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Carbon Dioxide Sorption and Transport in Miscible Cellulose/Poly(vinyl alcohol) Blends

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ABSTRACT: The sorption and transport properties of carbon dioxide gas in cellulose (CELL) poly(vinyl alcohol) (PVA), and three miscible blends containing 30, 50, and 70 wt percent CELL were investigated at pressures up to 1 atm at 25 °C. The sorption isotherms exhibit Henry's law behavior. The solubility, diffusion, and permeability coefficients are all lower than expected from the simple semilogarithmic additivity rule. The various results are interpreted in terms of theories which have been proposed to describe gas sorption and transport in miscible blends, and the sorption and transport coefficients are correlated in terms of blend composition.

Introduction

Several recent papers from our laboratory have examined the state of miscibility in a variety of cellulose/synthetic polymer blends.[1–7] For these studies initial efforts have been focused on synthetic polymers containing functional groups that can interact strongly with the hydroxyl groups of the cellulose chains. Such intermolecular interaction is well recognized as providing the driving force for the attainment of thermodynamic miscibility in polymer blend systems. Among the synthetic polymers that satisfy this condition are poly(vinyl alcohol), poly(acrylonitrile), poly(4-vinylpyridine), and poly(vinylpyrrolidone).

Recently, we have extended our investigations to explore how the gas transport properties of cellulose change during blending with some of these synthetic polymers. In this paper we assess the relationship between the gas transport properties and composition for binary blends of cellulose (CELL) with poly(vinyl alcohol) (PVA).

In previous studies of the CELL/PVA blends, a strong depression of the melting temperature of the PVA component in the blend was observed.[3,4] Analysis of the melting point depression data showed that the thermodynamic interaction parameter assumes a large negative value ($\chi_{12} = -0.985$ at 513 K). This result implies that the blends are thermodynamically miscible and is consistent with the presence of favorable interactions due to hydrogen bonding between the two different polymers. Such interaction undoubtedly contributes to the enhancement of the state of miscibility of this blend pair.

In the present experiments, gas transport information was obtained by following the kinetics of CO_2 sorption using a sensitive microbalance, for blends covering the whole composition range. From the data generated in these experiments the solubility, diffusion, and permeability coefficients were estimated. The results are interpreted in terms of mixing rules that have been developed to describe gas sorption and transport in homogeneous multicomponent polymer systems.

Experimental Section

Materials. The cellulose sample was a wood pulp with a degree of polymerization of 935. Poly(vinyl alcohol) was purchased from Polysciences Inc.; the nominal molecular weight was 78 000 and the saponification value was 99.7 mol %. Reagent grade *N,N*-dimethylacetamide (DMAc) (Aldrich Chemical Co. Inc.) was stored for about 1 week over potassium hydroxide before use. Lithium chloride (LiCl) (Aldrich Chemical Co. Inc.) was dried for 24 h at ~80 °C in a vacuum oven and stored in a vacuum desiccator until used. DMAc–LiCl used as a common solvent for both polymers was prepared at a salt concentration of 4.5 wt % by stirring a mixture of weighed amounts of DMAc and LiCl at about 50 °C.

Preparation of Samples. CELL/PVA blends were prepared from mixed polymer solutions in DMAc/LiCl according to a coagulation method described earlier.[3,4,7] In essence, two solutions, one of CELL and the other of PVA, were prepared at a concentration of about 1.5 wt % in DMAc–LiCl. The two solutions thus separately prepared were mixed in the desired proportions, so that the composition of the two polymers in the mixed solutions had values of 30/70, 50/50, and 70/30 in a ratio of weight percent, the first numeral referring to CELL. After stirring for several days, the mixed solutions were used to prepare blend films by coagulation with ethanol. The precipitated blend films were steeped for about 1 h in ethanol and washed in several changes of methanol to extract DMAc and LiCl thoroughly. Finally, the gel films were allowed to dry gradually at room temperature. The solid films thus obtained were further dried at ca. 55 °C overnight under high vacuum and stored in a desiccator until used. CELL and PVA homopolymer films were obtained by the same coagulation method. A typical film thickness for all samples was in the range 30–40 μm.

