Gas transport in miscible blends of ethylene–vinyl acetate copolymer and chlorinated polyethylene

J. A. Barrie and W. D. Webb
Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY, UK

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The sorption and permeation of carbon dioxide and methane have been studied in the range 25 to 60°C for blends of ethylene-vinyl acetate copolymer (EVA-45) and chlorinated polyethylene (H-48) reported as miscible. The dependence of both sorptive capacity and permeability on blend composition has been determined and examined in terms of models developed for miscible and heterogeneous blends. The analysis suggests the system is not well behaved and that some degree of phase separation may occur over part of the composition range. The dependence on blend composition and temperature of the ideal separation factor for carbon dioxide and methane has also been analysed.

(Keywords: sorption; permeation; gases; miscible polymer blends)

INTRODUCTION

With the continuing interest in miscible polymer blends there have been an increasing number of studies of the sorption and transport of small molecules in systems of this type[1]. Theoretical models which describe transport in such systems have been developed recently[2] and are most easily tested using a binary mixture of rubbery amorphous components. However, the number of studies on such systems is few[3-5]. Ethylene-vinyl acetate copolymer (EVA-45) and chlorinated polyethylene (H-48) have been reported as miscible[6]. Both polymers and their blends are amorphous and rubbery. In the present investigation gas transport in films of the pure components and of blends has been studied to provide additional information on this system.

EXPERIMENTAL

Ethylene-vinyl acetate copolymer (Levapren; $\bar{M}_n = 3.77 \times 10^4$) containing a nominal 45 wt% vinyl acetate was obtained from Bayer and is designated EVA-45. A sulpho-chlorinated polyethylene (Hypalon-48; $\bar{M}_n = 2.39 \times 10^4$) containing 44 wt% chlorine and a small number of SO_2Cl groups was supplied by Dupont UK. It is designated H-48. The purity of both polymers was checked by infrared spectroscopy (i.r.s.) and both were shown to be amorphous from X-ray diffraction measurements. Number average molecular weights were determined earlier by gel permeation chromatography (g.p.c.)[6].

Films with thickness in the range ~0.01–0.1 cm, were prepared by casting ~10% w/v dust free solutions in tetrahydrofuran on to a clean mercury surface and allowing complete evaporation. This was followed by outgassing at 40°C for two weeks in a vacuum oven. Checks for residual solvent were made with a thermogravimetric balance. No significant weight loss was recorded up to 100°C. At higher temperatures thermal degradation of the chlorinated polymer led to rapid loss of weight.

Densities of the pure components and of the blends were determined by displacement of water with error limits of $\pm 0.005\,g\,cm^{-3}$ at most. Glass transition temperatures (T_g) were measured by dynamic mechanical thermal analysis (Rheovibron DDV-11, Toyo Measuring Inst. Co., operating at 11 Hz) and by differential scanning calorimetry (d.s.c.) (Du Pont 990 operating at 10°C/min).

Carbon dioxide and methane with purity >99.96 mol% were used as penetrants. Sorption isotherms were measured with a vacuum electronic microbalance (Sartorius Instruments). Permeation rates were measured with a glass diffusion cell and a Baratron (MKS Instruments) capacitance manometer. The Baratron was interfaced to a microcomputer (Commodore PET 2001) which stored and analysed the data[7,8]. A similar system has recently been described[9].

RESULTS AND DISCUSSION

Glass transition temperature and density

It has been shown that blends of H-48 and EVA-45 are miscible with a minimum in the cloud point curve around 70°C[6]. In the present study, clear films were obtained for the pure components and for the blends which had a weight fraction of EVA-45 greater than 0.5. For weight fractions of EVA-45 less than 0.5 slight turbidity was observed. This increased as the EVA-45 content decreased. There was no evidence for any large scale ordering from X-ray diffraction measurements.

