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Europium(Ⅲ) Fluorescence Lifetime in Poly(methacrylic acid) Related to Its Conformational Transition

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The number of water molecules ($N_{\mathrm{H_2O}}$) in the inner-sphere of Eu(Ⅲ) complexed with poly(methacrylic acid) and poly(acrylic acid) was reported at various temperatures and α (degree of ionization) of these polyelectrolytes using laser-induced fluorescence spectroscopy. It is suggested that the conformational transition of poly(methacrylic acid) is reflected in the α dependence of $N_{\mathrm{H_2O}}$.

In some studies, the fluorescence lifetimes of Eu(Ⅲ) or Tb(Ⅲ), which are related to the number of water molecules in the inner-sphere of the lanthanide ions ($N_{\mathrm{H_2O}}$), have been utilized to study the interaction between polyvalent cations and polyelectrolytes.[1–3] These studies have shown the $N_{\mathrm{H_2O}}$ value at a specific degree of ionization (α) of polyelectrolytes. According to this paper and our preliminary study,[4] the $N_{\mathrm{H_2O}}$ value varies with the pH or α, especially in the Eu(Ⅲ)–poly(methacrylic acid) (PMAA) system. This fact indicates that the dependence of the $N_{\mathrm{H_2O}}$ value on the pH or α should be carefully examined to study the interaction between polyvalent cations and polyelectrolytes by this method. Besides, the present study suggests that the variation of the $N_{\mathrm{H_2O}}$ value in the Eu(Ⅲ)–PMAA system is possibly related to the conformation transition of PMAA, depending on the pH or α, which has been the subject of a number of studies.[4–6] In the present paper, we report on the α (or pH) dependence of $N_{\mathrm{H_2O}}$ at various temperatures (278, 298, and 318 K) for Eu(Ⅲ) species complexed with linear and cross-linked PMAA ($\mathrm{PMAA_l}$ and $\mathrm{PMAA_c}$, respectively) and poly(acrylic acid) ($\mathrm{PAA_l}$ and $\mathrm{PAA_c}$, respectively). The $N_{\mathrm{H_2O}}$ value was obtained from fluorescence lifetime of Eu(Ⅲ) (τ/ms) due to its f-f transition as $N_{\mathrm{H_2O}} = 1.07\ \tau^{-1}/\mathrm{ms}^{-1} - 0.62$.[7,8]

In the absence of polycarboxylate ligands, τ became very small (< 80 µs) at pH values above 6.5 due to the formation of inorganic Eu(Ⅲ) precipitates, where energy transfer among neighboring Eu(Ⅲ) ions occurs.[9] In that region, $N_{\mathrm{H_2O}}$ became larger than 9, which is not possible as Eu(Ⅲ) species, since the $N_{\mathrm{H_2O}}$ for the Eu(Ⅲ) aquo ion is 9.[7,8] In the presence of polycarboxylate ligands, the pH range which we studied was from pH 2 to 9, where τ is sufficiently large (> 110 µs), leading to reasonable $N_{\mathrm{H_2O}}$ values for the Eu(Ⅲ) species bound to polycarboxylates. If inorganic Eu(Ⅲ) precipitates also form in the polycarboxylate system, it is possible to distinguish the two species (precipitates and polycarboxylate complex) depending on their discrepant fluorescence lifetimes.[9] A shorter lifetime component, however, was not found in the polycarboxylate system, showing that inorganic Eu(Ⅲ) precipitates did not form in our experimental system.

