Calculation of the Complexity Constants for Complexes containing M^{3+} or M^{4+} Ions Co-ordinated to Monovalent Anions by the Cation-exchange Method: Salicylato-complexes of the Trivalent Lanthanides

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The graphical method for the calculation of stability constants of mononuclear complexes by the cation-exchange method has been modified and extended to include systems such as M^{3+}–A^- or M^{4+}–A^-, where two or three cationic complex species respectively would be sorbed by the exchange material. New functions have been derived for this purpose. The method has been applied to trivalent lanthanides with salicyclic acid. The stability constants were determined at 0·25M-$NaClO_4$ in 50% (v/v) acetone–water.

CATION-EXCHANGE methods have been frequently employed in an attempt to understand the complex chemistry of metal ions. A full description of the mathematical treatments have been reviewed in many monographs.[1-5] The computation of stability constants from cation-exchange data is straightforward where only one [6-8] or only two [9-12] cationic species are sorbed onto the exchanger. However, few attempts [13-19] have been made to calculate the stability constants for the case where three or four cationic species are sorbed. These methods are only approximate and involve some assumptions. The present paper is an attempt to calculate these constants without adopting any approximation and the calculations are also extended to include the M^{4+}–A^- system.

In the following discussion, the same notations are used as mentioned in previous texts [10-13] unless otherwise stated.

(i) *Calculation of the Complexity Constants for the System* M^{3+}–A^-.—As shown previously,[9] for the M^{2+}–A^- system, the values of β_j could be obtained by differentiating the product $\phi\cdot X$ twice with respect to A. In the M^{3+}–A^- system, this product is differentiated three times to give:

$$\phi_3\cdot X + 3\phi_2\cdot X_1 + 3\phi_1\cdot X_2 + \phi\cdot X_3 = 0 \qquad (1)$$

substituting for the values of X_n ($n = 1, 2,$ or 3) [12] we obtain:

$$\phi_3 + \sum_{=1}^{N} ([A]^{j}\cdot\phi_3 + 3j[A]^{j-1}\cdot\phi_2 + 3j(j-1)[A]^{j-2}\cdot\phi_1 + j(j-1)(j-2)[A]^{j-3}\cdot\phi)\beta_j = 0 \qquad (2)$$

From a simple graphic representation of ϕ_1, ϕ_2, and ϕ_3 as a function of [A], at N different values of [A], we get a system of N equations from which the complexity constants, β_j, can be computed. Using the values of the functions ϕ_1 and ϕ_2 and their limiting values (*cf.* Fronaeus [12]), Carlson and Irving [14] obtained the following equation:

$$\Delta\phi_2|[A] = \beta_1\Delta\phi_1|[A] + l'_2(\phi_1^{\circ} + \Delta\phi_1) - \beta_3 - X_4[A] \quad (3)$$

As a first approximation, they assumed that $X_4[A] \simeq l'_2\Delta\phi_1$ so that these would cancel out in equation (3). In another study of Gd^{3+} acetate and glycolate systems, Sonesson [15] showed that these two terms are functions of [A] and at low values of [A] can be regarded as correction terms so that approximate values of β_1 may be obtained as the slope of the linear representation of $\Delta\phi_2|[A]$ *vs.* $\Delta\phi_1|[A]$. On the other hand, Grenthe [16] showed that equation (3) could be rearranged into

$$\beta_1 = \frac{\Delta\phi_2}{\Delta\phi_1} + \beta_3\frac{[A]}{\Delta\phi_1} + \beta_4\frac{[A]^2}{\Delta\phi_1} - l'_2\phi_1\cdot\frac{[A]}{\Delta\phi_1} \qquad (3')$$

so that, to a first approximation β_1 is equal to $\Delta\phi_2/\Delta\phi_1$.

However, these mathematical approximations are not necessarily valid in all cases and might lead to erroneous results.

