Studies on the Sulfonation of Poly(phenylene oxide) (PPO) and Permeation Behavior of Gases and Water Vapor Through Sulfonated PPO Membranes. III. Sorption Behavior of Water Vapor in PPO and Sulfonated PPO Membranes

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SYNOPSIS

Water vapor absorption and desorption by poly(phenylene oxide) (PPO) and sulfonated PPO (SPPO) membranes were studied at a constant temperature of 30°C and over a broad range of water activity ($0.05 \leq a < 0.8$) by the weighing method. The experimental sorption isotherms of both PPO and SPPO possessed a general sigmoidal shape, which suggested that they belong to type II; thus, the data may be quantitatively analyzed according to the BET or GAB equation for multilayer sorption processes. The number of site-bound water molecules per monomeric unit was increased by a factor of 150 after sulfonation of PPO. The features of the reduced absorption and desorption curves of both PPO and SPPO suggested that the sorption processes were non-Fickian. The diffusion coefficient calculated from the slope of the initial linear part of the curves showed concentration dependence. The permeability of water vapor through SPPO was more pressure-dependent than was that through PPO. The Flory–Huggins interaction parameter derived from experimental data on SPPO had a smaller value compared with that of PPO and was a monotonic increasing function of water activity in the low-activity region and then leveled off at $a > 0.6$, showing a corresponding initial decrease of the polymer–water interaction, which then gradually reached a certain stable value. Water clustering for SPPO was much less than that for PPO, which is clear proof of its higher hydrophilicity. The results from this study showed that SPPO could be an excellent dehumidification membrane material. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In preceding work, we investigated the sulfonation of PPO and its physical properties including the permeation behavior of gases and water vapor through poly(phenylene oxide) (PPO) and sulfonated PPO (SPPO) membranes.[1,2] The present article is concerned with the equilibrium sorption of water by these two samples; such sorption data will be utilized in a discussion of the interaction between the polymer and water molecule and the mechanism of water sorbed.

The sorption isotherm was evaluated on the basis of three unrelated theories, i.e., the BET or GAB equation, the Flory–Huggins interaction parameter, X, and the cluster function G_{11}/v_1. Such examination of the data from various directions will aid in understanding properly the sorption mechanism for water into the two kinds of polymers whose structures differ only slightly from one another.

BACKGROUND AND THEORY

The permeation of most simple gases such as oxygen and nitrogen through a polymer matrix under normal conditions follows the Fickian mechanism and

is a coupled process involving the dissolution and diffusion of the gases. The permeability P of a polymer is therefore a function of the sorption level S (thermodynamic component) and the diffusivity D (kinetic component) of the permeating substance:

$$P = DS \qquad (1)$$

Typically, the solubility of water in hydrophobic polymers is relatively low, and the sorption follows Henry's law and the P is relatively unaffected by the surrounding water. The transport mechanism in these cases follows Fick's law.

On the other hand, the water-sorption level can be extremely high in hydrophilic polymers, and the P is greatly affected by the amount of water present, due to its hydrogen-bonding nature and other polar interactions with the polymer backbone, tending to follow different transport mechanisms.

There are three states of the water adsorbed in these cases:

1. Homogeneous sorption occurs in cases where the interaction between the polymer and water is uniform. The distribution can be described by the Flory–Huggins equation,[3] which is a product of a typical quasi-lattice theory in zero approximation:

$$\text{Ln } a = \text{Ln } \phi_1 + (1 - \phi_1) + \chi(1 - \phi_1)^2 \qquad (2)$$

   where a is the water relative activity in the environment; χ, the interaction parameter that is a function of the activity; and ϕ_1, the volume fraction of water in the binary system.

2. Localized multilayer sorption occurs when adsorbed water is tightly bound to the polymer molecules, and there exist two populations of water in the polymer: a bound and a liquid-like population. This multilayer sorption isotherm can be described by the BET equation[4,5]:

$$n_1/n_s = 1/(1 - a) - 1/[1 + (k - 1)a]$$

   or

$$a/n_1(1 - a) = 1/n_sk + (k - 1)a/n_sk \qquad (3)$$

Here, n_1 is the number of sorbed molecules per monomeric unit at a given relative activity a; n_s, the number of sorption sites per monomeric unit (first monolayer sorption capacity); and k, a parameter related to the energy difference of the sorbed molecules and in the other "liquid-like" layers; thus, it can be regarded as the ratio of the binding constants of a water molecule directly bound to the sorption site (first layer) and of one bound indirectly in the succeeding "liquid-like" layers.

