Thermodynamics of Ion Pairing of Nitrate and Chlorate with Metal Ions in Aqueous Solution

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Enthalpies of association of nitrate and chlorate with manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) have been determined by direct calorimetry in an aqueous medium at 25 °C and ionic strength $I = 1$ mol dm^{-3}. The corresponding entropy values have been obtained by using known values of the association constants. The thermodynamic parameters suggest formation of ion pairs of the outer-sphere type, and also indicate the importance of electrostatics in determining the association processes.

THERMOCHEMICAL studies of weak ionic interactions in aqueous solution have till now furnished an exiguous number of experimental data. This is mainly due to the difficulty of measuring reaction heats which are generally very small (because of the weakness of the bonds formed) and often complicated by interference from secondary, hard to eliminate, thermal phenomena caused by interactions among the other ions in solution. The weakness of these interactions affects the measured heats in two distinct ways: through the association constant and the corresponding molar enthalpy, both being in general very small.

As regards calorimetric studies of association equilibria in aqueous solution between nitrate and metal ions it must be noted that the only data in the literature refer to Sr^{II} and Ba^{II},[1] Cd^{II},[2,3] and Tl^{I} [4] and Tl^{III} [5] ions. No such data are available for the transition metals or for metal–chlorate interactions.[6] Previous conclusions about the nature of the association products between metal ions and the above anions are rather uncertain. In particular, Hutchinson and Higginson [7] determined association constants of a set of bivalent cations with some anions (nitrate and chlorate included) and attempted to extend this determination at two different temperatures to obtain the values of ΔH and ΔS. The formation of ion pairs of the outer-sphere type was suggested. These workers acknowledged the poor reliability of the thermodynamic data obtained (entropies especially) because of the too small variation in the stability constants with temperature, and they relied on a more precise evaluation of the thermodynamical quantities to clarify the nature of the interactions. It must be pointed out that in studies of metal complex-formation equilibria in aqueous solution the nitrates of the metals (especially in calorimetry) are often used, presuming that the use of these slightly associated salts reduces the interference of secondary thermal effects. Even if this assumption were true, particularly in the case of stable complexes, the determination of enthalpies of association between metal and nitrate ions is important in order to clarify this problem. In the present work direct calorimetry has been used to determine values of $\Delta H^{\ominus}$ and (by means of formation constants in the literature) of $\Delta S^{\ominus}$ for the association in aqueous solution

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[1] V. P. Vasil'ev, *Russ. J. Inorg. Chem.*, 1964, **9**, 354.

[2] V. P. Vasil'ev, *Russ. J. Inorg. Chem.*, 1962, **7**, 283.

[3] V. P. Vasil'ev and G. A. Lobanov, *Russ. J. Inorg. Chem.*, 1967, **12**, 463.

[4] F. Ya. Kul'ba, V. E. Mironov, I. F. Mavrin, and Y. B. Yakovlev, *Russ. J. Inorg. Chem.*, 1965, **10**, 1117.

[5] I. F. Mavrin, F. Ya. Kul'ba, and V. E. Mironov, *Russ. J. Inorg. Chem.*, 1967, **12**, 167.

[6] J. J. Christensen and R. M. Izatt, 'Handbook of Metal Ligand Heats,' M. Dekker, New York, 1970.

[7] M. H. Hutchinson and W. C. E. Higginson, *J.C.S. Dalton*, 1973, 1247.

between nitrate and chlorate and the metal ions Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. The measurements were made at 25 °C and ionic strength $I = 1$ mol dm^{-3}.

