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Thermodynamics of Association of Selenate and Sulfate with Bivalent Metals. Calculation, by Calorimetric Data, of the Water Molecules Displaced from a Cationic Sphere

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Enthalpy and entropy values have been determined, by direct calorimetry and by using the formation constants of the literature, for the associations of Zn^{2+} and Cd^{2+} with selenate and sulfate anions. The measurements have been performed in aqueous solution, at 25 °C and ionic strength $I = 0.5$ M. The examination of the present data (together with previous data for the associations of selenate and thiosulfate) leads to the following conclusions. (a) Selenate behaves like sulfate, with a predominantly electrostatic action toward metal ions. It forms mainly outer-sphere pairs with smaller cations (Zn^{2+}, Co^{2+}, Ni^{2+}) and inner-sphere pairs with the larger ones. The data indicate that one water molecule is displaced from Mn^{2+} and two molecules from Cd^{2+}. (b) Selenate and sulfate do not always behave as thiosulfate does. Sometimes thiosulfate forms covalent bonds with metals, as in the case of Zn^{2+} and Cd^{2+}. In these cases the desolvation process of the metal may be different from that observed for the other two anions.

In a previous paper[1] enthalpy and entropy values were determined by calorimetry for the association of thiosulfate with bivalent metals in aqueous solution. In that case it was possible to determine, from calorimetric data, whether contact (i.e., inner sphere) or solvent-separated ion pairs were formed. In the case of inner-sphere interactions it was also possible to calculate the number of water molecules displaced from the cationic hydration sphere. That method of calculation (as demonstrated also in a study of Larson[2]) seemed to be useful when precise entropy values are available for the formation of electrically neutral ion pairs between an anion and a set of metal ions.

In view of the above results, it seemed worthwhile to continue these studies. Therefore, in the present work enthalpy and entropy were determined for the association in aqueous solution of selenate and sulfate with Zn^{2+} and Cd^{2+}, under the same conditions used for thiosulfate ($T = 25$ °C, $I = 0.5$ M). Thus it is possible to compare the behavior of selenate (for which no direct calorimetric datum is available in the literature) with the behavior of the other two anions. In the second place, the above method of calculation, which was previously used for a single anion with various metals,[1] by means of the present results may be extended to the case of different anions. Finally, it should be noted that calorimetric data for sulfate are available in the literature, but they do not seem useful in the present case, inasmuch as they were determined under different experimental conditions and the results of the various investigations are inconsistent. For example, the heats of association of SO_4^{2-} obtained by Izatt et al.[3] by means of the "entropy titration" method are rather different from other values[2] obtained from the dilution heats of dilute solutions of metal sulfates.

Experimental Section

Reagents. Zn(II) and Cd(II) nitrates were used (C. Erba RPE). The concentrations of the solutions were determined by complexometric titration with EDTA (0.1 M solution, C. Erba RPE). Solutions of tetraethylammonium selenate, sulfate, and nitrate were prepared by neutralizing stock solutions of selenic, sulfuric, and nitric acids (C. Erba RPE) with tetraethylammonium hydroxide (20% solution, Merck). The nitrates of the metals were used instead of the perchlorates owing to the too low solubility of tetraethylammonium perchlorate in water.

Equipment. Calorimetric measurements were performed at 25.00 °C by an LKB 8700-2 Precision Calorimetry System and an LKB 8726-1 100-mL titration vessel, provided with a standard resistor (50 Ω) and a thermistor (2000 Ω). The accuracy of the instrument was checked by measuring the molar enthalpy of the reaction between tris(hydroxymethyl)methylamine and HCl in aqueous solution. The calorimeter was also equipped with a Radiometer ABU 12b autoburette for the addition of the titrant. The calorimetric experiments were performed in a room whose temperature was kept constant within ±0.3 °C. For the pH measurements a Metrohm Compensator E 388 potentiometer was used, at 25 °C.

Table I. Experimental Data for the Mixing of Metal and Ligand Solutions[a]

M^{2+}	A^{2-}	ΣV_T, mL	$10^{-3}C_{MA}$, M	$-\Sigma Q_c$, cal
Zn^{2+}	SO_4^{2-}	2.506	2.88	−0.110
		5.012	5.52	−0.193
		7.518	7.92	−0.271
Cd^{2+}	SO_4^{2-}	2.506	2.94	0.132
		5.012	5.62	0.250
		7.518	8.06	0.365
Zn^{2+}	SeO_4^{2-}	2.506	2.67	0.022
		5.012	5.10	0.033
		7.518	7.31	0.027
Cd^{2+}	SeO_4^{2-}	2.506	2.89	0.253
		5.012	5.53	0.489
		7.518	7.94	0.701

[a] Initial concentrations of Zn^{2+} and Cd^{2+} in the cell were 0.1691 and 0.1701 M, respectively.

