

Water-Swelling Behavior of an Ethylene-Vinyl Alcohol Copolymer in the Presence of Sorbed Sodium Chloride

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Synopsis

The swelling behavior of water in a poly(ethylene-vinyl alcohol) copolymer (70 mol % vinyl alcohol) has been characterized at 25°C by vapor and liquid sorption experiments over a range of water activities. The activity of the vapor phase has been varied by incrementing the pressure of the water vapor in the sorption cell. Alternatively, for the liquid phase experiments, aqueous sodium chloride solutions of different concentrations have been used to vary systematically the activity of the water in the salt solution and to introduce various concentrations of salt into the copolymer films. Relaxation-controlled sorption and Fickian diffusion have been observed as limiting cases of the water sorption behavior at high and low water activities, respectively. The effects of sorbed sodium chloride on water vapor sorption kinetics and equilibria were determined independently. A second salt phase forms within the previously homogeneous and seemingly single phase polymeric system, upon contacting the salt-loaded film with a water vapor activity above a threshold value corresponding to the activity of water in the salt solution used to introduce the salt into the films. The water and salt solubilities in the ethylene-vinyl alcohol copolymer have been measured systematically to describe the complex sorption equilibria associated with this three-component, multiphase system.

INTRODUCTION

A comprehensive study of the release kinetics of Sudan Red IV from glassy polystyrene films, following immersion of the films in *n*-hexane, indicated conclusively that the dye release was controlled quantitatively by the invasion of the *n*-hexane.¹ The sorption kinetics of *n*-hexane in these glassy polystyrene films are characterized by a constant rate (or case II) absorption associated with a front, advancing at a constant rate into the confines of the glassy polymer, which separates the essentially unpenetrated core from a uniformly swollen and dye-denuded shell.¹⁻⁴ The constant rate swelling, which quantitatively controlled the constant rate release, seemed to be a general response to the case II swelling of solute-containing glassy polymer systems, wherein the diffusion of swelling penetrant to and solute release from the advancing front are rapid compared with the rate of swelling.

The development of constant rate delivery devices suitable for the administration of biologically active solutes to aqueous media by a swelling-controlled mechanism, depends upon the formulation of solute in a glassy hydrophilic polymer which will respond to swelling in a manner quantitatively analogous to the *n*-hexane/polystyrene system. Typically, thermoplastic polymers which

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are sufficiently water-swellaable are also water-soluble and, therefore, formulation of controlled-release devices from these host polymers would ultimately result in the undesired liberation of the host polymer to the target organ. The exploitation of insoluble, crosslinked hydrophilic polymers (hydrogels) presents significant technological limitations associated with solute loading and the requisite crosslinking reactions.

The recent development of completely hydrolyzed ethylene-vinyl acetate copolymers forming ethylene-vinyl alcohol copolymers (with high vinyl alcohol contents) offers significant promise toward the ultimate development of swelling-controlled, constant rate delivery systems since these polymers are at once glassy and water-swellaable, but water-insoluble. Moreover, the family of ethylene-vinyl alcohol polymers are easily processed by conventional thermoforming techniques including extrusion and injection molding. This combination of potentially straightforward device fabrication technology, coupled with the confluence of glassiness, water swellability, and water insolubility, provides the motivation for the fundamental explorations reported and discussed in this paper.

This study presents a rather complete characterization of the complex equilibria associated with the three component multiphase system involving water, NaCl, and poly(ethylene-vinyl alcohol). The related absorption and desorption kinetics of water and salt are also described in an attempt to provide a fundamental basis for evaluation of poly(ethylene-vinyl alcohol) as a controlled release host matrix.

EXPERIMENTAL

Materials

An ethylene-vinyl alcohol copolymer film, 4.4×10^{-3} cm thick, containing 70 mol % vinyl alcohol was extruded from polymer supplied by Kuraray Co., Ltd. The vinyl acetate content in the polymer was less than 0.2 mol %. Distilled water was used in the sorption experiments. Dissolved gases were removed by repeated freeze-thaw cycling, under vacuum, using liquid nitrogen as a refrigerant. Reagent grade sodium chloride was used to prepare the aqueous salt solutions.