EXPERIMENTAL

Materials.—The metals investigated were used in the form of their perchlorates (Alfa and Fluka). Copper(II) perchlorate (Fluka, purum) containing small quantities of iron(III) was purified by means of repeated crystallization. The concentrations of the solutions were determined by compleximetric titrations with ethylenediaminetetra-acetic acid (Carlo Erba RPE). Nitrate and chlorate ions were used in the form of their sodium salts. A standard solution of sodium chlorate was prepared by weight from the pure salt (Fluka, puriss.) which had previously been dried at 120 °C for 3 h.[8] The concentration of the sodium nitrate solution (Carlo Erba RPE ACS), prepared by weight from the salt dried at 120 °C, was checked by reduction with Devarda's alloy followed by acidimetric titration of the ammonia produced.[9]

Procedure.—Heats of reaction were measured at 25.00 °C by means of an LKB 8700-2 precision-calorimetry system and of an LKB 8726-1 100 cm^3 titration vessel, provided with a standard resistor (50 Ω) and a thermistor (2 000 Ω). The accuracy of the instrument was checked by measuring the molar enthalpy of the reaction between tris(hydroxymethyl)methylamine and hydrochloric acid in aqueous solution. The calorimeter was also equipped with a Radiometer ABU 12b autoburette for the addition of the titrant.

To the metal perchlorate solution (*ca.* 0.33 mol dm^{-3}, 93.0 cm^3) contained in the titration vessel, two amounts (2.51 cm^3) of NaX solution ($X = NO_3$ or ClO_3; *ca.* 1 mol dm^{-3}) were added, and the corresponding heat was measured. For each of the reactions studied the above procedure was repeated twice under identical conditions; thus four values of the measured heats for each reaction were obtained. By using the above concentrations, solutions of ionic strength $I = 1$ mol dm^{-3} were always mixed. The ionic strength remained constant during the mixing, because of the negligible contributions made by the associations studied.[10,11] The pH of the solutions was always adjusted to 4.00 ± 0.03 before mixing, by adding NaOH or $HClO_4$ (Merck solutions, 2N and 60% respectively). At this pH hydrolysis of the metal ions investigated is avoided.

The heats of dilution of the titrants were measured in two different ways. First the heat was determined for the addition of two amounts (2.51 cm^3) of the same $Na[NO_3]$ and $Na[ClO_3]$ solutions to water (93.0 cm^3) at pH 4.00 ($HClO_4$). Secondly the same amounts of the titrant solutions were added to a solution of tetramethylammonium chloride (1 mol dm^{-3}, 93.0 cm^3) whose pH had been adjusted to 4.00 with HCl. In this manner the dilution was made at the same ionic strength as in the corresponding determination of the heat of reaction.

Treatment of the Experimental Data.—The two methods described above gave very different values for the heats of dilution. For example, for the dilution of 2.51 and 5.0 cm^3 of $Na[ClO_3]$ in water, −3.5932 and −7.2881 J respectively were obtained, while for the dilution in tetramethylammonium chloride (1 mol dm^{-3}) the absorbed heat amounted to −7.7320 and −14.7021 J. It is difficult to justify this result as due to the influence of the ionic strength over the heat of dilution. Such a difference may be better explained by the presence of secondary thermal effects due to ionic interactions, for example between chloride and sodium ions (by considering the dimensions of the chloride ion, which is smaller than chlorate and nitrate, and its high concentration). Adjustment of the ionic strength to 1 mol dm^{-3} by adding electrolytes (for which the presence of such interactions with the titrant is always possible), was therefore avoided and this was thought to make a smaller error in referring to the heat of dilution in water.

Now if we consider the heat measured during the reaction (Q_R) and during the corresponding dilution experiment in water (Q_D), we may write equations (1) and (2),