A single composition dependent glass transition temperature, T_g, was obtained from the maximum in the loss tangent with temperature for all compositions. D.s.c. also gave a single composition dependent T_g for blends containing more than 50 wt% EVA-45. For blends less

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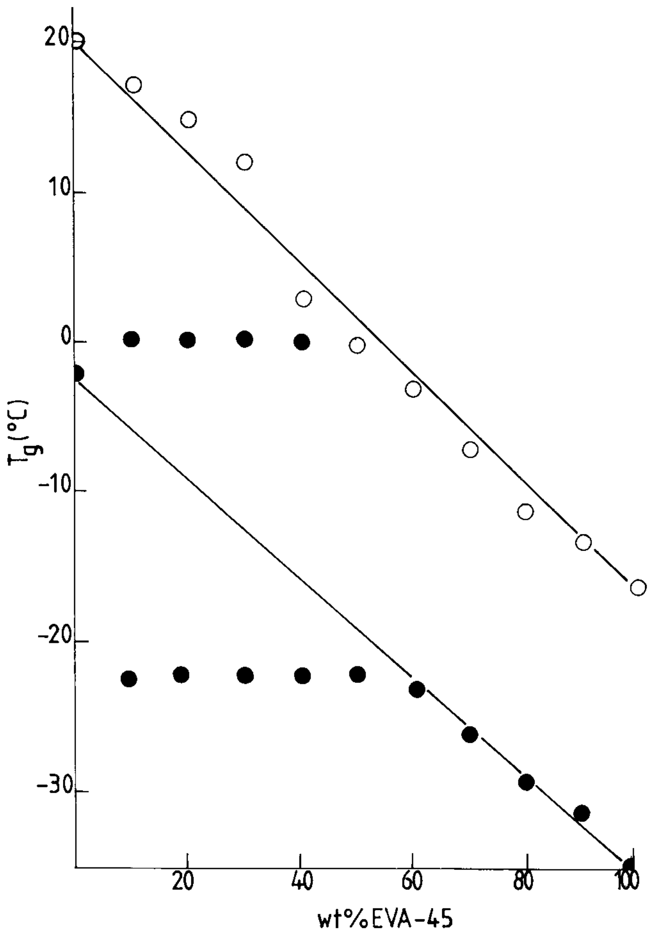

Figure 1 Glass transition temperature (T_g) as a function of blend composition. ○, Dynamic mechanical measurements; ●, d.s.c.

rich in EVA-45 there appeared to be two broad transition temperatures. The results are shown in *Figure 1* along with the Gordon–Taylor expression with the constant taken as unity[10]. The T_g from dynamic mechanical measurement lies reasonably close to the Gordon–Taylor line but there is an indication of a discontinuity in the results around 35 wt% EVA-45. Similar behaviour has been reported for other miscible blends[11]. Where d.s.c. produced a single T_g, there was a good linear dependence on composition. For the region 0 to ~50 wt% EVA-45, the d.s.c. results suggest a phase separation into almost pure H-48 and a 50:50 blend consistent with the slight turbidity of films in this range of composition. The discrepancy with the dynamic mechanical measurements which gave a single composition dependent T_g in this region is unresolved. Further work on this sytem suggests that it is not simple and that phase separation may occur over part of the composition range[12].

In *Figure 2* the specific volume is plotted against composition. Departure from the line corresponding to zero volume change on mixing is barely significant. This implies that the interaction between the two components is relatively weak.

Sorption of carbon dioxide

Equilibrium sorption isotherms for the pure components and the blends were measured in the temperature range 25–55°C and for pressures of 0 to 25 cmHg. In all cases, Henry's law, $C = kp$, where k is solubility and p is pressure, was obeyed. A representative set of isotherms is shown in *Figure 3*. A selection of k values is given in *Table 1*. Semi-logarithmic plots of k *versus* $1/T$ were linear. The dependence on blend composition of the heat of solution $\Delta H_s = -R\mathrm{d}\ln k/\mathrm{d}1/T$ was weak as is shown in *Figure 4*.