Density Measurements. The densities of the samples at 25 °C were measured by a density gradient column containing sodium bromide solution.

Sorption Apparatus. Equilibrium sorption and kinetic sorption experiments were made by a gravimetric method similar to that described by other authors.[8,9] The measurements were made with a Cahn recording electrobalance (Model C2000) enclosed in a glass chamber with connections through a vacuum line to a CO_2 tank, a mercury pressure gauge, and a Pirani/Penning vacuum gauge. The vacuum line comprised a glass manifold connected via a liquid nitrogen trap to a diffusion pump and an oil rotary pump. A 12 L glass reservoir was included in the vacuum system to maintain constant pressure during the sorption of the gas by the polymer films. The polymer samples (600–800 mg) were suspended in a light aluminum pan by thin glass fibers near the bottom of a 20 cm hang down tube. The buildup of static charges in the sample tube was prevented with a radioactive material 500 μC PO 210. The electrobalance and the associated vacuum system was enclosed in a thermostated wooden box in which a constant temperature of 25 ± 0.5 °C was maintained by a forced air heating system. The balance was used as 1 μg sensitivity.

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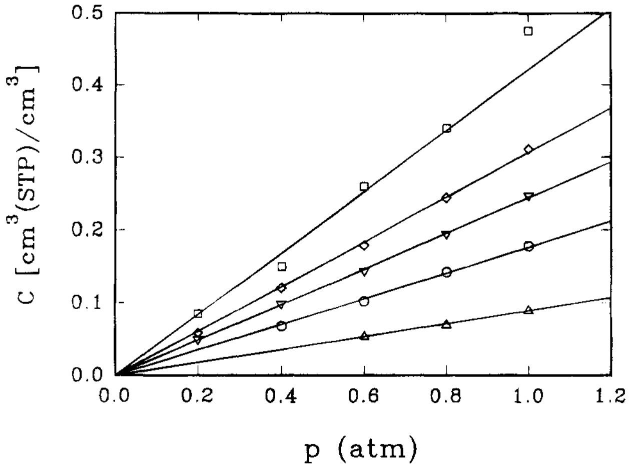

Figure 1. Sorption isotherms for CO_2 in CELL/PVA blends at 25 °C: (△) 0% CELL, (○) 30% CELL, (▽) 50% CELL, (◇) 70% CELL, (□) 100% CELL.

During an experiment the system was first fully evacuated via the liquid nitrogen trap and pumped on continuously at a pressure of $<10^{-3}$ mmHg to degas the sample and remove any adsorbed volatile material. The evacuation was continued until a constant sample weight was achieved. The system, excluding the balance chamber, was then charged with carbon dioxide gas to a selected pressure.

Finally, the sorption process was started by admitting the gas to the electrobalance chamber, and the sample mass was continuously monitored with a strip chart recorder. Due to the large gas volume and the small sample size, sorption caused a negligible change in pressure during the experiment. The sample mass initially increased linearly with the square root of time and then leveled off to a plateau value. The equilibrium sorption levels were obtained from the plateau value, and the diffusion coefficients were derived by methods to be described later. Here it may be noted that it was found essential that the carbon dioxide be completely free of water vapor, since otherwise the plateau portion of the curve never reached a constant value but continued indefinitely to increase slowly. To remove all traces of water vapor from the carbon dioxide, it was passed through four dry ice/acetone traps packed with glass wool before admittance to the vacuum system.

