

PROPERTIES OF DILUTE ELECTROLYTE SOLUTIONS FROM CALORIMETRIC MEASUREMENTS

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Abstract - The enthalpies of dilution of 2:2 electrolytes in water and 1:1 electrolytes in n-propanol have been measured at 25°C with a sensitive and accurate flow calorimeter. Since the electrolytes studied are partially associated, the data analysis of the dilution measurements yields both the heat of ion-pair formation ΔH_A^0 and the association constant K_A . On the basis of a recently proposed association model, including both coulombic and non-coulombic interactions, the non-coulombic functions ΔG_A^* , ΔH_A^* and ΔS_A^* of ion-pair formation are obtained. These functions are related to the changes in the cospheres of the ions undergoing ion-pair formation.

INTRODUCTION

Interactions in electrolyte solutions have been investigated by various experimental methods: by thermodynamic and spectroscopic methods and by the measurement of transport properties (Ref.1,2). Calorimetric investigations belong to the most precise among the thermodynamic methods yielding information on ion-ion and ion-solvent interactions. This is mainly due to modern developments (Ref.3,4,5) in the design of sensitive and accurate calorimeters. Figure 1 shows some of the most frequently applied calorimetric methods in the field of electrolyte solutions. The heat of solution at zero concentration ΔH_{sol}^0 of an electrolyte with the composition $Y \equiv C_{V+}^{Z+} A_{V-}^{Z-}$ in water (w) as a solvent or in a non-aqueous solvent (s) is obtained by dilution of the

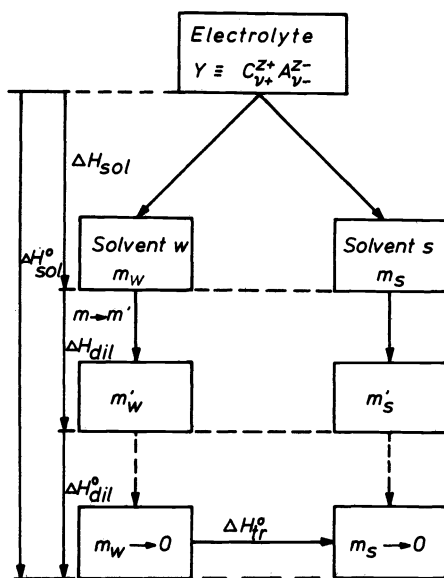


Fig. 1 Calorimetry of electrolyte solutions.

electrolyte solution from a concentration m to a series of concentrations m' followed by an appropriate extrapolation to infinite dilution. From $\Delta H_{\text{sol}}^{\circ}$ and the lattice enthalpy $\Delta H_{\text{lat}}^{\circ}$ the enthalpy of solute-solvent interactions $\Delta H_{\text{s-s}}^{\circ}$ can be calculated by means of

$$\Delta H_{\text{s-s}}^{\circ} = \Delta H_{\text{sol}}^{\circ} + \Delta H_{\text{lat}}^{\circ} \quad (1)$$

$\Delta H_{\text{s-s}}^{\circ}$ can be divided into its individual ion contributions on the basis of an extrathermodynamic assumption. Lattice enthalpies, however, are often unknown. Using water as the reference solvent, the difference of the corresponding solution enthalpies in nonaqueous solvent (s) and in water (w) yields the heat of transfer $\Delta H_{\text{tr}}^{\circ}$.

$$\Delta H_{\text{tr}}^{\circ} = \Delta H_{\text{sol}}^{\circ}(\text{s}) - \Delta H_{\text{sol}}^{\circ}(\text{w}) \quad (2)$$

This quantity is valuable in comparing the solvation properties of nonaqueous solvents with respect to those for water. The calorimetric methods described here and also other methods such as the heat of mixing (Ref.6) and heat capacity measurements (Ref.1,2,7) can be used to investigate the ion-ion as well as ion-solvent interactions.

This contribution deals with the heat of dilution of associated electrolytes at low concentration. When such a solution is diluted, heat is produced by the dissociation of ion-pairs (IP) to form 'free' ions (FI) and a contribution to $\Delta H_{\text{dil}}^{\circ}$ results.

THE HEAT OF DILUTION OF ASSOCIATED ELECTROLYTES

A chemical equilibrium is assumed between the 'free' ions of a symmetric electrolyte and the uncharged ion-pair which is considered as a species with a specific chemical potential. The association constant K_A is given by

$$K_A = \frac{1-\alpha}{\alpha^2 c y_{\pm}^2} \quad (3)$$

where α is the degree of dissociation, c the molar concentration and y_{\pm} the mean activity coefficient of the 'free' ions.

