A new viscometric approach to the interpolymer complexes

G. Staikos[*], P. Antonopoulou, and E. Christou

Department of Chemical Engineering, University of Patras, GR-26110 Patras, Greece

SUMMARY

A new viscometric approach for the investigation of the formation and the structure of interpolymer complexes has been proposed. This method has been applied on the complexation of polyacrylic acid with polyethyleneoxide or polyacrylamide. The influence of the molecular weight and of the degree of neutralization of polyacrylic acid and of the ionic force of the solution on the complexation with polyethyleneoxide have been examined.

INTRODUCTION

During last years there is an increasing interest in characterizing interpolymer complexes formed between polyacids and polybases. The stabilization of such complexes is due to the cooperative formation of hydrogen bonds between acid and base groups (1,2). It has been known that poly(acrylic acid), PAA, formes in aqueous solutions complexes with polymers acting as proton acceptors, e.g.polyethyleneoxide, PEO, (3-7) or polyacrylamide, PAM, (8).

Different methods, such as viscometry (3-5), fluorescence (5-6) and potentiometry (4,5,7,8) have been used for the study of formation, stoichiometry and structure of the interpolymer complexes. In this work we have used the variation of the reduced viscosity, η_{red}, of the proton acceptor polymer, PEO or PAM, as a function of its concentration, c, using as solvent a binary mixture of water and PAA of constant composition, in order to investigate the formation and the structure of the interpolymer complexes. Moreover we studied the influence of different parameters, such as the molecular weight and the degree of

*To whom offprint requests should be sent

neutralization of PAA or the presence of a salt on the formation of PEO-PAA complexes.

EXPERIMENTAL

The POE sample used is an Aldrich product. Its molecular weight has been determined viscometrically in water (9) and has been found equal to 143000. The PAM sample was synthesized in a water-methanol mixture 50% by volume with hydrogen peroxide as initiator(10) at $50^{\circ}C$. Its molecular weight has been determined viscometrically in water(11) and has been found equal to 148000.

The two PAA samples used, PAA-50 and PAA-150, were solutions 25% in water of Polyscience. These were purified by ultrafiltration and freeze dried. Their molecular weights have been determined viscometrically in NaBr 0,5 M after 100% neutralization (12) and have been found equal to 49500 and 149000 correspondingly in excellent accordance with their nominal values. The partial neutralization of PAA samples used has been made by NaOH 0,100 M.

Water used for the preparation of the solutions was deionized by an ion exchange resin and then purified by a Millipore norganic cartridge equipped with a 0,45 μm filter.

The polymer solutions were prepared 24 hours before viscosity measurements, which were performed at $25^{\circ}C$ with an automated viscosity measuring system, AVS 310 Schott-Geräte, equipped with an Ubbelhode type viscometer.

RESULTS AND DISCUSSION

The reduced viscosity, η_{red}, of a polymer in solution, defined by the formula,

