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Investigations of aqueous solutions of dextran–poly(ethylene glycol) and dextran–poly(vinyl pyrrolidone) near the binodial curve

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The dependences of the refractive indices of aqueous solutions of dextran (D), poly(ethylene glycol) (PEG), and poly(vinyl pyrrolidone) (PVP), and D–PEG and D–PVP mixtures, on the polymer concentration has been investigated in order to study structural and conformational changes as a function of the increasing polymer concentration. It is shown that in contrast to solutions of single polymers, conformational changes are not observed in aqueous solutions of mixed polymers, even at high concentrations, and the phase separation which is observed is due to a change of structure or state of the water. We have determined the rates of the processes of the phase separation in these aqueous biphasic polymer systems. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Polymer solutions attract widespread attention not only because of their widespread practical use, but also in view of the theory of compatibility (mutual dissolution) of polymers being highly viscous liquids in the amorphous state[1,2]. The high viscosities of polymer liquids makes the achievement of the equilibrium in such systems difficult, and macroseparation does not occur in polymer mixtures even when the mixture is really a two-phase system, or its separation is brought about thermodynamically.

We note that a nucleation of the second phase occurs in any system long before aspects of the phase transition appear. This assumption should also be valid in the case of mixed polymer solutions where one would expect corresponding changes in the supermolecular structure of the solution at concentrations lower than the limit of mutual dissolution[3].

For the purposes of studying the separation mechanism of polymer mixtures in aqueous media, the two-phase aqueous polymer systems, D–PEG and D–PVP were investigated by Zaslavsky and coworkers[4–6]. They proposed the hypothesis that phase separation of an aqueous polymer system occurs as a result of a change of structure or state of the water under the effect of these polymers[6].

Aqueous solutions of organic and inorganic compounds, as well as polymer solutions, are one of the main subjects of refractometric studies[7]. Investigations with dilute solutions have shown that ideal solutions obey the mixing law, i.e. the refractive indices can be calculated according to the additivity law from the component refractions[8]. However, while investigating more concentrated solutions, researchers have observed deviations from ideality, and thus deviations from the additivity principle are also expected. Taking into account the above concentrations, aqueous solutions of dextran, poly(ethylene glycol) and poly(vinyl pyrrolidone), and mixtures of these polymers in aqueous media, have been investigated by refractometry in order to confirm the above hypothesis. In an aqueous medium of two polymers, phase separation takes place over a short period of time when compared to other solvents[9]. The aim of this present work was to investigate the state of the aqueous polymer solutions of D–PEG (I) and D–PVP (II) near the binodial curves, and by employing the empirical relationship we have attempted to calculate the rates of the processes of phase separation.

EXPERIMENTAL

Materials

The polymers used were dextran-70 ($M_w = 57\,200$, $M_n = 28\,400$; Minmedprom, Moscow; lot 680480), poly-(vinyl pyrrolidone) (PVP) ($M_w = 12\,700$; Minmedprom,

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Moscow; lot 135-84) and poly(ethylene glycol) (PEG-20 000) (M_n ca. 20 000; Serva Fine Biochemicals, Heidelberg; lot 419-80). The water used in the experiments was doubly distilled in quartz vessels.

Methods

Method for the determination of phase separation points. Stock aqueous solutions of the polymers were made up by weight (polymer concentration expressed as wt of polymer (g) per 100 g of solution, i.e. wt%). Stock solutions of the two polymers were mixed to provide a given polymer concentration ratio. A known amount of water was added and the whole was mixed thoroughly. After each addition, the system, after mixing, was centrifuged for 30 min at 1200 g in order to determine if the system was in the two-phase state. The first appearance of a clear solution indicated that the system was about to enter the single-phase condition. With a knowledge of the polymer concentrations of the initial mixtures and the amount of water added, the point on the binodial curve could be determined.

