Conductometric and Viscometric Investigation of Poly(*N*-Vinylimidazole)–Metal Ion Complex Formation

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ABSTRACT: The complexation of copper (Cu^{2+}), cobalt (Co^{2+}), and cadmium (Cd^{2+}) ions with poly(*N*-vinylimidazole) (PVIm) and its protonated form in aqueous solution was studied conductometrically and viscometrically. From the conductometric and viscometric curves, it was found that four imidazole units were coordinated with one metal ion in the complex systems. Both studies showed that the complex formation tendency decreased in the following order: $Cu^{2+} > Co^{2+} > Cd^{2+}$. Complex properties of metal ions with imidazole group were explained by referring to Pearson's treatment, as hard and soft acids and bases. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 376–384, 2002

Key words: Poly(*N*-vinylimidazole); conductometry; viscometry; metal ion

INTRODUCTION

The elucidation of essential characteristics of complex formation with various metal ions and low molecular weight compounds (such as stability constants, structure, and composition of complexes) was the subject of numerous investigations. Complex formation with metal ions and synthetic polymers containing functional groups capable of interacting with metal ions has started to receive increasing attention.[1–5] A recently published review gives an overview on the selective complexation of metal ions with polymer-supported reagents.[6]

Many investigators reported that polymer–metal complexes show high catalytic activity in redox reactions in solution, but the details of the catalysis were not clarified because of the complexity of the catalytic system. To study the polymer–catalyst system, it is necessary to clarify the form of the polymer–metal complexes in solution.

In general, metal complexes, which act as catalysts are labile, so that analysis of the complex must be made in solution.

The polymer complexes could be of interest in both coordination chemistry and biochemistry. It was demonstrated[7] that the Cu^{2+}–poly(4-vinyl pyridine) complex exhibits, in oxidation of ascorbic acid, catalytic efficiency that is two orders of magnitude higher than that of the aqua–copper complexes. Besides biochemistry studies, polymer–metal complexation is highly important in heavy metal-ion separation studies for the environmental purposes. Various polymeric ligands, which contain functional groups, are used to remove transition metal ion pollution from aqueous systems. The complexation of poly(vinyl pyrrolidone) and gelatine with some transition metal ions is reported and the effect of metal ions in complex formation were found as $Hg^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+}$ for poly(vinyl pyrrolidone) and $Zn^{2+} > Co^{2+} > Cd^{2+} > Hg^{2+}$ for gelatine solutions.[8] In another study,[9] both poly(methacrylic acid) and poly(acrylic acid) interacted with some metal ions (Ca^{2+}, Co^{2+}, and Zn^{2+}) and the geometry of complex formation was discussed.

New polymeric materials containing chelating groups, which sorb heavy metal ions, were recently developed to selectively remove Cu^{2+} and Hg^{2+},[10] Co^{2+} and Cs,[+11] chromium ions,[12] and Pb^{2+} and Hg^{2+} ions.[13]

The complexation of poly(*N*-vinylimidazole) (PVIm) with Cu^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions was described spectrophotometrically in our recent article.[14] In this study, the complexation of PVIm with bivalent metal ions of copper (Cu^{2+}), cobalt (Co^{2+}), and cadmium (Cd^{2+}), in aqueous solutions, was studied by using conductometry and viscometry techniques. Formation and stability of polymer–metal complexes were discussed by experimental data on the basis of Pearson's treatment.

EXPERIMENTAL

Materials

The preparation and fractionation of PVIm ($\hat{M}_v$ = 65,000) were previously described.[14] All metal salts, $CuCl_2 2H_2O$, $CoCl_2 6H_2O$, and $CdCl_2 2\frac{1}{2}H_2O$, used in this study were commercial analytical grade (BDH, England) and used without further purification.

Polyelectrolyte PVIm was prepared by protonation of PVIm with diluted HCl solutions. Detailed information about protonation was reported elsewhere.[15]

Viscometric Measurements of the Complex Solution

Metal ion (Me^{2+}) solutions were prepared by using metal ion salts in the interval of 1.0×10^{-3}–$1.6 \times 10^{-2}M$ concentrations. Viscometric measurements were carried out with an Ubbelohde-type capillary viscometer at $25 \pm 1°C$ at constant Me^{2+} ion concentrations with varying polymer amounts (g/dL) in solutions. Viscometric behavior of protonated PVIm was also investigated similarly.

Conductometric Measurements of the Complex Solution

First, the conductivities of different concentrations of Me^{2+} ion solutions were measured by a Crison model 522 conductometer at a constant polymer concentration and the decrease of conductivity of Me^{2+} solutions was recorded twice.