$$\eta_{red} = (\eta-\eta_o) / \eta_o \, c$$

where η_o is the viscosity of the solvent, η is the viscosity of the solution and c is the concentration, is a very useful and popular parameter in the study of polymer solutions. Its limiting value at infinite dilution is the intrinsic viscosity $[\eta]$, which is related to the hydrodynamic volume of the macromolecule. The dependence of η_{red} on c is linear and it is usually described by the Huggins equation
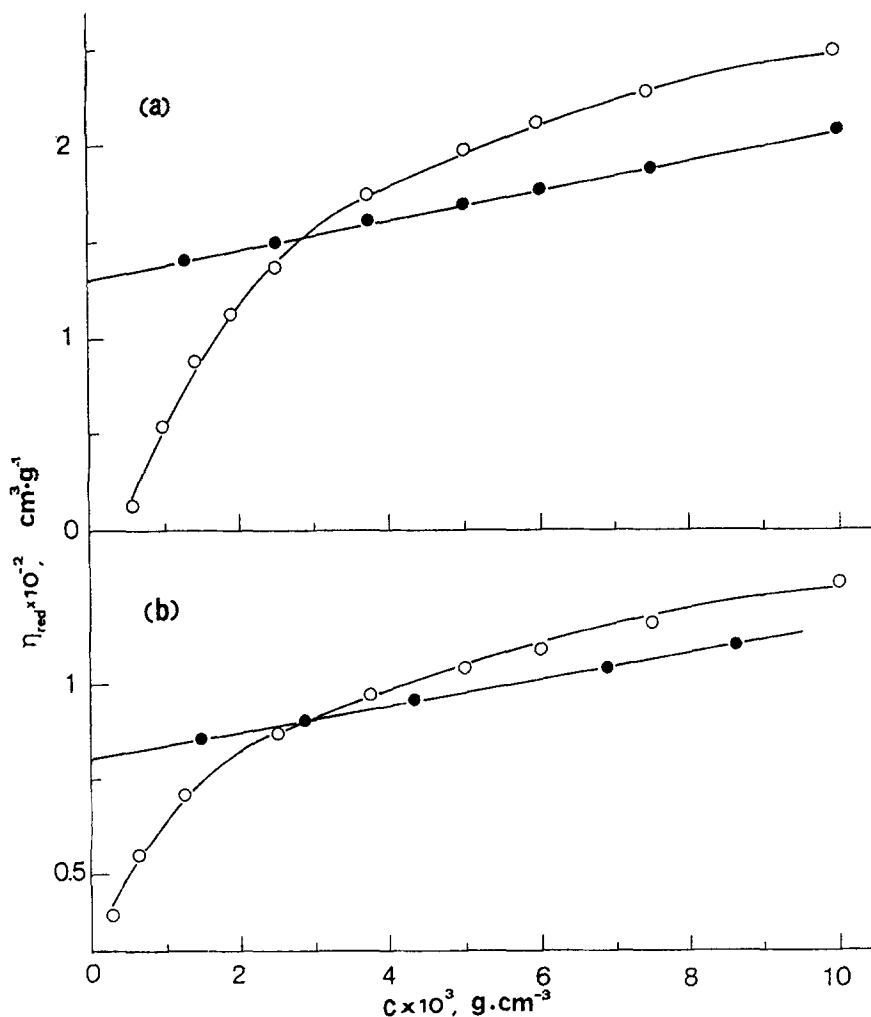
$$\eta_{red} = [\eta] + K' [\eta]^2 c$$

Fig.1 (a) Variation of the reduced viscosity, η_{red}, of PEO vs. concentration, c, in $5,0 \times 10^{-3}$ M NaBr (●) and in $5,0 \times 10^{-3}$ NaBr, $1,0 \times 10^{-3}$ g/cm^3 PAA-150 (○), water solutions.

(b) Variation of η_{red} of PAM vs. c in $5,0 \times 10^{-3}$ M NaCl (●) and in $5,0 \times 10^{-3}$ M NaCl, $1,0 \times 10^{-3}$ g/cm^3 PAA-150 (○). The degree of neutralization of PAA, a, is equal to 0,05 in both cases.

where K´ is a constant, which usually varies between 0,4 and 0,7, while higher values indicate association (13).

Fig.1 presents the variation of η_{red} versus c of POE (a)

and of PAM (b) in NaBr $5,0 \times 10^{-3}$M and NaCl $5,0 \times 10^{-3}$M correspondingly (full circles, ●) and in the same solvent containing now $1,0 \times 10^{-3}$ g/cm^3 PAA-150, 5% neutralized (open circles, O). We observe that the presence of PAA-150 provokes a great displacement of η_{red} of PEO and PAM towards very low values, in the region of low concentrations (low [POE]/[PAA-150],[PAM]/[PAA-150] ratios) and a relatively smaller displacement to higher values in the region of higher concentrations. This behaviour could be explained by the formation of a compact complex between POE or PAM and PAA-150 in the region of low [POE]/[PAA-150] or [PAM]/[PAA-150] ratios, which is gradually transformated to a entangled gel-like complex of a loose structure (5) as the concentration of POE or PAM increases.

