The Effect of Hydrogen Bonding on Vapor Diffusion in Water-Soluble Polymers

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ABSTRACT: Water-vapor transport in poly(acrylic acid)(PAA), poly(*N*-vinyl-2-pyrrolidone)(PVPo), and their 2 : 1 interpolymer complex was measured between 30 and 50°C. It was found that the formation of interpolymer hydrogen bonding not only caused the T_g of the complex to be higher than those of the individual components, but also affected vapor-sorption behaviors. In the high vapor pressure region ($P_r > 0.5$), sorption isotherms in pure PAA and PVPo follow the Flory–Huggins solution theory and the sorbed water molecules may form clusters around the COOH groups in PAA and C=O groups in PVPo. However, sorption in the complex is almost linear for the entire range of water activities. The binary polymer–polymer interaction parameter between PAA and PVPo in the complex, $\chi_{\text{PAA–PVPo}}$, is less than zero, which is indicative of favorable interaction between PAA and PVPo. At lower water activities, sorption behaviors for water in the three polymers can be approximated by Henry's law and vapor-diffusion coefficients can be ranked as PVPo > complex > PAA. The water vapor diffusion coefficients in each system decrease with increasing P_r in the region of $P_r > 0.5$ because the proportion of immobilized water molecules increases with vapor concentration. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 279–291, 1997

Key words: poly(acrylic acid); poly(*N*-vinyl-2-pyrrolidone); hydrogen bonding; water diffusion in glassy and rubbery polymers; clustering function

INTRODUCTION

Interpolymer complexes are formed through secondary bonding forces and often exhibit, as a result of molecular association, unusual properties.[1–3] For example, both poly(acrylic acid)(PAA) and poly(*N*-vinyl-2-pyrrolidone)(PVPo) are water soluble; however, it is well known that they form a water-insoluble interpolymer complex through interchain hydrogen bonding.[4] The glass transition temperature (T_g) of the complex exceeded the average value of the component T_g's.[5,6] It is therefore expected that water-transport properties in the complex would deviate from the rule of average. However, only a few publications addressed this subject.[7]

In the present research, water was used as a diffusional probe to study the effects of hydrogen bonding between PAA and PVPo on the structure of the complex. The interaction between the component polymers was deduced from the equilibrium sorption, the diffusion coefficient, and the clustering function of water vapor in the complex film.

BACKGROUND

Water-diffusion Coefficients and Sorption Isotherms

When a solvent-free polymer is placed in contact with a fluid phase, the sorbate will be taken up

by the polymer until the activities of the diffusant in both phases become identical. The concentration profile of the diffusant along the direction in film thickness during the transient-state sorption process is given by Fick's second law.[8,9] If the diffusion coefficient is independent of concentration, the amount of diffusant, M_t, taken up by a plane sheet of thickness L in time t is given by the equation

$$\frac{M_t}{M_\infty} = 4\left(\sqrt{\frac{Dt}{L^2}}\right)\left(\frac{1}{\sqrt{\pi}} + 2\sum_{n=0}^{\infty}(-1)^n ierfc\frac{nL}{2\sqrt{Dt}}\right) \quad (1)$$

where M_∞ is the equilibrium sorption attained theoretically at infinite time. The fractional sorption is typically linear with $t^{1/2}/L$ for at least half of the total sorption (or desorption) for systems obeying Fickian transport kinetics.[9] The diffusion coefficient, D, can be obtained from the initial gradient of a graph of M_t/M_∞ as a function of $(t^{1/2}/L)$:

$$D = \frac{\pi}{16}\left(\frac{d\left(\dfrac{M_t}{M_\infty}\right)}{d\left(\dfrac{\sqrt{t}}{L}\right)}\right)^2. \quad (2)$$

In many polymer systems, the diffusion coefficient varies either linear or exponentially with concentration. For a solvent–polymer system, a series of experiments usually produce a set of curves, one for each experiment, indicating that the diffusion coefficient is concentration-dependent. The initial gradient of each sorption curve yields a mean value $\bar{D}$, which is the average diffusion coefficient over the range of concentrations appropriate to that experiment:

$$\bar{D} = \frac{1}{C_0}\int_0^{c_0} D\, dC \quad (3)$$

Theories of Polymer Solutions

Several models have been proposed to describe the experimental sorption equilibrium as a function of diffusant activity. For polymer solutions, the Flory–Huggins theory[10] expressed by eq. (4) has found wide application:

$$\ln a_A = \ln(1 - \Phi_B) + \left(1 - \frac{1}{r}\right)\Phi_B + \chi\Phi_B^2 \quad (4)$$

where a_A is the activity of the solvent; Φ_B, the volume fraction of the polymer; r, the number of segments in the polymer; and χ, the Flory–Huggins interaction parameter. In many cases, especially in polar systems, χ changes with polymer concentration.[11]

A different approach which was particularly useful in the understanding of the state of association of the dissolved solvent molecules was the analysis developed by Zimm and Lundberg[12] to determine the extent of clustering in a binary solution. The analysis, when applied to water–polymer mixtures, yields important insights because water molecules are strongly associated in the liquid state with its neighbors and form clusters in relatively nonpolar materials.[9] The clustering function can be obtained from equilibrium data using the relation

$$\Phi_A\frac{G_{AA}}{v_A} = (1 - \Phi_A)\left(\frac{\partial \ln \Phi_A}{\partial \ln a_A}\right)_{PT} - 1 \quad (5)$$

where G_{AA}, v_A, a_A, and Φ_A denote the cluster integral, the partial molecular volume, the activity of component A, and the volume fraction of component A, respectively. For an ideal solution, $G_{AA}/v_A = -1$, which means that a particular type A molecule excludes it own volume to other molecules but otherwise does not affect their distribution. If the quantity $(\Phi_A G_{AA}/v_A)$ is greater than $-\Phi_A$, the concentration of type A molecules is higher in the neighborhood of a type A molecule. Thus, it indicates a tendency of molecules A to form clusters.

