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The Properties of Water in Solutions of Hydrophilic Polymers

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Abstract—The properties of water in solutions of hydrophilic polymers were compared with those in solutions of their monomeric analogues. The properties of polar groups grafted to polymeric molecules were known to remain unchanged. A comparison of the properties of water in solutions of polymers and the corresponding monomers under equal conditions therefore allowed us to obtain information about the influence of polymeric bonds on the properties of water in solutions of polymers. Proceeding from this, we analyzed the influence of polymeric chains and three-dimensional polymeric network on the activity and concentration of water in solutions of polymers.

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INTRODUCTION

When hydrophilic polymers interact with water, they first swell and then in the majority of cases dissolve to produce solutions. However, fairly frequently, solution stops at the stage of swelling. This usually occurs because of the presence of bonds (cross-links) between polymeric molecules. These cross-links limit the distance between polymeric chains and therefore hinder solution. The natures of bonds can be different. These can be H-bonds, as, e.g., with polyvinyl alcohol [1], or covalent bonds, which cross-link polymers in ion-exchange resins and membranes [2]. H-bonds break as the temperature increases, and polymers dissolve. Covalent bonds withstand heating. Polymers cross-linked this way do not dissolve under any conditions.

In a water vapor atmosphere, all hydrophilic polymers adsorb water, but complete solution does not occur under these conditions. The amount of sorbed water (at constant temperature and pressure) depends on the nature of the polymer and relative vapor pressure; it is described by sorption isotherms. The sorption of water by cross-linked polymers is accompanied by the appearance of electrical conductivity [3, 4]. Since neither dry polymers nor water are conductors, the appearance of electrical conductivity can only be related to the dissociation of polymer polar groups. The appearance of electrical conductivity also shows that the sorption of water by a polymer is accompanied by the formation of one common volume; that is, a polymer swollen in water possesses all the necessary properties of a solution. In what follows, we call this system a polymer solution (PS). This is the state of polymers that is considered below.

Linear (not cross-linked) polymers are known to dissolve completely when placed in water, whereas, with cross-linked polymers, the degree of swelling increases. It was, however, shown in [5–7] that an increase in the degree of cross-linked polymer swelling was not related to changes in the concentration of polymer solutions. Swelling increases because of the formation of a new phase in polymers, the water phase or (generally) the external solution phase. The concentration of the polymer solution phase remains unchanged.

The properties of polar groups in polymers are almost indistinguishable from their properties in low-molecular-weight compounds (LMWCs) [8, 9]. It follows that a comparison of the equilibrium data on the LMWC–vapor and PS–vapor systems can be used to determine the contribution of polymer chain and three-dimensional polymer network effects on the amount and activity of water in PSs.

It follows from interphase equilibrium conditions that, if vapor pressures over two different solutions are equal, water activities in these solutions are also so. This leads us to suggest that, at a given vapor pressure, the activity of water and its concentration should be equal in a solution of a polymer and a solution of its monomeric analogue. A mere comparison of these values, however, shows them to be noticeably different.

The reason for such differences was analyzed in [10]. The suggestion was made that cross-linked polymer chains act on water between them like capillary walls. Water is therefore under the action of not only atmospheric but also capillary pressure. It was shown that, if the radius of the capillary was constant, the activity of water in the PS phase was related to the relative vapor pressure over the PS through water distribution constant K_d.

Since the degree of polymer swelling depends on the amount of the cross-linking agent, the influence of cross-linking on K_d was given special attention. It was found [11] that, for polyelectrolytes based on styrene with divinylbenzene (DVB) as a cross-linking agent,

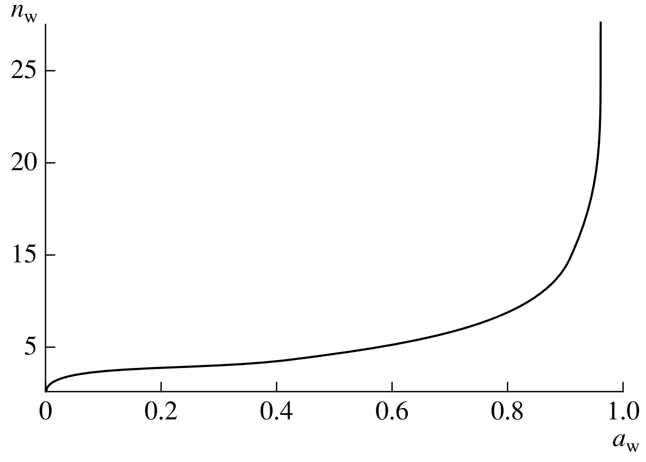

Fig. 1. Dependence of the specific amount of water (mol H_2O/mol LMWC) on the activity of water in solutions of LMWCs.

