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DETERMINATION OF THE STABILITY CONSTANTS OF THORIUM NITRATE COMPLEXES WITH ANION-EXCHANGE RESINS

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J. DANON

CENTRO BRASILEIRO DE PESQUISAS FISICAS

Av. Wenceslau Braz, 71

RIO DE JANEIRO

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J. DANON
Escola Nacional de Química
Centro Brasileiro de Pesquisas Físicas

The determination of the sucessive stability constants of nitrato complexes of thorium has been investigated by solvent-extraction methods. Using thenoyl-trifluoro-acetone as extracting agent from 0.5 ionic strength nitrate media Day and Stoughton[1] found the value 4.73 for the first nitrate complex of thorium. Zebrosky, Alter and Heumann[2] using the same solvent at $\mu = 5.97$ have found the constants 2.83 for $Th(NO_3)^{+3}$ and 1.41 for $Th(NO_3)_2^{+2}$.

V. V. Fomin and E.P.Maiorova[3] investigated the distribution of trace amounts of thorium between HNO_3 solution at $\mu = 2$ and varying concentrations of tri-butyl-phosphate in benzene. These authors have found the constants of $Th(NO_3)_x^{4-x}$ for x = 1 to 4 equal respectively to 6 ± 0.5, 13 ± 1, 10 ± 0.5, and 5.5 ± 0.5. Further studies[4] have

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shown that these values for the stability constants remain valid at high concentrations of thorium nitrate, suggesting that in such conditions thorium forms only mononuclear complexes with the nitrate ligand.

The knowledge of the stability constants of the negatively charged complexes of thorium, which has not been possible to derive from the solvent-extraction data, appears to be of interest. Several properties of thorium in concentrated nitrate solutions, such as the formation of $M_2Th(NO_3)_6$ compounds, the extraction with oxigenated organic solvents[5], the migration in the electric field, and the anion-exchange behaviour[6,7] are apparently influenced by the presence of complexes of negative charge.

A rigorous treatment of the sorption by anion-exchange resins of metal anion complexes from aqueous solutions has been recently develloped by Marcus and Coryell[8,9,10]. On this basis these authors derived a method for the evaluation of stability constants which is particularly suitable for the determination of constants of the species formed in the neighborhood of the neutral complex.

DISCUSSION AND RESULTS

The adsorption of thorium by Dowex-1, 8% DVB, 50-100 mesh in the nitrate form was investigated with thorium 234 (beta, gama, 24.1 days period). This isotope was separated from large amounts of uranium with Dowex-1 columns in 8 M HCl solution[11]. Further purification was made by adsorbing Th 234 in a small Dowex-1 column from 7 M HNO_3 solution followed by elution with water. All measurements were made

in a scintillation counter.

We shall assume the following mechanism for the adsorption of thorium in nitrate media by the anion-exchange resin. The neutral complex $Th(NO_3)_4$ is transfered from the aqueous solution to the resin phase

$$ThL_4\ (sol.) \rightleftarrows ThL_4\ (res.) \qquad (1)$$

followed by the reaction with the resin ligands

$$ThL_4\ (res.) + 4\ RL = R_4ThL_8 \qquad (2)$$

where L stands for the nitrate ligand. The number of resin ligands was choosen in order to form the coordinatively saturated complex in the resin phase. As has been shown by Katzin and all.[12] the coordination number of Th^{+4} is in general 8.

From (1) and (2) we can write for the thermodynamic equilibrium equation of the adsorption process

$$K_r = a_{R_4ThL_8} \cdot a^{-1}_{ThL_4} \cdot a^{-4}_{RL} \qquad (3)$$

or

$$K_r = \left[R_4ThL_8\right] \cdot \gamma_{R_4ThL_8} \cdot a^{-1}_{ThL_4} \cdot a^{-4}_{RL} \qquad (4)$$

where brackets represent concentrations and γ the corresponding activity coefficients.

The distribution coefficient D is given by

$$D = \frac{\left[R_4ThL_8\right]}{\left[Th^{+4}\right] + \left[ThL^{+3}\right] + \left[ThL_2^{+2}\right] + \ldots.} \qquad (5)$$

The sum in the denominator extends to all species present in aqueous solution.