In order to obtain more accurate values of the constant β_j, the following treatment is suggested. A new function ϕ_3 may be derived where:

$$\phi_3 = \frac{l_0\cdot\phi^{-1}[\{\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2)\}[A] - (\beta_1 - l'_1)] + \phi_1}{[A]^2} \qquad (4)$$

The values of l_0, $(\beta_1 - l'_1)$, and $\{\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2)\}$ are obtained as the limiting values of the graphical representations of the functions $\phi([A])$, $\phi_1([A])$, and $\phi_2([A])$ respectively. It is easily shown that ϕ_3 is given by:

$$\phi_3 = \beta_1\phi_2 - \beta_2\phi_1 + X_3 \qquad (5)$$

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A plot of the function $\phi_3([A])$ extrapolated to $[A] = 0$, gives $\phi_3{}^\circ$ as the limiting value where:

$$\phi_3{}^\circ = \beta_1\phi_2{}^\circ - \beta_2\phi_1{}^\circ + \beta_3 \qquad (6)$$

From equations (5) and (6), β_3 can be eliminated and a relation for the differences in ϕ_3, ϕ_2, and ϕ_1 obtained,

$$\Delta\phi_3 \,.\, \Delta\phi_1{}^{-1} = \beta_1 \cdot \Delta\phi_2 \cdot \Delta\phi_1{}^{-1} - \beta_2 \qquad (7)$$

assuming that only three complex species are formed. A plot of $\Delta\phi_3/\Delta\phi_1$ *versus* $\Delta\phi_2/\Delta\phi_1$ gives a line of slope β_1 and intercept β_2.

TABLE 1

Ion-exchange measurements for the scandium–salicylate system in 50% (v/v) acetone–water solvent

(I = 0.250)

c'_M / mmol l^{-1}	1.52		2.28		3.04		4.56	
[A] / mmol l^{-1}	$c_{MR}.10^5$ / mol g^{-1}	$\phi.10^3$ / l g^{-1}	$c_{MR}10^5$ / mol g^{-1}	$\phi.10^3$ / l g^{-1}	$c_{MR}10^5$ / mol g^{-1}	$\phi.10^3$ / l g^{-1}	$c_{MR}10^5$ / mol g^{-1}	$\phi.10^3$ / l g^{-1}
0.674	13.01	59.47						
1.348	11.06	26.69	17.31	31.60				
2.022	9.06	14.76	14.43	17.25				
2.696	7.33	9.32	12.67	12.51	18.00	14.52		
3.033	6.50	7.50	10.40	8.75				
3.707			9.30	7.25				
4.044	4.43	4.11	8.34	5.77	13.06	7.53	23.99	11.01
5.392	2.80	2.26	5.84	3.44	9.19	4.33	19.01	7.15
6.066							16.51	5.68
6.740			3.50	1.81	6.37	2.65		
8.088					4.27	1.63	10.00	2.81
9.436							7.23	1.88

TABLE 2

Corresponding values of ϕ, ϕ_1, ϕ_2, ϕ_3 and other related functions at different values of [A] and constant c_{MR} (= 1.3 × 10^{-4} mol g^{-1})

[A] / mmol l^{-1}	$\phi.10^3$ / l g^{-1}	$\phi_1.10^{-3}$ / mol^{-1} l	$\phi_2.10^{-6}$ / mol^{-2} l^2	$\phi_3.10^{-9}$ / mol^{-3} l^3	$\frac{\Delta\phi_2/\Delta\phi_1}{mol^{-1}\ l} \cdot 10^{-3}$	$\frac{\Delta\phi_3/\Delta\phi_1}{mol^{-2}\ l^2} \cdot 10^{-6}$
0.000	160.00	1.800	2.400	3.400		
0.674	59.50	2.506	3.463	4.437		
1.348	30.00	3.215	4.737	5.981		
2.022	17.50	4.027	6.147	7.812		
2.696	11.50	4.790	7.513	9.599	1.710	2.074
3.033	10.00	4.946	7.865	10.068	1.737	2.120
3.707	8.00	5.125	8.329	10.702	1.783	2.196
4.044	7.25	5.210	8.534	10.986	1.799	2.225
5.392	5.50	5.210	8.745	11.326	1.861	2.325