The apparent molal heat content ϕ_H of a solution containing an associated electrolyte can be separated into the contributions for the 'free' ions and the ion-pair (Ref.8).

$$\phi_H = \alpha \phi_H(\text{FI}) + (1-\alpha) \phi_H(\text{IP}) \quad (4)$$

Since only 'free' ions exist at infinite dilution

$$\lim_{m \rightarrow 0} \phi_H = \phi_H^{\circ}(\text{FI}) \quad (5)$$

The relative apparent molal heat content ϕ_L is the difference between the corresponding ϕ_H values at a finite concentration and that at infinite dilution.

$$\phi_L = \phi_H - \phi_H^{\circ} = \alpha \phi_H(\text{FI}) + (1-\alpha) \phi_H(\text{IP}) - \phi_H^{\circ}(\text{FI}) \quad (6)$$

ϕ_L is related to the limiting heat of dilution by

$$\phi_L = -\Delta H_{\text{dil}}^{\circ} \quad (7)$$

Neglecting any concentration dependence of $\phi_L(\text{IP})$ for dilute solutions

$$\phi_H(\text{IP}) = \phi_H^{\circ}(\text{IP}) \quad (8)$$

and introducing the enthalpy of ion association

$$\Delta H_A^{\circ} = \phi_H^{\circ}(\text{IP}) - \phi_H^{\circ}(\text{FI}) \quad (9)$$

the following relation is obtained

$$\phi_L = \alpha \phi_L(\text{FI}) + (1-\alpha) \Delta H_A^{\circ} \quad (10)$$

In our experiments dilution is performed from an initial concentration m of about 10^{-2} mol kg^{-1} to a series of final concentrations m' ending at about $5 \cdot 10^{-4}$ mol kg^{-1} . The change in heat content observed for such an experiment is given by the relation

$$\Delta \bar{\phi}_L = \bar{\phi}'_L - \bar{\phi}_L = \alpha' \bar{\phi}'_L(\text{FI}) - \alpha \bar{\phi}_L(\text{FI}) + (\alpha - \alpha') \Delta H_A^{\circ} \quad (11)$$

All data related to the variable final state are primed.

In order to analyze heat of dilution data for a system containing an associated electrolyte, it is necessary to use the activity coefficient γ'_{\pm} of the 'free' ions and the association constant K_A in a consistent way. A set of consistent relations for K_A and γ'_{\pm} including non-coulombic forces is given by Barthel (Ref.9)

$$K_A = 4\pi N_A \cdot 10^{-3} \left\{ \exp\left[-\frac{\Delta G_A^*}{RT}\right] \int_a^{R^*} r^2 \exp\left[\frac{2q}{r}\right] dr + \int_{R^*}^R r^2 \exp\left[\frac{2q}{r}\right] dr \right\} \quad (12)$$

$$\gamma'_{\pm} = \exp\left[-\frac{\kappa q}{1 + \kappa R}\right] \quad (13)$$

Eqs. (12) and (13) assume a region $a \leq r \leq R$ around an ion which is considered to be free of net charges.

$$\kappa^2 = 16\pi q N_A \alpha c \cdot 10^{-3} \quad (14)$$

$$q = \frac{e_0^2 z^2}{2\epsilon kT} \quad (15)$$

'a' is the center-to-center distance of cation and anion in contact, R^* the distance which limits the non-coulombic interaction potential of mean forces, w_{ij}^* , in the vicinity of an ion. With N_A as Avogadro's number the relationship

$$\Delta G_A^* = N_A \cdot w_{ij}^* \quad (16)$$

is obtained.

R^* and R are assumed to be given by the center-to-center distance 'a' in the contact ion-pair and the dimension 's' of the orientated solvent molecule.

$$R^* = a + s, \quad R = a + ns \quad (17)$$

As a consequence of the association model (Ref.9) used in this contribution the R parameter in eq. (13) is approximately independent of temperature. At low concentrations ($m \leq 0.01$ mol kg^{-1}) the activity coefficients in the molar and molal concentration scales are equal within the limits of accuracy of our measurements: $\gamma'_{\pm} = \gamma_{\pm}$. Using eq. (13) and the well-known equation

$$\bar{\phi}_L(\text{FI}) = -\nu RT^2 \frac{1}{m} \int_0^m \left(\frac{\partial \ln \gamma'_{\pm}}{\partial T}\right)_P dm \quad (18)$$

the following relation is obtained

$$\bar{\phi}_L(\text{FI}) = -\nu RT^2 \left\{ \left[\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P + \frac{1}{T}\right] \frac{\kappa q}{1 + \kappa R} + \frac{1}{3} \left(\frac{\partial \ln \rho_0}{\partial T}\right)_P \kappa q \sigma(\kappa R) \right\} \quad (19)$$

where ν is the sum of the stoichiometric coefficients ν_+ and ν_- and ρ_0 the density of the solvent. The σ -function (Ref.10) is defined by

$$\sigma(\kappa R) = 3(\kappa R)^{-3} [1 + \kappa R - (1 + \kappa R)^{-1} - 2 \ln(1 + \kappa R)] \quad (20)$$

EXPERIMENTAL

Heat of dilution measurements were carried out by means of a flow calorimeter of the heat conduction type. Figure 2 shows the block diagram of the calorimeter and of the electronic instrumentation.

