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Complex formation between poly(vinyl ether of diethyleneglycol) and polyacrylic acid

I. Effect of low molecular salts and phenols additives

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Abstract

Complex formation between poly(vinyl ether of diethyleneglycol) and polyacrylic acid has been studied in aqueous solutions. The influence of non-ionic polymer nature on the complex formation ability with polycarboxylic acids and composition of complexes is discussed. The effect of low molecular salts and phenols additives on the complexation was studied. Addition of low molecular salts to solutions of starting polymers favors the complexation due to the deterioration of solvent quality. Addition of phenol molecules is unfavorable for interpolymer interactions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Interpolymer complex; Hydrophobic interactions; Poly(acrylic acid)

1. Introduction

Interpolymer complex formation reactions between polycarboxylic acids and proton-accepting non-ionic polymers are the subject of intensive studies of the seventies and eighties [1–4], and in the present time [5]. A number of complex forming systems has been studied both in aqueous and organic solutions. The role of hydrophobic interactions in stabilization of compact structure of interpolymer complexes (IPC) was demonstrated.

It is well known that hydrophobic interactions can be affected by addition of different low molecular substances into the aqueous solutions. Many papers have been published about the influence of low molecular salts [6,7], organic solvents [8,9], phenols [10], saccharides [11], surfactants [12] on lower critical solution temperatures of some linear polymers and phase transition temperatures of hydrogels.

The effect of addition of different organic solvent additives on the stability of hydrogen bonded IPC also was studied by different authors. Usually the addition of proton-accepting solvents to IPC solutions leads to their destruction [3,5,13].

However, very little is known about the influence of different additives such as low molecular salts and phenols on hydrogen bonded IPC in aqueous solutions. Frenkel with co-workers published several papers about the influence of ionic strength of solution on complexation. They noted that the presence of low molecular salts in aqueous solutions disturbs the complexation of polyacrylic acid (PAA) with polyvinyl alcohol [14] and oxyethylcellulose [15]. Turro with co-workers [16] also demonstrated the unfavorable action of inorganic salts on the complex formation between polyacrylamide and polycarboxylic acids. At the same time Staikos with co-workers [17,18] and Iliopoulos with co-workers [19] showed that the presence of low molecular salts, i.e. increase of the ionic strength of the solution, favors the formation of compact IPC.

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Subotic et al. [20] reported that the presence of phenol enhances the interaction between PAA and polyvinylpyrrolidone in dimethylformamide making the complexation process more like that in an aqueous medium. Thus, the analysis of the literature shows that there is no systematic study of the influence of different low molecular additives on complexation of polycarboxylic acids with nonionic polymers.

In the present work we studied the complexation process between PAA and poly(vinyl ether of diethyleneglycol) (PVEDEG) in aqueous solutions and clarified the effect of different salts and phenols additives.

2. Experimental

Polyvinyl ether of ethyleneglycol (PVEEG) and PVEDEG were synthesized by γ-irradiation polymerization as described in Ref. [21]. The molecular weight of polymers determined by viscometric measurements [22] was ranged within 40 000–60 000. Polyacrylic and polymethacrylic acids (PMAA) ($M_W = 250\,000$) were purchased from Aldrich Chem. Corp. Inc and used without further purification.

The viscosity measurements were carried out in an Ubbelohde viscometer at 298 ± 0.1 K. Turbidimetric measurements were carried out with the help of the spectrophotometer KFK-2-UHL-4.2 (USSR) at the wavelength $\lambda = 400$ nm and at room temperature.

The pH of solutions was adjusted with a very small amount of 0.1 M HCl and determined using an EV pH-meter (USSR). Low molecular salts (NaCl, KCl, NH_4Cl) as well as phenol and hydroquinone were analytical grade and used without further purification.

3. Results and discussion

Poly(vinyl ethers of glycols) represent a new family of non-ionic water soluble polymers [21–23]. They are able to form IPC with polycarboxylic acids in aqueous as well as in organic solutions due to the presence of proton-accepting hydroxyl and etheric groups in their elementary units [24–30].