Substituting for the values of β_1 and β_2 in the equations[14] for $\phi_1{}^\circ$ and $\phi_2{}^\circ$, the constants l'_1 and l'_2 could be determined accurately. Knowing β_1, β_2, and l'_2, the polynomial X_2 is easily calculated from the following relationship:

$$\begin{aligned} X_2 &= \beta_1\phi_1 - \phi_2 + l'_2(\phi_1[A] + 1) \qquad (8) \\ &= \beta_2 + \beta_3[A] + \ldots + \beta_j[A]^{j-2} \end{aligned}$$

Other values of β_j are obtained from the corresponding $X_j([A])$ functions.

EXPERIMENTAL

All chemicals used were of analytical grade reagents. Stock solutions of $Ln[ClO_4]_3$ (Ln = Sc, Y, La, or trivalent rare-earth ion) were prepared by dissolving the metal oxide in the least amount of perchloric acid, evaporation of the solution almost to dryness, and then its dilution to the appropriate volume The final concentration was then checked compleximetrically.[20]

Recrystallised sodium salicylate was used to prepare the ligand solution.

Sodium perchlorate solution was prepared by dissolving the appropriate amount of AnalaR sodium perchlorate monohydrate in twice distilled water. The exact molarity was determined by exchanging a small aliquot with a H-form Dowex-50 resin and the resulting acid was determined titrimetrically

The air-dried cation exchanger Dowex 50, X-8 (50—100 mesh and 21% moisture content) was employed. The cation-exchange measurements were obtained by equilibrating v litres of the composition: c'_M [mmol of $Ln(ClO_4)_3$], c'_A (mmol of NaSal), c_H (mmol of $HClO_4$) to adjust the final pH to 4.5 and ($250-c_H-c'_A$) mmol of $NaClO_4$ in 50% (v/v) acetone–water solvent with a mass m of resin. The load c_{MR} on the exchanger was computed indirectly using the relationship:

$$c_{MR} = v/m(c'_M - c_M\delta)$$

where c'_M is the initial concentration of the metal ion, c_M is the concentration at equilibrium, and δ is the swelling factor. The value of δ was found to be 0.97 for the v/m value = 0.1 l g^{-1}. Series with varying c'_A were performed at four different values of c'_M. At equilibrium the final metal-ion concentration was determined compleximetrically using standard methods.[20]

Since the salicylate ion is the conjugate base of a weak acid, the initial ligand concentration [A] was given by:

$$[A] = \{([H^+] \cdot k_A{}^{-1}) + 1\}^{-1}c'_A \cdot \delta^{-1}$$

where k_A is the acid dissociation constant [1.072×10^{-4} as determined potentiometrically at 0.25 ionic strength in 50% (v/v) acetone–water solvent] and δ is a correction for the swelling of the resin phase.

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RESULTS AND DISCUSSION

Tables 1 and 2 summarise the data obtained for the scandium–salicylate system. It is obvious from the results that at a given value of c_A, the function ϕ increases with decreasing c_{MR} values. Extrapolation of the function $\phi(c_A)_{c_{MR}}$ gives the limiting value l_0 as 0.160 l g^{-1}. The values of ϕ_1, ϕ_2, and ϕ_3 (Table 2 columns 3, 4, and 5 respectively) are calculated as has been described before.