The Flory–Huggins solution theory for a ternary system comprising solvent (3) and two polymers (1) and (2) yields in the limit of zero concentration of solvent

$$\ln k = \phi_{10}\ln k_{31} + \phi_{20}\ln k_{32} + \chi'_{12}\phi_{10}\phi_{20} \qquad (1)$$

where k is the Henry law constant for the solvent in the miscible polymer blend; k_{31} and k_{32} are the corresponding constants for the pure polymer components and ϕ_{10} and ϕ_{20} are the volume fractions of

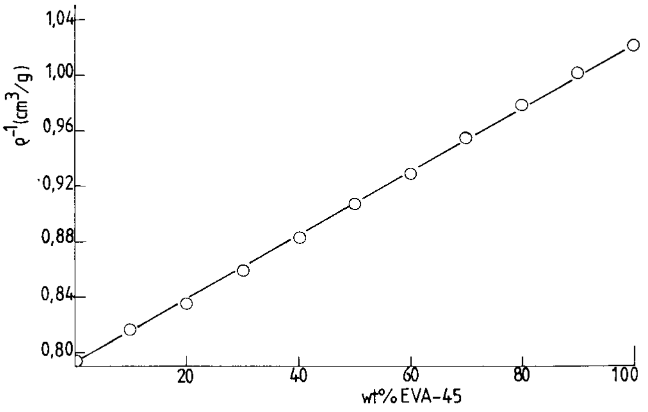

Figure 2 Specific volume as a function of blend composition

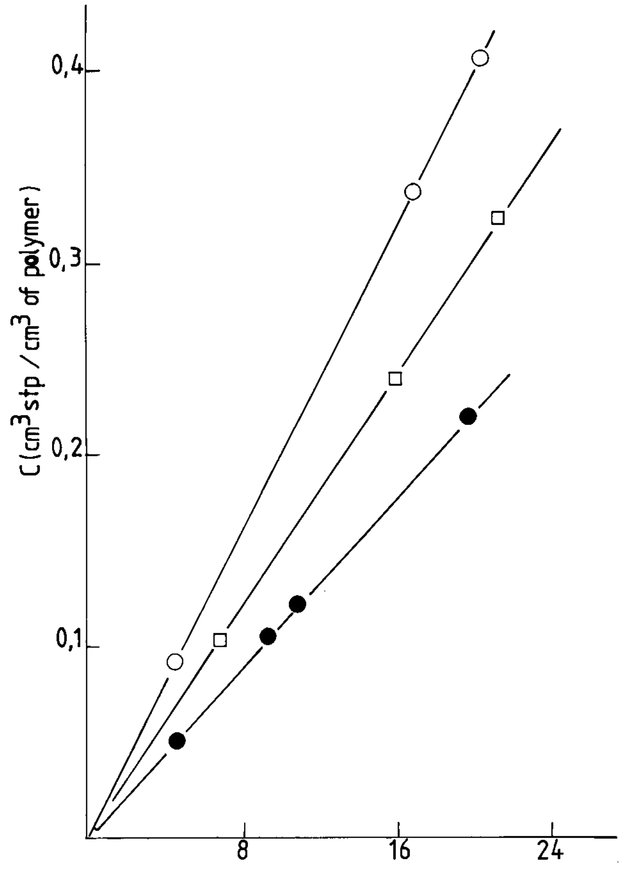

Figure 3 Henry law isotherms for carbon dioxide at 30°C; ○, 100 wt% EVA-45; □, 50 wt% EVA-45; ●, 100 wt% H-48

Table 1 Solubility k^a and permeability P^b of carbon dioxide in blends of EVA-45 and H-48

		30°C		40°C		50°C	
wt% EVA-45	ϕEVA-45	k	$10^{10}P$	k	$10^{10}P$	k	$10^{10}P$
100	1.0	0.020	113	0.0173	168	0.0148	241
90	0.920	0.0187	77.5	0.0159	121	0.0138	176
80	0.837	0.0181	53.1	0.0157	83.9	0.0137	124
70	0.750	0.0171	44.0	0.0144	71.6	0.0126	106
60	0.658	0.0156	32.6	0.0135	52.8	0.0118	82.0
50	0.562	0.0152	22.0	0.0132	38.6	0.0117	66.4
40	0.461	0.0142	18.5	0.0122	32.6	0.0108	53.4
30	0.355	0.0133	12.5	0.0115	21.2	0.0100	35.7
20	0.243	0.0127	6.42	0.0110	12.1	0.0098	20.1
0	0.0	0.0110	2.16	0.0096	4.62	0.0085	8.47

