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Thermodynamics of Swelling of Poly(N-vinylpyrrolidone)-Poly(ethylene glycol) Complex Due to Water Sorption

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Summary: The deformation of sorbent caused by the sorption is new method of quantitative investigation "in situ" of interaction in system host-quest. The deformation of PVP-PEG complex, φ_{PEG}=0.36 and φ_{PEG}=0.20 due to water sorption has been studied by the measuring of the relative elongation of the polymer samples and the isotherms of water sorption simultaneously. The investigation of the sorption deformation gives the possibility of direct estimation of polymer sample free volume and it's variation during sorption, also the variation of Gibbs energy of system due to sorption according to the vacancy solution theory. The glassy-plastic state transition of polymer during water sorption has been observed.

Keywords: glass transition; polymer free volume; poly(N-vinyl pyrrolidone)-poly(ethylene glycol) blends; thermodynamics of swelling of polymer; water sorption

Introduction

Thermodynamic parameters of water sorption by polymer blends - of poly(N-vinyl pyrrolidone)-poly(ethylene glycol)(PVP-PEG) were investigated using the method of quantitative estimation of interaction in the system host-quest "in situ" by the studies of polymer swelling in water vapours. The interaction of water molecules (sorbate-solvent) with atoms of polymer (sorbent) leads to variation in bond lengths of polymer molecules and the volume of polymer is changed. There are the expansion and contraction of every sorbents, especially polymers due to sorption process. PEG molecules bonded to comparatively long PVP chains are forming the supramolecular gel network [1]. The interaction of elastic chains of PEG with chains of PVP forms the free volume of PVP. The sorption of water leads to variation in volume of the polymer blend. The sorption, thermodynamic properties and free volume of supramolecular structure of PVP-PEG blends depend on the composition of blend, water content and thermal treatment. The formalized theoretical treatment of isotherms based on the assumption of the inert character of sorbent has usually ignored the existence of variation of sorbent volume, as well as the variation of energy of sorbent during the sorption and is not appropriate for analysis of sorption of swelling polymers. The phenomenon of sorption deformation has been interpreted

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using the model of vacancy solution [2]. Both the contraction and the expansion of sorbent due to sorption are consistently explained by the special thermodynamic theory, based on the model of binary vacancy solution. The theory connects the sorption deformation and Gibbs potential of two component system sorbent-sorbate by a relationship. The study of sorption deformation allows to elaborate the thermodynamic function of sorption process which takes into account the variation of the chemical potential of sorbate, as well as of sorbent . That gives the possibility of direct estimation of free volume of polymer sample and it's variation during sorption, as well as the variation of Gibbs energy of system due to sorption.

The present communication deals with the investigation of variation of volume of sorbents - PVP-PEG blends - during water sorption, and demonstrates the possibilities of this method for thermodynamic description of sorption and swelling process, the variation of free volume of system polymer-water, the transition of polymer into plastic state caused by sorption.

Experimental

The deformation of polymer blends PVP-PEG, φ_{PEG}=0.36 and φ_{PEG}=0,20 due to water sorption has been studied by the simultaneous measuring of the variations of linear dimensions (relative elongation and contraction) of the polymer sample and the isotherms (at 20 ^{0}C) of water sorption after the thermal and vacuum treatment of polymer sample. Poly(N-vinyl pyrrolidone) $M_w=10^6$ g/mol, Poly(ethylene glycol) with M_w=400 g/mol were mixed to obtain the blend with 36% and 20% PEG. These blends were dried at 100 °C after that the pellet of polymer (length 30 mm) was placed into the vacuum automatic microbalance with sensitivity 10^{-5} g. The variations of linear dimensions (relative elongation or contraction) of the sample placed into microbalance were measured with an accuracy of 0,05% during the sorption process. Before the water sorption the sample was outgassed in vacuum up to constant weight at 20 ^{0}C . After water sorption-desorption experiment the sample was outgassed at 100 ^{0}C, and at low filling the second and the third sorption- desorption experiments were performed for PVP-PEG-36 blend.

Results and discussion

The sorption, sorption deformation, thermodynamic properties and free volume of supramolecular structure of PVP-PEG blends depend on the composition of blend, the water content and thermal and vacuum treatment of polymer blend before the investigation.The experimental data obtained are given as the value of relative elongation of the pellet $\Delta L/L_0$ on the sorption value (Figure 1). The thermal treatment of polymer leads both to the decrease of free volume of polymer and the free energy of system.

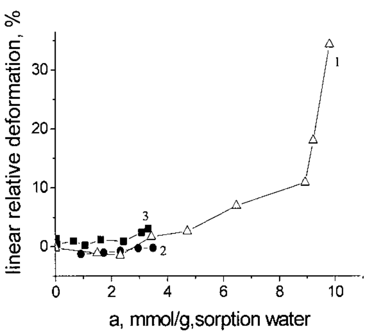

Figure 1. The deformation of PVP-PEG-36% caused by water sorption: 1- after outgassing, 2- heat treatment, 3-two heat treatments at 100 °C .

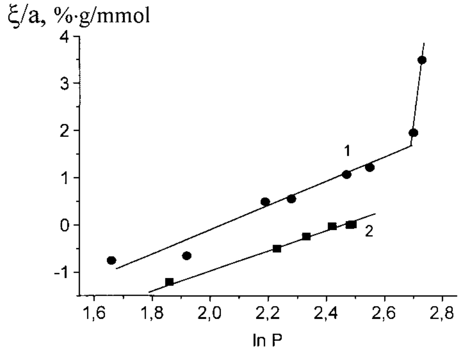

Figure 2. The ratio of relative volume deformation ξ to sorption *a* as a function of lnP : 1- outgassing, 2 – heat treatment (according to Equation 3).