the constant value depended on the amount of DVB in the polymer. Subsequent studies of polymer swellability, however, led the authors to conclude that the amount of the cross-linking agent not always influenced the water distribution constant.

In this work, differences in the properties of water between solutions of polymers and monomers are explained by the influence of the nature of polymeric molecules. More exactly, by fixed distances between polar groups in polymer chains, which means that, when a polymer is brought in contact with pure water, there is a limiting minimum PS concentration, which does not change when the amount of water increases.

THEORY

An analysis of handbook data [12–14] shows that the dependence of the amount of water (n_w) on water activity (a_w) (or on relative vapor pressure p/p_0) in solutions of low-molecular-weight compounds, $n_w = f(a_w)$, is fairly general in character and S-shaped (Fig. 1).

The analysis showed that the equation that described the dependence of the specific amount of water in a solution on water activity had the form

$$n_w = G(a_w)F(a_w), \tag{1}$$

where F and G are some functions that describe the asymptotic behavior of n_w as $a_w \longrightarrow 0$ and as $a_w \longrightarrow 1$, respectively.

By the physical meaning of Eq. (1), the mechanisms of water interaction with the substance undergoing solution differ depending on the amount of water. Water molecules that first interact with this substance are known to get bound with it much more strongly and orientatively than subsequent molecules. As a result, the bond energy and orientation of the nearest molecules noticeably differ from the bond energies and orientations of the other molecules. The number of "the first" molecules depends on the nature of the solute and usually does not exceed several H_2O molecules per low-molecular-weight compound molecule. Subsequent molecules interact with the low-molecular-weight compound by another mechanism. They are oriented according to the scheme of dipole-dipole interactions around the dipole of the already hydrated substance. These differences explain the S-shaped dependence of the amount of water on the relative vapor pressure. To describe such a behavior of water, Eq. (1) is written in the form

$$n_w = \alpha(a_w)^{\beta}[\tan(a_w\pi/2)]^{\gamma}, \tag{2}$$

where α, β, and γ are some coefficients adjusted empirically using handbook data on the properties of solutions of the monomer. Equation (2) fairly well describes the curves that illustrate the influence of the activity of water on the concentration of solutions of such low-molecular-weight compounds as ethanol, ethylbenzenesulfo acid and its salts, and tetramethylammonium chloride, which are monomeric analogues of the polymers studied in this work.

The influence of polymer chains on the properties of water in PSs can be determined by comparing the specific amounts and activities of water in a PS and a solution of the corresponding low-molecular-weight compound under equal external conditions. Since the properties of the polar groups of a polymer do not differ from the properties of the corresponding monomer, equilibrium activities and component concentrations in solutions of the polymer and monomer should be equal under equal external conditions. It is, however, known that the concentration of a PS under these conditions is always higher than the concentration of a solution of the monomer; that is, the influence of polymer chains is quite obvious.

At equilibrium, the chemical potentials of water in these solutions are equal, and the activities of water are related via the water distribution constant K_d,

$$K_d = \bar{a}_w/a_w, \tag{3}$$

where $\bar{a}_w$ and a_w are the activities of water in the PS phase and a solution of the low-molecular-weight compound, respectively. The distribution constant is therefore a value that shows how the activity of water in a PS changes under the action of polymer bonds. Because of these bonds, there exists a limiting minimum concentration of the PS, which remains constant no matter how much water is added. This limiting concentration exists because of a fixed distance between polar groups in polymer molecules. This distance depends on the nature of the polymer and determines the minimum PS concentration.

