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Preferential sorption of polyvinylpyrrolidone (PVP) in the binary solvent mixture water/DMF

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ABSTRACT

In this paper we have studied the behaviour of polyvinyl pyrrolidone (PVP) in the water(1)/DMF(2) binary mixture by differential refractometry and laser light scattering. No inversion has been found on the preferential sorption: the water is adsorbed on polyvinyl pyrrolidone over the whole composition range.

INTRODUCTION

When a polymer is dissolved in a binary liquid mixture, usually one of the liquids preferentially solvates the polymer. Systematic work on polymers in binary solvent mixtures was only started a few years ago(1-3). These systems present theoretical and experimental problems of various kinds, some of them similar to those for single solvents, and other specific of ternary systems, such as preferential sorption, unperturbed dimensions variation, conformational transitions, etc.(4-8). Earlier work(9) on these ternary systems has indicated that the behaviour of polymer in a mixed solvent is influenced largely by the thermodynamic properties of the binary liquid mixture. Preferential solvation investigations provide valuable informations about the interactions of the components of the solvent with the polymer and the dimensions of the macromolecules in solution. In the present paper, the behaviour of polyvinylpyrrolidone in the very polar binary mixture water/DMF is examined.

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EXPERIMENTAL PART

Samples. All polyvinylpyrrolidone samples were from Janssen Chimica. Molar masses determinations by membrane osmometry (MO), laser light scattering (LLS) and gel permeation chromatography (GPC) are shown in Table 1.

Table 1. Characterization of PVP samples used in this work

Polymer	$M_w x 10^{-4}$ g.mol^{-1} LLS	$M_n x 10^{-4}$ g.mol^{-1} MO	M_w/M_n GPC
PVP-1	36.0	30.0	1.20
PVP-2	4.0	3.4	1.19
PVP-3	1.5	-	

Liquids. DMF (Merck p.a.) was purified and distilled before use, by standard methods(10). The binary mixtures were prepared by volumetry, their compositions corresponding to their volume fractions before mixing. We assign the subscript 1 to water and 3 to the polymer.

Laser light scattering. Laser light scattering measurements were in a modified FICA P.G.D. 42,000 instrument at 298 K, equipped with a Spectra Physics Helio-Neon laser emitting at 633 nm with a power of 17 mW. The solutions and the pure liquids were clarified by centrifugation at 14,000 rpm for 1.5 hr. The results were evaluated by the extrapolation method of Zimm(11). The photogonioduffusometer was calibrated with benzene.

Refractive index increment. The specific refractive index increment of PVP with concentration (dn/dc_2) with respect to the binary mixture composition was determined with a BP-2000 Brice-Phoenix differential refractometer at 298 K equipped with a Helio-Neon laser as already specified(12). In Figure 1 we can see the variation of dn/dc as a function of % DMF in the solvent binary mixture. The instrument was calibrated using standard KCl solutions(13). The refractive indices of the pure liquids and their mixtures were determined with an Abbé refractometer at 298 K.

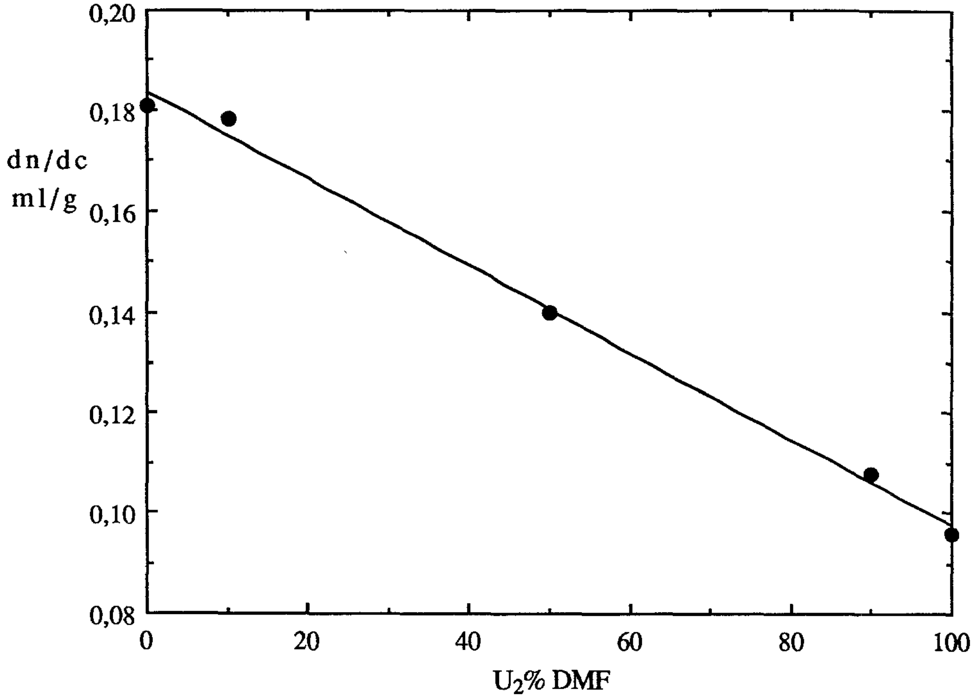


Figure 1. Variation of dn/dc of polyvinylpyrrolidone as a function of % DMF in the solvent binary mixture.

