polymer reports

Acrylic copolymer–polyelectrolyte interactions: hydrodynamic and electrochemical studies in dimethylformamide–water mixtures

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Intermacromolecular complex formation has been studied between polyethyleneimine and methacrylic acid–methacrylamide copolymer in water–dimethylformamide (DMF) mixtures of different compositions. Preferential solvation coefficients (λ/C) have been calculated for the various compositions of the solvent mixtures. At a specific composition of the solvent (e.g. 50% water + 50% DMF by volume), the intrinsic viscosity of the copolymer had a maximum value which coincided with the minimum value of λ/C and the minimum value of the reduced viscosity of the complexes. Interpretations have been sought in terms of conformational change of the copolymer and the interpolymer complex at a specific composition of the solvent mixture.

(Keywords: methacrylic acid–methacrylamide copolymer; polyethyleneimine; preferential solvation coefficient)

INTRODUCTION

Interaction between two complementary polymer molecules takes place through secondary binding forces[1,2]. Interpolymer complexes formed as a result of such interactions are unique substances in view of their potential applications in various fields[3–6]. In aqueous medium, stabilization of complexes of methacrylic acid–methacrylamide (MA–MAm) copolymer, is expected to also involve hydrophobic interaction due to the presence of methyl groups. The stability and stoichiometry of such interpolymer complexes in organic solvents are likely to be affected due to the weakening of the hydrophobic interactions[7]. Therefore, in water–organic solvent mixtures, one can expect a change in configurational environment as well as preferential solvation[8]. Both these factors are likely to influence interpolymer complex formation. Keeping this in mind, we have studied the interaction of MA–MAm copolymer with a typical polyelectrolyte, e.g. polyethyleneimine (PEI) in water–dimethyl formamide (DMF) mixtures of different compositions. One can expect that the presence of varying quantities of organic solvent may influence their configuration and ultimately affect the interpolymer complex formation. In this report, the significance of some interesting observations made in hydrodynamic properties in terms of the factors mentioned above are discussed.

EXPERIMENTAL

MA–MAm copolymer

The MA–MAm copolymer was prepared by free radical polymerization using $K_2S_2O_8$ as an initiator[9]. The MA and MAm comonomers were taken in the ratio of 9:1 (w/w) in aqueous medium (100 ml) with 0.1% $K_2S_2O_8$, and heated in a nitrogen atmosphere at 70°C for 50 min. As soon as the product precipitated, it was separated and dissolved in acetone and reprecipitated with ether. The process was repeated three times to remove unreacted monomers. The composition of the copolymer was determined by the electrometric titration technique[10] and was found to have respective monomeric units in the ratio 0.60:0.40 (i.e. 0.60 unit mol of MA and 0.40 unit mol of MAm).

PEI

PEI was supplied by BDH Chemicals Ltd, Poole, UK, in the form of a 50% viscous water solution.

Solvent

DMF–water mixture. The two solvents are miscible in all proportions. For all experimental measurements double distilled water and BDH (AR) DMF were used as solvents.

Viscosity

The viscosity of the mixed solutions of the MA–MAm copolymer (1×10^{-3} unit mol l^{-1}) and (5×10^{-3} unit mol l^{-1}) at various unit mol ratios was determined at 30 ± 0.05°C by an Ubbelohde viscometer for which the kinetic energy correction was negligible.

Potentiometric titrations

The potentiometric titrations were carried out with an EC digital pH meter (model pH 5651) using a combination electrode. The apparent pH of the system in mixed solvent was measured at various stages of the addition of PEI to the MA–MAm copolymer solution. The reproducibility of the values was checked and found

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to be within ±2%. The concentration of polymer used for these titrations was 5×10^{-3} unit mol l^{-1}.

RESULTS AND DISCUSSION

The interaction of the MA–MAm copolymer with PEI has been studied in water–DMF mixtures of different compositions. In order to probe the interaction between the copolymer and the polyelectrolyte (e.g. PEI), and also to study the role of solvent composition on this interaction, the variation of apparent pH was studied during the various stages of interaction in solvents of different compositions.

Figures 1 and *2* depict the variation of apparent pH of the MA–MAm copolymer solution on the addition of increasing concentrations of PEI solution in water–DMF mixtures of various compositions and also in pure aqueous medium. When the composition of the medium was in the range of 45–55% water, three distinct stages of interaction were observed. At the first stage of interaction [i.e. 1:0.6 unit mol ratio (umr)] a 1:1 complex is formed between the MA units of the copolymer with PEI. At 1:1 umr, both the comonomer units (e.g. MA and MAm units) of the copolymer are involved in the complex formation. Finally, a break was observed at 1:1.6 umr (MA–MAm : PEI), which may be assigned to a 1:2 (MA:PEI) complex in addition to a 1:1 (MAm:PEI) complex. However, if the same complexation is carried out in pure aqueous medium or in a medium containing 80% water or in a medium containing 20% water, the different stages of interaction are not so pronounced, and the formation of the 1:2 (MA:PEI) complex is not indicated (cf. *Figure 2*). Obviously, these observations indicate that solvent mixtures of specific compositions play a significant role in the interaction between the MA–MAm copolymer and PEI.

