

## Gas Permeation of Polymer Blends. III. Poly(vinyl Chloride) (PVC)/Chlorinated Polyethylene (CPE)

YOUNG J. SHUR and BENGT RÅNBY, *Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden*

### Synopsis

The permeability  $P$ , diffusivity  $D$ , and activation energy for diffusion,  $E_D$ , of He, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were determined for blends of PVC/chlorinated polyethylene (CPE), where the chlorine content of the CPE components varied: 36 wt-% for CPE-1, 42 wt-% for CPE-2, and 48 wt-% for CPE-3. The difference in thermal expansion coefficients  $\Delta\alpha$  above and below the glass transition temperature  $T_g$  of the polymers and the fractional free volume  $V_g$  of the polymers at their  $T_g$  were determined. Density and crystallinity measurements for the blends were also carried out as in the earlier work (Shur and Rånby, *J. Appl. Polym. Sci.*, **19**, 1337(1975)). Dynamic mechanical measurements of the blends were made using a torsion pendulum at about 1 Hz.  $P$  and  $D$  decreased, but  $E_D$  increased with increasing Cl content of CPE in the blends.  $P$  and  $D$  for the blends showed no additivity. The permeability indicated phase inversion for blend compositions at about 10% of CPE-1 and CPE-2 by weight. The experimental and the calculated densities were largely the same for PVC/CPE-1 blends; but for PVC/CPE-2 and PVC/CPE-3 blends, the experimental values were higher than the calculated ones. The  $\Delta\alpha$  and  $V_g$  values for PVC and the three CPE samples decreased with increasing Cl content in the polymers. Dynamic mechanical measurements indicate that PVC/CPE-1 and PVC/CPE-2 blends form largely incompatible blends, while PVC/CPE-3 blends are compatible to some extent. There is some weak interaction between PVC and CPE-3 giving a low level of compatibility. The solubility of gases obtained from time-lag measurements of diffusion for 50/50 blends decreased for He, O<sub>2</sub>, and N<sub>2</sub>, but increased for CO<sub>2</sub> with increasing Cl content in CPE. The solubility of He, O<sub>2</sub>, and N<sub>2</sub> shows a positive correlation with the Lennard-Jones force constant  $\epsilon/\kappa$ . However, a deviation from the linear relation between  $\epsilon/\kappa$  and  $\ln S$  was observed for CO<sub>2</sub> and the deviation became larger with increasing Cl content in CPE. The abnormally high solubility of CO<sub>2</sub> is probably due to the high polarizability of this gas. The heat of solution  $\Delta\bar{H}_s$  indicates that for He the sorption process may be a molecular slip process (endothermic), but for other gases the sorption may proceed by a dissolution process (exothermic). There is a large difference between the calculated solubility for the blends assuming incompatibility and the experimental values from time-lag measurements. This may partly be due to the uncertainty of sorption values obtained from the time-lag method and/or partly to changes of sorption modes by interaction between PVC and CPE in the blends. The resulting transport behavior of the blends is discussed on the basis of the free volume concept and of phase-phase interaction in the blends.

### INTRODUCTION

In our previous studies,<sup>1,2</sup> the kinetic factor of gas transport, i.e., the rate of diffusion  $D$  through polymer blends, was discussed mainly with relation to changes in segmental mobility of the polymer chains due to interaction between the molecules of the blend components. Improved additivity of gas

permeability  $P$  was attributed to increased compatibility of the two polymers in the blends.

An alternative treatment of diffusion and sorption of gases in polymers is based on the concept of free volume.<sup>3-8</sup> For a system of hard spheres diffusing through a liquid medium, Cohen and Turnbull<sup>3</sup> have assumed in their theory that the diffusion process is due to a redistribution of free volume and not the result of an activated process. The redistribution of free volume is mainly related to random density fluctuations of the medium through which the permeant molecules are diffusing. The following relationship has been proposed:<sup>3</sup>

$$D = D_0 \exp(-rV/V_f) \quad (1)$$

where  $r$  is a constant,  $V_f$  is the fractional free volume of the polymer, and  $V$  is the critical volume of the voids just large enough for a permeant molecules to pass through the medium. The  $V$  values can be approximated as  $(\pi/4) d_G^2 l_D$  according to Meares,<sup>9</sup> where  $d_G$  is the collision diameter of the permeant molecules and  $l_D$  is the length of diffusion path. Bueche<sup>4</sup> has derived the same relationship for diffusivity based on free volume using the concept of segment jumping. However, the unactivated diffusion process according to Cohen and Turnbull is not directly applicable to an actual diffusion process where permeant molecules diffuse through solid polymer membranes. At least, this is true when the gas transport process is carried below the glass transition temperature of the polymer.

