	Benzene	2.27	21.57	9	8.9	4.7	46.15
$Bu_4N \cdot NO_3$	Benzene	2.27	21.81	9	8.3	4.6	47.7
$Bu_4N \cdot ClO_4$	Benzene	2.27	21.63	9	8.1	4.6	49.1
$(Isoamyl)_4N \cdot NO_3$	Dioxane–water	2.38	20.4	3	9.0 est	4.6	48.5
		2.56	18.1	3	9.0 est	4.7	48.5
		2.90	15.5	3	9.0 est	4.6	48.5
		3.48	12.6	3	9.0 est	4.4	48.5
		4.42	10.0	3	9.0 est	4.0	48.5
		5.80	7.8	3	9.0 est	3.5	48.5

Entropy changes on the formation of ion triplets were calculated from the statistical eq 7–9 assuming the triplet to be linear. The rotational entropy is now, however, dependent on the symmetry of the molecule, and a symmetry number, σ, must be introduced in eq 8. The vibrational entropy will contain contributions from bending as well as stretching modes. Consideration of the vibrational contributions of linear triatomic molecules of known vibrational frequencies (*e.g.*, CO_2, CS_2) demonstrates that only the doubly degenerate bending mode makes a substantial contribution to the entropy at room temperature and this is small (~5%) compared with the total. Since the change in entropy of the association reaction is the important quantity for eq 4, stretching components can be ignored since for reaction 10 the difference in entropy, from this source, between AB and ABA is very small indeed. The bending frequency was calculated from the force constant, which was itself calculated from the second derivative of the potential energy with respect to the angle of the A–B–A bonds. Typical values for the total entropy changes are shown in Table III. Two different ion triplets are actually possible, ABA and BAB. From a simple Coulombic model they will have the same potential energies but will have different entropies resulting from different molecular weights and moments of inertia. However, calculation shows that the differences are generally negligible; *e.g.*, for $((isoamyl)_4N)_2 \cdot NO_3$ and $(isoamyl_4)N \cdot (NO_3)_2$ the values are, respectively

$$\Delta S = S_3^T + S_3^R + S_3^V - 2S_A - S_B$$

$$-48.2 = 45.4 + 22.8 + 7.9 - 2 \times 43.0 - 38.3 \text{ eu}$$

$$-48.9 = 44.0 + 19.7 + 7.0 - 2 \times 38.3 - 43.0 \text{ eu}$$

These values are well within the experimental error, and the mean value (−48.5) was chosen. No distinction was therefore made between the two possible formation constants for the triplets. As with ion-pair formation, the entropy changes are only slightly dependent on small changes in r_3 so that, using measured association constants for the association reaction the

$$2A + B \longrightarrow ABA \quad \beta_3 = [ABA]/[A]^2[B] \qquad (11)$$

internuclear separations were calculated by eq 4 for the compounds considered. Values are shown in Table III.

The r_3 values calculated by this technique are considerably closer in magnitude to the corresponding r_2 values (Table II) than those obtained by other treatments. In general, experimental values of r_3 appear to be slightly larger than r_2, as would be expected of a model based on the Coulombic interaction of charged

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(21) M. R. Truter, *Acta Cryst.*, **14**, 318 (1961).

(22) Gottfried and Schusterius, *Z. Krist.*, **84**, 65 (1932).

Table IV. Ion-Quadrupole Energies at 0°K

	r_2,[20] A	r_3,[a] A	r_4,[a] A	r_4,[15] A	V_4[14]	V_4[15]	V_4[a]	($V_4 - 2V_2$), kcal Ref 23	($V_4 - 2V_2$), kcal *a*
NaCl	2.36	2.67	2.60	2.60	302.3	297.4	307.1	50.6	52.8
NaBr	2.50	2.85	2.76	2.75	287.2	286.8	294.5	45.5	51.6
NaI	2.71	3.12	2.99	2.94	267.4	274.2	276.3	42.8	49.5
KCl	2.67	2.99	2.96	2.93	267.4	270.1	268.1	43.8	43.7
KBr	2.82	3.18	3.12	3.07	255.6	260.0	255.1		42.1
KI	3.04	3.44	3.38	3.29	240.2	247.5	239.7	37.3	37.9
RbCl	2.79	3.12	3.10	3.06	255.2	261.3	256.0	42.0	41.3
RbBr	2.95	3.31	3.27		244.6		243.3		39.5
RbI	3.18	3.60	3.52		230.3		227.5		37.6
CsCI	2.91	3.27	3.22	3.17	242.3	254.2	246.7	37.3	39.6
CrBr	3.07	3.46	3.42		232.8		233.5		37.5
CsI	3.32	3.75	3.69		220.1		217.2		35.2

[a] This work, energies in kcal/mole.

spheres. The close agreement between r_2 and r_3 clearly indicates that there is no drastic change in solvent separation or apparent ionic sizes on ion-triplet formation. As with ion-pair formation, this treatment will only apply to solvents of low dielectric constant (*e.g.*, r_3 values for (isoamyl)$_4$N·NO$_3$ begin to drop as D increases).

