Sorption and diffusion of water vapour in hydrogen-bonded polymer blends

W. P. Hsu, R. J. Li, A. S. Myerson* and T. K. Kwei
Department of Chemical Engineering, and Department of Chemistry, Polytechnic University, Brooklyn, NY 11201, USA

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Water vapour was used as a diffusional probe to study segmental mobility in hydrogen-bonded polymer blends. Modified polystyrenes containing 4-hydroxystyrene as comonomer units were blended with poly(methyl methacrylate). The diffusion coefficient of water decreased with increasing concentration of the diffusant. Clustering of water molecules in the polymer rendered a fraction of the sorbed water comparatively immobile. A partial immobilization model was used to estimate the diffusion coefficient of the clusters. Interpolymer hydrogen bonding acted as physical crosslinks, which decreased the diffusivity of clusters. However, the positive excess volume of mixing for one blend composition seemed to have nullified the restrictive effect of hydrogen bonding on cluster diffusivity.

(Keywords: sorption; diffusion; blends; water vapour; hydrogen bonding)

INTRODUCTION

In an earlier study[1], water vapour was used as a diffusional probe to study the interaction and segmental mobility in hydrogen-bonded polymer blends. Modified polystyrene containing *p*-(hexafluoro-2-hydroxyisopropyl) groups as hydrogen-bond donors were blended with poly(methyl methacrylate) as acceptors. In a number of blends, the diffusion coefficients were higher than the 'average' values of the component polymers. The deviation in diffusion coefficient was opposite in sign to the deviation in the activation energy of diffusion from its 'average' value. The residual activation energy was proportional to the excess volume of mixing.

The study has now been extended to a related polymer pair using, instead of *p*-(hexafluoro-2-hydroxyisopropyl)-styrene (HHIS), *p*-hydroxystyrene (HS) as the hydrogen-bond donor in the styrene copolymer. Although both the HHIS and HS groups have strong affinities for hydrogen bonding with the carbonyl groups of poly(methyl methacrylate) (PMMA) to result in miscible blends[2], the phenol groups have a greater tendency towards self-association[3]. Accordingly, the relative concentrations of the hydroxyl moiety in the free, self-associated and hydrogen-bonded (with carbonyl) states in the blends are likely to be different when *p*-hydroxystyrene is used as the donor. The motivation at the beginning of this study was to determine whether water vapour as a diffusional probe could reveal subtle differences in the segmental mobilities of the two blend systems. However, our attention was soon diverted to a second aspect of the diffusion phenomenon, that is, the decrease in the magnitude of the diffusion coefficient as the concentration of the diffusant increases.

EXPERIMENTAL

Materials

The two poly(styrene-*co*-*p*-hydroxystyrene) (PHS) copolymers used for this study contained 5 and 15 mol% of HS units, respectively, and were synthesized by using a procedure described previously[4]. The M_n and M_w/M_n values for the two copolymers, designated as PHS-5 and PHS-15, are 84 900 and 1.70, and 85 600 and 1.47, respectively. The PMMA polymer was purchased from Scientific Polymer Products; its number-average molecular weight is 46 400 and the M_w/M_n ratio is 2.01.

Film preparation

Thin films of individual polymers and their blends were prepared by solution casting from toluene or 1,4-dioxane on glass plates. The final drying step took place in a vacuum oven for one day at 130°C, which was 15–25°C above the glass transition temperatures of the polymers. All the films were transparent. However, unlike the procedure used in ref. 1, the films were not hot pressed at 160–165°C after vacuum drying. Unexpectedly, the apparently innocuous difference in the film preparation procedures altered the concentration dependence of the diffusion coefficient of water in PMMA.

Glass transition temperatures

The glass transition temperatures (T_g) of the polymers were determined with the use of a Perkin–Elmer DSC-7 calorimeter. The heating rate was 20°C min^{-1}. The midpoint of the jump in the specific heat in the second thermal scan was taken as T_g.

Infra-red spectroscopy

The conversion of the free hydroxyl group in poly(styrene-*co*-*p*-hydroxystyrene) to the hydrogen-bonded

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* To whom correspondence should be addressed

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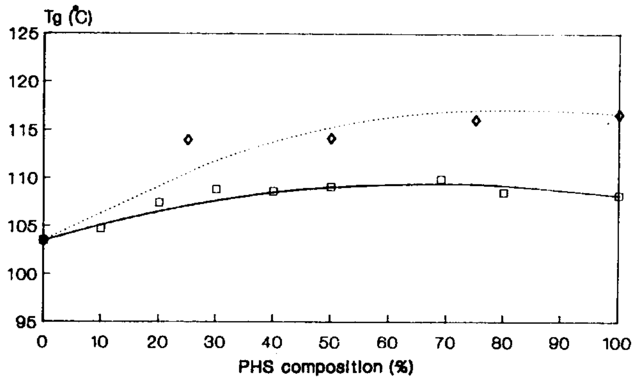

Figure 1 Glass transition temperatures of polymer blends: (□) PMMA/PHS-5; (◇) PMMA/PHS-15

species (with carbonyl) was observed qualitatively by infra-red spectroscopy using an FTS-60 *FT*i.r. spectrometer. Spectra were obtained with 64 scans at a resolution of $4\,cm^{-1}$. Only the 3200–$3700\,cm^{-1}$ region due to hydroxyl absorption was scanned.

