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Investigations of polyelectrolyte-transition metal ion association in mixed solvents

S. K. Chatterjee*, F. H. Rajabi, B. V. Farahani, and N. Chatterjee

Department of Chemistry, University of Delhi, Delhi 110007, India

SUMMARY

Association between a typical polyelectrolyte, e.g. poly(acrylic acid), and a divalent metal ion (e.g. Cu(II)) has been studied using different water-methanol mixtures. Preferential solvation coefficients (λ/c) have been calculated for various solvent compositions. Excellent agreement has been observed between minimum (λ/c), lowest [η] and reduced viscosity (η_{sp}/c) of the complexes at a specific composition of the solvent. Interpretations have been sought in terms of polyelectrolyte conformational change at this solvent composition.

INTRODUCTION

Polyelectrolyte-divalent metal ion interactions have been widely studied in aqueous medium by numerous methods. Among polycarboxylic acids, the most extensively investigated have been poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) (1-3). Measurements of thermodynamic properties indicated formation of stable complexes between polycarboxylic acid and divalent metal ions (4). This is especially so when compared with complexes of simple dicarboxylic acid (5). It is also known that chelation increases with increase in pH due to changes in the charge density along the polymer chain (6). In less polar solvents like methanol, ethanol, DMSO, the interaction due to polyelectrolyte and solvent is considerable, thereby reducing its interactions with metal ions. Therefore, in a mixed solvent like water-methanol mixture, the extent of ionization of polycarboxylic acid will depend on the composition of the medium. The polyelectrolyte chain dimensions undergo little change at low degree of ionization, then within a narrow composition range of solvent an increase in charge density leads to an abrupt transition to a highly expanded state. The "local compact structure" due to hydrophobic aggregation possibly breaks down due to the presence of alcohol as observed in case of denaturation of globular proteins (7). Keeping this fact in mind we have studied the change in hydrodynamic behaviour during the interaction of PAA with Cu(II) in water-methanol mixtures of different compositions. The aim of this investigation was to study the influence of configurational environment and preferential solvation on the chelation between PAA and Cu(II) ions and to discuss the

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*To whom offprint requests should be sent significance of observations made in the hydrodynamic properties in terms of some of the factors mentioned above.

EXPERIMENTAL

PAA was obtained by polymerizing purified acrylic acid (distilled twice in vacuo) in moist dioxane-methanol mixtures using benzoyl peroxide initiator under nitrogen. The polymer was characterized by calculating weight average molecular weight by (8):

$[\eta]=4.22 \times 10^{-4}\ \bar{M}w^{-0.604}$ in 2m aqueous NaOH solution at 25°C

thus $\bar{M}w = 4.5 \times 10^{5}$ g/mol.

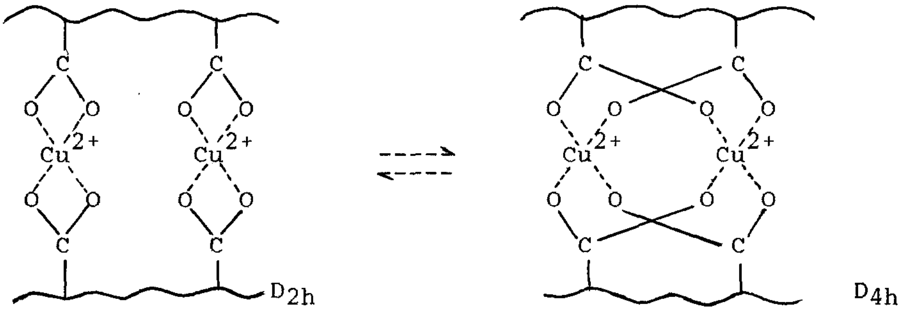
Conductometric and potentiometric measurements were carried out with a Leeds and Northrup 4959 electrolytic conductance bridge and an ECIL digital pH meter (Model pH 5651).

The viscosity of solutions was measured using an Ubbelohde viscometer at 30°C ± 0.05°C.

Double distilled water and analytical grade methanol were used as solvents.

RESULTS AND DISCUSSION

Polycarboxylic acids, such as PAA and PMA interact with Cu(II) in aqueous medium, to form a D_{4h} or D_{2h} type complex (9) :



Structure of Cu(II) - PAA complex

The equilibrium between D_{4h} and D_{2h} symmetry can be shifted in either direction depending on the nature of environment (6). Mixtures of methanol-water of several compositions are likely to provide different configurational environments as well as varying dielectric constants. Both factors are likely to influence the chelation of Cu(II) with PAA. Keeping these facts in mind, we have studied the variation of apparent pH and conductance of PAA with increasing concentration of Cu(II) in pure methanol and in aqueous medium,respectively (cf. Fig. 1). In both media a two stage interaction is indicated resulting in the formation of 1:2 and 1:1 (Cu:PAA) (umr) complexes. In both media, the pH curves (cf. curves C & D of Fig.1) showed a distinct fall during the interaction. This is understandable in view of the fact that complex formation between PAA and Cu(II) involves deprotonation (10). However, the conductance curve in methanol solution showed a fall during interaction with Cu(II). This may be attributed to ion association in low dielectric constant medium.

