

THE EFFECT OF MOLECULAR WEIGHT OF POLYMERS AND SOME MONOHYDRIC ALCOHOLS TO PHASE DIAGRAM OF TWO-PHASE SYSTEM DEXTRAN-POLYVINYLPIRROLIDONE-WATER

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In this paper, we investigated the effects of some monohydric alcohols (methanol, ethanol, propanol) on the phase diagram of the aqueous two-phase system. PVP-dextran-water and the influence of the molecular weight PVP on the phase separation of the aqueous two-phase system of dextran-PVP was investigated. It was found that the phase diagram of binodals in the presence of methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) the binodals are mixed in the direction of increasing the heterogeneous region of the phase diagram. The results can be explained as follows: The phase forming components of the system, and PVP and the dextran, to some extent structure the water. With the presence of alcohols, their hydroxyl groups entering into a hydrogen bond with water molecules to some extent destroys the structure of water, which leads to an improvement in the compatibility of the phase-forming components.

Keywords: water-two-phase system, dextran, polyvinylpyrrolidone, monohydric alcohols, phase separation.

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As is known, when mixing aqueous solutions of two polymers at certain concentrations of components, the mixtures split into two liquid phases. This phenomenon was first observed in [1]. In the future it became known that there are also other pairs of polymers that are thermodynamically incompatible in one common solvent (water) and above certain concentrations of these polymers the systems are divided into two phases [2]. Studies of water-soluble polymers in a common solvent confirmed that phase separation in polymer mixtures in water is a common phenomenon [3] and the solvent in both phases is water, while its content in each phase can be 70 or more percent, and each of the phases System is enriched with one of the polymers.

For the first time, aqueous two-phase systems formed by two incompatible pairs of polymers were systematically investigated by Albertson, the results of which were presented in the form of a monograph [5]. The method of nonuniform distribution of matter in two-phase aqueous-polymer systems, which was used in [5], allowed separation and purification of biological materials of different nature (proteins, nucleic acids, cellular organelles, viruses, bacteria, etc.).

Swedish researcher Albertson [2] for the first time has extensively investigated polymer-polymer-water two-phase systems with water solubility, and has demonstrated their capability to study medicine, pharmacology and biotechnology. It was revealed that, when solubilizing biological substances such as proteins, nucleic acids, viruses, etc. in two-phase systems, these substances are distributed unequally between the phases in the equilibrium. Since water is the basis of both phases of water-polymer systems, these systems allow for the soft separation of particles while maintaining the natural properties of weakly-denatured biological substances.

It should be noted that polymers incompatibility in the same solvent there have been conflicting

opinions in the scientific literature for a long time and are still encountered. Some authors highlight the role of system-forming components (polymers) in the solvability of the system if the mixtures of the two polymers in any solvent form a two-phase system, then this process should also be observed in the mixing of solutions with other solvents. However, recently analyzing the contradictions between the results of scientific research done in this area by E. Masimov, B.Zaslavski and others, [9-11] hypothesis that water plays a key role in the formation of two-phase water-polymer systems and in these system insoluble in each other, the presence of two different structures water [12]. This hypothesis has been repeatedly confirmed by the authors and many other researchers.

To investigate two-phase systems, P. Albertson used a phase diagram (containing binodal curves, connecting lines, their lengths, and angles) to represent the polymeric components of the system.

Processes in two-phase systems for a complete, systematic analysis it is important to study the effects of a number of external factors — temperature, molecular weight of the polymer, and the effects of various additives on the physical and chemical properties of the system.

Recently, aqueous two-phase polymer-water-salt systems have been widely used for separation and purification of various substances and fractionation of high-molecular compounds. As salts use both inorganic and organic salts. Such systems are characterized by a relatively high rate of separation and a significant cheapness of the materials used. The role of the study of aqueous two-phase systems and the method of distribution of substances in such systems has increased significantly after the possibility of this method was demonstrated in [6] for evaluating the relative hydrophobicity of aqueous solutions of various substances, a very important parameter that determines the stratification process

and also the possibility of directed control of the separation. The ability of these aqueous two-phase systems (polymer-polymer-water, polymer-salt-water).

According to the recently developed concept of the origin and separation properties, determined by the difference properties of the coexisting phases of the water two-phase systems, the differences in the water structure of the equilibrium phases of the system are.