Vapour absorption and diffusion

The amount of water vapour absorbed by a polymer was measured by a Cahn 2000 microbalance. The sensitivity of the measurement was $\pm 1\,\mu g$. The temperature of the sorption chamber was controlled to $\pm 0.2°C$. The successive sorption method was applied to study solubility and diffusivity.

RESULTS AND DISCUSSION

Glass transition temperature

The glass transition temperatures of the blends are displayed in *Figure 1*; all the values are higher than the weighted averages of the component T_g values. Several empirical equations have been proposed to describe the composition dependence of T_g for miscible blends that involve strong specific interaction. Three recent publications[5–7] offered theoretical insights into the underlying reasons for the experimental observations. In the limiting case, these equations reduce to a simple expression[8]:

$$T_g = W_1 T_{g1} + W_2 T_{g2} + q W_1 W_2 \qquad (1)$$

where W_1 and W_2 denote respectively the weight fractions of the components 1 and 2, and q is a parameter that depends on the net polymer–polymer interaction. Equation (1) fits our data very well with q values of 13.4 for PHS-5 and 23.1 for PHS-15 blends.

Infra-red spectroscopy

The infra-red spectra of blends of PHS and poly(alkyl methacrylates) have been documented extensively by Coleman and Painter[9]. In a series of papers, they have analysed the competitive equilibria between hydrogen bonding of the hydroxyl group with carbonyl group and with itself, i.e. self-association. Experimental data on the fraction of bound carbonyl are in complete accord with their theoretical calculations. Because we did not measure i.r. spectra in the carbonyl absorption region, but only in the hydroxyl stretching region (*Figure 2*), we resorted to Coleman and Painter's theory and repeated the calculation for our blends. The results, which are self-explanatory, are given in *Table 1*. A comparison of the values in columns 2 and 3 indicates that, in blends containing up to 50% PHS, at least 85% of the total OH groups are engaged in hydrogen bonding with carbonyl groups. Only in the two PHS-rich blends are the hydroxyl groups still present in significant quantities in the free and associated states.

The number of moles of bound carbonyl groups per 100 g of blend listed in the fourth column is also of interest because it represents the number of physical crosslinks in the system. The density of physical crosslinks increases with increasing amount of PHS in the blend, as would be expected. The increase from 20% PHS-5 (or 25% PHS-15) to 50% PHS is almost twofold; however, further increase to 80% PHS-5 (or 75% PHS-15) is comparatively minor.

Specific volumes

The specific volumes of the component polymers and their blends were measured by a density gradient column containing an aqueous solution of sodium bromide, as listed in *Table 2*. The measured specific volume of the

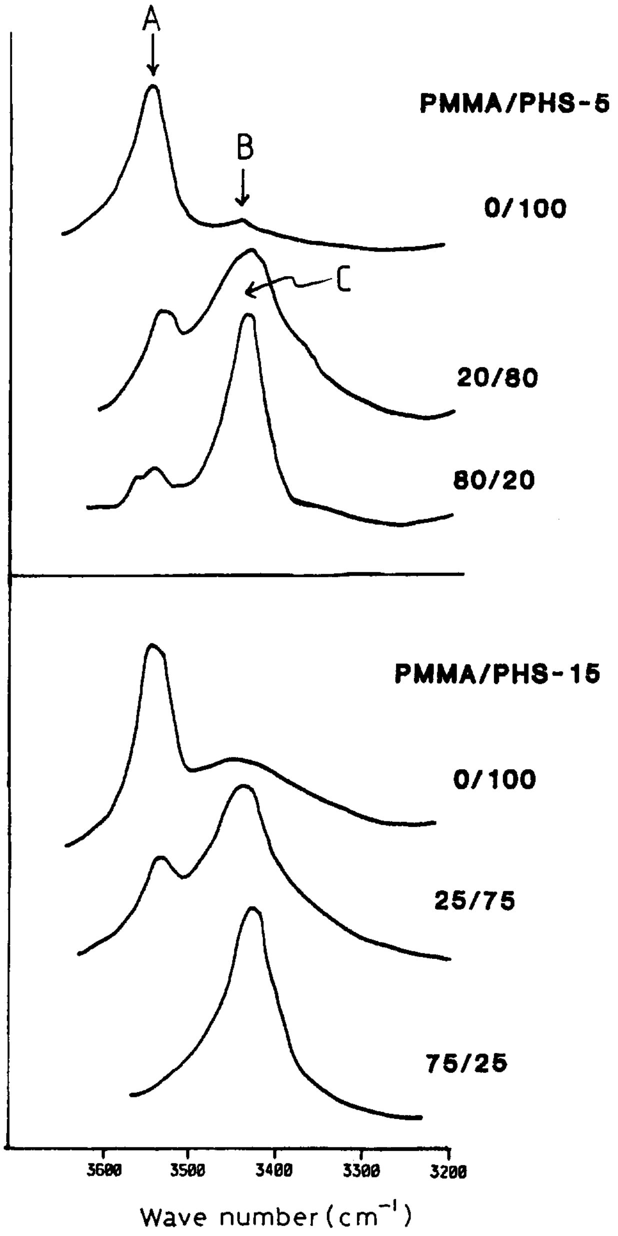

Figure 2 *FT*i.r. spectra in the hydroxyl stretching region: (A) free OH; (B) self-associated OH; (C) self-associated OH plus C=O...HO