However, in almost all cases, the BET plots are linear only over the lower half of the range of activity of the sorbate ($0.05 < a < 0.35$–0.40). This weakness has been corrected in terms of a modified BET isotherm, the so-called GAB isotherm,[6] which reproduces the experimental data up to $a \leq 0.8$–0.9:

$$n_1/n_s = 1/(1 - fa) - 1/[1 + (k - 1)fa]$$

or

$$a/n_1(1 - fa)$$
$$= 1/n_skf + (k - 1)a/n_sk \qquad (4)$$

where the constant f is the measurement of the difference between the standard chemical potentials of the molecules in the second sorption stage (over second layer) and in the pure liquid stage. If f is < 1, a lower sorption than that demanded by the BET model is predicted and allows the GAB isotherm to be successful up to the limit stated above, leading to a considerable improvement over the BET equation.

For a strongly sorbing substance, $k \gg 1$ and eq. (4) becomes very simple for the inverse of n_1:

$$1/n_1 = (1 - fa)/n_s \qquad (5)$$

The two constants n_s and f can readily be determined by extrapolating to $1/n_1 = 0$, giving $1/f$ directly as the intercept with the a axis, and to $a = 0$, giving $1/n_s$ at the ordinate.[7]

3. The cluster function that originates in the general statistical theory of binary liquid mixtures accounts for the association of water molecules in the polymer. In clusters, water molecules can associate with other water molecules, but not necessarily with polymer molecules.

The experimental sorption isotherm data may be analyzed on the basis of the Zimm–

Lundberg theory that correlates the cluster function G_{11}/v_1 with the solvent activity according to the following equation[7]:

$$G_{11}/v_1 = -\phi_2[\partial(a/\phi_1)/\partial a]_{P,T} - 1 \quad (6)$$

where v_1 is the partial molar volume of type 1 (solvent) molecules, and ϕ_2, the volume fraction of type 2 (polymer matrix) molecules. The quantity G_{11}/v_1 is considered as a measure of clustering tendency, scaled in units of molecular volume, i.e., $G_{11}/v_1 = -1$ means that the solvent molecule excludes its own volume to the other molecules of the same type but does not otherwise perturb their distribution; the higher values of the clustering function show a trend of the solvent molecules to cluster.

In multilayer adsorption, molecular segregation at low coverage, going over to clustering at higher coverage, should be reflected by the clustering function for adsorbed molecules increasing from much less than -1 to values greater than -1.

The clustering function for adsorbed molecules obtained from the BET isotherm [eq. (3)][8] is as follows:

$$G_{11}/v_1 = -\phi_2\{[1 - 2/k - 2a$$
$$\times (1 - 1/k)]v_s/v_1 + 1\} - 1 \quad (7)$$

where v_s is the partial molecular volume of the adsorption site.

The value of v_s/v_1 can be derived from following equation[8]:

$$\phi_1 = (1 + n_s v_s/n_1 v_1)^{-1}$$

i.e.,

$$v_s/v_1 = n_1/n_s(1/\phi_1 - 1) \quad (8)$$

The quantity $N_c = \phi_1(G_{11}/v_1) + 1$ can be regarded as a measure of the mean cluster size.

EXPERIMENTAL

The preparation and characterization of SPPO membranes have been described in detail in Part I of this series.[1]

The absorption and desorption experiments were carried out at 30°C by the weighing method. The amount of water at absorption equilibrium and the rates of absorption and desorption were measured using a high-vacuum apparatus (0.4 Pa) equipped with an electromagnetic microbalance (Model GAB-1, Chyo Balance Corp., Japan) (accuracy ± 0.005 mg). The pressure of water vapor was measured with a Baratron pressure transducer (Type 221A, MKS).

The values of relative vapor pressure, p/p_0, at which the sorption data were obtained, were 0.114, 0.248, 0.408, 0.617, and 0.792 for PPO and 0.047, 0.104, 0.267, 0.383, 0.603 and 0.751 for SPPO samples. The activity of water, a, was set equal to p/p_0. The order of measurements using the same sample membrane had no effect on the values of concentration of water, indicating that the conformation of the polymer chains is in a rather stable glassy state under the experimental conditions.

RESULTS AND DISCUSSION

Characterization of Samples

Two membrane samples were used in the study. One is the original PPO membrane with a density of 1.061 g/cm³ and T_g of 210°C; another is the sodium form of the SPPO membrane with a sulfonation degree of 28.8 mol % and density of 1.254 g/cm³ and T_g of 240°C.