Experimental Procedures

Water sorption kinetics and equilibria were determined by means of a quartz spring microbalance serviced by a standard vacuum system. The quartz springs, with a 2.0 mm/mg sensitivity, were obtained from the Ruska Corp., Worden Quartz Products Div., Houston, Texas. The sample temperature was maintained constant by circulating thermostated water through a water jacket surrounding the sorption cell. Various water activities have been maintained in the system by imposing and controlling different pressures of water vapor monitored by a mercury differential manometer.

Gravimetric liquid sorption measurements were performed by weighing film samples repeatedly on an analytical balance following immersion in water maintained at constant temperature. The samples were removed from the water, blotted, placed in a weighing bottle, weighed, and finally replaced in the constant temperature water bath.

The "as received" polymer films were heated under vacuum at a temperature of 190°C, about 20°C above the melting temperature of the isomorphous copolymer crystals, for 10 min and then rapidly cooled to room temperature. This procedure was used to erase the effects of the aging achieved under the unknown previous storage.⁵ The glass transition temperature and degree of crystallinity of the copolymer after the thermal treating were 58°C and 68%, respectively.⁵ The films appeared clear and glassy.

Sodium-chloride-loaded samples were prepared by equilibrating the films in salt solutions of different concentrations at 25°C for at least 1 week. The films were subsequently dried to constant weight under vacuum at room temperature for 2 weeks.

All samples were stored in a desiccator containing anhydrous calcium chloride. The sodium chloride content of the films, equilibrated in salt solutions, was determined by quantitative sequential extraction of salt into a large volume of pure water and subsequently measuring the salt concentration of the resulting solutions with an ion exchange chromatographic technique using a Model 10 Dionex Ion Chromatograph.

RESULTS AND DISCUSSION

Water vapor sorption experiments have been carried out on this films of a 70 mol % vinyl alcohol ethylene-vinyl alcohol copolymer at 25°C and various external water vapor activities. The corresponding water uptake kinetics are plotted as a linear function of time in Figure 1. Sorption curves at high values of the external water activity are characterized by limiting case II sorption since a linear dependency of water uptake on time is observed. The initial Fickian

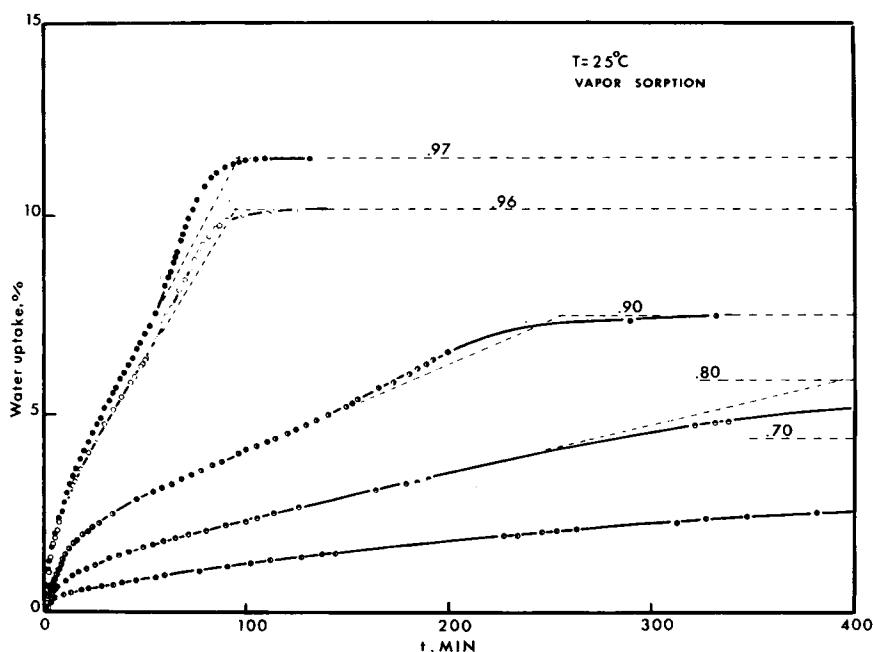


Fig. 1. Water vapor sorption kinetics in 70 mol % vinyl alcohol ethylene-vinyl alcohol copolymer at various penetrant activities.