If the dependence of the solvent concentration on relative pressure is close to linearity, the following semiempirical equation has been found to be useful[13]:

$$\Phi_A^{-1} = K_1\left(\frac{P_A}{P_0}\right)^{-1} - K_2 \quad (6)$$

where P_A and P_0 are the vapor pressure of a solvent and its saturated vapor pressure at the same temperature, respectively. Three cases were noted, depending on the magnitude of K_2. For $K_2 = 0$, the equation obeys Henry's law, whereas K_2

> 0 indicates the formation of clusters and K_2 < 0 corresponds to the Langmuir equation. However, we note that a Langmuir-type isotherm is generally not found for polymer–solvent systems.

Change from Glassy to Rubbery States During Sorption

The sorption isotherms curve of the penetrant in rubbery polymers are concave from the pressure axis as the penetrant pressure is increased so that[14]

$$\left(\frac{\partial^2 W_A}{\partial P_A^2} \right)_T > 0 \qquad (7)$$

where P_A is the pressure of the penetrant in the gas phase; W_A, the mass fraction of the penetrant in the solution; and T, the temperature of the sorption process. On the other hand, the second derivatives of the isotherms for sorption in glassy polymers are usually negative or close to zero.

During sorption, the glass transition temperature of the polymer–penetrant mixture, T_{gm}, which decreases with increasing mass fraction of the penetrant, may become lower than the experiment temperature when a sufficient amount of the penetrant has been imbibed, i.e., the mixture now enters the rubbery state. The mass fraction W_A at which this transition to rubberlike sorption behavior prevails depends on the specific polymer–penetrant combination. Although our polymers (PAA and PVPo) are initially in the glassy state, it will be seen that sorptions shift to rubbery-state characteristics at $P_r > 0.5$ due to high water solubilities in these polymers.

EXPERIMENTAL

Materials

An aqueous solution containing 5 wt % poly(acrylic acid) (PAA, Aldrich Chemical Co., USA, $MW = 250,000$) was prepared by adding the polymer into deionized water with constant stirring for 24 h. The resultant solution was placed in aluminum dishes and dried by passing an air stream for 24 h at room temperature. The film was placed in a vacuum oven at 1 Torr and 100°C for 1 week to ensure removal of the residual solvent. An aqueous solution containing 5 wt % poly(N-

Table I   Elemental Analysis of PAA–PVPo Complex Obtained from Aqueous Solution

Sample	Concentration of Polymers (mmol/100 g Solution)		Elemental Analysis of the Precipitate (Wt %)	
	PAA	PVPo	C (%)	N (%)
1	6.94	4.50	52.54	5.43
2	20.8	4.50	55.26	5.20
		Calcd[a]	54.60	5.48

[a] The calculated value is based on 2 : 1 molar ratio of PAA to PVPo.

vinyl-2-pyrrolidone) (PVPo, Aldrich Chemical Co., USA, $MW = 40,000$) was prepared by following the same processes.

The elemental analysis of the complex samples which precipitated in mixed aqueous solutions is presented in Table I. The molar ratio of PAA ($MW = 250,000$) to PVPo ($MW = 40,000$) in the complex is close to 2 : 1 (stoichiometry higher than 1 : 1 has been reported in the literature[4]). The precipitated 2 : 1 complex from aqueous solution, however, does not have the desired shape for our sorption experiments. Therefore, we resorted to the following procedures to prepare a film of the same 2 : 1 composition from organic solvents:

One hundred grams dimethyl sulfoxide (DMSO, Fisher Chemical Co., USA) solution containing 0.04 mol of PAA and 0.02 mol of PVPo was prepared by adding the polymers slowly to DMSO with constant stirring for 24 h. The resultant solution was placed in aluminum dishes and dried by passing an air stream for 2 days at 60°C and then dried for 2 days at 100°C in a vacuum oven. To minimize the amount of residual casting solvent, the transparent films were immersed in deionized water for 24 h and then dried again for 2 days at 100°C in a vacuum oven. The membranes were about 100 μm in thickness.

Measurements

A Perkin-Elmer differential scanning calorimeter (DSC) was used for the measurement of T_g. Specimens are heated at 10°C/min. The temperature at which an abrupt increase in heat capacity occurred was designated as T_g.

Films of PVPo, PAA, and their complex for IR measurements were prepared by casting the re-

Table II Glass Transition Temperature of PAA, PVPo, and Their Complex

Material	T_g (°C)
PAA	108
PVPo	163
Complex	155
Weight-average value	132

spective aqueous solutions on KBr crystal windows. The IR spectra were obtained by the use of a Perkin-Elmer 1600 FT-IR spectrometer.

The densities of PAA and PVPo, needed for the calculation of volume fractions, were estimated by using the relation of the molar refraction property[6] to be 1.41 and 1.13 g/cm³, respectively. The method seemed to give reasonable estimates because the calculated densities of polystyrene (PS), poly(vinyl chloride)(PVC), and poly(vinyl alcohol)(PVA) are in good agreement with the data cited in the *Polymer Handbook*.[15] In any case, errors in the estimated densities are not expected to result in gross inaccuracies in the calculated volume fraction values. The estimated density of the complex is based on weight-averaging.