Procedure. Several sets of measurements were carried out, each set being performed in the following manner. Successive amounts of 2.506 ± 0.0025 mL of tetraethylammonium sulfate or selenate (0.17 M) were added to 88.00 mL of metal nitrate solution ($C_M = 0.17$ M) contained in the titration cell of the calorimeter, and the heat for each addition was measured. The pH value of all solutions had been previously brought to 5.0. The heat of dilution was measured by adding the same amounts of titrant to 88.00 mL of 0.50 M tetraethylammonium nitrate solution, without metal, at pH 5.0. The following results were obtained under these conditions: (a) an ionic strength constant at $I = 0.5$ M in the calorimetric cell, for both the metal–ligand reactions and the dilutions (the decrease in the I value resulting from the association reactions was calculated and was shown to cause a negligible variation in the total I); (b) the absence of species of the MA_2^{2-} type, owing to the strong excess of metal; (c) the absence of protonated anionic species, with $pK_a = 1.4$ for both of the ligands[4,5] (these values were determined at 25 °C and corrected to $I = 0.5$ by means of Davies' equation, see below); (d) the absence of hydrolysis products of the metals. Finally, by using tetraalkylammonium salts it was possible to eliminate some disturbing association processes, which would have been present with alkaline metal salts.[3]

Treatment of the Experimental Data. Table I collects the following experimental data for the mixing of metal and ligand solutions: cumulative volume of titrant added ($\sum V_T$); the ion pair's concentration after each addition (C_{MA}); cumulative heat corrected for the dilution ($\sum Q_c$). The molar enthalpies of association were obtained from $\sum Q_c$

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Table II. Thermodynamics for the Association Reactions in Aqueous Solution at 25 °C and $I = 0.5$ M

reaction	log *k*	$-\Delta G°$,[a] kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, gibbs mol^{-1}
$Zn^{2+} + SO_4^{2-} \rightarrow ZnSO_4$	0.99 ± 0.02[b]	1.35 ± 0.03	−0.37 ± 0.01	3.3 ± 0.1
$Cd^{2+} + SO_4^{2-} \rightarrow CdSO_4$	1.01 ± 0.03	1.38 ± 0.04	0.48 ± 0.01	6.2 ± 0.1
$Zn^{2+} + SeO_4^{2-} \rightarrow ZnSeO_4$	0.91 ± 0.02	1.24 ± 0.03	0.05 ± 0.01	4.3 ± 0.1
$Cd^{2+} + SeO_4^{2-} \rightarrow CdSeO_4$	0.99 ± 0.03	1.35 ± 0.04	0.94 ± 0.01	7.7 ± 0.1
$Zn^{2+} + S_2O_3^{2-} \rightarrow ZnS_2O_3$	1.12	1.53	2.20 ± 0.03	12.5
$Cd^{2+} + S_2O_3^{2-} \rightarrow CdS_2O_3$	2.64	3.60	−0.04 ± 0.01	11.9

[a] The results are expressed by means of the thermochemical calorie, equal to 4.1840 absolute J. [b] The uncertainty in each case is given as the standard deviation. log *k* values for thiosulfate were reported[10] without the standard deviations.

and from the formation constants of literature.[6,7] These constants were corrected to $I = 0.5$ M by means of Davies' equation: $-\log f = Az^2[I^{1/2}/(1 + I^{1/2}) - 0.2I]$. The calculations of $\Delta H°$ and its standard deviation were made by two different methods reported previously:[8,9] (a) the numerical method of minimization of the function U, i.e., the error square sum for n measurements, $U = \sum_{i=1}{}^{n} w_i(\sum Q_i + V\sum_{j=1}{}^{n}\sum_{k=1}{}^{j}[ML_j]\Delta H°_k)^2$; (b) a graphical method derived from the equations of Leden and Fronaeus. The standard deviation of the measured heats was also calculated; it ranged from 4×10^{-3} to 12×10^{-3} cal. The above two methods of calculation gave $\Delta H°$ values in good accordance. The entropy variation values were obtained by $\Delta G° = \Delta H° - T\Delta S°$.