Activated diffusion is a highly specific process, dependent both on the mobility of polymer segments and the solubility of permeant molecules in bulk polymer. In a more explicit way, Roger et al.<sup>5,6</sup> have proposed the following relationship:

$$D \sim \exp(-V_1/BV_f) \exp(-E_D/RT) \simeq D_0 \exp(-E_D/RT) \quad (2)$$

where  $V_1$  is the molar volume of the permeant,  $B$  is a constant depending on the system, and  $E_D$  is the activation energy for diffusion. For many polymers, relation (3) is valid according to the WLF equation,<sup>10</sup>

$$V_f = V_g + \Delta\alpha(T - T_g) \quad (3)$$

where  $V_g$  is the fractional free volume of the polymer at the glass transition temperature  $T_g$  and  $\Delta\alpha$  is the difference between the thermal expansion coefficients of the polymer phase above and below  $T_g$ , i.e.,

$$\Delta\alpha = \alpha_{T>T_g} - \alpha_{T<T_g} \quad (4)$$

$V_g$  can be obtained in different ways, e.g., using the WLF equation,<sup>10</sup> the Simha-Boyer (S-B) equation,<sup>11</sup> and the Gibbs-DiMarzio (G-DiM) equation.<sup>12</sup>

The thermodynamic factor of gas transport, i.e., the solubility  $S$ , has also been studied on the basis of the free volume theory.<sup>13-16</sup> Draibach et al.<sup>13</sup> have found that the solubility of  $H_2$  in poly(ethylene terephthalate) passes through a minimum at the  $T_g$  of the polymer. Meares<sup>14-16</sup> has observed that the solubilities of  $H_2$ , He, Ne, and  $O_2$  in poly(vinyl acetate) have minima at temperatures about 9°C below  $T_g$ . He observed that the changes in solubility above and below  $T_g$  depend on the nature of the permeants and the  $\Delta\alpha$  of the polymer. Stannett et al.<sup>17</sup> have recently reported similar data for poly(methyl acrylate).

These results seem to indicate that an increase in free volume provides extra sites for gas absorption, which leads to an increase in the solubility of gases. This assumption agrees well with Kwei-Arnheim's sorption model,<sup>8</sup> where the sorption of simple molecules, like those of inert gases, proceeds by locating the dissolved gas molecules in the free volume of the polymer phase without disruption of polymer-polymer contacts. According to Peterlin et al.,<sup>18</sup> the change in initial sorption at zero concentration,  $S_0$ , is directly related to the change in fractional free volume of polymer and is given as  $S_0 = AV_f$ , where  $A$  is a constant. This relationship is also in agreement with the Kwei-Arnheim's sorption equation

$$S = (273/eT)V_f \exp(-\Delta H_s/RT) = S_0 \exp(-\Delta H_s/RT) \quad (5)$$

where  $e$  is the base of natural logarithms ( $\sim 2.7183$ ) and  $\Delta H_s$  is the enthalpy of solution.

In the present work, measurements of gas transport through polymer blends of poly(vinyl chloride) (PVC) and chlorinated polyethylene (CPE) are presented and the data related to the compatibility of the blends. The diffusivity  $D$  and solubility  $S$  of the gases are discussed on the basis of the free volume concept.