Water-sorption experiments were carried out with a Cahn electrobalance Model 2000 with a sensitivity of 1 μg. The balance was enclosed in a glass vacuum system with service lines to a vapor (or gas) source, a reservoir bulb, a mercury manometer, a weighing unit, and a high-vacuum pumping system. The entire assembly was placed in a thermostated box. Before water-absorption experiments were performed, the polymer membranes were vacuum-dried again for 12 h at 50°C in the chamber. Sorption equilibria were determined from the final weight of penetrant absorbed by the membranes. To examine the effect of water vapor concentration on the diffusion coefficient, the average D were measured using the method of successive sorption by a stepwise small increment of the vapor pressure in each sorption step.[16]

RESULTS AND DISCUSSION

Glass Transition Temperature and IR Spectra

The glass transition temperatures of PAA, PVPo, and the complex are listed in Table II. The experiment was repeated at least twice for each specimen. The measured T_g of the complex was higher

by 23°C than the calculated weight-average value of the T_g of the components ($T_g = W_1 T_{g1} + W_2 T_{g2}$); the increase in T_g was due to hydrogen bonds acting as physical crosslinks.[5,7,17]

In the IR spectra of PVPo and PAA, the C=O stretching band is located at 1716 cm⁻¹ for PAA and 1670 cm⁻¹ for PVPo. The complex shows two bands at 1716 and 1630 cm⁻¹. The shift from 1670 to 1630 cm⁻¹ indicates the formation of hydrogen bonds between the carboxyl groups (—COOH) of PAA and carbonyl groups (C=O) of PVPo. Since the molar ratio of PAA to PVPo is 2 from elemental analysis of the precipitated complex, not all the COOH groups of PAA bond with the C=O groups of PVPo; therefore, the band at 1716 cm⁻¹ can still be seen.

Water-sorption Isotherms

The experimental data of equilibrium sorption isotherms for water vapor in the PVPo film at 30, 40 and 50°C are presented in Figure 1. Up to a relative pressures (P_r) of about 0.4 and about 10% weight gain, the three isotherms coincide and obey an approximately linear relationship. Beyond this activity (P_r), there is a greater increase of vapor solubility with further increase of vapor activity, i.e., $(\partial^2 W_A / \partial P_A^2) > 0$. A visual superposition of the three isotherms indicates that the heat of solution is close to zero at $P_r < 0.4$. Further examination of the sorption isotherms for PVPo in the region $P_r < 0.2$ shows that the absorption behavior can be classified approximately as athermal (zero enthalpy of mixing) and that the interaction parameter χ approaches zero[11] at all three temperatures in the limit of zero relative pressure. However, the higher water solubilities at lower temperatures at $P_r > 0.6$ imply a negative heat of solution in this activity range. Theoretical curves for the ideal solution, $a_A = \Phi_A$, and for the athermal solution (i.e., $\chi = 0$) grossly overestimate the amount of absorbed water.

Kambour et al.[18] found that the equilibrium solubility of n-hexane in glassy polymers was essentially a linear function of the penetrant activity until a penetrant concentration was sufficient to lower the T_g of the solvent−polymer mixture to the experimental temperature. The effective T_g's of n-hexane equilibrated samples measured by differential thermal analysis was found to correspond quite well with the estimated T_g's by analysis of the shape of the sorption isotherms.[19] Based on the above reasoning, it is suggested here that
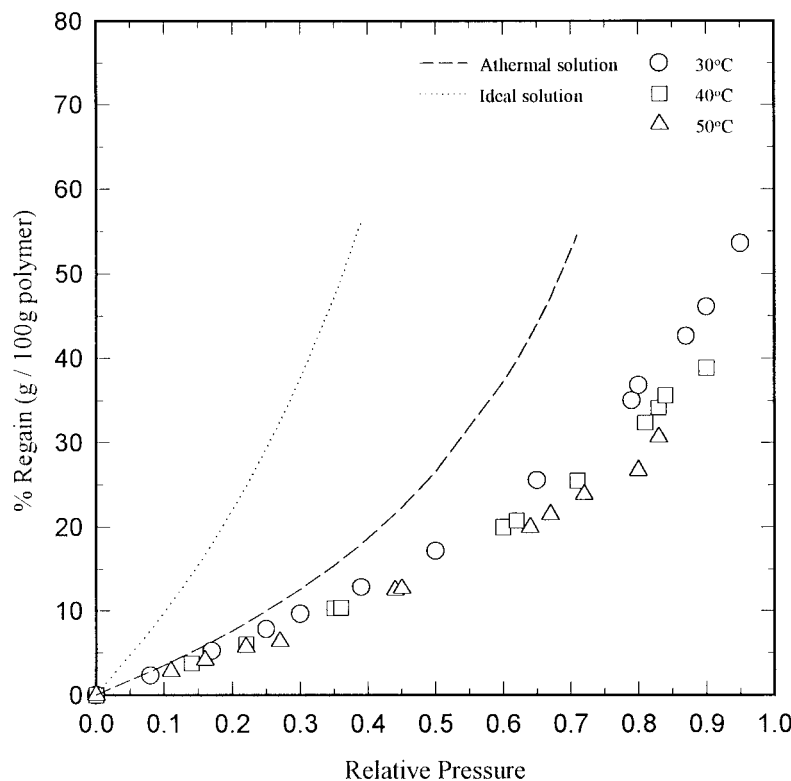
Figure 1 Equilibrium sorption isotherms for water vapor in PVPo.

the change in the water sorption behavior at P_r > 0.4 is due to the lowering of the T_g of the penetrant–polymer mixture to the experiment temperature, i.e., the mixture is now in the rubbery state.