Since the water in such complex systems is influenced by many factors (temperatures, the nature of the phase-forming components, various additives, the molecular-mass distribution of the polymer component of the system, etc.) to study the influence of these factors, individually or jointly, on the water structure. And, accordingly, on the properties of aqueous two-phase systems is very important for understanding the mechanism of phase separation of the system into two phases and controlling the

separation ability of such systems. For the description of aqueous two-phase systems, it is customary to use phase diagrams (binodal curves, line connectors, etc.) of these systems where the ordinate axis contains the content of one polymer (in weight concentrations), the abscissa of the content of another polymer or salt. Of great importance is the study of the influence of various substances on the phase diagrams of aqueous two-phase systems, both from a practical and theoretical standpoint. We have studied the effects of some monohydric alcohols (methanol, ethanol, propanol) on the phase diagram of the aqueous two-phase system PVP-dextran-water). The results are shown in Fig1. As follows from the figures in the presence of methanol (CH₃OH), ethanol (CH₃CH₂OH) and propanol (CH₃CH₂CH₂OH) the binodals are mixed toward the increase in the heterogeneous region of the phase diagram.

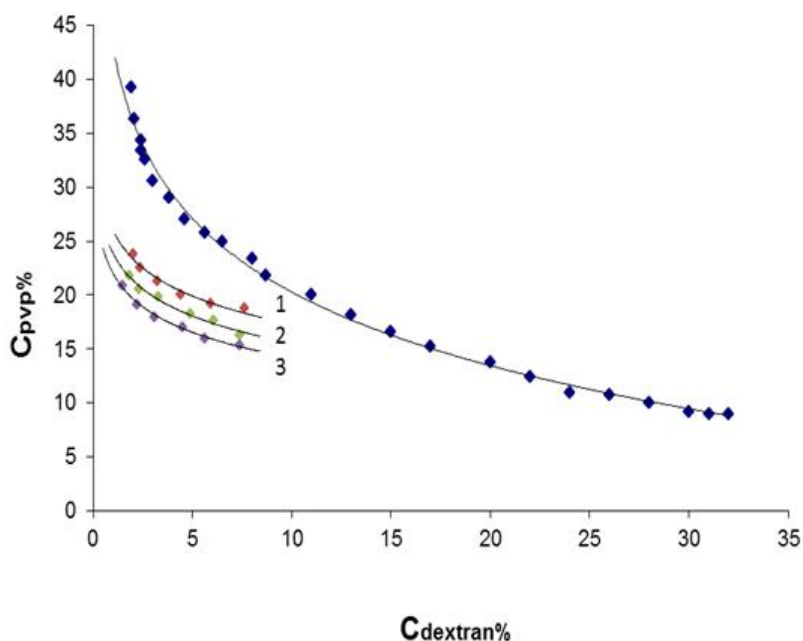


Fig.1. Influences of some alcohols on the phase diagram of the two-phase system PVP-dextran-water (basic binodal, 1-methanol, 2-ethanol, 3-propanol).

The results can be explained as follows: The phase forming components of the system, and PVP and the dextran, to some extent structure the water. With the presence of alcohols, their hydroxyl groups entering into a hydrogen bond with water molecules to some extent destroys the structure of water, which leads to an improvement in the compatibility of the phase-forming components. However, hydrophobic functional groups of alcohols naturally structure water, reducing the exchange frequencies between water molecules. Connected with molecules of alcohols and between bulk water molecules.

This process leads to a deterioration in the compatibility of phase-forming components. The first of these processes, the occurrence of hydrogen bonds between hydroxyl groups of alcohols and water molecules, destroying the structure of water, leads to

an improvement in the compatibility of the phase-forming components, and the second process due to the hydrophobic hydration of the non-polar functional groups of alcohols leads to a deterioration in the compatibility of the phase-forming components of the two-phase system. In the competition between these two processes, as shown by the results of the experiments, the influence of hydroxyl groups of alcohols, which first destroys water structures, prevails first, then with the increase in hydrophobic groups of alcohols, the influence of these groups compensates for the effects of OH groups and further exceeds the effects of a single hydroxyl group of alcohols.

In the next step of work the physical-chemical properties of the dextran-polyvinylpyrrolidone-water two-phase system were studied. Polymers selected as research objects-dextran and polyvinylpyrrolidone

widely used in medicine, and these polymers are water soluble.