Results and Discussion

Equilibrium Sorption. Figure 1 shows the equilibrium sorption isotherms for CO_2 in CELL, PVA, and for CELL/PVA blends with compositions of 30, 50, and 70 wt % cellulose. The sorption curves for the blends lie intermediate to those for the pure components. The isotherms exhibit linear behavior over the accessible pressure range. This behavior may be interpreted in terms of Henry's law which states that

$$C = k_D p \tag{1}$$

where C is the equilibrium concentration of the penetrant gas in the polymer, p is the penetrant pressure at equilibrium, and k_D is the Henry law constant in cm^3(STP)/cm^3(polymer). The values of k_D derived from the slope of the curves are listed in Table 1.

Many studies of gas sorption in polymers at temperatures below their glass transition temperature show that the sorption isotherms do not conform to Henry's law, but rather follow the dual mode sorption model,[10] which stipulates that the sorbed penetrant exists in two populations; one dissolved according to Henry's law (concentration = C_D), and the other sorbed according to a Langmuir isotherm (concentration = C'_H) due to the presence in the specimen of pre-existing microvoids. This is expressed by the well-known equation

$$C = k_D p + \frac{C'_H bp}{1 + bp} = C_D + C_H \tag{2}$$

where k_D and p have the significance given above, C'_H is the total sorption capacity of the polymer for the penetrant in the Langmuir sorption mode in cm^3(STP)/cm^3 of polymer, and b is the affinity constant of the penetrant for the Langmuir sites in (cm Hg)$^{-1}$.

Table 1. Sorption Parameters for CO_2 in Cellulose/PVA Blends at 25 °C

wt % PVA	k_D [cm^3(STP)/ m^3 atm]	k_D/α [cm^3(STP)/ (cm^3 atm)]	k_D/α [10^{-6} cm^3(STP)/ (cm^3 Pa)]
100	0.0893	0.192	1.89
70	0.179	0.248	2.45
50	0.245	0.279	2.75
30	0.310	0.310	3.06
0	0.463	0.463	4.58

The dual mode model predicts that the isotherm should be concave to the pressure axis. In the present experiments, the observation temperature is below the glass transition temperature of both components of the blends (for PVA, T_g = 358 K, and for CELL, T_g = 525 K), so the pure components and the blends are expected to be glassy. Since many polymer systems show dual mode behavior at pressures less than 1 atm,[11-14] it is also possible that the structure of the specimen films may be such that the Langmuir sorption mode is not operative. However, a more plausible explanation is that the absence of curvature in the observed isotherms may simply reflect the fact that at the low pressures accessible for the experiments, only the initial linear portion of the total isotherm is probed.

It is noteworthy that the absolute level of the CO_2 equilibrium sorption is relatively low in comparison with the sorption levels observed in other polymers. From Figure 1 it is seen that for a CO_2 pressure of 1 atm the concentration of gas in the pure components and the blends is less than 0.5 cm^3(STP)/cm^3 of polymer. In comparison, for a variety of polymers, including polystyrene, poly(ethylene terephthalate), polycarbonate, and cellulose acetate,[15] at the same pressure the corresponding concentration of CO_2 lies in the range 2–7 cm^3(STP)/cm^3. The low values of the equilibrium CO_2 sorption in the present experiments may be due to extensive hydrogen bonding in the samples or to residual crystallinity.

Mixing rules, developed for ternary systems on the basis of Flory–Huggins theory, allow the interaction between the blend components to be characterized. For this purpose it is important to recognize that the CELL/PVA blends are semicrystalline. This has been demonstrated in earlier DSC studies[3] which showed that blends containing more than 30% PVA exhibit well-defined PVA melting peaks. Because of the method used for preparing the blends the cellulose component is essentially amorphous.[7] Accordingly, since the sorption takes place only in the amorphous regions, we need to know the volume fraction of the amorphous phase, α, in the blends. Following Chiou and Paul,[16] α is given by the expression

