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ION ASSOCIATION OF Cl^- WITH Na^+, K^+, Mg^{2+} AND Ca^{2+} IN AQUEOUS SOLUTION AT $10 \leqslant T \leqslant 45\,^\circ C$ AND $0 \leqslant I \leqslant 1$ mol l^{-1}. A LITERATURE DATA ANALYSIS

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ABSTRACT

The formation constants of $[Na(Cl)]^0$, $[K(Cl)]^0$, $[Mg(Cl)]^+$ and $[Ca(Cl)]^+$ ion pairs have been calculated by using literature data obtained from different techniques at different temperatures and ionic strengths.

Results are reported together with estimated errors, and their reliability is discussed.

Formation enthalpies and entropies are calculated from the dependence on temperature of formation constants.

A computer program for the calculation of dependence on temperature and ionic strength of thermodynamic parameters is described.

INTRODUCTION

There is no field related to the speciation of natural fluids in which the formation of weak ion pairs between alkali and alkaline earth metal ions and the chloride anion can be neglected without making restrictive assumptions.

In fact, chloride anions are present in considerable amounts, together with alkali and alkaline earth metal ions in all natural fluids (blood plasma, urine, sea-water, etc.).

Therefore, the quantitative knowledge of $[M(Cl)]$ ion pair stability is of primary importance in the building of model systems for these fluids.

The formation and stability of $[Na(Cl)]^0$, $[K(Cl)]^0$, $[Mg(Cl)]^+$ and $[Ca(Cl)]^+$ complexes have been studied by several authors using different techniques [1–15].

Since these complexes are very weak, the formation constants are very sensitive to assumptions made concerning the activity coefficients (and on their dependence on ionic strength) during their derivation, and relevant discrepancies can be observed among values reported by various authors.

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Since we considered the matter worthwhile for a further investigation, we report here an analysis of literature data, together with the calculation method used.

METHOD

All the data collected from various authors [1–15] were elaborated by the least squares computer program, REGIS.

This program calculates the empirical parameters for the general equation:

$$\begin{aligned} y_{I,T} = {} & y_{I',\theta} + g_T(y_{I'}) + \{ p^*[c_{0,\theta} + g_T(c_0)] + z^*[c_{1,\theta} + g_T(c_1)] \} \\ & \times (I - I') + \{ p^*[d_{0,\theta} + g_T(d_0)] + z^*[d_{1,\theta} + g_T(d_1)] \} \\ & \times (I^{3/2} - I'^{3/2}) + \{ p^*[e_{0,\theta} + g_T(e_0)] \\ & + z^*[e_{1,\theta} + g_T(e_1)] \} (I^2 - I'^2) - z^*[a_\theta + g_T(a)] \\ & \times \left\{ \frac{I^{1/2}}{1 + \mathring{a}[b_\theta + g_T(b)] I^{1/2}} - \frac{I'^{1/2}}{1 + \mathring{a}[b_\theta + g_T(b)] I'^{1/2}} \right\} \end{aligned} \tag{1}$$

where the function $g_T(x)$, ($x = y_I$, a, b, c_0, c_1, d_0, d_1, e_0 and e_1) represents the temperature dependence of the empirical parameters:

$$g_T(x) = x_{0,\theta} + \sum_p x_{p,\theta}(t - \theta)^p \tag{2}$$

I' and θ are the ionic strength and temperature reference, respectively, p^* and z^* are integers dependent on the stoichiometry of the reaction:

$$\left.\begin{aligned} p^* &= \Sigma(\text{reactants}) - \Sigma(\text{products}) \\ z^* &= \Sigma(\text{charge of reactants})^2 - \Sigma(\text{charge of products})^2 \end{aligned}\right\} \tag{3}$$

and $\mathring{a}$ is the dimensional parameter of the Debye–Hückel equation.

Equation (1) can be used in calculating the dependence on temperature and ionic strength of a large variety of thermodynamic parameters (such as formation constants, densities, partial molal volumes, formation enthalpies, etc.) from both experimental and literature data.