Before the beginning of a dilution experiment, the temperature of the heat sink is set exactly at the temperature of the precisely controlled thermostat. The calorimeter unit is enclosed by an evacuated brass container. These precautions ensure that the drift of the base line is negligible and that the power produced in the calorimeter cell is nearly exclusively exchanged via the thermopile on the heat sink.

Piston pumps driven by quartz-controlled stepper motors deliver very constant flow rates of both the pure solvent and the electrolyte solution. The voltage of the thermopile, which is proportional to the power produced by the dilution process in the calorimeter cell, is amplified by a chopper amplifier and digitalized by a voltage to frequency-converter.

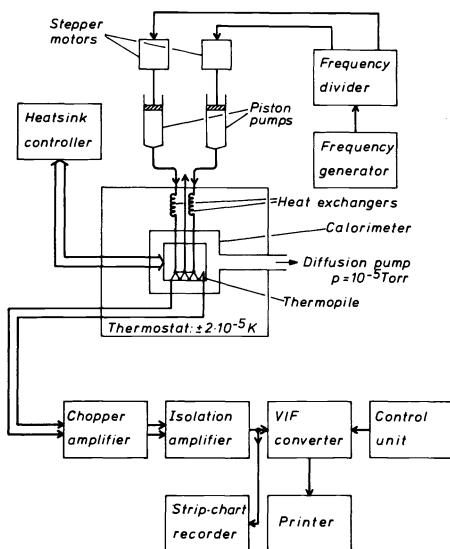


Fig. 2 Block diagram of the calorimetric assembly. Sensitivity: $\pm 1\text{nW}$, reproducibility: $\pm 5\text{nW}$, response time (90%): 60s.

THERMODYNAMIC DATA OF ION-PAIR FORMATION OF 2:2 ELECTROLYTES IN WATER

Experimental $\Delta\phi_L$ data are analyzed by a least square fit using eqs. (3,11,13, 19). The parameters adjusted are K_A , ΔH_A° and R . The great advantage of this method for determining thermodynamic data of ion-pair formation by heat of dilution measurements is that consistent data are obtained from measurements at only one temperature, 25°C. In contrast, conductance measurements must be carried out over a great temperature range to obtain reliable values for the association enthalpy ΔH_A° (Ref.11). Figure 3 shows a plot of the dependence of the standard deviation of the fit (σ_{fit}) on R as observed for MgSO_4 in water. It should be pointed out that parabolic curves as shown in Fig. 3 are only obtained when the precision of all the experimental data used in the fit is better than 0.1%, otherwise, curves with ill defined minima or two minima result which do not permit a unique value for R_{exp} to be established. Significant minima of the type of Fig. 3 are found for all the sulfates we have investigated.

Table 1 summarizes the experimental results K_A , ΔH_A° and R_{exp} for the sulfates of some divalent cations in water.

The R_{exp} values must be identical with both the upper limit R of the integral in eq. (12) and the distance parameter R in eq. (13). The association model assumes that R is given by the distance of closest approach 'a' and the length of the orientated solvent molecule. In a protic solvent, the directional nature of the hydrogen bond leads to some internal structure. Ions cannot approach each other without displacing solvent molecules. This is effected by breaking the strong hydrogen bonds. Therefore, an equilibrium between 'free' ions, solvent-separated ion-pairs (SSIP) and contact ion-pairs (CIP) may be assumed (Ref.14,15). In hydroxylic solvents the ions of a SSIP are

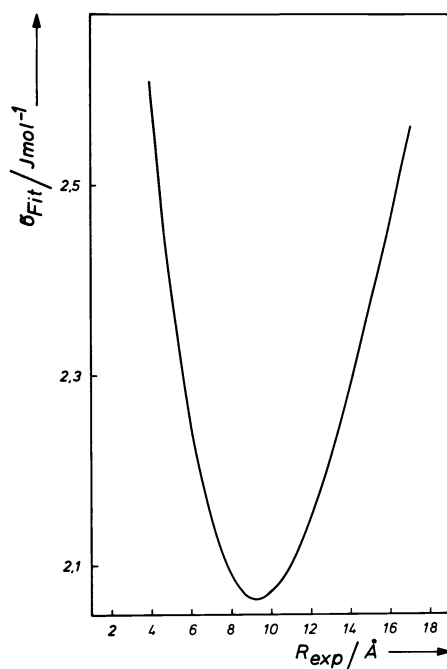


Fig. 3 The dependence of σ_{fit} on the distance parameter R .