The three sorption isotherms for water in PAA are presented in Figure 2. The isotherms are visually linear up to P_r = 0.4 but the weight of sorbed water is only 3% at P_r = 0.5. The observation of the unexpectedly low sorptive capacity of PAA in this pressure range was not unique. Similar results was reported for polyamides.[20] Presumably, interchain hydrogen bonds were sufficiently strong to resist breakage by water. However, the plasticization effect of water molecules eventually loosens the PAA structure and sorption shifts to rubberlike isotherms at P_r > 0.5.

Strikingly different from the sorption behaviors of vapor in PVPo or PAA, the isotherms for the complex are almost linear over the complete range of relative pressures and the data at three different temperatures fall on a single line (Fig. 3). It seems that the effective T_g of the penetrant–complex mixture remained above the experimental temperatures over the entire range of pene-

trant activities. Therefore, the water regain in the complex at P_r > 0.5 is less than the average value expected from individual components. Interpolymer hydrogen bonding, which is responsible for the high T_g value of the complex, is believed to be also responsible for the decreased amount of sorbed water.

Since the temperature effect on equilibrium sorption is minor in the three polymers but the physical states of PAA and PVPo change from glassy at P_r < 0.5 to rubbery at P_r > 0.5, we shall compare the absorption behaviors in these polymers only at 40°C but at two different ranges of vapor activity: below P_r = 0.3 and above P_r = 0.5.

Sorption Behaviors at P_r < 0.3

The three sorption isotherms for water in PAA, PVPo, and their complex in the low vapor pressure region are plotted in Figure 4. The essentially linear relationships indicate that the sorption behaviors for water in the three membranes can be approximated by Henry's law, i.e., the absorbed water molecules prefer to occupy nonspecific sites in these systems at P_r < 0.3. The water
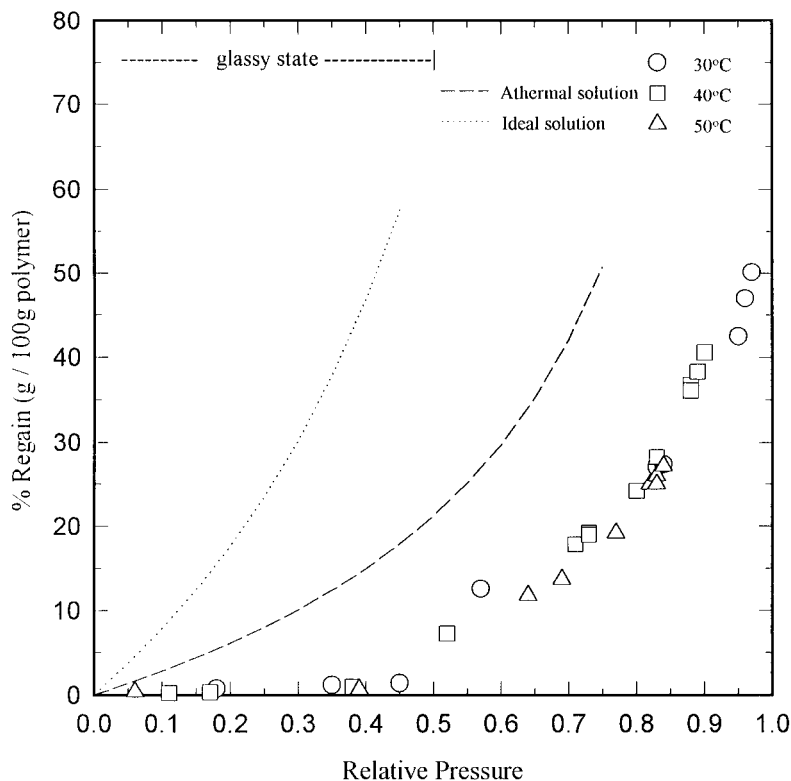
Figure 2 Equilibrium sorption isotherms for water vapor in PAA.

solubilities in the three systems at $P_r < 0.3$ can be ranked as PVPo > complex > PAA. Since the population of water molecules following Henry's law is assumed to be nonspecifically absorbed in the polymers, the ranking is in agreement with the estimated densities because greater density implies smaller free volume.

The average diffusion coefficients of water vapor in PVPo, PAA, and their complex at 40°C are shown in Figure 5, and it is seen that the diffusion coefficient in the complex is intermediate between the values for PAA and PVPo. The diffusion coefficients are nearly constant in PVPo and in the complex up to $P_r = 0.3$. Since $\bar{D}$ is composed of two terms, the thermodynamic term $\partial(\ln a)/\partial(\ln C)$ and the intrinsic mobility term B,[9] the latter must be independent of concentration in both cases because the $\partial(\ln a)/\partial(\ln C)$ terms are constant.

Interestingly, the water-diffusion coefficient in PAA increases with P_r in this pressure range. Because $\partial(\ln a)/\partial(\ln C)$ is constant, B is now dependent on vapor concentration. This may result from an increase in the free volume of PAA, as water molecules enter the matrix.

