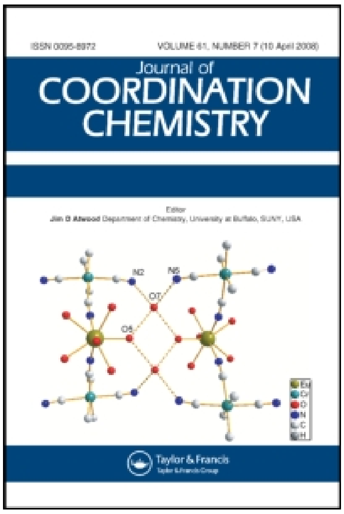

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FORMATION CONSTANT OF THE CALCIUM $(ATP)_2$ COMPLEX

E-I. Ochiai[a]; R. Morand[a]
[a] Department of Chemistry, Juniata College, Huntingdon, PA, USA

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COMMUNICATION

FORMATION CONSTANT OF THE CALCIUM $(ATP)_2$ COMPLEX

E-I. OCHIAI and R. MORAND
Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA.

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Although there is some indication that a complex $[Ca(ARP)]_2^{6-}$ exists,[1,2] no definitive evidence for it has been produced nor has its formation constant been reported. We have investigated its formation by means of conductometric titration and a Ca-specific electrode. The formation constants for other calcium-ATP complexes, $[Ca(ATP)]^{2-}$ and $[Ca_2(ATP)]^0$ have been reported by several authors.[3-5]

EXPERIMENTAL

Conductometric titration:

500 cm^3 of a 2×10^{-4} M Na_4 ATP solution was titrated by a 5×10^{-3} M Ca $(NO_3)_2$ solution at 25° and monitored continuously using conductivity techniques.

Determination of formation constants of Ca-ATP complexes:

The Ca-specific electrode (Orion 93-20) was used to monitor the titration of a 10^{-2} M ATP solution by a 10^{-3} M Ca $(NO_3)_2$ solution. The ionic strength of the solution was adjusted by addition of a known amount of $NaNO_3$, and its pH was adjusted to 9.1 ± 0.1 by adding a 0.06 M NaOH solution. The electrode potential reading was converted to the activity of free Ca(II) species by utilizing a calibration curve.

Calculation:

The calculation of the formation constants K(1) and K(2) for $[Ca(ATP)]^{2-}$ and $[Ca_2(ATP)]^0$ was carried out in the same way as Mohan and Rechnitz.[3] The method of calculation of the formation constant K(3) for $Ca(ATP)_2^{6-}$ is as follows:

$$Ca(II) + ATP^{4-} \rightleftharpoons [Ca(ATP)]^{2-};\ K(1) \quad (1)$$

$$[Ca(ATP)]^{2-} + Ca(II) \rightleftharpoons [Ca_2(ATP)]^0;\ K(2) \quad (2)$$

$$[Ca(ATP)]^{2-} + ATP^{4-} \rightleftharpoons [Ca(ATP)_2]^{6-};\ K(3) \quad (3)$$

K(3) is to be determined in terms of activities of the entities involved and can be evaluated by the following formula in terms of both molar concentrations and activity coefficients, (*4*),

$$K(3) = [Ca(ATP)_2^{6-}]\gamma^4/[Ca(ATP)^{2-}][ATP^{4-}] \quad (4)$$

where γ is the activity coefficient for a species carrying 2+ or 2– charge. The basic mass balances are given in (*5*) and (*6*).

$$\mathrm{T(Ca)\ (= total\ calcium\ concentration)} = [\mathrm{Ca(II)}] + [\mathrm{Ca(ATP)^{2-}}] + [\mathrm{Ca(ATP)_2^{6-}}] \qquad (5)$$

$$\mathrm{T(ATP)} = [\mathrm{ATP^{4-}}] + [\mathrm{Ca(ATP)^{2-}}] + 2[\mathrm{Ca(ATP)_2^{6-}}] + [\mathrm{Na(ATP)^{3-}}] \qquad (6)$$

In these equations $[\mathrm{Ca_2(ATP)}]$ is ignored, because these calculations are to be done for the points in which $\mathrm{T(ATP)/T(Ca)} > 1$ and for such a point $[\mathrm{Ca_2(ATP)}]$ has been shown to be negigibly small. The only experimental value directly obtainable is the activity of free Ca(II), $a_{\mathrm{Ca^{2+}}}$, other than T(C) and T(ATP). $[\mathrm{Ca(ATP)_2^{6-}}]$, $[\mathrm{Ca(ATP)^{2-}}]$, $[\mathrm{ATP^{4-}}]$ and the activity coefficient value are calculated by the following procedure.

$$[\mathrm{Ca(II)}] = a_{\mathrm{Ca}}/\gamma \qquad (7)$$

$$[\mathrm{ATP^{4-}}] = (\mathrm{T(APT)} - 2\mathrm{T(Ca)} + 2[\mathrm{Ca(II)}]) /(1 + K\gamma^2[\mathrm{Na(I)}] - \mathrm{K(1)}[\mathrm{Ca(II)}]\gamma^4) \qquad (8)$$

$$(\text{where } \mathrm{K} = [\mathrm{Na(ATP)^{3-}}]/[\mathrm{Na(I)}][\mathrm{ATP^{4-}}] = 229\ 1/\mathrm{M})\ [\mathrm{Na(ATP)^{3-}}] = \mathrm{K}[\mathrm{ATP^{4-}}][\mathrm{NA(I)}] \qquad (9)$$

$$[\mathrm{Ca(ATP)^{2-}}] = 2\mathrm{T(Ca)} - \mathrm{T(ATP)} - 2[\mathrm{Ca(II)}] + [\mathrm{ATP^{4-}}] + [\mathrm{Na(ATP)^{3-}}] \qquad (10)$$

$$[\mathrm{Ca(ATP)_2^{6-}}] = (1/2)(\mathrm{T(ATP)} - [\mathrm{Na(ATP)^{3-}}] - [\mathrm{ATP^{4-}}]) \qquad (11)$$