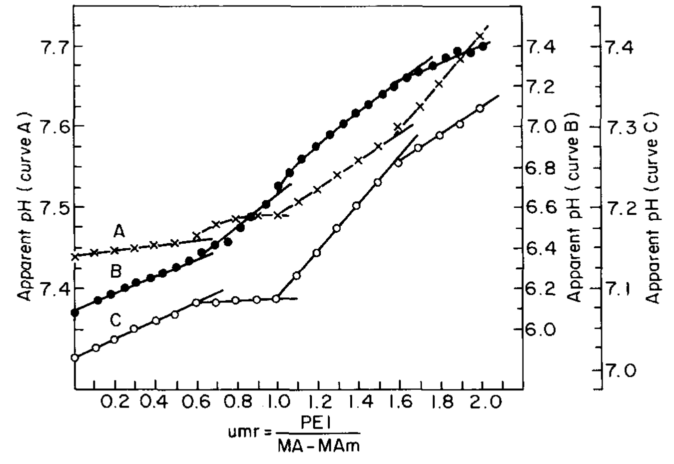


Figure 1 Variation of apparent pH with unit mole ratio of PEI:MA-MAm. Medium: (A) 45% H_2O + 55% DMF; (B) 50% H_2O + 50% DMF; (C) 55% H_2O + 45% DMF

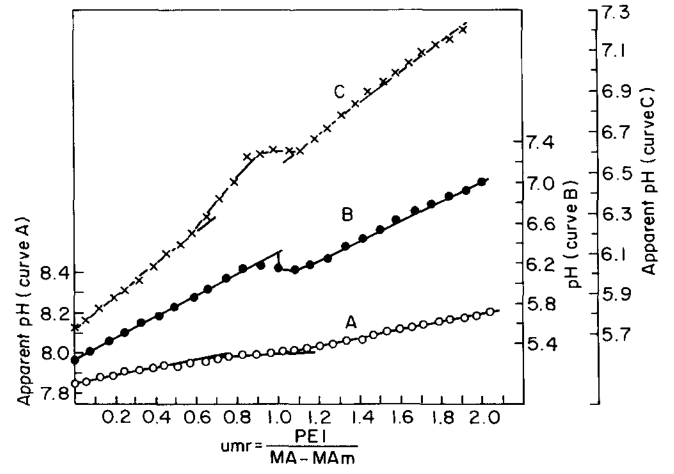


Figure 2 Variation of apparent pH with unit mol ratio of PEI:MA-MAm. Medium: (A) 20% H_2O + 80% DMF; (B) pure aqueous medium; (C) 80% H_2O + 20% DMF

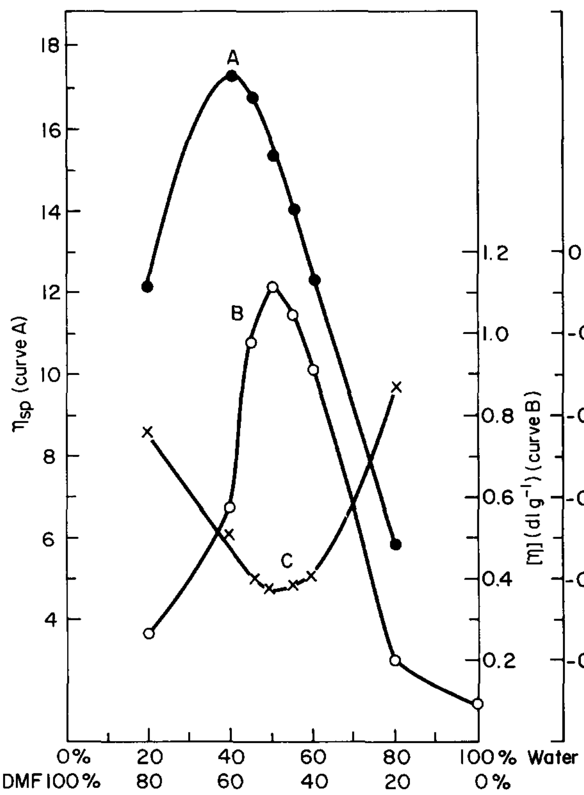


Figure 3 Variation of (A) η_{sp} of various solvent mixtures in the absence of polymer; (B) $[\eta]$ of the MA-MAm copolymer; (C) λ/C, with solvent composition