We have also used the same viscometric approach in order to investigate the influence of different parameters, such as the molecular weight of PAA, the degree of neutralization of PAA
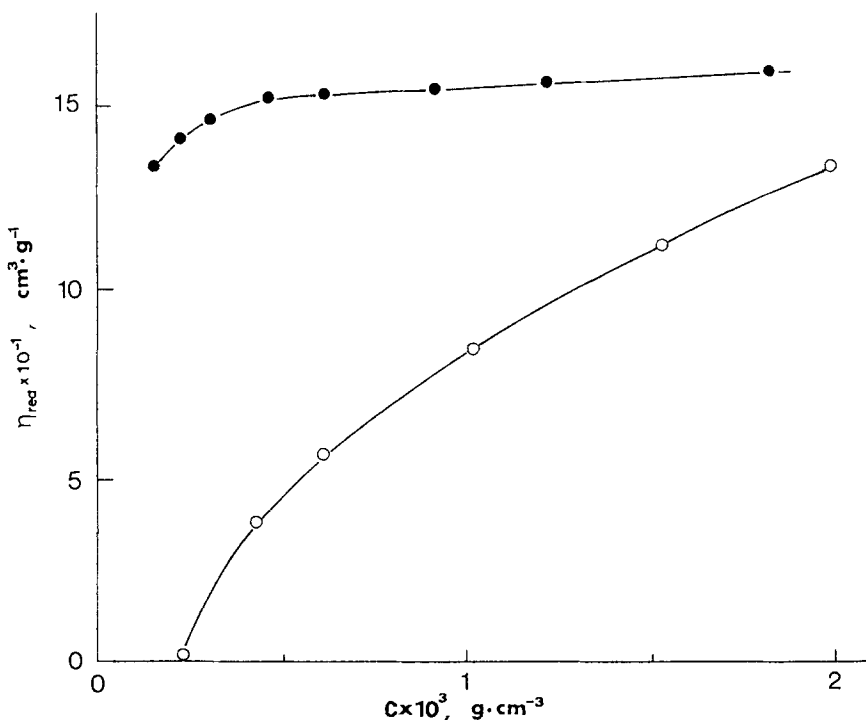

Fig.2. Variation of η_{red} of PEO vs. c in $2,0 \times 10^{-3}$ g/cm^3 PAA-50. a=0,15 (●), a=0,05 (O).

and the presence of a salt, on the formation of the POE-PAA complex.

Fig.2 shows the variation of η_{red} of PEO versus c in 0,2% PAA-50, 15% neutralized (●) and 5% neutralized (○). We observe that when the degree of neutralization of the polyacid is high the η_{red} of POE presents only a slight downward curvature at low concentrations and remains in general high indicating that when the neutralization of PAA-150 exceeds 15% the complex cannot be formated. On the other hand the great displacement to lower values of η_{red} of POE in PAA-150, 5% neutralized, indicates that the diminution in the degree of neutralization favours the formation of a compact POE-PAA complex.

In Fig.3 the influence of the molecular weight of PAA on the formation of the POE-PAA complex is depicted. It is directly concluded that the increase of the molecular weight of PAA
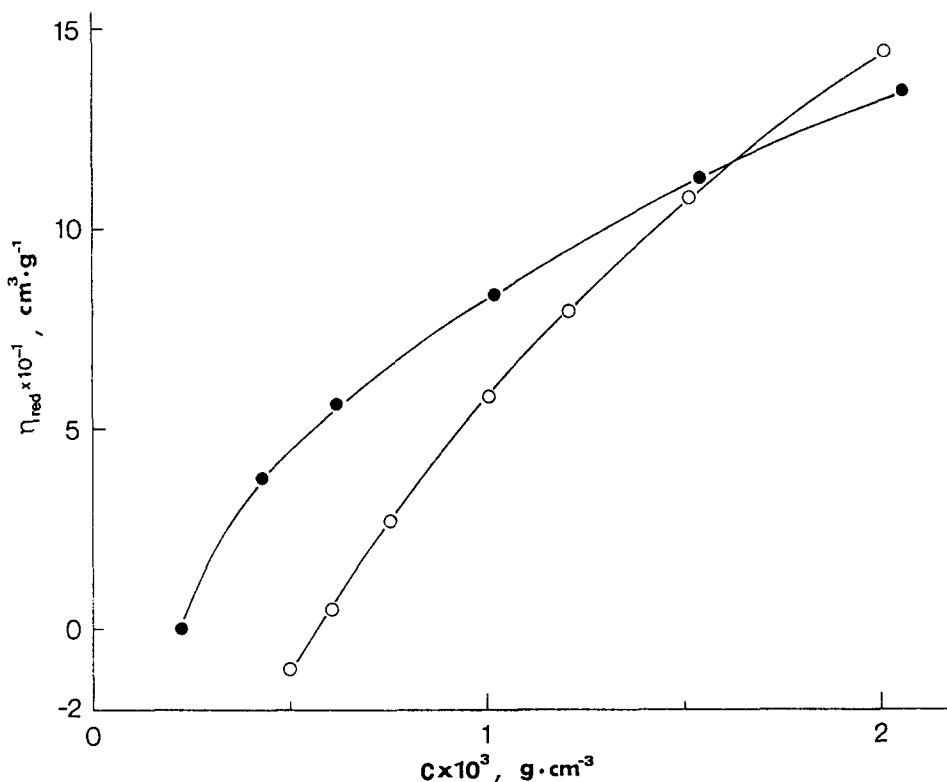