From (4) and (5) we obtain

$$D = K_r \cdot \gamma^{-1}_{R_4ThL_8} \cdot a^4_{RL} \cdot \frac{1}{\frac{[Th^{+4}]}{a_{ThL_4}} + \frac{[ThL^{+3}]}{a_{ThL_4}} + \ldots} \qquad (6)$$

We shall now define the formations of a complex by relating it to the neutral complex

$$ThL_4 \rightleftharpoons ThL^i_{4-i} + iL \qquad (7)$$

The index i gives the charge of the complex.

The thermodynamic equilibrium constant for (7) is

$$\beta_i = a_{ThL^i_{4-i}} \cdot a^i_L \cdot a^{-1}_{ThL_4} \qquad (8)$$

which gives

$$\frac{[ThL^i_{4-i}]}{a_{ThL_4}} = \beta_i \gamma^{-1}_i a^{-i}_L \qquad (9)$$

Introducing (9) in (6) we get

$$D = K_r \cdot \gamma^{-1}_{R_4ThL_8} \cdot a^4_{RL} \cdot \left(\sum \beta_i \gamma^{-1}_i a^{-i}_L\right)^{-1} \qquad (10)$$

We shall now make the following assumptions:

1) The activity of nitrate in solution is given by

$$a_L = [L] \cdot \gamma^{\pm}(LiNO_3) \qquad (11)$$

where $[L]$ is the concentration of nitrate ion in the aqueous phase and $\gamma^{\pm}_{LiNO_3}$ the corresponding mean ionic activity coefficient of $LiNO_3$.

2) The activity of the nitrate ion in the resin phase is given by[13]

$$a_{RL} = a_L \cdot [L]_R^{-1/2} \cdot [Li]_R^{-1/2} \qquad (12)$$

where a_L is the activity in the aqueous phase according to (11), $[L]_R$ and $[Li]_R$ the concentrations of nitrate and lithium respectively in the resin phase. The reference state for the activity a_{RL} is taked arbitrarely as a^o_{RL} for $a_L = 1$.

Relation (12) can be derived from Donnan equilibrium of the electrolyte between the aqueous solution and the resin phase[13].

3) The activity coefficients $\gamma_{R_4ThL_8}$ and γ_i are independent of the value of a_L. The justification for these assumptions are given in Marcus and Coryell papers.

Introducing the above assumptions in (10) we find

$$\log D = \log \left(K_r \cdot \gamma^{-1}_{R_4ThL_8} \cdot a^o_{RL} \right) + 4 (\log a_{RL} - \log a^o_{RL}) - \log \sum \beta_i \gamma_i^{-1} a_L^i \qquad (13)$$

We shall now make

$$K^*_r = K_r \cdot \gamma^{-1}_{R_4ThL_8} \cdot a^o_{RL} \qquad (14)$$

$$\beta^*_i = \beta_i \gamma_i^{-1} \qquad (15)$$

and we define a correction function F (a) as

$$F(a) = \log a_{RL} - \log a^{o}_{RL} \qquad (16)$$

Introducing (14), (15) and (16) into (13) we find

$$\log D = \log K_r + 4\, F(a) - \log \sum \beta^{*}_{i}\; a_L^{-i} \qquad (17)$$

The difference $\log D_o = \log D - 4\, F(a)$ gives the distribution coefficients corrected from the invasion effects of the supporting electrolyte in the resin phase:

$$\log D_o = \log D - 4F(a) = \log K_r - \log \sum \beta^{*}_{i}\; a_L^{-i} \qquad (18)$$

It is easily calculated that

$$\frac{d \log D_o}{d \log a_L} = 4 - \bar{n} = \bar{f} \qquad (19)$$

where $\bar{n}$ is the mean number of ligands as defined by Bjerrum, and $\bar{i}$ the mean charge number of the complex species.

The values of the distribution coefficients as a function of the $LiNO_3$ molarity are given in Table I. This data was obtained in equilibration experiments (24 hours) with the resin at room temperature ($25^{o} \pm 3$ C). The concentration of the $LiNO_3$ solutions was measured in a flame photometer. All $LiNO_3$ solutions were made 0.07 M in HNO_3 in order to avoid hydrolysis of thorium nitrate. However, even at these acidities hydrolytical reactions appear to occur at $LiNO_3$ molarities lower than 2 M[14].