TABLE 1. Thermodynamic functions of ion-pair formation. Sulfates of divalent cations in water at 25°C.

Electrolyte	$\frac{K_A}{\text{dm}^3 \text{mol}^{-1}}$	$\frac{\Delta H_A^0}{\text{J mol}^{-1}}$	$\frac{R_{exp}}{\text{Å}}$	$\frac{R_{calc}}{\text{Å}}$ *)
MgSO ₄	161.2(±0.5)	5776 ± 2	9.30(±0.05)	8.79
CaSO ₄	192.0	6665 ± 4	9.45	9.12
ZnSO ₄	203.9	6202 ± 3	9.20	8.87
CdSO ₄	238.8	8389 ± 4	9.60	9.10
MnSO ₄	194.1	7769 ± 3	9.35	8.93
CoSO ₄	202.7	5712 ± 2	9.35	8.85
NiSO ₄	209.6	5440 ± 3	9.10	8.82

*) Radii of the cations taken from (Ref.12), radius of the sulfate anion (2.53 Å) calculated from (Ref.13).

separated by OH-groups. Therefore, the length 's' of an orientated solvent molecule is given by the van der Waals length of the OH-group (Ref.16). Values R_{calc} as calculated according to $R = a + 2s$ are given in the last column of Table 1. The calculated and experimental values differ only by less than 0.5 Å. This observation proves the assumption made for R and therefore all further evaluations carried out for aqueous solutions of 2:2 electrolytes are based on the calculated R values ($R^* = a+s$, $R = a+2s$).

The precision obtained in ΔH_A^0 is remarkably high - the standard deviation of the mean is less than 0.1%. The estimated error for K_A given in parentheses is also very small. The agreement of the K_A values compared with those from conductance measurements is excellent when the same R values are used in both methods. For instance, the association constant K_A for MgSO₄ in water as obtained by us is 161 dm³ mol⁻¹, whereas a data analysis of conductance data

(Ref.17) by means of the Fuoss-Justice equation (Ref.18) yields $160 \text{ dm}^3 \text{ mol}^{-1}$ when the experimental R value given in Table 1 is used as distance parameter.

In Fig. 4 ϕ_L for MgSO_4 in water as calculated from eqs. (3,10,11,13,19) and from the experimental data for K_A , ΔH_A^0 and R, is plotted against $m^{1/2}$. The concentration range of our measurements is shown by the unbroken part of the line. The concentration dependence of ϕ_L of an associated electrolyte is completely described by the parameters K_A , ΔH_A^0 and R. For comparison, the Debye-Hückel limiting law (DHLL) slope is also shown. Only at very low concentrations the DHLL is approached.

The thermodynamic data of ion-pair formation are difficult to discuss because they include both coulombic and non-coulombic contributions. Only after the separation of the coulombic part, the rest gives some insight into the chemical behavior of the electrolyte solution.

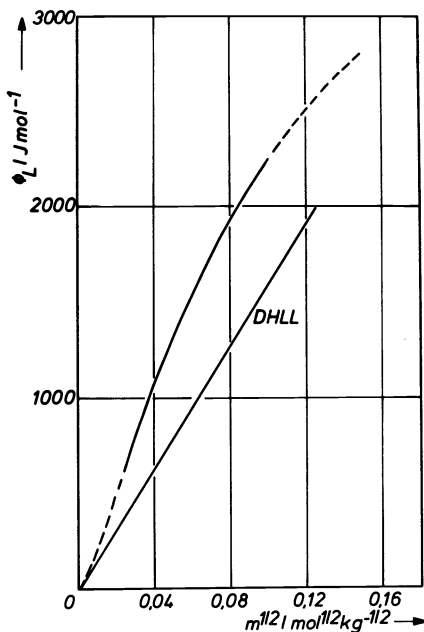


Fig. 4 ϕ_L for MgSO_4 in water.

