Complex Formation of Poly(Acrylic Acid) with Lead(II) Ion

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Synopsis. The equilibrium constants of Poly(acrylic acid)-Pb(II) complex formation reactions were evaluated from stoichiometric equations by means of pH titration with a Pb(II) ion selective electrode. The thermodynamic parameters were obtained from the temperature dependence of the equilibrium constants. The Poly(acrylic acid)-Pb(II) complexes seem to be stable due to an exothermic process.

There are many investigations on the interaction between divalent metal ions and polyelectrolytes.[1–4] Many workers have extensively discussed the stability of polyelectrolyte complexes from the equilibrium constants of complex formation reactions. Gregor and co-workers have shown that the Bjerrum method of pH titration for the evaluation of formation constants of complexes may be applied to the divalent metal–polyelectrolyte complex systems.[1]

On the other hand, the amount of complexed metal ions in aqueous solution can be evaluated from the amount of free metal ions. However, it is not so easy to determine this amount, although several methods have been proposed. Yamashita et al. showed that the potentiometric titration by use of a copper(II) ion selective electrode(Cu-ISE) is useful to investigate the complex formation in the copper(II) ion-polycarboxylic acid system. Cu-ISE is able to detect free metal ion alone. The values of equilibrium constants of complex formation reactions were evaluated from stoichiometric equations.[4]

In this paper, the complex formation in the lead(II)–poly(acrylic acid) system was investigated potentiometrically. On the basis of the data from pH titration by a lead(II) ion selective electrode(Pb-ISE), stability constants were evaluated from stoichiometric equations. Thermodynamic parameters were evaluated from the temperature dependence of stability constants for complex formation reactions.

Experimental

Materials. Poly(sodium acrylate)(PAANa) was purchased from Nakarai Chemical Co. PAANa was dissolved in distilled water and transformed to poly(acrylic acid)(PAA) by addition of excess hydrochloric acid. The aqueous solution of PAA was refined by dialysis. The molecular weight of PAA was 5.2×10^5 by viscometric measurement.[5] The other chemicals and lead(II) perchlorate used were of guaranteed reagent grade. The concentration of lead perchlorate stock solution was determined by chelatemetric titration with Xylenol Orange(XO) as the indicator.

Potentiometric Titration. The pH measurements were carried out in a nitrogen atmosphere at 15.0, 25.0, and 35.0 (±0.1)°C and ionic strength of 0.1 mol dm^{-3} $NaClO_4$ by use of a digital ion meter (Orion 801A) with glass and calomel electrodes. The activity measurements of lead(II) ion were performed with a digital ion meter (Orion Model 801A) with lead selective (Orion 948200) and calomel electrodes.

Double junction salt bridges of 1.0 mol dm^{-3} with sodium perchlorate agar and ammonium chloride-saturated agar were used between a glass (or Pb-ISE) and a reference calomel electrode in order to avoid the formation of Pb(II) chloride complex. The concentration of lead(II) ions was determined with the calibration curve obtained for the system without any polymer. The limit of detection for Pb-ISE was 10^{-6} mol dm^{-3}.

The lead perchlorate solution was added to the PAA solutions neutralized with a sodium hydroxide solution in order to avoid the precipitation. The potentiometric titration was thus carried out with a perchloric acid solution.

Results and Discussion

The average coordination number($\bar{n}$) obtained from the pH titration curve is given as follows:

$$\bar{n} = \sum i[PbA_i]/[Pb], \tag{1}$$

where [Pb] and [PbA_i] represent the total concentrations of lead ion and 1:i lead-carboxylate complex, respectively. Calculation of $\bar{n}$ was done by the method of reference plot contrived by Mandel et al.[2] $\bar{n}$ and the fraction of free lead ion determined with Pb-ISE are shown in Fig. 1 as two functions of the degree of dissociation of carboxyl group (α). $\bar{n}$ increased with α and reached nearly 1.8 in contrast to the decrease in fraction of free lead ion. An almost complete binding occurred above 0.3 of α. At α=0.1, 70% of lead ions was

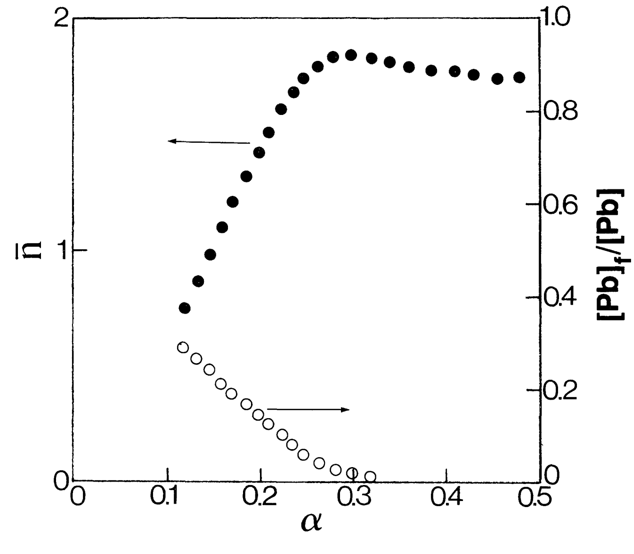

Fig. 1. Formation curve of PAA-Pb(II) complex at 25 °C: ●; $\bar{n}$ (average coordination number), ○; $[Pb]_f/[Pb]$ (fraction of free lead ion). [PAA]= 1.00×10^{-2} mol dm^{-3} [Pb]=1.01×10^{-3} mol dm^{-3}.

already bound to polymer, indicating that Pb(II)–PAA complex is stable. Below 0.1 of α, the precipitation occurred.

