Complex formation and adsorption of V$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$ ions with poly($N$-vinylimidazole)

Abstract The complex formation of soluble poly ($N$-vinylimidazole) (PVIm) with trivalent metal ions in aqueous solution was studied by using UV–vis spectroscopy. Formation constants of PVIm–metal complexes were calculated by applying the “molar ratio” method. It was found that the interaction between PVIm and trivalent metal ions follows 4(base unit):1(metal ion) stoichiometry. The stability constants for the complexes of PVIm with trivalent transition-metal ions were in agreement with the Irving–William series. The biggest formation constant was found for the PVIm–Fe$^{3+}$ complex system. The capacity of adsorption for these metal ions was investigated using cross-linked PVIm. Cross-linked PVIm hydrogels were prepared by irradiating binary mixture of $N$-vinylimidazole–water with a $^{60}$Co $\gamma$-ray source having a dose rate of 4.5 kGy/h. Adsorption studies were performed at different pH and metal ion concentrations at room temperature. It was observed that the same sequence for the metal ions was verified by adsorption studies.

Keywords Poly($N$-vinylimidazole) · Molar ratio method · Trivalent metal ions · Adsorption

Introduction

Polymer–metal complexes (composed of a metal ion and its coordinating ligands) are currently attracting considerable attention for a variety of applications [1, 2], such as developments in nuclear chemistry, organic synthesis, wastewater treatment, pollution control, hydrometallurgy, polymer drug grafts, preconcentration and recovery of trace metal ions [3]. In addition, they are also used as mechanochemical systems and as models of bioorganic and bioinorganic systems [4].

Interactions in polymer–metal complexes consist mainly of various weak binding forces, such as coordination bonds, hydrogen bonds, charge-transfer interaction, hydrophobic interaction and so forth. These interactions are weak, but significant, and act multiply and dynamically. Because they are plural, these binding forces cooperatively play an important role in polymer–metal complexes. The electron-transfer processes of the complex moieties of polymer–metal complexes are often affected by the dynamic conformational change of the molecular environment around the complexes. As a result, various kinds of electronic interactions are observed in polymer–metal complexes [5].

A polymeric ligand is usually used in an insoluble resin form to separate a specific metal ion from a liquid containing metal ions. Various polymeric ligands which contain functional groups are used to recover metal ions from aqueous systems. In recent years, we prepared amidoxime containing various polymeric resins for the recovery of uranium [6–8]. Santos et al. [9] synthesized gallium chelating agents for the application of radiodiagnosis and antitumor activity studies. In other work related with the complexation of metal ions with polymeric ligands, it has been reported that new bifunctional chelating agents toward radioisotopes of lead can be used in radioimmunotherapy and radioimmunoimaging [10].

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The stoichiometries of polymer–metal complexes in solution have been calculated on the basis of data obtained using UV–vis, IR, NMR, electron spin resonance, etc., methods [11], by using various evaluation methods such as the continuous variation method, the molar ratio method and the slope ratio method. Harvey and Manning [12] proposed a reliable method, the molar ratio method, for establishing the stoichiometries of polymer–metal complexes.

Several decades ago, it was found that imidazole groups of histidine were binding sites for the combination of some proteins with metals. This discovery was the driving force for further studies on the ion binding capacity of imidazole [13] and soluble poly(N-vinylimidazolone) (PVIm) [14]. However, there have only been a few studies [15, 16] on the complexation of PVIm with divalent metal ions, except for Cu$^{2+}$ and Zn$^{2+}$ ions, and there are no published results on the interaction between PVIm and trivalent metal ions.

In this study, we investigated the complexation and adsorption of PVIm with trivalent metal ions such as vanadium (V$^{3+}$), chromium (Cr$^{3+}$) and iron (Fe$^{3+}$). V$^{3+}$ is essential to some species, including humans, although we require very little – less than the 0.04 mg we take in each day. Cr$^{3+}$ is an essential element for humans because it helps us to use glucose. We take in about 1 mg a day; foods such as brewer’s yeast, wheat germ and kidney are rich in chromium. Fe$^{3+}$ is also an essential element for all forms of life. The average human contains about 4 g, a lot of which circulates as haemoglobin in the blood, the job of which is to carry oxygen from our lungs to where it is needed. If the diet does not contain the 6 mg iron needed each day anaemia will eventually develop. Foods such as liver, kidney, molasses, brewer’s yeast, cocoa and liquorice contain a lot of iron [17].

