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ORIGINAL CONTRIBUTION

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

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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 γ-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*-vinyl imidazole) · 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].

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*-vinylimidazole) (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.

Experimental

Materials and methods

PVIm was prepared by radical polymerization of *N*-vinylimidazole in benzene with azobis(isobutyronitrile) 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 $\bar{M}_v = 65000$ using the equation $[\eta] = 1.22 \times 10^{-3} M^{0.51}$[18]. The concentration of PVIm used in the complexation experiments was 6×10^{-2} ground mole/l, in aqueous solution. All the metal chlorides (VCl_3, $CrCl_3 \cdot 7H_2O$, $FeCl_3$) 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 γ-ray source.

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

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

$$Me^+ + nPL \rightleftharpoons Me(PL)_n^+ \ ,$$

where Me^+ is the metal ion, 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]

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

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 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):

$$A = \frac{c_0 - c}{w} V \frac{1}{1000} \ , \qquad (2)$$

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 litre), 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 λ_{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 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 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

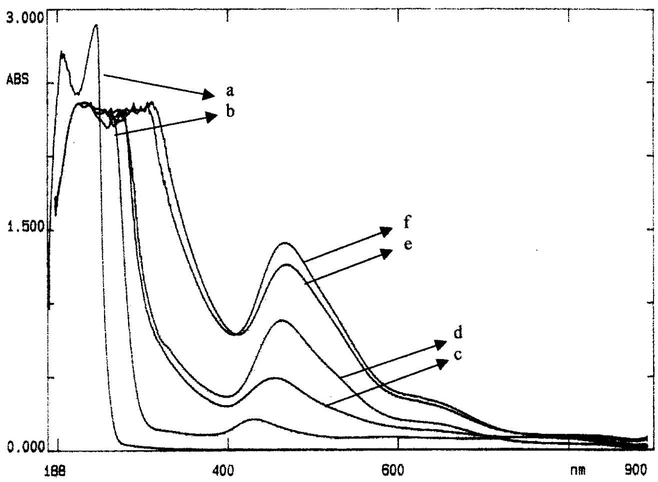

Fig. 1 UV spectra of **a** poly(*N*-vinylimidazole) (PVIm), **b** V^{3+} and PVIm–V^{3+} complex solutions containing different ground concentrations of PVIm: **c** 1×10^{-2}, **d** 2×10^{-2}, **e** 4×10^{-2}, **f** 6×10^{-2}

462.4 nm, while a newly formed band was observed at 623 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)/ 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}). The absorption spectra of the solutions containing 1.0×10^{-2} M V^{3+} and different concentrations of PVIm are represented in Fig. 1c–f. Absorbance values recorded at λ_{max} for each spectrum were plotted against the molar ratio of the concentration of VIm to the concentration of Me^{3+}. The molar ratio curves for the PVIm–Me^{3+} systems are shown in Figs 2, 3 and 4. The common characteristic of these graphs is that PVIm combines with all the metal ions in the same proportion. In other words, the formation curves of the PVIm–Me^{3+} complexes appear to extrapolate to a maximum coordination number of $n = 4$. In our previous work [20], we studied the complexation of PVIm with divalent metal ions such as Cu^{2+}, Co^{2+}, etc. and found the same coordination number in these polymer–metal complexes. In living organisms, imidazole groups take part in proteins such as histidine. The imidazole group and its analogues have fourfold coordination in metal complexes, such as iron in porphyrin and cobalt in corrin molecules. This real situation agrees with our experimental results.

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

	λ_{max} values (nm)		
	PVIm	Metal ion	PVIm–metal ion[a]
V^{3+}	204.8, 244.8	228, 429.6	462.4^s, 623^n
Cr^{3+}	204.8, 244.8	439.2, 572	577.6^s
Fe^{3+}	204.8, 244.8	445.6, 527.2	483.2^s

