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Solvent effect on the complex formation of polyvinylpyrrolidone and polymonomethyl itaconate

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SUMARY

The influence of solvent on polyvinylpyrrolidone (PVP) and polyitaconic acid monomethylester (PMMI) sterecomplex formation was studied by means of laser light scattering and viscometry. Several phase changes were observed, from homogeneous solution to precipitates and gels. Responsible of this behaviour are hydrogen bonding, Coulombic forces, or hydrophobic interaction in aqueous medium.

INTRODUCTION

Interpolymer complexes were obtained simply by mixing the two solutions of polymers. They were formed due to some secondary binding forces in solution. The capacity of PVP to form complex with polyacrylates and polymethacrylics is well known(1-3). The medium has a great influence on interpolymer interaction.

The proton-donating character of PMMI makes us think that complex formation with PVP (proton-acceptor) is possible. Mixtures of both polymers have been studied in different protics medium. Polymer complexes are formed in alcohols, water and DMF.

The size of the complexes depends on the solvent and the total polymer concentration, as it can be deduced of laser light scattering measurements. In the DMF/water mixtures, the complex formation depends on the proportion of these liquids in the mixture.

EXPERIMENTAL PART

Polymer samples. Commercial PVP (Janssen Chimica) were used without any purification. Average weight molar masses, quoted by manufactures are: 3.6×10^5, 4.0×10^4 and 1.5×10^4 g/mol for PVP-1, PVP-2 and PVP-3, respectively. The samples of PMMI used were synthesized, fractionated and characterized by ourselves. The average weight molar masses are: 10^5 and 2×10^4 g/mol for PMMI-1 and PMMI-2, respectively.

Solvents. Methanol, ethanol and DMF (Panreac) were purifyed by

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standard methods. Twice distilled and desionizated water was used. The values of dielectric constants for the solvents are: 32.70, 24.55, 78.39 and 36.71 for methanol, ethanol, water and DMF, respectively. The values of the dielectric constants we have found for the mixtures of DMF/water are: 40.88, 57.55 and 67.22 for the % in water of 10, 50 and 90 %, respectively.

EXPERIMENTAL

Viscometry. The reduced viscosity, η_{red}, was measured in an Ubbelhode viscometer, at 25.00±0.05°C. Lower values of η_{red} than theoretical, shows polymer complex formations(4):

$$\eta_{red,\ theo} = \eta_{red(p_1)}\ x_1 + \eta_{red(p_2)}\ x_2$$

where x_i is the molar fraction of the polymer i.

Laser light scattering. The solutions were studied using a modified FICA 4200 light scattering photometer, at 25.00±0.05°C. The light source and the optical block of the incident beam were replaced by a He-Ne laser (Spectra Physics, emission wavelength 633 nm, power 3 mw). The polymer solution was clarified by centrifugation previous to mixing. Parameters of polymer mixtures were determined from the Zimm plots.

Differential refractometry. The refractive indices increment, dn/dc, of the complex were determined using a Brice-Phoenix differential refractometer, at 25.00±0.05°C. As a light source at 633 nm we used a He-Ne laser (Spectra Physics model 156 power 1 mW).

RESULTS

Mixtures of PVP-PMMI were prepared from each polymer solutions in methanol in the range 0-100% weight fraction of PMMI. The initial total polymer concentration was 2.5×10^{3} g/mL. An interpolymer complex was at once observed like a gel. On decreasing the total polymer concentration only until reaching 0.4×10^{-3} g/mL. From this concentration downwards, a gel is first observed and afterwards a precipitate. We obtained the same results when mixing solutions of both polymers in ethanol.

The mixtures prepared from polymer solutions in DMF were homogeneous with time, even for total polymer concentration upper 2.5×10^{-3} g/mL. The mixtures prepared from the polymers solutions in water were also homogeneous at the range concentration of 10^{-3} g/mL. For higher total polymer concentrations, (10^{-2} g/mL), a gel was observed with time.

For solvent mixtures DMF/water, 10, 50 and 90% in volume of water, polymer mixtures were also homogeneous in the range of total polymer concentrations above indicated. Interpolymer complex were also formed in DMF, water and DMF/water mixtures, but the size of this complex are abviously smaller than complexes formed using alcohols as solvents.

DISCUSSION

The viscometric measurements, of homogeneous polymer mixtures, give us information about the complex interpolymer formation and the interactions between polymers. The obtained experimental values of η_{red} in DMF are shown in Table 1. As it can be seen except for 10% of PMMI sample, the observed values were smaller than the theoretical ones, indicating that complexation exists. Differences between theoretical and experimental decrease as the molar mass of PVP decreases.

