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Complexation behavior of poly(acrylic acid) and lanthanide ions

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ABSTRACT

The complexation behavior of PAA and lanthanide (Ln) ions was schematically investigated. As pH increased, the complexation between PAA and Ln ions will greatly strengthen because COO^- groups exhibit much stronger interaction with Ln ions than COOH. When the pH values are higher than 2.5, where the ionization of PAA is about 2.0%, the PAA–Ln complex would precipitate out from the solution. The precipitation is a direct indicator for the complexation between PAA and Ln ions. Besides pH values, the complex precipitation is related with the concentration, the molar ratio, and the operation procedure. At the extremely low concentration, there is no polymer–metal complex precipitation but fluorescence spectroscopy reveals that the complexation between PAA and Ln ions still exists when pH value is higher than 2.5. When the molar ratio of PAA and Ln ions exceeds the certain level, it would produce soluble polymer–metal complex, even at the high concentration of Ln ions.

1. Introduction

Understanding the interaction of polymer and metal ion has significant meaning in terms of the potential applications in chemistry and technology, such as rare metal recovery, environment protection, heavy metal ion detection, medical therapy and functional material design [1–12]. Electrostatic force and coordination are two major interactions between polymer and metal. Metals are easy to lose electron to become ion while there are lots of negative charged polymers, so the electrostatic force is very common between polymers and metal ions. At the same time, metal ions have empty orbits in their atomic structure while the groups in polymer can provide electron lone pair, which will form coordination bond.

Lanthanides have 4f orbits in atomic structure, which make them exhibit special chemical and spectroscopic properties. Lanthanide doped materials are of great interest for the potential in the fields of catalysis and luminescence [13–18]. Some lanthanide ions, such as Terbium and Europium, have been widely used as luminescent probes and stains for molecular assembly and biomolecular structure [19,20]. The coordination of small molecules containing carboxylic acid groups has been deeply investigated, and many coordination modes have been reported, such as unidentate, simple chelating, bridging bidentates, and chelating tridentate [21,22]. Compared with small molecules, the coordination behavior of polymer and lanthanide ion is more complicated. Long chain structure of the polymer would affect coordination geometry and it is very hard to form highly ordered structure.

Poly(acrylic acid) (PAA) is a water soluble polymer and is the simplest synthetic poly(carboxylic acid). PAA and its derivatives are widely used for thickening, dispersing, suspending and emulsifying agents in pharmaceuticals, cosmetics and paints [23]. One PAA chain can provide many carboxylate groups which are among the most suitable ligands for lanthanides ions. Studies on PAA help more specifically in the interpretation of the behavior of polymers containing carboxylic acid group, such as the acidic polysaccharides, humic substance and proteins.

PAA is a weak polyelectrolyte and the ionization degree is pH sensitive [24–26]. The ionization degree strongly affects the chain conformation and chain mobility of PAA in aqueous solution [27,28]. As the pH value elevated, the ionization of PAA will increase and there will be more COO^- groups present. COO^- shows stronger interaction with lanthanide ions than COOH does. At the same time hydrolysis of lanthanide will strength as pH value increases, *i.e.* lanthanide ions would form $Ln(OH)_3$ to precipitate out from the solution. So if the pH value in the solution is too high, COO^- and OH^- will have competition to interact with lanthanide ions. There have been existed studies on interaction of PAA and lanthanide ions [29–39]. Montavon et al. studied the interaction between Eu^{3+} and PAA at pH 5.0 in 0.1 mol/L $NaClO_4$ with fluorescence spectroscopy

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[29–31]. Huang et al. prepared the polymer–metal complexes from PAA and several kinds of lanthanide ions at pH 6.0 [32]. They considered that at pH 6.0 PAA is fully ionized and the stoichiometric complex can be formed. In fact, at pH 6.0, PAA is partially ionized and its ionization degree is about 40–60% [23]. Lis et al. selected Nd^{3+} and Eu^{3+} as representatives to investigated interaction of lanthanide ions and PAA in the pH region from 2 to 12 with fluorescence spectroscopy, but which only revealed the complexation behavior in the dilute solution [33]. Generally, the fluorescence would quench as the concentration increased. So it is hard for the fluorescence spectroscopy to reveal the complexation behavior of the concentrated solution. In this paper, we applied different spectroscopic techniques to study the complexation of PAA and Ln ions from low concentration to high concentration, and investigated the effects of pH value and molar ratio on the complexation process.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA) (sodium salt, $M_w = 15{,}000$, 35 wt.% solution) was purchased from Sigma–Aldrich. Lanthanum chloride heptahydrate, Cerium chloride heptahydrate, and Praseodymium chloride were bought from Aladdin Chemistry Co. Ltd. Sodium hydroxide and other chemicals were analytical grade. All chemicals were used as received without the further purification.

2.2. Complexation of PAA and Ln ions

PAA and lanthanide were dissolved in deionized water. PAA's concentration was accounted with its repeat unit AA. The pH values of the solutions were adjusted with hydrochloric acid and sodium hydroxide under monitoring with a pH-meter (Mettler, SR-40).

