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Thermodynamics of Water Sorption in Acrylic Homonetworks and IPNs

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Summary: The equilibrium thermodynamic properties of poly(hydroxyethyl acrylate) and poly(ethyl acrylate)-*i*-poly(hydroxyethyl acrylate) hydrogels are investigated starting from the water sorption isotherms of the systems. Partial enthalpy and entropy of the sorbed water in the gel differ markedly from the values of pure water at the lowest water contents, and tend to those of liquid water as saturation is approached. The residual mixing free energy is calculated, as a means of assessing the intensity of the water-polymer interaction. Its small positive magnitude shows that water-polymer hydrogen bonds are labile compared to water-water and polymer-polymer hydrogen bonds, and thus the stability of the gel state is still mainly due to the combinatorial entropic contribution to the mixing free energy. An equation correctly describing the sorption isotherms, when combined with the thermodynamic equations, can deliver the true water-polymer interaction parameter and its dependence on the polymer volume fraction in the gel.

Keywords: adsorption; hydrogels; interpenetrating networks (IPN); swelling; thermodynamics

Introduction

The swelling of polymer hydrogels is a topic of great scientific and technological interest because many of properties of these materials depend on the amount and the state of the water molecules they can retain. Most of the time this state is analysed in terms of the outcomes of dynamic (non-equilibrium) experimental techniques, such as DSC.[1-3] Such non-equilibrium experiments are processes involving a number of overlapped phenomena (rate dependence of phase transitions, glass transition of the gel, *etc.*) which make conclusions about the state of the water-polymer system difficult, and we believe that they should be complemented with a consideration of the equilibrium properties[4-6] of the gel and its components as functions of the water content of the system. In our contribution we study the thermodynamic properties of the gel (mixing Gibbs free energy and its residual part) and of water (partial enthalpy and entropy in the gel) when the system has been equilibrated at water activities ranging from zero up to

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saturation values (one). We perform this study based on experimental measurements on poly(hydroxyethyl acrylate) homonetworks and on poly(hydroxyethyl acrylate)-*i*-poly(ethyl acrylate) interpenetrating networks with different mass ratios of the hydrophilic and the hydrophobic components.

Materials and Methods

A poly(2-hydroxyethyl acrylate)—PHEA in what follows—network was prepared by UV-light initiated copolymerization of HEA monomer and a 1% (weight) ethylene glycol dimethacrylate (EGDMA). The same mass ratio of the cross-linking comonomer EGDMA was used in the preparation of a poly(ethyl acrylate)—PEA—network and for each one of the components of four sequential PEA-*i*-PHEA IPNs, as described elsewhere.[7] Water sorption isotherms were determined by the standard gravimetric method of equilibrating samples in conditions of controlled known relative humidity (RH) at 40°C;[7] for the PHEA hydrogel isotherms were measured also at 10°C, 26°C, 32°C, 45°C and 56°C.

Results and Discussion

Figure 1 shows three of the experimental sorption isotherms for PHEA as an example. The isotherms could be well described by Guggenheim-Anderson-de Boer's equation,[8,9]

$$\mathrm{w} = \mathrm{w}_m \frac{cfa_1}{(1 - fa_1)(1 + (c-1)fa_1)} , \qquad (1)$$

in which c, f and w_m are adjustable parameters, a_1 is the activity of water (which can be identified with RH/100) and w is m_1/m_2, the ratio of the mass of the sorbed water in the gel to the mass of the dry polymer. For the temperature values investigated in this work these parameters obeyed (in the case of pure PHEA)

$$\mathrm{w}_m = 0.0878 - 1.581 \cdot 10^{-4} \cdot T \ , \quad c = 7.963 - 1.810 \cdot 10^{-2} \cdot T \ , \quad f = 0.930 + 1.423 \cdot 10^{-5} \cdot T \ , \quad (2)$$

with T temperature in Kelvin. From thermodynamics it is well known that the equilibrium properties of a mixed system (the hydrogel in our case) are completely determined by the dependence of its Gibbs free energy on temperature and composition. In particular, the stability of the homogeneous gel state requires that the mixing Gibbs free energy be negative and its second derivative with respect to the composition variable be positive. The sorption isotherm