$$\alpha = 1 - \varrho X_C/\varrho_C \tag{3}$$

where ϱ is the density of the blend and ϱ_c is the density

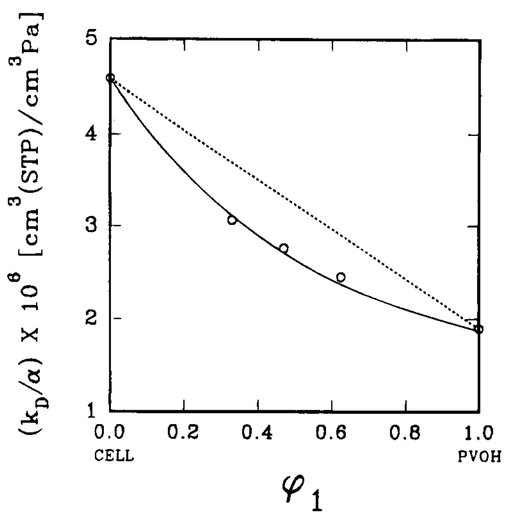

Figure 2. Henry's law solubility coefficient plotted against volume fraction of PVA in the amorphous phase φ_1 for CELL/PVA blends at 25 °C. The solid line was drawn using eq 5 with $B = -4.3$ cal/cm^3, which agrees well with experimental results.

Table 2. Thermal and Volumetric Properties of Cellulose/PVA Blends

wt % PVA	ΔH_m (cal/g)	X_c	ϱ (g/cm^3)	α	φ_1
100	18.7	0.552	1.297	0.466	1
70	9.4	0.277	1.357	0.719	0.624
50	4	0.118	1.399	0.877	0.470
30	0	0	1.440	1	0.330
0	0	0	1.505	1	0

of 100% crystalline PVA taken as 1.34 g/cm^3,[4,17] and X_c is the weight fraction crystallinity for the blends. For the blends studied here X_c was determined from the observed heat of fusion, where 33.9 cal/g was taken as the value of ΔH for 100% crystalline PVA.[4] The volume fraction of PVA in the amorphous phase φ_1 was calculated from the following expression, which assumes volume additivity in the mixed amorphous phase

$$\varphi_1 = V_{1a}/(V_{1a} + V_2) \tag{4}$$

where V_{1a} is the volume of amorphous PVA and V_2 is the volume of cellulose; both V_{1a} and V_2 are expressed per unit mass of blend. Values of the specific volumes of amorphous PVA and CELL were taken as 0.7874 and 0.6645 cm^3/g, respectively.[4] Values of the various parameters used in these calculations are listed in Table 2.

According to ternary solution theory,[18-20] for a miscible blend the composition dependence of the solubility coefficients can be related to those of constituent polymers by the equation

$$\ln k_D = \varphi_1 \ln k_{D1} + \varphi_2 \ln k_{D2} + (BV_3/RT)\varphi_1\varphi_2 \tag{5}$$

where R is the gas constant, B is the interaction energy density, V_3 is the molar volume of the penetrant gas, and the subscripts 1 and 2 indicate the two components.

According to eq 5, when $B = 0$ the relation between $\ln k_D$ and blend composition should be linear. Since B is negative for miscible blends, the values of k_D are expected to be smaller than those calculated from the semilogarithmic additivity rule when $B = 0$.

The composition dependence of the observed Henry's law coefficients is shown in Figure 2, where the solubility coefficients have been divided by the factor α in order to account for the fact that the sorption takes place only in the amorphous phase.[21,22] The experimental points show the negative deviation from the tie line expected for miscible blends. By taking $V_3 = 55$ cm^3/mol for CO_2,[23] nonlinear regression analysis of the data gives $B = -4.3$ cal/cm^3. This may be compared with a value of $B = -9.4$ cal/cm^3 obtained from melting point depression data.[4] The difference between the two values may be due to experimental errors caused by the inherently low solubility levels in the sorption measurements. For most miscible blend systems with mild to strong interactions, the value of B is typically less than -5 cal/cm^3.[24] For the present system the interactions probably involve strong specific hydrogen bonding between the hydroxyl groups of the constituent polymers.