Table 1 Calculated fraction of bound carbonyl groups

PMMA/PHS-x	$(OH/C{=}O)_{blend}$[a]	$(C{=}O)_{blend}$[b]	No. H bond/100 g blend[c]	$(OH)_{f+sa}$[d]
$x=5$: 80/20	0.012	0.012	9.6×10^{-3}	0.033
50/50	0.048	0.044	0.022	0.083
20/80	0.191	0.142	0.028	0.257
$x=15$: 75/25	0.047	0.045	0.034	0.043
50/50	0.141	0.120	0.060	0.149
25/75	0.423	0.254	0.064	0.399

[a] $(OH/C{=}O)_{blend}$: stoichiometric ratio of total OH groups to C=O groups in the blend
[b] $(C{=}O)_{blend}$: fraction of bonded C=O groups in the blend
[c] No. H bond/100 g blend: moles of bonded C=O groups per 100 g of blend
[d] $(OH)_{f+sa}$: fraction of free plus self-associated OH groups

Table 2 Specific volumes of blends

	V (cm^3 g^{-1})		$V^e = V-(W_1V_1+W_2V_2)$	
PMMA/PHS-x	Measured	Corrected	Measured	Corrected
$x=5$: 100/0	0.8453	0.8422		
80/20	0.8648	0.8627	−0.0017	−0.0013
50/50	0.8954	0.8944	−0.0030	−0.0022
20/80	0.9291	0.9286	−0.0011	−0.0006
0/100	0.9514	0.9510		
$x=15$: 100/0	0.8453	0.8422		
75/25	0.8664	0.8643	−0.0009	−0.0006
50/50	0.8894	0.8881	0	0.0006
25/75	0.9132	0.9124	+0.0018	+0.0022
0/100	0.9334	0.9329		

PMMA film, 0.8453 cm^3 g^{-1}, is comparable to literature values[10,11] but is larger than that reported in the previous study[1], in which the film was hot pressed after vacuum drying. The lower density of the PMMA film is probably responsible for the slightly lower T_g and, unexpectedly, also for different water sorption and diffusion behaviours.

Since the volume of mixing plays an important role in the interpretation of our sorption and diffusion data, it is necessary to ascertain at this point that our specific-volume measurements are not rendered invalid by the absorption into the polymer of the fluid (water) of the density gradient column. Therefore, we have made the following corrections. In the density range of our interest, the activity of water in the gradient column is about 0.95 to 0.99. We did not have experimental water sorption data at such activities. The correction for PMMA was made by assuming the amount of water absorbed by PMMA in the column to be the same as the value reported by Bueche[12] for sorption in 100% water vapour, 0.02 g g^{-1}, which represented the upper limit. The 'true' specific volume of PMMA was then calculated by assuming zero volume of mixing of the polymer and water. For the two modified polystyrenes and their blends, we assumed that the amount sorbed by the specimen in the gradient column could be estimated as 0.02 g g^{-1} multiplied by the ratio of water vapour sorption at $a_1=0.40$ by the specimen to that by PMMA. The 'corrected' specific volumes and the attendant excess volumes are listed in *Table 2*. It is seen that, although the correction for individual specific-volume measurement may be sizeable, the magnitude of the excess volume is altered to a much smaller extent. In fact, the correction is within the experimental uncertainty of ±0.0005 cm^3 g^{-1}. For this reason, we believe that at least the sign (positive or negative) of the excess volume is not in error.

The excess volumes of mixing are negative for the PHS-5 blends. On the other hand, the volume of mixing for the PHS-15 blends changes from a slightly negative value to a positive one when the PHS content increases from 25 to 75%. Similar trends were found for the blends of HHIS copolymers; the excess volumes become more positive when the amount of hydroxyl groups in the styrene copolymer increases[1]. While negative excess volumes appear to be the norm for miscible blends, positive values have been reported only for a few cases[1,13,14]. The explanation proposed in ref. 1 was based on considerations of chain packing. Central to the interpretation was the assumption that volume shrinkage to be expected from the formation of a hydrogen bond between a free hydroxyl group and a carbonyl group was diminished to some extent by the poor packing of the styrene and methyl methacrylate segments in the immediate neighbourhood of the interacting sites. Consequently, the net volume shrinkage is small. However, the dissociation of the self-associated hydroxyl groups is accompanied by a volume increase. If the establishment of an OH····O=C bond cannot overcome the volume increase caused by the break-up of self-association and poor chain packing, the excess volume becomes positive.

We have seen in the previous section on infra-red spectroscopy that the hydroxyl groups in PHS-5 are almost all in the free state, but a significant fraction of the groups are self-associated in PHS-15. Therefore, the explanation offered in ref. 1 is also applicable to the results of this study. As it turns out, the positive excess volume found for the 75% PHS-15 blend is one of the factors that influence strongly the concentration dependence of the diffusion coefficient, which will be described later.

