Sorption Behavior of Water Vapor into Polyelectrolyte Complex of Poly(Acrylic Acid) / Poly(4-Vinylpyridine)

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Synopsis

The sorption of water vapor into the polyelectrolyte complex of poly(acrylic acid)/poly(4-vinylpyridine) has been investigated. The sorption isotherm was evaluated on the basis of various theories; BET equation, Flory–Huggins interaction parameter χ_1, and cluster function G_{11}/v_1. The behavior of the BET plot, χ_1, and G_{11}/v_1 was considered in terms of the structure of the complex, while the crosslink density and charge density were determined from the carbonyl absorption in IR spectra. The reasonable conclusion drawn from the available data is as follows. The interaction of water with specific polymer sites plays an important role in the sorption. The sorbed water plasticizes this material, and it enables the expansion of the network. The large amounts of water incorporated by the expansion cannot be dispersed homogeneously in the network, and indicate clustering tendency.

INTRODUCTION

Polyelectrolyte complexes have been noted as new polymer materials, because of their characteristic physicochemical properties.[1,2] Incidentally, all of such properties were examined for the complex membranes saturated with moisture. On the other hand, only slight attention was given to the sorption of water vapor into these materials; at the present stage little is known about the sorption mechanism of water vapor or the structure associating with moisture sorption.

Thus, in the preceding work we have investigated the sorption kinetics of water vapor into the complex of poly(acrylic acid)/poly(4-vinylpyridine), and discussed the morphological structure of the complex and chain mobility of the network.[3] The present paper is concerned with the equilibrium sorption of water by the complex; such sorption data will be utilized for the discussion of the interaction between the complex and water and the feature of water sorbed.

The sorption isotherm was evaluated on the basis of three unrelated theories; i.e., BET equation, Flory–Huggins interaction parameter χ_1, and cluster function G_{11}/v_1. The BET equation is based on the view of a localized multilayer sorption. The Flory–Huggins equation is a product of a typical quasilattice theory of solution in zero approximation. The cluster function originates in the general statistical theory of binary liquid mixtures. Such examination from various directions for the data will be favorable to understand properly the feature of sorption of water into the complex.
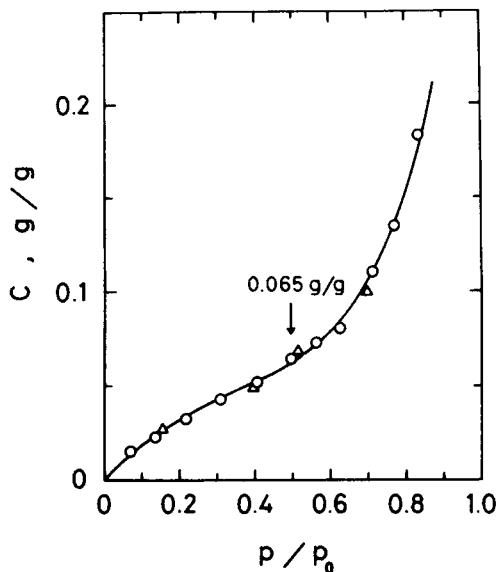
Fig. 1. Sorption isotherm for the system poly(acrylic acid)/poly(4-vinylpyride)-water at 30°C: (○,△) data obtained from successive differential sorption and integral sorption, respectively. The arrow sign indicates the concentration at which polymer–vapor mixture changes from glassy to rubbery state.[3]

The behavior of the BET plot, χ_1, and G_{11}/v_1 is considered in terms of the structure of the complex; the crosslink density and charge density evaluated from IR spectra were useful for consideration.

EXPERIMENTAL

The details of the preparation of sampled films and sorption experiments have been described elsewhere[3]; the complex is composed of equimolar amounts of poly(acrylic acid) and poly(4-vinylpyridine). The densities needed for the calculation of the Flory–Huggins interaction parameter were determined with a density-gradient tube containing ethylacetate and carbon tetrachloride; $d = 1.32$ g/cm³. The infrared spectra of the complex film were measured by using the cell (Shimazu Seisakusho Ltd., Japan) in which humidity can be varied arbitrarily[4]; 85% relative humidity was prepared by the saturated salt solution of potassium chloride.

