Eur. Polym. J. Vol. 29, No. 12, pp. 1601–1602, 1993
Printed in Great Britain

0014-3057/93 $6.00 + 0.00
Pergamon Press Ltd

CONCENTRATION DEPENDENCE OF WATER VAPOUR DIFFUSION IN HYDROGEN-BONDED POLYMER BLENDS

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(Received 4 January 1993; accepted 3 February 1993)

INTRODUCTION

In a previous investigation [1], water vapour was used as a diffusional probe to study polymer–polymer interaction and segmental mobility in hydrogen-bonded polymer blends. Modified polystyrenes containing 5 or 15% 4-hydroxystyrene as comonomer units (designated as PHS-5, PHS-15) were blended with poly(methyl methacrylate) (PMMA). The diffusion coefficient of water was found to decrease with increasing concentration of the diffusant because of water clustering. Additionally, the concentration dependence is influenced by blend composition via the effect of hydrogen bonds acting as physical cross-links.

In this communication we report a simple relation which links the concentration dependence of water vapour diffusion to diffusant–diffusant interaction (water clustering) and the density of hydrogen bonds. The tendency for water molecules to form clusters can be evaluated from the sorption isotherms and the density of hydrogen bonds can be calculated theoretically. These calculations will be discussed below.

ISOTHERM EQUATION

A number of equations have been proposed to fit sorption isotherms of water in polymers. Since water clustering appears to play an important role in our system, Dole's multilayer model including internal partition functions was used to fit our sorption data.

Dole has extended the localized model to allow for different partition functions in each "multilayer" [2]. He has derived the following general isotherm:

$$m/m_0 = x(\phi'/\phi) \qquad (1)$$

$$\phi = 1 + C_1 x + C_1 C_2 x^2 + C_1 C_2 C_3 x^3 + \cdots \qquad (2)$$

$$\phi' = \mathrm{d}\phi/\mathrm{d}x$$

where m is the amount of sorbed water per unit mass of polymer, m_0 is the monolayer capacity, x is the relative vapour pressure and the constant C_i $(i = 1, 2, \ldots, m)$ is the ratio of the internal partition function of the sorbed molecules in the ith layer to the partition function of the molecule in the pure liquid state. If all the C_i values are equal to k, and $k < 1$ or $kx < 1$, equation (3) for infinite number of layers reduces to

$$x/m = 1/km_0 - x/m_0 \qquad (3)$$

A plot of x/m vs x can be used to estimate k and m_0.

Sorption data of Ref. [1] were used to calculate k and m_0. The correlation coefficient was found to be always >0.99. Not surprisingly, k values were found to have almost the same rank order as the cluster functions in Ref. [1]. The k values for PMMA/PHS-5 blends can be arranged in the order: 100% PHS-5 > 80% PHS-5 > 50% PHS-5 > PMMA > 20% PHS-5; those for PMMA/PHS-15 blends in the order: PMMA > 100% PHS–15 > 50% PHS-15 > 25% PHS-15 > 75% PHS-15. The k values were used to represent the extent of water–water interaction in later analysis.

DENSITY OF HYDROGEN BONDS

There are two types of hydrogen bonds in our system, the interaction between the carbonyl and the hydroxyl groups and the self-association of hydroxyl groups. The number of each type of hydrogen bonds can be calculated from i.r. spectra or from the equation of Painter and Coleman [3]. The self-association of hydroxyl groups in PMMA/PHS-5 blends is insignificant (both from i.r. spectra and from calculation) and the mole of H-bonds per 100 g blend, h, can be calculated in a straightforward manner (Table 1). In PMMA/PHS-15 blends, both OH · · · · OH and C═O · · · · OH bonds are important and the calculated h values which are the sum of the two types of hydrogen bonds are also listed in Table 1.