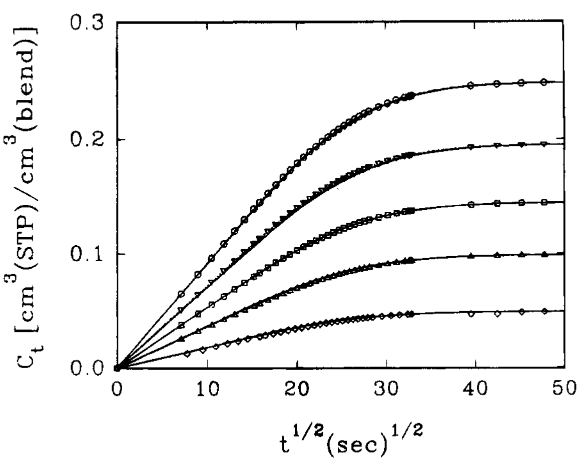

Figure 3. Sorption rate curves for CO_2 in a 50/50 blend at various pressures: (◇) 0.2 atm, (△) 0.4 atm, (□) 0.6 atm, (▽) 0.8 atm, and (○) 1.0 atm. The points correspond to observed values. The solid lines calculated from eq 8 using D_I and D_E are coincident.

Transport. Figure 3 shows sorption rate curves, as plots of solubility, C_t, versus $t^{1/2}$ for a CELL/PVA 50/50 blend at various pressures up to 1 atm. These rate curves are representative of the behavior of the pure components as well as of the blends with compositions of CELL/PVA 70/30 and CELL/PVA 30/70. From these sorption rate curves diffusion coefficients were calculated by two well-known methods.[25] In the first method, the calculations were made by using the short time solution of the diffusion equation for conditions such that $C_t/C_e < 0.5$, where C_t is the solubility at time t and C_e is the equilibrium solubility. In this case C_t/C_e is given by

$$C_t/C_e = \frac{4}{l}\left(\frac{D_I t}{\pi}\right)^{1/2} \tag{6}$$

where D_I is the diffusion coefficient and l is the sample thickness. The value of D_I was obtained from the slope of the initial linear region of plots of C_t/C_e versus $t^{1/2}$ using eq 6.

In the second method, the diffusion coefficient D_E was calculated from the long term solution of the diffusion equation for conditions where $C_t/C_e > 0.5$. The value of D_E was derived from the relation

$$\ln(1 - C_t/C_e) = \pi^2\frac{D_E t}{l^2} \tag{7}$$

so that a plot of $\ln(1 - C_t/C_e)$ vs t should give a straight line with a slope of $\pi^2 D_E/l^2$. If the diffusion of gas in the polymer is Fickian, the two diffusion coefficients D_I and D_E should be equal. The values of the two diffusion

Table 3. Results of CO_2 Sorption Experiments for Cellulose/PVA Systems at 25 °C

	pressure (atm)	C_e[a] (cm^3 of CO$_2$/cm^3 of blends)	10^9D_I[b] (cm^2/s)	10^9D_E[b] (cm^2/s)	$10^{15}P_I$[c] [(cm^3 cm)/(cm^2 s Pa)]	$10^{15}P_E$[c] [(cm^3 cm)/(cm^2 s Pa)]
100% PVA						
	0.6	0.054	2.47	2.73	2.18	2.41
	0.8	0.070	2.50	2.70	2.20	2.38
	1.0	0.090	2.80	3.00	2.47	2.64
70% PVA						
	0.4	0.068	2.54	2.55	4.47	4.49
	0.6	0.102	2.68	2.69	4.72	4.74
	0.8	0.142	2.54	2.55	4.47	4.49
	1.0	0.178	2.60	2.61	4.58	4.60
50% PVA						
	0.2	0.049	2.59	2.60	6.26	6.28
	0.4	0.099	2.58	2.48	6.23	5.99
	0.6	0.144	2.54	2.55	6.13	6.16
	0.8	0.194	2.47	2.58	5.97	6.23
	1.0	0.247	2.56	2.60	6.18	6.28
30% PVA						
	0.2	0.059	2.86	2.86	8.74	8.74
	0.4	0.121	2.91	2.92	8.90	8.93
	0.6	0.179	2.92	2.93	8.93	8.96
	0.8	0.244	3.11	3.12	9.51	9.54
	1.0	0.311	3.55	3.57	10.9	10.9
0% PVA						
	0.2	0.085	3.26	3.60	14.9	16.5
	0.4	0.150	3.24	3.50	14.8	16.0
	0.6	0.260	3.30	3.70	15.1	16.9
	0.8	0.340	3.42	3.90	15.6	17.8
	1.0	0.475	3.45	3.95	15.8	18.1