As can be seen, all these metal ions are very essential and beneficial for our life. In this study, the complexation of these metal ions with PVIm was investigated using UV–vis spectroscopy. Complex formation constants and stoichiometric ratios were calculated using the molar ratio method. Cross-linked PVIm hydrogels were used for the adsorption of metal ions. The affinity of the metals towards PVIm for complexation is discussed in terms of the adsorption results.

Calculations

In the complexation study, the formation constants of the polymer–metal complexes were calculated using the following equations. For a typical complex formation reaction

\[ \text{Me}^+ + n\text{PL} \rightleftharpoons \text{Me(PL)}_n^+, \]

where \( \text{Me}^+ \) is the metal ion, \( \text{PL} \) is the chelating unit of the polymer ligand and \( n \) is the coordination number of the metal ion.

The equilibrium constant, \( K_F \), can be expressed by the following equation [19]

\[ K_F = \frac{[\text{Me(PL)}_n^+]}{[\text{Me}^+][\text{PL}]^n}, \]

where \( n \) is the dissociation constant, which is calculated as the ratio of the absorbance for a defined coordination number to the theoretical absorbance value for maximum coordination and \( c \) is the concentration of the complex.

In the adsorption study, PVIm hydrogels ground to fine powder (0.01 g) were added to 10 ml buffered metal chloride solution. The mixture was stirred for about 3–5 days at 25 °C in a closed vessel. The amount of metal ions remaining was determined using a UV–vis spectrophotometer at the maximum absorption wavelength of the corresponding metal ion. The adsorption capacity of the PVIm hydrogels was calculated from Eq. (2):

\[ A = \frac{(c_0 - c) V}{w} \times \frac{1}{1000}, \]

where \( A \) is the amount of adsorbed Me$^{3+}$ (grams) per dry gel (grams), \( c_0 \) and \( c \) are the initial and equilibrium concentrations of the Me$^{3+}$ ion solutions (milligrams per liter), respectively, \( V \) is the volume of the Me$^{3+}$ ion solution (litres) and \( w \) is the weight of the dry gel (grams).

Results and discussion

Complexation studies

The absorption spectra from 200 to 900 nm of PVIm, Me$^{3+}$ and Me$^{3+}$ complexes with PVIm were recorded using a UV–vis spectrophotometer and \( \lambda_{\text{max}} \) values for each system were determined. Examples of the UV spectra of PVIm, V$^{3+}$ and PVIm–V$^{3+}$ complex solutions are shown in Fig. 1. The absorbency of PVIm was measured at 204.8 nm for the \( \pi-\pi^* \) transition of the C–N group on the imidazole ring and at 244.8 nm for the \( \pi-\pi^* \) transition of the same group. Maximum absorbance values of V$^{3+}$ were obtained at 228 and 429.6 nm. As PVIm solution was added to the V$^{3+}$ ion solution, the band observed at 429.6 nm shifted to

Experimental

Materials and methods

PVIm was prepared by radical polymerization of N-vinylimidazole in benzene with azobisisobutyronitrile as initiator at 70 °C in a N$_2$ atmosphere. Analytical grade reagent of N-vinylimidazole and benzene were used. The polymers were obtained in the form of a white powder and were dried in a vacuum oven at 30 °C. The viscosity-average molecular weight was determined in 0.1 M NaCl at 25 °C with an Ubbelohde-type viscometer. The viscosity-average molecular weight of the polymer was found to be \( M_v = 65000 \) using the equation \( [n] = 1.22 \times 10^{-1}M_v^{0.5} \)[18]. The concentration of PVIm used in the complexation experiments was \( 6 \times 10^{-2} \) ground mole/l, in aqueous solution. All the metal chlorides (Cl$_2$, CrCl$_2$, 7H$_2$O, FeCl$_3$) used in this study were supplied by BDH. For the metal ion adsorption, cross-linked PVIm hydrogels were synthesized by irradiating aqueous solution of N-vinylimidazole with a $^{60}$Co $\gamma$-ray source.

The visible and UV spectra were recorded using a Philips 8715 model PU UV–vis spectrophotometer in the region 200–900 nm.