The ionic strength, I, of the solution is calculated by taking into consideration all of the ionic species present in the solution, (*12*).

$$\mathrm{I} = (1/2)\{36[\mathrm{Ca(ATP)_2^{6-}}] + 16[\mathrm{ATP^{4-}}] + 9[\mathrm{Na(ATP)^{3-}}] + 4[\mathrm{Ca(ATP)^{2-}}] + 4[\mathrm{Ca(II)}] + [\mathrm{NO_3^-}] + [\mathrm{OH^-}] + [\mathrm{Na(I)}]\} \qquad (12)$$

The γ value is then calculated by a Debye-Huckel formula (*13*), with $z = 2$.

$$\log \gamma = -0.5091 \times z^2 \times \{\sqrt{\mathrm{I}}/(\sqrt{\mathrm{I}} + 1) - 0.31\} \qquad (13)$$

The first assumption is that $\gamma = 1$; the calculation, equation (*8*) to (*13*) is then carried out based on this assumption. This will lead to a new value of γ. The calculation is then repeated using this new γ value. Similar iterations are carried out until the difference between two consecutive γ values becomes insignificant. K(3) then can be evaluated using this final set of values.

RESULTS AND DISCUSSION

Log K(1) and log K(2) values obtained are 6.56 ± 0.04 (95% confidence limit) and 2.89 ± 0.04 (95% confidence limit), respectively, at pH = 9.1 and 25°. These values are comparable to the values (log K(1) = 6.37, log K(2) = 3.04) reported by Mohan and Rechnitz.[3]

A typical result of a conductometric titration is given in Fig. 1. It shows inflections at T(Ca)/T(ATP) = 1/2 and 1, clearly indicating the formation of a

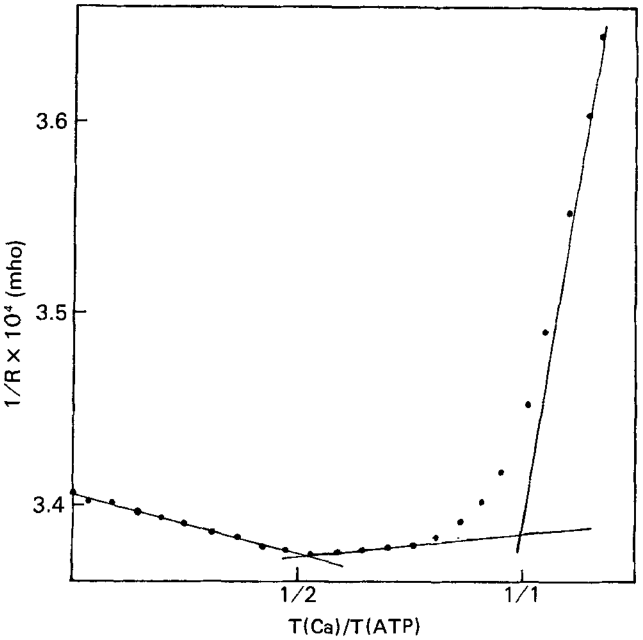

FIGURE 1 Typical results for the conductimetric titrations.

$[Ca(ATP)_2]^{6-}$ species as well as $[Ca(ATP)]^{2-}$. The result of K(3) determinations are given in Table I. K(3) was determined to be 196 ± 25, log K(3) = 2.29 ± 0.05 (95% confidence limit).

The K(3) value is enormously reduced compared to the K(1) value; this is most likely due to the strong repulsive effect between the highly negatively charged ATP ligands. The repulsive effect may be estimated roughly by equation (*14*)

$$E = z_1z_2e^2/4\pi\varepsilon Dr \qquad (14)$$

where z_1e and z_2e are the electric charges of the ligands, ε the vacuum permittivity, D the dielectric constant of the medium, and r the distance between the two

TABLE I
K(3) Determination (examples).

T(ATP)/T(Ca)	T(ATP) (mM)	T(Ca) (mM)	K(3)[†]
1.14	1.20	1.05	187
1.25	1.80	1.50	212
1.25	2.40	1.92	191
1.26	0.82	0.65	198
1.32	0.82	0.62	180
1.32	1.40	1.06	207
1.33	2.16	1.62	201
1.50	1.86	1.24	176
1.50	2.84	1.89	169
1.59	3.27	2.06	229

[†] At the 95% confidence limit K(3) = 196 ± 25 (24 data points)

charges. Taking the four O^- charges on each ATP Molecule into consideration and assuming that a set of proximal oxygen atoms (two on each ligand) is 500 pm apart and the other set is 1500 pm apart (on average), E can be estimated to be 1.89E4 J mol^{-1}. This corresponds to log K = − 3.3. The intrinsic value of K(3) is expected to be little smaller than K(1). The average of the difference between the corresponding log K(1) and log K(3) values in ethylenediamine complexes of various divalent metals in whcih the electrostatic repulsive effect between ligands may be negligible is about 1.1. If this value is adopted here, the intrinsic value of log K(3) would be about 5.5 (= 6.6 − 1.1), and the expected log K(3) value is 2.2 (= 5.5 − 3.3), if the electrostatic repulsive effect is taken into account. This is to be compared to the observed value 2.3. This agreement between the observed and the estimated values of K(3) would indicate that the reduced value of K(3) is mainly due to the repulsive effect between the negative charges on the ligands, as postulated, and that the value of K(3) obtained here is reasonable.

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