## EXPERIMENTAL

### Materials

The properties of PVC and CPE samples used are listed in Table I. The PVC was a suspension-polymerized commercial grade, supplied by Kema-Nord AB, Sweden, and previously used.<sup>1,2</sup> The CPE samples were manufactured by chlorination of high-density polyethylene suspended as a slurry and supplied by Dow Chemical Co., U.S.A. The method of preparation of the various blend compositions is described in previous work.<sup>1</sup>

### Measurements

Permeation measurements (giving  $P$  values) for He, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were carried out for thin membranes (thickness about 0.03 mm) at two temperatures (25° and 50°C) using the isostatic gas permeation meter (GPM-200) described in our previous work.<sup>1</sup> The diffusion coefficients  $D$  were determined

TABLE I  
Polymer Characteristics

	CPE-1	CPE-2	CPE-3	PVC
Cl content, wt %	36	42	48	57
Density at 25°C, g/ml	1.16	1.22	1.25	1.39
Crystallinity, %	<10	<10	<10	<10
$T_g$ from max. $\tan \delta$ , °C <sup>a</sup>	-2	16	25	83
Designation	Dow QX 2243.16	Dow XP 2243.31	Dow CPE 4814	Pevikon S655

<sup>a</sup> By torsion pendulum with 1 Hz.

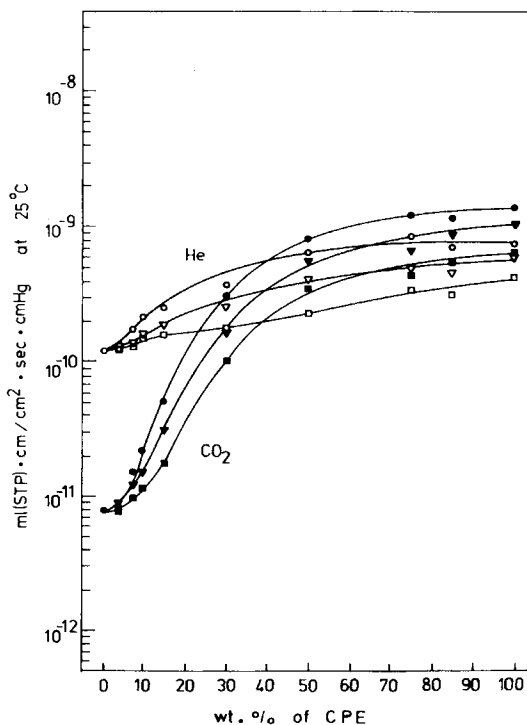


Fig. 1. Permeability coefficients of He and  $\text{CO}_2$  vs. polymer blend composition.  $P$  of He: (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $P$  of  $\text{CO}_2$ : (●) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

from the same experiments by the time-lag method. The solubility coefficients  $S$  were calculated from the formal relation  $P = S \times D$ . No separate solubility measurements were made.

In addition to permeation measurements, measurements of density with gradient column and crystallinity with x-ray diffraction were also made like in previous work. The volumetric thermal expansion coefficients were obtained by dilatometry. Measurements of loss tangent,  $\tan \delta$ , for the blends were made with a torsion pendulum described by Petersen and Rånby<sup>19</sup> with free oscillations at about 1 Hz and at temperatures from  $-160^\circ$  to  $+120^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The results of the gas transport measurements for He,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  through the membranes are presented in Figures 1–4. The data show that  $P$  and  $D$  decrease, but the activation energy for diffusion,  $E_D$ , increases for the blends with increasing chlorine content in the CPE components (Figs. 8 and 9). A linear relation of  $P$  or  $D$  versus blend composition has previously been defined as the additivity of these parameters.<sup>1,2</sup> In this case, no noticeable indications of the additivities of  $P$  and  $D$  for the PVC/CPE blends have been found. There are some indications of phase inversion of the PVC/CPE-1 and PVC/CPE-2 blends at about 10 wt-% of CPE in the blends. The  $P$  values of