Sorption Behaviors at $P_r > 0.5$

Interaction Parameters Between Water and Polymers

If the interpolymer complex is treated as a single component, the three interaction parameters can be replaced by χ_c[21]:

$$\chi_c = \chi_{12}\Phi_{20} + \chi_{13}\Phi_{30} - \chi_{23}\Phi_{20}\Phi_{30} \qquad (8)$$

where χ_{12} and χ_{13} are the interaction parameters between water 1 and pure polymers 2 and 3, respectively, and χ_{23} is the polymer–polymer interaction parameter. Φ_{20} and Φ_{30} represent the volume fraction of each polymer based on the solvent-free composition of the complex.

The relations between the interaction parameters χ and the volume fractions of vapor in the three materials are shown in Figure 6. It is seen that χ increases approximately linearly with Φ_A for water absorption in PVPo and the complex for the entire activity range but decreases slightly with the increasing Φ_A in PAA at $P_r > 0.6$, with the relations
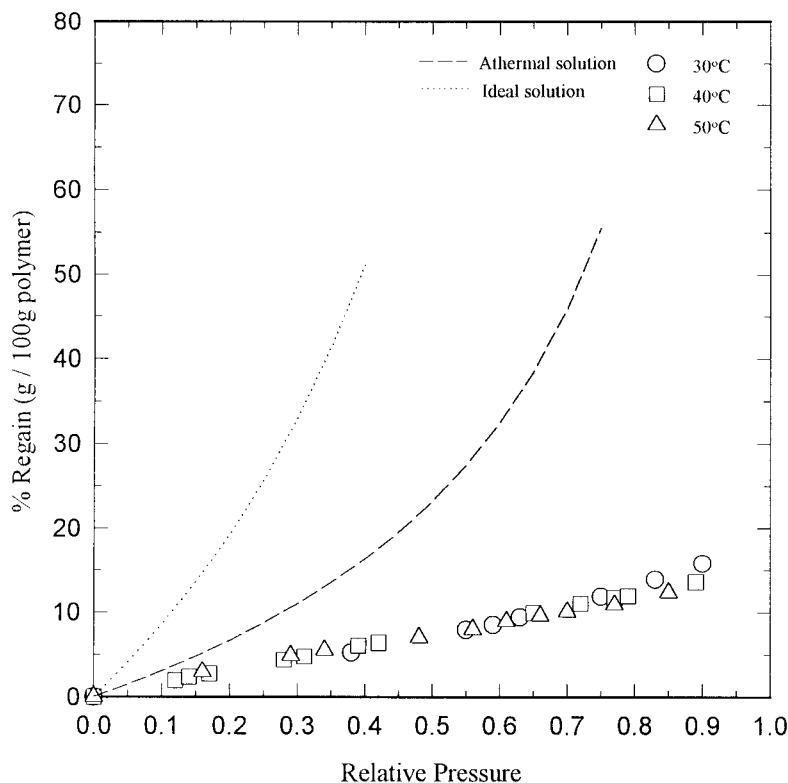
Figure 3 Equilibrium sorption isotherms for water vapor in the PAA–PVPo complex.

$\chi = 1.73\Phi_A + 0.23$ (water in PVPo)

$\chi = 5.24\Phi_A + 0.50$

(water in PAA–PVPo complex)

$\chi = -0.39\Phi_A + 0.80$ (water in PAA at $P_r > 0.6$)

When χ_C is larger than both χ_{12} and χ_{13}, it is evident from eq. (8) that $\chi_{23} < 0$ and the interaction between polymers 2 and 3 is favorable. This is the case for the complex (Fig. 7); the two polymers are brought together by hydrogen bonding, so that their complex is relatively less attracted to water compared to pure PVPo and PAA.

Although the water solubilities (wt %) are about 1.5 times higher in PVPo than in PAA in the region $P_r = 0.6$–0.8, $\chi_{\text{PAA–water}}$ decreases slightly with increasing P_r in this pressure range whereas $\chi_{\text{PVPo–water}}$ increases. This can be rationalized by assuming that most of the intercarboxyl hydrogen bonds in PAA are broken by virtue of interaction with water at about $P_r = 0.5$, and the sorption process becomes increasingly favorable energetically. In contrast, the linear increase of $\chi_{\text{PVPo–water}}$ with Φ_A indicates the average affinity between water and PVPo actually decreasing with

increasing P_r, although there are larger amounts of sorbed water.

Cluster Function

Plots of reciprocal Φ_A vs. reciprocal P_r in the $P_r > 0.5$ range, according to eq. (6), are approximately linear from which the values of K_2 are obtained as 1.15 for PVPo, 5.56 for PAA, and close to zero for the complex. Since K_2 is positive but small for PVPo, the sorbed water molecules may form clusters only to a minor extent in the polymer. The larger K_2 value for PAA is indicative of a different situation. In the following, the Zimm–Lundberg cluster function will be used to analyze sorption data.