Water vapour absorption

The sorption isotherms for the component polymers and their blends are shown in *Figures 3* and *4*. All the curves are concave upwards. The curvature in the isotherm for PMMA is in contrast with the direct proportionality between the amount absorbed and vapour pressure (up to relative vapour pressure of 0.5) reported in ref. 1. Again, this may be attributed to the difference in the film preparation procedures. The PHS-5 copolymer absorbs less water vapour than does PMMA. In the PHS-5 blends, sorption decreases when the

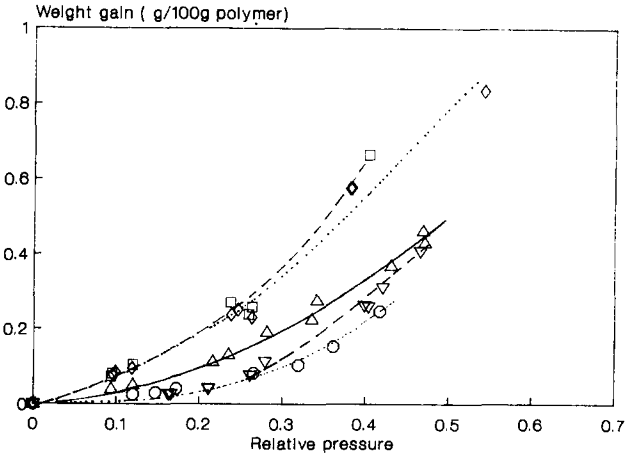

Figure 3 Water vapour sorption curves of PMMA/PHS-5 blends at 31°C: (□) 0% PHS, (◇) 20%, (△) 50%, (○) 80%, (▽) 100%

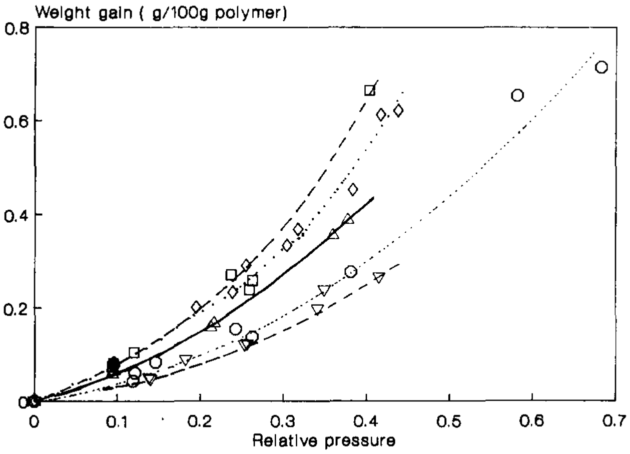

Figure 4 Water vapour sorption curves of PMMA/PHS-15 blends at 31°C: (□) 0% PHS, (◇) 25%, (△) 50%, (○) 75%, (▽) 100%

copolymer content increases, but the 80% copolymer blend absorbs slightly less water vapour than does PHS-5 itself. The PHS-15 copolymer, having more hydroxyl groups, absorbs more water vapour than does PHS-5. The trend of increasing water solubility with increasing polar-group content in styrene copolymers has also been recorded in ref. 1. However, even with 15% hydroxyl groups, PHS-15 still absorbs less water than does PMMA. When PHS-15 is blended with PMMA, water vapour solubilities decrease in an orderly manner with increasing amount of the copolymer.

It is well known that, in relatively non-polar polymers, there is a tendency for the sorbed water molecules to associate or form clusters. The extent of clustering in a binary solution can be evaluated from the sorption isotherm by using the Zimm–Lundberg analysis[15]. The cluster integral, G_{AA}, is defined by:

$$\frac{G_{AA}}{V_A} = -(1-v_A)\left(\frac{\partial(a_A/v_A)}{\partial a_A}\right) - 1 \qquad (2)$$

or

$$v_A\frac{G_{AA}}{V_A} = (1-v_A)\left(\frac{\partial \ln v_A}{\partial \ln a_A}\right) - 1 \qquad (3)$$

where V_A and a_A denote, respectively, the partial molar volume and the activity of water, and v_A is the volume fraction. The quantity $v_A G_{AA}/V_A$ is a measure of the mean number of water molecules in excess of the mean concentration of water in the neighbourhood of a given water molecule. For an ideal solution $G_{AA}/V_A = -1$. When the value of G_{AA}/V_A is greater than -1, there is a tendency for water molecules to cluster. Since the volume fraction of sorbed water is less than 0.01 in every experiment, clustering tendency is indicated by $v_A G_{AA}/V_A$ values larger than -0.01. The calculated values are plotted in *Figures 5* and *6*.

Composed predominantly of styrene units, the PHS-5 polymer is relatively non-polar and the tendency for sorbed water molecules to form clusters is the highest. The cluster functions are much smaller for PMMA. The $v_A G_{AA}/V_A$ values in the blends decrease with decreasing amounts of PHS-5. However, the trend is not a simple one; rather, the clustering tendency can be arranged in the order: 100% PHS-5 > 80% PHS-5 > 50% PHS-5 = PMMA > 20% PHS-5. We do not have a simple, convincing explanation of the trend reversal of the values in the 20% PHS-5 blend and PMMA.