The influence of configurational environment and dielectric constant of the medium on this interaction has been studied by choosing methanol-water mixture of different compositions. Fig. 2 depicts the variation of apparent pH of PAA with increasing concentration of Cu(II) in methanol-water mixtures of different compositions. As expected, the nature of the curve is entirely different from that observed in the case of aqueous or pure methanol. In addition to 1:2 and 1:1 complexes between PAA and Cu(II), formation of 1:4 complex (Cu:PAA) is also indicated in mixed solvents. Moreover, the different stages of interaction become more distinct (cf. Fig. 2).

Addition of Cu(II) to PAA results in chelation between ionized carboxylate and Cu(II) leading to a reduction in interionic repulsion within PAA molecule. This facilitates the molecule to assume a folded conformation. One would expect this behaviour to be reflected on the reduced viscosity of the solution during the different stages of interaction of PAA with Cu(II).

The abrupt change in the pattern of viscosity curves with solvent composition leads us to believe that methanol and water do not form an ideal mixture. This could be seen from the change in viscosity of solvent mixture with composition (cf. curve A of Fig. 3). It can be seen from this curve that water-methanol is in highly associated form in the composition range 40-60% water (by volume). The presence of varying proportion of methanol in the medium is likely to influence the conformation of the polyelectrolyte (e.g. PAA) in solution. One can expect it to be reflected in the intrinsic viscosity of PAA in various solvent mixtures. In fact a sharp variation of intrinsic viscosity of PAA could be observed with the solvent composition as shown in Fig. 3, curve C. The intrinsic viscosity curve showed a pronounced minimum at 60% H_2O + 40% methanol. The sharp variation of intrinsic viscosity may be due to preferential solvation of PAA or to an abrupt change in the conformation in various solvent mixtures. Preferential solvation was calculated on the basis of (11) :

$$\lambda / C = 1 / [\eta_1] - 1 / [\eta_o]$$

where λ is preferential solvation coefficient, C is a characteristic constant and depends on polymer-solvent system, $[\eta_1]$ is the intrinsic viscosity of PAA in mixed solvent, and $[\eta_o]$ is its intrinsic viscosity in water. A plot of λ/C vs. composition of solvent is shown in Fig. 3, curve B. A distinct minimum is observed for the preferential solvation coefficient (λ/C) at the same composition of the solvent, i.e. 60% water + 40% methanol.

One would also expect that the presence of varying quantities of methanol in the medium is likely to influence the chelation of Cu(II) with PAA. This is due to the fact that

Fig.1. Variation of conductance and pH with unit mole ratio (umr); Aqueous medium : (A) Conductance, (D) pH; Methanol medium : (B) Conductance, (C) Apparent pH.

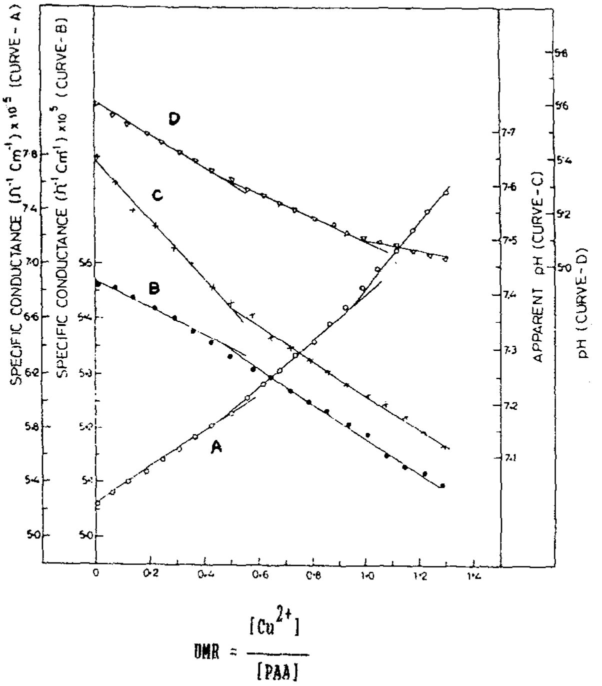


Fig.2. Variation of apparent pH with unit mole ratio (umr) : (A) 80% Methanol+ 20% Water, (B) 60% Methanol + 40% Water, (C) 40% Methanol+60% Water, (D) 20% Methanol+ 80% Water.