Earlier [27,29,30] we studied the complex formation between PVEEG and PAA in aqueous and alcohol solutions. The formation of stoichiometric IPC was detected by viscometry and turbidimetry methods. It occurred only below some critical pH values in aqueous solutions. The influence of polymer concentrations and ionic strength of the solutions on critical pH values was shown.

It was also reported [24] that PVEDEG possesses higher complexation ability (PVEDEG) than PVEEG in respect to PMAA. In the present work we studied the complexation between PVEDEG and PAA in aqueous solutions in comparison with previously studied systems.

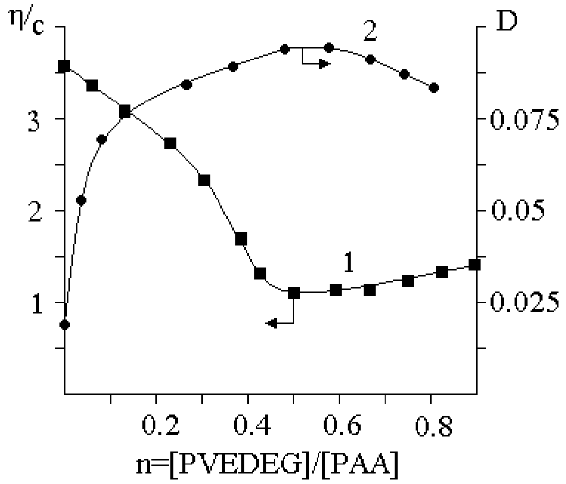

Fig. 1. Viscometric and turbidimetric titration curves of PAA by PVEDEG. [PAA] = [PVEDEG] = 0.05 M.

The titration of 0.05 M PAA aqueous solution by 0.05 M PVEDEG solution is accompanied by noticeable increase of turbidity and decrease of viscosity, indicating the complex formation (Fig. 1). Earlier [23], the complexation in this system was not observed. In our present study we used more concentrated solutions of polymers at pH = 3.0 that favors the complex formation due to the depressing of PAA ionization. It is seen from the figure the minimum of viscosity and maximum of turbidity indicate the formation of non-stoichiometric polycomplex. The same composition of IPC was observed earlier for the system PMAA–PVEDEG [24].

Usually the interaction of polycarboxylic acids with non-ionic polymers such as polyvinyl alcohol, polyethylene oxide, polyvinylpyrrolidone, polyvinylmethyl ether, polyacrylamide, etc. is accompanied by formation of stoichiometric complexes [4]. In our case the composition of IPC is highly deviated from 1:1. Probably the presence of both etheric and hydroxylic groups in every monomeric unit of PVEDEG makes it possible to bind two units of PAA per each PVEDEG one according to the scheme (Fig. 2). One can suppose that the presence of several proton-accepting sites in every unit of PVEDEG favors its higher complexation ability in respect to PAA in comparison with PVEEG.

Tsuchida et al. [4] reported about the existence of some critical pH values for formation of polycomplexes between polycarboxylic acids and nonionic polymers. We determined the critical pH values for complexes of PMAA and PAA with PVEEG and PVEDEG in aqueous solutions (Fig. 3). It is seen that complexes containing PVEDEG are characterized by higher values

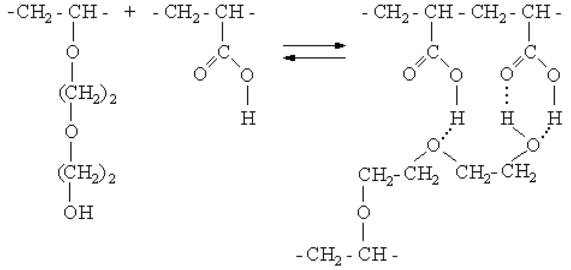

Fig. 2. Postulated complex formation mechanism.