All experimental points were determined about 3 min. after mixing the components, the time needed for complete mixing and filling the Ubbelhode viscometer. The total concentrations of polymer were 2.5×10^{-3} g/mL. The optimal composition of polymer mixture in order to a maximum complexation is function of molar mass of PVP. Thus, the proportion of PVP in the polymer blend decreases as its molar mass increases.

Table 1. Reduced viscosity as a function of PMMI composition in DMF, at 298 K

	η_{red}(dL/g)					
% PMMI-1	PVP-1		PVP-2		PVP-3	
	Exp.	Theor.	Exp.	Theor	Exp.	Theor.
0	1.548	1.548	0.249	0.249	0.300	0.300
10	1.624	1.481	0.365	0.224	0.415	0.270
30	0.760	1.348	0.216	0.439	0.262	0.475
50	0.295	1.215	0.194	0.565	0.355	0.591
60	0.236	1.148	0.210	0.628	0.377	0.649
70	0.298	1.082	0.249	0.692	0.426	0.707
90	0.409	0.948	0.382	0.818	0.521	0.824
100	0.882	0.882	0.882	0.882	0.882	0.882

For the PVP-1 systems, the optimal composition are 1/1.3. However, we have not found any dependence with PMMI molar mass. These results evidence a complex formation in DMF, and furthermore indicates that in order to form a stable complexe, it is necessary for PVP to have a sufficiently long chain (i. e., a sufficiently high number of active sites). As the reduced viscosity decreases drastically at a certain chain length, it is found that a critical chain length, L_c, of PVP exists for complexation in every case. The values of η_{red} of polymer mixtures are smaller than the ones observed for each polymer in the solvent. Figure 1 shows these differences for a blend of 60% in PMMI. These values are evidence that interactions between PVP and PMMI separately. The non linear relation observed for η_{red} with total polymer concentration make evident the occurrence of electrostatic forces in the interpolymer complex.

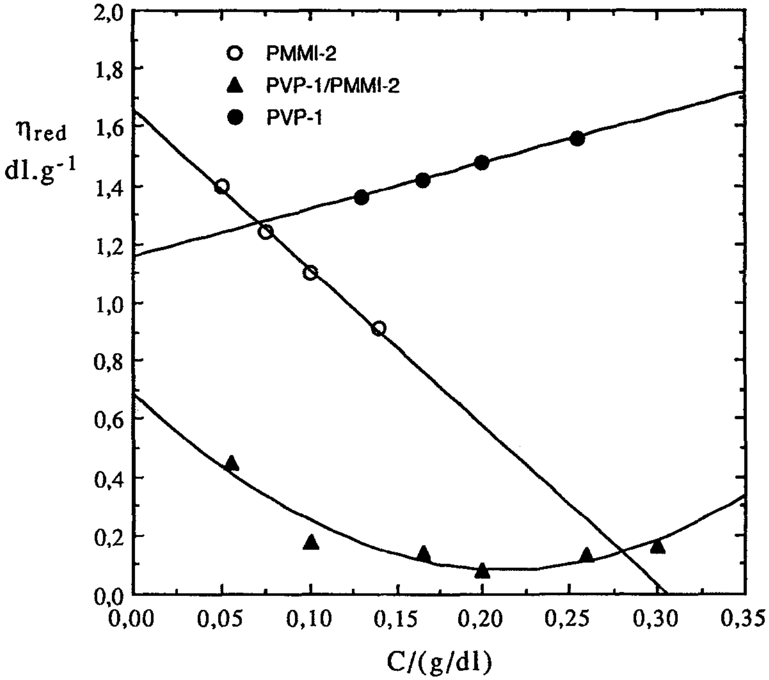


Figure 1. Variation of η_{red} as a function of total polymer concentration in DMF for PVP-1 and PMMI-2 and for the mixture.

The PMMI does not dissociate in organic solvents, but in presence of PVP, dissociation is possible. A similar behaviour has been observed for other systems (5). The values of η_{red} for the polymer mixtures in water and solvents mixtures of DMF/water at 10% and 90% in water were also smaller than theoretical ones, Figure 2. For the solvent DMF/water at 50%, the experimental and theoretical values were concident, indicating that complex polymer were not formed.