establishment of a step concentration profile and the final sorption acceleration, apparent in the curves of Figure 1, are characteristic of thin samples undergoing relaxation controlled sorption.¹⁻⁴ The lower equilibrium water uptake, corresponding to decreasing vapor activities, are reached in increasingly longer times. The progressively slower polymer relaxations associated with the intermediate activity experiments are consistent with the decreased driving force for swelling expected at lower equilibrium water contents.⁶

At intermediate external penetrant activities both polymer relaxation and Fickian diffusion may contribute to the sorption behavior. The anomalous sorption behavior evident at intermediate penetrant activities is apparent in Figure 2 where the sorption data are replotted as a function of the square root of time. An experiment performed at a substantially lower activity of 0.38 is also presented in Figure 2. Completely Fickian behavior is apparent in the experiment performed at an activity of 0.38.

The influence of the external penetrant activity has been determined also in sorption experiments carried out by direct contacting of the copolymer film with aqueous sodium chloride solutions of different concentrations. The overall weight gain kinetics (salt and water) are plotted in Figure 3 as a function of the square root of time. The numbers on the curves refer to the corresponding water activities of the respective salt solutions. The anomalous character of the sorption is evident although less pronounced than in the vapor sorption experiments. This might be explained by the simultaneous occurrence of salt inhibition by ordinary diffusion in the swollen polymer⁷ during the swelling of the glass. The equilibrium salt content of samples equilibrated in the different aqueous solutions has also been determined by subsequently monitoring desorption from the film into a large volume of pure water.

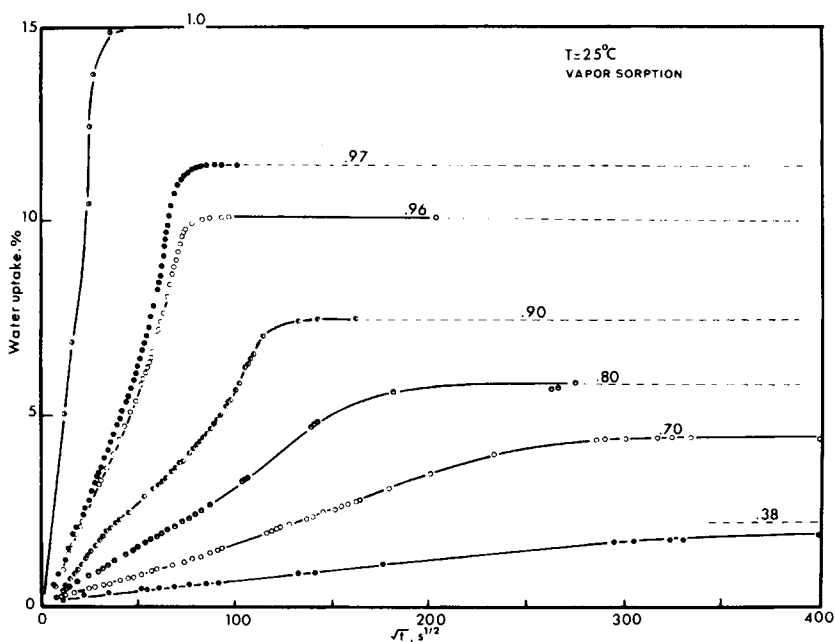


Fig. 2. Water vapor sorption kinetics in the 70 mol % VA ethylene-vinyl alcohol copolymer at various penetrant activities plotted as a function of a square root of time abscissa.