[a] k (cm^3 stp/cmHg cm^3 of polymer)
[b] P (cm^3 stp cm/cm^2 s cmHg)

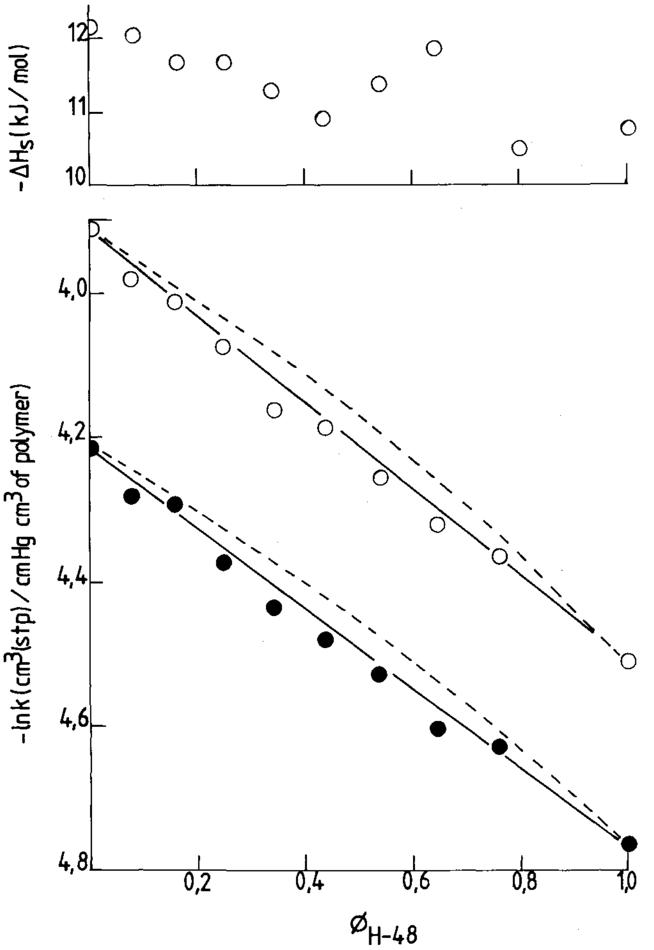

Figure 4 Henry law constant k and heat of sorption ΔH_S (upper graph) as a function of blend composition ($\phi_{H\text{-}48}$): ○, 30°C; ●, 50°C; ———, equation (1) with $\chi'_{12}=0$; – – –, equation 2

(1) and (2) in the dry blend. The interaction parameter χ_{12} for the polymer pair is related to χ'_{12} by $\chi'_{12}=\chi_{12}V_3^0/V_1^0$ where V_1^0 and V_3^0 are the molar volumes of (1) and (3) respectively[13].

In *Figure 4*, ln k is plotted against blend composition as suggested by equation (1). The experimental points tend to lie slightly below the line of equation (1). This indicates a small negative χ'_{12}. Because the pure component solubilities differ by less than a factor of 2 there are large errors and scatter in the individual χ'_{12} values. Average values of -0.10 and -0.08 were obtained at 30 and 50°C, respectively. For a heterogeneous blend comprising phases of the pure polymeric components

$$k=\phi_{10}k_{31}+\phi_{20}k_{32} \tag{2}$$

This is shown as a dotted line in *Figure 4*. Equation (2) does not represent the data as well as equation (1) although the difference between the two models is small in this instance.

Steady state permeation and diffusion

The permeability P of carbon dioxide in H-48, EVA-45 and the series of blends was measured for upstream pressures of less than 20 cmHg and in the temperature range 25–60°C. The permeability was independent of the upstream pressure. The representative values given in *Table 1* are the averages of four or more measurements at different pressures. The permeability in EVA-45 at 50°C is in reasonable agreement with an earlier value of 2.11×10^{-8} cm^3 stp cm/cm^2 s cmHg (ref. 14).