$$Q_R = Q_{\mathrm{ass}} + Q_{\mathrm{dil}} + Q_{\mathrm{oth}} \tag{1}$$

$$Q_D = Q_{\mathrm{dil}'} + Q_{\mathrm{oth}'} \tag{2}$$

where Q_{ass} is the heat of association between M^{2+} and X^- ($X = NO_3$ or ClO_3), $Q_{\mathrm{dil}(\prime)}$ is the heat of dilution of the titrant, and $Q_{\mathrm{oth}(\prime)}$ is the heat due to thermal effects, *e.g.* temperature differences between the two solutions, the heat of stirring, *etc.* When the measurements of the heats of reaction and dilution are made under the same experimental conditions and within a short time, $Q_{\mathrm{oth}} = Q_{\mathrm{oth}'}$. As regards the comparison between Q_{dil} and $Q_{\mathrm{dil}'}$, it is necessary to take into account some literature data,[12,13] according to which sodium nitrate and chlorate in aqueous solution give rise to associations which, notwithstanding their weakness, are not negligible in work such as this (on the other hand it was not possible to use these two anions in the form of their tetra-alkylammonium salts because on mixing with the metal solution tetra-alkylammonium perchlorate would have precipitated). By considering the nature of these interactions it is clear that the quantities Q_{dil} and $Q_{\mathrm{dil}'}$ must be regarded as being made up of two parts, one determined by the separation of the charges of the dissociated electrolyte, the other by the extent of dissociation of $Na[NO_3]$ and $Na[ClO_3]$ present in the titrant. The heat of dissociation arising from the latter should be different in the two measurements because dissociation of NaX is more complete during reaction than during the dilution. In the case of the reaction the equilibria (3) and (4) coexist, the latter removing X^- ions

$$NaX \rightleftharpoons Na^+ + X^- \tag{3}$$

$$M^{2+} + X^- \rightleftharpoons [MX]^+ \tag{4}$$

from the solution. The evaluation of this difference between the heats of dissociation was as follows. Assuming $k_{\mathrm{ass}} = 0.25$ dm^3 mol^{-1} for the reaction between Na^+ and $[NO_3]^-$ (ref. 12) and $k_{\mathrm{ass}} = 0.32$ dm^3 mol^{-1} for Na^+ and $[ClO_3]^-$ (ref. 13) (these data refer to 25 °C and $I = 0$), the variation in the number of moles of the associated species $Na[NO_3]$ and $Na[ClO_3]$ in the case of the reaction and of the dilution of the titrant respectively was calculated. The values of k_{ass} used in the calculations were corrected to the

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[8] L. Meites, 'Handbook of Analytical Chemistry,' McGraw-Hill, New York, 1963.

[9] F. P. Treadwell, 'Chimica Analitica–Analisi Quantitativa,' F. Vallardi, Milano, 1966.

[10] M. B. Kennedy and M. W. Lister, *Canad. J. Chem.*, 1966, **44**, 1709.

[11] R. Aruga, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3779.

[12] C. W. Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.

[13] A. D'Aprano and I. D. Donato, *Electrochim. Acta*, 1972, **17**, 1175.

ionic strength of the solutions by means of Davies' formula, $-\log f = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.2I]$. The decrease in the number of moles of NaX in the reaction differs from the corresponding decrease during the dilution by $\leqslant 3\%$ (3.1% on the average for Na[NO_3] ion pairs, and 2.8% for Na[ClO_3]). This is also valid for the corresponding heats of dissociation, which are proportional to the number of dissociating ion pairs. Consequently, within the limits of the above approximation and of the influence of the ionic strength over the heat of dilution, $Q_{dil} = Q_{dil'}$. It follows that $Q_R - Q_D = Q_{ass}$, that is the difference between the heats obtained in the two measurements is due to the association process (4).