[a] C_e = equilibrium solubility. [b] D_I = diffusion coefficient (initial sorption rate), D_E = diffusion coefficient (near sorption equilibrium rate). [c] P_I = permeation coefficient (from D_I), P_E = permeation coefficient (from D_E).

coefficients thus obtained were substituted into the solution of the Fickian diffusion equation for sorption into a thin flat membrane[26] in order to obtain theoretical sorption rate curves for comparison with the experimental results.

$$C_t = C_e\left\{1 - \frac{8}{\pi^2}\sum_{n=0}^{n=\infty}\frac{\exp[D(2n + 1)^2\pi^2 t/l^2]}{(2n + 1)^2}\right\} \qquad (8)$$

Figure 3 shows a representative example of the results obtained. It is seen that the sorption rate curves calculated as described above using D_I and D_E in eq 8 show excellent agreement with the experimental values over the entire range of measurement. It follows that the sorption kinetics for CO_2 in CELL, PVA, and their blends satisfies the criterion for Fickian diffusion. Values of the diffusion coefficients D_I and D_E obtained as outlined above for CELL, PVA, and their blends are listed in Table 3.

Figure 4 shows D_I as a function of CO_2 pressure. The data points show some scatter, but it seems acceptable to conclude that there is little or no concentration dependence over the accessible concentration (pressure) range. Normally, for glassy polymers the diffusion coefficient increases initially with pressure and then reaches an equilibrium value at higher pressures. The apparent constancy of the observed diffusion coefficients with pressure implies that the dual mode immobilization model is not applicable for the range of pressures accessible in these experiments.

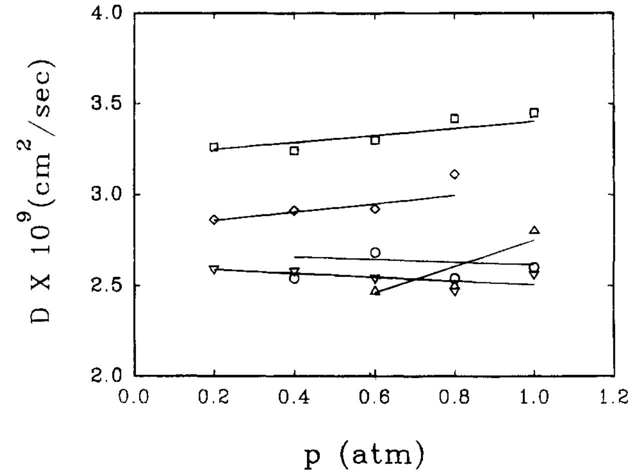

Figure 4. Diffusion coefficient (D_I) for CO_2 in CELL/PVA blends at 25 °C versus pressure: (△) 0% CELL, (○) 30% CELL, (▽) 50% CELL, (◇) 70% CELL, (□) 100% CELL.