Figure 1a shows that $N_{\mathrm{H_2O}}$ decreased from 4.5 to 2.5 along with an increase in α for $\mathrm{PAA_l}$ ($0.1 < \alpha < 1$). Since one carboxylate can exclude two water molecules hydrated to Eu(Ⅲ) in this system,[10] the $N_{\mathrm{H_2O}}$ value shows that there are more than two Eu(Ⅲ) species interacting with the $\mathrm{PAA_l}$; some Eu(Ⅲ) ions bind to two carboxylate ligands, while the other to three carboxylates. The decrease of $N_{\mathrm{H_2O}}$ at a larger α may show that the Eu(Ⅲ) species binding to three carboxylates relatively increase among all Eu(Ⅲ) species. A decrease of $N_{\mathrm{H_2O}}$ vs α was similarly observed for $\mathrm{PAA_c}$ (Fig. 1b). However, there is a difference in the temperature dependence between these two systems. The $\mathrm{PAA_l}$ system shows a slight temperature effect, whereas $N_{\mathrm{H_2O}}$ at higher temperature is lower for the $\mathrm{PAA_c}$ system. This indicates that a larger number of carboxylates are associated with Eu(Ⅲ) in the $\mathrm{PAA_c}$ system at higher tempera-

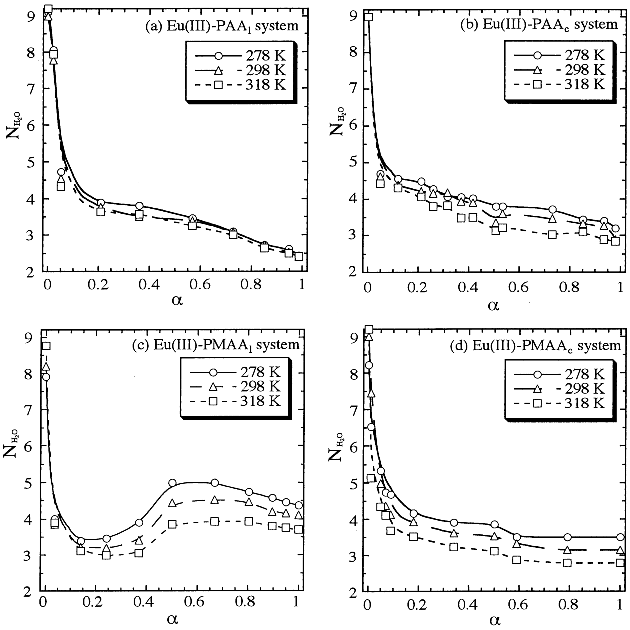

Fig. 1. The α {= degree of dissociation of poly(methacrylic acid) or poly(acrylic acid)} dependence of $N_{\mathrm{H_2O}}$, the number of water molecules in the inner-sphere of Eu(Ⅲ), in the various systems of (a) Eu(Ⅲ)–$\mathrm{PAA_l}$ {linear poly(acrylic acid)}, (b) Eu(Ⅲ)–$\mathrm{PAA_c}$ {cross-linked poly(acrylic acid)}, (c) Eu(Ⅲ)–$\mathrm{PMAA_l}$ {linear poly(methacrylic acid)}, and (d) Eu(Ⅲ)–$\mathrm{PMAA_c}$ {cross-linked poly(methacrylic acid)} at 278, 298, and 318 K. Total concentrations of carboxylate and Eu(Ⅲ) were 0.30 eq/dm^3 and 1.5 mmol/dm^3, respectively. Concentration of supporting electrolyte (NaCl) was 0.020 mol/dm^3.

ture, suggesting that the entropic effect may have a larger influence on complexation in the PAA$_c$ system than that in the PAA$_l$ system.