The clustering of sorbed water molecules is reduced in PHS-15, which contains a larger amount of polar groups than in PHS-5. The cluster function in PHS-15 is almost

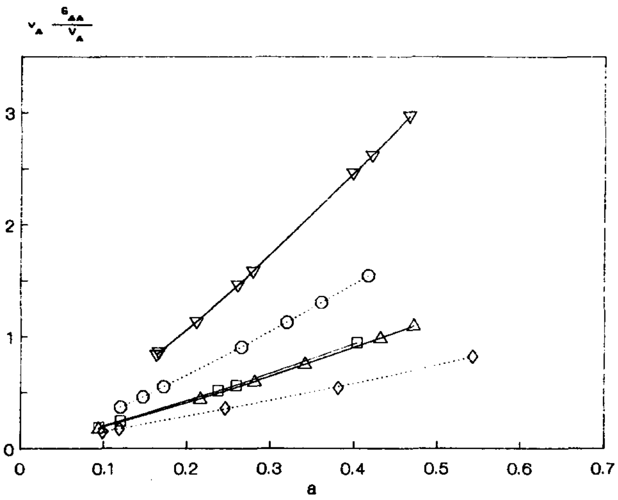

Figure 5 Cluster functions $v_A G_{AA}/V_{AA}$ of PMMA/PHS-5 blends. Data symbols as in *Figure 3*

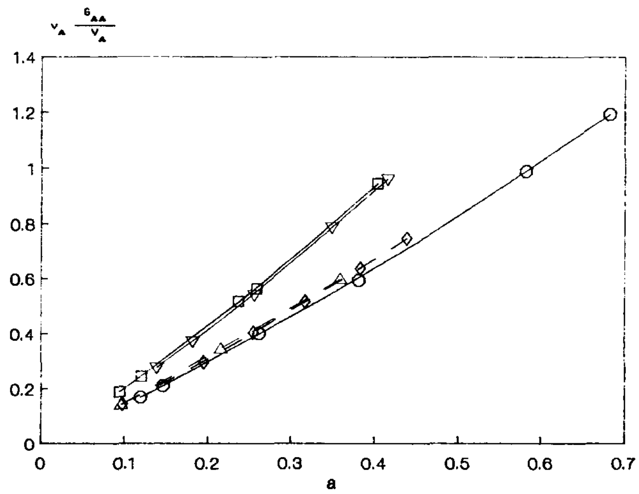

Figure 6 Cluster functions $v_A G_{AA}/V_{AA}$ of PMMA/PHS-15 blends. Data symbols as in *Figure 4*

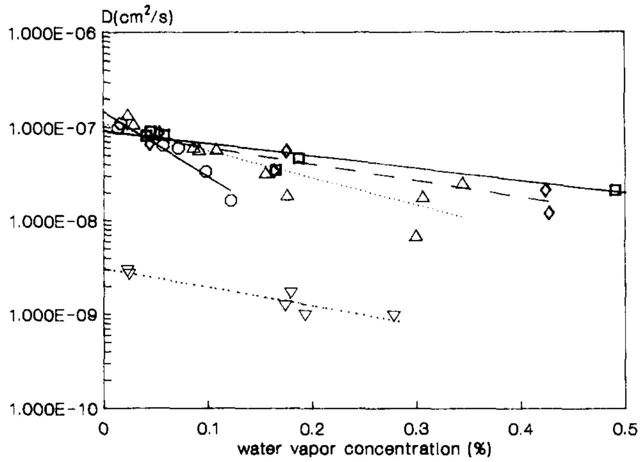

Figure 7 Water vapour diffusion coefficients D of PMMA/PHS-5 at 31°C. Data symbols as in *Figure 3*

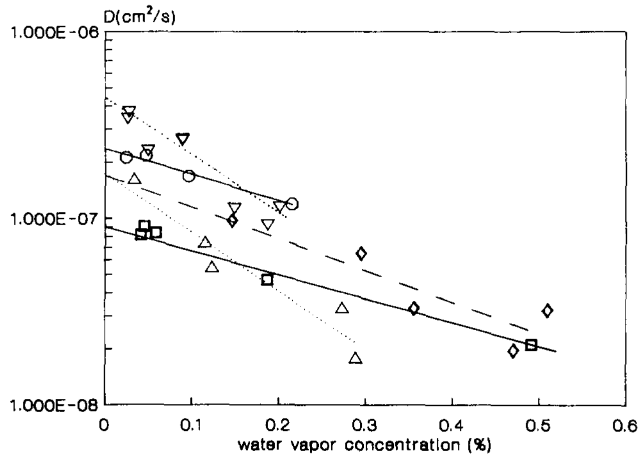

Figure 8 Water vapour diffusion coefficients D of PMMA/PHS-15 at 31°C. Data symbols as in *Figure 4*

indistinguishable from that in PMMA. The three blends have essentially the same $v_A G_{AA}/V_A$ values.