All measurements were done at $25 \pm 1°C$. In addition, precipitation points for each Me^{2+} ion was determined from conductometric measurements. In a similar way, the effect of Me^{2+} ions on conductivity of protonated PVIm was investigated. In addition, solutions having different [Ligand]/[Me^{2+}] ratios were prepared and the complex stoichiometry of polymer–metal complexes was calculated from the conductivity curves.

RESULTS AND DISCUSSION

To study the strength of formed complexes between Me^{2+} and PVIm and its protonated form in aqueous solutions, viscometric measurement was carried out for the PVIm, protonated PVIm, and those of Me^{2+} complexes. In the concentration range studied, the reduced viscosity (η_{sp}/C_p) can be generally represented by the well-known relation.[16] $\eta_{sp}/C_p = [\eta] + K_H[\eta]^2 C_p$, where $[\eta]$ is the intrinsic viscosity, k_H is the Huggins constant, and C_p is the polymer concentration. Intrinsic viscosity is a measure of hydrodynamic volume of polymer coil in solution and represents the polymer/solvent and polymer/solvent/additive interactions, depending on the nature and concentration of the cosolute in the studied systems. Extrapolation of the reduced viscosity to infinite dilution using this empirical dependence gives the intrinsic viscosity values of the expanded polymer coils.

Viscometric evaluations were done at two different concentration regions. The deviation from linearity was observed in low concentrations (<0.08 g dL^{-1}), whereas linear behavior was observed in the interval of 0.08–0.15 g dL^{-1} concentration. The dependence of the reduced viscosity of PVIm in water on dilution is illustrated in Figure 1(a) which did not produce a straight line, although a typical curve for polyelectrolytes could be expected because of the polar groups pendant to the polymer backbone. Concerning this behavior, Scheme 1 represents the chemical structure of PVIm (**I**) and its resonance form (**II**).

According to structure **II**, PVIm is expected to show typical polyelectrolyte behavior in aqueous solutions, which can be verified by viscometric studies of its dilute solutions. The use of a strong electrolyte can eliminate the polyelectrolyte effect of PVIm. The ionic strength of the solution has a strong influence on the value of the reduced viscosity.[17] It may be seen that an addition of NaCl
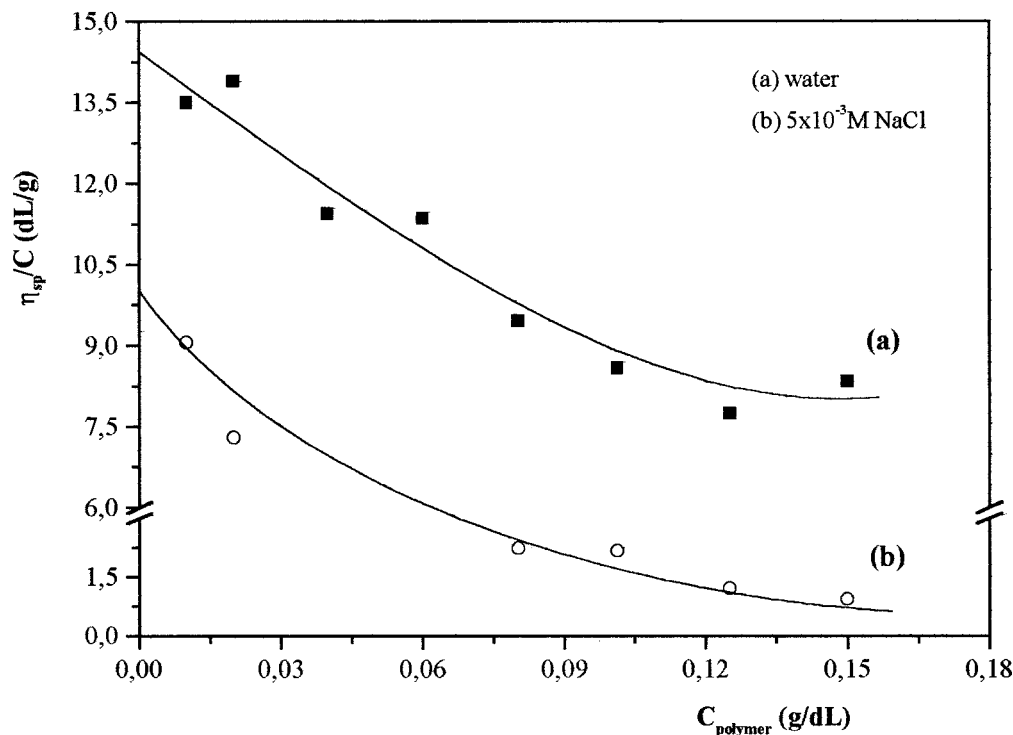
Figure 1 The reduced viscosity of unprotonated PVIm in water (a) and in NaCl solution (b).