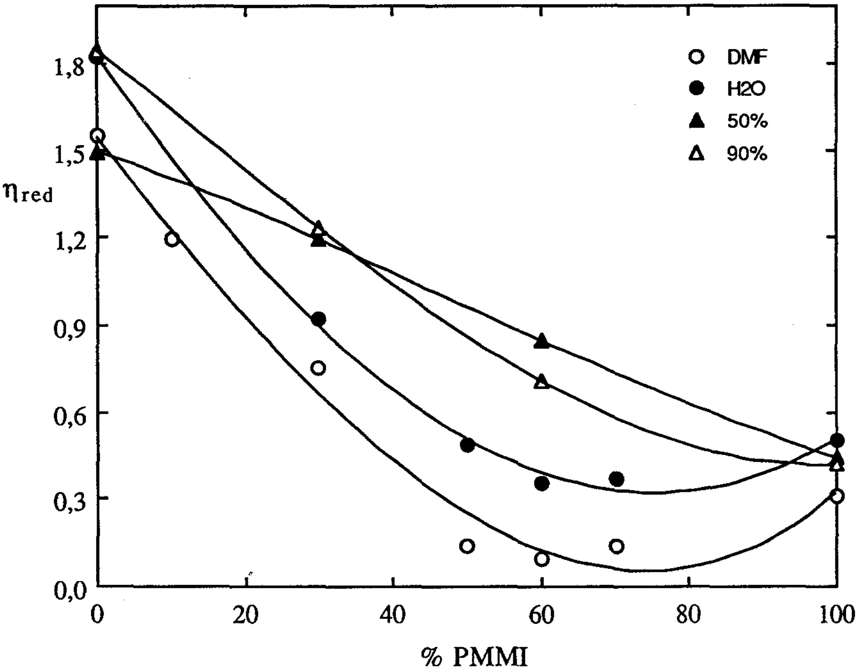
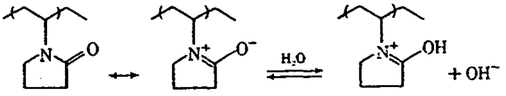


Figure 2. Variation of η_{red} as a function of % weight of PMMI for the PVP-1/PMMI-2 mixture in several solvents.

The explanation of results obtained in aqueous systems is possible considering the basic character that PVP shows in water. The presence of a negative charge on the PMMI generally results in formation of a polymer-polymer complex, because of the cationic nature of the nitrogen atom of the pyrrolidone ring in the following the scheme proposed by Takagishi (6):



The oxygen atom is strongly hydrated because it is not shielded. But the neighbour hydrocarbon groups shield the nitrogen atom and its hydratation is not possible. The hydrofobic part includes the methyl groups of chain and methyl groups of pyrrolidone ring. The importance of hydrofobic interactions in binding PVP is also evidenced in the literature (7). In aqueous environment, coulombic forces and hydrophobic interactions contribute to polymer complex formation, while in organic solvents these interactions decrease, while strengthening the electrostatic forces. In the systems DMF/water(50%), none of these interactions noted are strong and complexation do not take place. The size of the complex is considered to be dependent on the kind of solvent nature. In order to examine this prediction, laser light scattering spectra was applied. The weight average molar mass and second virial coefficient found are apparent values.

A rather strange scattering behaviour was observed for the systems PVP/PMMI/DMF. We found that the intensity of the scattered light would not fulfill the Rayleigh scattering theory but increased with the angle. Thereby R_g could not be derived from the slope of Zimm plot as it is negative. A similar behaviour was reported by Koetsier at al.(8), for polymer mixture systems.

However, the exact reason for these results is still unknown. In our systems, we think that the basic character of DMF(9-13) would cause ionization of some carboxylic groups of uncomplexed PMMI chain, which are always present in stable complex particles to some extent. Therefore, the complex particles can become compact. The values reported in Table 2 are characteristics for compact particles.

Table 2. M_w*, A_2* and dñ/dc values for PVP-1/PMMI-1 system in DMF as a function of PMMI composition.

	M_w^*	$A_2^* \times 10^4$	dñ/dc
% PMMI-1	g/mol	$cm^3.mL.g^{-1}$	mL/g
0	613,000	1.93	0.0958
30	406,000	-1.03	0.0878
50	429,600	-3.68	0.0752
60	1,205,000	-1.22	0.0647
100	95,910	-0.13	0.0677

All values are obtained for the smallest experimental time after the mixing. The larger value of M_w* was found for the polymer mixtures PVP/PMMI (60% in PMMI). Zimm plots obtained for the polymer mixture in the binary mixture DMF/water and in water have positive slopes. The values of M_w* for the mixture PVP-1/PMMI-2 (60% in PMMI) in the different solvents are shown in Table 3. These values are not absolute because of the fact that stereopolymer formation depends on concentration, as can be seen in figure 2. So, the values given in Tables 2 and 3 would be qualitative values, for the fact that concentration is a factor that exerts influence on the complex formation and their size was not considered. Studying this dependence as a function of the concentration can be see in Table 4, values of M_w*

calculated for different concentration, in different solvents. From these data we can classify the solvents used in three groups according to their capacity to form complexes between the PVP and PMMI.

Table 3. Apparent molar mass for PVP-1 (40%)/PMMI-2 (60%) mixtures in several solvents.