We next determined the total concentrations required for phase separation to occur (total critical points $C_{\Sigma c}$) in the aqueous mixtures of the polymers D and PEG (system I), i.e. $C_{\Sigma c}^I = C_c^D + C_c^{PEG}$ and D and PVP (system (II), i.e. $C_{\Sigma c}^{II} = C_c^D + C_c^{PVP}$; C_c^D and C_c^{PEG} are the concentrations of D and PEG required for phase separation to occur in the D–PEG system, while C_c^D and C_c^{PVP} are the concentrations required for phase separation to occur in the D–PVP system. The critical points of the polymers in the aqueous mixtures were determined at five different temperatures.

Refractometric method. The refractive index measurements were made at wavelengths of 436 and 546 nm, by using an IRF-23 refractometer (LOMO, St. Petersburg, Russia). In some of the experiments, the aqueous dextran solutions were investigated by polarimetry, using a Polamat-A instrument (Carl-Zeiss Yena, Germany), with $(\alpha)_D = 212°$. All experiments were carried out at a temperature of 23°C. The total concentration of the polymers in the aqueous D–PEG mixtures was taken as $C_{\Sigma_i} = C_{D_i} + C_{PEG_i}$, with C_{PEG_i}/C_{D_i} being kept constant for each measurement. Similarly, for the aqueous D–PVP mixtures the total concentration of the polymers was taken as $C_{\Sigma_i} = C_{D_i} + C_{PVP_i}$, and for each measurement C_{PEG_i}/C_{D_i} was also kept constant.

RESULTS AND DISCUSSION

This paper is based on the assumption that polymer solvent interactions cause changes in the structure of aqueous biphasis polymer systems. It is known that the determining factor of phase incompatibility in the polymer mixtures is the result of two different structures of water solvent, which differ from each other in behaviour as well as in energy of hydrogen connection[6]. These structures are a result of interaction of macromolecule polymers with water molecules, and even if there is a non-essential difference in interaction energies then this polymer mixture is layered in two phases.

Taking into account the importance of the energy of the systems we have calculated an energy parameter, which characterizes the rates of the processes of

separation in aqueous biphasic polymer systems. On the basis of a modified Arrhenius equation, we suggest that for aqueous biphasic polymer systems the following relationships apply:

$$C_{\Sigma c}^I = A \exp(-E^I/KT)$$

and

$$C_{\Sigma c}^{II} = A \exp(-E^{II}/KT) \qquad (1)$$

where E^I and E^{II} are energy parameters which characterize the rates of the processes of phase separation for aqueous mixtures of D and PEG, and D and PVP, respectively, $C_{\Sigma c}^I$ and $C_{\Sigma c}^{II}$ are the total polymer concentrations required for phase separation to occur in systems I and II, respectively, T is the temperature of the system and K is the molar gas constant.

The total concentrations of the polymers required for phase separation to take place in these systems at various temperatures are given in *Table 1*. The data in this table indicate that an increase in the temperature of the system increases the total polymer concentration required for phase separation to occur, i.e. decreases the polymer incompatibility in the D–PEG and D-PVP aqueous solutions.

By using this temperature effect on the phase separation in these systems and equation (1) we can calculate the rates of the processes from *Figure 1*, and obtain values of E of 0.92 and 1.15 kJ mol^{-1} for the D–PEG and D–PVP systems, respectively. These results show that the rate of the process of phase separation for the aqueous system I is slower than that of aqueous system II.

Therefore, the component polymers of system I are thermodynamically much more incompatible, than those of system II, and hence for this system to acquire a structure which corresponds to a phase separation a smaller amount of energy is needed (cf. system II). In the latter system, the fact that more energy of interaction of the polymers with water is needed led to structure differences in the interphase region. In these systems one may neglect the interactions of the component polymers[3,5,6], and hence the deciding factor for phase separation is the interaction between the polymers and water.