Dependence of D, S, and P on Water Vapor Activity

The typical reduced sorption curves, M_t/M_∞, vs. $(t/x^2)^{0.5}$ at 30°C are given in Figure 1; M_t is the amount of water sorbed in time t, and M_∞, the corresponding limiting value at equilibrium; x is the thickness of the dry membrane, presumed constant over the whole sorption process. The curves show some of the characteristics of Fickian diffusion process: (a) Absorption curves exhibit a straight line up to at least 0.6 of M_t/M_∞ and, also, desorption curves exhibit a linearity up to 0.2 or more of $(1 - M_t/M_\infty)$, and (b) curvature concave to the abscissa axis following the linear increase. However, the sorption and desorption curves intersect at a certain activity (at $a = 0.617$ for PPO and at $a = 0.383$ for SPPO), indicating that the sorption and desorption of water in both PPO and SPPO are of non-Fickian type, which has been ascribed to slow relaxation motions of polymer chains that occur within a time scale comparable to that of the concurrent diffusion process. However, since deviations from the Fickian behavior are not so pronounced, it may be permissible to estimate the apparent diffusion coefficient D by analyzing these curves.[9]
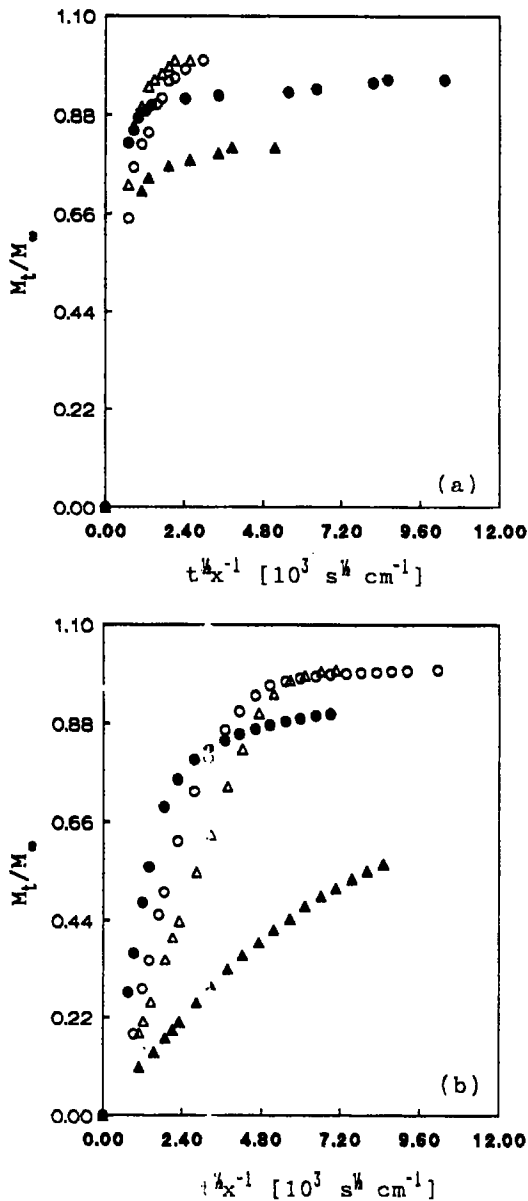
Figure 1 Typical reduced sorption and desorption curves of water vapor in (a) PPO and (b) SPPO membranes at 30°C. Open and filled symbols refer to sorption and desorption, respectively. ($\triangle$, $\blacktriangle$) for (a) PPO at vapor activity $a = 0.408$ and (b) SPPO at $a = 0.047$; (O, ●) for (a) PPO at $a = 0.792$ and (b) SPPO at $a = 0.751$.

Thus, the apparent diffusion coefficient for the sorption mode, D_a, is

$$D_a = (\pi/16)R_a^2$$

Similarly, that for the desorption mode, D_d, is

$$D_d = (\pi/16)R_d^2$$

where R_a and R_d are the slopes of the initial linear part of the adsorption and desorption curves, respectively. The arithmetic mean of D_a and D_d may be taken as approximately equal to the integral diffusion coefficient Dw.[7,9]

