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COMPLEXATION CONSTANTS OF LANTHANIDE IONS WITH POLY(METHACRYLIC ACID) AND ITS COPOLYMERS

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ABSTRACT

Complexation of some lanthanide ions with poly(methacrylic acid) and its copolymers was studied by potentiometric titration. Poly [methacrylic acid-*co*-oligo(ethylene oxide)methacrylate] and poly(methacrylic acid-*co*-acrylamide) formed tris-carboxylate coordinate lanthanide complexes with large overall complexation constants, while poly(methacrylic acid)s and copolymer with higher content of the methacrylic acid residue formed bis-coordinate ones. It was concluded that the comonomer residues in the copolymer chains decreased the steric hindrance for the complexation and/or acted as co-coordinating groups of the carboxylic group to lanthanide ions. Very large positive and favorable entropy changes were observed for the complexation with poly(methacrylic acid) and its copolymers. This contribution of thermodynamic parameters to the complexation was contrary to that for the analogous monomeric methacrylic acid complex and is assumed to be induced by dehydration of the polymers through the lanthanide ion complexation.

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INTRODUCTION

Complexation constants of transition metal ions, such as copper and cobalt ions, with poly(carboxylic acid)s, such as poly(methacrylic acid) and poly(acrylic acid), have been well studied to explore the complexation behavior of polymers [1, 2]. The complexation of trivalent lanthanide ions with low molecular weight carboxylic acids has been also well studied and summarized [3, 4], but less attention has been given to the complexation constants of lanthanide ions with polymers in aqueous solution. These complexation constants are relevant to the preparation of polymer-lanthanide complexes, which represent an attempt to give an organic polymer with the physicochemical properties of lanthanide [5].

In this paper, poly(methacrylic acid) and its copolymers were used as polymer ligands, and europium (Eu), gadolinium (Gd), and terbium (Tb) ions as lanthanide ions. Their complexation constants and thermodynamic parameters for complexation in aqueous solution were estimated by potentiometric titration. The effects of the polymer ligand on complexation with trivalent and "large" lanthanide ions are discussed.

EXPERIMENTAL

Materials

Poly(methacrylic acid) (PMA), oligo(methacrylic acid) (OMA), poly(methacrylic acid-*co*-acrylamide) (MAA), and poly[methacrylic acid-*co*-oligo(ethylene oxide) methacrylate] (MAE) were prepared by free-radical polymerization. Composition and molecular weight of the polymers were determined by elemental analysis and gel permeation chromatography, respectively. Suffixes indicate the mole fraction of the methacrylic acid residue in the copolymer. MW of PMA = 5.1×10^5 , OMA = 6.4×10^3 , MAA_{0.45} = 2.0×10^5 , MAA_{0.28} = 3.5×10^5 , and MAE_{0.69} = 9.0×10^5 . Methacrylic acid (MA) was used after distillation. Oligo(ethylene oxide) methacrylate, $\text{CH}_2\text{C}(\text{CH}_3)\text{COO}-(\text{CH}_2-\text{CH}_2\text{O})_n\text{H}$ ($n = 7-8$), was a gift from Nihon Fat and Oil Co. Europium, gadolinium, and terbium nitrate of analytical reagent grade were used.

Potentiometric Titrations

All titrations were conducted in a jacketed vessel maintained at constant temperature (10-40°C) under N₂ atmosphere with CO₂-free water. Hydrogen

ion activities were determined with a glass electrode and a TOA HM-15A type pH meter. Sodium nitrate was added as a supporting electrolyte (0.1 *M*).

RESULTS AND DISCUSSION

Potentiometric titration was carried out in aqueous solutions of Eu, Gd, and Tb with PMA, OMA, MAA, MAE, and MA. Since PMA, OMA, MAA, and MAE themselves as well as their Eu, Gd, and Tb complexes behave as poly-electrolytes in aqueous solution, the modified Bjerrum method reported by Gregor [1] was used for the calculation of complexation constants. Examples of modified Bjerrum formation curves for the lanthanide complexes are shown in Fig. 1.