Solvent	M_w*.10^5 (g/mol)
DMF	21.51
DMF/water(%)	5.16
DMF/water(50%)	2.60
DMF/water(90%)	2.23
Water	9.17

Table 4. Apparent molar mass for PVP-1/PMMI-2 as a function of concentration in several solvents.

	M_w*(g/mol)			
c_2x10^3 (g/mL)	0.65	1.50	2.01	2.50
DMF	518,200	790,500	990,100	1,370,000
DMF(90%)/H_2O (10%)	460,000	241,000	228,600	228,600
DMF(50%)/H_2O(50%)	266,700	232,600	213,900	215,100
DMF(10%)/H_2O(90%)	329,500	720,400	1,085,400	1,884,200

DMF and water belong to the first group, they help the complex formation. The second group are the solvents where there is feeble complex formation. In our systems, the mixtures DMF/water to 10% and 90% in water belong to this group. And the mixture DMF/water to 50% is in the third group. In this system no complex formation is observed. We can relate this complexing power to the properties of solvents. The relationship between reduced viscosity of solutions and the dielectric constant, ε, for solvents is shown in Figure 3, for the system PVP-1/PMMI-2 (60% in PMMI). The total concentration of polymer is always 2.5x10^{-3} g/mL.

From this study, we can conclude that the polymer interactions between PVP and PMMI depend on the medium. Coulombic forces, hydrogen bonding and hydrophobic interaction (in aqueous medium) are the principal responsible for the complex formation. We can separate the complexing process in three steps i) primary complexing (Coulombic forces and hydrogen bonding taken part in this first step), ii) the second step is one intramolecular redistribution (in this step take place the new bonds and/or complex torsion), and iii) The third step is the intercomplex addition, through specific interactions.

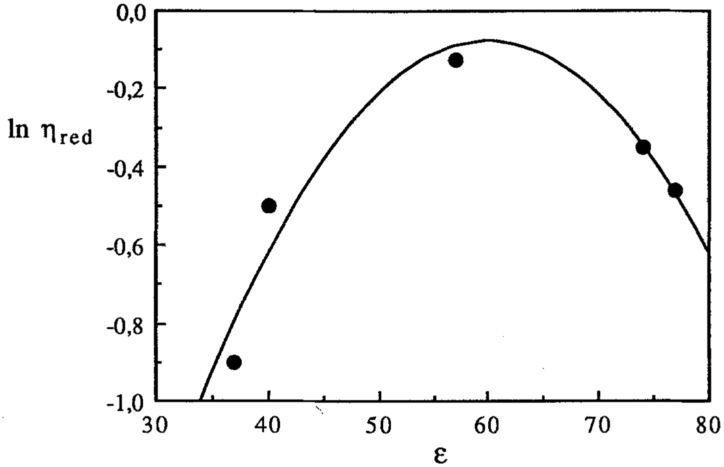


Figure 3. Relation between ln η_{red} and dielectric constant, ε, of the solvent for PVP-1/PMMI-2 (40/60% w/w) mixture, at 298 K.

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REFERENCES

1. I.M. Papisov, V.A. Kabanov, Y. Osaba, Vysokomolek. Soedin., **A14**, 2462 (1972)
2. A.D. Antipina, V.Y. Baranouskii, I.M. Papisov, V.A. Kabanov, Vysokomolek. Soedin., **A14**, 941(1972)
3. Y. Fergusen, C. Mcleod, Eur. Polym. J., **10**, 1083(1973)
4. K. Abe, H. Ohno, E. Tsuchida, Makromol. Chem., **179**, 2285 (1977)
5. R.L. Darcus, D.O. Jordan, T. Knucsen, M.L. Martin, J. Polym. Sci., Polym. Chem. Ed., **3**, 1941(1965)
6. T. Takagiski, N. Kuroki, J. Polym. Sci., Polym. Chem. Ed.,**11**,1889 (1973)
7. I.M. Klotz, K. Shikama, Arch. Biochem. Biophys., **123**, 551(1968)
8. D.W. Koetsier, G. Challa, Y.Y. Tan, Polymer, **22**, 1709(1981)
9. R.L. Benoit, C. Louis "*The Chemistry of Non-aqueous Solutions*", Academic Press, New York 1978
10. I. Katime, J.R. Quintana, Eur. Polym. J., **24**, 775(1988)
11. J.R. Quintana, I. Katime, J. Chem. Soc., Faraday Trans. 1, **82**,1333 (1986)
12. I. Katime, J. Quintana, C.Strazielle, Makromol. Chem., **187**,1441 (1986)
13. I. Katime, J.R. Quintana, R. Valenciano, C. Strazielle, Polymer, **27**, 742 (1986)

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