Of course, the concentration of a solution of a polymer can be treated as the concentration of polymer chains. A solution of a linear polymer can have an arbitrary concentration. It, however, follows from the results of spectral, calorimetric, and other studies [15] that part of water in polymers swollen in water has activity equal to one, that is, the activity of pure water. Water in polymers is therefore divided into "free" and "bound." Bound water is related to the PS phase. This shows that a polymer swollen in water contains two types of water simultaneously. It follows that the determination of the concentration of a polymer as the concentration of polymer chains is incorrect. A solution of polymer chains is a two-phase system in the simplest case consisting of a PS and water. If the concentration of polymer chains is fairly high, such a mixture is called a gel.

Bearing this in mind, we arrive at the conclusion that the influence of polymer chains on the activity and amount of water in a PS should influence the curve that describes the relation between the concentration of water in the polymer and water vapor pressure over the polymer (this curve is the isotherm of water sorption by the polymer). On the one hand, this curve should be similar to the curve for the corresponding monomer, on the other, it should differ from it because the solution of a polymer has a certain minimum concentration at a water activity of one.

There are two possible variants of the behavior of such a curve.

According to the first variant, the polymeric framework does not influence the properties of polymer polar groups until it is fully stretched. The initial monomer and polymer curve portions then coincide, and this coincidence extends from zero to a certain vapor pressure value. The curve for the polymer then goes parallel to the abscissa axis until the $a_w = 1$ value is reached.

In the second variant, polymer chains influence the properties of water at arbitrary a_w values. The dependence for the polymer should then be related to the dependence for the monomer by some coefficient, which, in addition, predicts a certain n_w value at $a_w = 1$. As is known, the second variant is observed in practice.

The experimental isotherm of water sorption by a polymer and the dependence of water activity on the concentration of a solution of the corresponding monomer can be described by an equation of type (2) with an identical set of α, β, and γ coefficients if the influence of the polymer chain is taken into account. For instance, we can introduce the water distribution constant as an additional coefficient,

$$n_w = \alpha(K_d a_w)^\beta[\tan(K_d a_w \pi/2)]^\gamma. \quad (4)$$

By changing K_d in (4), we can bring the "theoretical" water sorption isotherm in coincidence with the experimental dependence and thereby determine K_d for a particular polymer.

EXPERIMENTAL

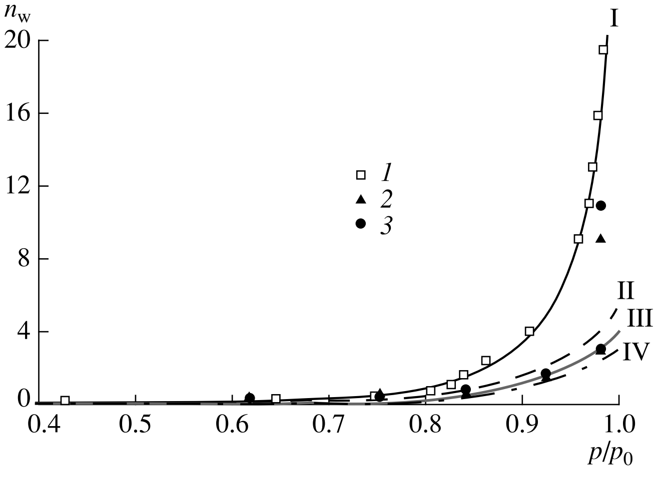

Fig. 2. Determination of water distribution constants K_d for PVA. Lines correspond to approximation by (4) at various K_d values; (*1*) found from the data [14, p. 350] and (*2, 3*) water sorption isotherms for PVA-10 and PVA-20 (respectively) determined in isopiestic experiments; K_d = (I) 1, (II) 0.93, (III) 0.91, and (IV) 0.89.

To check the correspondence of theoretical isotherms calculated according to (4) to experimental isotherms of water sorption and desorption, we performed a series of experiments by the isopiestic [16] and dynamic desorption porosimetry (DDP) [15, 17] methods. These methods were used to obtain water sorption (desorption) isotherms for several polymers at atmospheric pressure and 298 K.