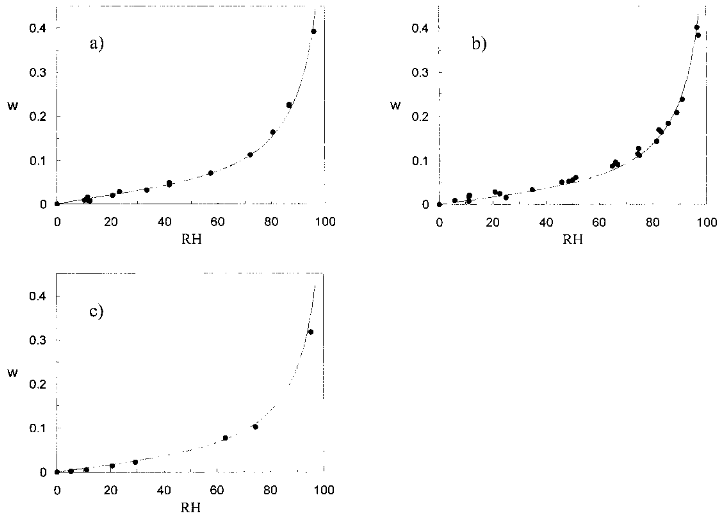

Fig. 1. Experimental sorption isotherms for PHEA at: a) 10°C, b) 40°C and c) 56°C. Mass of sorbed water per unit mass of polymer *versus* relative humidity (RH). Continuous lines are the predictions of the GAB equation.

(1) yields a knowledge of the dependence on temperature and water content of the activity of water, $a_1 = a_1(w, T)$, and thus of the difference between the chemical potentials of water in the gel and pure liquid water, $\Delta\bar{\mu}_1 = \bar{\mu}_1 - \mu_1 = RT \ln a_1$; making use of Gibbs-Duhem's equation, $\Delta\bar{\mu}_2$ can be calculated as a function of w at constant T, and then the Gibbs mixing free energy of the gel is obtained from

$$\Delta_m g = g - \omega_1 \mu_1 - \omega_2 \mu_2 = \omega_1 \Delta\bar{\mu}_1 - \omega_2\, \Delta\bar{\mu}_2 \ , \tag{3}$$

where $\omega_1 = m_1/(m_1 + m_2)$ is the mass fraction of water in the gel. From the Gibbs-Helmholtz equation one obtains the difference between the partial enthalpy of water in the gel and of pure liquid water $\Delta h_1 = h_1 - h_1$ as

$$\Delta h_1 = -RT^2 \frac{\partial \ln a_1}{\partial T} \ , \tag{4}$$

and then the partial entropy of water is obtained as

$$\Delta\bar{s}_1 = \bar{s}_1 - s_1 = \frac{\Delta\bar{h}_1 - \Delta\bar{\mu}_1}{T} \; . \qquad (5)$$

The calculations involved in equations (3-5) can be performed explicitly when (1) is employed as the equation giving the relationship between activity and water content.[10]

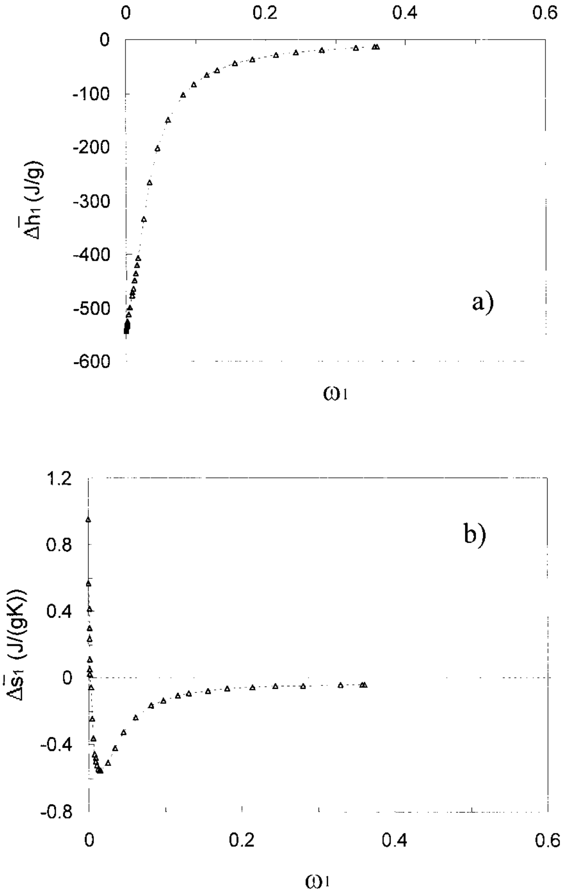

Fig. 2. a) Specific partial enthalpy and b) specific partial entropy of water in the gel as a function of water mass fraction, at 40°C.