TABLE 3

Values of the overall stability constants of Sc, Y, La, and some rare-earth salicylato-complexes

Element	log β_1	log β_2	log β_3
Sc	3.23	5.92 ± 0.002	8.91 ± 0.27
Y	2.56	4.60 ± 0.002	6.20 ± 0.01
La	2.17	3.52 ± 0.005	4.01 ± 0.14
Pr	2.69	4.65 ± 0.007	5.40 ± 0.25
Sm	2.57	4.33 ± 0.020	6.40 ± 0.55
Gd	2.31	3.33 ± 0.016	5.64 ± 0.05
Er	2.42	4.24 ± 0.003	5.92 ± 0.03
Lu	2.53	4.27 ± 0.003	5.86 ± 0.01

Since the limiting values ϕ_1°, ϕ_2°, and ϕ_3° are known, the differences $\Delta\phi_1$, $\Delta\phi_2$, and $\Delta\phi_3$ can be calculated. The values of β_1 and β_2 were then obtained as the slope and intercept of the linear function $(\Delta\phi_3/\Delta\phi_1) \cdot (\Delta\phi_2/\Delta\phi_1)$ respectively. Assuming that only three complex species are formed, the value of β_3 is obtained using equation (5). In Table 3, the values of the overall stability constants obtained have been summarised.

The trivalent lanthanides differ significantly one from another in the number of 4*f* electrons and the ionic radius. If the bonding in the rare-earth chelates is purely electrostatic, stability should be determined by the relationship $\Delta E = (e^2/2r)(1 - D^{-1})$ where ΔE is the energy change on complexation of a gaseous ion of charge e and radius r in a medium of dielectric constant D. Accordingly, log K_1 is expected to vary linearly with $1/r$ (ref. 21). In these salicylato-complexes, such linearity characterises the sub-groups (La, Y, and Sc) and (La, Gd, Er, and Lu). The trend in stability resembles that obtained for other rare-earth complexes [22-27] in that the heavy rare-earth elements have nearly comparable stabilities. The sharp variation in log K_1 values for the light elements cannot be explained by the electrostatic theory and may be interpreted in terms of the ligand-field effects.[28-31] Considering the electronic configurations of Pr^{3+} ($4f^2$) and Sm^{3+} ($4f^5$) ions, the former is expected to be more stable than the latter one and those elements which have no ligand-field stabilisation, *e.g.* La^{3+} ($4f^0$), Gd^{3+} ($4f^7$), and Lu^{3+} ($4f^{14}$), should vary in stability linearly with ionic radii which is the case. The marked stability of Sc and Y is referred to the small size of the former and possibly, polarisability effects or/and a minor contribution of covalent bonding in the latter ion.[32]

In general, the values of log K_1 obtained are in good agreement with other values determined conductimetrically [33,34] or by the glass-electrode method.[35]

Calculation of the Complexity Constants for the System M^{4+}–A^-.—The mathematical treatment for this system is more complicated but similar deduction of the equations is followed here.

The distribution ratio, ϕ, is given by

$$\phi = l_0/\mathrm{X}(1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3) \qquad (9)$$

The numerators ϕ_1 and ϕ_2 are computed according to Fronaeus' definitions. Therefore:

$$\phi_1 = \frac{(\beta_1 - l'_1) + [\mathrm{A}](\beta_2 - l'_2) + [\mathrm{A}]^2(\mathrm{X}_3 - l'_3)}{1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3} \qquad (10)$$

and

$$\phi_2 = \frac{l_0 \cdot \phi^{-1}[(\beta_1 - l'_1)[\mathrm{A}] - 1] + 1}{[\mathrm{A}]^2}$$

$$= \beta_1\phi_1 - \mathrm{X}_2 + \{l'_2 + l'_3[\mathrm{A}]\}\{\phi_1[\mathrm{A}] + 1\} \qquad (11)$$

Substituting for the value of ϕ in the original equation, we get:

$$\phi_2 = \frac{\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2) - [\mathrm{A}](\mathrm{X}_3 - l'_3) + (\beta_1 - l'_1)(\beta_2[\mathrm{A}] + \mathrm{X}_3[\mathrm{A}]^2)}{1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3} \qquad (12)$$