As shown in Figure 2, D_a and D_d for PPO are equal except at $a > 0.6$, indicating that the sorption at $a < 0.6$ is Fickian, whereas for SPPO, D_a is larger than D_d at $a < 0.4–0.5$ and just the opposite at $a > 0.5$. With increasing activity, D_a passed through a maximum at $a \approx 0.3$ and then decreased, sug-
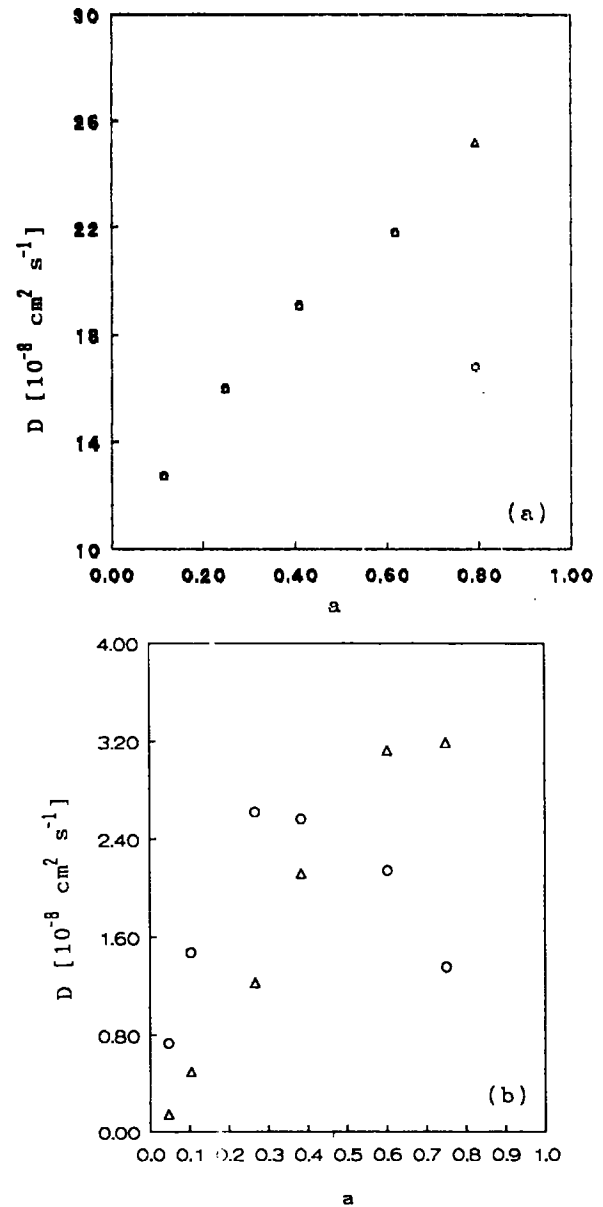

Figure 2 Activity dependence of diffusion coefficients for (O) sorption and ($\triangle$) desorption of water vapor in (a) PPO and (b) SPPO membranes at 30°C.

gesting that the relaxation of the SPPO chains caused by dissolved water occurs even at the early stage of sorption.

It is obvious from Figure 3 that D_w for SPPO exhibits strong concentration dependence in the low concentration region, due to its hydrogen-bonding nature and ion interaction between water molecules and —SO_3Na groups in the polymer backbone, and reaches a maximum at a certain concentration and then slightly decreases. On the other hand, the value of D_w for PPO is 10 times larger than that for SPPO and exhibits less concentration dependence. The great disparity in concentration dependence of D_w for PPO and SPPO may be attributed to the difference in molecular structure of their polymer chains. The —SO_3Na groups introduced into PPO molecular chains may protrude sufficiently into the interchain volume such that, for a given amplitude of rotational motions, the average gap size generated is reduced. Furthermore, the —SO_3Na groups on adjacent chains may directly suppress torsional motions in the polymer by interfering with one another, leading to an increase of chain stiffness, as reflected by T_g going up from 210°C for PPO to 240°C for SPPO, and further reduce the size of transient molecular openings, which reduces the diffusivity considerably.
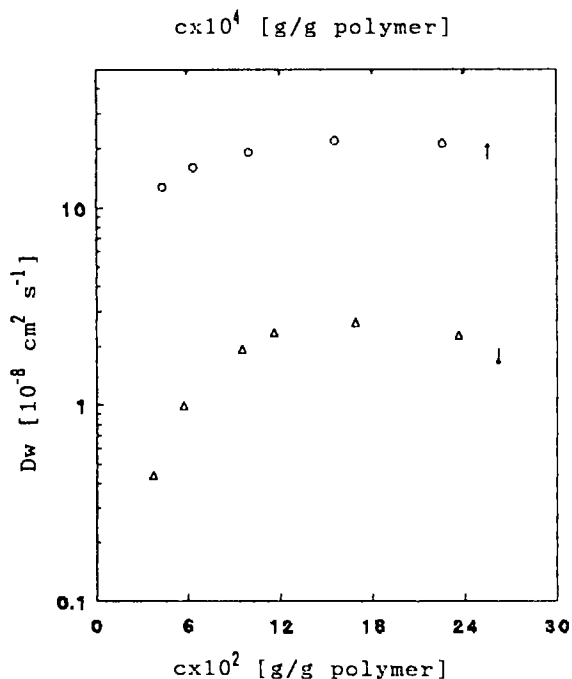