The dependence of the partial enthalpy of water in the hydrogel on water content in Figure 2 shows that $\Delta\bar{h}_1$ is negative and increases monotonically towards 0 as ω_1 tends to 1. This means that, even well below saturation, from a certain water content on the partial enthalpy of water in the gel is practically equal to that of liquid water, suggesting that the sorbed state of water at these concentrations is similar to the condensed water state. However for the lowest water contents h_1 is significantly smaller that the value h_1 of liquid water. According to multilayer sorption theories[9,11] these water contents correspond to the completion of the first sorption layers, where a direct interaction of water with the polymer chains is expected to occur. In particular the limit $\bar{h}_1$ for ω_1 tending to 0 is the enthalpy of the water molecules directly attached to the sorption sites. Also in Figure 2 can be seen that $\bar{s}_1$ rapidly approaches the value of liquid water as water content of the gel increases, as happened with the enthalpy. At lower water contents, on the contrary, $\Delta\bar{s}_1$ is first positive, rapidly decreases reaching a negative minimum, and then monotonically increases towards 0. The partial entropy of water reflects its mobility and order as a component of the gel. A minimum of partial entropy of an adsorbate is frequent in adsorption processes and is thought to correspond to the completion of the first sorption layer.[11] That minimum would mean a loss of mobility and/or an increase of order of the water molecules that are completing the first sorption layer relative to their liquid state mobility and order. By contrast, the starting positive $\Delta\bar{s}_1$ values say that the very first sorbed water molecules are in a less correlated state, occupying a more random location, than in the more ordered liquid state (water molecules in the liquid state are known to possess a short range order, with a mean coordination number of four[12]).

Figure 3 collects the mixing free energy values for PHEA, for PEA, and for the IPN hydrogels, calculated according to (3) from the experimental isotherms,[7,13] as explained above. The negative values and convex shape of these functions determine the water content interval where the homogeneous hydrogel state is stable. The saturation water mass fraction ω^*_1 of each sample corresponds to water activity $a_1 = 1$ and the experimental curves at those abscissas have as tangent the straight line joining the saturation point with the point (1,0) representing liquid water, as demanded by the thermodynamic equilibrium condition $\bar{\mu}_1(\omega_1^*) = \mu_1$. The water mass fraction that saturates each sample is seen to be dependent on its PHEA content; in fact, the sorption isotherms for the IPN samples could be fitted to the GAB equation (1) employing the same c and f parameters as in PHEA and a monolayer parameter $w_m(x)$ for each IPN, of PHEA mass fraction $x = m_{\mathrm{PHEA}}/(m_{\mathrm{PHEA}} + m_{\mathrm{PEA}})$, given by

$$w_m(x) = x \cdot w_m(\mathrm{PHEA}) \ , \tag{6}$$

where w_m(PHEA) is the monolayer parameter of PHEA. This finding is consistent with the phase separated structure of the IPNs, which could be confirmed in scanning electron micrographs of the samples,[13] and makes the amount of sorbed water at equilibrium in each IPN proportional to its PHEA phase mass fraction. It also implies that, essentially, this PHEA phase in the IPNs behaves as regards water sorption as does pure PHEA.[7]

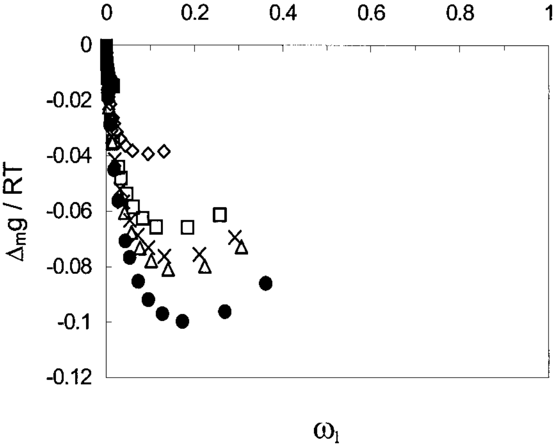

Fig. 3. Normalized mixing free energy as a function of water mass fraction for PHEA (circles), IPN with PHEA mass fraction equal to 0.78 (triangles), equal to 0.72 (crosses), equal to 0.613 (open squares), equal to 0.378 (diamonds) and for PEA (full squares), at 40°C.

The values of the mixing free energy $\Delta_m g$ inform about the stability of the homogeneously mixed state (the gel state) but the reasons for this stability are due both to an entropic-combinatorial contribution and due to the interactions between the system's components. In order to specifically address the nature of the water-polymer interaction in a gel state one must subtract from $\Delta_m g$ the combinatorial part $\Delta_m g^{\mathrm{comb}}$, which is independent of the interactions between the system's components and which, independently of their nature, is always negative and always contributes to miscibility. The remaining part of the mixing free energy is called the residual mixing free energy,

$$\Delta_m g^{\mathrm{res}} = \Delta_m g - \Delta_m g^{\mathrm{comb}} \quad , \tag{7}$$

