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Studies on Sulphate Complexes.
Part I. Potentiometric Investigation of Li^+, Na^+, K^+, Rb^+ and Cs^+ Complexes at 37 °C and $0.03 \leq I \leq 0.5$

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The formation of complexes between sulphate ion and the alkali metal ions ($M^+ = Li^+$, Na^+, K^+, Rb^+ or Cs^+) was investigated. The experiments were carried out measuring potentiometrically the hydrogen ion concentration, at t = 37 °C and variable ionic strengths ($0.03 \leq I \leq 0.5$ mol dm^{-3}). For each alkali metal ion, in addition to the value of the stability constant, we obtained the parameters which define the dependence of the stability constant on ionic strength. The order of stability for $[M(SO_4)]^-$ complexes is $Li^+ > Na^+ < K^+ < Rb^+ < Cs^+$.

The results seem to confirm that the differences in the protonation constants obtained using different ionic media may be explained in terms of complex formation between the ligand and the alkali metal ions.

Introduction

The presence of sulphate ion in all the natural fluids is not negligible: its concentration is 28 mmol Kg^{-1} in seawater, 0.2 mmol dm^{-3} in blood plasma, and very often higher than 10 mmol dm^{-3} in urine. Therefore knowledge of the sulphate complexes and their stability constant values is necessary when calculating the speciation of natural fluids by mathematical simulation [1]. In the natural systems the alkaline and alkaline earth metal ions are present in high concentration and then they are the most important, even if the stability of their complexes is not very high.

We have studied the complexes of all the alkali metal ions with sulphate, at 37 °C and different ionic strengths, since the investigations reported up to now [2–11] are not always sufficient for the speciation of multicomponent systems, which often have ionic strengths very different from each other.

Experimental

The measurements were performed by means of potentiometric measurements of hydrogen ion concentration (c_H) with a model E 600 Metrohm potentiometer, equipped with glass and silver–silver chloride electrodes, at t = 37.0 ± 0.1 °C and $0.03 \leq I \leq 0.5$ mol dm^{-3}. The glass electrode was calibrated by titrating HNO_3 solutions with carbonate free KOH; with respect to background salt and to the initial value of c_H the composition of the standardization solution was the same as in the solutions in which the complexes were studied. In this way the value of E° and of the liquid junction potential could be carefully determined. The pH reproducibility was ±0.005. The experimental points used in the calculations ranged from $-\log c_H \cong 1.9$–2.0 to $-\log c_H \cong 2.7$–3.0.

Sulphuric acid and the alkali metal nitrates, *p.a.* Merck products, were used without further purification.

Other experimental details are as reported elsewhere [12, 13].

Calculations and Results

The potentiometric data obtained in the different ionic media were first analyzed by using the program ACBA [14], without considering the interactions between sulphate and alkali metal ions. This program refines simultaneously the protonation constants and

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TABLE I. SO_4^{2-} Protonation Constants in $LiNO_3$, $NaNO_3$, KNO_3, RbI and $CsNO_3$ Aqueous Solutions, at 37 °C, without allowing for $[M(SO_4)]^-$ Complex Formation and some Experimental Details of Potentiometric Measurements.