In the case of a single reaction *, equation (1) becomes:

$$\begin{aligned} \log \beta_{I,T} = {} & \log \beta_{I,\theta} + g_T(\log \beta_{I'}) - z^* I^{1/2}(2 + 3I^{1/2})^{-1} \\ & + [C_\theta + g_T(C)](I - I') + [D_\theta + g_T(D)](I^{3/2} - I'^{3/2}) \end{aligned} \tag{4}$$

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* Equations (1)–(3) may be used for calculating the dependence on ionic strength for a series of different reactions [16,17], having different z^* and p^* values: in this case the differences $y_{I,T} - y_{I',\theta}$ are considered.

with $a = 0.5$, $åb = 1.5$, $p^* = 1$, $C_\theta = p^* c_{0,\theta} + z^* c_{1,\theta}$ and $D_\theta = p^* d_{0,\theta} + z^* d_{1,\theta}$.

This equation is widely used for studies on the dependence on ionic strength of formation constants [16,17 *] and of formation enthalpies [18].

The REGIS program can refine all parameters of equation (1) by minimizing the error squares sum:

$$U = \Sigma(y - y_{\text{calc}})^2$$

A first analysis of available data on chloride complexes of Na^+, K^+, Mg^{2+} and Ca^{2+} revealed that the term in $I^{3/2}$ of equation (4) was not necessary, owing to the high dispersion of log β values.

RESULTS AND DISCUSSION

Firstly, the data relative to the association of NaCl and KCl were elaborated **.

Very similar values for both $[Na(Cl)]^0$ and $[K(Cl)]^0$ were obtained, $0.25 \leqslant \beta \leqslant 0.38$ mol^{-1} l in the range $0 \leqslant I \leqslant 1$ mol l^{-1}, where

$$\beta = c_{MCl}(c_M c_{Cl})^{-1} \tag{5}$$

Although the estimated errors are quite large in their absolute value (14–30%), they should be regarded as very low in practice, if difficulties inherent in the determination of formation constants < 1 mol^{-1} l are considered.

Before analysing the data relative to $MgCl_2$ and $CaCl_2$, we corrected the formation constant values obtained in NaCl or KCl solutions without allowing for $[Na(Cl)]^0$ and $[K(Cl)]^0$ complex formation.

The stability of $[Mg(Cl)]^+$ and $[Ca(Cl)]^+$ complexes is higher (about six times) than that of alkali metal chloride complexes, $0.9 \leqslant \beta \leqslant 1.5$ mol^{-1} l.

Also, in this case, errors associated with formation constants are acceptable.

The formation constants of $[Na(Cl)]^0$, $[K(Cl)]^0$, $[Mg(Cl)]^+$ and $[Ca(Cl)]^+$ complexes, at different temperatures and ionic strengths, are reported in Table 1.

From β values we obtained the degree of dissociation α, defined as:

$$\alpha = c_M / C_M \tag{6}$$

by the general equation:

$$\beta C \alpha^2 + \alpha[1 + (z_M - 1)\beta C] - 1 = 0 \tag{7}$$

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* See also refs. in ref. 17.

** All formation constants were converted, when necessary, from molal to molar scale. The values reported in this work are always in the molar scale.