TABLE 1

Experimental data obtained on mixing NaX and M[ClO_4]$_2$ solutions

Reaction	c_M / mol dm^{-3}	ΣV_T / cm^3	$10^3 c_{MX}$ / mol dm^{-3}	$\Sigma Q_{corr.}$ / J
$Mn^{2+} + [NO_3]^- \longrightarrow [Mn(NO_3)]^+$	0.34	2.505	4.98	2.2516
		5.01	9.39	4.3762
		2.505	4.98	2.3101
		5.01	9.39	4.2538
$Co^{2+} + [NO_3]^- \longrightarrow [Co(NO_3)]^+$	0.325	2.505	4.83	2.2807
		5.01	9.09	4.2564
		2.505	4.83	2.2602
		5.01	9.09	4.2907
$Ni^{2+} + [NO_3]^- \longrightarrow [Ni(NO_3)]^+$	0.34	2.505	7.40	2.4564
		5.01	13.91	4.9781
		2.505	7.40	2.4343
		5.01	13.91	4.8488
$Cu^{2+} + [NO_3]^- \longrightarrow [Cu(NO_3)]^+$	0.32	2.505	4.90	2.1924
		5.01	9.22	4.2597
		2.505	4.90	2.2016
		5.01	9.22	4.2576
$Zn^{2+} + [NO_3]^- \longrightarrow [Zn(NO_3)]^+$	0.335	2.505	5.20	2.2602
		5.01	9.80	4.3727
		2.505	5.20	2.3891
		5.01	9.80	4.6656
$Mn^{2+} + [ClO_3]^- \longrightarrow [Mn(ClO_3)]^+$	0.34	2.505	4.03	1.9811
		5.01	7.585	3.9145
		2.505	4.03	2.0313
		5.01	7.585	3.8434
$Co^{2+} + [ClO_3]^- \longrightarrow [Co(ClO_3)]^+$	0.325	2.505	8.98	2.2481
		5.01	16.84	4.6693
		2.505	8.98	2.3276
		5.01	16.84	4.5405
$Ni^{2+} + [ClO_3]^- \longrightarrow [Ni(ClO_3)]^+$	0.34	2.505	3.44	1.7130
		5.01	6.47	3.3203
		2.505	3.44	1.7639
		5.01	6.47	3.4148
$Cu^{2+} + [ClO_3]^- \longrightarrow [Cu(ClO_3)]^+$	0.32	2.505	3.33	2.0050
		5.01	6.27	3.9547
		2.505	3.33	2.1004
		5.01	6.27	4.1175
$Zn^{2+} + [ClO_3]^- \longrightarrow [Zn(ClO_3)]^+$	0.335	2.505	5.27	2.1121
		5.01	9.91	4.4254
		2.505	5.27	2.1933
		5.01	9.91	4.2509

TABLE 2

Thermodynamics * of ion-pair formation in aqueous solution at 25 °C and I = 1 mol dm^{-3}

Reaction	$-\log k$	$\Delta G^\ominus$ / kJ mol^{-1}	$-\Delta H^\ominus$ / kJ mol^{-1}	$-\Delta S^\ominus$ / J K^{-1} mol^{-1}
$Mn^{2+} + [NO_3]^- \longrightarrow [Mn(NO_3)]^+$	0.15 ± 0.06	0.86 ± 0.34	4.74 ± 0.10	18.8 ± 1.2
$Co^{2+} + [NO_3]^- \longrightarrow [Co(NO_3)]^+$	0.15 ± 0.08	0.86 ± 0.46	4.86 ± 0.08	19.2 ± 1.6
$Ni^{2+} + [NO_3]^- \longrightarrow [Ni(NO_3)]^+$	−0.08 ± 0.08	−0.46 ± 0.46	3.53 ± 0.09	10.3 ± 1.6
$Cu^{2+} + [NO_3]^- \longrightarrow [Cu(NO_3)]^+$	0.13 ± 0.07	0.74 ± 0.40	4.70 ± 0.01	18.3 ± 1.3
$Zn^{2+} + [NO_3]^- \longrightarrow [Zn(NO_3)]^+$	0.12 ± 0.05	0.68 ± 0.28	4.69 ± 0.16	18.0 ± 1.1
$Mn^{2+} + [ClO_3]^- \longrightarrow [Mn(ClO_3)]^+$	0.27 ± 0.13	1.54 ± 0.74	5.21 ± 0.07	22.6 ± 2.5
$Co^{2+} + [ClO_3]^- \longrightarrow [Co(ClO_3)]^+$	−0.21 ± 0.08	−1.20 ± 0.46	2.73 ± 0.09	5.1 ± 1.6
$Ni^{2+} + [ClO_3]^- \longrightarrow [Ni(ClO_3)]^+$	0.35 ± 0.08	2.00 ± 0.46	5.30 ± 0.09	24.5 ± 1.6
$Cu^{2+} + [ClO_3]^- \longrightarrow [Cu(ClO_3)]^+$	0.34 ± 0.08	1.94 ± 0.46	6.51 ± 0.18	28.4 ± 1.7
$Zn^{2+} + [ClO_3]^- \longrightarrow [Zn(ClO_3)]^+$	0.12 ± 0.05	0.68 ± 0.28	4.37 ± 0.15	16.9 ± 1.1

* The uncertainty in each case is given as the standard deviation.