Diffusion coefficients

The diffusion coefficients of water in polymers were calculated from the initial slopes of the successive sorption curves[16]. To our surprise, the diffusion coefficient D in the PMMA film was found to decrease with increasing concentration of sorbed water, whereas in the previous paper we reported D as being essentially independent of concentration. There are conflicting reports in the literature about the concentration dependence of the water diffusion coefficient in PMMA[12,17]. Our results underscore the importance of the sample preparation procedure. The diffusion coefficients in the two copolymers and in the blends also decrease when the concentration of sorbed water increases. The results are shown in *Figures 7* and *8*.

The mutual diffusion coefficient $\bar{D}$ for a polymer–solvent system determined over a sufficiently small concentration interval can be represented by a relation of the form[18]:

$$\bar{D}(C) = D_0 \exp(\alpha C) \tag{4}$$

where D_0 is the diffusivity extrapolated to zero penetrant concentration, α is a constant and C is the average concentration. The average concentration has been approximated as $\frac{1}{2}(C_i + C_f)$, where C_i and C_f are the initial and final concentrations of the sorption experiment[18]. When the diffusion coefficient decreases with increasing penetrant concentration, $\bar{D}$ approximates the value of D at $C = C_i + 0.56(C_f - C_i)$, according to Vrentas and Duda[19]. In constructing semilogarithmic plots of $\bar{D}$ vs. C, we found little difference whether C was taken as $\frac{1}{2}(C_i + C_f)$ or $[C_i + 0.56(C_f - C_i)]$; the plots shown in *Figures 7* and *8* were based on the latter. For the sake of convenience, the symbol D will be used in the ensuing discussion instead of $\bar{D}$.

The dependence of D_0 value on blend composition is expressed graphically in *Figure 9*. The D_0 values of the PHS-5 blends far exceed the average values of the component polymers; the three blends have nearly the same D_0 as PMMA. On the other hand, within the limit of accuracy, D_0 equals the average value for each of the three PHS-15 blends.

Paul and coworkers[20] have discussed the diffusion coefficients of gases in polymer blends in the contexts of both the activated-diffusion and the free-volume theories. In our previous paper, we used Paul's equation, which related $(\ln D - \phi_1 \ln D_1 - \phi_2 \ln D_2)$ to $(E_D - \phi_1 E_{D1} - \phi_2 E_{D2})$, where E_D is the activation energy of the diffusion process and ϕ_1 and ϕ_2 denote, respectively, the volume fractions of the component polymers 1 and 2 in the blend. In the present study, we did not determine the activation energy of diffusion. Therefore, we shall resort to the free-volume theory in an attempt to analyse the D_0 data.

Paul[21] has noted that the term $(\ln D - \phi_1 \ln D_1 - \phi_2 \ln D_2)$ is always positive if the free volume of the blend obeys the additivity rule. The free-volume derivation can be easily extended to the more general case in which the additivity rule is not obeyed. We shall begin with the expressions[22]:

$$D = A \exp(-v^*/v_f) \tag{5}$$

and

$$v_f = \phi_1 v_{f1} + \phi_2 v_{f2} + \delta \tag{6}$$

where v_f is the free volume of the polymer, v^* is the critical free volume required for a diffusional jump, and δ can be either positive or negative. A combination of

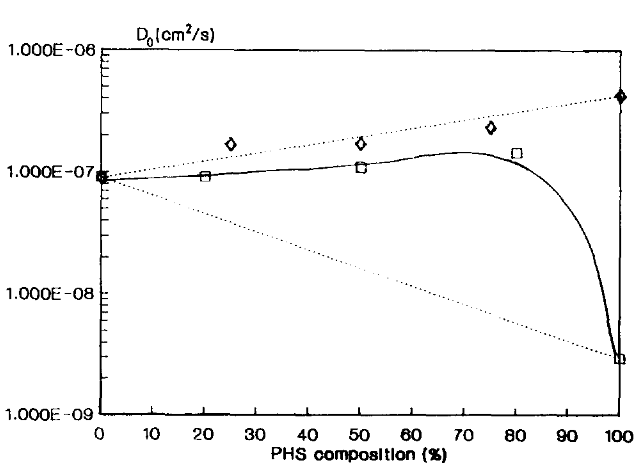

Figure 9 Relationship between D_0 and blend composition. Data symbols as in *Figure 1*

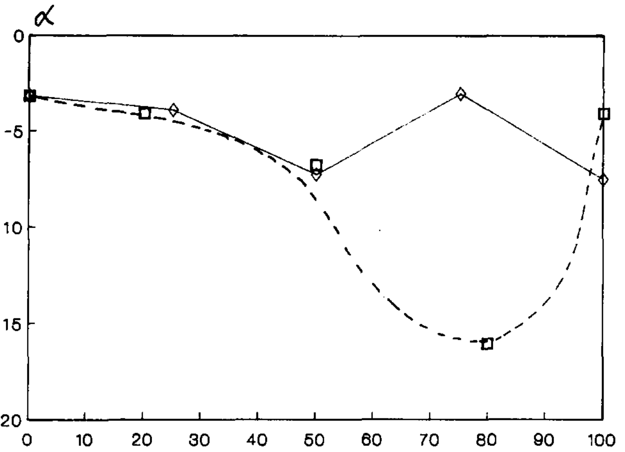

Figure 10 Relationship between α and blend composition. Data symbols as in *Figure 1*

the two equations results in the following equation:

$$(\ln D-\phi_1\ln D_1-\phi_2\ln D_2) = \frac{v^*}{v_f v_{f1} v_{f2}}[\phi_1\phi_2(v_{f1}-v_{f2})^2+\delta(v_f-\delta)] \quad (7)$$