CONCENTRATION DEPENDENCE

The thermodynamic diffusion coefficient, D_T is defined [4]:

$$D_T = \bar{D}(\mathrm{d}\ln v/\mathrm{d}\ln a)/(1 - v) \qquad (4)$$

where v is the volume fraction of the diffusant and a is the activity of the diffusant. In our case, $1 - v \cong 1$ and $(\mathrm{d}\ln v/\mathrm{d}\ln a)$ is nearly identical to $(\mathrm{d}\ln C/\mathrm{d}\ln a)$. The term $(\mathrm{d}\ln C/\mathrm{d}\ln a)$ can be readily calculated from the sorption data, and D_T was then calculated from equation (4) accordingly.

An exponential function of D_T with respect to C [expressed $D_T = D_0 \exp(\alpha' C)$] was found to represent

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Table 1. Parameters used in the simplified approach

PMMA/PHS-x	α'	k	h
$x = 5$			
100/0	−2.42	1.43	0
80/20	−3.49	1.09	0.010
50/50	−6.59	1.30	0.022
20/80	−10.35	1.76	0.028
0/100	−1.17	2.00	0
$x = 15$			
75/25	−3.19	1.12	0.034
50/50	−6.15	1.15	0.064
25/75	−0.62	0.96	0.081
0/100	−5.02	1.35	0.042

well the diffusion data of Ref. [1]. The calculated α' values are listed in Table 1. The quantity α' is negative in all cases, i.e. the diffusion coefficient decreases with increasing diffusant concentration. In our search for a physical interpretation of the concentration dependence, we came across at least three types of important interactions in our system, namely, water–water interaction, polymer–polymer interaction and polymer–water interaction. Therefore, α' is dependent on at least three parameters. As a first approximation, clustering or water–water interaction, is replaced by k in the multilayer model. The polymer–polymer interaction is assumed to be a monotonic function of the density of hydrogen bonds expressed as the number of H-bonds per 100 g blend, h. For polymer–water interaction, we have no estimated value.

The exact functional form of α' in terms of k and h is not known. However, since large k and h values tend to decrease diffusivity, we have plotted the ratio $|\alpha'/k|$ vs h. (Because h is almost zero for PHS-5 and $h = 0$ for PMMA, there are two values of $|\alpha'/k|$ at $h = 0$.) An almost linear relationship is observed in Fig. 1 for the two blend series except the 75% PHS-15 system. The latter system is unusual in that there is a large positive volume of mixing while the volume changes upon mixing are either slightly negative or zero for the other blends. We believe that the extra free volume [5] available for diffusion in the blend causes the deviation from the correlation. We also speculate that the smaller slope of the plot for the PMMA/PHS-15 blends than that for the PMMA/PHS-5 blends is probably related to the more hydrophilic nature of the former blends. Stronger polymer–water interaction i.e. the higher hydrophilicity of the polymer will weaken the dependence of diffusivity on concentration.

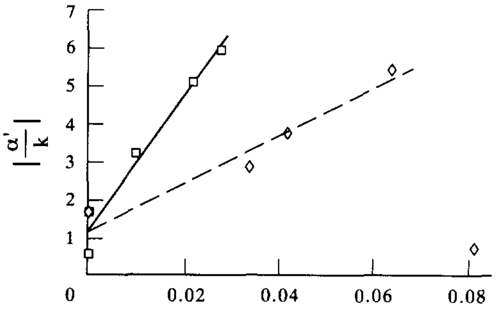

Fig. 1. $|\alpha'/k|$ vs H-bond density for PMMA/PHS blends. □, PMMA/PHS-5; ◇, PMMA/PHS-15.

Although a theoretical basis for the relationship between concentration dependence and molecular parameters is not offered in this communication, the simple correlation seems to justify further study.

CONCLUSION

Restricted segmental mobility caused by interpolymer hydrogen bonding and strong water clustering tendency are the two major reasons for decreasing vapour diffusivity with increasing concentration in PMMA/PHS blends. The result for the 75% PHS-15 blend indicates that free volume is also an important factor in determining the concentration dependence of diffusivity.

Acknowledgements—We gratefully acknowledge the support of this investigation by the National Science Foundation, Division of Materials Research, Grant 8820046. Acknowledgement is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

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