The influence of solvent composition on the stepwise interaction could possibly be explained in the following way. It can be seen from the specific viscosity of various solvent mixtures in the absence of polymer (cf. *Figure 3A*), that the water–DMF system is in a highly associated state in the composition range of 40–60% water (by volume). The presence of varying proportions of DMF in the medium is likely to influence the conformation of the copolymer molecule in solution. One can expect it to be reflected in the intrinsic viscosity of the copolymer in various solvent mixtures. In fact, a sharp variation in intrinsic viscosity of MA–MAm copolymer alone has been observed with the solvent composition (cf. *Figure 3B*). A similar variation in intrinsic viscosity of PEI with solvent ratio has also been observed. In pure organic solvents only molecular dimensions of polymer molecules may change but in a mixed solvent the intrinsic viscosity of polymers changes with solvent composition, perhaps due to the different nature of interactions between the polymers and the solvent components of the mixture. The variation of the molecular weights of the interpolymer complexes in organic solvents has been

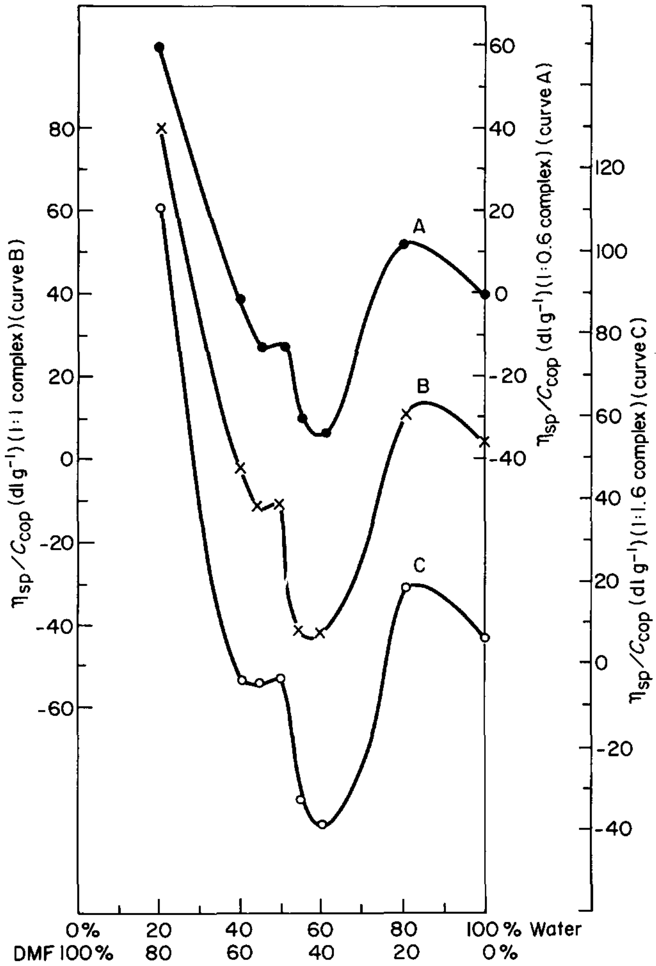
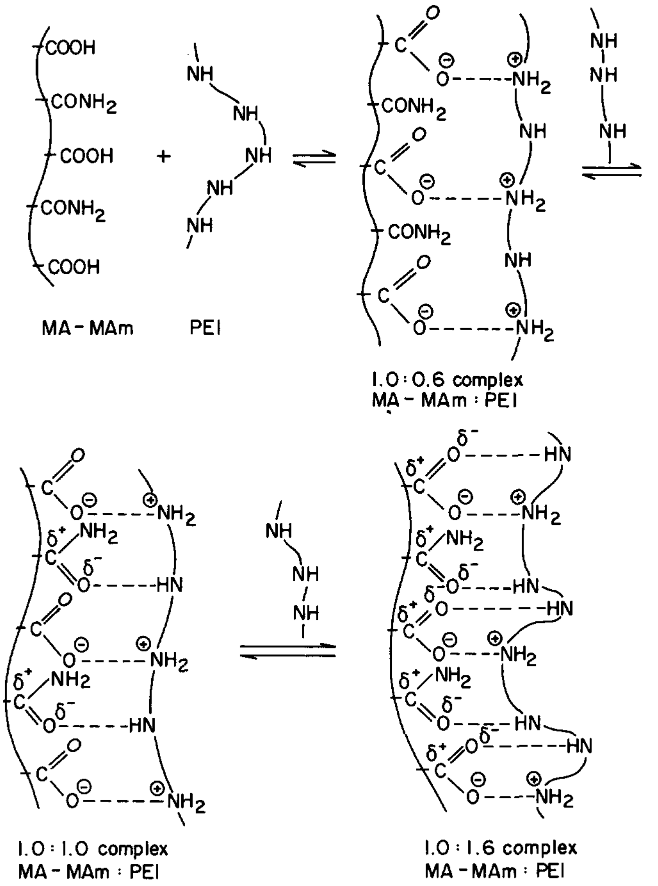