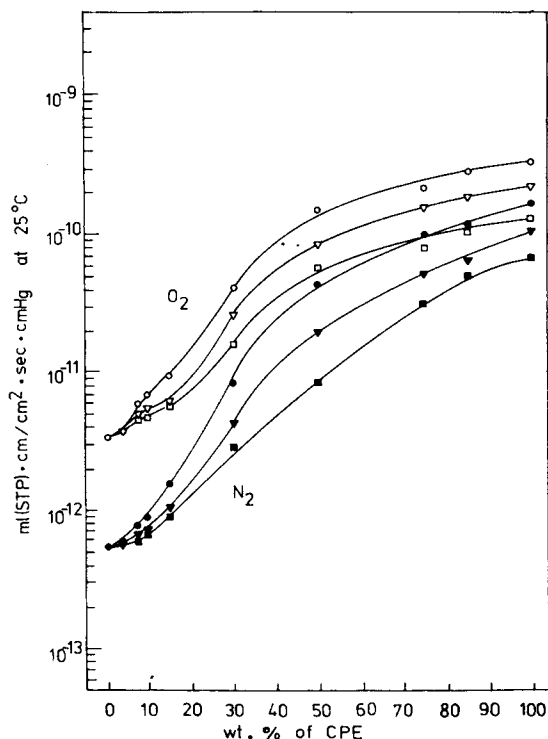


Fig. 2. Permeability coefficients of  $O_2$  and  $N_2$  vs. polymer blend composition.  $P$  of  $O_2$ : (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $P$  of  $N_2$ : (●) in PVC/CPE-1 blends; (▼) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

$O_2$ ,  $N_2$ , and  $CO_2$  were sharply increased in this composition range.

The mechanical and other physical properties of CPE depend largely on the structural heterogeneity and the Cl content of the polymer.<sup>20</sup> There are no repetitive units along the CPE polymer chains. The substitution of chlorine on the polyethylene chains is randomly distributed. CPE can thus be considered as a mixture of  $-CH_2-CH_2-$ ,  $-CH_2-CHCl-$ ,  $-CH_2-CCl_2-$ , and  $-CHCl-CH_2-CHCl-$  sequences. With increasing Cl content, crystallinity, and gas permeability decrease, but density, glass transition temperature, and melt viscosity increase. Crystallinity is largely due to the  $-CH_2-CH_2-$  sequences along the polymer chains.

The compatibility of CPE with other polar polymers is mainly an effect of Cl content. Paul et al.<sup>21</sup> have reported that the tensile impact strength of PVC/polyethylene binary blends was significantly improved than PVC/polystyrene blends by addition of CPE. The glass transition temperatures of PVC/CPE blends were also studied by Locke et al.<sup>22</sup> and by Zelinger<sup>23</sup> using dynamic mechanical measurements. They have observed that the  $T_g$  values of the PVC and CPE phases of PVC blends corresponding to PVC/CPE-1 and PVC/CPE-2 were not changed. For PVC blends corresponding to PVC/CPE-3, shifts in the  $T_g$  values were found to higher temperature for the CPE phase and to lower temperature for the PVC phase. The same results were observed in our measurements which were carried on the PVC/CPE

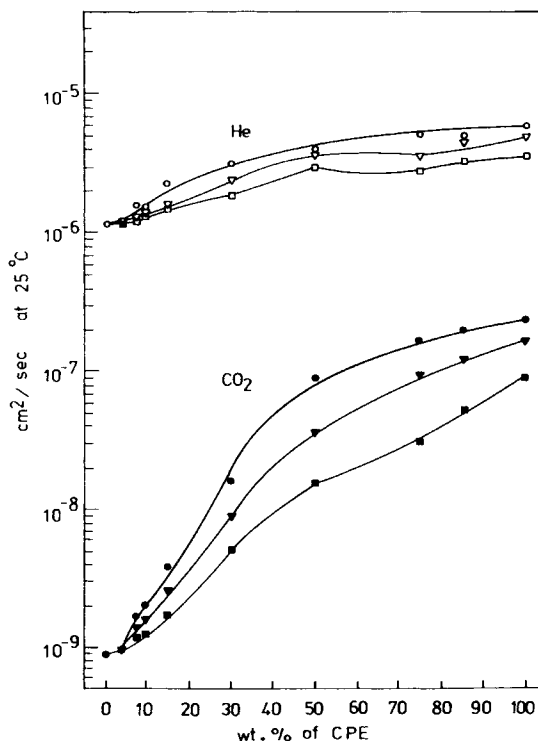


Fig. 3. Diffusion coefficients of He and  $\text{CO}_2$  vs. polymer blend composition:  $D$  of He: (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $D$  of  $\text{CO}_2$ : (●) in PVC/CPE-1 blends; (▼) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

blends having the compositions 75/25 and 50/50 and also for pure PVC and pure CPE (see Table II and Figs. 5–7). These results indicate that the interaction of PVC with CPE increases with increasing Cl content in CPE, e.g., with improved compatibility between the two polymers. Lock et al.<sup>21,22</sup> have interpreted the mechanical behavior of the blends as not due directly to the increased compatibility of the polymers in the blends but rather to better adhesion between the PVC and CPE phases. However, it is quite obvious that the interaction of PVC with CPE is increased with increasing Cl content in CPE, i.e., with lower crystallinity and increased polarity of the CPE. The low degrees of additivity of  $P$  and  $D$  for PVC/CPE blends compared with those of PVC/EVA-65<sup>1</sup> and PVC/NBR-3<sup>2</sup> are considered to be due to the low degree of interaction between PVC and CPE.