2.2.1. pH dependence

There were two procedures to investigate the pH effect on the complexation behavior of the PAA and Ln ions. *Procedure (a)*: First, PAA solution (0.25 mol/L) and lanthanide solution (0.25 mol/L) mixed at pH 1.0 with the same volume, and then the sodium hydroxide solution was added into drop-wisely to increase pH value. In the procedure, the pH meter was used to monitor the pH value change in the solution and an UV–Visible spectrometer was applied to measure turbidity of the solution as a function of pH value. *Procedure (b)*: Prepared a serial of PAA solutions (0.25 mol/L or 1.0×10^{-3} mol/L) and lanthanide solution at different pH values separately (pH 1.0, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0), and then mixed them at the same pH value point with the same volume. For example, the PAA solution of pH 2.0 and the Ln solution of pH 2.0 mixed. If there is precipitation, the sediment will be filtered out with quantitative filter papers (Hardened Low Ash Grades) and dried in vacuum at 50 °C. If there is no precipitation, the mixed solution will be freeze-dried to get solid samples. The solid samples were characterized by FT-IR and elemental analysis.

2.2.2. Molar ratio

At pH 6.0, the concentration of the PAA was fixed (0.25 mol/L) while the concentration of Ln ion was gradually decreased, and then the PAA solution and the Ln solution were mixed with the same volume. The complexation behavior was investigated at the molar ratios ([AA]/[Ce]) of 1.0, 2.0, 3.0, 5.0, and 10.0.

2.2.3. Concentration

At pH 6.0, the original PAA solution (0.25 mol/L) and the original Ln ion solution (0.25 mol/L) were diluted with the same times, and then mixed them to investigate complexation behavior.

2.2.4. Determine the ionization degree of PAA

The ionization degree of PAA was determined by IR spectroscopy. The PAA solutions of different pH values were frozen dried to get solid samples, which were milled with KBr powder and pressed into the standard disk for IR spectroscopy measurement. The C=O vibration of COOH in PAA is located at 1711 cm^{-1}, while asymmetric stretching of COO^- in PAA is centered at 1575 cm^{-1}. The band intensity was estimated by using the maximum peak height of each adsorption band. Assuming the same extinction coefficients for both bands, so the ionization degree of PAA at a given pH was calculated from $I = [\nu(COO^-)]/[\nu(COOH) + \nu(COO^-)] \times 100\%$.

2.3. Instrumental

UV–Vis spectra were obtained using a Shimadzu UV-2550 spectrophotometer. The emission and excitation fluorescence spectra were recorded at room temperature with Shimadzu 5301-RF machine. FT-IR characterization was performed on a Nicolet 8700 spectrophotometer. The lanthanide ion content in the complex was measured with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES, Prodigy, Leeman, USA). Powder X-ray diffraction (XRD) investigation was carried out with a Bruker D2 advanced diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å) at 30 kV and 10 mA. The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range of 10–90° with a scan step width of 0.02° and a fix time of 1 s/step.

3. Results and discussion

The metal ions in aqueous solution have trend to hydrolyze. As pH value of the solution increases, lanthanide ions will form $Ln(OH)_3$ and the solution will become cloudy and finally there will be precipitation. As shown in Fig. 1, when pH value is higher than 7.5, the $LnCl_3$ solutions became cloudy and absorbance signal in UV–Visible region suddenly increased, indicating $Ln(OH)_3$ formed. So in order to avoid $Ln(OH)_3$ precipitation, the complexation behaviors of the PAA and lanthanide ions were investigated in the pH value region less than 7.5. Two procedures were applied to investigate the pH effect on the complexation of PAA and Ln ions.

In Procedure (a), the PAA solution and the Ln chloride solution mixed at low pH 1.0, and then the sodium hydroxide solution was drop-wise added into the mixed solution. At pH 1.0, the mixed solution was homogeneous and clear. As the sodium hydroxide solution added into the mixed solution, the pH value of the solution increases. When pH value is higher than 2.5, the mixed solution became cloudy and the absorbance signal of the solution abruptly increases. The increment of absorbance in the UV–visible spectrum is due to the PAA chains and the Ln trivalent ions form the complex which makes the solution cloudy. As shown in Fig. 1, La^{3+}, Ce^{3+}, and Pr^{3+} showed the same complexation behavior with PAA chains. In the lanthanide series, there are 15 elements, and all of them exhibit trivalent. The Ce^{3+} was selected as the representative of Ln ions to further investigate the complexation behavior with PAA chains.

In Procedure (b), the PAA solution and the $CeCl_3$ solution were mixed at a serial of pH value points. Before mixing, the PAA solution and the $CeCl_3$ solution were adjusted to the same pH value. Eight pH value points were selected: pH 1.0, 2.0, 3.0, 3.5, 4.0, 5.0, 6.0 and 7.0. It was found that at pH 1.0, 2.0 and 3.0, the mixed solution was homogeneous, while at pH 3.5 or higher than 3.5, after mixing, the solution become cloudy and finally there is precipitation formed, as shown in Table 1. In Procedure (b) the precipitation happened at the higher pH values than that happened in Procedure (a). If PAA chains and Ln ions form the complex to precipitate out from the solution, the first step is nucleation. In Procedure (a), with the sodium hydroxide solution adding into the solution, locally there will be