[a] s: shifting band; n: newly formed band

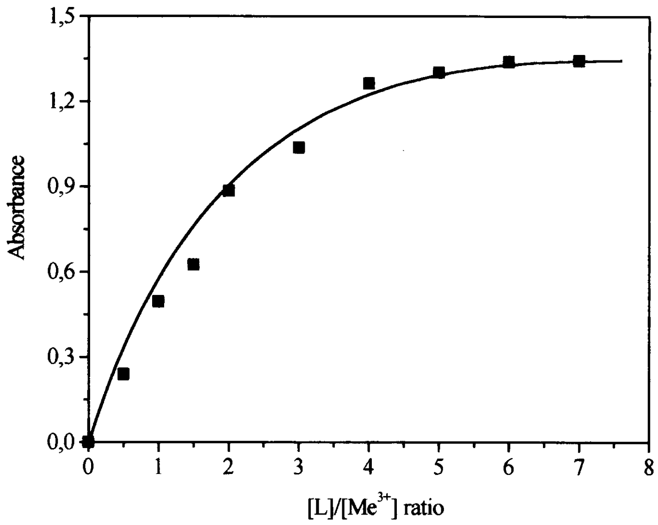

Fig. 2 Formation curve of the PVIm–V^{3+} complex system. Absorbance measured at $\lambda_{max} = 462.4$ nm

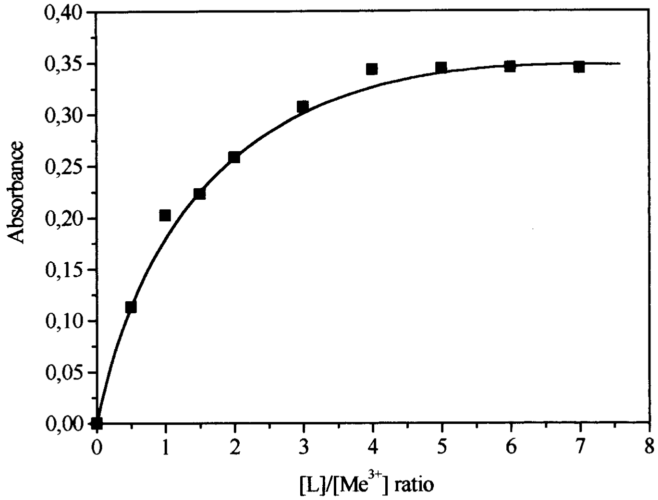

Fig. 3 Formation curve of the PVIm–Cr^{3+} complex system. Absorbance measured at $\lambda_{max} = 577.6$ nm

In aqueous solution the formation of a complex between a Me^+ and PL to give the complex $Me^+(PL)_n$ is characterized by the formation constant K_f. The magnitude of the formation constant tells us what

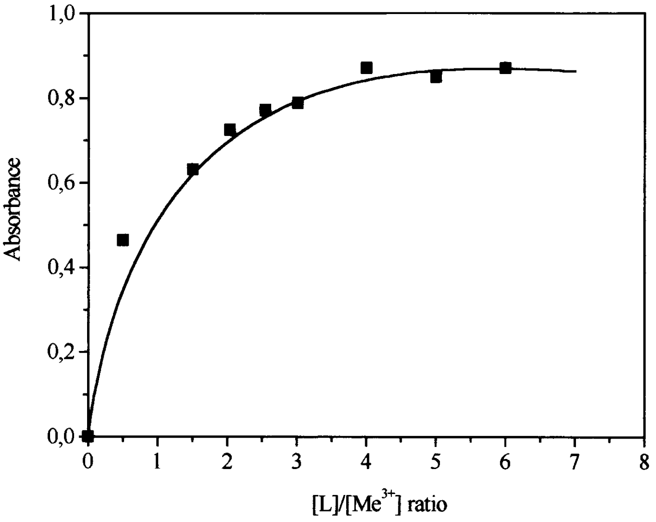

Fig. 4 Formation curve of the PVIm–Fe^{3+} complex system. Absorbance measured at $\lambda_{max} = 483.2$ nm

proportion of the metal ions is present as $Me^+(PL)_n$ at equilibrium. A high K_f value indicates that a large proportion of the metal ions will, at any given instant, be found associated with the ligand and only a small amount will be present as free Me^+. K_f also indicates the strength of complexing ability of metal ions with polymeric ligand, namely complex stability constants. K_f values calculated from Eq. (1) for V^{3+}, Cr^{3+} and Fe^{3+} are given in Table 2. As can be seen from Table 2, PVIm forms relatively stable complexes with Fe^{3+} ions and to a lesser extent with Cr^{3+} and V^{3+}, respectively. This result can be explained by the nature of the bonding, which influences the stability of polymer–metal complexes. There are two components in any complexation reaction, the metal and the complexing agent, and both contribute to the formation of the complex and both have their own characteristics. Only if these characteristics match is a strong bond formed between the two.

Once the metals and ligands have been split into hard and soft the prediction of the stability of the complex is based on the preference of hard acids for hard bases and soft acids for soft bases [21, 22].