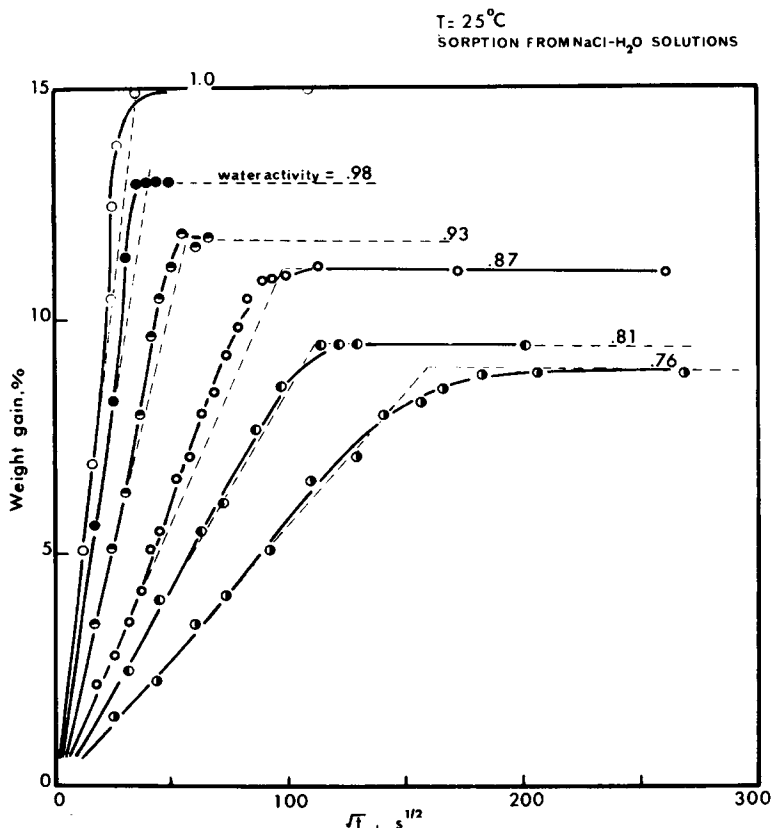


Fig. 3. Weight gain as a function of the square root of time describing liquid sorption from aqueous sodium chloride solutions. Numbers on the curves refer to water activities of the aqueous solutions.

The isotherm describing salt sorption in the copolymer is reported in Figure 4 (open circles); the water activity corresponds to the equilibrating solution. A nearly linear dependency between salt uptake and water activity is found over the entire range of water activities. The curve is not defined below an activity of 0.75, which corresponds to the activity of a saturated aqueous sodium chloride solutions. The salt-water isotherm is coplotted in Figure 4 in a similar form, from data obtained in the literature.⁸ These combined data permit direct estimation (assuming linear additivity) of the water absorption in salt-loading films resulting from exposure to vapors of various activities.

After drying, salt-loaded films appear clear and glassy. The detailed nature of molecular dispersion of metal salts in hydrophilic polymeric glasses has been recently studied and reported.⁹⁻¹³ In particular, for poly(vinyl alcohol), metal salts have been described to be coordinated chemically to the polymer backbone by the pendant hydroxyl oxygen atoms.¹³ The salt loaded PVOH films were reported to be optically transparent, indicating a very fine scale dispersion of the salt, further substantiated by small angle X-ray diffraction studies.¹³ The EVOH copolymer studied here is also transparent and interacts strongly both with water molecules and salt ions.⁹