Ion-Quadrupole Formation. The potential energies of symmetrical ion quadrupoles, (AB)$_2$, in the vapor phase have been calculated by various workers in studies of alkali halide vapors.[14–16] Equations similar to those set up by O'Konski and Higuchi[13] were used, but incorporating repulsion terms in $B/r_4^{6.9}$ for each interionic repulsion where B values were taken from the corresponding ion-pair potential energies. The ions are found to favor a planar arrangement as in Figure 1 and the diagonal a, and hence the geometry of the rhombus, was calculated by minimizing the full potential energy expression using a range of values for a. The value of a was adjusted in steps of 0.1 r, then 0.01r, and finally 0.001r, keeping r constant, to give a final value accurate to about 0.001 A. The angles were then calculated and, assuming this geometry, the value of r was adjusted to give a minimum energy by using an iterative procedure in r. Using this new value for r, the value of a was readjusted to obtain an energy minimum and final values for $r(r_4)$ were then calculated. These calculations were carried out with the aid of a Control Data 1604 computer. Results for some alkali halide quadrupoles (dimers) are shown in Table IV, together with those calculated by Berkowitz[15] and Milne and Cubicciotti.[14] Reasonable agreement is found in all cases other than very small ions (*i.e.*, fluorides and, to a lesser extent, other lithium salts). In these cases the exponent in the repulsion term (6.9) is clearly inaccurate and they have therefore been omitted. For larger ions the agreement found justifies the above treatment and indicates that the potential energy expression used is acceptable for an ion quadrupole.

Experimental values for the potential energy change in the reaction

$$2AB \longrightarrow (AB)_2 \tag{12}$$

for several alkali halides are available and are summarized by Datz, Smith, and Taylor (at 1300°K)[23] and by Milne and Klein (at about 900°K).[24] Since this energy is the difference between two large quantities (*i.e.*, $V_4 - 2V_2$), good agreement cannot be expected between experimental and calculated values. The experimental values show a large scatter, *e.g.*, for (NaCl)$_2$ the range of values at 930° is 44.7–51.8 kcal[25] which corresponds to a range of 47.0–54.5 kcal at 0°K. The latest results available[23] corrected to 0°K are shown in Table IV together with the results calculated in this work. Surprisingly good agreement is found, better, in fact, than the agreement between experimental results and those calculated more rigorously by Berkowitz. Considering the possible errors involved, this agreement is fortuitous. For most ions studied in solution, polarizability values are not known accurately so that the potential energy equation cannot be used rigorously; its use for the alkali halides was to demonstrate that it was, in fact, a reliable expression of the energy. For larger ions polarization has only a minor influence on the total energy so that small errors are unimportant. In most cases the volume in A^3 was quite acceptable as the polarizability and, for larger ions, it could be neglected completely.

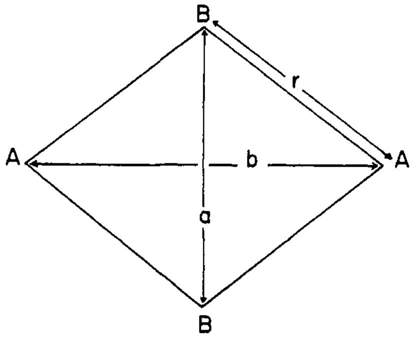

Figure 1. Symmetrical ion quadrapole.

Entropy charges can again be calculated as before. The translational entropy can be found accurately and the rotational entropy can be calculated provided the three moments of inertia about the three space axes (I_A, I_B, and I_C) and the symmetry number (σ) are known, *i.e.*

$$S_R = R\left[1 + 8\pi^2 \frac{(8\pi^3 I_A I_B I_C)^{1/2}}{\sigma h^3}(kT)^{3/2}\right] \tag{13}$$

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(23) S. Datz, W. Smith, and E. Taylor, *J. Chem. Phys.*, **34**, 558 (1961).

(24) T. A. Milne and H. Klein, *ibid.*, **33**, 1628 (1960).

(25) S. Bauer, R. Diner, and R. Porter, *ibid.*, **29**, 991 (1958).