TABLE 1

Formation constants of Ca^{2+}, Mg^{2+}, Na^+ and K^+ chloride complexes

I (mol l^{-1})	log K				
	T(°C)	10	25	37	45
	Ca^{2+}				
0		0.34(11) [a]	0.40(11)	0.45(11)	0.48(11)
0.1		−0.03(10)	0.03(9)	0.07(9)	0.10(10)
0.3		−0.08(9)	−0.04(7)	−0.01(8)	0.02(9)
0.5		−0.05(10)	−0.02(6)	0.01(8)	0.02(10)
1		0.12(19)	0.13(11)	0.14(14)	0.14(19)
		[0.58] [b]	[0.53]	[0.48]	[0.46]
	Mg^{2+}				
0		0.53(8)	0.57(8)	0.61(8)	0.63(8)
0.1		0.13(7)	0.18(7)	0.21(7)	0.24(7)
0.3		0.04(7)	0.08(6)	0.11(6)	0.14(7)
0.5		0.02(9)	0.07(6)	0.10(6)	0.12(8)
1		0.09(17)	0.13(10)	0.16(11)	0.18(16)
		[0.37]	[0.36]	[0.36]	[0.35]
	Na^+				
0		−0.23(11)	−0.30(8)	−0.35(9)	−0.39(11)
0.1		−0.43(9)	−0.50(7)	−0.56(7)	−0.59(10)
0.3		−0.50(9)	−0.57(6)	−0.62(7)	−0.66(9)
0.5		−0.53(9)	−0.59(7)	−0.65(8)	−0.68(10)
1		−0.54(15)	−0.61(13)	−0.66(13)	−0.70(15)
		[0.1]	[0.1]	[0.1]	[0.1]
	K^+				
0		−0.25(11)	−0.29(7)	−0.32(8)	−0.34(11)
0.1		−0.44(10)	−0.48(6)	−0.50(7)	−0.52(10)
0.3		−0.47(8)	−0.51(6)	−0.54(6)	−0.56(8)
0.5		−0.46(9)	−0.50(6)	−0.53(7)	−0.54(10)
1		−0.39(18)	−0.42(11)	−0.45(14)	−0.46(20)
		[0.26]	[0.26]	[0.27]	[0.27]

[a] > 95% confidence interval in parentheses.

[b] In brackets are reported the values for the parameter C.

In addition, the estimated error ϵ_α can be calculated from the equation:

$$\epsilon_\alpha = \frac{C\alpha[\alpha + (z_M - 1)\beta]}{\beta C\alpha(z_M + 1) + 1}\epsilon_\beta \tag{8}$$

(where ϵ_β is the estimated error in β), and the real ionic strength from the equation:

$$I = Cz_M[\alpha + (z_M - 1)/2] \tag{9}$$

As an example, some calculations relative to $[Na(Cl)]^0$ formation are reported in Table 2.

TABLE 2

Association of sodium chloride at 25 ° C

C_{NaCl} (mol l^{-1})	I (mol l^{-1})	β (mol^{-1} l)	α	ϵ_α^a
0.010	0.010	0.41	0.996	
0.040	0.039	0.36	0.986	
0.090	0.088	0.32	0.973	
0.160	0.153	0.29	0.957	
0.250	0.235	0.28	0.939(0.956) [b]	0.01
0.360	0.331	0.27	0.919(0.940)	
0.490	0.440	0.26	0.898(0.930)	
0.640	0.561	0.25	0.876(0.905)	0.02
0.810	0.691	0.25(0.26) [c]	0.853(0.886)	
1.000	0.829	0.25	0.829(0.867)	0.05

[a] Estimated error in α (> 95% confidence interval).

[b] From Millero, ref. 15.

[c] From Johnson and Pytkowicz, refs. 9 and 10.

All the values of α were fitted, for each metal ion, by the equation:

$$\alpha = 1 - [a_1 + a_1'(T - 25)]C^{1/2} - [a_2 + a_2'(T - 25)]C + a_3C^{3/2} \tag{10}$$

and the results are reported in Table 3.

In Fig. 1 α versus C_M and I is shown and, from the temperature dependence of log β, ΔH^0 and ΔS^0 values have been drawn.

Owing to the high uncertainties of formation, constant values of ΔH^0 and ΔS^0, reported in Table 4, are to be considered only as indicative.

As a conclusion of this investigation, two points must be discussed: the first dealing with the reliability of the results obtained here, and the second regarding the influence of chloride complexes of Na^+, K^+, Mg^{2+} and Ca^{2+} on model systems for natural fluids.

In our opinion, the reliability of the reported values is acceptable on the basis of the estimated errors of log β and α (Tables 1 and 2) and considering that the original works, from which we calculated the various formation constants, used very different techniques (potentiometry with ion selective electrodes, conductimetry, freezing point measurements, density measure-

TABLE 3

Parameters for equation (10) defining the dependence of α on total concentration of NaCl, KCl, $MgCl_2$ and $CaCl_2$

M	a_1	a_2	a_3	a_1'	a_2'
Na^+	0.033	0.219	0.079	−0.0009	−0.0004
K^+	0.027	0.246	0.059	−0.0005	-0.0001_5
Mg^{2+}	0.416	0.812	0.628	0.0039	−0.0032
Ca^{2+}	0.258	0.765	0.230	0.0046	−0.0055