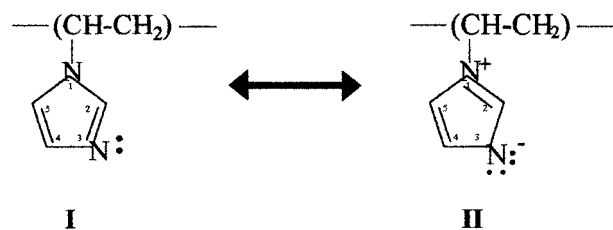**Scheme 1** PVIm chemical structure (**I**) and its resonance form (**II**).

as a strong electrolyte partially suppressed the polyelectrolyte effect of PVIm [Fig. 1(b)]. Thus, the concentration dependence of the reduced viscosity deviated somewhat from linear character within the studied concentration range. This means that there is an essential change in the conformation of the polymer chains, thus ensuring a shielding of the polyelectrolyte chain with an exclusion of any important intermolecular electrostatic effect.

The effect of different metal ions and their concentrations on viscosity of polymer (η_{sp}/C_p) are shown in Figures 2–4. As can be seen, Cu^{2+} ion is more effective than the other two metal ions in

decreasing the viscosity of the polymer solution. However, although decreasing viscosities are observed with increasing Me^{2+} concentration for a given polymer concentration, at high Cu^{2+} concentration ($1.6 \times 10^{-2}M$) even in dilute polymer solution PVIm shows linear behavior. Besides Me^{2+} concentration, if the type of the cation is also considered, Cu^{2+} displays the most important role in decreasing the viscosity in dilute region, whereas Cd^{2+} is the least effective cation.

Viscometric observations mainly represent the polymer/additive interactions/complexation tendency depending on the nature and concentration of cation in the PVIm/additive aqueous solution system. The reduced viscosities were observed to decrease with increasing Me^{2+} ion concentration. This stipulation can be interpreted by the interaction/complexation between Me^{2+} ion and polymer segments, resulting in the contraction of the polymer coil by increasing Me^{2+} ion concentration in solution.

