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SHORT COMMUNICATION

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Investigation of complex formation between poly(*N*-vinyl imidazole) and various metal ions using the molar ratio method

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Abstract The complex formation of poly(*N*-vinyl imidazole) (PVIm) with various metal ions was studied. UV-vis spectroscopy was employed to study the interaction of PVIm and metal ions in aqueous solution. Formation constants of PVIm-metal complexes were calculated by applying a "mole ratio" method. The stoichiometric ratios between polymer and metal ions were found to be 4. The stability constants for the complexes of PVIm with bivalent transition metal ions were in agreement with the Irving-William series. The biggest formation constant was found for the PVIm-Cu^{2+} complex system.

Key words Poly(*N*-vinyl imidazole) – Complexation – Molar ratio method – UV spectroscopy

Introduction

Metal ions are not only valuable intermediates in metal extraction, but are also important raw materials for technical applications. Accordingly, complexation of metal ions is an important technique for recovering metals from various sources (hydrometallurgy) and for the removal of metal ions from solutions in municipal and industrial waste. As a consequence, complexation, separation, and removal of metal ions have become increasingly attractive areas of research and have led to new technological approaches.

The development of polymeric materials for metal ion complexation and removal has dramatically accelerated [1–3]. A polymeric ligand is used to selectively bind a specific metal ion in a mixture in order to isolate important metal ions from wastewater. This is based on different complex formation constants between the polymeric ligand and various metal ions or molecules [4]. A polymeric ligand is usually used in an insoluble resin form to separate a specific metal ion from a liquid containing metal ions. For example, uranium is a potential environmental pollutant especially in mining industry wastewater and the migration of uranium in nature is important in this context. New chelating polymers containing an amidoxime group show high selectivity towards uranium and separate easily from wastewater [5, 6]. In addition, various polymeric ligands which contain functional groups are used to remove transition metal ion pollution from aqueous systems. In the literature [7], the complexation of poly(vinyl alcohol) with Cu^{2+} and other metal ions is reported, and complex stability constants of polymeric ligand-metal ion systems were found to be in the order $Cu^{2+} > Ni^{2+} > Co^{2+}$. In another study [8], both poly(methacrylic acid) and poly(acrylic acid) were reacted with some metal ions (Ca^{2+}, Co^{2+}, and Zn^{2+}) and the geometries of the complexes formed were discussed.

Various methods have been applied to the investigation of the stoichiometries of polymer-metal complexes in solution, such as UV-vis, IR, NMR, ESR, viscosimetry, etc. [9, 10]. Stoichiometries of polymer-metal ion complexes have been calculated based on data obtained using these methods, by using various evaluation methods such as the continuous variation method, the molar ratio method and the slope ratio method. Harvey and Manning [11] proposed a reliable method, the molar ratio method, for establishing the stoichiometries of polymer-metal complexes.

There are only a few studies [12, 13] on the complexation of poly(*N*-vinyl imidazole) (PVIm) with other metal ions besides PVIm-Cu^{2+} complexation studies [4, 14]. In this study, the complexation of PVIm with the bivalent metal ions lead(Pb^{2+}), cadmium(Cd^{2+}), copper(Cu^{2+}), and cobalt(Co^{2+}) has been studied using UV-vis spectroscopy. Complex formation constants and stoichiometric ratios were calculated. The affinity of the metals for complexation with PVIm was discussed.

Experimental

PVIm was prepared by free radical polymerization of *N*-vinyl imidazole in benzene with azobisisobutyronitrile as initiator at 70 °C in a nitrogen atmosphere. Polymers in the form of white powder were dried in a vacuum oven at 30 °C. The viscosity average molecular weight of the polymer was determined to be $M_v = 65{,}000$ using the equation $[\eta] = 1.22 \times 10^{-3}\ M^{0.51}$ [15].

All metal salts ($CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$, and $PbCl_2$) used in this study were supplied by BDH. In the complexation studies, UV-vis spectra of the solutions were recorded with a Philips model 8715 UV-vis spectrophotometer.

Results and discussion

The chemical structure of PVIm is shown in Fig. 1. The complexing properties of PVIm are due to the electron donor nitrogen at position 3 of the imidazole ring [16].