The effect of the presence of this second component, NaCl, on the water-

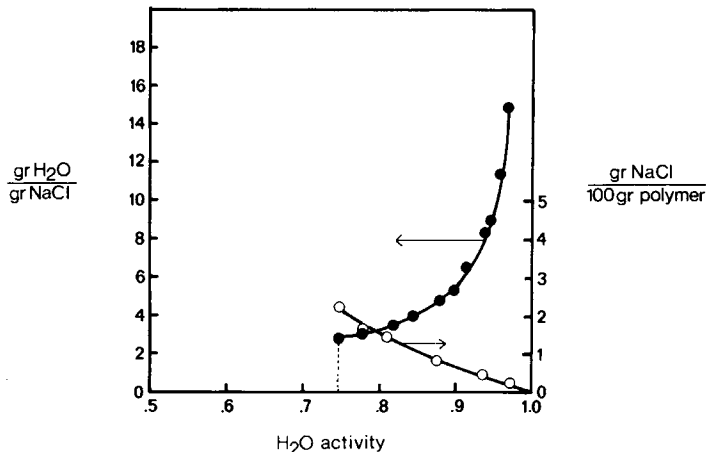


Fig. 4. Equilibrium sodium chloride uptake in the copolymer as a function of the water activity in the external salt solution (open circles). Full circles refer to equilibrium water per gram of NaCl to form the aqueous solution of the corresponding water activity (data from Ref. 7).

swelling behavior of the seemingly one-phase, glassy polymeric systems has been explored with vapor sorption experiments, determining both the equilibrium water uptake and associated absorption kinetics. A saturated sodium chloride solution, which corresponds to a water activity of 0.75,⁸ and a 3-M solution, which corresponds to a water activity of 0.89,⁸ were chosen to equilibrate the samples used in the subsequent water-vapor sorption experiments on salt-loaded film samples.

The sorption kinetics describing water vapor absorption are compared in Figure 5 for salt-loaded and unloaded films in experiments carried out at an activity of 0.97. Salt-loaded samples sorb more and faster than the unloaded films, but they show similar relaxation-controlled behavior. The higher water-sorption rates are consistent with the correspondingly higher sorption driving forces. Equilibrium sorption isotherms for the salt loaded and unloaded copolymer are compared in Figure 6. For the unloaded polymer, the increased water solubility achieved at higher water vapor activities most likely reflects an increased plasticization and subsequent swelling undergone by the bulk polymer. In the range of activities in which positive deviations from the initial linearity of the isotherm are significant, relaxation-controlled sorption is, in fact, observed.

For the salt-loaded samples, higher water solubilities in the film are associated with increasing initial salt loadings. Upon contact with water activities equal to and higher than the water activity of the solution in which the sample has been originally equilibrated (the "threshold" activity) the salt, previously completely dissolved in the polymer, starts to segregate and ultimately forms a separate phase within the film. The phase separation is manifested by a progressive whitening of the sample suspended in the sorption cell. Light microscopic observations confirmed the presence of salt crystals within the film. If the water activity in the vapor phase is subsequently reduced to values lower than the threshold level, the salt is again sorbed in the polymer and a clear film results. In general, the three components of the polymeric system redistribute to accommodate the equilibrium constraints corresponding to the external water activity and the initial salt loading.