Membrane osmometry. The number-average molar mass, M_n, of polyvinylpyrrolidone was measured in methanol solution with a Knauer osmometer using membranfilter Gottingen Allerfeinst and S-S08 Carl Schleicher and Schuell membranes. The membrane conditioning was carried out by using mixtures of water/methanol.

The following equation was used to calculate M_n(14):

$$\frac{\pi}{c_2} = \frac{RT}{M_n}(1 + A_2^* c_2 + \cdots\cdot) \qquad (1)$$

where A_2^* is the apparent second virial coefficient. Yamakawa (15) showed that for low concentrations of the second solvent a simple relation ecists between true and apparent values:

$$A_2 = A_2^* \frac{M_w^*}{M_w} \qquad (2)$$

RESULTS AND DISCUSSION

From laser light scattering it is possible to determine the preferential sorption coefficient, λ, by the expression(16):

$$\lambda = [(\frac{M^*}{M})^{1/2} - 1] \frac{dn/dc_2}{dn/d\Phi_2} \qquad (3)$$

where M* is the apparent molar mass of the polymer determined in the water/DMF binary mixture and M is the real molar mass of the polyvinyl pyrrolidone determined in various single solvents. The extrapolation method proposed by Zimm has been used in all cases for molar mass determinations. dn/dc_2 is the specific refractive index increment of the polymer in the binary mixture at constant composition, obtained using a Brice-Phoenix diferential refractometer at a wavelength of 633 nm and $dn/d\Phi_2$ is the variation of the refractive index of the binary solvent mixture with the composition.

From figure 2 it can be seen that the preferential sorption coefficient, λ, does not remain constant but changes as the composition of water-DMF binary mixture vary.

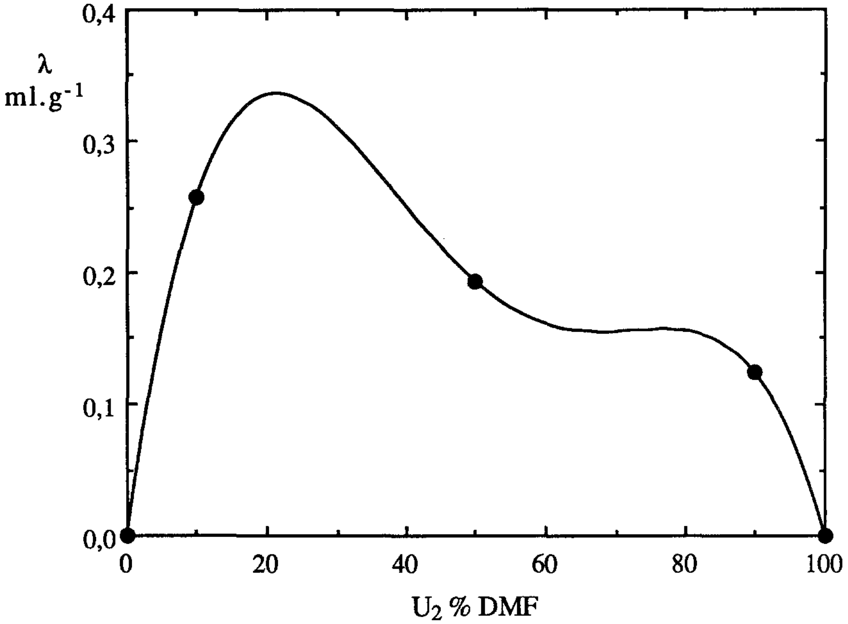
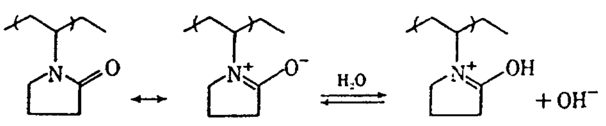


Figure 2. Variation of preferential sorption coefficient, λ, as a function of % water.

At Φ_2 = 10% DMF, preferential sorption coefficient reach the absolute maximum value. As can be seen in the whole composition range is always the water the solvent adsorbed into the macromolecular coil. This behaviour means that the polyvinylpyrrolidone prefers to interact more with water than DMF may be due to the more polar character of water and for the possibility to form hydrogen bonds. The amphipatic nature of the polymer is responsible for the high binding capacity. This can explain the higher value of preferential sorption coefficient of polyvinyl pyrrolidone at the composition Φ_2 = 90% water. On the other hand, the excess Gibbs free energy, G^E, for mixtures of water with organic liquids is, in general, positive and high. This means that both components are incompatibles and prefers interact with himselfs. The adition to water of any molecules containing inert groups such as CH_3- (methylene) must reduce the total number of hydrogen bonds, even if the inert group is itself attached to a highly polar group such hydroxil OH. Takagishi et al.(17) has showed that the polyvinylpyrrolidone in aqueous solutions behaves as:



If this mechanism is true, it is possible to understand the high values of preferential sorption coefficient found for this system.