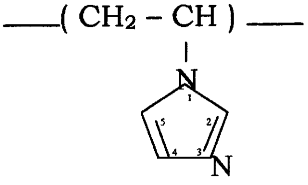

Fig. 1 Chemical structure of poly (*N*-vinyl imidazole) (*PVIm*)

Absorption spectra of PVIm, metal ion and PVIm-metal ion complex solutions were recorded on a UV-vis spectrometer and λ_{max} values for each system were determined. Examples of the UV spectra of PVIm, Cu^{2+}, and PVIm-Cu^{2+} complex solutions are shown in Fig. 2. The absorbancy of PVIm was measured at 204.8 nm for the π-σ^* transition of the C=N group on the imidazole ring and at 244.8 nm for the π-π^* transition of the same group. Maximum absorbance values of Cu^{2+} were obtained at 207.2 nm, 227.2 nm, 251.2 nm, and 795.2 nm. As Cu^{2+} was added to PVIm solutions, the band at 244.8 nm shifted to shorter wavelengths (238.4 nm), while a newly formed band was observed at 290.4 nm. Similar results were obtained with the other metal ions and the results are given in Table 1.

The molar ratio method renders it possible to determine the dissociation constant spectrophotometrically. In this method, the maximum absorption values of the complex solution at different concentrations are plotted versus the molar ratio of polymeric ligand to metal ion and molar ratio curves are obtained. In this study, solutions with polymer ligand(monomeric unit)/

Table 1 λ_{max} values of poly (*N*-vinyl imidazole) (*PVIm*), metal ion, and PVIm-metal ion systems

	λ_{max} values (nm)		
	PVIm	Metal ion	PVIm-metal ion[a]
Cu^{2+}	204.8, 244.8	227.2, 251.2, 795.2	238.4^s, 290.4^n
Co^{2+}	204.8, 244.8	198.4, 284.8, 512.8	224.4^s
Cd^{2+}	204.8, 244.8	203.0	190.0^s, 217.0^n
Pb^{2+}	204.8, 244.8	205.6, 244.0	238.4^s

[a] s, shifting band and n, newly formed band

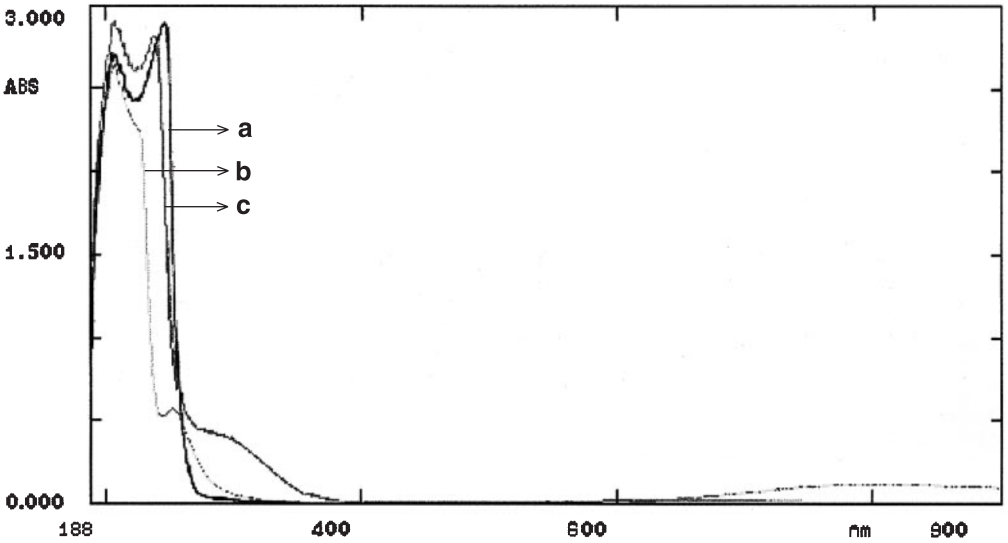

Fig. 2 UV spectra of PVIm (*a*), Cu^{2+} (*b*), and PVIm-Cu^{2+} complex (*c*), solutions