As is shown in Fig. 1, $\overline{n}$ does not exceed 2; it indicates that 2 is the maximum number of carboxylate groups bound to a lead ion. Assuming that both monocarboxylate (1:1) and dicarboxylate complexes (1:2) are formed, the following equation holds:

$$[\mathrm{Pb}] = [\mathrm{Pb}]_f + [\mathrm{PbA}] + [\mathrm{PbA}_2], \qquad (2)$$

where $[\mathrm{Pb}]_f$, [PbA], and $[\mathrm{PbA}_2]$ represent the concentrations of free lead ion, monocarboxylate complex, and dicarboxylate complex, respectively. In the present study, the concentration of free lead ion can be determined by Pb–ISE, and Eq. 1 can be rewritten as

$$\overline{n}\,[\mathrm{Pb}] = [\mathrm{PbA}] + 2[\mathrm{PbA}_2]. \qquad (3)$$

The simultaneous Eqs. 2 and 3 purposely gave the concentrations of two species [PbA] and $[\mathrm{PbA}_2]$.

The fractions of PbA and PbA_2 are shown as two functions of α in Fig. 2. The fraction of PbA_2 increased with α in contrast to a decrease in the fraction of PbA, suggesting that each of complex formation reactions is stepwise as is in the case of the monomeric ligand. In a low α region, monocarboxylate complex predominated over dicarboxylate complex. As α increased, monocarboxylate complex changed to dicarboxylate complex under increasing carboxylate group concentration.

The stability constants of monocarboxylate and dicarboxylate Pb(II) complexes, K_1 and K_2 are given by

$$K_1 = [\mathrm{PbA}]/[\mathrm{Pb}]_f\,[\mathrm{A}] \qquad (4)$$

and

$$K_2 = [\mathrm{PbA}_2]/[\mathrm{PbA}]\,[\mathrm{A}], \qquad (5)$$

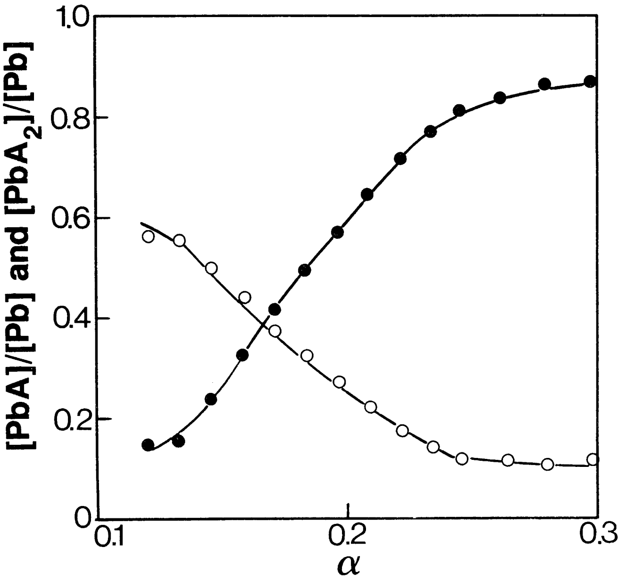

Fig. 2. Fractions of monocarboxylate and dicarboxylate Pb(II) complexes, [PbA]/[Pb] (○) and $[\mathrm{PbA}_2]$/[Pb] (●) as two functions of α.

where [A] represents the concentration of nonchelating carboxylate group determined by reference plot method proposed by Mandel and Leyte.[2] The values of K_1, K_2 calculated by the above equations in the α range of 0.1 to 0.3 are plotted in Fig. 3. The value of K_1 was nearly constant, whereas, the values of K_2 depended on α. K_2 increased with α and saturated at 0.25 of α. The behavior of K_2 is attributed to the change in negative charge density on each polymer chain, because the negative charge of carboxylate group adjacent to dicarboxylate complex raises the stability constant K_2. The stability constants of K_1 and K_2 at 0.15 of α ($\overline{n}=1.0$ in Fig. 1) were $10^{3.64}$ and $10^{3.11}$ dm^3 mol^{-1}, respectively.