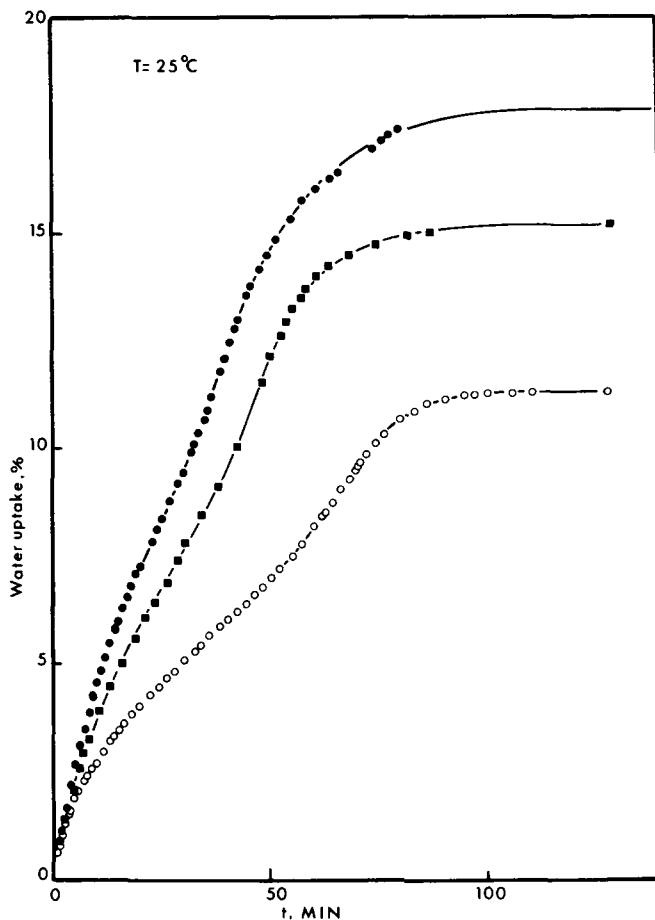


Fig. 5. Water vapor sorption at an external activity of 0.97 in unloaded (O) and NaCl loaded copolymer films. Salt loadings: (■) 0.6 g NaCl/100 g copolymer; (●) 2.25 g NaCl/100 g copolymer.

If an excess of dissolved salt is present, i.e., when an external water activity higher than in the solution in which the polymer was initially saturated is imposed, the excess salt migrates through the film where it phase-separates since the contiguous vapor phase will not accommodate further elution of the migrant salt. The actual water dissolved in the salt-loaded complex, above this threshold vapor activity could not be measured explicitly since the salt, as a second phase, independently tends to form an aqueous solution in equilibrium with the imposed water vapor activity, and the concentrations of both the polymeric system and the free salt are measured by the quartz spring microbalance.

The isotherms determined for the loaded samples are characteristic of intense clustering presumably associated with solvation of the highly hygroscopic free salt phase. The equilibrium water sorption/g salt, needed to form a solution in equilibrium with the imposed vapor phase activity, has been coplotted in Figure 4. The qualitative nature of the water sorption isotherm in the loaded films is quite similar to the form of the isotherm characterizing dissolution of salt and water.

The equilibrium sorption isotherms, obtained from the vapor sorption tests,

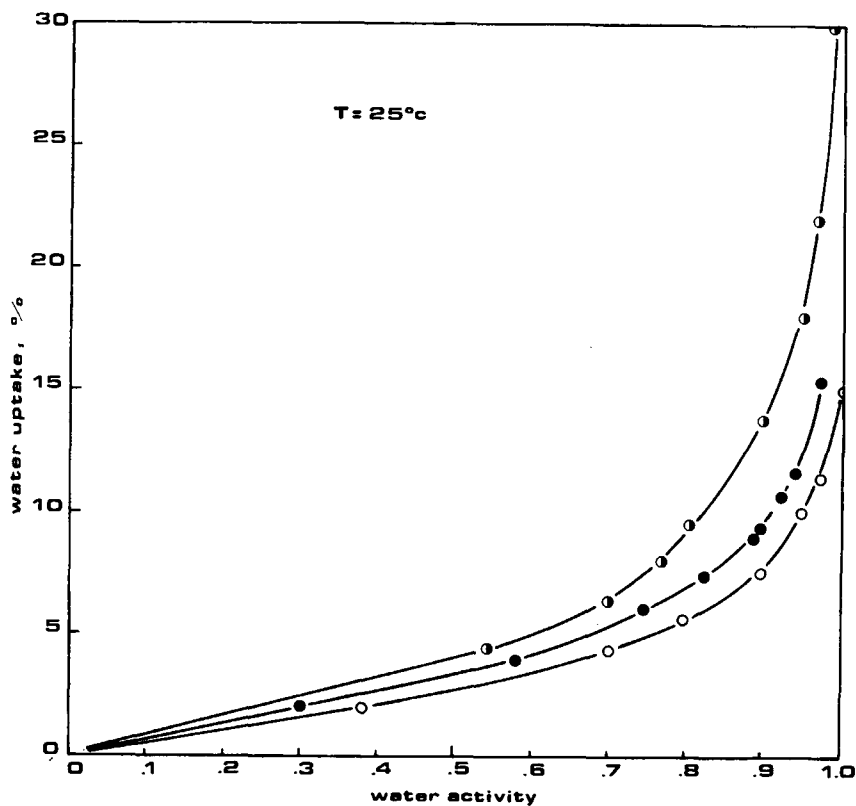


Fig. 6. Water vapor sorption isotherms for unloaded (○) and NaCl loaded copolymer films. Salt loadings: (●) 0.6 g NaCl/100 g copolymer; (○) 2.25 g NaCl/100 g copolymer.