The molar enthalpies for the association reactions were calculated from the measured heats, corrected for the dilution, and from the values of the association constants obtained by a kinetic method.[7] The constants determined in the previous work referred to 25 °C and ionic strength I = 1 mol dm^{-3} as used here. The entropy values were calculated from $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$. In determining the values of the thermodynamic parameters only the existence of 1 : 1 species has been taken into consideration, because of the excess of metal ion. The absence of MX_2 species was demonstrated, even with an excess of X^-, by Davis and Chong,[14] where the association constant between Cu^{2+} and $[NO_3]^-$ was determined by Raman spectroscopy.

In Table 1 the following experimental data are collected: initial concentration of metal ion in the titration cell (c_M); cumulative volume of titrant added (ΣV_T); concentration of $[M(NO_3)]^+$ and $[M(ClO_3)]^+$ ion pairs present after each addition (c_{MX}); and cumulative heat of reaction corrected for the dilution ($\Sigma Q_{corr.}$, expressed in joules). The initial volume of the $M[ClO_4]_2$ solution was 93.0 cm^3; and the concentrations of the titrant solutions were 1.015 ($Na[NO_3]$) and 1.028 mol dm^{-3} ($Na[ClO_3]$).

RESULTS

The thermodynamic quantities for the association reactions are listed in Table 2. The only possible comparison with previous thermochemical data concerns the reaction between cobalt(II) and nitrate ions, for which, by the method of temperature variation of the formation constant, the following values were obtained:[15] $\Delta H_1 = -1.7 \pm 1.2$ kcal mol^{-1} (-7.1 ± 5.0 kJ mol^{-1}) and $\Delta S_1 = -9.3 \pm 4.2$ Gibbs mol^{-1} (-38.9 ± 17.6 J K^{-1} mol^{-1}), at 15, 25, and 35 °C, and $I = 1$ mol dm^{-3}. These values are in fairly good accordance (if we consider the different methods used) with those of the present work.

DISCUSSION

From the data listed in Table 2 it follows that the ion pairs studies are all enthalpy stabilized, while the entropy term, always negative, is unfavourable to the formation process. This fact seems to demonstrate that the ion pairs are of the outer-sphere (or solvent-separated) type.[15] In fact the slightly exothermic value of $\Delta H^\ominus$ may be a consequence of the formation of a weak metal–ion bond, without displacement of water molecules from the first hydration shell of the cation. This hypothesis justifies the negative values of $\Delta S^\ominus$. In fact, by also taking into consideration the poor solvent-ordering effect of $[NO_3]^-$ and $[ClO_3]^-$ (the respective crystal ionic radii being[16] 2.64 and 2.88 Å), it is reasonable to assume that the association process is in this case prevailing over the solvent structure breaking due to the partial neutralization of the charges.

It is interesting in this connection to compare these results with those of a previous paper[17] in which thermodynamic quantities were determined for the association in aqueous solution of fluoride ion with the five cations studied in this work. In that case the $\Delta H^\ominus$ and $\Delta S^\ominus$ values were all positive, as opposed to the present results. It is possible that the previous values are a consequence of the remarkable solvent-ordering ability of fluoride ion (which is much smaller than nitrate and chlorate; 1.36 Å crystal radius), and that they are determined by the stronger solvent structure-breaking process taking place when this anion is associated with metal ions.

Moreover the data in Table 2 show that as the stability of the ion pairs increases there is a decrease in exothermicity for the association process and a decrease in the negative entropy value. This means, even if enthalpy is the term favouring the complex formation, that it is the entropy factor which determines the differences in stability (see Figures 1 and 2). By considering more precisely log k and $\Delta S^\ominus$ values, it may be noted that their mutual trend allows some conclusions to be derived about the nature of the forces operating in the ion-pair formation.