M	C_M[a]	$10^3\ C_{SO_4}$	$\sigma\%_{SO_4}$[b]	$\log K^{H'}_{exp}$ (3σ)	$10^3\ \sigma_v$[b]	10^3 R[c]	$\bar{I}$[d]
Li^+[e]	0.03	5.972	0.05	1.762(13)	0.67	1.64	0.045
	0.03	4.587	0.04		0.42	1.26	0.043
	0.1	6.031	0.07	1.588(21)	0.88	2.11	0.115
	0.1	4.593	0.04		0.38	2.15	0.112
	0.3	3.494	0.05	1.351(18)	0.35	1.50	0.308
	0.3	5.273	0.04		0.46	1.27	0.313
	0.3	5.008	0.06		0.49	1.52	0.312
	0.3	6.920	0.05		0.46	0.98	0.32
	0.5	5.304	0.09	1.23(5)	1.02	2.75	0.511
	0.5	7.138	0.04		0.69	1.37	0.52
	0.5	6.975	0.03		0.39	0.82	0.52
Na^+	0.03	6.118	0.05	1.823(5)	0.58	1.46	0.046
	0.1	5.318	0.13	1.694(12)	0.70	3.88	0.114
	0.1	9.737	0.12		2.77	4.02	0.124
	0.3	5.345	0.11	1.567(9)	0.60	3.31	0.313
	0.3	4.871	0.04		0.50	1.49	0.312
	0.5	5.129	0.11	1.444(13)	0.55	3.23	0.511
	0.5	5.964	0.03		0.37	0.91	0.514
K^+	0.03	4.039	0.05	1.812(8)	0.34	1.25	0.041
	0.03	5.735	0.09		1.03	2.39	0.044
	0.1	4.835	0.09	1.665(11)	0.79	2.57	0.113
	0.1	6.391	0.05		0.53	1.23	0.116
	0.29	5.115	0.04	1.502(11)	0.55	1.51	0.303
	0.29	4.987	0.04		0.36	1.11	0.301
	0.5	4.021	0.05	1.395(14)	0.45	1.70	0.509
	0.5	5.766	0.04		0.42	1.03	0.512
Rb^+	0.03	10.731	0.11	1.791(13)	1.12	3.23	0.054
	0.1	10.679	0.05	1.645(8)	0.55	1.60	0.12
	0.3	10.647	0.11	1.467(13)	1.05	3.20	0.314
Cs^+	0.03	10.612	0.07	1.767(8)	0.71	2.06	0.053
	0.1	10.797	0.08	1.605(8)	0.83	2.30	0.12
	0.3	10.646	0.06	1.416(8)	0.52	1.53	0.314

[a]Concentrations in mol dm^{-3}. [b]Calculated by the computer program ACBA. [c]Hamilton's R factor, see ref. 14. [d]Mean ionic strength, in mol dm^{-3}, during the titration. [e]Alkali metal nitrates were used.

the analytical concentration of sulphate (C_{SO_4}). In Table I we report log K_1^H experimental values for each titration, together with the values of some statistical parameters. The percent standard deviation in C_{SO_4} is $\sigma(\%) = 0.065$ and the value of the statistical parameter R ($R = (\Sigma\epsilon^2/\Sigma v^2)^{1/2}$; ϵ = deviations from the volume of titrant, v = volume of titrant) is 0.19%: these results show that the potentiometric data are reliable.

The values of log K_1^H of Table I, together with those previously calculated in Et_4N^+ (tetraethylammonium cation) [15] are plotted in Fig. 1 *vs.* $\sqrt{I}$. It can be observed that i) in the presence of different alkali metal ions, different values of log K_1^H are obtained; ii) the dependence of the protonation constants on the concentration of alkali metal ion is noticeable, and is significantly heavier than we would expect on the basis of a different behaviour of the alkali metal and tetraethylammonium cations, as a function of the ionic strength. Previously [15] a relation was reported for log $K^H = f(I)$:

$$\log K^H = 1.808 - 2.092\left(\frac{\sqrt{I}}{1 + 1.5\sqrt{I}} - 0.214\right) + \\ + 1.21\,(I - 0.1) - 0.31\,(I^{1.5} - 0.0316) \qquad (1)$$

valid in the range $0.01 \leqslant I \leqslant 0.5$ mol dm^{-3}, at t = 37 °C (in eqn. (1) the reference ionic strength is 0.1 and therefore $\sqrt{0.1}/(1 + 1.5\sqrt{0.1}) = 0.214$ and

TABLE II. Log $K^{H'}$ Values Corrected according to Equation (8), log K^{M_i} Values calculated using Equation (5), log $^TK^{M_i}$ and C_i calculated using Equation (9), at 37 °C.