When the curves in Figure 2–4 were analyzed in relatively high polymer concentrations, 0.08–0.15 g/dL, a linear behavior can be observed. The extrapolation of linear portions of these curves to
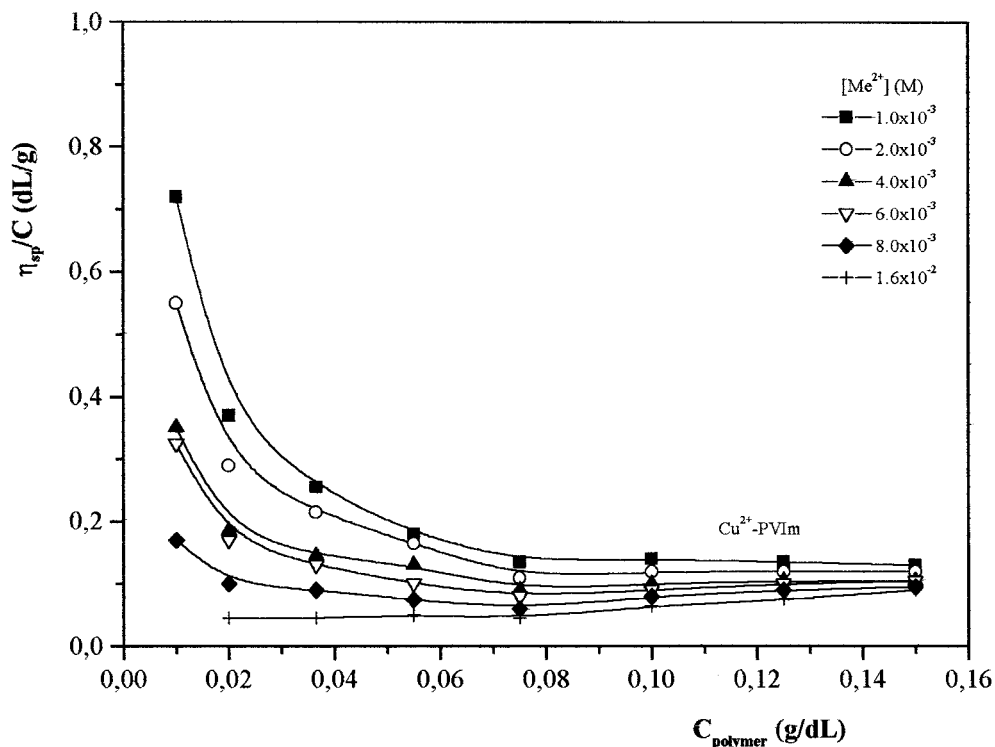
Figure 2 The effect of Cu^{2+} ion concentration on viscosity of PVIm.
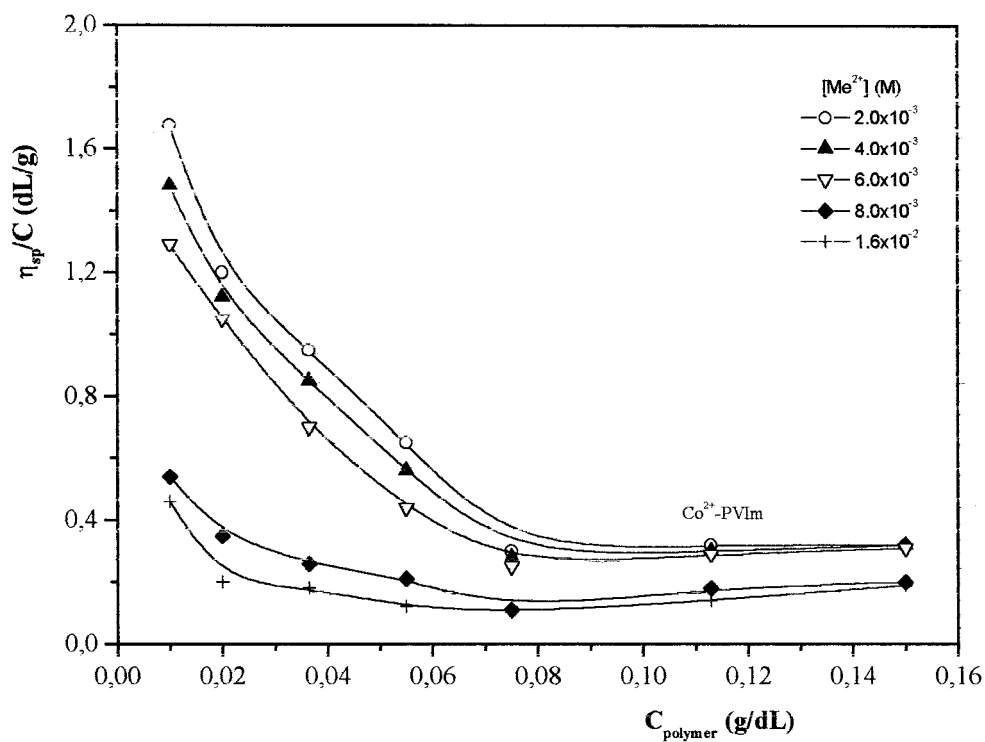

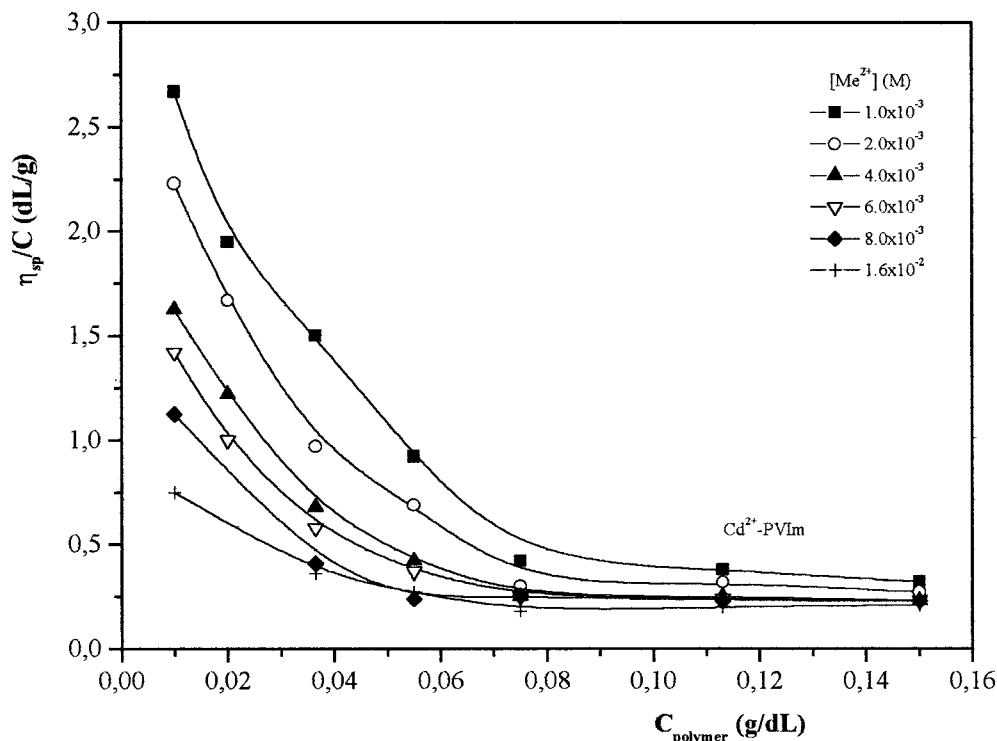**Figure 3** The effect of Co^{2+} ion concentration on viscosity of PVIm.