Fig. 1 shows the values of log D as a function of log a_L. The values of log a_L where calculated from mean activity coefficients of $LiNO_3$ taken from Robinson and Stokes[15].

Fig. 2 shows the variation of the invasion function F(a) with log a_L. This data was obtained with Dowex-1, X-8, 50-100 mesh in the nitrate form with resin from the same batch used in the equilibration experiments with thorium, according to the procedure described by Kraus and Nelson[13]. Details about this data will be published in a next paper.

Fig. 3 shows the variation of the corrected distribution function log D as a function of log a_L.

In the range of activities investigated the values of $\bar{i} = \frac{d \log D_o}{d \log a_L}$ go from + 0.6 to -1.8 indicating the presence of ThL_3^{+1}, ThL_4^{o}, ThL_5^{-1} and ThL_6^{-2} successive species in solution.

Preliminary values of β^*_{+1}, β^*_{o}, β^*_{-1} and β^*_{-2} constants were derived from the relation:

$$\log \frac{\beta^*_i}{\beta^*_{i+1}} = - \log a_L \quad (\bar{i} = i - 1/2)$$

With the values obtained for β^*_{+1} and K_r we formed the equation in three parameters which was solved by curve fitting method of Sillén[16]:

$$\frac{1}{D_o} - \frac{\beta^*_{+1}}{K_r \cdot a} = \frac{1}{K} + \frac{\beta^*_{-1}}{K} \cdot a + \frac{\beta^*_{-2}}{K} \cdot a^2 \qquad (20)$$

With the values of K and β^*_{-2} obtained from (20) we solved the equation

$$\frac{K}{D_o} \cdot \frac{a}{\beta^*_{-2}} - a^3 = \frac{\beta^*_{+1}}{\beta^*_{-2}} + \frac{1}{\beta^*_{-2}} \cdot a + \frac{\beta^*_{-1}}{\beta^*_{-2}} a^2$$

By this procedure the following set of values were derived for the constants: $\log K_r = 1.22$; $\log \beta^*_{+1} = + 0.22$; $\log \beta^*_{o} = 0.00$; $\log \beta^*_{-1} = - 0.80 \pm 0.17$; $\log \beta^*_{-2} = 1.70 \pm 0.22$.

With these values the solid curves shown in fig. 1 and (2) were calculated from equations (17) and (18) respectively. The fitting of the experimental points is satisfactory. The data could also be fitted by a curve $\log D_o = \log K_r - \log (1 + \beta^*_{-1} a + \beta^*_{-2} a^2)$ which would mean that no $Th(NO_3)^{+1}_3$ species are present at the lower activity range investigated. However at low $LiNO_3$ activities the hydrolytical reactions of thorium nitrate tend to increase the values of the distribution coefficient. For this reason the value found for β^*_{+1} may be considered as the upper limit of the association constant.

The comparison between the values of stability constants β_i (refered to the neutral complex) calculated from Fomin and Maiorova's data[3] and those obtained by anion-exchange is shown in table 2[17].

The values obtained for β^*_{-1} and β^*_{-2} show that the formation of negatively charged complexes of thorium nitrate occur at high concentrations of nitrate ion ($\geq$ 3 M). This is in agreement with the results of Fomin and Maiorova[3] which have shown that the extraction behaviour of thorium nitrate by TBP until 2.2 M nitrate ion was essentially not influenced by the formation of negatively charged complexes.

No evidence was found in the range of activities investigated for the presence of complexes with charge more negative than -2, although the possible existence of such species at higher activities of nitrate ion cannot be ruled out uniquely on the basis of the anion-exchange data.

The overall stability constant for the reaction

$$Zr^{+4} + 6\ NO_3^{-1} = Zr(NO_3)_6^{-2}$$

was investigated by solvent-extraction studies with TBP[18] and its value was found to be $\beta_6 = 0.02$ at $\mu = 4$. From Fomin and Maiorova's data and the results from the present study we found for the analogous reaction for Th^{+4} the value $\beta_6 = 0.11$. This shows an increasing tendency in the stability of the negatively charged nitrato complexes with increasing ionic radius in going from Zr^{+4} to Th^{+4}. The same trend was observed with the first nitrato complexes of these elements[19].