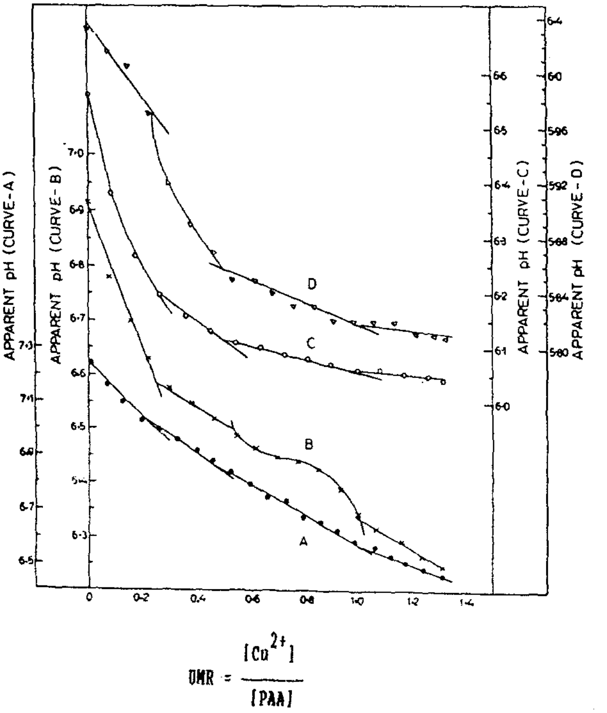


Fig.4. Variation of reduced viscosity ($\eta_{sp/C}$) of (A) 1:1 complex, (B) 1:2 complex, (C) 1:4 complex, with solvent composition.

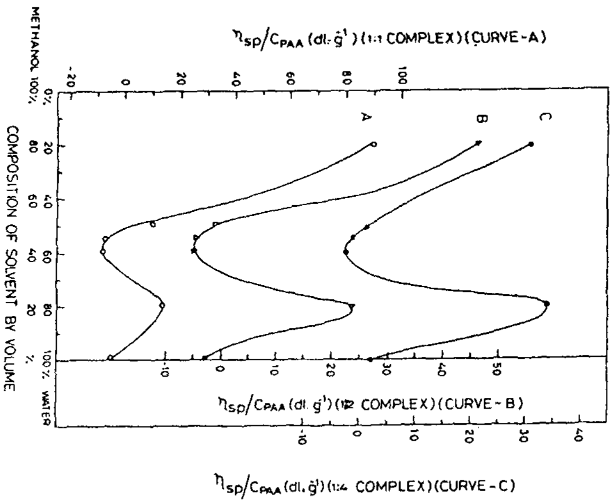
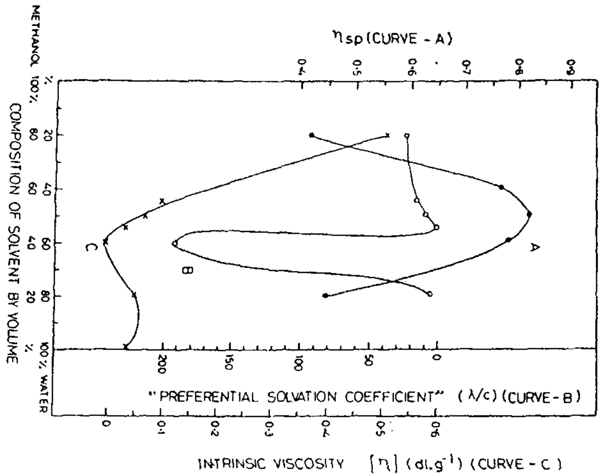


Fig.3. Variation of : (A) η_{sp} (B) Preferential solvation coefficient, (C) Intrinsic viscosity, with solvent composition.



PAA may assume different conformations in different solvent mixtures. This is reflected in the variation of reduced viscosity of PAA ($\eta_{sp/c}$) on the addition of Cu(II) in different solvent mixtures. The absolute values of $\eta_{sp/c}$ at different stoichiometries of the complex (e.g. 1:1, 1:2 and 1:4) (COOH:Cu(II)) have been plotted against the composition of the solvent mixtures (cf. curves A,B, & C of Fig. 4). All the complexes showed a distinct minimum in reduced viscosity ($\eta_{sp/c}$) at 60% water + 40% methanol. It is known that during binding, in almost all systems, there is an enthalpy gain (6,12). We believe that at this solvent composition the enthalpy gain is likely to be maximum due to desolvation of the PAA. In fact, this is reflected by the minimum of the preferential solvation curve (cf. curve B of Fig. 3). Both factors, e.g. desolvation and folded or coiled conformation of PAA, are likely to favour chelation with Cu(II). The distinct stages of interaction of PAA and Cu(II) as observed in various solvent mixtures (cf. Fig. 2) certainly indicate the validity of these arguments.

In conclusion, the hydrodynamic behaviour during association of polyelectrolytes with divalent metal ion is entirely different from that observed in aqueous medium or in pure organic solvents. The coincidence of lowest value of preferential solvation coefficient, minimum intrinsic viscosity of the polyelectrolyte and the minimum value of reduced viscosity of the various complexes at a specific composition of solvent can be attributed to abrupt conformational change of the polyelectrolyte/complex at this composition of the medium.

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