metal ion molar ratios varying from 1 to 7 were prepared and absorbance values were measured at the maximum wavelength of the complex (λ_{max}). UV spectra of PVIm-Cu^{2+} complex solutions containing different amounts of PVIm are given in Fig. 3 as examples. Absorbance values were recorded at λ_{max} for each UV spectrum and plotted against the polymer ligand concentration to the metal ion concentration ratio, and are collected in Figs. 4–7. The common characteristic of these graphs is that PVIm combines with all metal ions in the same proportions. In other words, the formation curves of the PVIm-metal complexes would appear to extrapolate to a maximum coordination number of $n = 4$. One metal ion is coordinated by four PVIm rings.

For a typical complex forming reaction

$$Me^+ + nPL \overset{K_f}{\rightleftharpoons} Me(PL)_n^+ \ ,$$

where

Me^+ = metal ion,
PL = chelating unit of the polymer ligand, and
n = coordination number of the metal ion.

The equilibrium constant, K_f, can be expressed by the following equation [10]

$$K_f = \frac{[Me^+(PL_n)]}{[Me^+][PL]^n} = \frac{1-\alpha}{\alpha(\alpha nC)^n} \ , \qquad (1)$$

where α 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 complex concentration.

K_f values calculated from Eq. (1) for all metal ions are given in Table 2. As can be seen from Table 2, PVIm forms stable complexes with Cu^{2+} ions and to a lesser extent with Co^{2+}, Cd^{2+}, and Pb^{2+}, respectively. This result can be explained by some factors which affect polymer-metal complex formation. These factors are