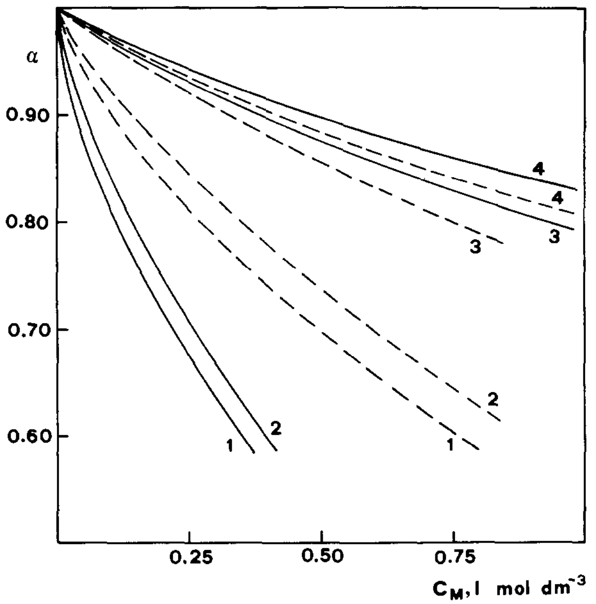

Fig. 1. α versus C_M (———) and α versus I (- - - - -) at 25 °C: 1 = $MgCl_2$; 2 = $CaCl_2$; 3 = KCl; 4 = NaCl.

ments with partial molal volume determination, activity coefficients determination).

To verify how it may be important to consider Cl^- complexes, we

TABLE 4

ΔG^0, ΔH^0 and ΔS^0 values for the formation of $[Na(Cl)]^0$, $[K(Cl)]^0$, $[Mg(Cl)]^+$ and $[Ca(Cl)]^+$ complexes at 25 °C

M	I (mol l^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} °C^{-1})
Na^+	0	1.7(5) [a]	−8(4)	−33(15)
	0.5	3.4(4)	−7(3)	−35(10)
	1	3.5(5)	−7(5)	−35(17)
K^+	0	1.7(4)	−4(4)	−19(13)
	0.5	2.9(3)	−4(3)	−23(10)
	1	2.4(6)	−3.5(5.0)	−20(17)
Mg^{2+}	0	−3.3(5)	5(4)	28(14)
	0.5	−0.4(3)	5(3)	18(10)
	1	−0.7(6)	4(5)	16(16)
Ca^{2+}	0	−2.3(6)	7(5)	31(16)
	0.5	0.1(3)	3.5(3.0)	11(11)
	1	−0.7(6)	1(5)	6(16)

[a] > 95% confidence interval in parentheses.

TABLE 5

Distribution of species in a sea-water model [19]: (A) without considering M(Cl) ion pair formation; (B) considering chloride complexes

	M	Free ion (%)	$M(SO_4)$ (%)	$M(HCO_3)$ (%)	$M(CO_3)$ (%)	M(Cl) (%)
(A)	Ca^{2+}	76.6	21.7	1.4	0.3	–
	Mg^{2+}	74.7	23.8	1.1	0.4	–
	Na^+	98.0	1.9	0.1	0.0	–
	K^+	96.8	3.2	–	–	–
(B)	Ca^{2+}	53.0	18.4	1.1	0.3	27.3
	Mg^{2+}	50.2	19.6	0.8	0.4	29.0
	Na^+	87.3	2.0	0.1	–	10.6
	K^+	83.2	3.4	–	–	13.4

performed some calculation on a Garrels and Thompson [19] type model for sea-water by means of the computer program ES4EC [20] (calculation details are reported in Table 5).

We used the same values of the analytical concentrations and stability constants at $I = 0$ as in ref. 19, but a different approach [16,17] in estimating their values at $I = 0.7$.

As can be seen, the introduction of Cl^- complexes significantly alters the speciation of the simple Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, (Cl^-) systems, with particular regard to the percentage of free metal ions.

Preliminary calculations also showed that in urine speciation [21] chloride complexes should be taken into account [22].

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