V^{3+}, Cr^{3+} and Fe^{3+} are classified as hard acids according to Pearson [21]. Thus, if it were decided to design a ligand specific for these ions, hard donor atoms such as $-OH$ or $-NH_2$ containing ligand would be chosen for the best correlation in complexation. Moreover, the sp^2 hybridized nitrogen atoms of the imidazole group lead to greater character in the orbitals used for bonding to the metal ion and hence more covalent bonding, namely soft base. Therefore, there was no good complexation between these metals ions and imidazole. In our earlier work [20], we calculated K_f values of the order of 10^{18} owing to good complexation of PVIm with Cu^{2+}, Co^{2+}, etc. (these metal ions are borderline according to Pearson).

Table 2 K_f values for PVIm–metal ion systems

PVIm– metal ion system	$K_f(\times10^{-9})$
PVIm– V^{3+}	1.17
PVIm– Cr^{3+}	2.42
PVIm– Fe^{3+}	2.69

The stability of the metal complexes increases with the metal ion charge/radius ratio [23]. For all the metal ions used in this study, the charge/radius ratio increased in the order $V^{3+} < Cr^{3+} < Fe^{3+}$. The Fe^{3+} ion has the smallest ionic radius among the three metal ions [24] used in this study. Metal ions with smaller radii interact more easily with polymeric ligands. In addition, the Fe^{3+} ion has the highest electronegativity among these three metal ions; therefore, the unpaired electrons on the nitrogen atoms of the basic ligand should result in the easy formation of stable complexes with Fe^{3+}. As a result, it can be generally explained that the concentration of ligand is higher in the polymer domain, so once the metal ion is attached to one group on the polymer chain, the other ligands coordinate more readily.

Adsorption studies

The PVIm hydrogels were synthesized using ^{60}Co γ-rays to investigate the adsorption capacity of PVIm for the three metal ions used in the complexation studies. When monomer or *N*-vinylimidazole is irradiated with ionizing rays such as γ-rays, one double bond of $-C=C-$ on *N*-vinylimidazole is broken by the ionizing irradiation and free radicals are generated in the aqueous solutions. Random reactions of these radicals with the monomers lead to the formation of PVIm. When the irradiation dose is increased beyond a certain value the polymer chains cross-link and a gel is obtained [25]. The details of the procedure and the adsorption of divalent metal ions by PVIm hydrogels were reported in our previous articles.

The adsorption of metal ions was performed at different pH values using acetate buffer solutions and some factors affecting the adsorption of metal ions were investigated. It is well known that pH has two kinds of influence on metal uptake: an effect on the solubility and speciation of the metal ion in aqueous solution and an effect on the overall charge of the sorbents. Accordingly, the affinities of PVIm hydrogels for V^{3+}, Cr^{3+} and Fe^{3+} were investigated by a batch study at different pH and the results are given in Table 3. In highly acidic media (pH 0–3), there no adsorption occurred, owing to the protonation of the imidazole group, resulting in

Table 3 Adsorption values for each metal ion with PVIm hydrogel at different pH (c_0 [Me^{3+}] = 750 ppm, 25 °C)

Me^{3+} ion	*A* (g/g) at different pH				Distilled water (pH 6, non-buffered system)
	4	5	6	7	
V^{3+}	–	0.161	0.228	0.243	0.327
Cr^{3+}	–	0.214	0.336	0.178	0.440
Fe^{3+}	0.290	–	–	0.351	0.520

positively charged pendant groups causing electrostatic repulsion. At pH 4, the adsorption capacity of PVIm is limited by partial protonation of nitrogen atoms at the 3 position of imidazole ring. However, in a weakly acidic solution, the adsorption of metal ions increases with pH. Whatever the pH, Fe^{3+} ions are always more strongly adsorbed than are Cr^{3+} and V^{3+} ions. This observation could be explained by the periodical properties of these metal ions as before. In the adsorption experiments, nonbuffered systems were used for the adsorption kinetic and concentration dependence because it is known that buffers complex the metal ions, causing a shift in equilibrium other than that produced by the acid.

Using distilled water (at pH 6 of the nonbuffered system) the contact time, in other words the adsorption kinetics, was studied. Figure 5 shows that the amount of metal ions adsorbed per gram of sorbent increase sharply during the first 5 h and equilibrium is reached after 48 h of contact under prevailing experimental conditions.