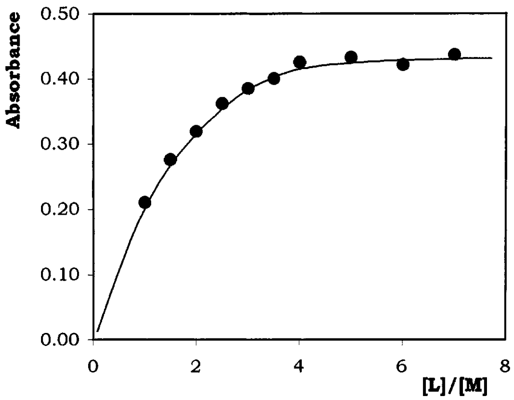

Fig. 4 Formation curve of the PVIm-Cu^{2+} complex system

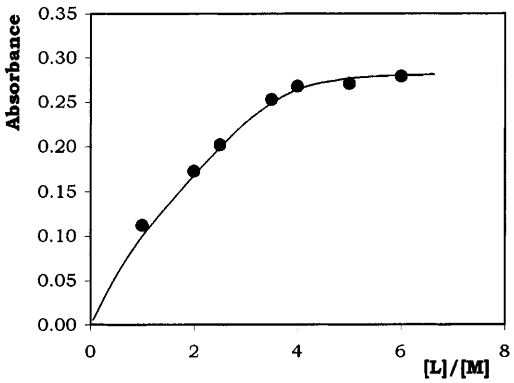

Fig. 5 Formation curve of the PVIm-Co^{2+} complex system

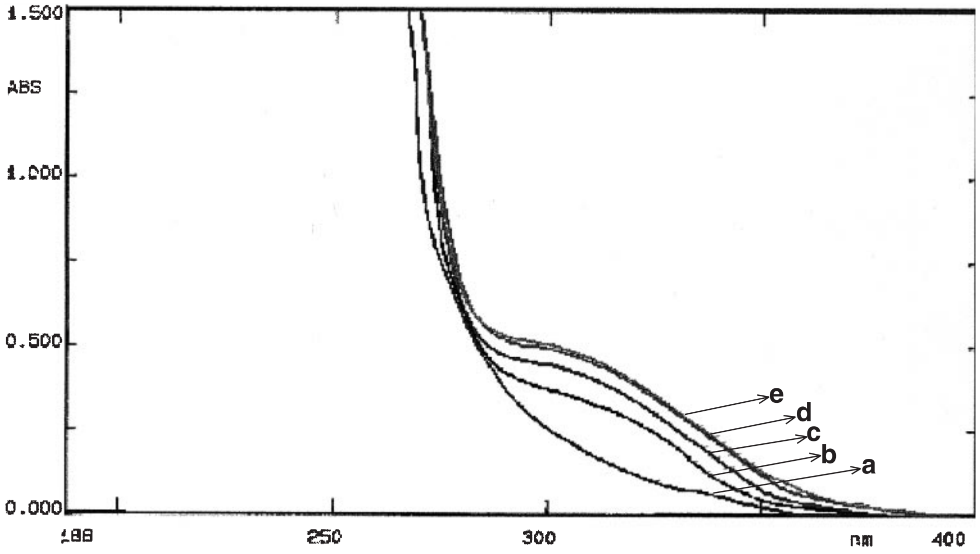

Fig. 3 UV spectra of PVIm-Cu^{2+} complex solutions containing different amounts of PVIm. [L]/[M] ratio for *a*: 1, *b*: 2, *c*: 3, *d*: 4, and *e*: 5

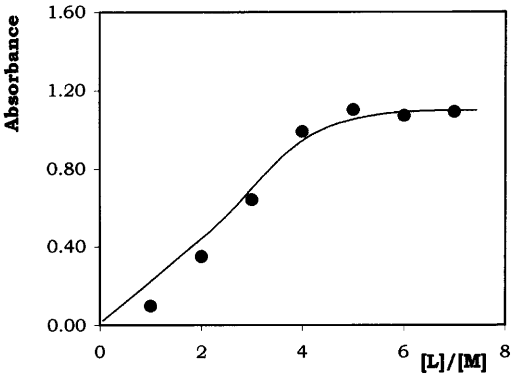

Fig. 6 Formation curve of the PVIm-Cd^{2+} complex system

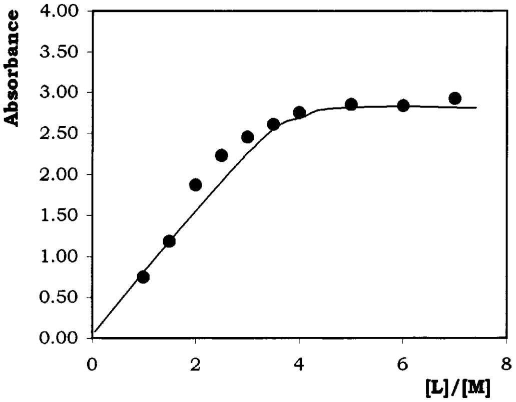

Fig. 7 Formation curve of the PVIm-Pb^{2+} complex system

1. The basicity of the chelating unit on the polymeric ligand.
2. The electronegativity of donor atoms at basic groups of the chelating ligand.
3. Metal ion properties.

Table 2 K_f values for PVIm-metal ion systems

PVIm-metal system	K_f ($\times 10^{-18}$)
PVIm-Cu^{2+}	82.00
PVIm-Co^{2+}	7.00
PVIm-Cd^{2+}	0.62
PVIm-Pb^{2+}	0.46

Complexation of PVIm occurred through the basic nitrogen atoms at position 3 of the imidazole ring. The stability of the metal complex formed increases with the metal ion charge/radius ratio [17]. For all metal ions used in this study, the charge/radius ratio increased in the order $Pb^{2+} < Cd^{2+} < Co^{2+} < Cu^{2+}$. When the stability constants of PVIm-metal ion complexes are considered, the sequence for the ions complies with our experimental results. The Cu^{2+} ion has the smallest ionic radius of the metal ions [18]. When the complex formation between polymeric ligands and metal ions is discussed, metal ions with smaller radii interact more easily with polymeric ligands; However, the acidic properties of the Cu^{2+} ion have a greater effect than those of the other metal ions. In other words, acidic Cu^{2+} ions easily react with the basic chelating unit of PVIm.

On the other hand, the Pb^{2+} ion has the highest electronegativity. Therefore, the unpaired electrons on the nitrogen atoms of the basic ligand should result in the easy formation of stable complexes with Pb^{2+}; however, in this study it was observed that the Pb^{2+} ion has the smallest K_f value. This result is caused by steric hindrance of the Pb^{2+} ions decreasing of basic chelating group activity [19].

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