It follows that $(\ln D-\phi_1\ln D_1-\phi_2\ln D_2)$ is positive if the following conditions are met:

$$\delta \geqslant 0 \quad (8)$$

or

$$\delta<0, \quad |\delta(v_f-\delta)|<|\phi_1\phi_2(v_{f1}-v_{f2})^2| \quad (9)$$

Equality between $\ln D$ and $(\phi_1\ln D_1+\phi_2\ln D_2)$ occurs when:

$$\delta\geqslant 0, \quad \text{both } \phi_1\phi_2(v_{f1}-v_{f2})^2 \text{ and } \delta(v_f-\delta)\approx 0 \quad (10)$$

or

$$\delta<0, \quad |\delta(v_f-\delta)|=|\phi_1\phi_2(v_{f1}-v_{f2})^2| \quad (11)$$

In principle, the condition for $\ln D<(\phi_1\ln D_1+\phi_2\ln D_2)$ also exists, i.e. $\delta<0$ and $|\phi_1\phi_2(v_{f1}-v_{f2})^2|<|\delta(v_f-\delta)|$. In the following, the D_0 data displayed in *Figure 9* will be discussed in the context of the above analysis.

The magnitude of v_f can be estimated as the difference between the specific volume of the polymer at temperature T and the occupied volume at 0 K. The latter is often approximated as 1.3 times the van der Waals volume, according to Bondi[23]. Without going into the details of the calculation, it suffices to say that the δ values are negative for the PHS-5 blends because the excess volumes of mixing are negative. The positive deviation of $\ln D$ from its average value then most likely reflects the condition given by equation (9). For the PHS-15 blends, the excess volume varies from a slightly negative to a positive value. If we assume that δ follows the same trend as excess volume, then the experimental results of $\ln D\approx(\phi_1\ln D_1+\phi_2\ln D_2)$ correspond to the conditions represented by equations (10) and (11).

The values of α that describe the concentration dependence of the diffusion coefficients are plotted in *Figure 10*. The α value becomes more negative, i.e. the concentration dependence of the diffusion coefficient becomes stronger, as PHS-5 content increases in the blend. We attribute the trend to the increasing number of OH···O=C bonds present in the blend (*Table 1*). Acting as physical crosslinks, the hydrogen bonds restrict segmental mobility, in particular the modes of motion that are responsible for the diffusion of clustered water molecules. An analysis based on the partial immobilization model will be given in the next section.

We had expected the α values of the PHS-15 blends to follow a similar trend as that of the PHS-5 blends. However, there was a trend reversal for the blend containing 75% PHS-15. The positive excess volume found from this blend probably compensated for the effect of interpolymer hydrogen bonding.

Partial immobilization model

As early as 1947, Rouse[24] proposed that the decrease in D with increasing concentration could be explained by postulating clustering of the sorbed water molecules so that a fraction of the penetrant became comparatively immobile. Several specific models have been proposed[25,26]; a simple version will be used below. We shall assume that the diffusant molecules can be classified into two species, mobile and partially immobilized. The concentration of the mobile species is C_1 and that of the partially immobilized species is C_2. The mobile species is characterized by a diffusion constant D_1 and the partially immobilized one by D_2, which is an average quantity for clusters of various sizes. The diffusional flux J can be written according to Fick's law as:

$$J=-D\frac{\partial C}{\partial x}=-D_1\frac{\partial C_1}{\partial x}-D_2\frac{\partial C_2}{\partial x} \quad (12)$$