The ion-pair formation of 2:2 electrolytes in water is assumed to be described by a two-step process



The overall association constant K_A is given by

$$K_A = K_1 + K_1 K_2 \quad (22)$$

Assuming that non-coulombic forces are involved only in the last step the constant K_A is given by

$$K_A = K_1^C + K_1^C K_2^C K_A^* \quad (23)$$

where K_1 is calculated by taking into account only coulombic forces (K_1^C). The equilibrium constant K_2 , however, is determined by both coulombic (K_2^C) and non-coulombic (K_A^*) interactions. A comparison of eq. (23) with eq. (12) yields the relations

$$K_1 = \frac{4\pi N_A}{1000} \frac{a+2s}{a+s} \int r^2 \exp\left[\frac{2q}{r}\right] dr \quad (24)$$

$$K_1^C K_2^C K_A^* = \frac{4\pi N_A}{1000} \exp \left[-\frac{\Delta G_A^*}{RT} \right] \int_a^{a+s} r^2 \exp \left[\frac{2q}{r} \right] dr \quad (25)$$

The upper limits R and R^* of the integrals in eq. (12) are assumed to be given by $a+s$ or $a+2s$, respectively. ΔG_A^* is obtained by means of eqs. (23, 24, 25) and the value of K_A determined by the dilution measurements.

On the other hand, ΔH_A^O can be divided into its coulombic and non-coulombic parts as follows

$$\Delta H_A^O = RT^2 \frac{\partial}{\partial T} [\ln(K_1^C + K_1^C K_2^C K_A^*)] \quad (26)$$

$$\Delta H_A^O = \Delta H_1^C + \frac{K_1^C K_2^C K_A^*}{K_1^C + K_1^C K_2^C K_A^*} (\Delta H_2^C + \Delta H_A^*) \quad (27)$$

Neglecting non-coulombic interactions the enthalpy of association is given by the relation

$$\Delta H_A^{OC} = \Delta H_1^C + \frac{K_1^C K_2^C}{K_1^C + K_1^C K_2^C} \Delta H_2^C \quad (28)$$

ΔH_A^{OC} and ΔH_1^C are calculated from the expressions for the corresponding equilibrium constant. The value for ΔH_2^C obtained in this way permits the evaluation of ΔH_A^* by means of eq. (27).

In Table 2 the non-coulombic functions of ion-pair formation of the aqueous 2:2 electrolytes of Table 1 are recorded.

TABLE 2. The non-coulombic part of the thermodynamic functions for ion-pair formation in solutions of sulfates of divalent cations in water at 25°C.

Electrolyte	$\frac{\Delta G_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta H_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta S_A^*}{J \text{ mol}^{-1} \text{ K}^{-1}}$	$\frac{r_+}{\text{\AA}}$
MgSO ₄	3380	339	-10.20	0.66
CaSO ₄	1540	1920	1.27	0.99
ZnSO ₄	2180	695	- 4.98	0.74
CdSO ₄	895	3840	9.88	0.97
MnSO ₄	2150	3190	3.49	0.80
CoSO ₄	2290	- 8	- 7.71	0.72
NiSO ₄	2260	- 535	- 9.37	0.69

The data are related to the second step of the two-step mechanism described by eq. (21). The free energy ΔG_A^* is always positive and increases with decreasing radius of the cation. Therefore, one could state, that the association behavior of the aqueous sulfates is controlled by the desolvation of the cation. However, comparing the ΔS_A^* values of MgSO₄ and CaSO₄, one recognizes that the value found for MgSO₄ is less by about 11 J mol⁻¹ K⁻¹. Since the formation of a CIP involves some desolvation of the ions, the highest positive ΔS_A^* would be expected for MgSO₄. But through undergoing ion association the cospheres of the ions influence one another. In aqueous solution the Mg²⁺ ion is a strong structure maker and the SO₄²⁻ ion a weak structure breaker. In the ion-pair the structure is increased resulting in a decrease of ΔS_A^* . As proved by the observations made for ZnSO₄ / CdSO₄ and for NiSO₄ / CoSO₄ / MnSO₄ this effect is relatively large when small cations are involved. ΔH_A^* increases with increasing radius of the cation. This result provides additional evidence that ion association of the sulfates of

divalent cations is influenced mainly by effects resulting from cosphere overlapping rather than by desolvation.

THEMODYNAMIC DATA OF ION-PAIR FORMATION OF ALKALI SALTS IN n-PROPANOL

In many respects the behavior of alkali salts in n-propanol is similar to the behavior of the sulfates of divalent cations in water. The energies of coulombic interactions are nearly the same and both hydroxylic solvents are structured. Since the ions of alkali salts are solvated in n-propanol, the two-step mechanism used to describe the association behavior of 2:2 electrolytes in water can be applied to alkali salts in n-propanol.

In Table 3 the thermodynamic data of the ion-pair formation of alkali salts in n-propanol are summarized.