The equilibrium isothermal data are used to evaluate the clustering function, $\Phi_A G_{AA}/V_A$, from eq. (5) by assuming the volume of mixing to be negligible. The relations between the Zimm–Lundberg cluster functions and the volume fractions of vapor in the polymers at $P_r > 0.5$ are shown in Figure 8. As noted previously, the condition $\Phi_A G_{AA}/V_A > -\Phi_A$ indicates water-cluster formation in the polymer. We find that the quantities $\Phi_A G_{AA}/V_A$ are only slightly greater than $-\Phi_A$ for water
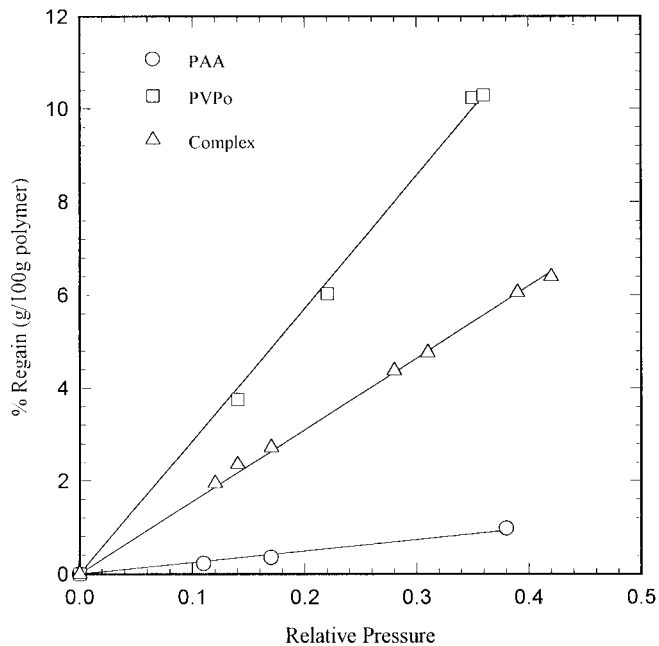
Figure 4 Equilibrium sorption isotherms for water vapor in PAA, PVPo, and the complex at 40°C and $P_r < 0.5$.

absorption in PVPo and this conclusion is consistent with the magnitude of K_2. In comparison, both the K_2 and $\Phi_A G_{AA}/V_A$ values are greater for PAA. It is obvious that water clustering in PAA
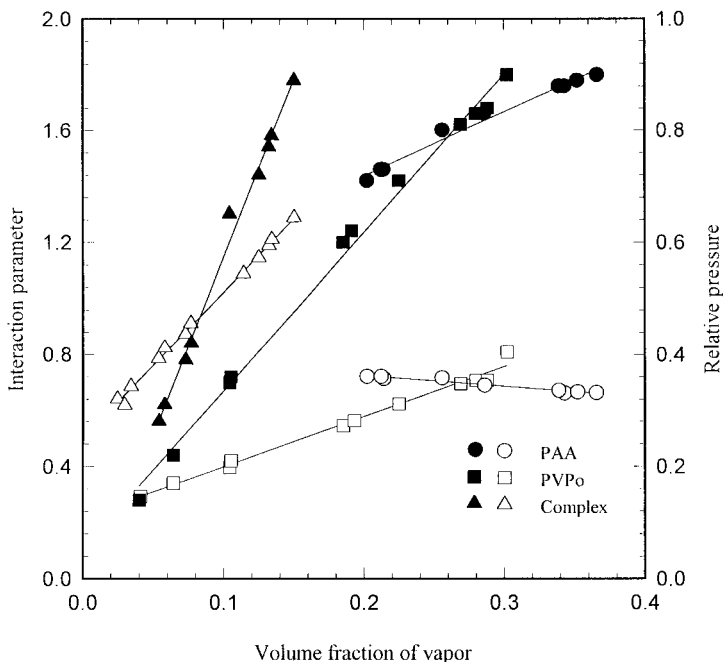
is stronger than that in PVPo due to hydrogen bonding between carboxyl group of PAA and water.

For the complex, the magnitudes of both K_2 and
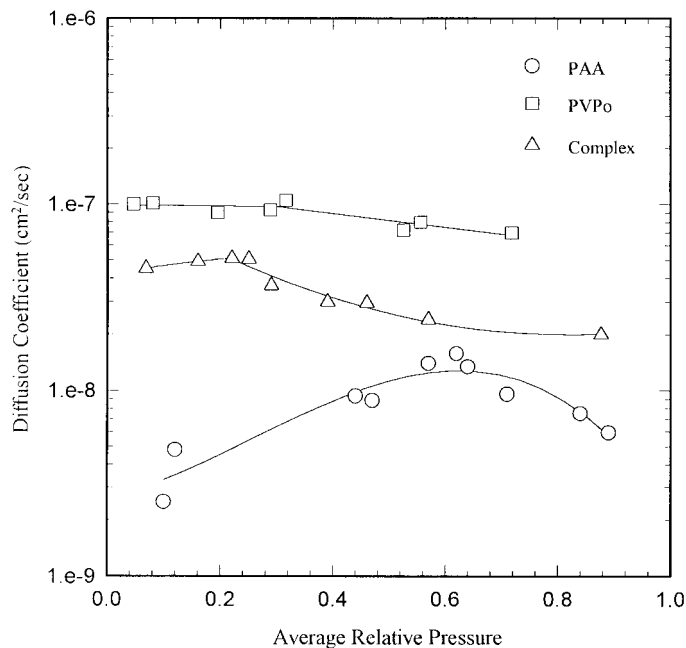
Figure 5 Diffusion coefficient for water vapor in PAA, PVPo, and their complex at 40°C.