M	$I = C_M$	log $K^{H'}$	log K^M	
Li^+	0.03	1.81	0.89	$\log {}^TK^{Li} = 1.13$; $C = 1.21$
	0.1	1.60	0.77	$r = 0.9976$[a]
	0.3	1.35	0.81	
	0.5	1.24	0.87	
Na^+	0.03	1.86	0.51	$\log {}^TK^{Na} = 0.71$; $C = 1.43$
	0.1	1.71	0.36	$r = 0.9915$
	0.3	1.57	0.41	
	0.5	1.45	0.59	
K^+	0.03	1.85	0.61	$\log {}^TK^{K} = 0.85$; $C = 1.34$
	0.1	1.68	0.50	$r = 0.9978$
	0.29	1.50	0.58	
	0.5	1.40	0.65	
Rb^+	0.03	1.84	0.69	$\log {}^TK^{Rb} = 0.93$; $C = 1.29$
	0.1	1.66	0.58	$r = 0.9963$
	0.3	1.47	0.62	
Cs^+	0.03	1.83	0.77	$\log {}^TK^{Cs} = 1.03$; $C = 1.24$
	0.1	1.62	0.71	$r = 0.9975$
	0.3	1.42	0.70	

[a] r is the linear correlation coefficient.

$0.1^{1.5} = 0.0316$). The values of log K^H that we can calculate by eqn. (1), as well as the experimental ones of Fig. 1, are always much higher than those obtained in alkali metal salts. This fact means that if the activity coefficients are considered constant at the same ionic strength in the different media ionic (this assumption will be discussed below), sulphate ion forms weak (but not negligible) complexes with alkali metal ions.

When weak complexes are formed between a ligand A and the alkali metal ion (M^+), the apparent equilibrium concentration c'_A must be diminished by c_{MA} (equilibrium concentration of alkali metal complex), and then:

$$c_A = c'_A - c_{MA}$$

If the alkali metal salt is in great excess with respect to the analytical concentration of the ligand (C_A), then c_{MA} may be considered constant. Therefore the contribution to the conditional (or apparent) stability constant* due to a background salt may be considered constant when the alkali metal ion and its concentration are fixed.

The mass balance equations can be written in two different ways, according to whether the alkali metal complexes are taken into account (a), or not (b); for sulphate, in the most general case with M_1, M_2, ..., M_n alkali metal ions, they are:

$$\text{(a)}\ C_{SO_4} = c_{SO_4} + K^H c_{SO_4} c_H + K^{M_1} c_{SO_4} c_{M_1} + \ldots$$
$$\ldots + K^{M_n} c_{SO_4} c_{M_n} \qquad (2)$$

$$\text{(b)}\ C_{SO_4} = c'_{SO_4} + K^{H'} c'_{SO_4} c_H \qquad (3)$$

where C_{SO_4} is the analytical concentration, c_H, c_{M_i} and c_{SO_4} are the equilibrium concentrations of H^+, M^+ and SO_4^{2-} respectively and K^{M_i} is the stability constant of the complex formed by the ligand and M_i. By comparing eqns. (2) and (3) the following equations can be obtained:

$$(K^{H'} c_H)^{-1} = (K^H c_H)^{-1} + \sum_{i=1}^{n} K^{M_i} c_{M_i} (K^H c_H)^{-1} \qquad (4)$$

or

$$\log K^H = \log K^{H'} + \log\left(1 + \sum_{i=1}^{n} K^{M_i} c_{M_i}\right) \qquad (5)$$

when $C_{SO_4} \ll C_{M_i}$ it can be assumed that $c_{M_i} \cong C_{M_i}$.