TABLE 3. Thermodynamic functions for ion-pair formation of alkali salts in n-propanol at 25°C.

Electrolyte	$\frac{K_A}{\text{dm}^3 \text{mol}^{-1}}$	$\frac{\Delta H_A^0}{\text{J mol}^{-1}}$	$\frac{\Delta S_A^0}{\text{J mol}^{-1} \text{K}^{-1}}$	$\frac{R_{\text{exp}}}{\text{\AA}}$	$\frac{R_{\text{calc}}^*)}{\text{\AA}}$
NaBr	314(±1)	22136±10	122.04(±0.05)	9.2(±0.1)	8.53
NaI	206	18930±12	107.76	9.7	8.77
NaClO ₄	390	16516± 9	105.00	9.7	9.02
KI	374	19055± 7	113.15	9.9	9.13
RbI	527	17545± 8	110.93	9.5	9.27

*) $R_{\text{calc}} = a + 2 d_{\text{OH}}$. Radii of alkali and halide ions from (Ref.12), radius of ClO₄⁻ from (Ref.19).

The data sets recorded are valid in combination with the experimental values R_{exp} obtained. The values were determined in the same way as described for the aqueous electrolyte solutions. The agreement of the experimental R values with the calculated values is fairly satisfactory. This observation proves again the assumption made on the R values, and for this reason all further evaluations are based on the calculated R values given in the last column. The non-coulombic contributions to the ion-pair formation of some alkali salts in n-propanol are recorded in Table 4.

TABLE 4. The non-coulombic part of the thermodynamic functions for ion-pair formation in solutions of alkali salts in n-propanol at 25°C.

Electrolyte	$\frac{\Delta G_A^*}{\text{J mol}^{-1}}$	$\frac{\Delta H_A^*}{\text{J mol}^{-1}}$	$\frac{\Delta S_A^*}{\text{J mol}^{-1} \text{K}^{-1}}$	$\frac{r_+}{\text{\AA}}$	$\frac{r_-}{\text{\AA}}$
NaBr	1270	4849	12.00	0.97	1.96
NaI	1730	4200	8.28	0.97	2.20
NaClO ₄	-1080	669	5.87	0.97	2.45
KI	-1280	4250	18.5	1.33	2.20
RbI	-2640	2577	17.5	1.47	2.20

The process of ion-pair formation of alkali salts in n-propanol is greatly influenced by non-coulombic interactions as indicated by ΔG_A^* , going from 1270 J mol⁻¹(NaBr) to -2640 J mol⁻¹(RbI). The ΔG_A^* values observed are the result of effects due to both desolvation and to cosphere overlap.

In the series of alkali iodides ΔS_A^* increases and ΔH_A^* decreases with increasing radius of the cation. Since the iodide anion is weakly solvated, its cosphere may be reinforced by undergoing ion association with a

structuremaking cation. The ability of a cation to influence the structure around an anion decreases with increasing radius of the cation. The influence of the desolvation of the cations, however, would lead to tendencies which are contrary to the observed ones. These observations are similar to those made for the sulfates of divalent cations in water.

The association behavior of the sodium salts seems to be mainly controlled by the desolvation of the anions. This explains the increase in ΔS_A^* for Br^- compared to ClO_4^- . However, the negative ΔG_A^* observed for NaClO_4 and the fact that ΔG_A^* for NaI is greater than that for NaBr would seem to indicate the influence of cosphere overlapping.

THERMODYNAMIC DATA ON ION-PAIR FORMATION OF TETRAALKYLAMMONIUM SALTS IN n-PROPANOL

Tetraalkylammonium salts in n-propanol as a solvent are weakly solvated and, consequently, an one-step mechanism has been used to describe the ion-pair formation of these salts.

In Table 5 the thermodynamic data of ion-pair association of some symmetric and asymmetric tetraalkylammonium salts are recorded.

TABLE 5. Thermodynamic functions for ion-pair formation in solutions of tetraalkylammonium iodides in n-propanol at 25°C.

Electrolyte	$\frac{K_A}{\text{dm}^3 \text{mol}^{-1}}$	$\frac{\Delta H_A^{\circ}}{\text{J mol}^{-1}}$	$\frac{\Delta S_A^{\circ}}{\text{J mol}^{-1} \text{K}^{-1}}$
Et_4NI	535 (± 2)	6623 \pm 9	74.45 (± 0.04)
Pr_4NI	513	6000 \pm 9	72.02
Bu_4NI	534	5670 \pm 12	71.24
i- Am_4NI	581	5150 \pm 9	70.21
n- Am_4NI	536	5570 \pm 14	70.93
$\text{Me}_2\text{Bu}_2\text{NI}$	691	6954 \pm 8	77.69
MeBu_3NI	597	6406 \pm 8	74.63
EtBu_3NI	535	5904 \pm 10	72.03
i- Am_3BuNI	559	5343 \pm 10	70.52