The variation of permeability with blend composition for representative temperatures of 30°C and 50°C is shown in *Figure 5*. A number of expressions have been developed to describe the dependence of the gas transport parameters on composition for a miscible blend[10]. Assuming that the activation energy for diffusion (E_D) can be expressed as $E_D=\phi_1E_{D_1}+\phi_2E_{D_2}+\Delta E_{12}$ and using, $D=D_0\exp(-E_D/RT)$ and the empirical relation $\ln D_0=aE_D+b$, it follows that

$$\ln D=\phi_1\ln D_1+\phi_2\ln D_2+(aRT-1)\Delta E_{12}/RT \tag{3}$$

Equation (3) combined with equation (1) yields

$$\ln P=\phi_1\ln P_1+\phi_2\ln P_2+(aRT-1)\Delta E_{12}/RT+\chi'_{12}\phi_1\phi_2 \tag{4}$$

An alternative approach is based on the empirical relation, $P=Ae^{-B(V-V_0)}$, where V is the specific volume and V_0 the 'occupied' volume of the polymer. From correlations of P with $V-V_0$ for various polymers, A and B to a first approximation can be regarded as constants for a given gas[2,15]. The assumption of additivity of free volume then leads to

$$\ln(P/A)=\left\{\frac{\phi_1}{\ln(P_1/A)}+\frac{\phi_2}{\ln(P_2/A)}\right\}^{-1} \tag{5}$$

This expression can be modified to accommodate a

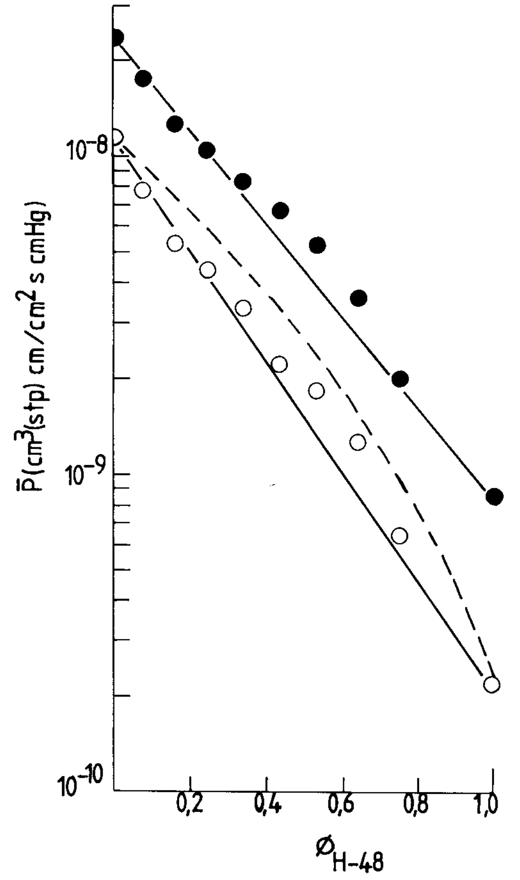

Figure 5 Permeability ($\bar{P}$) as a function of blend composition ($\phi_{H\text{-}48}$): ○, 30°C; ●, 50°C; ———, equation (6); – – –, equation 5

volume change on mixing. When ΔE_{12} and χ'_{12} are zero equation (4) reduces to the simple expression given in equation (6).

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{6}$$

Similarly, when $\ln A \gg \ln P_i$ or when P_1 and P_2 are similar in magnitude equation (5) reduces to the same expression which has been used as an empirical description of transport in miscible blends. None of these expressions rests on rigorous theoretical foundations. As indicated[2] it would be more instructive to apply free volume theory to D rather than P, although the availability of free volume parameters for penetrant and polymers is a limiting factor.