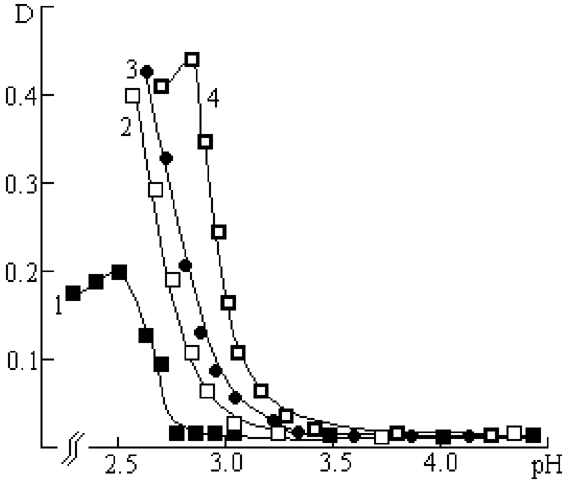

Fig. 3. Dependencies of turbidity of PAA–PVEEG (1), PMAA–PVEEG (2), PAA–PVEDEG (3), PMAA–PVEDEG (4) solutions on pH. [polymers] = 0.01 M.

of critical pH. In our opinion the critical pH value can be considered as some criterion of complexation ability for complexes of polycarboxylic acids with non-ionic polymers in aqueous solutions. The more critical the pH value is, the higher the ability of the system to form complexes is.

We checked the influence of polymer concentrations of PVEDEG–PAA system on the critical pH values (Fig. 4). It is seen that an increase of polymer concentrations shifts the critical pH values to the higher pH region. Probably the ionization of PAA is suppressed with increase of polymer concentrations and complexes can be readily formed at higher pH values. All critical pH values for PAA–PVEDEG system are higher than that the corresponding values for PAA–PVEEG one. This is the indication of higher complexation ability of PVEDEG in comparison with PVEEG.

In aqueous solutions IPC are additionally stabilized by hydrophobic interactions. These interactions can be enhanced by increase of hydrophobicity of interacting macromolecules [3,4,23], increase of temperature [3,4], and addition of different low molecular salts. We studied the influence of low molecular salt additives on critical pH values. The dependencies of solution turbidity on pH in the presence of NaCl are plotted in the Fig. 5. An increase of NaCl concentration considerably increases the critical pH values. Probably the action of NaCl is concerned with deterioration of solvent quality in respect to polymers. In this case the polymer–solvent interactions became weaker and polymer–polymer

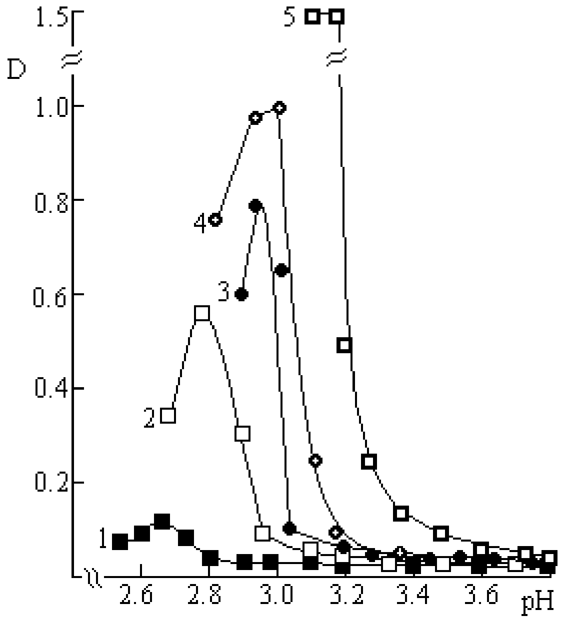

Fig. 4. Dependence of turbidity of PAA–PVEDEG (2:1) solutions on pH at different concentrations. [PAA] = [PVEDEG] = 0.001 M (1), 0.01 M (2), 0.025 M (3), 0.05 M (4), 0.1 M (5).

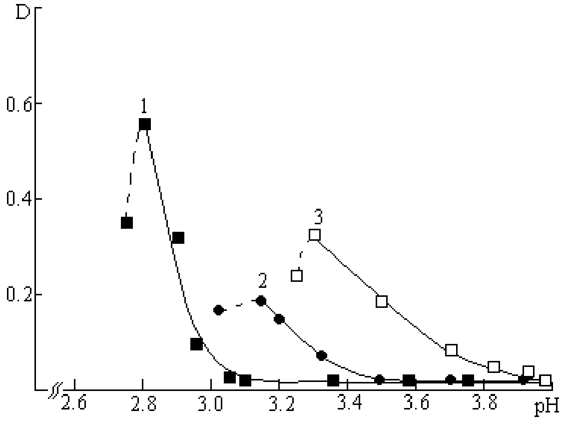

Fig. 5. Dependencies of turbidity of PAA–PVEDEG (2:1) solutions on pH in the presence of NaCl. [PAA] = [PVEDEG] = 0.01 M, [NaCl] = 0 M (1), 0.1 M (2), 0.25 M (3).