Figure 6 (Empty symbols) Flory–Huggins interaction parameter and (solid symbols) relative pressure for water in PAA, PVPo, and their complex.

the cluster function suggest that there is little cluster formation although there is a stoichiometric excess of the carboxyl groups. For reasons yet to be understood, the excess carboxyl groups do not behave in the same way in the sorption process as do the COOH groups in PAA. It seems that interpolymer hydrogen bonding in the complex exercises a severe constraint to swelling and
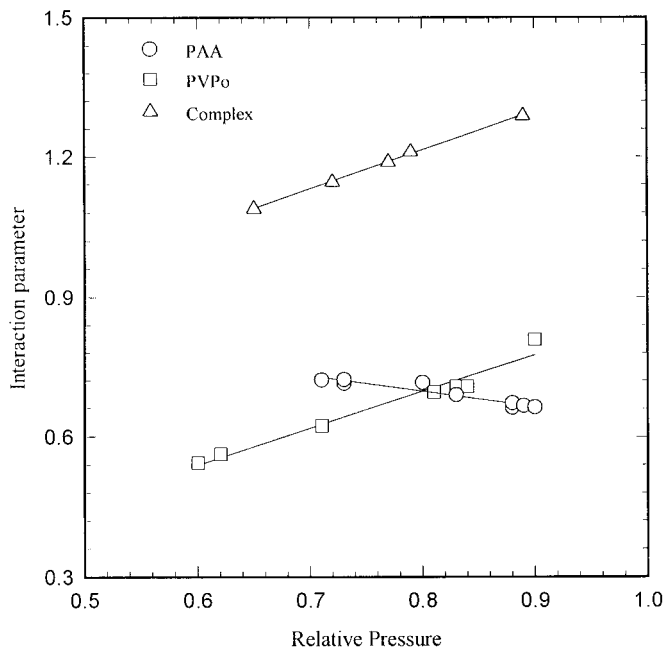
Figure 7 Pressure dependence of the Flory–Huggins interaction parameter for water vapor in PAA, PVPo, and their complex at 40°C.
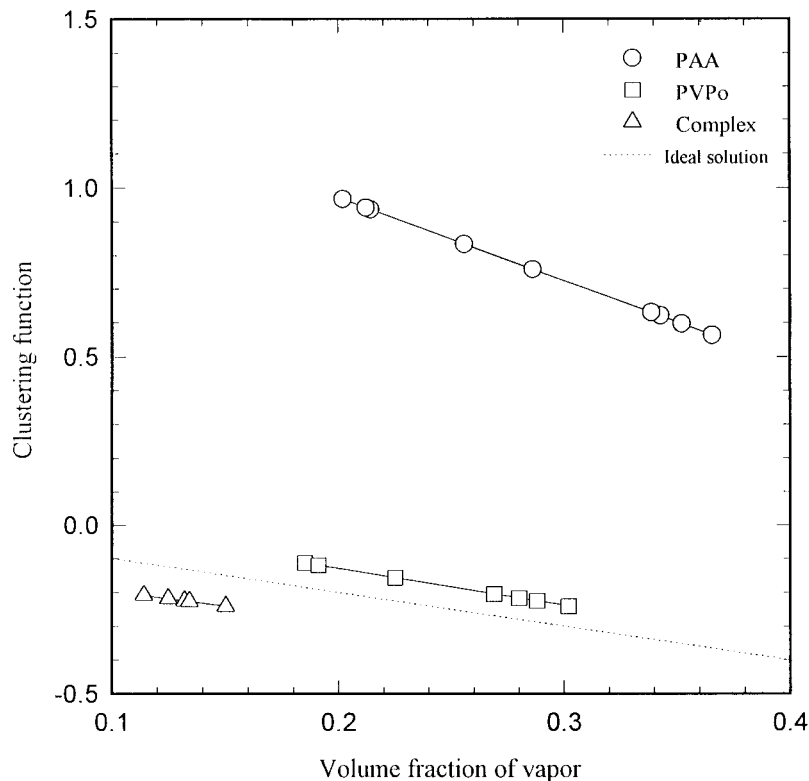
Figure 8 Cluster function of sorbed water in PAA, PVPo, and their complex at P_r > 0.5.

the excess carboxyl groups are not as accessible to water molecules as in PAA.

Vapor-Diffusion Coefficient

The average diffusion coefficients ($\overline{D}$) of water vapor in PAA and PVPo in the $P_r > 0.5$ region were found to decrease with increasing vapor pressure (Fig. 5). A possible mechanism leading to the decreases of $\overline{D}$ with increasing vapor pressure is that the proportion of immobilized water molecules increases as a result of water clustering.[9] The stronger dependence in PAA is in agreement with the analysis of K_2 and clustering function values. Additionally, the vapor diffusion coefficient in PVPo is one order of magnitude higher than that in PAA at $P_r = 0.7$. This again leads to the suggestion that water molecules are more strongly associated with the COOH groups than with the C$=$O groups in PVPo and causes more extensive clustering and lower diffusion coefficients.

Interestingly, water vapor diffusion coefficients in the complex were found to decrease somewhat with increasing water activities. Since $\chi_{\text{complex}-\text{water}}$ increases with vapor concentration at $P_r > 0.5$, the decrease of $\overline{D}$ with vapor concentration possibly results from the increase of the proportion of immobilized water molecules. We noted that the complex had a relatively high degree of water swelling but a low diffusion coefficient when compared to other polymer membranes[22]; therefore, it is suggested that hydrogen bonds are formed among the two polar groups, COOH and C$=$O, and water molecules in the complex.