Unlike the other systems studied, no significant dependence of σ_{fit} on the R value used as a parameter was found. This is probably due to the empirical term in $m^{3/2}$ added to the expression for the apparent molal heat content ϕ_L (FI) defined by eq. (19). Such an extra term was only required to describe the heat of dilution data of tetraalkylammonium salts. The value of this term increases with increasing radius of both the cation and the anion, indicating it would be reasonable to assume that the concentration dependence of structural interactions are taken into account by the empirical $m^{3/2}$ term. The value of R was fixed to a+s. 's' is the van der Waals length of a n-propanol molecule (Ref. 20). Although this assumption is somewhat arbitrary, the results change very little when R is varied in a reasonable range.

In Table 6 the non-coulombic functions for the ion-pair formation of tetraalkylammonium iodides in n-propanol are recorded.

ΔG_A^* has been calculated by means of the equation (Ref.20)

$$K_A = \frac{4\pi N_A}{1000} \exp \left[-\frac{\Delta G_A^*}{RT} \right] \int_a^{a+s} \exp \left[\frac{2q}{r} \right] r^2 dr \quad (29)$$

which describes an one-step process.

TABLE 6. The non-coulombic part of the thermodynamic functions for ion-pair formation in solutions of tetraalkylammonium iodides in n-propanol at 25°C.

Electrolyte	$\frac{r_+}{\text{Å}}$	$\frac{\Delta G_A^*}{\text{J mol}^{-1}}$	$\frac{\Delta H_A^*}{\text{J mol}^{-1}}$	$\frac{\Delta S_A^*}{\text{J mol}^{-1} \text{K}^{-1}}$
Et ₄ NI	4.00	- 4314	- 1440	9.64
Pr ₄ NI	4.52	- 4380	- 1510	9.63
Bu ₄ NI	4.94	- 4581	- 1460	10.48
i-Am ₄ NI	4.94	- 4791	- 1980	9.45
n-Am ₄ NI	5.29	- 4658	- 1273	11.35
Me ₂ Bu ₂ NI	3.47	- 4728	- 1795	9.84
MeBu ₃ NI	3.47	- 4365	- 2343	6.78
EtBu ₃ NI	4.00	- 4314	- 2159	7.22
i-Am ₃ BuNI	4.94	- 4694	- 1787	9.76

ΔH_A^* has been obtained from the relation

$$\Delta H_A^O = \Delta H_A^C + \Delta H_A^* \quad (30)$$

where ΔH_A^C has been calculated considering only coulombic interactions.

The negative ΔG_A^* observed indicate that the ion association of all tetraalkylammonium iodides is favored by non-coulombic interactions. A possible explanation will be given at the end of this paper. Since the shape of all symmetric cations is similar, one expects that the corresponding ΔH_A^* should vary continuously. However, unexpected fluctuations are observed that cannot be attributed to unprecise data. The ionic radii we have used (Ref.10) could be incorrect. Whereas the radius of Et₄N⁺ is calculated from bond lengths, the radii of the larger ions are derived from the molar volumes of the corresponding isosteric alkanes. Since the conformation of the alkyl chains is somewhat dependent on the intermolecular forces, these radii are unreliable. For asymmetric ions, the shortest distance possible between the positive center of charge and the end of the alkyl chain was taken as the ionic radius. Provided that the approach of the anion to the end of the shortest alkyl chain is not hindered by the larger alkyl groups, the distance of closest approach calculated from these 'radii' is correct. This is certainly the case for Me₂Bu₂NI.

ΔS_A^* for Et₄NI and Me₂Bu₂NI are equal, although the shape of the cations is quite different. Since the precision of the ΔS_A^* values is about 1%, this observation is not the result of an accidental error. Therefore, one may assume that for all the tetraalkylammonium iodides the same ΔS_A^* can be found provided that the radius of the cation is correct. This assumption is confirmed by the fact that within the symmetric tetraalkylammonium iodides the variation of ΔS_A^* is small and correlated to the expected deviation of the cationic radii. Taking the ΔS_A^* for Et₄NI as a reference, all the other cation radii were adjusted and given in Table 7.