From the log $K^{H'}$ of Table I and those calculated by eqn. (1), it is possible to obtain approximate

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*We define 'conditional' the stability constant values not corrected for the formation of alkali metal complexes.

values of K^K, for the species $[K(SO_4)]^-$, by using eqn. (5). Since all the alkalimetric titrations were performed using K[OH] as titrant, a correction is necessary when the determinations are carried out in the presence of alkali metal ions other than K^+. This correction $\delta^{(K)}(\log K^{H'}) \cong \log(1 + K^K C_K)$ is possible if the value, even approximate, of $\log K^K$ is known. Furthermore the mean ionic strength during the titrations ($\bar{I}$) may be different from the concentration of background salt, especially when $I < 0.1$ mol dm^{-3}, therefore the $\log K^{H'}$ values were also corrected ($\delta^{(I)}(\log K^{H'})$), according to eqn. (7), derived from eqn. (1):

$$\delta^{(I)}(\log K^{H'}) = 2.092\left(\frac{\sqrt{\bar{I}}}{1 + 1.5\sqrt{\bar{I}}} - \frac{\sqrt{C_M}}{1 + 1.5\sqrt{C_M}}\right) - \\ - -1.21\,(\bar{I} - C_M) + 0.31\,(\bar{I}^{1.5} - C_M^{1.5}) \qquad (7)$$

Hence, if $[C_{M_j} = 0]_{j \neq i}$ and we put $I = C_{M_i}$, the corrected value is:

$$\log K^{H'} = \log K^{H'}_{exp} + \delta^{(I)}(\log K^{H'}) + \delta^{(K)}(\log K^{H'}) \quad (8)$$

where $\log K^{H'}_{exp}$ is the value directly obtained by the calculation, without any correction.

The values of $\log K^{H'}$, corrected according to eqn. (8) are listed in Table II. Log K^{M_i} values, calculated by using eqn. (5) (the $\log K^H$ values, at the different ionic strengths, are those calculated by eqn. (1)), are shown in the same Table.

The dependence on ionic strength was investigated by the function Y (eqn. (9)):

$$Y = \log K^M(I) + 2.092\,\frac{\sqrt{I}}{1 + 1.5\sqrt{I}} - \\ - DI^{1.5} = \log {}^TK^M + CI \qquad (9)$$

where $\log {}^TK^M$ is the stability constant at zero ionic strength and D is made equal to −0.4, as found in a previous investigation [15]. The above function is the equation of a straight line, the coefficients of which, together with the correlation coefficient, are reported in Table II for each alkali metal.

Log K^{M_i} was also determined by two computer programs [11–14] namely: a) Modified MINIQUAD 76A [16, 17]. This program refines the formation constants values and the parameter C, which defines the dependence on ionic strength of log K^{M_i} (the parameter D is kept constant (−0.4) on the basis of our previous results [15]), according to eqn. (10):

$$\log K(I) = \log K(I') - Az^*\left(\frac{\sqrt{I}}{1 + 1.5\sqrt{I}} - \frac{\sqrt{I'}}{1 + 1.5\sqrt{I'}}\right) + \\ + C(I - I') + D(I^{1.5} - I'^{1.5}) \qquad (10)$$

TABLE III. Formation Constants for $[M(SO_4)]^-$ Complexes, at 37 °C, calculated using Different Methods.

M	$\log K^M$ (I = 0.1)	C	D	Method
Li^+	0.79	1.21	−0.4	eqn. (9)
	0.77(6)[a]	0.95	−0.4	MINIQUAD
	0.77	1.25	−0.4	ACBA[b]
Na^+	0.39	1.43	−0.4	eqn. (9)
	0.40(3)	1.41	−0.34	ACBA
	0.42(6)	1.44	−0.4	MINIQUAD
	0.41	1.25	−0.4	ACBA[b]
K^+	0.52	1.34	−0.4	eqn. (9)
	0.55(3)	1.29	−0.43	ACBA
	0.55(3)	1.31	−0.4	MINIQUAD
	0.53	1.25	−0.4	ACBA[b]
Rb^+	0.60	1.29	−0.4	eqn. (9)
	0.61(8)	1.00	−0.4	MINIQUAD
	0.60	1.25	−0.4	ACBA[b]
Cs^+	0.69	1.24	−0.4	eqn. (9)
	0.72(8)	1.05	−0.4	MINIQUAD
	0.69	1.25	−0.4	ACBA[b]

[a] 3σ in parenthesis. [b] Values calculated using for all the complexes C = 1.25 and D = −0.4.