Figure 3 Concentration dependence of diffusion coefficients of water vapor in (O) PPO and (△) SPPO membranes at 30°C.
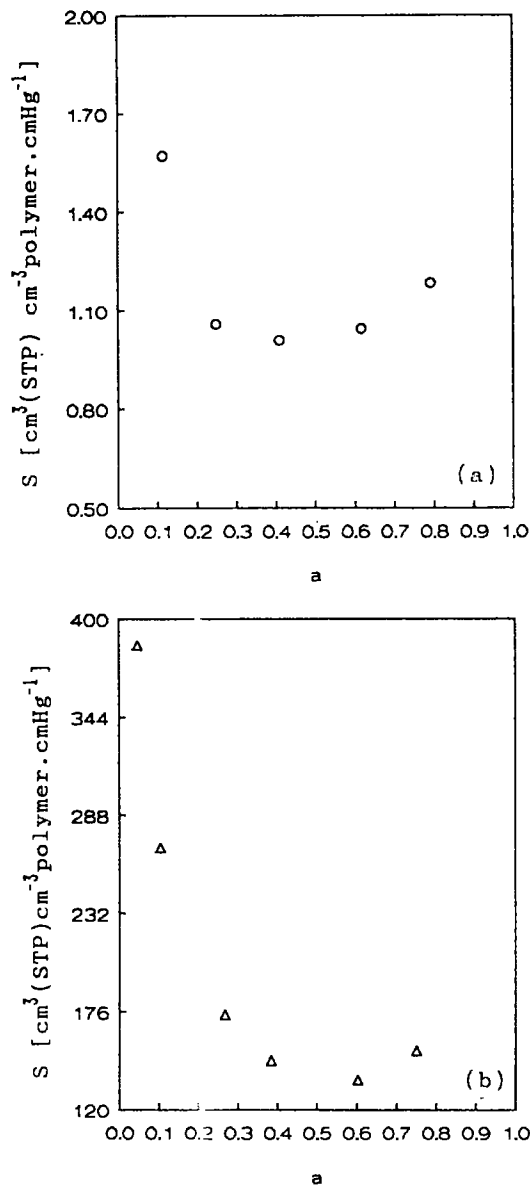

Figure 4 Activity dependence of solubility of water in (a) PPO and (b) SPPO membranes at 30°C.

Figure 4 shows the dependence of solubility (S), derived from the secant slope of the plots of concentration against pressure, on water activity in both membrane samples at 30°C. With increasing activity, S initially decreases rapidly and then increases slightly. It appears to be a plasticization effect caused by dissolved water. Making a comparison between Figure 4(a) and (b), we find that the solubility of water in SPPO is higher than that in PPO by a factor of at least 120, which can be attributed to the strong interaction between —SO_3Na groups in SPPO and water molecules. As a result, the per-
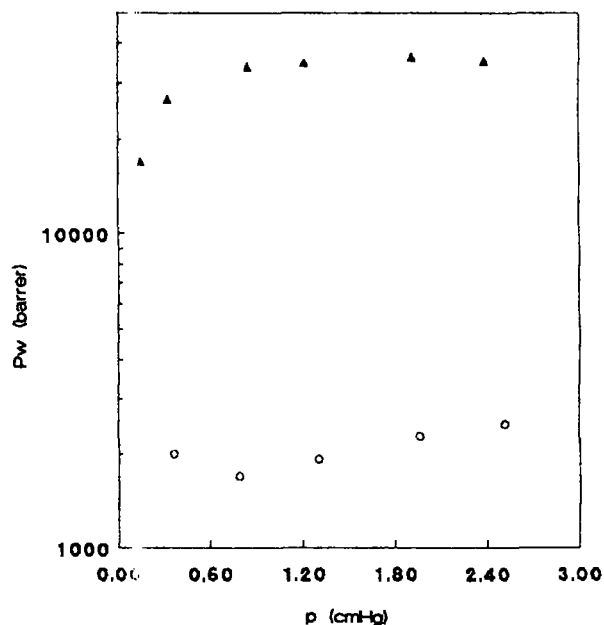
Figure 5 Pressure dependence of permeability to water vapor through (O) PPO and (▲) SPPO at 30°C.

meability $(P = DS)$ of water through the SPPO membrane, shown in Figure 5 as a function of pressure, is more than 10 times higher than that through the PPO membrane. It is also seen from Figure 5 that the permeability of water through SPPO is pressure-dependent at $a < 0.3$ (or $p < 1$ cmHg), mainly due to the strong concentration dependence of Dw and becomes pressure-independent at $a > 0.3$, owing to the contrary tendency to change of S and Dw, whereas the permeability for PPO is relatively unaffected by pressure.