Results

The thermodynamics for the association reactions are listed in Table II, together with the values for thiosulfate.[1]

The only comparison to be made with literature data regards sulfate. The values of Table II for this anion seem to be in rather strong disagreement with the previous calorimetric data.[2,3] However, considering that the previous data refer to $I = 0$ M and correcting the results of Table II to this ionic strength, it can be shown that the present values are in satisfactory agreement with those of Izatt and co-workers.[3] In fact for Zn^{2+} and Cd^{2+} with SO_4^{2-} a $\Delta H_0°$ of 0.60 and 1.45 kcal mol^{-1}, respectively, was found from the values of Table II, against 0.63 and 0.98 of ref 3; for $\Delta S_0°$, 12.4 and 15.3 gibbs mol^{-1} of the present work compare with 13.5 and 15.0. The above quantities were corrected by using

$$\Delta H_0° = \Delta H° + RT^2\textstyle\sum \nu_i \partial(\ln \gamma_i)/\partial T \qquad (1)^{11}$$

$$\Delta S_0° = \Delta S° + R[T\textstyle\sum \nu_i \partial(\ln \gamma_i)/\partial T - \sum \nu_i \ln \gamma_i] \qquad (2)^{11}$$

and by considering

$$\sum \nu_i \partial(\ln \gamma_i)/\partial T = -\tfrac{3}{2}\left(\frac{1}{D}\frac{\partial D}{\partial T} + \frac{1}{T}\right)\sum \nu_i \ln \gamma_i \qquad (3)$$

where ν_i is the number of moles of the species i with the activity coefficient γ_i, and D is the dielectric constant of the solvent. The values of R, D, and $\partial D/\partial T$ are those reported by Harned and Owen.[12]

Discussion

The enthalpies in Table II, which are a little more endothermic for selenate than for sulfate, suggest a different intensity of electrostatic interaction between cation and anion, as a consequence of the larger dimension of SeO_4^{2-} in relation to SO_4^{2-} (3.05 and 2.90 Å respectively for crystal radius[13]). On the contrary, very different are the values for thiosulfate, in which the S^- group demonstrates a strong covalent action[1] toward Zn^{2+} and Cd^{2+}.

In order to examine more particularly the structure of these ion pairs, it is necessary to recall briefly the previous calculations for thiosulfate and to refer to the above-mentioned papers[1,2] for greater details. Let us consider an association reaction between a metal and an anion, both in the hydrated form, from which an electrically neutral ion pair is formed with the displacement of p water molecules from the cation (eq 4)

$$M_I(H_2O)_n{}^{q+}(aq) + A^{q-}(aq) \rightarrow M_I(H_2O)_{n-p}A(aq) + pH_2O \qquad (4)$$

and an analogous reaction between another metal and the same anion, with the displacement of m water molecules (eq 5).

$$M_{II}(H_2O)_n{}^{q+}(aq) + A^{q-}(aq) \rightarrow M_{II}(H_2O)_{n-m}A(aq) + mH_2O \qquad (5)$$

With $\Delta S_I°$ and $\Delta S_{II}°$ being the entropy variations for reactions 4 and 5

$$\Delta S_I° - \Delta S_{II}° = \bar{S}'(M_I(H_2O)_{n-p}A(aq)) - \bar{S}'(M_{II}(H_2O)_{n-m}A(aq)) + \bar{S}°(M_{II}(H_2O)_n{}^{q+}(aq)) - \bar{S}°(M_I(H_2O)_n{}^{q+}(aq)) + (p - m)S°(H_2O) = \Delta S_{ex}° \qquad (6)$$

where $\bar{S}'$ is a "corrected" entropy content of the ion pair,[14] because this content does not include the entropy of the water molecules displaced in the reaction, and $\Delta S_{ex}°$ refers to exchange reaction 7, obtained from the difference between (4)

$$M_I(H_2O)_n{}^{q+}(aq) + M_{II}(H_2O)_{n-m}A(aq) \rightarrow M_I(H_2O)_{n-p}A(aq) + M_{II}(H_2O)_n{}^{q+}(aq) + (p - m)H_2O \qquad (7)$$

and (5). By simple rearrangements we obtain[1]

$$\Delta S_I° - \Delta S_{11}° = \Delta S_{ex}° = \Delta S_{p-m}° + \bar{S}°(M_{11}(H_2O)_n{}^{q+}(aq)) - \bar{S}°(M_I(H_2O)_n{}^{q+}(aq)) \qquad (8)$$