For CPE polymers, as shown in Table III, the  $\Delta\alpha$  and  $V_g$  values decrease while  $T_g$  increases with increasing Cl content. An increase in free volume of a polymer is expected to give increased segmental mobility. The increased segmental mobility will then cause a decrease in the energy required to overcome the interaction between adjacent polymer chains for the gas diffusion process. If PVC/CPE blends were incompatible like in Higuchi's model,<sup>24</sup> i.e., no interaction between the two phases, the overall gas transport will mainly be governed by the nature of each polymer phase in the blend. Hence,  $P$  and  $D$  would be expected to increase with increasing free volume of

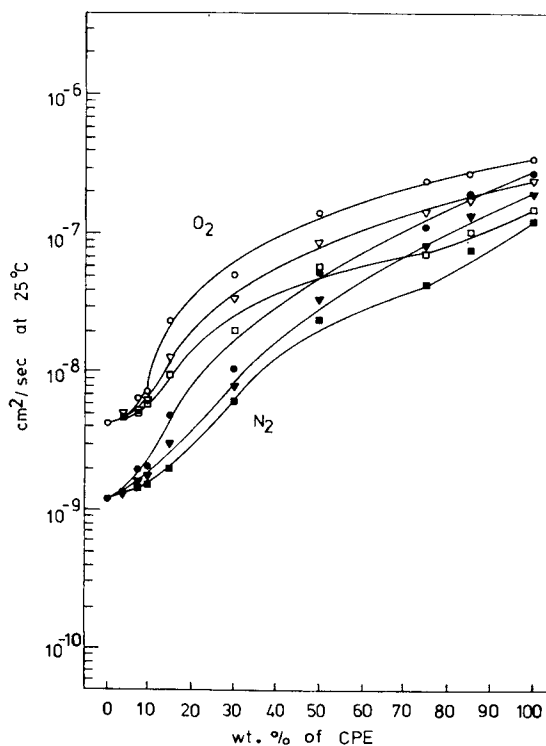


Fig. 4. Diffusion coefficients of  $O_2$  and  $N_2$  vs. polymer blend composition:  $D$  of  $O_2$ : (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $D$  of  $N_2$ : (●) in PVC/CPE-1 blends; (▼) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

CPE and increasing CPE content in the blends. However, if there is interaction between the two phases, the transport properties will be influenced by the changed molecular properties at the interphase. For PVC/CPE blends, it is very difficult to separate the effect on  $P$  and  $D$  of the change in the free volume of CPE and of the varied interaction between PVC and CPE. There are probably contributions from both factors.

The interaction between PVC and CPE is, in principle, better explained in terms of thermal expansion coefficients and activation energies of diffusion than in terms of  $P$  and  $D$  values. The thermal expansion coefficients for

TABLE II  
 $T_g$  ( $^{\circ}C$ ) of PVC/CPE Blends<sup>a</sup>

	PVC/CPE = 75/25		PVC/CPE = 50/50	
	CPE phase	PVC phase	CPE phase	PVC phase
PVC/CPE-1	-2	83	-2	83
PVC/CPE-2	15	82	16	80
PVC/CPE-3	31	78	38	74

<sup>a</sup>  $T_g$  for pure PVC,  $83^{\circ}C$ ; for pure CPE-1,  $-2^{\circ}C$ ; for pure CPE-2,  $16^{\circ}C$ ; and for pure CPE-3,  $25^{\circ}C$ .