In order to determine the change in enthalpy and entropy of the complex formation, the temperature dependence of stability constants was measured. The gross stability constant of the dicarboxylate Pb(II) complex, β_2 is given by

$$\beta_2 = K_1K_2. \qquad (6)$$

The logarithmic values of β_2 were 6.86, 6.75, and 6.66 at 15, 25, and 35 °C under the conditions of 0.15 of α,

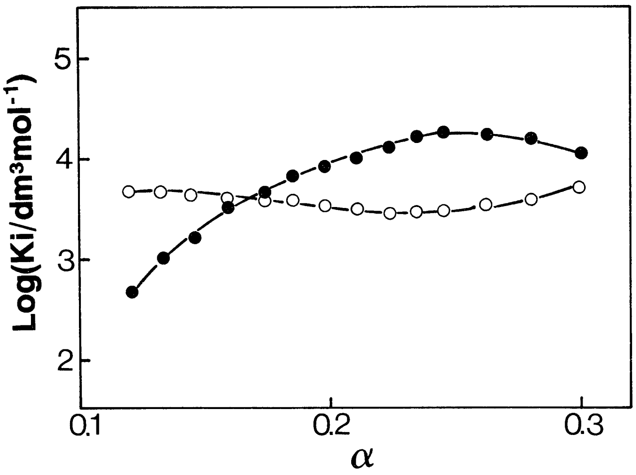

Fig. 3. Stability constants of monocarboxylate and dicarboxylate Pb(II) complexes, K_1 (○) and K_2 (●) as two functions of α.

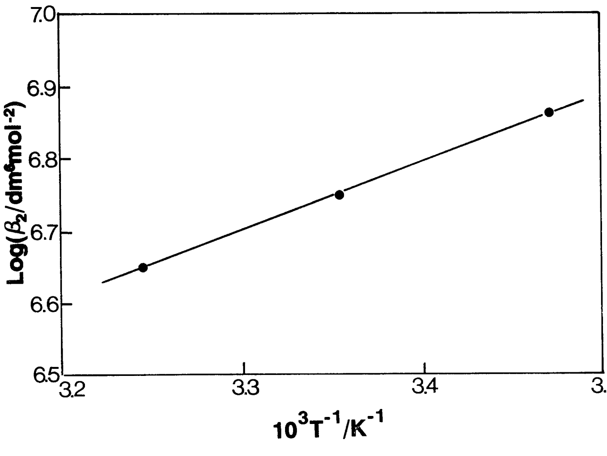

Fig. 4. Plots of log β_2 vs. T^{-1}.

Table 1. Gross Stability Constants and Thermodynamic Parameters

Metal ion	Ligand	β_2	$\Delta G^\ominus$	$\Delta H^\ominus$	$\Delta S^\ominus$
		$dm^6\ mol^{-2}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$J\ mol^{-1}\ K^{-1}$
Pb^{2+}	PAA	$10^{6.75}$	−38.5	−18.0	67
Pb^{2+}[a)]	Acetic acid	$10^{3.62}$	−20.5	−0.6	67
Cu^{2+}[b)]	PAA	$10^{5.86}$	−33.5	2.1	117

a) Data taken from Ref. 6. b) Data taken from Ref. 7.

respectively. Figure 4 gives the plot of log β_2 vs. T^{-1}. Log β_2 values were on the straight line between 15 and 35 °C, indicating that the enthalpy change is constant. The standard enthalpy change (ΔH) was obtained from Eq. 7:

$$\Delta H = -\ 2.303\ R\ \mathrm{d}\,(\log \beta_2 / T^{-1}), \tag{7}$$

where T is the absolute temperature, and R is the gas constant. The free energy change (ΔG) obtained from the value of log β_2 at 25 °C and the entropy change (ΔS) was calculated by $(\Delta H - \Delta G)/T$. Gross stability constants and the thermodynamic parameters obtained by the present analysis are summarized in Table 1, together with the literature values for the corresponding lead acetate,[6)] and copper–PAA[7)] as a comparison. The dicarboxylate complex is 10^3 times as stable as the Pb(II) acetate complex. Standard enthalpy changes for Pb(II)–PAA complex and Pb(II) acetate complex were negative, indicating that the formation of a chelate between one lead ion and two carboxylate groups is an exthothermic process. The absolute value of enthalpy change was favorable of the formation of Pb(II)–PAA complex. In the polymer–metal system, the standard enthalpy change is more negative than that in the monomeric analogue–metal ion system, so that the metal ions are more tighly bound to the polymer than to the monomeric analogue.[8)]

The standard entropy change for Pb(II)–PAA complex is smaller than that for Cu(II)–PAA complex which is the most stable one among divalent metal–PAA complexes investigated, the entropy change was favorable of Cu(II)–PAA complex, whereas the enthalpy change for the former is larger than that for the latter. It is known that enthalpy change for transition divalent metal-polycarboxylate complexes are positive.[9)] These comparisons show that the lead–PAA complex must be stabilized by a highly exthothermic process. It is concluded that Pb(II)–PAA complex is the most stable one of the divalent metal ion–PAA complexes which have been investigated in accord with the order of magnitude of stability constant for the divalent metal ion–monomeric carboxylate complex, that is Pb>Cu>Cd.[10)]

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