Equilibria of Complex Formation in Aqueous Solution between Lead(II) and Thallium(I) Ions, and Cyclic and Linear Polyethers

Mutsuo KODAMA[1] and Eiichi KIMURA*

Department of Chemistry, College of General Education, Hirosaki University, Bunkyo, Hirosaki 036

**Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, Kasumi, Hiroshima 734*

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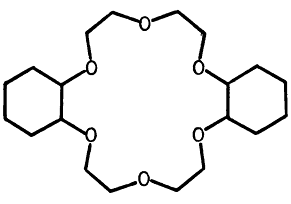
log K, ΔH and ΔS values were polarographically determined for the interaction in aqueous solution of Pb^{2+} and Tl^{+} ions with a cyclic polyether, 1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6), and a linear polyether, tetraethylene glycol dimethyl ether(tetraglyme). The stability constant of a 1: 1 Pb^{2+} complex with the macrocyclic ligand is four figures higher than that with the linear ligand. This macrocyclic effect is explained in terms of entropy.

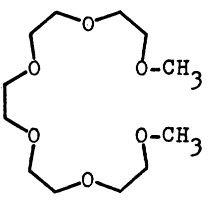
The stability of a complex between a given cyclic polyether and a cation is dependent on the cation diameter, as illustrated by a case in which the preference of 18-membered cyclic hexaether **1** and **2** (2.6—3.2 Å macrocycle hole cavity) for divalent metal ions decreases in the order; $Pb^{2+}(2.4) > Ba^{2+}(2.7) > Sr^{2+}(2.3) > Hg^{2+}(2.2) > Ca^{2+}(2.0\text{ Å})$.[2] The size selectivity is determined by several effects such as electrostatic attraction between metal ion and ligand, ligand conformational change, changes in total particle number, dehydration of the metal ion and ligand, or hydration of the metal-ligand complex. In the thermodynamic study on the 1: 1 complexes of **1** and **2** with divalent metal ions, Izatt *et al.* showed that the complexation with Sr^{2+} is more favorable entropically but less so enthalpically than with Ba^{2+}.[3] This suggests that the dominant effects in determining size selectivity are the endothermic removal of water from the hydration sheath with an accompanying gain in entropy, both of which are known more pronounced for the more strongly hydrated Sr^{2+} ion.[4] However, for the complex formation with Pb^{2+} ion which stands linking between Sr^{2+} and Ba^{2+} in terms of ionic diameter, no thermodynamic functions have been reported as yet.

A macrocyclic effect of $\approx 10^4$-fold stability enhancement was found between $K^{+}(2.7\text{ Å})$ complex of an open-chain hexaether, **3**, and those of the macrocyclic analogs such as **1** or **2**.[5] It was postulated that entropic forces work against complete envelopment of the cation by the non-cyclic polyether. However, recent studies on the macrocyclic tetramine system[6–8] disclosed the fact that thermodynamic parameter ΔH often plays more important role in the macrocyclic effect which is linked to ligand solvation effects.[9]

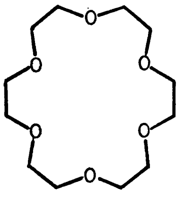
In order to investigate the complexing properties and a major source of the macrocyclic effect, the present polarographic study was undertaken on the interaction of Pb^{2+} with 1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6), **4**, and tetraethylene glycol dimethyl ether (tetraglyme), **5**, in aqueous solution. Stability constant K, ΔH and ΔS values have also been determined for Tl^{+} complex formation with **4**. The studies constitute a part of our investigations into the macrocyclic effects.[8,10,11] Similar studies have been reported on the metal ion complexes containing analogous ligands, $H_{3-n}(CH_2CH_2OCH_2CH_2OCH_2CH_2)_nNH_{3-n}$, **6**.[12–15]



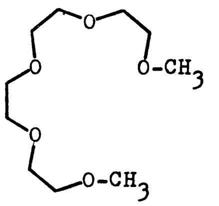
Dicyclohexyl-18-crown-6
1. isomer A **2**. isomer B



3. Pentaglyme



4. 18-Crown-6



5. Tetraglyme

Experimental

Reagents. A standard solution of thallium(I) perchlorate was prepared by dissolving pure thallium metal in a reagent grade perchloric acid. A standard lead(II) nitrate solution was prepared by dissolving pure lead(II) nitrate crystals in redistilled water. Tetraethylammonium perchlorate(TEAP) was prepared by the method given by Fujinaga, Izutsu and Takaoka,[16] and purified by recrystallization from water. 18-Crown-6, **4**, (Aldrich Chemical Company, Inc.) was recrystallized from acetonitrile. The ionic strength of the sample solutions was adjusted to 0.10 by adding an appropriate amount of TEAP. The other reagents were of analytical reagent grade and were used without further purification.