Generally, it is found that permeabilities are less than predicted by equation (6) for miscible blends but permeabilities are greater than predicted for copolymers. Permeabilities calculated from equation (6) and from equation (5) using a value of $A = 3 \pm 2 \times 10^{-6}$ cm^3 (stp)cm cm^{-2} s^{-1} (ref. 15) are included in *Figure 5*. Equation (5) overestimates P and the agreement is better with equation (6), especially in the composition range 0 to 50 wt% H-48. Good agreement with equation (6) has also been obtained for several gases in blends of poly(methylacrylate) and poly(epichlorohydrin), both of which are rubbery and amorphous, although the differences in component permeabilities were considerably smaller[4].

Slight turbidity of the films was observed at higher H-48 contents. In *Figure 6* a comparison is made with the permeability calculated from the Maxwell and Böttcher expressions developed for heterogeneous dispersions of one component in a continuum of the other[7,16]. The corresponding apparent activation energies for permeation are shown in *Figure 7*. Clearly, equation (6) is

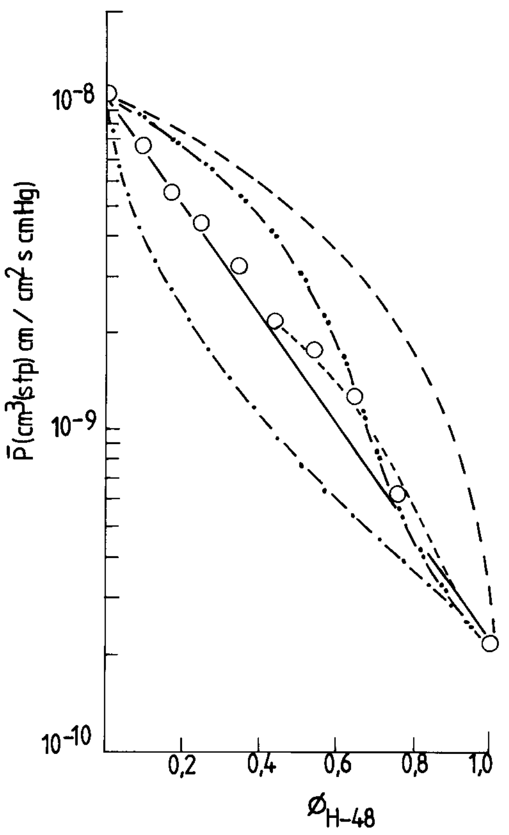

Figure 6 Permeability ($\bar{P}$) as a function of blend composition ($\phi_{H\text{-}48}$) at 30°C: ○, expt; ———, equation (6); – – –, Maxwell equation with EVA-45 continuous phase; –·–·–, Maxwell equation with H-48 continuous phase; –··–··–, Böttcher equation for pure EVA-45 and H-48 phases; -----, Böttcher equation for phases comprising pure H-48 and a 50–50 blend

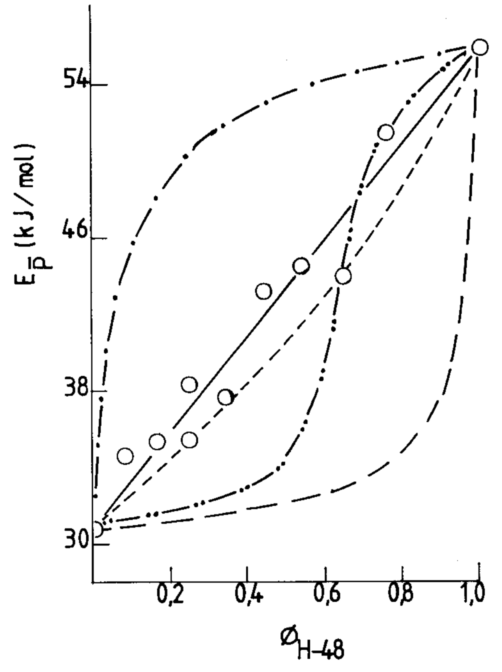

Figure 7 Apparent activation energy for permeation $E_{\bar{P}}$ as a function of blend composition ($\phi_{H\text{-}48}$): ○, expt; ———, equation 6; ·····, equation (5); –·–·–, Maxwell equation with H-48 continuous phase; – – –, Maxwell equation with EVA-45 continuous; –··–··–, Böttcher equation for pure EVA-45 and H-48 phases