and it reflects the influence on miscibility of differences in free volume and in intermolecular forces between the system's components.[14] In the case of liquids which associate through physical bonds the residual mixing free energy basically reflects the balance between the formation of heterobonds 12 between molecules of different species and the destruction of homobonds 11 and 22 between molecules of the same species in the system.[4-6,14,15] We accept Flory-Huggins's expression for the combinatorial mixing free energy, $\Delta_m G^{\mathrm{comb}} = RT\cdot(n_1\cdot\ln \phi_1 + n_2\cdot\ln \phi_2)$, which, on a unit gel mass basis, reduces to

$$\Delta_m g^{\mathrm{comb}} / RT = \omega_1 \ln \phi_1 \tag{8}$$

with the approximation that the number of polymer moles n_2 is 0 (since the polymer network is a single molecule; notice that R in (8) is the quotient of the gas constant through the molar mass of water). Subtracting (8) from (3) one obtains $\Delta_m g^{\mathrm{res}}$ shown in Figure 4. The residual mixing free energy is positive, though small, for all water contents. This means that, in the mean, the water-polymer interactions are not stronger than the water-water or the polymer-polymer interactions, and that even in the case of these hydrophilic polymers the affinity of water to mix homogeneously with them is due to the combinatorial increase of entropy which mixing affords, which outweighs the positive $\Delta_m g^{\mathrm{res}}$ to give the negative $\Delta_m g$ values of Figure 3.

The Flory-Huggins theory of polymer solutions[16] expresses the mixing free energy in terms of an interaction parameter χ_{12} according to

$$\Delta_m G = \Delta_m G^{\mathrm{comb}} + RTn_1\phi_2\chi_{12} \ .$$

Thus, the water-polymer interaction parameter is a reduced normalized residual mixing free energy:

$$\chi_{12} = \frac{\Delta_m g^{\mathrm{res}}}{RT\omega_1\phi_2} \ . \tag{9}$$

The equation for the sorption isotherm (1), which determines $\Delta_m g^{\mathrm{res}}$ as explained, then determines also the true interaction parameter and its dependence on the gel composition through (9). This function has been included in Figure 4. It must be remarked that, starting from the experimental isotherms, the methodology here employed allows the determination of the true interaction parameter, and not only the apparent interaction parameter[17] as is usual. The positive values of the interaction parameter for all gel compositions indicate again the labile nature of the water-polymer interaction in the mean. After a maximum value attained around the water mass fraction corresponding to the completion of the first sorption layer (*i.e.*, around w_m), the function decreases monotonically with water content, which might reflect the predominance, from that water content on, of water-water interactions in the multilayered structure of the sorbed water.

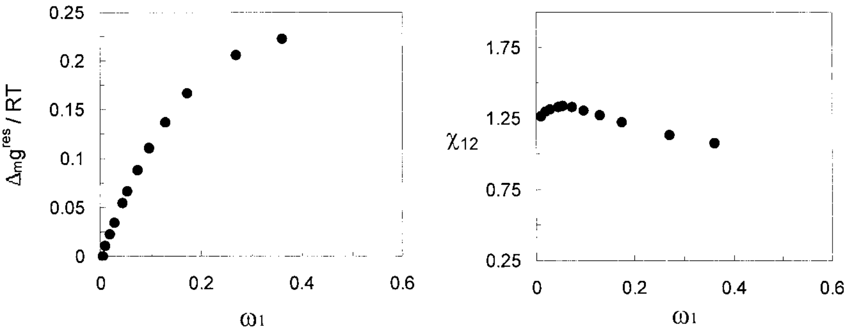

Fig. 4. Left: Normalized specific residual mixing free energy of the gel as a function of water mass fraction, at 40°C. Right: Flory-Huggins water-polymer interaction parameter as a function of water mass fraction, at 40°C.

Conclusions

A methodology based on the combination of mixture thermodynamics and an equation describing the sorption isotherms of a water-polymer system can deliver the equilibrium properties of the hydrogel and its components. It gives, in particular, the composition dependence of the mixing free energy and of its residual part. This last shows that the water-polymer interaction cannot be regarded as a strong interaction. The same conclusion can be read from the values of the Flory-Huggins interaction parameter, whose true values and composition dependence can be determined from the general relationships. The partial enthalpy and entropy values of the sorbed water in the gel show that the thermodynamic properties of this water are very similar to those of liquid water already at relatively low water contents, and that they differ appreciably at the 0 limit of ω_1 corresponding to water molecules located at the first sorption layer. The completion of this first sorption layer and the subsequent formation of sorbed water multilayers is specifically reflected in the composition dependence of different thermodynamic functions (partial entropy, Flory-Huggins interaction parameter).

Acknowledgements

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