Apparatus and Experimental Procedures. The d.c. current-voltage curves were obtained by using a manual polarograph similar to that of Kolthoff and Lingane[17] or a Yanagimoto P-8 pen-recording polarograph. For all the measurements, we used a dropping mercury electrode with an m value of 0.915 mg/s and a drop time, t_d, of 5.00 s in an air-free 0.10 M $NaClO_4$ solution at the mercury height of 65 cm, with an open circuit. A saturated calomel electrode (SCE) with a large area was used as a reference electrode. All the free ligands we used gave no reduction wave. In order to prevent the precipitation of metal ions as hydroxides, the pH of the sample solutions were adjusted to 2.00 by adding $HClO_4$. The oxygen dissolved in the sample solution was removed by bubbling pure nitrogen gas through the solution.

Results

Polarographic Behavior of Pb^{2+} and Tl^{+} in Solutions Containing 4. Crown ligand **4** lowered the surface tension at the interface of a mercury-electrolyte solution, changing the electrocapillary curve considerably in the potential range from −0.30 to −1.40 V *vs.* SCE (Fig. 1).

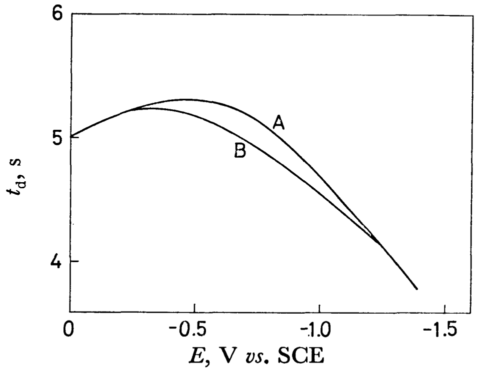


Fig. 1. Electrocapillary curves (A) without and (B) with **4** of 2.50×10^{-3} M at I=0.10 M (TEAP), pH=2.00.

The lowering was found to be independent of the solution pH and the nature of supporting electrolyte. Although no tensammetric wave was observed, the depression of the electrocapillary curve may be indicative of an adsorption of **4** at the mercury electrode surface. This was supported by the effect of the adsorbed **4** on the d.c. polarogram of cadmium(II) ion (Fig. 2). However, **4** had no depressing effect on the d.c. polarographic behavior of Pb^{2+} and Tl^{+} even at concentration above 50×10^{-3} M.

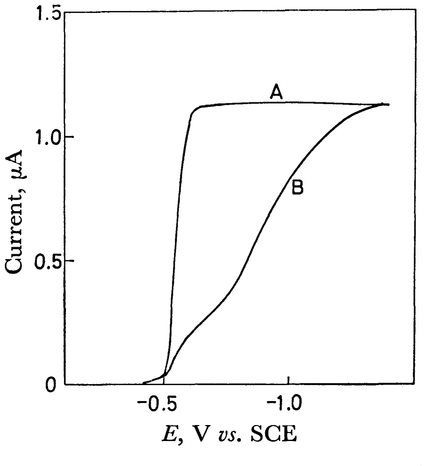


Fig. 2. Polarograms of Cd^{2+} (A) wthout and (B) with **4** of 21.8×10^{-3} M. I=0.10 M (TEAP) and pH=2.00.