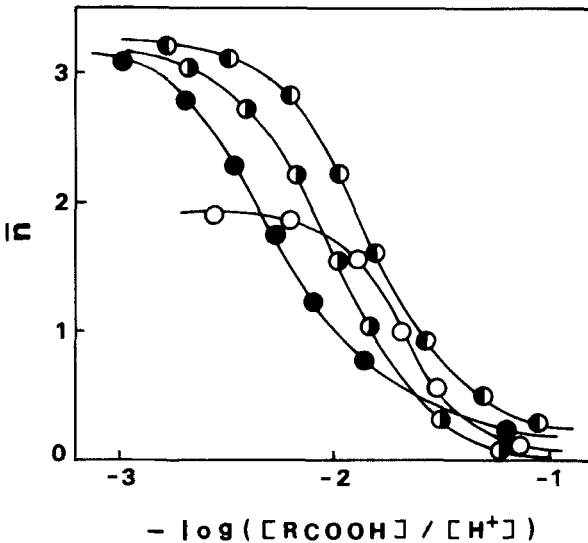
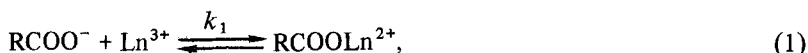


FIG. 1. Bjerrum formation curves for the Eu complexes at 30°C. (○) PMA, (◐) MAE_{0.69}, (○) MA, (●) MAA_{0.28}.



Successive formation constants k_i and overall formation constant

$$\beta_n = \prod_{i=1}^n k_i \quad (4)$$

for the complexation of lanthanide ions with carboxylates are summarized in Table 1.

TABLE 1. Complexation Constants of Poly(Methacrylic Acid) and Its Copolymers with Lanthanide Ions at 30°C

Lanthanide ion	Ligand	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_n$
Eu^{3+}	PMA	4.6	4.3	—	8.9
	OMA	4.7	4.4	—	9.1
	MAA _{0.45}	4.3	4.0	—	8.3
	MAA _{0.28}	4.1	3.8	3.4	11.3
	MAE _{0.69}	4.6	3.9	3.5	12.0
	MA	3.2	2.6	2.4	8.2
Tb^{3+}	PMA	4.5	4.2	—	8.7
	OMA	4.6	4.3	—	8.9
	MAA _{0.28}	3.9	3.6	3.5	11.0
	MA	3.1	2.6	2.4	8.1
Gd^{3+}	PMA	4.6	4.3	—	8.9
	MAA _{0.28}	4.3	3.8	3.5	11.6
	MA	3.2	2.7	2.5	8.4

The constants k_1 and k_2 for the lanthanide complexes with PMA were ~ 10 times larger than those with monomeric MA, but the third step of the carboxylate-complexation with Eu, Gd, and Tb was not observed, and the β_n values were limited to $\sim 10^9$. It is assumed that the PMA chain cannot easily form the tris-coordinate complexes with its three carboxylate groups due to the steric hindrance of the polymer chain and the "large" lanthanide ions. The k_n and β_n values for the OMA-lanthanide complexes were approximately equal to those of PMA, and molecular weight, at least in this molecular weight region, of the polymer ligand did not influence the complexation constants. In contrast, lanthanide ion complexation proceeded to the third step for MAA_{0.28} with $\beta_n \sim 10^3$ times larger than for PMA and MA, and MAA formed stable tris-coordinate complexes with lanthanide ions. It is considered that the comonomer residues in MAA decrease steric hindrance for the complexation.

Table 1 shows that the third step of carboxylate complexation was not observed for MAA_{0.45}, which, with its higher content of methacrylic acid residues, is similar to the homopolymer PMA. This suggests that the acrylamide residue effectively influences the complexation only when it makes up more than two-thirds of the polymer.

MAE_{0.69} gave extra large complexation constants compared to other polymers (Table 1). Shiokawa et al. reported that oligo(ethylene oxide)s form relatively weak complexes with lanthanide ions [6]. It is considered that the oligo(ethylene oxide) methacrylate residue in the copolymer chain increases the flexibility of the polymer ligand chain and/or acts as a co-coordinating group of the carboxylic group to lanthanide ions to stabilize the complex.

The temperature dependence of the complexation constants (van't Hoff isochore) is plotted in Fig. 2 for Eu complexation with the polymers and in Fig. 3 for that with the monomeric analog MA. These figures demonstrate that the temperature dependence, i.e., the enthalpy change, is markedly different for the polymeric and monomeric complexes.