BET and GAB Isotherms

The experimental sorption isotherms obtained by the weighing method for the PPO- and SPPO-water systems shown in Figure 6 are typical sigmoid shapes, which suggests that they belong to type II in the Brunauer classification[10]; thus, the data were analyzed according to the BET eq. (3) for multilayer adsorption. Although the BET plot is not presented here, the BET constants n_s and k derived from the initial slopes and intercepts of the BET plot[11] are listed in Table I.

On the other hand, the GAB plots (not presented here) after optimization of the f parameter are excellent straight lines both for PPO and SPPO over the whole range of activity under study. The GAB constants f, n_s, and k derived from the GAB plots are also listed in Table I.

No significant difference in values of parameter f between PPO and SPPO appears, due to the similar structure of the polymer chains, and the f values, being smaller than unity, reflect that indirectly bound water molecules are in a still more stable state than are the water molecules in the bulk liquid state. The values of parameter k for both PPO and SPPO are larger than 2, which is characteristic for type II sorption isotherms.[11] The value of n_s for SPPO is
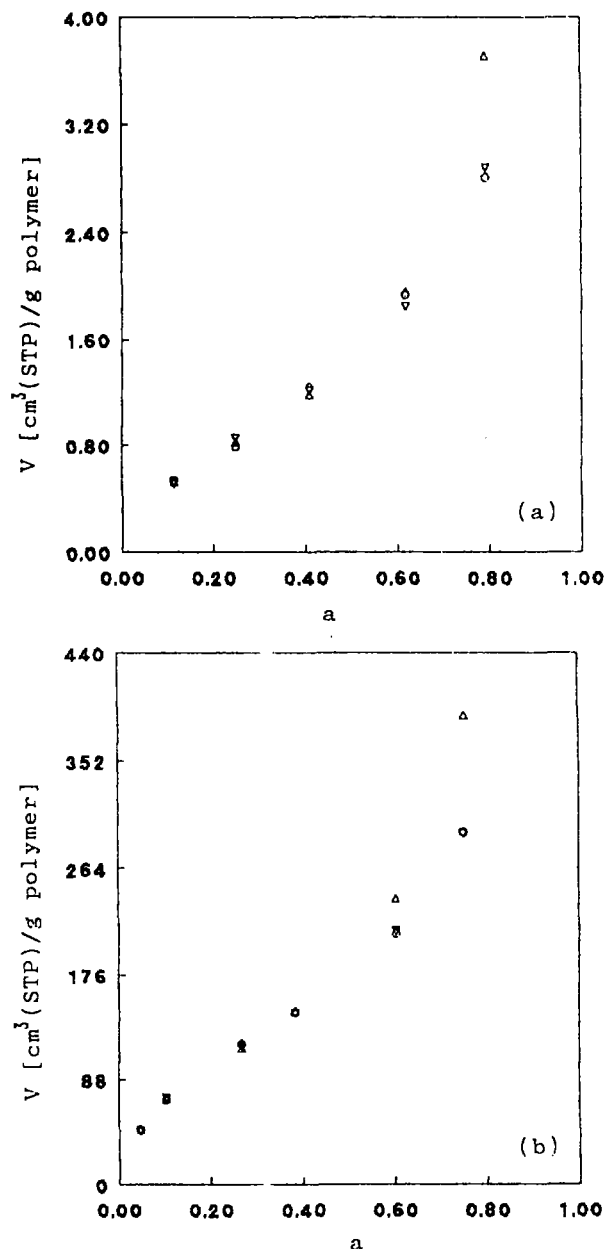

Figure 6 (O) Experimental and calculated sorption isotherms by the (△) BET and (▽) GAB of water vapor in (a) PPO and (b) SPPO at 30°C.

Table I   Sorption Isotherm Analysis According to BET and GAB Equations

	BET			GAB			
	n_s			n_s			
	cm³/g	Mol %	k	cm³/g	Mol %	k	f
PPO–H₂O	0.79	0.424	11.26	0.942	0.505	8.864	0.87
SPPO–H₂O	98.77	66.0	16.33	109.6	73.2	15.85	0.85

two orders of magnitude larger than that for PPO. Because the sulfonation degree of the SPPO sample is 28.8 mol % and the value of n_s is 73.2 mol/100 repeat units, each —SO₃Na group provides more than 2.5 monolayer sorption sites for water molecules. The higher k and n_s values of SPPO indicate that the hydrophilicity and strength of specific site binding increase significantly after sulfonation of PPO. This appears reasonable, taking into account the much higher solubility of the SPPO membrane compared with that of unmodified PPO.