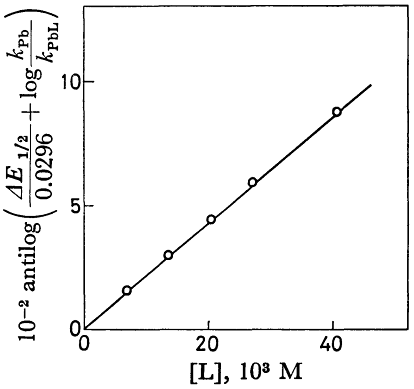


Fig. 3. Determination of the stability constant for Pb^{2+}–**4** complex. A plot of antilog ($\Delta E_{1/2}/0.0296+\log(k_{Pb}/k_{PbL})$) *vs.* [**4**]. $[Pb^{2+}]=0.25\times10^{-3}$ M, I=0.10 M, pH=2.00, 25 °C.

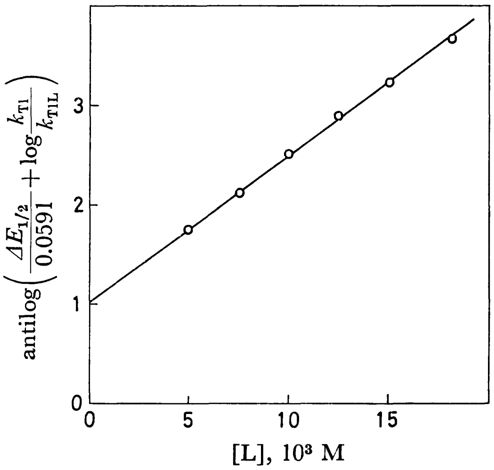


Fig. 4. Determination of the stability constant for Tl^{+}–**4** complex. A plot of antilog($\Delta E_{1/2}/0.0591+\log(k_{Tl}/k_{TlL})$) *vs.* [**4**]. $[Tl^{+}]=0.25\times10^{-3}$ M, I=0.10 M, pH=2.00, 25 °C.

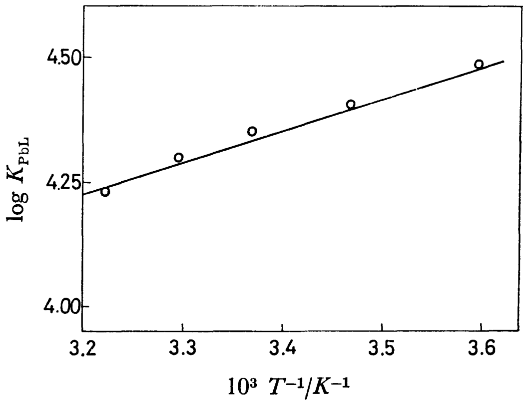


Fig. 5. Temperature dependence of the stability constant of Pb^{2+}–**4** complex.

The lead and thallium ions invariably gave single well-defined waves under the present experimental conditions. The plots of $\log(i/(i_l-i))$ *vs.* d.c. potential, E, gave straight lines with reciprocal slopes of −31—−32 mV and −58——61 mV for Pb^{2+} and Tl^{+}, respectively. Their limiting currents (i_l) were exactly proportional to their bulk concentrations and to the square root of the effective pressure on the dropping mercury electrode. Thus, the two electron reduction of Pb^{2+} and one electron reduction of Tl^{+} in the presence of **4** were polarographically defined to be reversible. The half-wave potential, $E_{1/2}$, and i_l underwent little pH effect within the range 1.0—3.0. Complexation was demonstrated by the negative shift of $E_{1/2}$, $\Delta E_{1/2}$, upon increasing the ligand concentration, [**4**]. The slope in

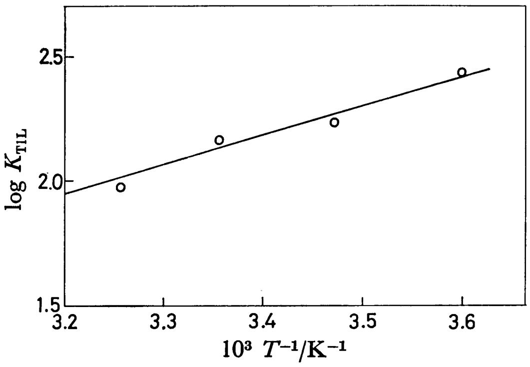


Fig. 6. Temperature dependence of the stability constant of Tl^+-**4** complex.