It is known that the relative hydrophobicity of the polymers being studied in this work decreases in the following order: PEG > PVP > D[10-12]. The relative polarity of PVP clearly exceeds those of the other polymers[13]. (It should be noted here that by the term 'relative polarity' we mean the relative capacity of the solute to participate in dipole–dipole interactions with water.) The relatively smaller E^I value for the aqueous biphasic D–PEG systems can be related to the relatively

Table 1 The total D–PEG and D–PVP concentrations required for phase separation to take place in aqueous mixtures of the polymers at various temperatures

$C_{\Sigma c}^I$ (mol kg^{-1})	$C_{\Sigma c}^{II}$ (mol kg^{-1})	T (°C)
1.4816	1.8669	10
1.5485	2.0331	23
1.5983	2.0510	30
1.6481	2.1790	38
1.6663	2.1625	52
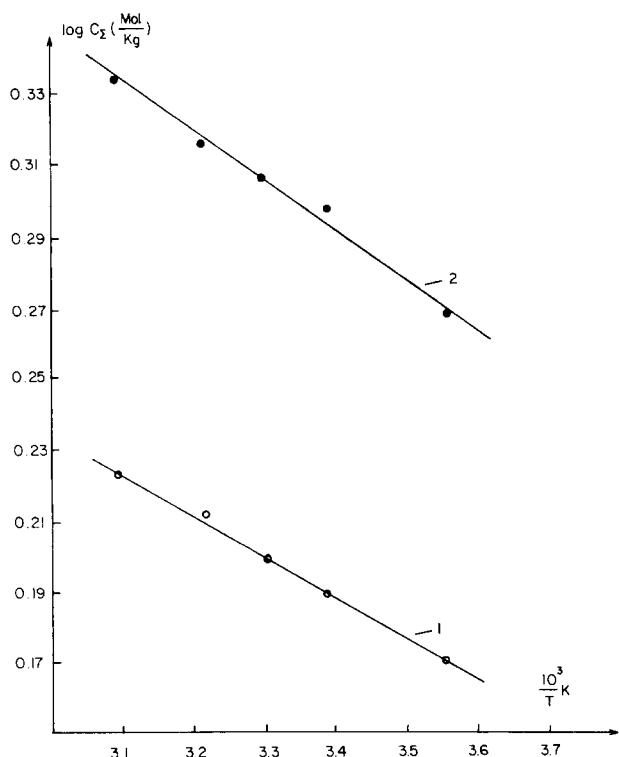
Figure 1 Plots of the logarithm of the total polymer concentration required for phase separation to take place in the aqueous polymers mixtures D–PEG (1) and D–PVP (2) as a function of the reciprocal temperature

high hydrophobic character of PEG, while the higher E^{II} value for the aqueous biphasic D–PVP system can be related to the highly polar character of PVP. Thus, the relatively high value of E^{II} for the latter biphasic system can result from strong connections between the carbonyl group of the PVP and a molecule of water, as follows:

$$>C=O \cdots H–O–H \quad \text{or} \quad >N \cdots H–O–H$$
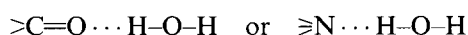
In other words, in order to bring the structure of the water in this system to one which corresponds to conditions of phase separation, higher energy is required.

The experimental results obtained from refractometry investigations on the component polymers yield the dependences shown in *Figure 2*. As can be seen in this figure, the concentration dependence of the refractive index is linear in all cases, even at high polymer concentrations, and gives the following:

aqueous D solution: $n_1 = 1.3335 + 1.55 \times 10^{-3} C_1$

$$(2)$$

aqueous PEG solution: $n_2 = 1.3334 + 1.54 \times 10^{-3} C_2$

$$(3)$$

aqueous PVP solution: $n_3 = 1.3332 + 1.43 \times 10^{-3} C_3$

$$(4)$$

where n and C are, respectively, the refractive index and concentration, and the subscripts 1, 2, and 3 refer to dextran, PEG and PVP, respectively. The correlation coefficient (R) was 0.999 for all of the experiments.
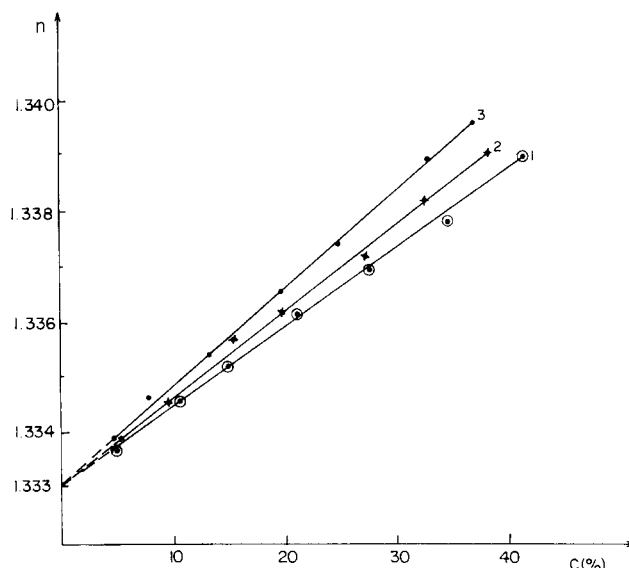
Figure 2 Dependence of the refractive index on polymer concentration for aqueous solutions of: (1) D; (2) PEG; (3) PVP
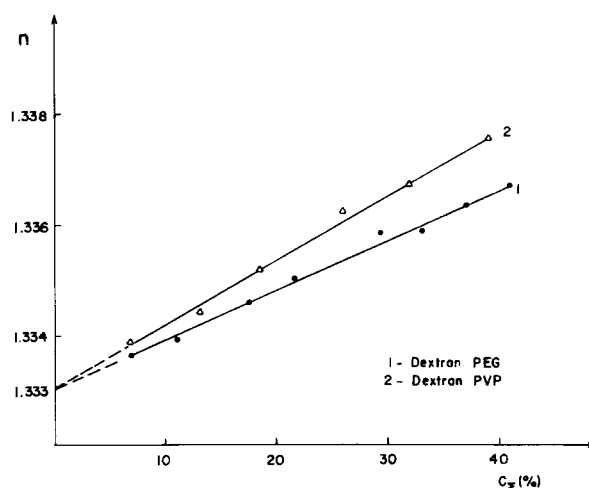
Figure 3 Dependence of the refractive index on total polymer concentration for aqueous polymer mixtures of D–PEG (1) and D–PVP (2)

These data indicate that in solutions of the above polymers no structural changes occur in the regions under study. For dextran solutions this was confirmed by a polarimetric method. Similar experiments were carried out for the two polymer mixtures, D–PVP and D–PEG, near the binodials in aqueous media, at fixed C_{PVP}/C_D and C_{PEG}/C_D concentrations. The results obtained are shown in *Figure 3*. As can be seen in this figure, as in the case of solutions of the component polymers, the refractive index depends linearly on the polymer concentration, and no conformational changes or interactions between the polymers occur, i.e. the additivity principle is retained. The following values for the refractive indexes were obtained:

PEG–D: $n^I = 1.3332 + 2.5 \times 10^{-3} C_\Sigma^I$ $\quad\quad (5)$

PVP–D: $n^{II} = 1.3339 + 1.31 \times 10^{-3} C_\Sigma^{II}$ $\quad\quad (6)$

where n and C_Σ are, respectively, the refractive index and total polymer concentration in the aqueous mixtures,

and the superscripts I and II refer to the D–PEG and D–PVP systems, respectively.

The results obtained in this study show that in the aqueous D–PEG and D–PVP mixed polymer solutions no associates are formed, even at high concentrations (near the binodial curves of the systems studied) between the polymers and hence one may neglect any interactions of these components. Phase separation in these aqueous polymer systems is the result of the occurrence of two different, co-existing, but mutually immiscible water structures which are formed by the effect of each of the phase-forming polymers on the structure and or the state of the water in the solution. We suggest, therefore, that the previously proposed hypothesis of Zaslavsky *et al.* is confirmed

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