RESULTS

Sorption Isotherm and BET Plot

Figure 1 gives the sorption isotherm for the poly(acrylic acid)/ poly(4-vinylpyridine) complex–water system at 30°C. The isotherm is a typical sigmoid shape which corresponds to the usual adsorption mechanism. The adsorption is most frequently described by the BET equation for multilayer adsorption.[5] The BET plot for the observations was linear below the relative vapor pressure (p/p_0) = 0.50. While the plot is not presented here, the BET
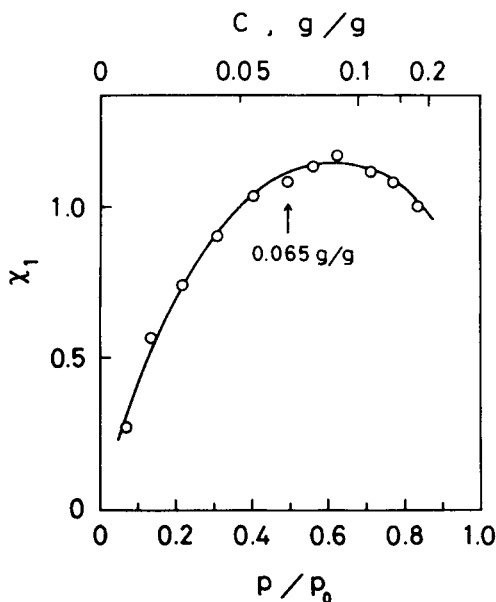
Fig. 2. Interaction parameter χ_1 of Flory–Huggins equation. The arrow sign indicates the concentration at which polymer–vapor mixture changes from glassy to rubbery state.

constants were obtained: the monolayer value n_m and energy factor c were 0.033 g/g and 9.5, respectively. Then n_m value is small as compared with the number of carboxyl groups and pyridine rings. The c value is of such magnitude as expected from the shape of the sorption isotherm.

Flory–Huggins Interaction Parameter

The Flory–Huggins equation is based on the assumption of random mixing and thus it does not account for the adsorption of the solvent molecules to binding sites and for the clustering of the solvent molecules[6]:

$$\ln x = \ln v_1 + (1 - v_1) + \chi_1(1 - v_1)^2$$

where x is the relative vapor pressure, v_1 is the volume fraction of the solvent molecules, and χ_1 is the apparent interaction parameter.

The χ_1 calculated from the sorption isotherm is shown in Figure 2; χ_1 is small in the low pressure range and has a maximum value at $p/p_0 = 0.60$. The increasing trend of χ_1 has often been observed for hydrophilic polymer–water systems. This phenomenon can be interpreted in terms of the decrease of contribution of adsorption mechanism; the adsorption refers to strong affinity between polymer and solvent, which will be predominant in the low pressure region. The decreasing tendency of χ_1 in the high pressure region has been observed for a few polymer–solvent systems, e.g., poly(vinyl alcohol)–water[7]; the decreasing tendency was interpreted in terms of the dissolution of an aggregate.
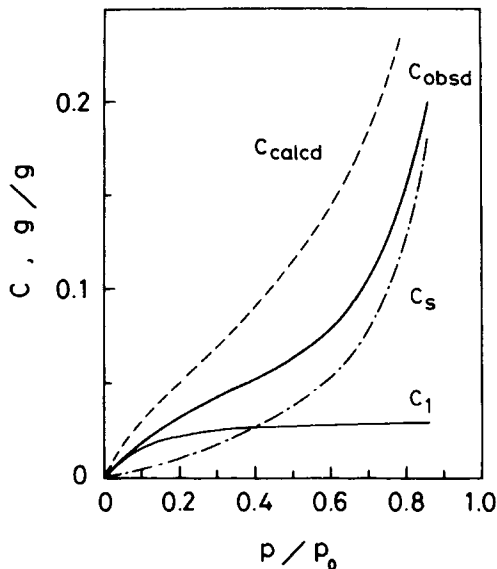
Fig. 3. Separation of experimental isotherm into adsorption part C_1 and dissolution part C_s. C_{calcd} is the curve calculated by Flory–Huggins theory with $\chi_1 = 0.80$.

Adsorption and Dissolution

The theory of solution accompanied by adsorption was reported by Takizawa[8]: It is based on the concept that an isotherm consists of the contribution of adsorption and dissolution. The application of the theory to the present sorption data would be helpful in understanding the sorption behavior.