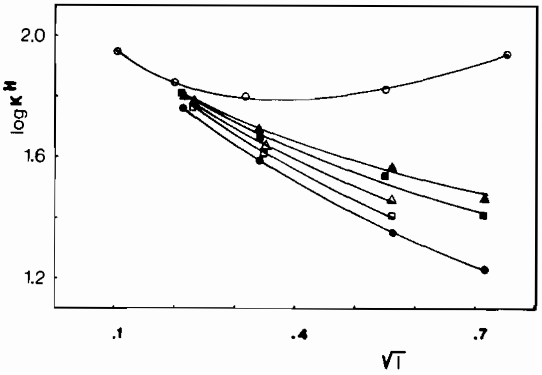

Fig. 1. Conditional protonation constants in different backgrounds: ○ Et_4N^+, ▲ Na^+, ■ K^+, △ Rb^+, □ Cs^+, ● Li^+.

where I′ is the reference ionic strength; A is the Debye–Hückel constant (A = 0.523 at 37 °C); z* is the square of the charge on each species summed over the formation reaction of a complex species (z* = 4, for the formation of $[M(SO_4)]^-$). The protonation constants used in this calculation are those obtained from eqn. (1). b) Modified ACBA [14,

TABLE IV. Mean Values of Stability Constants for the $[M(SO_4)]^-$ Complexes, Parameters for the Dependence on Ionic Strength (at 37 °C), and some Literature Data.

M	log K^M (I = 0.1)	C	–D	Literature data
Li^+	0.77(4)[a]	1.1(2)	0.4	1.1[c]
Na^+	0.40(5)	1.4(2)	0.4	0.72[d]
K^+	0.54(4)	1.3(2)	0.4	0.87[e] 0.5[f]
Rb^+	0.60(5)	1.2(2)	0.4	
Cs^+	0.70(5)	1.2(2)	0.4	

I	log K^{Li}	log K^{Na}	log K^K	log K^{Rb}	log K^{Cs}
0	(1.12)[b]	(0.72)	(0.87)	(0.94)	(1.04)
0.05	0.82	0.44	0.58	0.65	0.75
0.15	0.75	0.40	0.53	0.59	0.69
0.2	0.75	0.41	0.54	0.59	0.69
0.3	0.76	0.45	0.57	0.61	0.71
0.5	0.81	0.56	0.66	(0.68)	(0.78)
0.7	(0.88)	(0.69)	(0.77)	(0.77)	(0.87)

[a] >95% confidence limits in parenthesis. [b] Extrapolated values in parenthesis. [c] Calculated from Ramette and Stewart solubility data [9], I = 1, t = 25 °C. [d] Jenkins and Monk [8], I = 0, t = 25 °C, conductivity measurements. [e] Righellato and Davies [11], I = 0, t = 40 °C, conductivity measurements. [f] Chlebek and Lister [10], I = 0.1, t = 39 °C, K^+ glass electrode.

18]. This program, which was previously used only for the refinement of the protonation constants, can in the actual version also calculate the formation constants of weak complexes and the parameters C and D, by using eqns. (5) and (10).

The results of the analysis of the potentiometric data by means of the two above programs are listed in Table III.

In order to show the importance of these weak complexes, we calculated the distribution of the species. If we consider, as an example, a solution 0.1 mol dm^{-3} in $Na_2[SO_4]$ (I = 0.3), we found that for $-\log C_H$ values higher than 4, about 30% of sulphate ion is bound to Na^+.