In a series of recent papers by Vrentas and Vrentas,[23,24] the free-volume theory of diffusion was refined to account for solvent diffusion in glassy polymers and for the concentration dependence of the diffusion coefficient. With suitably chosen free-volume parameters, model calculations illustrate conditions for positive or negative concentration dependence of D and the effect of the transition from the glassy to the rubbery state. When the diffusion coefficients in Figure 5 are replotted against the concentration of the diffusant (W_1) in Figure 9, log D decreases with increasing W_1 in both PVPo (W_1 from 0.01 to 0.24) and the complex (W_1 from 0.01 to 0.13). However,

Weight fraction of the diffusants (W_1)
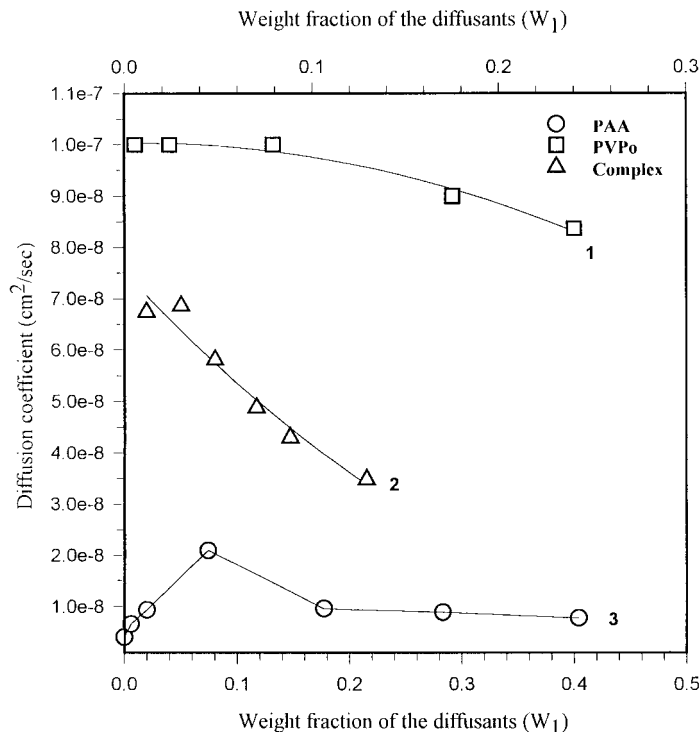
Figure 9 Diffusion coefficients for water vapor in PAA, PVPo, and their complex with respect to the weight fraction at 40°C. Curves 1 and 2 share the upper x-axis and curve 3 corresponds to the lower x-axis.

the concentration dependence is more complicated in PAA. In the high vapor pressure region in which the sorption behavior is rubberlike, the diffusion coefficient decreases in a regular fashion with increasing concentration. In the low vapor pressure region in which W_1 is small and the sorption isotherm is glasslike, the concentration dependence is reversed. Because of these complications which probably arise from hydrogen-bond-ing interaction, we have not applied the theory of Vrentas and Vrentas in the analysis of our results.

Summary of Water Absorption

To summarize the effects of hydrogen bonding on the behaviors of water absorption in the polymers, these results are assembled in Tables III and IV. Interchain hydrogen bonding prevails in PAA at

Table III Water Absorption in PVPo, PAA, and Their Complex

	$P_r < 0.5$			$P_r > 0.5$		
	PVPo	PAA	Complex	PVPo	PAA	Complex
State	G	G	G	R	R	G
Interchain H-bonding	No	Yes	Yes	No	—	Yes
K_2	—	—	—	> 0	> 0	< 0
Water clustering	No	No	No	Yes	Yes	No
Sorption mechanism	H	H	H	F–H	F–H	$\sim$ H
Diffusion coefficient	High	Low	Inter.	High	Low	Inter.

G: glassy state; R: rubbery state; H-B: hydrogen bonding; F–H: Flory–Huggins model; H: approximate Henry's law; Inter: intermediate.

Table IV   Water Absorption in PAA

	$P_r < 0.5$	$P_r > 0.5$
Structure	PAA–PAA (hydrogen bond)	Hydrogen bond was broken
State	Glassy	Rubbery
$(\partial^2 P_A / \partial W_A^2)_T$	> 0	< 0
Isotherms	Low capacity	Slope increases with P_r
χ	Higher values	Lower values
K_2	—	> 0, water clustering
Cluster function	—	$> -\Phi_A$, water clustering
Sorption mechanism	H	Clustering
Diffusion coefficient	Lower, increase with P_r	Higher, decrease with P_r

$P_r < 0.5$ and in the PAA–PVPo complex over the entire water activities.

CONCLUSIONS

1. The T_g of the complex is much higher than the weight-average component T_g values. The weight of sorbed water in the complex, on the other hand, is much less than the weight-average value at high vapor pressure. These observations can be explained by the hydrogen-bonding formation between the PAA and PVPo chains in the complex.
2. Since the relative strengths of polymer–polymer, polymer–water, and water–water bonds are important factors in deciding the total regain, the strong hydrogen bonds formed between PAA and PVPo reduce substantially the total regain and increase the magnitude of Flory–Huggins interaction parameter $\chi_{\text{complex–water}}$.
3. Hydrogen bonding between polymer chains also influences the sorption mechanism. When it is absent, as in the case of PVPo, sorption follows the Flory–Huggins equation in the $P_r > 0.5$ region but sorbed water molecules show a tendency toward clustering. When interpolymer interaction is strong, as in the case of the complex, the sorption mechanism is close to Henry's law.
4. The degree of clustering of water in the polymer depends on the polar groups in the polymer. Clustering is believed to be more extensive in the neighborhood of the carboxyl groups of PAA than that in the neigh-

borhood of carbonyl groups (C=O) of PVPo. In the PVP–PAA complex, the clustering tendency is also small.

5. At low vapor activities, sorption behaviors in these systems approach Henry's law, and the vapor diffusion rate in the complex is intermediate between the values for PAA and PVPo.
6. Up to $P_r = 0.3$, the diffusion coefficients of water change very little in PVPo and in the complex but increase in PAA, possibly because of an increase in the free volume. In the region $P_r > 0.5$, the diffusion coefficients in the three systems all decrease with increasing diffusant concentration because the proportion of immobilized water molecules increase.

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