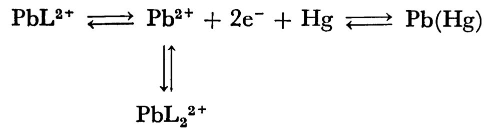
the linear relation between antilog($n\Delta E_{1/2}/0.0591+\log(k_M/k_{ML})$) and [**4**] immediately allowed the estimation of the 1 : 1 complex stability constant for both metal ions, where logarithm of the diffusion current constant ratio, k_M/k_{ML}, was 0.06 for Pb^{2+} and 0.04 for Tl^+ system (Figs. 3 and 4). Stability constants, K_{PbL} and K_{TlL}, were measured at various temperatures (5—35 °C) to estimate thermodynamic functions (Figs. 5 and 6). The results are summarized in Table 1.

TABLE 1. STABILITY CONSTANTS (I=0.10 M. 25 °C) AND THERMODYNAMIC FUNCTIONS

Complex	log $K^{a)}$	$-\Delta H^{a)}$ kcal mol^{-1}	$\Delta S^{a)}$ cal K^{-1} mol^{-1}
Pb^{2+}–(18-Crown-6)	4.4±0.1	3.1±0.2	9.7±1
Tl^+–(18-Crown-6)	2.2±0.1	5.4±0.3	−8.3±1
Pb^{2+}–Tetraglyme	0.5±0.1 (log β_1)	3.2±0.2	−8.3±1
Pb^{2+}–(Tetraglyme)$_2$	1.6±0.1 (log β_2)	6.4±0.3	−14.3±2

a) Uncertainties are the standard deviations.

Polarographic Behavior of Lead(II) in Tetraglyme **5** *Solution.* The solution containing Pb^{2+}, **5**, and 0.1 M TEAP also gave a reversible polarographic wave. As in the case of the cyclic ligand system, the increase in the concentration of **5**, [**5**], caused a negative shift of $E_{1/2}$. However, a plot of [antilog($\Delta E_{1/2}/0.0296+\log(k_{Pb}/k_{PbL})-1$]/[**5**] instead of antilog($\Delta E_{1/2}/0.0296+\log(k_{Pb}/k_{PbL})$) *vs.* [**5**] gave a straight line with an intercept of finite value (Fig. 7). The electrode reaction mechanism is thus written as



$$\begin{tikzcd} PbL^{2+} \arrow[r, shift left] & Pb^{2+} + 2e^- + Hg \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & Pb(Hg) \arrow[l, shift left] \\ & PbL_2^{2+} \arrow[u, shift left] & \end{tikzcd}$$

and the shift of the half-wave potential is expressed in the form

$$\Delta E_{1/2} = 0.0296 \log(1+K_{PbL}[5]+K_{PbL}K^*_{PbL_2}[5]^2) + 0.0296 \log \frac{k_{PbL}}{k_{Pb}}$$

where K_{PbL} and $K^*_{PbL_2}$ denote the first and second successive formation constants, respectively, of lead(II)-tetraglyme complex. From the intercept and slope of the above linear relation, $K_{PbL}(\beta_1)$ and $K_{PbL}K^*_{PbL_2}(\beta_2)$ values were determined. They were also measured at various temperatures (10—35 °C) in order to determine the thermodynamic parameters (Table 1 and Fig. 8). The polarography of Tl^+ ion in the tetraglyme solution was also studied. However, little evidence indicating the complex formation was obtained.

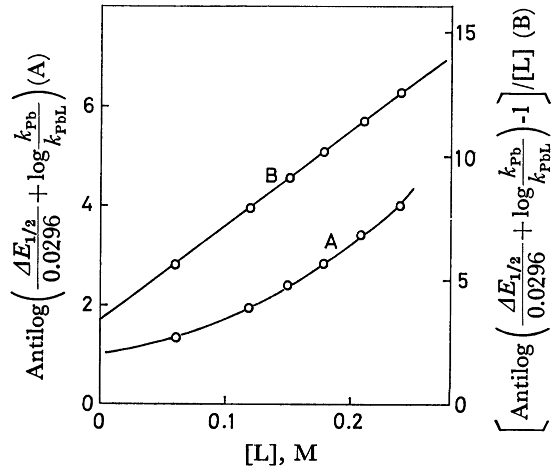


Fig. 7. Determination of the stability constants for Pb^{2+}-**5** complexes. Plots of [antilog($\Delta E_{1/2}/0.0296+\log(k_{Pb}/k_{PbL})$)−1]/[**5**] and antilog($\Delta E_{1/2}/0.0296+\log(k_{Pb}/k_{PbL})$) *vs.* [**5**]. $[Pb^{2+}]=0.40\times10^{-3}$ M, I=0.10 M, pH=2.00, 25 °C.