Polyvinylpyrrolidone with a molecular mass of 12,000 is used as a blood substitute, 0.5% of polyvinylpyrrolidone aqueous solution is used as an antioxidant. Therefore, the study of two-phase polymer water systems with dextran and aqueous solutions of polyvinylpyrrolidone is very relevant. Here, the molecular mass of polyvinylpyrrolidone, and some sugars effect on dextran-polyvinylpyrrolidone-water two-phase system on the diagram have been investigated. In this work, were used polyvinylpyrrolidone produced by the German firm "Applichem" and dextran produced by Russia. The molecular mass of dextran is kept constant ($M_n \approx 70000$), and molecular masses of polyvinylpyrrolidone were used with fractions of 10000, 30000, 40000, and 54000. The binodal curves of each of these systems

are constructed by the known method [13], the inclination angles of the binodal connecting lines are determined, the results are shown in Figure 2. As you can see in the picture, as the molecular weight of polyvinylpyrrolidone increases, the binodal curve shifts to the beginning of the coordinate, the area of the heterogeneous region of the diagram increases. In other words, when the molecular weight of polyvinylpyrrolidone increases, phase separation (non-uniformity) results in smaller concentrations of components. As the molecular weight of binodal increases sliding to the beginning of the coordinate related to for an arbitrary point taken on binodals in a constant concentration of phase-forming components number of monomers ($-\text{CH}_2\text{-CHO}-$) per unit mass of solution regardless of the molecular mass despite being stable when the molecular mass is small the number of molecules will be greater.

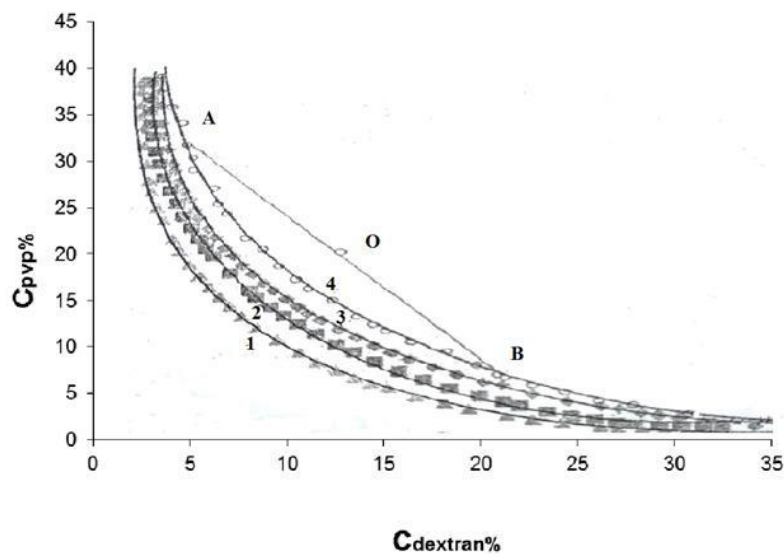


Fig. 2. Binodal curves and connecting lines for different molecular masses of dextran- polyvinylpyrrolidone-water two-phase system.

$M_n \approx 54000$; 2- $M_n \approx 40000$; 3- $M_n \approx 30000$; 4- $M_n \approx 10000$.

Small molecular mass polyvinylpyrrolidone molecules are more likely to hydrate, as a result, they are more conformed with its own water coverage. This formation decreases as the molecular weight of the polymer increases, and phase separation occurs at a smaller concentration of the polymer (binodal curve moves towards the beginning of the coordinate).

For the systems that were also investigated, is the dependence of the main characteristic of the two-phase system the angular coefficients of binodal connecting lines on the molecular mass of polyvinylpyrrolidone. For the polyvinylpyrrolidone molecular mass $M_n \approx 10000$, the mean value of the dextran-polyvinylpyrrolidone-water two-phase system connecting line is $\text{tg}\alpha_{BX} = -0.97$.

Thus, the effect of the molecular weight of the polymer on the process of phase separation in dextran-polyvinylpyrrolidone-water binodal systems has been investigated, and it has been shown that as the molecular weight of the polymer increases, phase

separation occurs at a smaller concentration of components. To explain this fact, we must note that under the influence of each of the phase-forming components in the water, the structure (state) of water in the system changes two different water structures are formed which is the core of the formation phases at greater value than the specified value of component concentration phase separation occurs. As the molecular mass increases, the number of water molecules in the hydrate layer of the polymer increases, the number of free water molecules in the system decreases and phase separation occurs more quickly. In the studied system, and also in the dextran-peg-water two-phase system influence of sugars on sucrose, glucose, maltose and others on the phase separation process. It is assumed that affected sugars does not affect the binodal curves of the systems in the studied concentration range. This fact can be explained by the fact that, one component of both systems is dextran, dextran is a polysugar and almost

screened the effects of other sugars. Thus, the results of the study confirm the hypothesis that water plays a

key role in the phase separation of polymer-water two-phase systems.

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