Thermodynamic data for the Eu complexation are summarized in Table 2. MA gave negative enthalpy changes for each step as well as the overall complexation. This means that the MA-Eu complexation is favored by the energy gain accompanying formation of the coordination bonds. The polymer ligands, PMA, MAA_{0.28}, and MAE_{0.69}, show a drastic effect on the thermodynamic parameters for the Eu complexation. In contrast to the monomeric MA complex, the polymer ligands give very large positive entropy changes for each step of the complexation and make a significant favorable entropic contribution to the complexation. Eu complexation

TABLE 2. Thermodynamic Parameters of the Eu Complexes

Ligand	k_1		k_2		k_3		β_n	
	ΔH_i kcal/mol	ΔS_i eu	ΔH_i kcal/mol	ΔS_i eu	ΔH_i kcal/mol	ΔS_i eu	ΔH_i kcal/mol	ΔS_i eu
PMA	4.2	35	4.6	35	—	—	8.8	70
MAA _{0.28}	3.8	31	4.0	30	4.3	30	12.1	91
MAE _{0.69}	2.9	30	2.1	25	2.3	24	7.3	79
MA	-5.9	-5	-8.7	-17	-9.5	-20	-24.1	-42

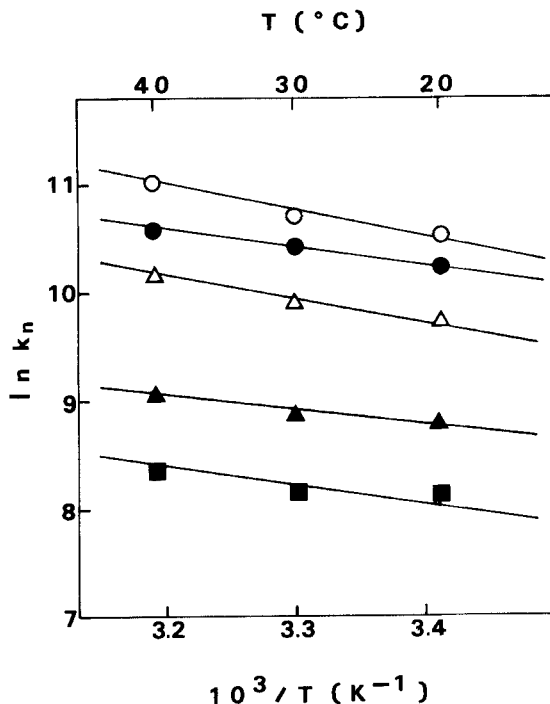


FIG. 2. Van't Hoff plots for the complexation constants of Eu ion with the polymers. (○) k_1 , (△) k_2 , (□) k_3 ; open symbols, PMA; closed symbols, MAE_{0.69}.

with the polymers is disfavored enthalpically compared with the monomeric MA complex, but this is compensated by the large favorable change in the entropy. This positive and favorable entropy change is considered to be caused by dehydration of the polymer ligand (the anionic polycarboxylic acid) and of the trivalent cationic Eu ion through complex formation.

MAE_{0.69} gave not only large and positive entropy changes but also relatively favorable enthalpy changes, corresponding to the specially large complexation constants of MAE_{0.69}. This suggests that the oligo(ethylene oxide) methacrylate residue increases flexibility and hydration of the polymer chain and/or acts as a co-coordinating group for Eu ion. In any case, the polymer ligand produces a large effect on the stability of the Eu complex through its entropic contribution.

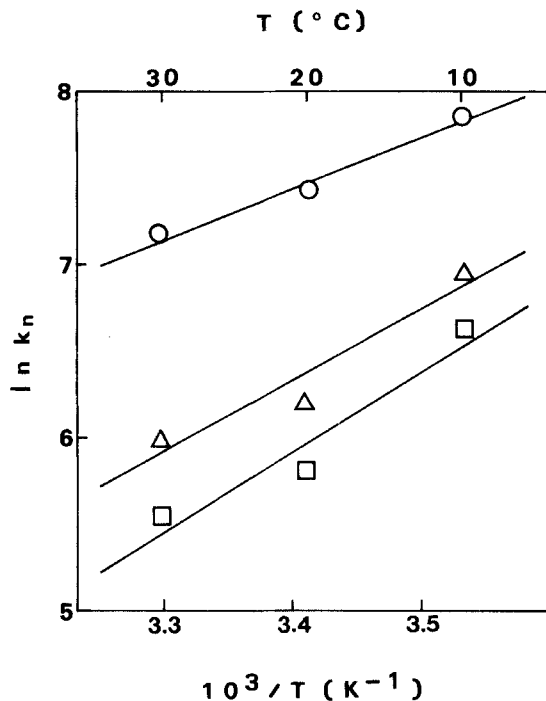


FIG. 3. Van't Hoff plots for the complexation constants of Eu ion with MA. (○) k_1 , (△) k_2 , (□) k_3 .

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