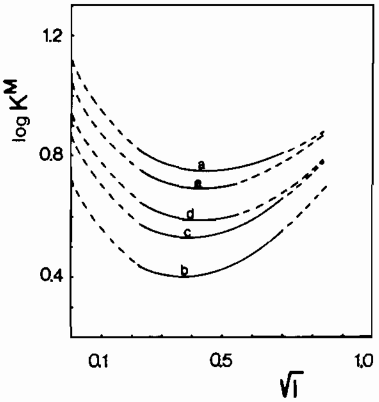

Fig. 2. log K^M *vs.* $\sqrt{I}$ (Full lines refer to the range experimentally studied, dotted lines are extrapolated). a) Li^+, b) Na^+, c) K^+, d) Rb^+, e) Cs^+.

Discussion

Log K_M values reported in Table III are in good agreement with the literature data [2–11, 19, 20], even if many of them were obtained by indirect techniques (for example, from activity [19] or osmotic coefficients [20]). The standard deviations seem to be so low that the values of the stability constants can be used for both a correct speciation of the natural fluids and a characterization of the stability of $[M(SO_4)]^-$ complexes: the order (Li > Na < K < Rb < Cs) is well shown by the plot of Fig. 2, in which the full lines are calculated in the ranges experimentally studied.

It is interesting to remark that the dependence on ionic strength is very similar for all five metal ions studied. In fact, by considering a mean value of C = 1.25, the stability constant values estimated at I = 0.1 mol dm^{-3} (see Table III) are very close to those obtained with a different C for each metal ion. The analysis of variance, applied to the five systems examined has shown that there are no significant differences, as concerns the dependence on ionic strength, among these systems. A similar behaviour was already observed in previous investigations on protonation constants of organic and inorganic acids [15] and on complex formation between citrate and alkali metal or ammonium ions [21].

TABLE V. Protonation Constants of Sulphate and $[Na(SO_4)]^-$ Formation Constants using Different Sets of Measurements (ref. 15 and this work), at 37 °C (D = –0.4).[a]

Measurements	$\log K^H$ (I = 0.1)	C	$\log K^{Na}$ (I = 0.1)	C
$C_{Na} = 0.03-0.5$, $C_{Et_4N} = 0.03-0.5$	1.804(2)[b]	1.29(2)	0.42(1)	1.43(3)
$C_{Na} = 0.03-0.5$, $C_{Et_4N} = 0.03-0.3$	1.804(2)	1.29(2)	0.42(1)	1.44(4)
$C_{Na} = 0.03-0.5$, $C_{Et_4N} = 0.03-0.1$	1.804(3)	1.28(5)	0.42(2)	1.43(6)

[a]Calculations performed by MINIQUAD program. [b]Standard deviations in parenthesis.

The mean values of the stability constants obtained by the different methods, together with the parameters for the dependence on ionic strength, are listed in Table IV. Some values calculated at different ionic strengths, including extrapolated values as well (in parenthesis), are also reported.

Finally the assumption, according to which the differences in the protonation constants (and consequently in the apparent activity coefficients) are due for the most part to the complex formation with alkali metal ions, must be discussed. It seems to be supported by three factors: i) The literature values for sodium– and potassium–sulphate complexes [2–11], determined by independent techniques (see Table IV), are in excellent agreement with ours*. ii) The parameters for the dependence on ionic strength have practically the same values for the protonation of sulphate and for the complex formation with alkali metal ions. This fact seems to be, rather than a coincidence, an indirect demonstration that the effects due to ionic strength and to the interactions ligand–background salt can be separated when considering the protonation constants. iii) Both the protonation constant of sulphate and the formation constant of $[Na(SO_4)]^-$ can be calculated by taking into account the pH-metric data in Et_4N^+ [15] and in Na^+. We have considered separately, first all the data up to $C_{Et_4N} = 0.1$, then up to $C_{Et_4N} = 0.3$ and finally up to $C_{Et_4N} = 0.5$ mol dm^{-3}. The results of this refinement are reported in Table V: there is no difference either in the values of the stability constants or in the values of the statistical parameters. If significant specific interactions, different from complex formation, were present, the behaviour would have been different in the three cases.

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*Furthermore, evidence for $Li^+-SO_4^{2-}$ complex formation was also obtained by Raman spectra [22].