Figure 6 shows a direct comparison of the experimental data with the isotherms calculated using the values of n_s, k, and f given in Table I. There are significant differences between experimental data and the BET equation for both PPO and SPPO at the higher water activity. However, the amended GAB equation avoids this drawback and accounts for the experimental results for both PPO and SPPO over the whole range of activity under study.

The Flory–Huggins Interaction Parameter X

The Flory–Huggins theory (lattice model) assumes random mixing in polymer–solvent mixtures and, obviously, it cannot hold for a multilayer sorption process; it remains, however, of definite interest to point out any concentration dependence of the apparent interaction parameter X. Such a dependence is precisely ascribed in most cases to an inhomogeneous distribution of solvent molecules and polymer segments throughout the solution.

The X values derived from the sorption isotherm according to eq. (2) are shown in Figure 7. X values for PPO are much higher than for SPPO and have a maximum at $a = 0.4$, but the change in X over the whole range under study ($a < 0.8$) is very small (only 10%). This indicates that hydrophilicity and strength of specific site binding for PPO are less than for SPPO, thus leading to a much higher diffusion coefficient for water molecules. X for SPPO is a monotonically increasing function of the water

activity at the low-activity region, levelling off as a becomes > 0.6 and showing a corresponding initial decrease of the polymer–water interactions gradually reaching a stable value. The trend of increasing X has often been observed for hydrophilic polymer water systems. It can be interpreted in terms of a decrease of site binding contribution, which relates to a strong affinity between polymer and water and will be predominant in the low-activity region. The negative X values for SPPO observed at low activity may be ascribed to rather strong site binding due to the sulfonate anion (hydrogen-bond acceptor).

Clustering Function

The G_{11}/v_1 and N_c values calculated from the BET sorption isotherm are shown in Figures 8 and 9, respectively. The large negative values of G_{11}/v_1 in the low-activity region suggest the interaction of
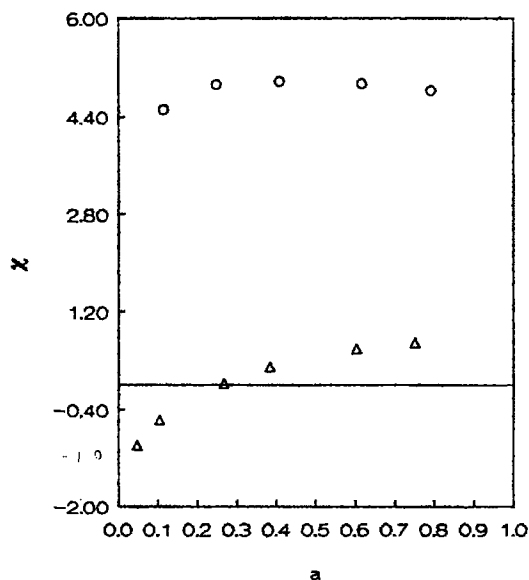

Figure 7 Activity dependence of the interaction parameter X in (○) PPO and (△) SPPO membranes at 30°C.