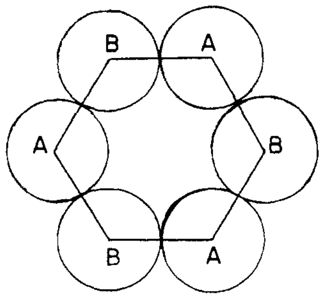

Figure 2. Symmetrical sexapole.

The vibrational entropy is much more difficult to estimate on account of the six normal vibration modes possible. Berkowitz has carried out a complete analysis for some alkali halides,[15] Bauer, Diner and Porter have used a less rigorous calculation,[25] and Rice and Klemperer have used an approximation method.[26] From the point of view of ion-quadrupole formation in solution at room temperature, the rigorous treatment is not essential so a simplified form of the Bauer, Diner, and Porter treatment was used. Using their notation, the triply degenerate ν_3 vibration contributes approximately the same entropy as the singly degenerate vibration, ν_2 (which is also approximately the same as the bending contribution to the entropy of the corresponding triplet). Using Bauer, Diner, and Porter's equation for the force constant corresponding to ν_2, it was possible to obtain an approximate value for the total vibrational entropy charge for reaction 12; *i.e.*, $\Delta S = 4S_v^{(\nu_2)}$. Hence the total entropy change may be estimated and, by substituting in eq 4, the association constant may be related to the interionic separation, r_4.

Only a few measurements of ion-quadrupole formation constants in solution have been published. Attempts to treat them theoretically by the Bjerrum treatment have been made by Fuoss and Kraus,[5] but they were unable to give values for the interionic separations. The simple D.R. treatment gives separations in the region of 25–40 A, distances far too large to have any physical significance since, at the concentrations concerned, normal "space crowding" would lead to a closer mean separation. If the full expression (eq 4) is used on the available data, the results shown in Table V are obtained. Few results are available, since cryoscopy has been used in most studies, and the precision of the measurements is unsufficient for quantitative treatment unless very refined techniques have been used. However, the results available indicate interionic separations very similar to those found in ion pairs and ion triplets, suggesting that the ions in the quadrupole are in contact and are not solvent separated.

Table V. Ion-Quadrupole Formation in Solution

Solute	Solvent	D^a	Log β_4	r_4, A	$\Delta S/2$ mole, eu
$NaClO_4$	HAc	6.13	11.4	4.2	−70
$HClO_4$	HAc	6.13	10.5	4.4	−70

[a] From ref 28.

Higher Aggregate Formation. Experimental data indicate that, when the dielectric constant is very low, ion-quadrupole formation is always accompanied with more extensive association, eventually resulting in crystallization as the concentration increases. Five ions in an aggregate do not form a very stable group since the resulting ion will be charged and no simple arrangement can be visualized. The sexapole (*e.g.*, $(AB)_3$) would be expected to have a much higher stability. Such species have been detected in solution[27,28] and in the vapor phase and potential energies calculated assuming a planar hexagonal arrangement.[16] Still larger aggregates must certainly form before crystallization takes place, but a theoretical treatment for such species is not possible because of the uncertainty in the geometries of the higher aggregates. In order to give approximate formation constants for the sexapoles (β_6), the symmetrical arrangement suggested by Milne and Cubicciotti was adopted (Figure 2) and a simple potential energy expression used, considering only ion–ion interactions and interionic repulsions of B/r^6[9] for each contact repulsion. The hexagon was assumed to be regular (*i.e.*, in Milne and Cubicciotti's notation, $\delta = 0$). Translational and rotational entropy charges may be calculated comparatively accurately, but vibrational entropy charges were estimated at 10 eu for the formation from six free ions. Substitution in eq 4 at 25° then gives the approximate relationship

$$\log \beta_6 = \frac{772.9}{r_6 D} - 12$$

Applying this equation to the available association constants allows calculation of r_6. Values of r_6 for solutes in anhydrous acetic acid are as given in Table VI. Considering the large uncertainty in the entropy changes and the approximations in the potential energy expression, this agreement with r_2 values is surprisingly close, again indicating actual contact between the ions.

Table VI. r_6 in Anhydrous Acetic Acid

Solute[a,b]	Log β_6	r_6, A
$HClO_4$	16.0	4.5
H_2SO_4	21.7 (19.2)	3.8 (4.1)
Diethylanilinium perchlorate	17.3	4.3

[a] See footnote *d*, Table I. [b] Reference 26.