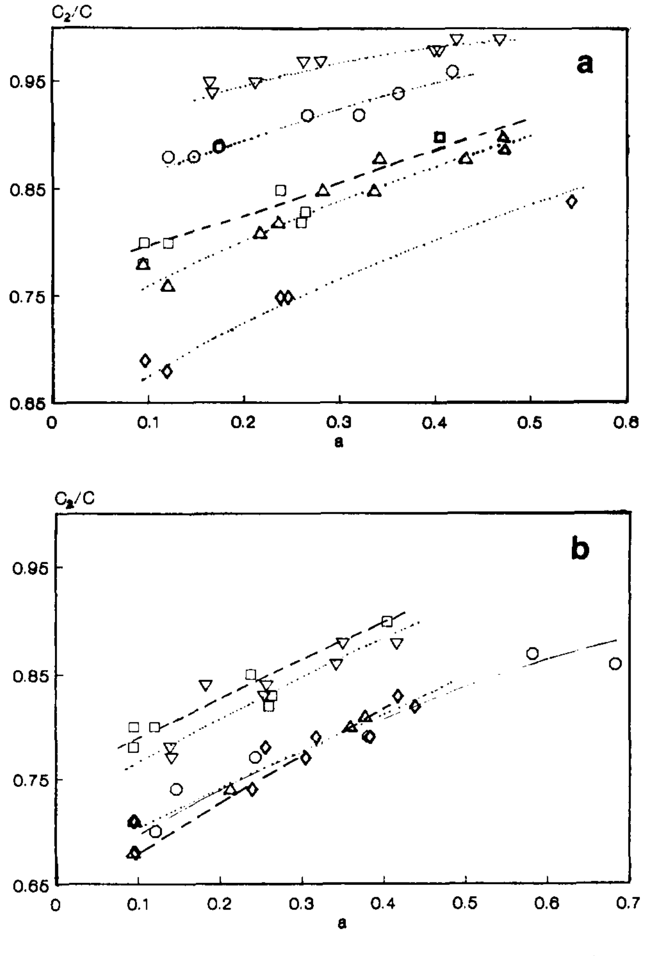

Figure 11 Fraction of partially immobilized water C_2/C in polymer blends: (a) PMMA/PHS-5, data symbols as in *Figure 3*; (b) PMMA/PHS-15, data symbols as in *Figure 4*

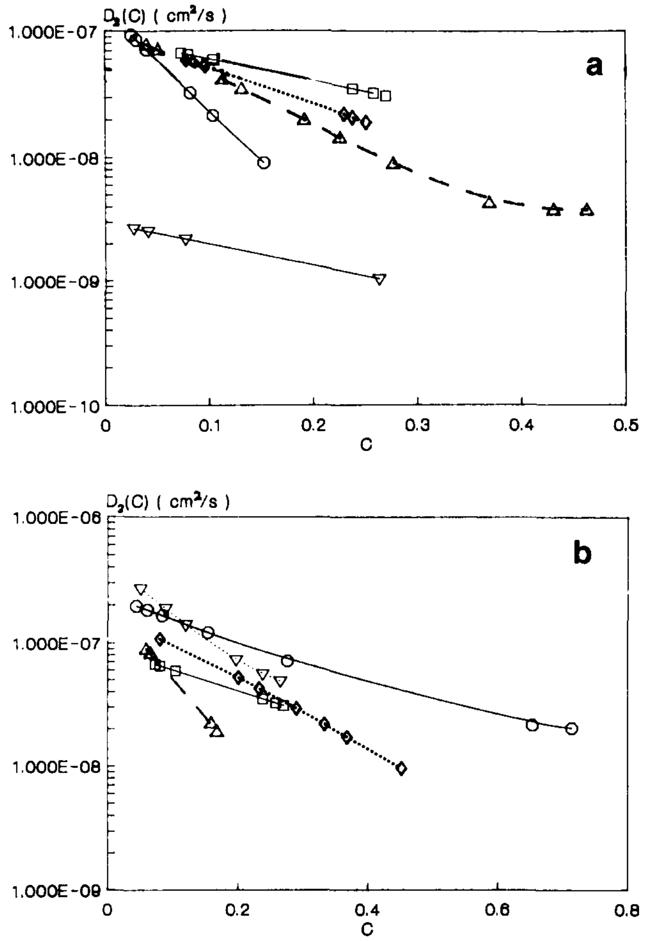

Figure 12 Diffusion coefficients of partially immobilized water $D_2(C)$ in polymer blends: (a) PMMA/PHS-5, data symbols as in *Figure 3*; (b) PMMA/PHS-15, data symbols as in *Figure 4*

It follows that:

$$D(C)=D_1\frac{\partial C_1}{\partial C}+D_2(C)\frac{\partial C_2}{\partial C} \tag{13}$$

We further assume that D_1 equals D_0 in *Figure 9*, i.e. the value of D at infinite dilution. The quantities C_1 and C_2 are evaluated by expressing C as a power series of vapour activity a_A:

$$C=C_1+C_2=k_1a_A+(k_2a_A^2+k_3a_A^3+\ldots) \tag{14}$$

from which the concentration of C_1 is determined from the Henry's law term. The calculation of C_2, $\partial C_1/\partial C$, $\partial C_2/\partial C$ and D_2 is then straightforward. The results of the calculation are shown in *Figure 11* for the fractions of partially immobilized water, C_2/C_1, and in *Figure 12* for the corresponding diffusion coefficients, D_2. The fractions C_2/C in the different polymers have the same rank order as the cluster integrals. The functional dependence of D_2 on C is linked to α. It is gratifying to note that the internal consistency of our calculations is confirmed by the coincidence of D_0 with the D_2 value extrapolated to zero diffusant concentration. We conclude from the above that interpolymer hydrogen bonds, while having little effect on the diffusivity of mobile species, cause a decrease in the diffusion coefficients of the clusters. The exception to the rule found for the 75% PHS-15 can be ascribed to volume expansion during mixing.

CONCLUSIONS

The tendency of sorbed water molecules towards cluster formation in PMMA, PHS and their blends is revealed by the cluster integral and the decrease of the diffusion coefficient with increasing concentration of the diffusant. Interpolymer hydrogen bonding decreases the diffusion coefficient of water clusters. However, in the 75% PHS-15 blend the positive excess volume of mixing seems to nullify the restrictive effect of hydrogen bonding.

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