where $\Delta S_{p-m}°$ is the entropy variation for the displacement of $(p - m)$ water molecules from the cationic hydration sphere in exchange reaction 7. By knowing the entropy variation for the displacement of one water molecule from a cation (about 7.3 gibbs mol^{-1}) and by taking into consideration eq 8, the value of $(p - m)$ can be obtained. It is also possible, by knowing p or m for a certain cation taken as reference, to obtain the number of water molecules removed in the association of other metals with the same anion. Moreover, it must be noted that reaction 7 takes place without variation of the electric charges between reactants and products. This fact (see eq 2) shows that the value of $\Delta S°$ for (7) is not influenced by the ionic strength of the solution. Therefore $\Delta S°$ values can be used in the present calculations, referred to any value of I, provided that this value is constant and determined. On the contrary, in the previous calculations of Larson[2] for the associations of sulfate, $\Delta S°$ values referred to $I = 0$ must be used. The above calculations give a $\Delta S_{p-m}°$ value of 12.4 gibbs mol^{-1} for the exchange reaction of sulfate (see Table III, reaction 9). This value (by remembering the amount of 7.3 gibbs for 1 mol of displaced water) is in satisfactory agreement with $p - m = 2$. An interaction of the outer-sphere type having been previously demonstrated[2] between Zn^{2+} and SO_4^{2-} (m

Table III. $\Delta S_{p-m}°$ Values for Exchange Reactions

no.	reaction	$\Delta S_{p-m}°$, gibbs mol^{-1}	$p - m$
9	$Cd^{2+} + ZnSO_4 \rightarrow CdSO_4 + Zn^{2+}$	12.4	2
10	$Cd^{2+} + ZnSeO_4 \rightarrow CdSeO_4 + Zn^{2+}$	12.9	2
11	$ZnSO_4 + SeO_4^{2-} \rightarrow ZnSeO_4 + SO_4^{2-}$	2.4	0
12	$Mn^{2+} + CoSeO_4 \rightarrow MnSeO_4 + Co^{2+}$	7.3	1
13	$Mn^{2+} + NiSeO_4 \rightarrow MnSeO_4 + Ni^{2+}$	10.5	1

= 0), the formation of contact ion pairs is also confirmed by the present data for Cd^{2+} and SO_4^{2-}, with a bidentate action ($p = 2$) by the latter.

The analogous exchange of selenate (Table III, reaction 10) gives $\Delta S_{p-m}° = 12.9$ gibbs mol^{-1}, in agreement with $p - m = 2$. In this case neither p nor m are known. We can therefore take as reference the case of the association between Zn^{2+} and SO_4^{2-} (for which the absence of displacement processes has already been demonstrated) and calculate $\Delta S_{p-m}°$ for anion-exchange reaction 11 in Table III. For this reaction $\Delta S_{p-m}° = 2.4$ gibbs mol^{-1}. This value, if it is taken into account that $\bar{S}°(SeO_4^{2-}(aq))$ is known only rather approximately (see below), satisfactorily agrees with $p - m = 0$. Hence it follows that selenate acts in like manner as sulfate with both Zn (outer-sphere interaction) and Cd, with the displacement of two water molecules from the hydration sphere of the latter metal. It must be noted that these calculations, in the case of anion exchange, require the knowledge of the partial molal entropy for both of the anions. For SO_4^{2-} the experimental value of 4.4 gibbs mol^{-1} was used.[15] For SeO_4^{2-} it was calculated by using the empirical equation (14) obtained

$$\bar{S}° = {}^{3}\!/_{2}R \ln M + 66 - 81Zf/r_{12} \qquad (14)$$

by Cobble[14] for inorganic oxyanions, where R is the ideal gas constant, M is the ionic mass, Z is the absolute integral charge of the anion, f is a structural constant (0.74 for selenate[14]), and r_{12} is the Se–O interatomic crystal distance (ca. 1.6 Å). It was obtained that $\bar{S}°(SeO_4^{2-}(aq)) = 5.8$ gibbs mol^{-1}.

It may be interesting to extend the above calculations to the $\Delta S°$ values obtained previously by Ghosh and Nair[16] for the association of Mn^{2+}, Co^{2+} and Ni^{2+} with SeO_4^{2-}. These values were obtained by the method of log k variation with temperature and refer to $I = 0$ M. Two conclusions were drawn in that paper: (a) the interactions studied are of electrostatic type; (b) in these interactions solvent-separated ion pairs are formed, owing to the inability of selenate to remove water molecules from the three examined cations. For reactions 12 and 13 in Table III a $\Delta S_{p-m}°$ value of 7.3 and 10.5 gibbs mol^{-1}, respectively, is obtained (by using[17] the $\Delta S°$ values of ref 16). If we assume that for the Co^{2+} and Ni^{2+} associations with SeO_4^{2-} it is really $p = 0$ (both for an analogy with SO_4^{2-} and because of their small dimensions[1]), the above values of $\Delta S_{p-m}°$, and particularly the former, are in close agreement with the formation of a contact ion pair between Mn^{2+} and SeO_4^{2-}, as a consequence of the displacement of one water molecule from this cation. Therefore the conclusions of Ghosh and Nair seem to be in accordance with the experimental data in the case of Co and Ni but not for Mn.