The limiting values of ϕ_1^0 and ϕ_2^0 may then be introduced into a third function ϕ_3, where,

$$\phi_3 = \frac{l_0 \cdot \phi^{-1}[\phi_2^0[\mathrm{A}] - \phi_1^0] + \phi_1}{[\mathrm{A}]^2} \qquad (13)$$

Alternatively, ϕ_3 would be rewritten as,

$$\phi_3 = \beta_1\phi_2 + \mathrm{X}_3 - \beta_2\phi_1 \cdot l_0 l'_3/\phi \qquad (14)$$

$$= \frac{\beta_1[\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2)] - \beta_2(\beta_1 - l'_1) + (\beta_3 - l'_3) +}{1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3}$$

$$\frac{[\mathrm{A}]\mathrm{X}_2\{\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2)\}}{1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3} - \frac{[\mathrm{A}]\{\mathrm{X}_3(\beta_1 - l'_1) - \mathrm{X}_4\}}{1 + l'_1[\mathrm{A}] + l'_2[\mathrm{A}]^2 + l'_3[\mathrm{A}]^3} \qquad (15)$$

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Hence:

$$\lim_{[A]\to 0}\phi_3 = \phi_3^0 = \beta_1\{\beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2)\} + (\beta_3 - l'_3) - \beta_2(\beta_1 - l'_1)$$
$$= \beta_1\phi_2^0 - \beta_2\phi_1^0 + (\beta_3 - l'_3) \quad (16)$$

subtracting equation (16) from equation (14) and dividing by [A], then

$$\Delta\phi_3/[A] = \beta_1\Delta\phi_2/[A] + X_4 - l'_3\Delta\phi_1 - l'_3\phi_1^0 \quad (17)$$

In agreement with the earlier attempts,[17–19] it is reasonable to obtain β_1 as the slope of the linear function of $\Delta\phi_3/[A]$ *versus* $\Delta\phi_2/[A]$ in the low region concentration of [A].

The authors [17–19] modified the calculations by assuming some successive approximations in order to obtain the other β_j values.

By differentiating the product $\phi{\cdot}X$ in equation (9)

$$\phi_4{\cdot}X + 4\phi_3{\cdot}X_1 + 6\phi_2{\cdot}X_2 + 4\phi_1{\cdot}X_3 + \phi{\cdot}X_4 = 0 \quad (18)$$

another function ϕ_4 is introduced, where

$$\phi_4 = \beta_1\phi_3 - \beta_2\phi_2 + \beta_3\phi_1 - X_4$$
$$= \frac{l_0 \cdot \phi^{-1}\{\phi_3^0[A]^2 - \phi_2^0[A] + \phi_1^0\} - \phi_1}{[A]^3} \quad (19)$$

The limiting value ϕ_4^0 is obtained from a plot of $\phi_4([A])$ function:

$$\lim_{[A]\to 0}\phi_4 = \phi_4^0 = \beta_1\phi_3^0 - \beta_2\phi_2^0 + \beta_3\phi_1^0 - \beta_4 \quad (20)$$

if only four complex species are formed, then combination of equations (19) and (20) gives

$$\Delta\phi_4 = \beta_1\Delta\phi_3 - \beta_2\Delta\phi_2 + \beta_3\Delta\phi_1 \quad (21)$$

then introducing the value of β_1 in equation (21), it follows,

$$(\Delta\phi_4 - \beta_1\Delta\phi_3)/\Delta\phi_2 = \beta_3\Delta\phi_1/\Delta\phi_2 - \beta_2 \quad (22)$$

A plot of the function $(\Delta\phi_4 - \beta_1\Delta\phi_3) \cdot \Delta\phi_2^{-1}$ *vs.* $\Delta\phi_1/\Delta\phi_2$ should give a straight line of slope β_3 and intercept β_2. From the values of β_1, β_2, and β_3 the constants l'_1, l'_2, and l'_3 could be determined accurately and consequently the polynomial X_2 from equation (11).

All the above equations have been deduced on the assumption that no polynuclear species are formed either in the resin phase or in solution.

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