The dimensions of polyvinylpyrrolidone are influenced largely by the thermodynamic properties of the binary liquid mixture. In Figure 3 we have plotted the variation of the mean square radius of gyration, R_g, with binary mixture composition. As can be seen there is an initial decrease of R_g between 0% and 18% DMF. As the DMF proportion increases above 18% methanol, we can observe again an increase of R_g. The maximum is obtained at 60% DMF. At that point another decrease is observed in R_g.

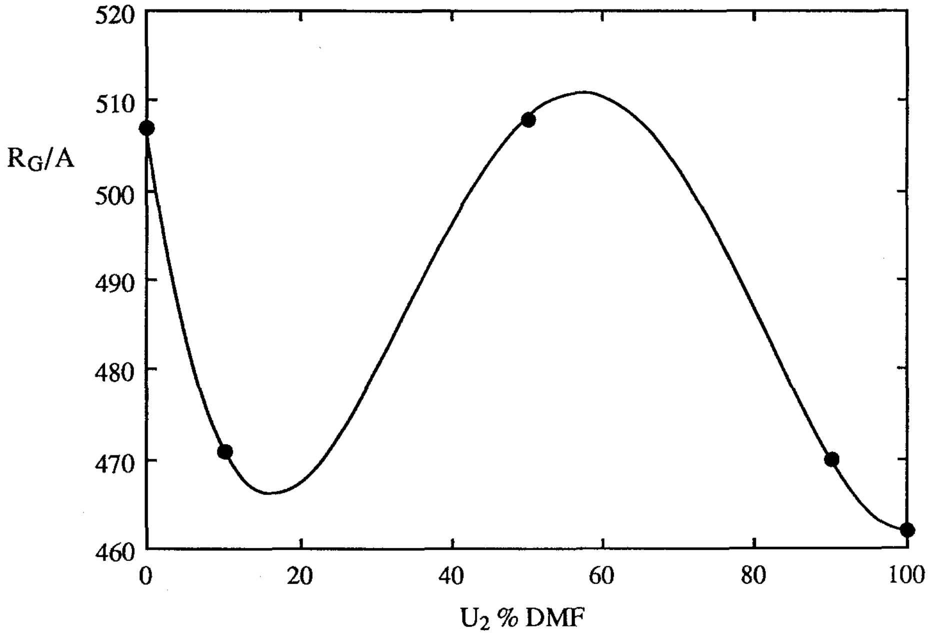


Figure 3. Variation of mean square radius of gyration, R_g, of poly vinyl pyrrolidone as a function of percentage of DMF.

Figure 4 shows the variation of second virial coefficient, A_2, with composition of DMF. As can be seen, A_2 remains constant in the interval $10 < U_2 < 90\%$ DMF. This behaviour can indicate that in this composition interval the polymer-binary solvent intermolecular interactions remains constant.

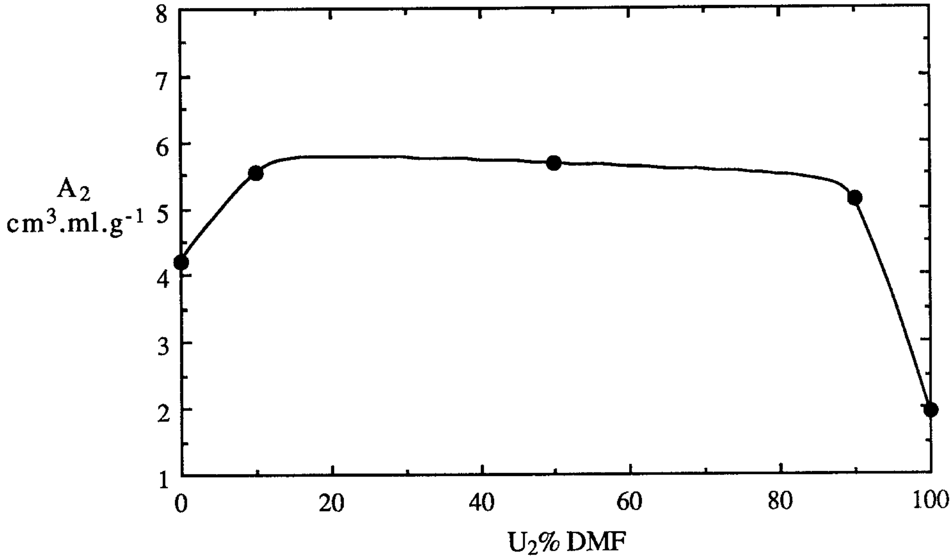


Figure 4. Variation of second virial coefficient, A_2, of polyvinyl pyrrolidone as a function of percentage of DMF.

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