It is worth mentioning that, in the past, other methods were proposed for the calculation of the number of water molecules displaced in complex formation reactions. For example, an empirical equation (15) of Cobble[11,14] can be used for this

$$\bar{S}° = 49 - 99z[f/(r_1 + r_2)] + nS_{H_2O}° \qquad (15)$$

purpose, which is analogous to (14), where $\bar{S}°$ is the partial molal entropy of the inorganic complexes; i.e., $\bar{S}° = \Delta S_0° + \bar{S}°(M^{q+}(aq)) + \bar{S}°(A^{z-}(aq))$ (z is the absolute integral charge of the anion A^{z-}), f is a structural constant, r_1 and r_2 are the crystal radii of the cation and anion, n is the number of water molecules removed from the cationic sphere in the complex formation, and $S_{H_2O}°$ is the partial molal entropy of water. The calculation of n by (15), besides various experimental quantities, requires the knowledge of f, a structural factor with rather indeterminate characteristics, which is not always easy to evaluate. It might be thought, in the present case, to determine f for a reaction for which n is known and then to give this value of f to other similar association reactions, thus obtaining n for each of them. By taking as reference the association Zn^{2+}/SO_4^{2-} ($n = 0$) and operating in this manner, $n = 0.5$ is obtained for Cd^{2+}/SO_4^{2-}, and $n = 0.6$ for Cd^{2+}/SeO_4^{2-}. These values are in disagreement with the previous conclusions. It is probable that the difference of structure between an inner-sphere and an outer-sphere pair is so great that it makes the above method of calculation inapplicable. On the contrary, by comparing pairs of the same type ($ZnSO_4$ as reference for $ZnSeO_4$, $CdSO_4$ for $CdSeO_4$), $n = 0.0$ is obtained for the association between Zn^{2+} and SeO_4^{2-}, and $n = 2.0$ for Cd^{2+} and SeO_4^{2-}, in perfect accordance with the previous results. Therefore it can be concluded that the empirical equations considered above may be useful in the case of (14), where the simple structures examined allow a sufficiently precise evaluation of structural parameters. On the contrary, in the case of (15), the practical significance of these equations is lost for the most part, at least for reactions of the type here examined. In fact the evaluation of f becomes uncertain, because it requires a knowledge of very specific structural characteristics of the product of association, as, for example, knowing whether the complex is of outer- or inner-sphere type.

Registry No. Zn^{2+}, 20214-91-9; Cd^{2+}, 22537-48-0; SO_4^{2-}, 14808-79-8; SeO_4^{2-}, 14124-68-6.

References and Notes

(1) R. Aruga, *J. Inorg. Nucl. Chem.*, **36**, 3779 (1974).
(2) J. W. Larson, *J. Phys. Chem.*, **74**, 3392 (1970).
(3) R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc. A*, 45, 47 (1969).
(4) S. Kilpi, A. Nurmi, and Y. Rinne, *Suom. Kemistil. B*, **23**, 31 (1951).
(5) R. W. Gelbach and G. B. King, *J. Am. Chem. Soc.*, **64**, 1054 (1942).
(6) W. H. Banks, *J. Chem. Soc.*, 1010 (1934).
(7) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).
(8) L. G. Sillén, *Acta Chem. Scand.*, **16**, 159 (1962).
(9) R. Aruga, *J. Inorg. Nucl. Chem.*, **39**, 2159 (1977).
(10) T. O. Denney and C. B. Monk, *Trans. Faraday, Soc.*, **47**, 992 (1951).
(11) J. M. Austin, R. A. Matheson, and H. N. Parton, "The Structure of Electrolytic Solutions", W. J. Hamer, Ed., Wiley, New York, N.Y., 1959, pp 370, 375.
(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York, N.Y., 1950, pp 116, 118.
(13) E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).
(14) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443, 1446 (1953).
(15) W. M. Latimer, K. S. Pitzer, and W. V. Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938).
(16) R. Ghosh and V. S. K. Nair, *J. Inorg. Nucl. Chem.*, **32**, 3041 (1970).
(17) Some errors are contained in Table 8 of ref 16. A $\Delta S°$ value used in the present calculations had to be recalculated.