In Figure 5 the diffusion coefficients for CELL, PVA, and the blends are plotted semilogarithmically versus the volume fraction of PVA in the amorphous phase, φ_1. As in the case of the solubility coefficients in Figure 2, the values of D have been divided by the factor α, since the diffusion occurs only in the amorphous phase. The significance of these plots can be understood on the basis of the activated state theory for blends,[27] which predicts that the diffusion for penetrant molecules in a miscible blend is given by the expression

$$\ln D = \varphi_1 \ln D_1 + \varphi_2 \ln D_2 + (aRT - 1)\Delta E_{12}/RT \qquad (9)$$

where a is a constant, R is the gas constant, T is the temperature, and ΔE_{12} is the excess activation energy for diffusion in the blend, defined by

$$E_D = \varphi_1 E_{D1} + \varphi_2 E_{D2} + \Delta E_{12} \qquad (10)$$

where E_D is the activation energy for diffusion in the blends and E_{D1} and E_{D2} refer to the pure components.

It is seen that the experimental diffusion coefficients for the blends are significantly lower than those calculated from the additivity rule to which eq 9 reduces when the excess term is omitted. According to McGregor,[28] aRT is on the order of 0.5–0.6 so that the value of $(aRT - 1)$ in eq 9 is approximately −0.5. It follows that ΔE_{12} must be positive, which means that gas

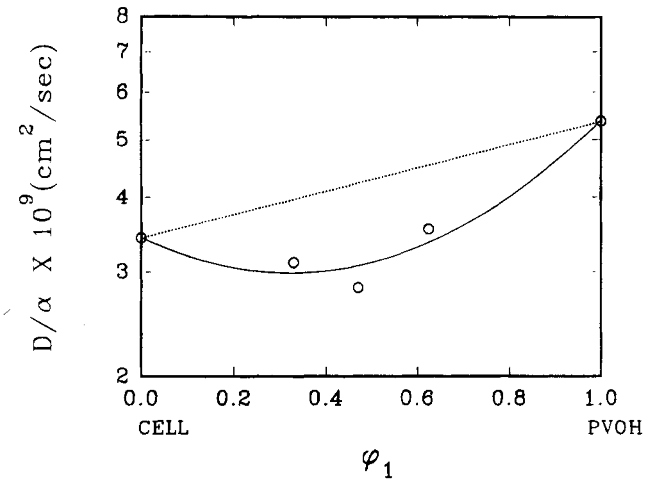

Figure 5. Semilogarithmic plots of CO_2 diffusion coefficient (D_I) at 0.8 atm plotted against the volume fraction of PVA in the amorphous phase φ_1 for CELL/PVA blends at 25 °C.

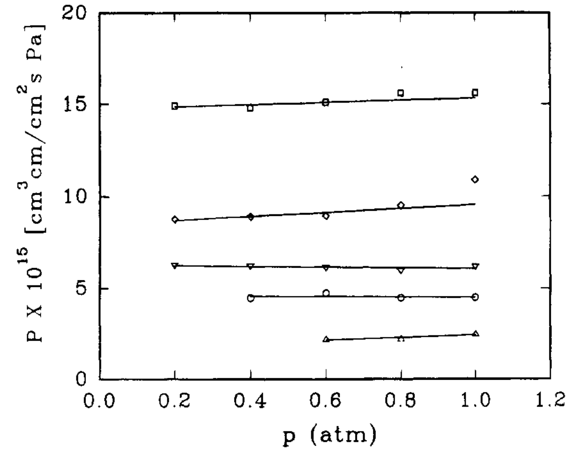

Figure 6. Pressure dependence of the permeability coefficient (P_I) for CO_2 in CELL/PVA blends at 25 °C: (△) 0% CELL, (○) 30% CELL, (▽) 50% CELL, (◇) 70% CELL, (□) 100% CELL.