Calculations and the construction of theoretical water sorption isotherms at various K_d values were based on the literature data on the dependence of the specific amount of water on its activity in solutions of the corresponding monomers. Ethanol was selected as a monomeric analogue of polyvinyl alcohol (PVA), ethylbenzenesulfo acid and its salts, as monomeric analogues of strongly acid cationites based on styrene cross-linked with divinylbenzene, and tetramethylammonium chloride, as a monomeric analogue of the chloride form of strongly basic anionites also based on styrene and divinylbenzene.

At the first stage, we studied the swellability of cross-linked PVA in a water vapor atmosphere. Cross-linked PVA was prepared by cross-linking linear PVA with epichlorohydrin as described in [18]. This procedure was used to synthesize two polymers, PVA-10 and PVA-20 (10 and 20 wt % epichlorohydrin in the initial mixture for cross-linking). The isotherms of water sorption for PVA-10 and PVA-20 were obtained by the isopiestic method. The corresponding experimental data are shown in Fig. 2.

According to Fig. 2, neither the method for obtaining the isotherms (sorption or desorption) nor the amount of the cross-linking agent influences the specific sorption of water by this polymer. For all these cases, one common curve was obtained, which was evidence that only the relative vapor pressure influenced the sorption of water from vapor by this polymer.

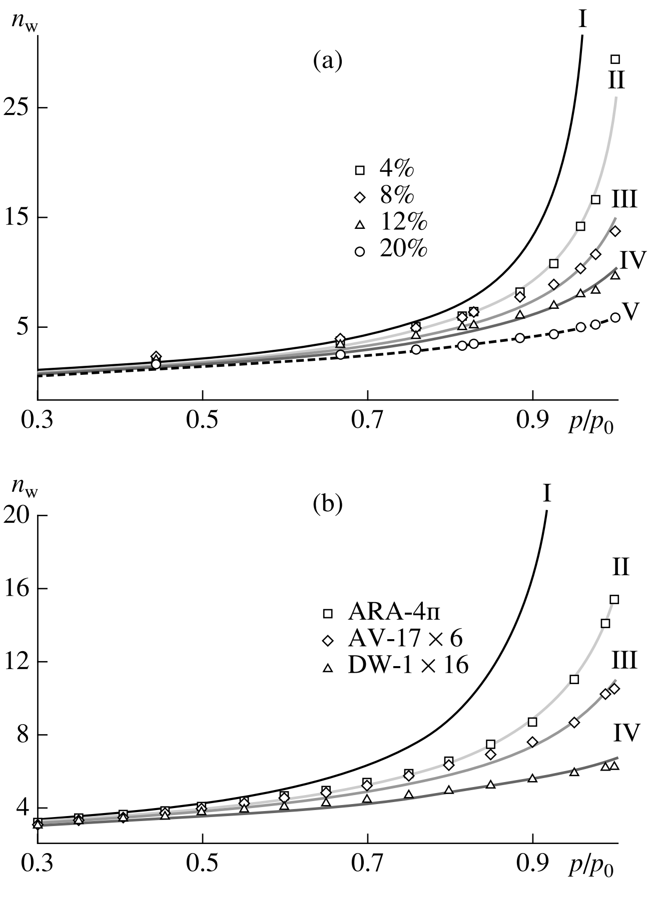

Fig. 3. Determination of water distribution constants K_d for (a) polystyrene–sulfo acid and (b) polystyrene–trimethylammonium chloride with different degrees of cross-linking. Lines correspond to approximation by (4) at various K_d values: (a) (I) 1, (II) 0.95, (III) 0.91, (IV) 0.87, and (V) 0.77 and (b) (I) 1, (II) 0.89, (III) 0.84, and (IV) 0.72. (a) Water sorption isotherm values according to [19] and (b) values determined by the DDP method.

Handbook data on the activity of water in solutions of ethanol [14, p. 350] were substituted into (2) to determine the α, β, and γ coefficients. The coefficients obtained this way were $\alpha = 3.33$, $\beta = 8.51$, and $\gamma = 0.51$. Next, we used these values to construct a curve for a solution of the monomer (Fig. 2).

Various K_d values were substituted into (4) to find that the theoretical isotherm with $K_d = 0.91$ corresponded to the experimental curve.