The N_{H_2O} in the PMAA$_l$ system showed similar results to the PAA$_l$ system in the range of $0 < \alpha < 0.2$ (Fig. 1c). However, the α dependence of the N_{H_2O} in the PMAA$_l$ system has a maximum value around $\alpha = 0.5$, which was not found in the PAA$_l$ system. Although similar lanthanide(III) fluorescence studies have reported the N_{H_2O} value at a specific α value so far,[1–2] the present study indicates that we need to be careful to employ the N_{H_2O} value for the PMAA$_l$ system due to its variation depending on α. The maximum N_{H_2O} value was not found in other Eu(III) complexes binding with polycarboxylates of poly(maleic acid), poly(α-hydroxyacrylic acid), and PAA.[3] Among these polycarboxylates, a sharp conformational transition is peculiar to PMAA, which is estimated from pH titration,[4–6] viscometry,[5,6] and neutron and X-ray small angle scattering.[6] The scattering study clearly showed that a conformational change undergoes from $\alpha = 0.2$ to 0.5.[6] The α dependence of N_{H_2O} in the PMAA$_l$ system found in this study can be well explained by the conformational transition of PMAA$_l$ from a compact coiled conformation at lower α to an elongated conformation at higher α.[4–6] The maximum value can be given when the conformational change into the elongated form is terminated ($\alpha = 0.5$). In the elongated conformation, the Eu(III) ion is more exposed to the bulk aqueous solution, allowing more water molecules to interact with Eu(III). Although the N_{H_2O} value provides information on the local structure of the Eu(III) ion, it is suggested that Eu(III) fluorescence can be used as a probe for the conformational transition of PMAA$_l$.

Both the PMAA$_l$ and PMAA$_c$ systems showed a similar temperature dependence to the PAA$_c$ system: the N_{H_2O} decreases as the temperature increases (Fig. 1). It must be noted that the increment of N_{H_2O} in PMAA$_l$ from a minimum value (around $\alpha = 0.2$) to a maximum value (around $\alpha = 0.5$) is larger at lower temperatures. From the temperature dependence of the dissociation behavior and the viscosity of PMAA$_l$, the conformational transition of PMAA$_l$ is caused by intramolecular hydrogen bonding between the ionized and unionized carboxylate groups.[5,11] This implies that a conformational transition of PMAA$_l$ occurs more distinctively at lower temperatures.[5] This fact is also consistent with the present N_{H_2O} results concerning the temperature dependence of the N_{H_2O} value in the Eu(III)–PMAA$_l$ system. At larger C_s (supporting electrolyte concentration), the maximum value in the N_{H_2O} variation in Eu(III)–PMAA$_l$ system was less pronounced,[3] as is also suggested from a titration study showing that the transition occurs moderately at a larger C_s region.[4] Both the temperature and the C_s dependence also support that the sharp conformational transition of PMAA$_l$ is reflected in the α dependence of the N_{H_2O} in the Eu(III)–PMAA$_l$ system.

On the other hand, a similar maximum value was not observed for the PMAA$_c$ system. This fact seems to be reasonable, since the cross-linked structure of PMAA$_c$ may inhibit such a conformational transition, probably due to the rigidity of PMAA$_c$ compared with PMAA$_l$.[12] It is speculated that, because of the rigidity, the PMAA$_c$ molecule does not let more water molecules hydrate to Eu(III) to produce a maximum value of N_{H_2O} in the α dependence.

As can be seen from the results above, the N_{H_2O} value of Eu(III) seems to be closely related with the conformation of polyelectrolyte interacting with Eu(III). This study implies that the careful application of an Eu(III) fluorescence probe can be a useful tool to clarify the conformation of polyelectrolyte.

Experimental

PAA$_l$ (mean molecular weight (MW): 250,000) and PMAA$_l$ (MW: 100,000) were obtained from Aldrich Chem. Co., Inc. and from Polyscience Inc., respectively. PAA$_c$ and PMAA$_c$ were IRC-76 and IRC-50, respectively, obtained from Rohm and Haas Co. The relation between pH and α was obtained by pH titration.

A polyelectrolyte solution ([–COO$^-$]: 0.30 eq/dm^3) was mixed with Eu(III) (total Eu(III) concentration: 1.5 mmol/dm^3). C_s was adjusted by NaCl at 0.020 mol/dm^3. The pH of the solution was adjusted with a small amount of a NaOH or HCl solution. Fluorescence measurement was conducted as similarly to our previous studies.[3,9] The temperature of each solution was kept at 278, 298, and 318 K overnight, and was maintained at each value during a measurement by soaking the lower part of a quartz cell in a bath at a proper temperature.

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