The small values of r_6 for sulfuric acid are not surprising since sulfuric acid in acetic acid is only dissociated $10^{-2.4}$ times as much as perchloric acid in the solvent acetic acid,[22] and probably exists only partially in the ion-paired form. Thus β_6 must be corrected for the equilibrium constant for the reaction between molecular sulfuric acid and ion-paired acetonium bisulfate. Assuming that the equilibrium constant

$$H_2SO_4 + HAc \rightleftharpoons H_2Ac^+ \, HSO_4^-$$

for the analogous reaction involving perchloric acid is very large, β_6 should be corrected by a factor of

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(26) S. Rice and W. Klemperer, *J. Chem. Phys.*, **27**, 643 (1957).

(27) S. Bruckenstein and L. Pettit, *J. Am. Chem. Soc.*, **88**, 4780 (1966).

(28) J. Kenttamaa, *Suomen Kemistilehti*, **B32**, 9, 220 (1959).

$10^{2.4}$. This is the value log β_6 listed above in parentheses. The value of r_6 corresponding to the corrected β_6 is 4.1 A.

Ionic Solutes in a Solvent of Low Dielectric Constant. Association of ions in solution will take place by a stepwise mechanism as the concentration increases. Treatment of aggregates up to sexapoles has been outlined above. If average entropy charges are taken, and internuclear distances of 4 A accepted while polarizabilities are neglected, eq 4 may be simplified to

$$\begin{aligned}\log\beta_2 &= \frac{52.1}{D} - 3.7\\ \log\beta_3 &= \frac{75.1}{D} - 6.9\\ \log\beta_4 &= \frac{121.3}{D} - 7.5\\ \log\beta_6 &= \frac{193.2}{D} - 12\end{aligned} \tag{14}$$

For a univalent solute, AB, the total concentration, C_I ($= 2C_{AB}$), will be made up as follows

$$C_I = [I] + 2[I_2] + 3[I_3] + 4[I_4]\ldots\text{etc.} \tag{15}$$

where [I] represents to the equilibrium concentration of the free ion and $[I_n]$ the concentration of an ion aggregate of containing n ions. If only hexapoles and below are considered, eq 14 and 15 can be combined to give

$$C_I = [I] + 2[I]^2\beta_2 + 3[I]^3\beta_3 + 4[I]^4\beta_4 + 6[I]^6\beta_6 \tag{16}$$

Hence the concentrations of the various species, for a given total concentration and dielectric constant, can be calculated. The results are shown in Figure 3, which gives a qualitative picture of an ionic solute in a solvent of low dielectric constant. Since small variations in eq 14 will modify the graphs considerably, rigorous interpretation is not possible but several points emerge clearly. Apart from the monomer, A^+ or B^-, charged species play only a very small part in the total equilibrium; the concentrations of the ion triplets, ABA^+ or BAB^- (and presumably of the quintuplets such as $A_3B_2^+$), are always too small to show on the graphs, and data are available on their existence purely as a result of their ability to conduct electricity. At low concentrations (*e.g.*, 10^{-5} *M*) solutions of almost pure ion pairs can be found (*i.e.*, $D = 4$) but at higher concentrations a mixture of species will always be present. Ion quadrupoles, in particular, only contribute a small percentage toward the total equilibrium mixture, which explains why cryoscopic studies are difficult to interpret in terms of simple equilibria of the type

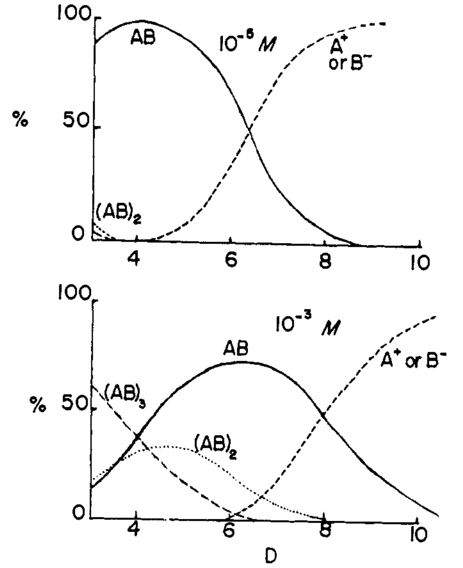

Figure 3. The effect of dielectric constant upon the association of a simple salt, A^+B^-. Internuclear separation = 4 A at 25°.

$$2AB \rightleftharpoons (AB)_2$$

The greater stability of the sexapole compared with the quadrupole is also supported by experiment. The graphs of Figure 3 have not been extended below a dielectric constant of 3 since much more extensive association will take place in this region. Since the equilibria are so complicated, cryoscopic data can only be treated quantitatively with the aid of a computer (or lengthy iterative hand calculation) and, if the results are to be reliable, only data of the highest precision can be used.

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