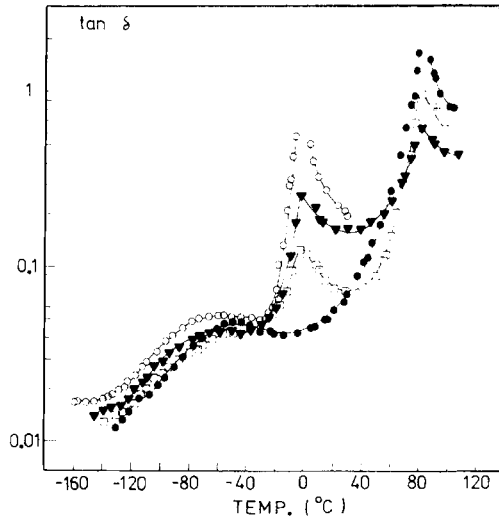


Fig. 5.  $\tan \delta$  vs. temperature from dynamic mechanical measurements: (●) PVC; (○) CPE-1; (□) 75/25(PVC/CPE-1); (▼) 50/50.

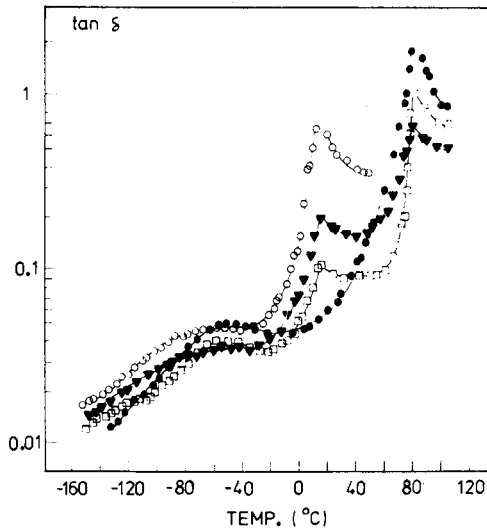


Fig. 6.  $\tan \delta$  vs. temperature from dynamic mechanical measurements: (●) PVC; (○) CPE-2; (□) 75/25(PVC/CPE-2); (▼) 50/50.

50/50 blends of PVC and CPE below the  $T_g$  of the PVC phase were  $1.67 \times 10^{-4}/^\circ\text{K}$  (PVC/CPE-1),  $1.56 \times 10^{-4}$  (PVC/CPE-2), and  $1.32 \times 10^{-4}$  (PVC/CPE-3).

As shown in Figures 8 and 9, the activation energy of diffusion of the PVC/CPE blends increases with increasing Cl content in the CPE component. This indicates that the mutual interaction between PVC and CPE increases with increasing Cl content in CPE. It is reasonable to expect that strong intermolecular attraction between the two polymers in a blend would decrease the thermal expansion of the mixed polymer phase. This could be interpreted as a decrease in the fractional free volume of the blend. The de-



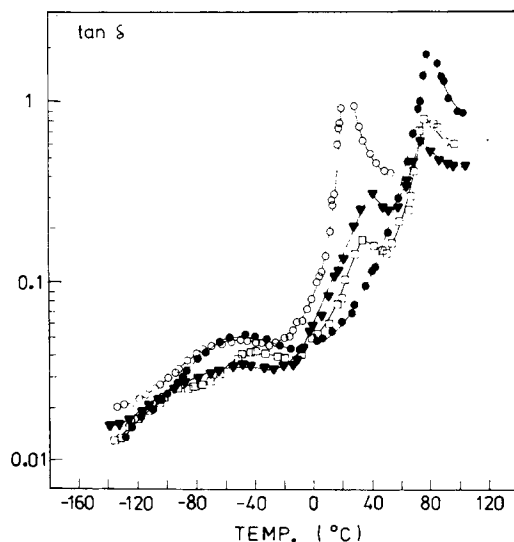


Fig. 7.  $\tan \delta$  vs. temperature from dynamic mechanical measurements: (●) PVC; (○) CPE-3; (□) 75/25 (PVC/CPE-3); (▼) 50/50.

crease of  $\Delta\alpha$  and the increase of  $E_D$  for the blend with increasing Cl content in the CPE component also suggest that the PVC blended with CPE containing high Cl content may relax more slowly under comparable conditions than the blends with CPE of low Cl content. This interpretation is probable since the hindrance to segmental mobility of PVC is expected to be enhanced by increased interaction between PVC and CPE. This conclusion is well in line with the apparent decrease in  $P$  and  $D$  and the increase in  $E_D$  with increasing Cl content. These results are of a general nature and Roger's diffusion equation, eq. (2), seems to be applicable to our system.