Figure 4   The effect of Cd^{2+} ion concentration on viscosity of PVIm.

zero concentration yielded $[\eta]$ values from the intercept of the graphs. Thus, it was observed that the intrinsic viscosity value decreased with increasing Me^{2+} ion concentration (Fig. 5). Regarding this decrease in intrinsic viscosity values, the greatest effect was observed to result from Cu^{2+} ion (as expected, the complexation of Cu^{2+} ion with PVIm is much faster for two reasons: it is a light cation of small size and its binding constant is higher than those for Co^{2+} and Cd^{2+} ions[14]), whereas the least effect comes from Cd^{2+} ion.

The viscosity behavior of protonated PVIm was also investigated and is shown in Figure 6. The reduced viscosity of protonated PVIm is not significantly affected by Me^{2+}–salt concentrations and Me^{2+} type, because there is no interaction between Me^{2+} ions and PVIm due to the large amounts of H^+ ion in solution. This observation is caused by repulsive forces between two positively charged ions (H^+ and Me^{2+}) in aqueous solutions. Furthermore, the viscosity behavior of protonated PVIm with the addition of metal ion can be explained better by using Pearson's approach.

In Pearson's empirical classification,[18] hard acids (acids, mostly the cations) are mentioned as

strong acceptors, whereas soft acids are weak. Hard bases (bases, organic functional groups, their anions, and anionic species) are strong donors, whereas soft bases are weak. A general principle was proposed, in which hard acids coordinate best with hard bases and soft acids coordinate best with soft bases.

Hancock and Martell[19] classified various ligands containing nitrogen and oxygen atoms as hard and soft acids and bases depending on the charge density and the resonance form. According to their classification, in aqueous solution, the unsaturated nitrogen donor imidazole group is a *weaker base* than the saturated nitrogen donors. This must arise partly from the inability to disperse the charge in the solvent. Moreover, the imidazole group has the ability to induce rigidity to the ligand system, because of the rigidity of aromatic ring systems. In Pearson's classification, Cu^{2+} and Cd^{2+} are known as soft acids and Co^{2+} is borderline. However, H^+ is classified as a hard acid. From this approach, maximum interaction should be expected between PVIm and Cu^{2+} and Cd^{2+}, but, from viscometric measurements, interaction with PVIm was found in the following order: $Cu^{2+} > Co^{2+} > Cd^{2+}$. This discrepancy may