have been coplotted in Figure 7 with the equilibrium water uptake obtained upon contacting the films with aqueous solutions of different salt concentrations. The

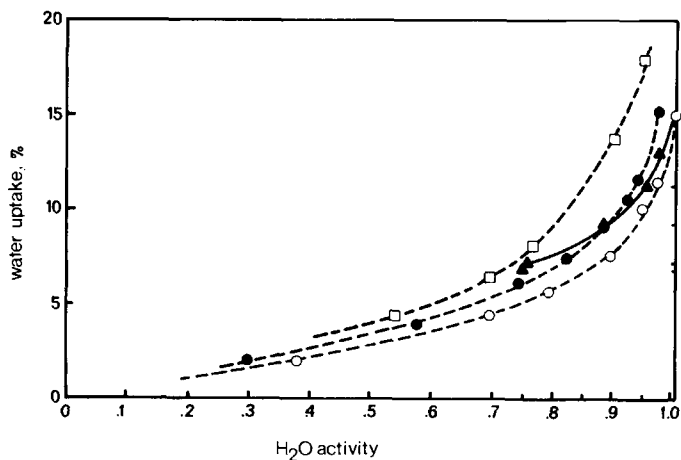


Fig. 7. Water sorption isotherms for unloaded (○) and NaCl loaded copolymer films. Salt loadings: (●) 0.6 NaCl/100 g copolymer; (□) 2.25 g NaCl/100 g copolymer. Full triangles refer to water sorption from aqueous NaCl solutions; all other data refer to sorption from the vapor phase.

data corresponding to the liquid sorption experiments are represented by the full triangles. For convenience and clarity, the vapor sorption isotherms at high activities, presented previously as Figure 6, are presented in Figure 7 as dotted lines to insure that the points of intersection of the vapor and liquid data are not obscured. The vapor sorption isotherm for each sample intersects the liquid isotherm at an activity which closely corresponds to the salt compositions of the aqueous solution with which the loaded polymers were equilibrated prior to vapor sorption testing.

These results confirm that equilibrium is achieved independent of path and that the activity of the contiguous vapor or liquid phase is an appropriate and convenient correlating parameter for data presentation and interpretation. These results are consistent, moreover, with the notion offered previously, that the mobile components redistribute to accommodate the internal constraints imposed upon the system under the diverse experimental conditions explored here.

In all cases, however, the equilibrium water vapor sorption in the salt-loaded films is significantly less than the water content predicted by simple additivity corresponding to the combined equilibria for water dissolution of salt and water sorption in unloaded copolymer, respectively. As previously discussed, metal salts coordinate with hydroxyl-containing polymers through the pendant hydroxyl groups.¹³ The decreased water solubility observed, with respect to simple additivity predictions, could reflect the more highly structured polymer network resulting from the formation of a metal complex which reduces the number and accessibility of the free, uncomplexed hydroxyl groups.⁹

In summary, at low activity in the vapor sorption tests the salt-loaded polymer accommodates an equilibrium water content corresponding to the imposed external water activity and the original salt loading. Up to the threshold value of the external water vapor activity, a three-component, single-phase polymer system is most likely responsible for and, therefore, consistent with the observed behavior. At higher values of the water vapor activity, salt separates as a separate phase, but remains within the confines of the polymer serving as a sink for additional water sorption. Conversely, if the identically loaded polymer-salt system is contacted with a dilute salt solution, corresponding to the identical low water activity used in the vapor sorption experiments, this excess salt is eluted to the contiguous sink of dilute liquid solution and, therefore, the observed sorption is less than observed in the seemingly identical vapor phase experiment.

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