We studied the sorption of water from vapor by polyelectrolytes based on polystyrene cross-linked by DVB with different cross-links and different types of polar groups. The isotherms are shown in Fig. 3. It is clearly seen that the specific sorption of water was influenced by both the amount of DVB in the polymer and the type of polar groups in the ionites. The coefficients and constants calculated for these isotherms are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

The results show that, in all instances, the $n_w = f(a_w)$ dependences for solutions of monomers and the isotherms of water sorption by the corresponding polymers are interrelated. This relation is described by the water distribution constant K_d and extends over the whole interval of vapor pressures studied. We see that the concentration of PSs is always higher than the concentration of solutions of the corresponding monomers under equal external conditions.

It was found that the specific amount of water sorbed by PVA only depended on vapor pressure and was independent of the presence of cross-links. The concentration of PVA solutions was higher than the concentration of solutions of ethanol, which is a monomeric analogue of PVA, under the same conditions. This difference can be explained by the influence of polymer chains or, more exactly, the influence of a fixed distance between polar groups in polymer molecules. In addition, the concentration of a PS is influenced by the molecular weight of the polymer. Because of a large molecular weight, polymer chains act on water molecules situated between them like capillary walls, that is, influence the external pressure value.

For this reason, the standard chemical potential of water in a PS differs from the standard chemical potential of water under usual conditions. As a result, the activity and concentration of water in a PS differ from the corresponding values in usual solutions at equal vapor pressures [10].

Importantly, the properties of water in PSs remain unchanged when polymers are sank into water or aqueous solutions rather than surrounded by water vapor. This means that just the polymer framework influences the activity of water in PSs. It is its influence that decreases the external pressure on this phase. We call this effect the polymer effect by analogy with the capillary effect.

Table 1. Coefficients of Eq. (2) for solutions of ethylbenzenesulfo acid and its salts, tetramethylammonium chloride, and ethanol

Coefficient	$EtPhSO_3H$	$EtPhSO_3Li$	$EtPhSO_3K$	$C(CH_3)_4Cl$	C_2H_5IOH
α	2.47	1.75	0.37	2.32	3.33
β	−0.51	−0.85	−1.51	−0.88	8.51
γ	0.90	1.09	1.50	1.02	0.51

Table 2. Influence of the amount of DVB and ionite ionic form on the distribution constant of water

Cross-links, %	$RPhSO_3H$	$RPhSO_3Li$	$RPhSO_3K$	$RC(CH_3)_3Cl$	PVA
4	0.95 ± 0.01	0.96 ± 0.01	–	0.89 ± 0.01	–
8	0.91 ± 0.01	0.90 ± 0.01	0.91 ± 0.01	0.84 ± 0.01	–
10	–	–	–	–	0.95 ± 0.01
12	0.87 ± 0.01	–	–	–	–
16	–	–	–	0.72 ± 0.01	–
20	0.77 ± 0.02	0.79 ± 0.02	–	–	0.95 ± 0.01

The influence of the polymer effect decreases the external pressure on PSs and, as a consequence, specific equilibrium amount of water in them. As a result, the concentration of a PS is always higher than that of a solution of the corresponding monomer at equal external conditions and relative vapor pressures. Another consequence is a quite definite concentration of PSs, which do not become an infinitely dilute solutions as the relative vapor pressure tends to one.

Studies of the sorption of water by cross-linked polyelectrolytes revealed certain special features of the process. First, as distinct from solutions of PVA, where the amount of sorbed water is independent of cross-links, the amount of water sorbed by cross-linked polyelectrolytes based on polystyrene depends on the concentration of the cross-linking agent (DVB). Figure 3 shows that an increase in the number of cross-links in a polymer decreases the amount of water in the PS phase. Secondly, note that equal water distribution constants were obtained for the same ionite in different ionic forms. This is a strong argument for the absence of influence of the nature of counterions on the constant of water distribution in a particular polyelectrolyte.

The results obtained in this work lead us to conclude that if a polymer swells in solvent vapor, sorption and subsequent solvent condensation result in the formation of a solution of the polymer. The activity of the solvent in this solution and the relative vapor pressure over it are related by the distribution constant.

In addition, it was found that a polymeric gel cannot be obtained at equilibrium between the polymer and vapor, because the gel is a two-phase system in which the second phase is a pure solvent, for which the relative vapor pressure is one.

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