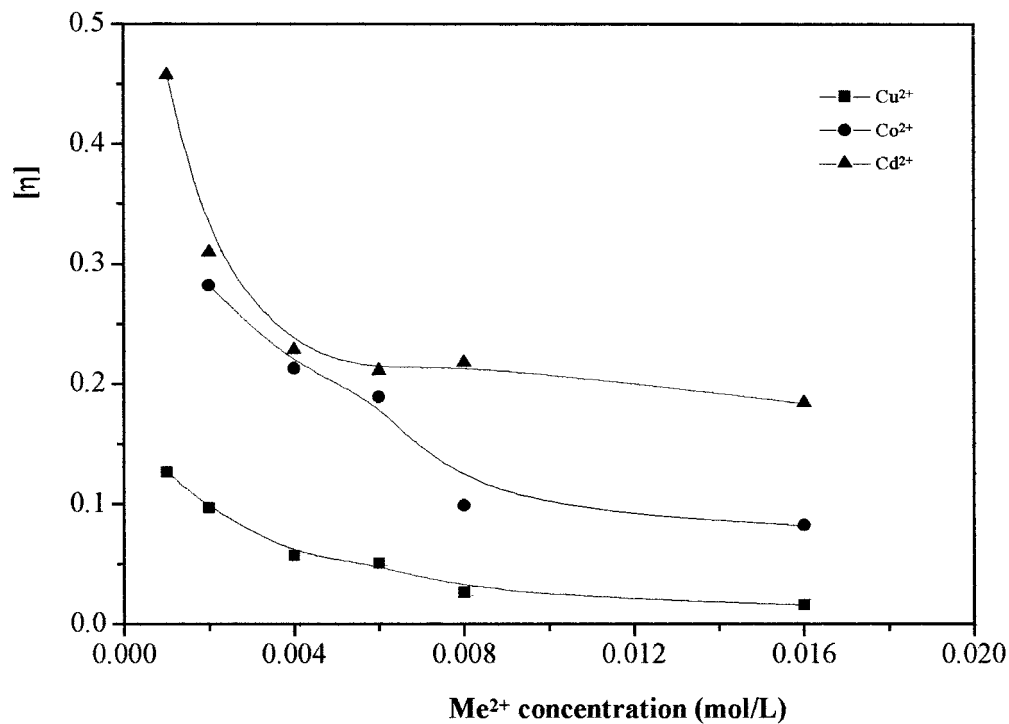**Figure 5** [η] values for different Me^{2+} ion concentrations.
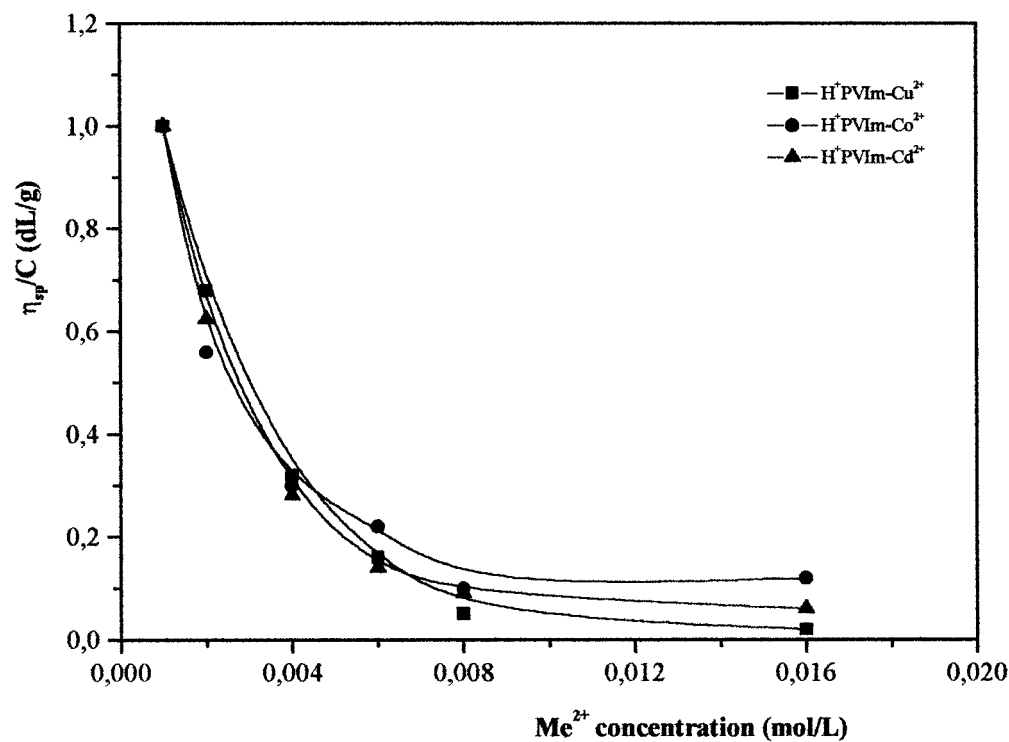