a much better overall fit to the data although there is a small but significant departure in the range ~40–~70% H-48. Assuming a separation of the blend in this region of composition into two phases comprising pure H-48 and a 50:50 blend respectively, as suggested by the d.s.c. results, then good agreement is obtained with the permeability calculated from the Böttcher expression as shown in *Figure 6*. Anomalous permeation behaviour may also arise if a gradient of chemical composition were to develop across the membrane of a miscible blend during the slow evaporation of solvent when casting. However, this would not account for the turbidity observed in some of the films. Satisfactory agreement was also obtained between time-lag and steady-state diffusion coefficients. This suggests that the structure was essentially uniform across the membrane.

The dependence of the steady-state diffusion coefficient and of the activation energy for diffusion E_D on blend composition is shown in *Figures 8* and *9*. Both sets of results suggest a small negative value for ΔE_{12}. Similar behaviour has been observed for propane diffusion in miscible blends of polystyrene and poly(vinyl methyl ether) in the rubbery state. However, for the poly(methyl acrylate)–poly(epichlorohydrin) system, ΔE_{12} was effectively zero for carbon dioxide[3,4]. In general, for miscible blends positive ΔE_{12} values are expected[2]. The small negative values reported here may reflect interference associated with imperfect mixing of the components. The question of imperfect mixing has also been raised for the polystyrene–poly(vinyl methyl ether) system[3].

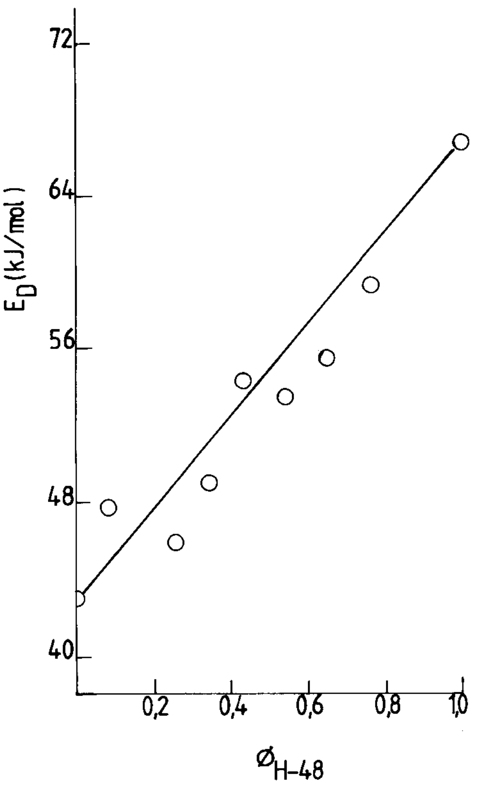

Figure 9 Activation energy for diffusion (E_D) as a function of blend composition ($\phi_{H\text{-}48}$). ○, expt; ———, $E_D = \phi E_{D_1} + \phi_2 E_{D_2}$