Figure 4 Variation of η_{sp}/C_{cop} *of* (A) 1:0.6 complex, (B) 1:1 complex and (C) 1:1.6 complex, with solvent composition



Scheme 1 Complexation between PEI and MA–MAm

reported in the literature[11]. However, in addition to association or aggregation of the complex molecules in mixed solvents, conformational change may also take place due to preferential solvation at a specific composition of the medium. Preferential solvation was calculated on the basis of the following equation[12]:

$$\frac{\lambda}{C}=\frac{1}{[\eta_1]}-\frac{1}{[\eta_0]}$$

where λ is the preferential solvation coefficient, C is the characteristic constant which depends on the polymer solvent system, $[\eta_1]$ is the intrinsic viscosity of the copolymer in the mixed solvent and $[\eta_0]$ is the intrinsic viscosity of the copolymer in water. A plot of λ/C *versus* solvent composition is shown in *Figure 3C*. The λ/C showed a distinct minimum at a specific composition of the solvent (e.g. 50% water + 50% DMF, by volume). This volume ratio corresponds to a 4:1 mol ratio (water:DMF). The lowest value of λ/C may be attributed to desolvation and a consequent change in conformation of the copolymer molecules. This is in fact reflected by the maxima in the intrinsic viscosity curve at the same solvent composition (cf. *Figure 3B*).

The variation of reduced viscosity ($\eta_{sp/C}$) of the copolymer solution with increasing PEI concentration has been studied in solvent mixtures of different compositions. The values of reduced viscosity of interpolymer complexes of distinct stoichiometries (e.g. 1:0.6, 1:1 and 1:1.6 umr MA–MAm:PEI) have been plotted against the composition of the solvent mixtures (cf. *Figure 4*). All three curves showed distinct minima (in reduced viscosity) at solvent compositions of around 60% water + 40% DMF, and also a distinct shoulder has been observed for all the complexes at an earlier solvent composition (e.g. 50% water + 50% DMF). This perhaps indicates that λ/C has a distinctly different effect on the interpolymer complex as compared to the pure copolymer (e.g. MA–MAm). This may be attributed to the presence of PEI in the complex which may be preferentially solvated by DMF. The proximity of DMF near the interpolymer complex molecule is likely to influence its conformation.

One can thus expect that the interpolymer complex molecules are likely to acquire a tightly coiled conformation. This is in fact reflected by the lowest value of reduced viscosity ($\eta_{sp/C}$) of all three complexes at this solvent composition (cf. *Figure 4*). The shoulder observed at 50% water + 50% DMF solvent composition for all three complexes perhaps indicates that the two-component polymers (e.g. MA–MAm and PEI) of the interpolymer complex are influenced differently by the organic solvent (e.g. DMF). As a result of this, shrinkage of polymer chains may take place which is likely to induce complexation due to higher co-operativity.

The probable mode of interaction between the MA–MAm copolymer and PEI could possibly be explained on the basis of *Scheme 1*.

Thus it can be concluded that hydrodynamic behaviour during interpolymer complex formation in mixed solvents is entirely different from that observed in the case of aqueous medium and in pure organic solvents. The solvent mixture of specific composition seems to play a significant role which leads to the coincidence of intrinsic viscosity maxima and reduced viscosity ($\eta_{sp/C}$) minima of the three interpolymer complexes.

REFERENCES

1 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99

2 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1982, **45**, 1

3 Grutsh, J. F. *Environ. Sci. Technol.* 1978, **12**, 1022

4 Ohno, H., Abe, K. and Tsuchida, E. *Makromol. Chem.* 1981, **182**, 1253

5 Ohno, H., Abe, K. and Tsuchida, E. *Makromol. Chem.* 1981, **182**, 1407

6 Abe, K. and Tsuchida, E. *Polym. J.* 1977, **9**, 79

7 Chatterjee, S. K., Yadav, J. B. and Sethi, K. R. *Angew. Makromol. Chem.* 1985, **133**, 171

8 Chatterjee, S. K., Malhotra, A. and Yadav, D. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 2591

9 Pinner, S. H. *J. Polym. Sci.* 1953, **10**, 379

10 Chatterjee, S. K., Pandith, R. L. and Pachauri, L. S. *Polymer* 1982, **23**, 1659

11 Ohno, H., Abe, K. and Tsuchida, E. *Makromol. Chem.* 1978, **179**, 755

12 Dondos, A. and Hebd, C. R. *Seances Acad. Sci., Ser. C* 1971, **272**, 1419