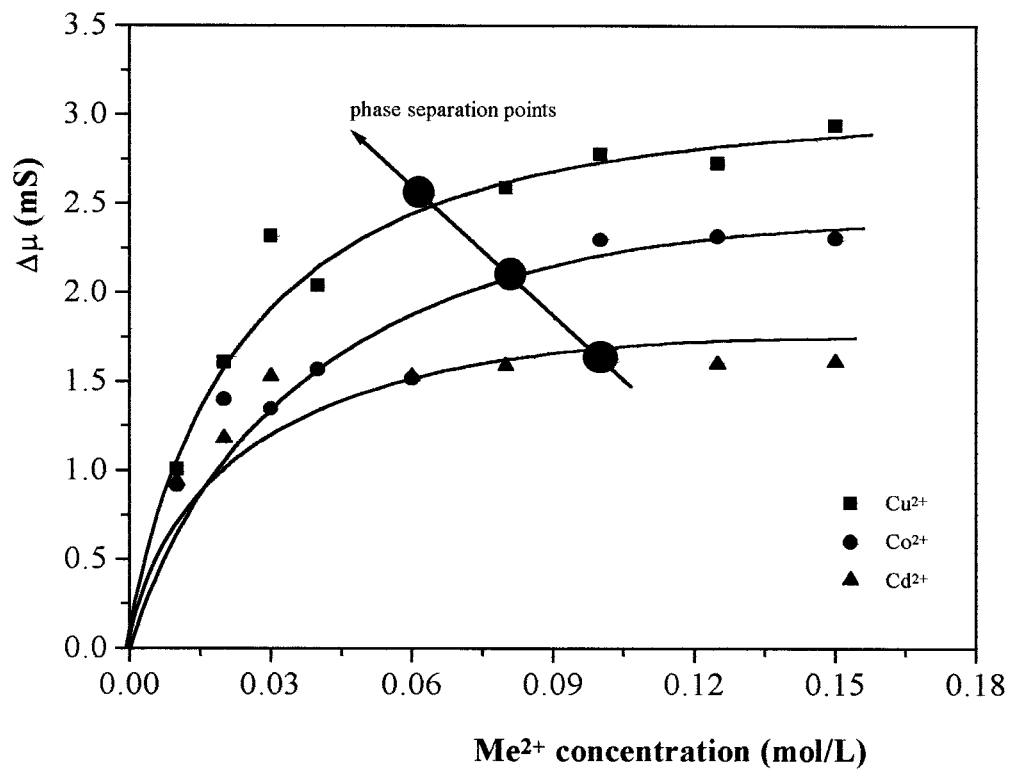**Figure 6** The viscosity behavior of protonated PVIm with different Me^{2+} ions.

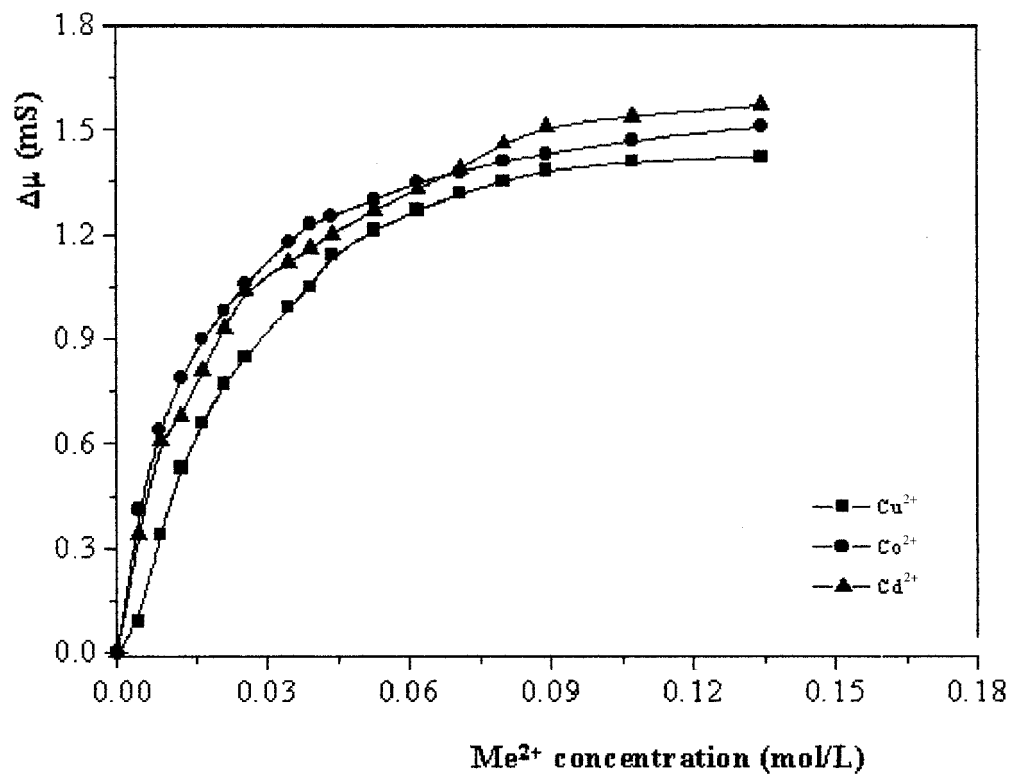**Figure 7** The change of PVIm's conductivity with the addition of Me^{2+} ion.