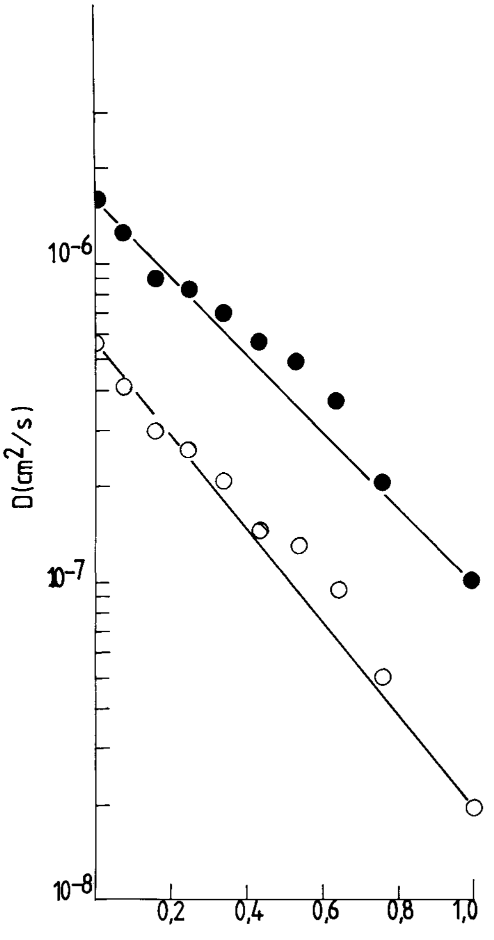

Figure 8 Diffusion coefficient (D) as a function of blend composition ($\phi_{H\text{-}48}$). ○, 30°C; ●, 50°C; ———, equation (3) with $\Delta E_{12} = 0$

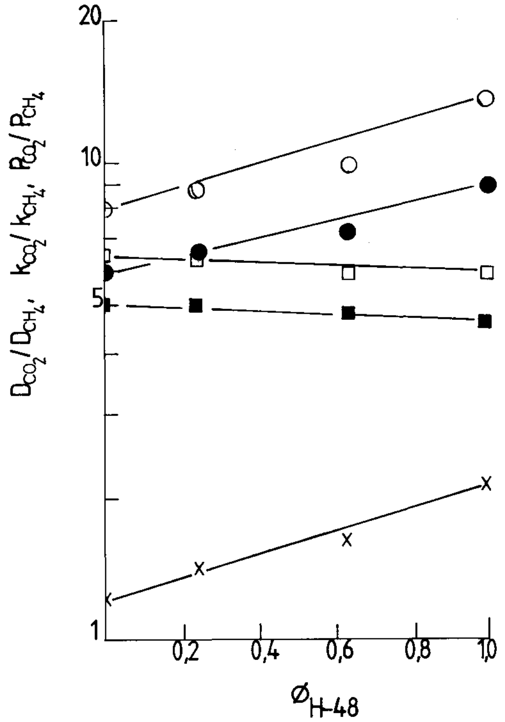

Figure 10 Selectivity ratios as a function of blend composition. P_{CO_2}/P_{CH_4} at ○, 30°C and ●, 50°C. D_{CO_2}/D_{CH_4} at ×, 30 and 50°C. k_{CO_2}/k_{CH_4} at □, 30°C and ■, 50°C

Separation factors for carbon dioxide and methane

Methane permeabilities for the pure components and two of the blends were also determined. Diffusion coefficients were obtained from time-lags. Solubilities

Table 2 Activation energies for diffusion (E_D) and permeation (E_P)

	E_P (kJ/mol)		E_D (kJ/mol)		$\Delta H_D = E_P - E_D$	
Wt% EVA-45	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
100	31	43	41	41	−10	2
70	35	48	45	50	−10	−1
30	44	57	53	56	−9	2
0	56	73	66	70	−10	3

were low and were obtained indirectly from $P = DS$. Semi-log plots of the solubility selectivity α_s ($= k_{CO_2}/k_{CH_4}$), mobility selectivity α_m ($= D_{CO_2}/D_{CH_4}$) and overall selectivity α ($= P_{CO_2}/P_{CH_4}$) are shown in *Figure 10*. Activation energies and heats of solution are given in *Table 2*. It can be seen that the composition dependence of α mirrors that of α_m because α_s has a very weak composition dependence. However, the temperature dependence of α is primarily due to the temperature dependence of α_s, which in turn reflects differences between ΔH_D for CO_2 and CH_4 at each composition. α_D is relatively unaffected by temperature because at any blend composition, the activation energies for diffusion, E_D (*Table 2*) are essentially equal for CO_2 and CH_4. It can be seen in this case that α_s provides the major contribution to α. Thus the separation performance is due chiefly to the difference in CO_2 and CH_4 solubilities. The small value of α_m indicates a weak ability to discriminate on the basis of molecular size and shape. This behaviour is typical of rubbery polymers. The relatively low value of α highlights the reason that few rubbery polymers have found applications as gas separation membranes.

It should also be noted that the separation performance of the blends is equal or less than that expected from a volume additivity relationship. Where blends exhibit strong interactive forces, separation properties which are superior to those exhibited by either of the pure components are feasible.

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