The procedure of analysis is as follows. The adsorption part is calculated as the value of the BET's first layer. The dissolution part is obtained by subtracting the adsorption part from the experimental isotherm. The χ_1 is calculated for the dissolution isotherm, and the value of extrapolation to $p/p_0 = 1$ is estimated. The calculated isotherm is determined by using this χ_1 value.

The results are given in Figure 3. This theory is suitable for protein–water systems: the calculated curves fit in with the experimental isotherms.[8] Figure 3 shows that the present system cannot be explained satisfactorily by the theory.

Cluster Function

An analysis of sorption behavior can be made on the basis of the cluster function G_{11}/v_1[9]:

$$G_{11}/v_1 = -\phi_2 \left[\partial(a_1/\phi_1)/\partial a_1 \right]_{p,T} - 1$$

where a_1, ϕ_1, and v_1 are the activity, volume fraction, and molar volume of type 1 molecules (solvent molecules), respectively. The quantity G_{11}/v_1 is considered as a measure of clustering tendency, scaled in units of molecular
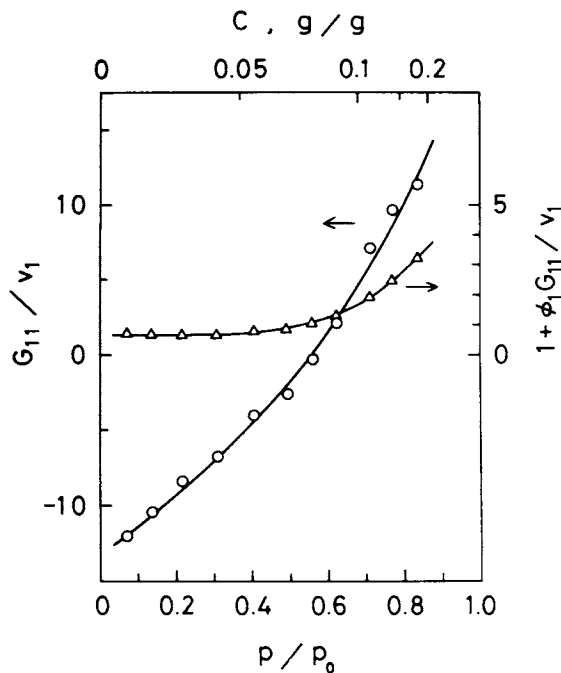
Fig. 4. Cluster function G_{11}/v_1 and mean cluster size $1 + \phi_1 G_{11}/v_1$ of water in the complex of poly(acrylic acid)/poly(4-vinylpyridine).

volume, that is, $G_{11}/v_1 = -1$, which means that a particular type 1 molecule excludes its own volume to other molecules but otherwise does not affect their distribution. When $G_{11}/v_1 > -1$, the concentrataion of type 1 molecules is higher in the neighborhood of a type 1 molecule; there is a tendency for type 1 molecules to cluster.

The G_{11}/v_1 values calculated from the isotherm are shown in Figure 4. The large negative values of G_{11}/v_1 in the low pressure region suggest the interaction of water with specific polymer sites. The large positive values in the high pressure region indicate the clustering of sorbed water molecules. Figure 4 includes also the quantity $\phi_1(G_{11}/v_1) + 1$, which is regarded as a measure of the mean cluster size: The size is about 3 molecules of water at $p/p_0 = 0.80$.