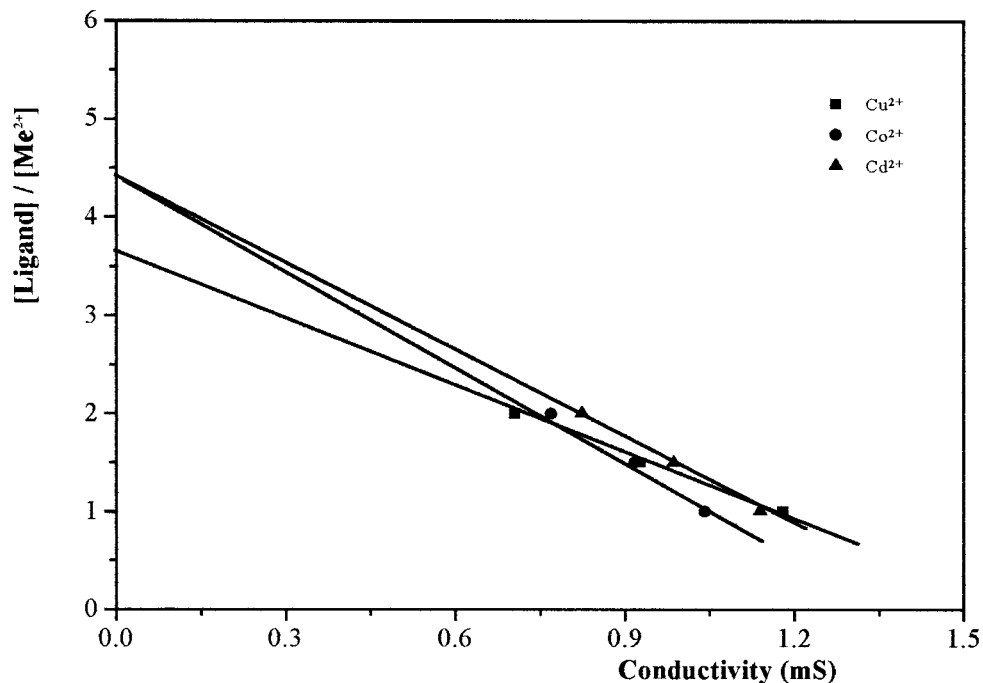**Figure 8** The change of protonated PVIm's conductivity with the addition of Me^{2+} ion.

Figure 9 Calculation of stoichiometric ratio for PVIm–Me^{2+} complexes by conductometry.

be explained by the steric hindrance of Cd^{2+} to interact with the pendant imidazole groups on PVIm because of their large size and difficult accessibility.

In light of these explanations, no effective interactions were expected between protonated PVIm (soft base) and metal ions, as shown in Figure 6.

Complex formation between PVIm and metal ions was also investigated by using conductometry. The conductivity of pure PVIm decreased with the addition of metal ions, depending on their concentrations. The conductometric differences ($\Delta\mu$) between conductivities of PVIm solutions and metal ion adducts are shown in Figure 7 for each metal ion. As can be seen from this figure, the largest difference between conductivities is caused by Cu^{2+}, and then Co^{2+} and Cd^{2+}, respectively. The same order obtained from viscosimetric studies was also retained in conductometric measurements. Another expected behavior results from the shrinkage of polymer chains caused by the interaction of ionic species with polymer segments. Eventually, turbidity was observed in polymer solutions at higher metal ion concentrations. Threshold concentrations of metal ions giving rise to turbidities were marked

on the respective curves in the figure. The type and metal ion concentration inducing turbidity also yielded the same order as discussed before.

Protonated PVIm was also investigated by using conductometry and a result similar to the one observed in Figure 7 was displayed in Figure 8. No significant difference can be seen in conductivity decreasing the effect of these metal ions in protonated PVIm solutions. Conductivity was measured by changing [Ligand]/[Metal ion] ratio for unprotonated PVIm and conductivity data were replotted versus [Ligand]/[Me^{2+}] ratio. When all experimental results were evaluated, the stoichiometric ratio was found to be around 4/1 for [Ligand]/[Me^{2+}] (Fig. 9).

CONCLUSION

Solution properties such as viscosity and conductivity of poly(*N*-vinylimidazole) are observed to be affected by the type and concentration of Me^{2+} ion. From both viscometric and conductometric methods, it was determined that the Me^{2+} ions gave much better interaction with unprotonated PVIm and the order of interaction was found to be the same in both methods. The strength of inter-

action between poly(N-vinylimidazole) and Me^{2+} ions is explained by Pearson's classification. According to this classification, hard acid–soft base interaction is not preferred; thus, there is no interaction between PVIm's protonated form and Me^{2+} ions. In conductometric investigations, [Ligand]/[Me^{2+}] ratio was found to be 4/1.

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