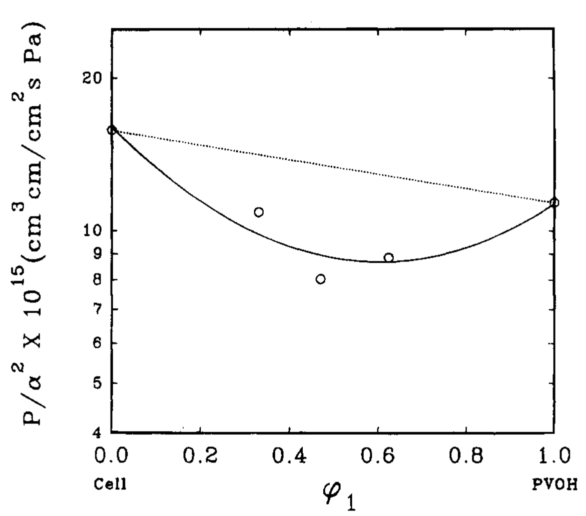

Figure 7. Semilogarithmic plots of CO_2 permeability coefficient divided by the square of the volume fraction of the amorphous phase against the volume fraction of PVA in the amorphous phase at 25 °C and 1.0 atm pressure.

diffusion in the blends requires a higher activation energy than predicted by simple additivity. For the CELL/PVA blends studied in the present work, the negative deviation of the diffusion coefficients corresponds to values of $\Delta E_{1/2}$ in the range of 180–500 cal/mol, depending on the pressure and blend composition.

The permeability coefficient can be estimated as the product of the solubility and diffusion coefficients, i.e.

$$P = Dk_D \tag{11}$$

Values of P thus obtained for CELL, PVA, and for the various blends are listed in Table 3. As shown in Figure 6, the permeability of CO_2 in the pure components and in the blends is essentially independent of pressure in the pressure range investigated. Although glassy polymers generally show permeability coefficients which decrease with pressure,[15,18,19,29,30] very little change is expected for the range of pressures used in the present experiments.[15]

It is also of interest to compare the CO_2 permeability coefficients for PVA and CELL with values reported in the literature. Widely different gas permeability coefficients, ranging from 0.075×10^{-15} to 3.15×10^{-15} (cm^3(STP) cm)/(cm^2 s Pa) have been reported for PVA. As pointed out by Aguilar-Vega et al.[31] these differences could be due to several factors including variations in the level of crystallinity, degree of hydrolysis, moisture content, and errors associated with the measurement of very low transmission rates. As seen in Table 3, the values obtained in the present studies are in the range of 2.4×10^{-15} (cm^3(STP) cm)/(cm^2 s Pa). This compares most favorably with the value of 3.15×10^{-15} (cm^3(STP) cm)/(cm^2 s Pa) reported by Bixler and Sweeting.[32]

For cellulose the observed permeability coefficients lie in the range $(15-18) \times 10^{-15}$ (cm^3(STP) cm)/(cm^2 s Pa) (Table 3). These values are significantly higher than the literature value of 0.35×10^{-15} (cm^3(STP) cm)/(cm^2 s Pa) reported for regenerated cellulose (Cellophane) at 0% relative humidity.[33]

Finally, by combination of eqs 5, 9, and 11 the permeability coefficient for a miscible blend can be related to that of the component polymers by the expression

$$\ln P = \varphi_1 \ln P_1 + \varphi_2 \ln P_2 + (aRT - 1)\Delta E_{12}/RT + (BV_3/RT)\varphi_1\varphi_2 \tag{12}$$

Figure 7 shows semilogarithmic plots of P/α^2 versus the volume fraction of PVA in the amorphous phase, φ_1. It is obvious that the negative deviation of the permeability coefficients from the semilogarithmic additivity rule arises from the last two terms in eq 12.

Conclusions

The main issue arising from the present work is the low levels of CO_2 absolute sorption in comparison with the sorption levels found in other polymers. This probably reflects the high level of hydrogen bonding in both the pure components and the blends. Although other gases (e.g. He, Ar, N_2, O_2, and CH_4) have not been studied, it can be anticipated that they would show even lower levels of sorption than CO_2.

The gas sorption and transport coefficients are lower than predicted from simple additivity relations. This behavior is consistent with that of other miscible systems in which there are strong intermolecular interactions.

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