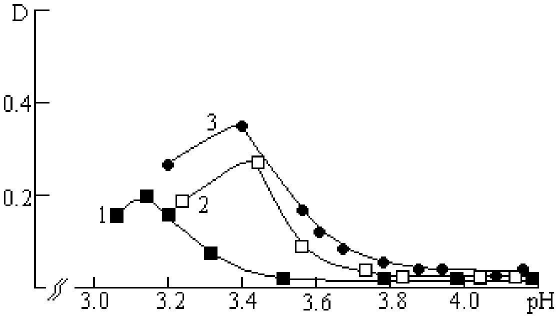

Fig. 6. Dependence of turbidity of PAA–PVEDEG (2:1) solutions on pH in the presence of NaCl (1), KCl (2), NH_4Cl (3). [PAA] = [PVEDEG] = 0.01 M, [salt] = 0.1 M.

interactions are more favorable. Our results confirm the viewpoints of Staikos et al. [17,18] and Iliopoulos et al. [19] about the favorable influence of ionic strength on complexation.

We checked the influence of nature of low molecular salts on critical pH values. It is seen from the Fig. 6 the salts can be arranged in the following order $NH_4Cl > KCl > NaCl$ by decreasing of their action on polycomplexes. It is interesting to note that the salt effectiveness to shift critical pH coincides well with the changing of ionic radiuses NH_4^+, K^+, Na^+.

The addition of low molecular organic compounds like phenol and hydroquinone also influences the complex formation (Fig. 7). However, unlike of low molecular salt additives, phenol and hydroquinone shift the critical pH values to the lower pH region. It is interesting to note that phenol and hydroquinone influence the critical pH values at comparatively low concentrations in solutions (0.01 M). According to Molyneux [31] it can be associated with the specific binding of their molecules by polymeric chains. Moreover, a number of papers has been published on the complexation of phenols with non-ionic water-soluble polymers like polyethyleneoxide, polyvinylpyrrolidone, polyvinyl alcohol, etc. [32–34]. Besides, such a complexation occurs more readily with polyphenols [31]. Probably, phenol and hydroquinone are also able to form hydrogen bonds with PVEDEG and their specific interactions compete with complexation between polymers. The detailed investigation of complexation between poly(vinyl ethers of glycols) and different phenols will be the subject of our further research.

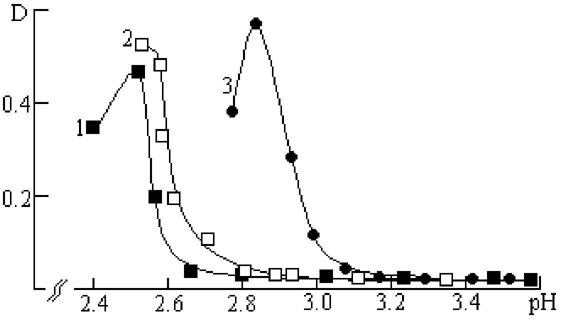

Fig. 7. Dependence of turbidity of PAA–PVEDEG (2:1) solutions on pH in the presence of phenol (2) and hydroquinone (1) and without additives (3). [PAA] = [PVEDEG] = 0.01 M, [phenols] = 0.01 M.

Thus, the ability to form IPC as well as the composition of complexes is strongly influenced by nature of non-ionic polymer. The more proton-accepting centers are in the elementary unit of non-ionic polymer, the higher the complexation ability of this polymer in respect to polycarboxylic acids.

The addition of different low molecular compounds influences the complexation between polycarboxylic acids and non-ionic polymers. Low molecular salt additives favor the complex formation due to the deterioration of thermodynamic quality of the solvent in respect to polymers. The addition of organic substances like phenol and hydroquinone does not prevent complexation but shifts the critical pH to the lower region. The mechanism of phenols action will be clarified in our further research.

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