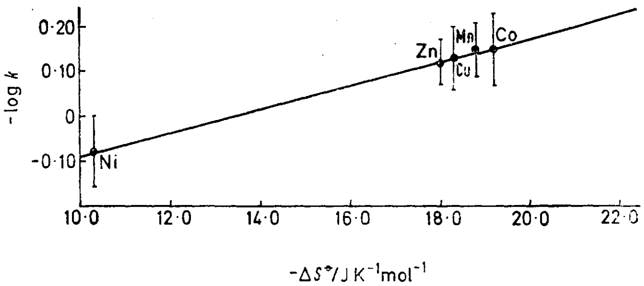

FIGURE 1 Plot of $-\log k$ against $-\Delta S^\ominus$ for the reaction $M^{2+} + [NO_3]^- \longrightarrow [M(NO_3)]^+$

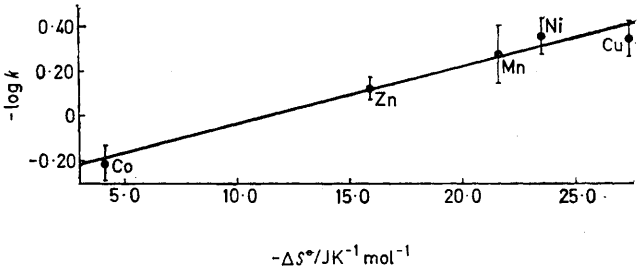

FIGURE 2 Plot of $-\log k$ against $-\Delta S^\ominus$ for the reaction $M^{2+} + [ClO_3]^- \longrightarrow [M(ClO_3)]^-$

If the Born and Bjerrum electrostatic theories[18-20] are used to explain the interaction, equations (5) and (6) can be written for $\Delta G^\ominus$ and $\Delta S^\ominus$, where Z^{n+} and Z^{m-} are

$$\Delta G^\ominus = -\frac{Z^{n+}Z^{m-}}{rD} \qquad (5)$$

$$\Delta S^\ominus = -\frac{\partial \Delta G^\ominus}{\partial T} = -\frac{Z^{n+}Z^{m-}}{rD}\left(\frac{\partial \ln D}{\partial T}\right)_P \qquad (6)$$

the charges of the positive and negative ions of the pair, assumed to be spherical, r is the distance of closest approach of the two ions, and D is the dielectric constant of the medium. Even if the applicability of the above equations to the individual thermodynamic parameters is not satisfactory, combination of (5) and (6) (expressing $\Delta G^\ominus$ in J mol^{-1} and $\Delta S^\ominus$ in J K^{-1} mol^{-1}, and using a value[21] of $(\partial \ln D/\partial T)_P$ of -4.579×10^{-3}) leads to the conclusion that a plot of log k against $\Delta S^\ominus$ should be linear, with a gradient of 0.04. Such plots are given in Figures 1 and

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[14] A. R. Davis and C. Chong, *Inorg. Chem.*, 1972, **11**, 1891.

[15] D. F. C. Morris and L. Vandersyde, *Radiochem. Radioanalysis Letters*, 1969, 123.

[16] E. R. Nightingale, jun., *J. Phys. Chem.*, 1959, **63**, 1381.

[17] R. Aruga, *Ann. Chim.* (*Italy*), in the press.

[18] R. W. Gurney, ' Ionic Processes in Solution,' Dover Publications, New York, 1953.

[19] E. J. King, 'Acid–Base Equilibria,' Macmillan, New York, 1965.

[20] R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc.* (*A*), 1969, 47.

[21] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1958.

2 for the association of the metal ions with nitrate and chlorate respectively. The gradient of the straight line corresponding to the experimental points, calculated by means of a least-squares method, is 0.03 in both cases. This value (*ca.* 0.12 if $\Delta S^{\ominus}$ is expressed in cal K^{-1} mol^{-1}) was obtained in a previous paper [20] on the association of metal ions with sulphate. The agreement (although only partial) of the experimental results with the values predicted by the above theories shows the importance of electrostatics in the associations and the relative values of the thermodynamic quantities.

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