The equilibrium dependence of variation in linear dimensions of pellet of PVP-PEG-36 blend on sorption shows the significant (up to -1,5 %) contraction at small water filling (Fig.1, curve 1). At higher fillings PVP-PEG complex expanded up to 35%. After thermal outgassing at 100 ^{0}C the contraction of polymer at low water filling is diminished (curves 2, 3 showed at low filling). The expansion of PVP-PEG-36 is more than that of PVP-PEG-20, but the contractions at low filling of these polymer blends are near 1,5%.

The contraction of the polymer sample at low water fillings may be associated with the sorption of water into hollow voids in polymer structure. It may be assumed, that this voids are similar to micropores. They were generated due to drying and thermal treatment. It was suggested, that the volume of this voids is polymer free volume. The water molecules interact with two opposite walls of micropore, and the polymer is contracted. The phenomenon of contraction of the sorbent due to sorption has been demonstrated by many careful studies [3], but the formalised theoretical treatments of sorption have usually ignored the existence of this deformation as well as the variation of energy in system caused by this deformation. The estimation of free energy of sorbent- sorbate system based only on the analysis of the isotherms of sorption has neglected the variation of energy of sorbent due to sorption. According to the investigation of sorption deformation the assumption of inert character of sorbent for polymer is mistaken. The phenomenon of sorption deformation has been interpreted by the special thermodynamic theory of vacancy solutions, which allows the indirect characterisation of the contraction of sorbent in low filling.

The deformation caused by the sorption is connected with variation of energy of binary system sorbent-sorbat according to the thermodynamic of vacancy solutions [2]. The deformation caused by sorption is determined by depends on the variation of the free energy Gibbs of binary system:

$$\xi = \Delta V/V_0 = \Delta G/K\,V_m = \Delta G\,a_m/KW_0 \qquad (1)$$

where V - the sorbent volume, V_0 - initial volume, V_m - partial molar volume of vacancy solution, W_0 - the summary pore volume, a_m - saturation sorption, K - modulus of elasticity, ΔG - the variation of free energy Gibbs of binary vacancy solution. The vacancy solution exists in osmotic equilibrium with free vacancies, and the chemical potential of vacancy in vacancy solution is zero [2]. According the model of vacancy solution, in equilibrium state chemical potential of sorbate in gas phase and in the vacancy solution are equal. Then the variation of chemical free energy Gibbs is:

$$\Delta G = x\mu + x^*\mu^* = x\mu = x\mu_g = (\mu_0^g + RT\ln P)\,a/a_m \qquad (2)$$

with $x = a/a_m$- molar fraction of sorbate and x^* - molar fraction of vacancy in vacancy solution and μ and μ^*- chemical potentials of sorbate and vacancies respectively. Substitution of Eq.1 with ΔG into Eq. 2 gives the expression for the deformation isotherm Eq.3:

$$\xi/a = \Delta G/\,a\,K\,V_m = B + RT/KW_0 \quad \ln P \qquad (3)$$

Here B is the constant dependent on the temperature and the standard chemical potential of sorbate in vacancy solution, R - gas constant and T - temperature. The experimental data were fitted with Eq. (3) as shown in Figure 2. The Eq.3 is the straight line in the interval of sorption value up to 8 mmol/g. For the higher sorption values the expansion is so large, that this phenomenon may be considered as the transition of glassy state of structure to plastic state. This dependence (3) has two parts, that indicates on the sharp transition of their thermodynamic properties. The modulus of elasticity for glassy state obtained by Eq.3 is $K = 1.3{*}10^7$ Pa. This value is adjusted with modulus of elasticity of N,N '-diethyl acrylamide - water, obtained by this method previously [4].

Furthermore the solution thermodynamic analysis of the system performed to Eq.(3) shows the similarity the sorption deformation curves and curves of the variation of Gibbs energy of polymer-water system, provided the linearity of the Eq.3 curve.

The measurements of the sorption deformation of polymer sorbent such as PVP-PEG blend gives the direct estimation of free volume of polymer sorbent and it's variation during the sorption. The curves of sorption deformation (Figure 1) demonstrate the contraction range. It may be assumed, that the volume contraction of -4 % corresponds to the filling of initial free volume of polymer sorbent - 0.0431 cm^3/g. After that the polymer expands up to 0.977 cm^3/g. During the sorption process the partial molar volume of sorbent is changed in accordance with the curve of sorption deformation. The heat treatment in vacuum at 100 ^0C leads to the increasing of sorption deformation. The second heat treatment leads to the diminishing of initial contraction and the maximum swelling volume due to the ageing of polymer (curve 3, Fig.1). The ageing of PVP-PEG blend was corroborated by NMR PFG measurements of self-diffusion [1].

Conclusion

The new method of quantitative estimation of interaction in system host-quest "in situ" by the studies of polymer swelling in water vapours gives the possibility of direct estimation of the variation of Gibbs energy of system sorbent-sorbate due to sorption, free volume of polymer sample and it's variation during sorption. According to the special thermodynamic theory of vacancy solutions the deformation of sorbent due to sorption is caused by the Gibbs potential of binary component sorbent-sorbate system. The variation in volume of PVP-PEG (36% and 20%) polymer blends caused by water sorption and isotherms of sorption were measured with and without the heat treatment of the sample. The contraction of sorbent at low water fillings gives the direct estimation of free volume of polymer and it's variation during sorption. The effect of thermal treatment upon the sorption deformation was shown. The modulus of elasticity due to water sorption was obtained for glassy state. The glassy-plastic state transition of polymer during water sorption was observed.

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