water with specific polymer sites. It is seen from Figure 8 that each of the first molecules of water added to PPO and SPPO excludes several hundred times and nearly 10 times, respectively, its molecular volume to the next molecule of water to be added. It is interpreted that the values of n_s, the first monolayer sorption capacity, of SPPO is more than 100 times higher than that of PPO (see Table I) due to an improvement in the hydrophilicity by introduction of the —SO_3Na group into PPO chains. For the same reason, the tendency for water in the
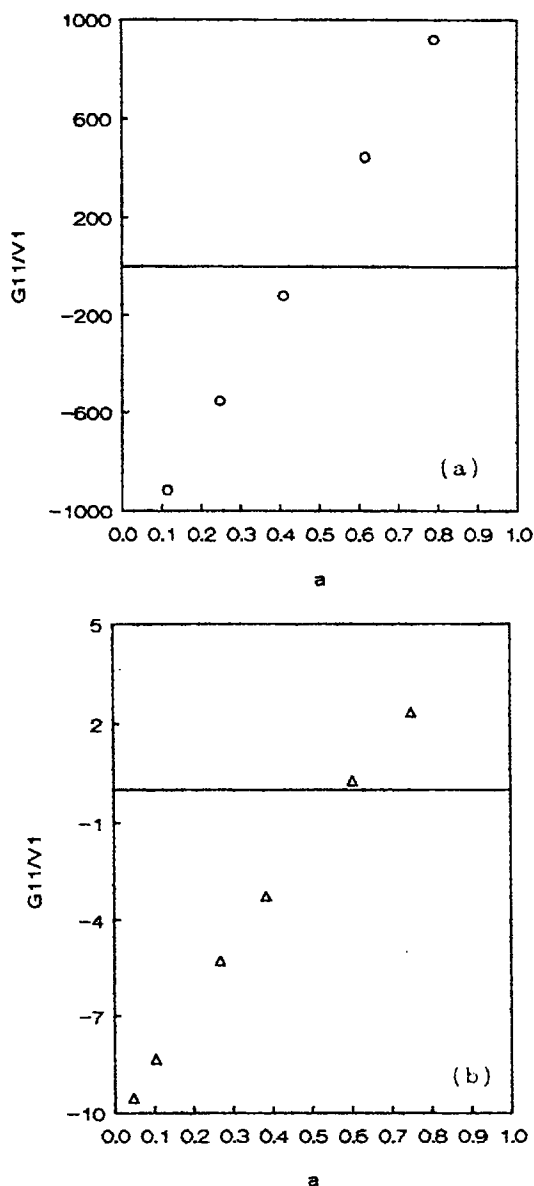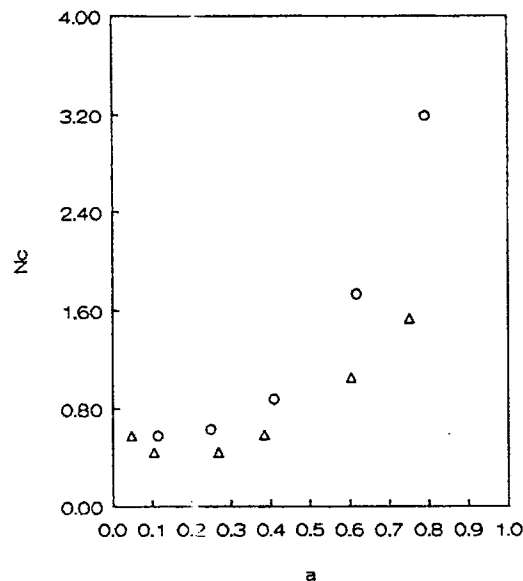

Figure 9   Mean cluster size of water in (O) PPO and (△) SPPO membranes as a function of water activity.

PPO sample to cluster is much larger than that in SPPO. It is obvious from Figure 9 that the value of N_c, the mean clustering size, of PPO is larger than that for SPPO. It is concluded from the above results that the state of water in SPPO is mainly direct site-binding, whereas in PPO, it is predominantly clustered; thus the former has high solubility and the latter has high diffusivity because the binding strength of water–water is much less than that of specific site binding.

CONCLUSIONS

In spite of slight variations in their chemical structure, the amorphous PPO and SPPO under study show a common multilayer sorption process over a broad range of water activity (0.05–0.8) at a constant temperature of 30°C, at which the physical state of the system is glassy. Diffusion of water is non-Fickian and the average diffusion coefficients derived from the slopes of the initial linear part of the reduced sorption curves show concentration dependence. The sorption isotherms belong to type II and may be quantitatively analyzed according to the GAB amended form of the BET equation. The Flory–Huggins interaction parameters and clustering function also can be derived from the sorption data.

Figure 8   Plot of clustering functions vs. water activity for (a) PPO and (b) SPPO membranes at 30°C.

The introduction of —SO_3Na groups into PPO chains results in significant differences in many aspects as compared with unmodified PPO:

1. The number of site-bound water molecules is 73.2 mol % and is about 150 times higher than that of PPO.
2. The energy difference between the site binding (negative χ values) and "liquid-like" layer for SPPO is twice as large as that for PPO.
3. The trend of clustering of water for SPPO, even at the highest water activity, is much less than that for PPO, which is clear proof of the higher hydrophilicity of SPPO.
4. The value of χ for SPPO is only one-seventh of that for PPO even in the high-activity region.
5. The above results led to significant increase in the solubility (more than 100 times) and to decreases in the diffusivity (about one-tenth), thus increasing the permeability to water (more than 10 times) for the SPPO membrane as compared with the PPO membrane.

Therefore, the sulfonated PPO could be an excellent dehumidification membrane material.

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