Fig.3. Variation of η_{red} of PEO vs. c in $2,0 \times 10^{-3}$ g/cm^3 PAA, a=0,05. PAA-50 (●), PAA-150 (○).
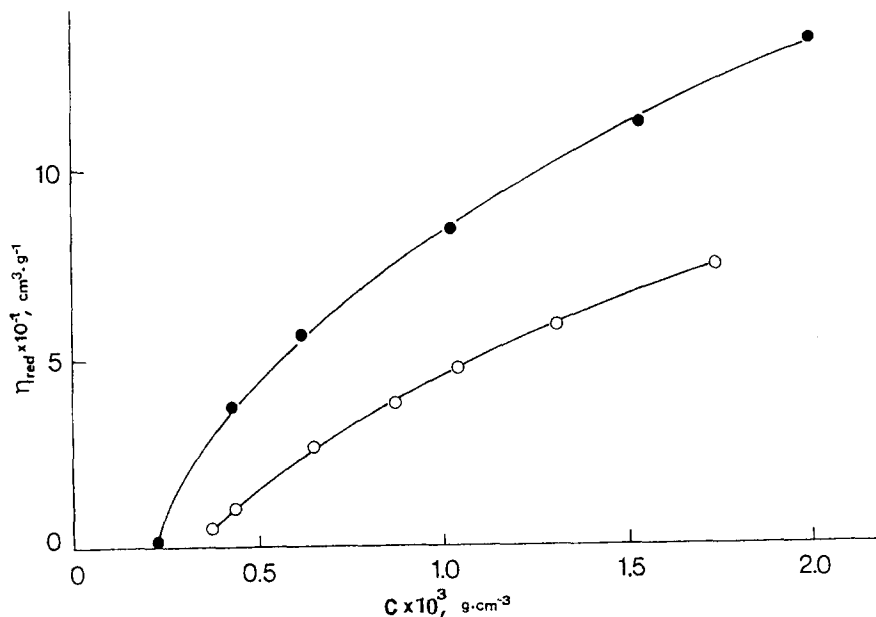
Fig.4. Variation of n_{red} of PEO vs. c in $2,0 \times 10^{-3}$ g/cm^3 PAA-50, a=0,05. Pure water (●), $5,0 \times 10^{-3}$M NaBr (○).

favours the complex formation. Fig.4 finally shows that the presence of a salt, i.e. increase of the ionic force of the solution, favours the formation of a compact POE-PAA complex.

CONCLUSIONS

We have demonstrated that, a new, more sensible, viscometric approach can be used, in order to investigate the formation and the structure of interpolymer complexes. Application of this method for the POE-PAA system shows that the complex formation is favoured by the lower degree of neutralization of PAA, and by its higher molecular weight in accordance with the results of Iliopoulos and Audebert (4,5). The complex formation seems also to be favoured by the presence of a salt, NaBr, in accordance with previous potentiometric results (7), but in disagreement with other fluorometric results (6) on the same system.

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