The difference between the radii calculated in this way and those taken from literature increases from Pr₄N⁺ to n-Am₄N⁺. This is probably due to a more compact structure of the tetraalkylammonium cations in solution compared with the structure of the isosteric alkanes in their pure state. The great deviation observed for n-Am₄N⁺ is diminished for i-Am₄N⁺ having the same composition, but the i-amyl group makes the contraction of the alkyl sphere more difficult than the n-amyl group. The 'a' values of the asymmetric tetraalkylammonium iodides are assumed to be equal to the shortest interionic distance possible. This assumption is proved for Me₂Bu₂NI but not for MeBu₃NI and EtBu₃NI. For these electrolytes it can be stated that the approach of the anion to the shortest alkyl group of the cation is hindered by the three large butyl groups.

TABLE 7. Radii of tetraalkylammonium ions.

cation	$\frac{r}{\text{\AA}}$	$\frac{r}{\text{\AA}}$	$\frac{\Delta r}{\text{\AA}}$
	(literature)	(adjusted)	
Et ₄ N ⁺	4.00	(4.00)	(0.00)
Pr ₄ N ⁺	4.52	4.53	+0.01
Bu ₄ N ⁺	4.94	4.73	-0.21
n-Am ₄ N ⁺	5.29	4.80	-0.49
i-Am ₄ N ⁺	4.94 ^{a)}	5.00	+0.06
Me ₂ Bu ₂ N ⁺	3.47 ^{a)}	3.44	-0.03
MeBu ₃ N ⁺	3.47 ^{a)}	3.96	+0.49
EtBu ₃ N ⁺	4.00 ^{a)}	4.51	+0.51
i-Am ₃ BuN ⁺	4.94 ^{a)}	4.91	-0.03

a) shortest possible distance

Figure 5 shows the dependence of ΔH_A^* on the cation radii we have evaluated. The ΔH_A^* values are recalculated on the basis of these cation radii. Smooth curves are obtained for both symmetric and asymmetric tetraalkylammonium iodides. With the values taken from the literature no correlation between ΔH_A^* and the ion size has been found. The shape of the curves is due to the superimposition of electrostatic interactions which decrease with increasing cationic radius and of structural interactions which increase with an increasing cationic radius.

As can be seen from the data recorded in Table 6, the ion-pair formation of tetraalkylammonium iodides is favored by non-coulombic interactions. These interactions exceed both the free energy and the enthalpy needed for the partial desolvation of the iodide anion. The assumption that the anion is partially desolvated in the process of ion-pair formation can easily be proved by considering the Bu₄N⁺ ion with different anions. In Table 8 the non-coulombic functions of ion-pair formation of some Bu₄N⁺ salts are recorded. ΔH_A^* varies from 397 J mol⁻¹ (Bu₄NBr) to -4151 J mol⁻¹ (Bu₄NClO₄).

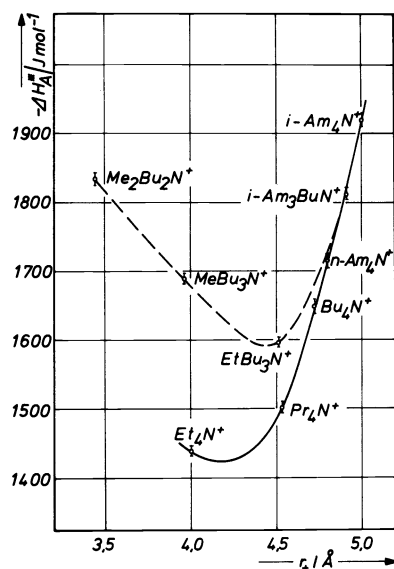


Fig. 5 ΔH_A^* of tetraalkylammonium iodides as dependent on the radius of the cation.

TABLE 8. The non-coulombic part of the thermodynamic functions for ion-pair formation in solutions of tetrabutylammonium salts in n-propanol at 25°C.

Electrolyte	$\frac{r_-}{\rho}$	$\frac{\Delta G_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta H_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta S_A^*}{J \text{ mol}^{-1} \text{ K}^{-1}}$
Bu ₄ NBr	1.96	- 3561	397	13.27
Bu ₄ NI	2.20	- 4532	- 1650	9.66
Bu ₄ NClO ₄	2.45	- 6125	- 4151	6.62
Bu ₄ NSCN	3.37	- 4581	- 1326	10.92

This dependence of ΔH_A^* is in accordance with the desolvation enthalpy of the corresponding anions. The ΔS_A^* observed also show that the anions are partially desolvated. The negative ΔG_A^* and ΔH_A^* observed for the tetraalkylammonium salts in n-propanol as a solvent which we investigated may be due to changes in structural solvation. The large tetraalkylammonium cations disturb the interactions of the solvent molecules, whereas their own interactions with the solvent molecules are only weak. The disturbance of solvent-solvent interactions is diminished by the formation of ion-pairs resulting in negative values for both ΔG_A^* and ΔH_A^* .

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