DISCUSSION

The behavior of the BET plot, χ_1, and G_{11}/v_1 in the low pressure range can be interpreted in the term "interaction of water with specific polymer sites." For the sorption in the high pressure region, these theories yielded inconclusive findings. A difficulty arose in the behavior of the interaction parameter and cluster function. The decreasing trend of χ_1 may be attributed to the dissolution of a polymer structure.[7] The dissolution would mean the appearance of new polar groups, and it will contribute to the increase of affinity between polymer and solvent. However, the data of G_{11}/v_1 indicated the clustering tendency of water molecules in the high pressure region; this is in conflict with the phenomenon of dissolution.
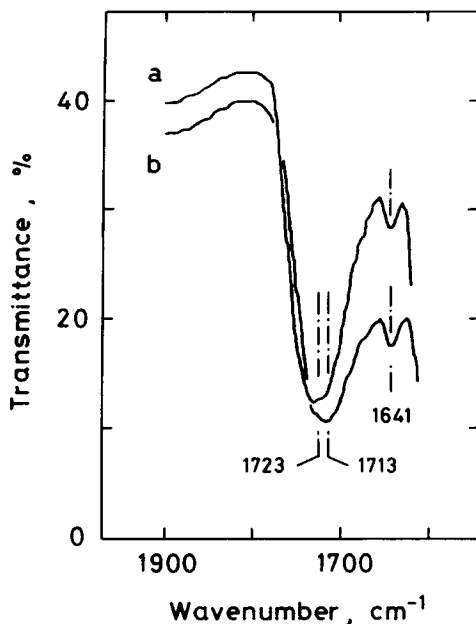
Fig. 5. Infrared spectra in the $\nu_{c=0}$ region of poly(acrylic acid)/poly(4-vinylpyridine) complex: (a) dried film; (b) film kept under 85% relative humidity.

As described above, the three theories are based upon quite different concepts and assumptions, and thus they each yield different findings. On the other hand, the examination of the rate process of sorption provides distinct findings from those presented above: The data of rate process demonstrate the rearrangement of polymer chains and plasticizing of polymer materials.[3] That is, a phenomenon can be expressed in alternative forms by differences of approaches to the problem, analysis of data, or sorption experiments. Therefore, the sorption data seem preferable to be considered on the basis of the structure of this material.

Figure 5 shows the infrared spectra in the $\nu_{c=0}$ region of the poly(acrylic acid)/poly(4-vinylpyridine) complex. The absorption at 1723 cm^{-1} corresponds to nonionized carboxyl groups, and the peak at 1641 cm^{-1} can be assigned to ionized groups.[10] Zezin and Rogacheva reported that the dissociation of carboxyl groups of poly(acrylic acid) is extremely small, and carboxyl groups are necessarily ionized by binding with pyridine rings.[11] Actually, this small peak cannot be observed for poly(acrylic acid); needless to say, poly(4-vinylpyridine) has no absorption in this region. Therefore, the absorption at 1641 cm^{-1} is correlated to the carboxyl groups, which are bound to pyridine rings and consequently ionized. From the peak intensity, the crosslink density and charge density are evaluated to be 5% as a fraction of carboxyl groups. This complex is composed of a loosely crosslinked and slightly ionized network structure. In addition, it is found from the spectra (b) that the crosslink is not broken by moisture sorption.

The figure shows also that the absorption at 1723 cm^{-1} is shifted towards lower frequencies by moisture sorption, while the peak at 1641 cm^{-1} is not

altered. The change in the carbonyl frequencies is often considered in connection with hydrogen bonding and its disruption. In the present case, two kinds of hydrogen bonding are imagined, hydrogen bonds between carboxyl groups in the complex and that between carboxyl groups and water molecules sorbed. The change of the frequencies may be presumed to be due to the disruption of hydrogen bonds between carboxyl groups caused by moisture sorption. However, the disruption of hydrogen bonds shifts the carbonyl absorption towards higher frequencies.[10] The shift of absorption at 1723 cm^{-1} can, therefore, be attributed to the bonding of water molecules on the carboxyl groups.

In view of the above facts on the structure, the reasonable conclusion can be drawn for the sorption of water into the complex. (i) The interaction of water with specific polymer sites plays an important role in the sorption. The data of the BET plot, χ_1, and G_{11}/v_1 in the low pressure region supported such a sorption mechanism. The adsorption will mainly occur on the ionized moiety and carboxyl groups. The shift of carbonyl absorption indicated the hydrogen bonding of water molecules on carboxyl groups. (ii) The sorbed water plasticizes this polymer material.[3] The plasticizing enables the expansion of the network; the expansion will permit the incorporation of large amounts of water. The loosely crosslinked network is favorable for such a phenomenon. The behavior of the interaction parameter χ_1 in the high pressure region is attributable to the sorption accompanied by the expansion of the network; the penetration of large amounts of water decreases χ_1 as it leads to the increase of affinity between the complex and water. (iii) The large amounts of water sorbed in this way cannot be dispersed homogeneously in the network, and the cluster is formed. This may be associated with the low charge density of the complex.

It would be interesting to examine the sorption behavior of water vapor into complexes having dense network structures and highly ionic character.

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