The adsorption is affected by the initial metal concentration as shown in Fig. 6. When this concentration increases, the adsorption of metal ions by PVIm hydrogels from solution increases strongly and then levels off. This plateau corresponds to the saturation of the imidazole group. The isotherms shown in Fig. 6 comply with Langmuir type for all the PVIm–Me^{3+} systems. The common characteristic of the Langmuir-type isotherm is that at first adsorption increases rapidly owing to easily available imidazole groups as they are not bound, they have immediate interaction with Me^{3+} ions, and eventually reaches a plateau region. At higher initial metal ion concentrations, polymer–metal ion interactions slow down as a result of increasing repulsion forces between adsorbed metal ions. The results given in Table 3 and Fig. 6 indicate that PVIm possesses a much higher affinity to adsorb Fe^{3+} than the other metal ions. The results obtained can be reasonably explained by considering that the Fe^{3+} ion has the smallest ionic radius among the other metal ions and coordinates imidazole groups readily and easily.

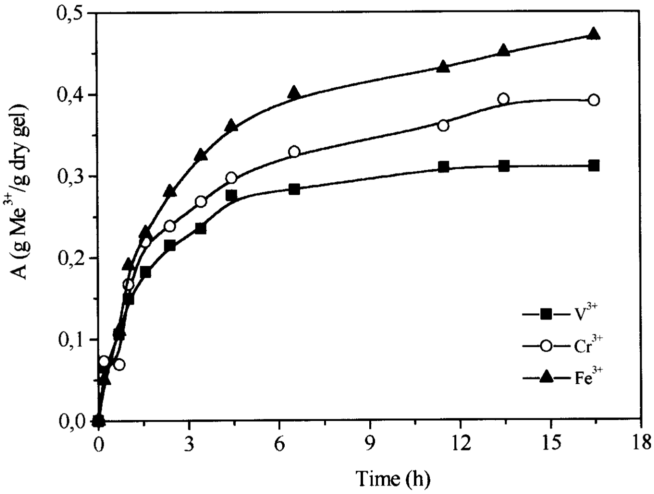

Fig. 5 Effect of contact time on the adsorbed amount of metal ions

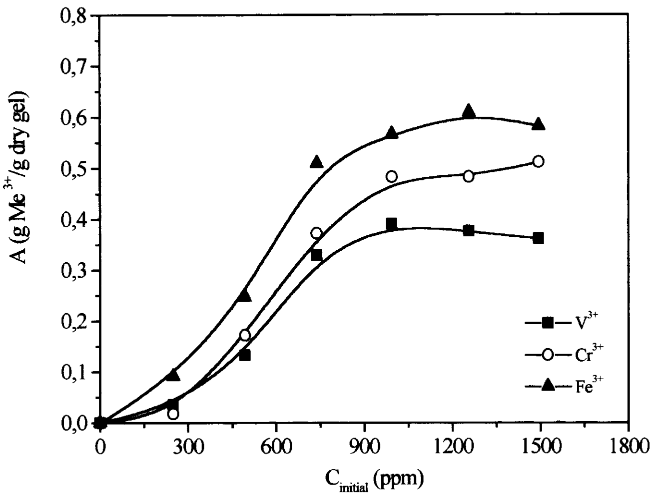

Fig. 6 Adsorption isotherms for all the PVIm–metal ion system

Conclusion

The complexation of PVIm with trivalent metal ions in aqueous solution was investigated. The stability constants for PVIm–Me^{3+} systems were calculated by applying the "molar ratio method" and that these constants increase in the order $V^{3+} < Cr^{3+} < Fe^{3+}$. All these indications allow us to estimate the structure of the complexes: A 4:1 complex is generated between each metal ion and the imidazole group.

PVIm hydrogels were prepared by γ-ray radiation to investigate the adsorption properties of insoluble PVIm towards trivalent metal ions. The ability of PVIm to adsorb metal ions increases with the concentration and tends to steady values because of the saturation of the imidazole groups. The influence of pH on the adsorption capacity of PVIm hydrogels was studied and it was observed that in the weakly acidic region (above pH 4) the adsorption increases with the pH. The maximum adsorption capacity was observed in the PVIm–Fe^{3+} system owing to properties of Fe^{3+} giving the best correlation with PVIm. Moreover, work on the interaction of Me^{3+} ions and PVIm is still under way and future work involving the selective adsorption from aqueous media containing these metal ions will conducted.

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