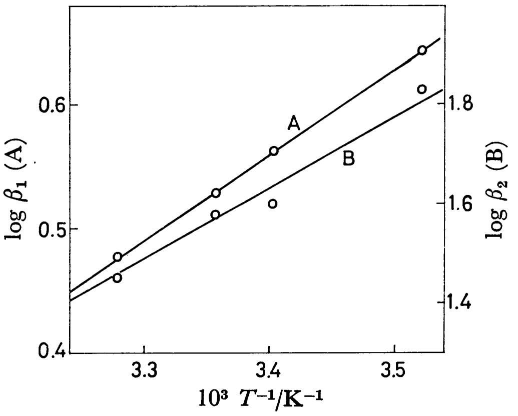


Fig. 8. Temperature dependence of stability constants for 1 : 1 (β_1) and 1 : 2 (β_2) Pb^{2+} -**5** complexes.

Discussion

Crown ether undergoes adsorption to the mercury electrode surface to block the electrochemical reactions of Cd^{2+}, but not of Pb^{2+} or Tl^+. This might be relevant in some way to the selective ion transport phenomena across cell membranes. The metal ions such as Pb^{2+} or Tl^+ may pass through the artificial membrane of the 18-crown-6 in complex forms possibly by repeating dissociation and complexation before reaching the electrode surface. On the other hand, Cd^{2+} ion shows the low permeability probably because of its low affinity for **4**. We observed that the presence of **4** similarly hindered the reduction of transition metal ions like

Cu^{2+}, which is known to be incapable of forming stable complexes with **4**.[2b]

The agreement of the stability constant of $10^{4.4}$ for the 1 : 1 Pb^{2+}–**4** complex with those for Pb^{2+}–**1** or –**2** (log K 4—5) determined by Christensen *et al.*[2a] is noteworthy in view of the difference in side groups as well as in the methods. A comparison of the present Pb^{2+} data with those of the alkali earth metal ion[3] discloses a remarkable entropic effect contributing to the Pb^{2+} complex stability. The special affinity of the bicylic polyoxadiaza ligand, **6** ($n=3$), for Pb^{2+} over Ba^{2+} or Sr^{2+} is similarly accounted for by the greater entropic contribution.[12] Considering the fact that the dehydration of Pb^{2+} ion causes the least entropic increase among the three divalent metal ions,[4] the major contribution to the large positive ΔS value upon the Pb^{2+} complex formation might result from other sources.

The measurement for a linear polyoxy ligand, **5**, was conducted in the identical conditions. No complication took place as in the case of **4**. It was found that **5** forms a 1 : 1 and a 2 : 1 complex with Pb^{2+} in aqueous solution. The second successive stability constant ($K^*_{\mathrm{PbL_1}}$) is greater than the first one. The large enthalpic gain due to small expenditure of energy for the dehydration of Pb^{2+}–**5** (1 : 1) complex outweighs the loss of entropy, making an overall free energy change for the additional ligation feasible.

Comparison of stability constants of 1 : 1 complexes for the linear (though short of one oxygen atom) and cyclic ligands allows the estimation of the macrocyclic effect of *ca.* 10^4-fold that is entirely accounted for by the favorable entropy contribution. The *macrocyclic effect* in the present case can be regarded as a synonym to *chelate effect*.

Thallium(I) ion forms with **4** a 1 : 1 complex having the stability constant of $10^{2.2}$ at $I=0.10$ and 25 °C. The high exothermicity exceeds the unfavorable entropy change. Unlike Pb^{2+} or smaller metal ions, Tl$^+$ is too large (2.8 Å diameter) to fit the macrocyclic cavity and has to lie above the plane of the six oxygen atoms, in analogy to Rb$^+$(2.9 Å).[18,19] Hence, the desolvation, a major factor contributing to positive entropy change upon complexation in some metal ions would not be sufficient for the ligand substitution of Tl$^+_{\mathrm{aq}}$.

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