ACKNOWLEDGMENTS

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TABLE I

M_{LiNO_3}	log D	M_{LiNO_3}	log D
1.55	1.10§	4.02	2.81
2.00	1.45§	4.35	2.91
2.39	1.72§	5.06	3.21
2.53	1.83	5.20	3.35
2.89	2.21	6.24	3.69§
3.40	2.36	6.32	3.67§
		8.44	4.33§

§ - Values with errors larger than $\pm$ 0.05 log units

TABLE 2

	$\log \beta^*_{+1}$	$\log \beta^*_{0}$	$\log \beta^*_{-1}$	$\log \beta^*_{-2}$
Fomin and Maiorova ($\mu = 2$)	+ 0.26	0.00	-	-
Present work (variable $LiNO_3$)	+ 0.22	0.00	-0.80	-1.70

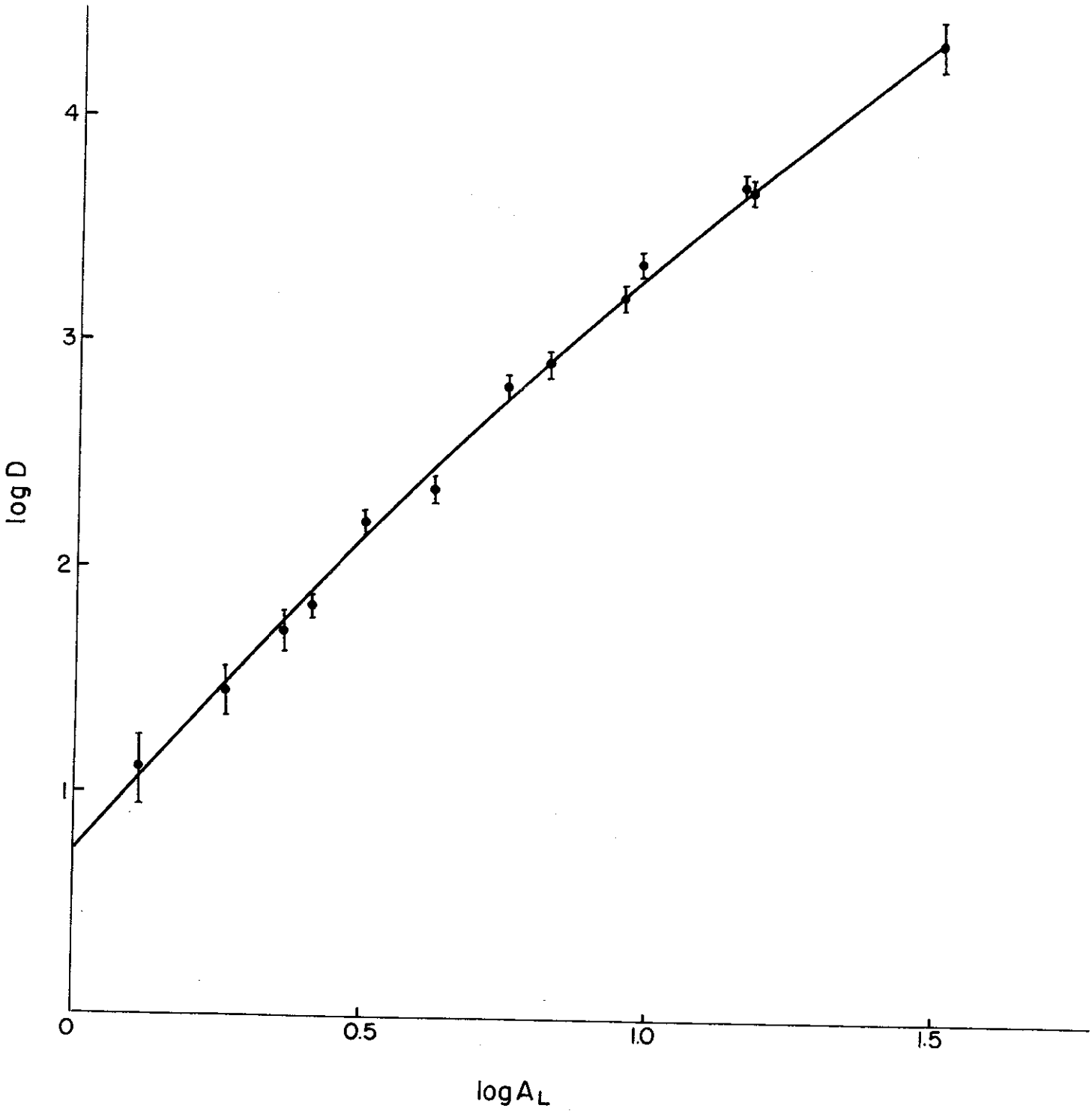

FIG. 1

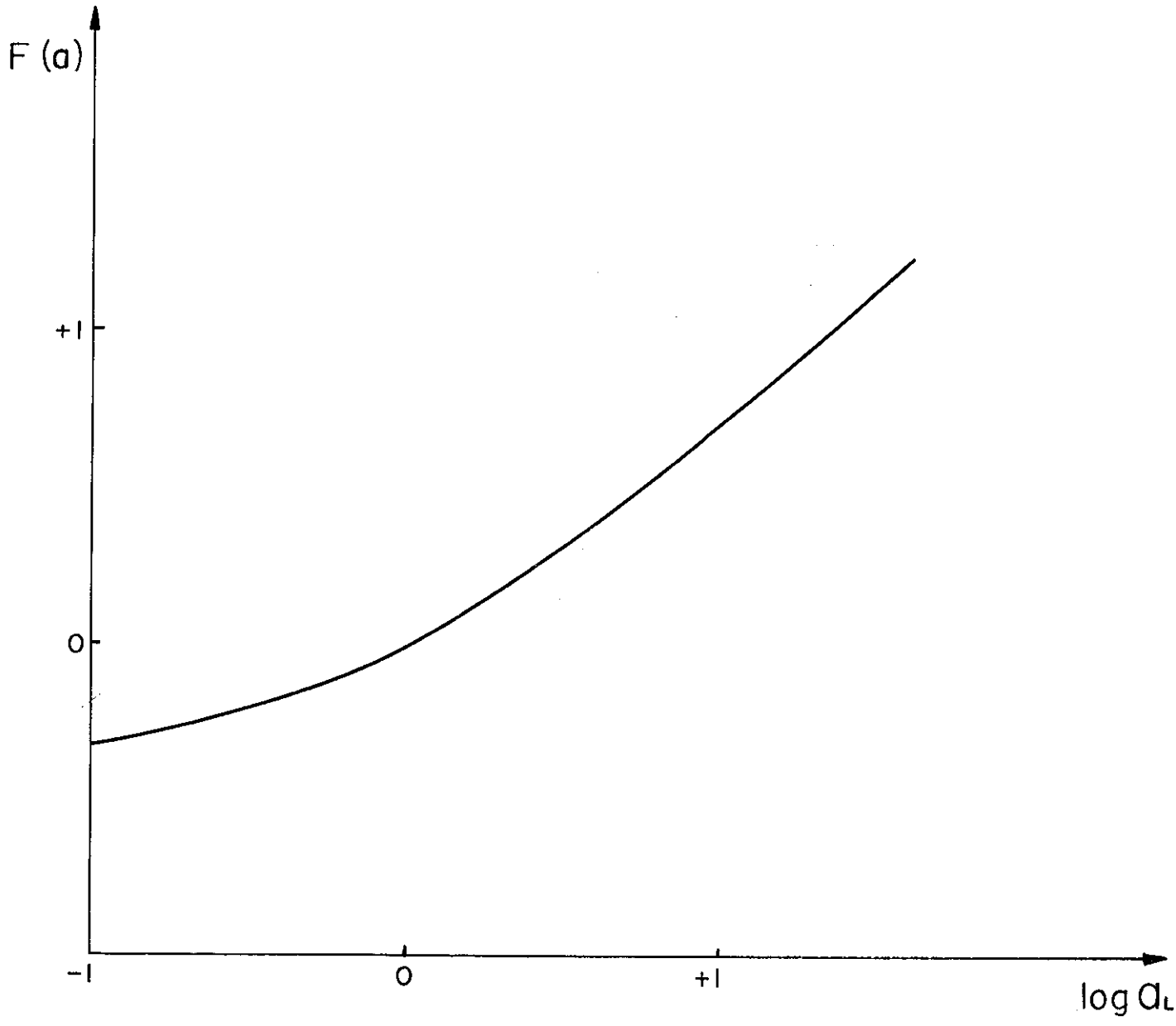

FIG. 2

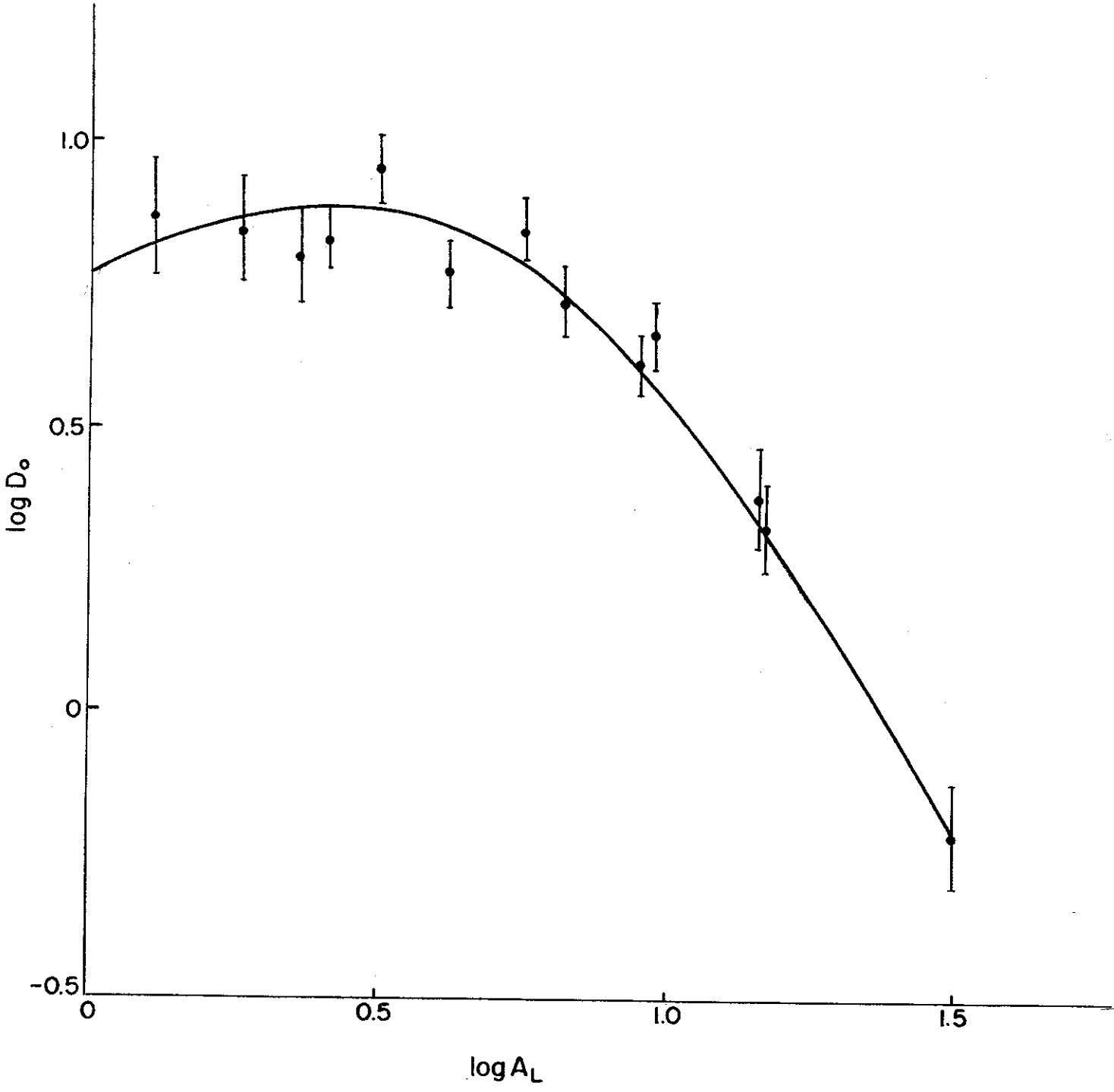

FIG. 3