Another independent indication of interaction between PVC and CPE is given by the measurements of density of the blends. The measured and the calculated densities (assuming volume additivity and incompatibility of PVC and CPE in the blends) are not very different for PVC/CPE-1. For the PVC/CPE-2 and PVC/CPE-3 blends, however, the measured densities are higher than the calculated values (see Fig. 10). The density differences become larger with increasing Cl contents in the CPE of the blends, and for the 50/50 blends they are 0.005 g/ml (PVC/CPE-1), 0.009 (PVC/CPE-2), and

TABLE III  
Glass Transition Temperature ( $T_g$ ), Change in Volume Expansion Coefficient at  $T_g$  ( $\Delta\alpha$ ), and Fractional Free Volume ( $V_g$ ) of Polymers

Polymer	$T_g$ , <sup>a</sup> °C	$\Delta\alpha \times 10^{-4}$ , °K <sup>-1</sup>	$V_g$		
			S-B	WLF	G-DiM
CPE-1	5	4.33	0.1212	0.0276	0.0374
CPE-2	24	4.01	0.1185	0.0268	0.0366
CPE-3	31	3.85	0.1170	0.0262	0.0361
PVC	87	3.14	0.1125	0.0238	0.0346

<sup>a</sup> By dilatometry.

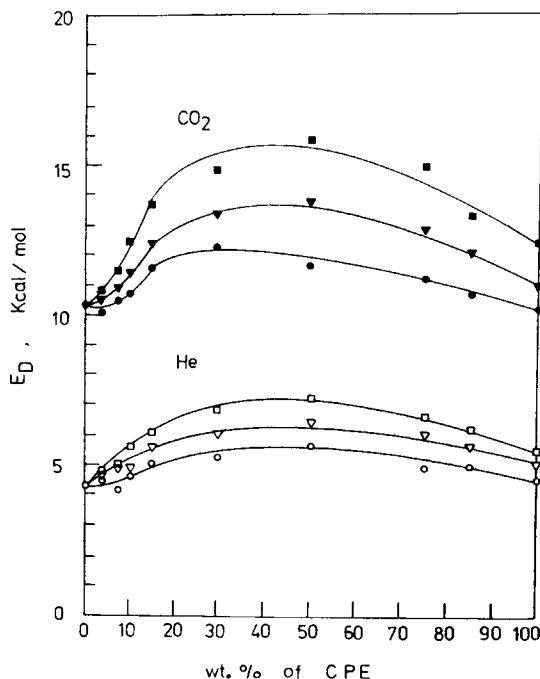


Fig. 8. Activation energy of diffusion for He and CO<sub>2</sub> vs. polymer blend composition.  $E_D$  of He: (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $E_D$  of CO<sub>2</sub>: (●) in PVC/CPE-1 blends; (▼) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

0.015 (PVC/CPE-3) at 25°C. X-Ray diffraction measurements showed that all samples are largely amorphous with crystallinities less than 10%. This is interpreted as indication that the crystallinity is not responsible for the change of densities. The results of the density measurements suggest that the polymer chains become closer packed in the blends with increasing Cl content in the CPE component of the blends.

In previous work,<sup>2</sup> we have observed that the permeant solubility values of the blends calculated from the  $P/D$  ratios were irregular when the blend compositions were varied. Michael et al.<sup>25-28</sup> have noticed that the solubility determined from the  $P/D$  ratio is less precise for polar permeants, e.g., CO<sub>2</sub> and organic vapors, than those determined by equilibrium sorption measurements. According to them, in a system where the dual sorption process<sup>29</sup> occurs, the time-lag method measures an *apparent diffusion coefficient* rather than the *actual diffusion coefficient*. The difference is due to deviations of the permeant transport from Fick's diffusion model. For Fick's gas diffusion, the determinations of  $D$  and  $S$  values using time-lag method are based on the assumption of an isotropic transport medium, independence of  $D$  on permeant concentration (or pressure), and a linear sorption isotherm, i.e., Henry's law is valid. In a polymer blend, the transport medium is in general considered to be nonisotropic compared with a single-component system. Furthermore, if the rates of equilibrium partition of a permeant molecule between the phases in the blend differ in the initial stage of gas permeation, this will alter the shape of the diffusion curve in the nonsteady state of diffusion, leading to errors in extrapolation to time-lag intercept. These deviations

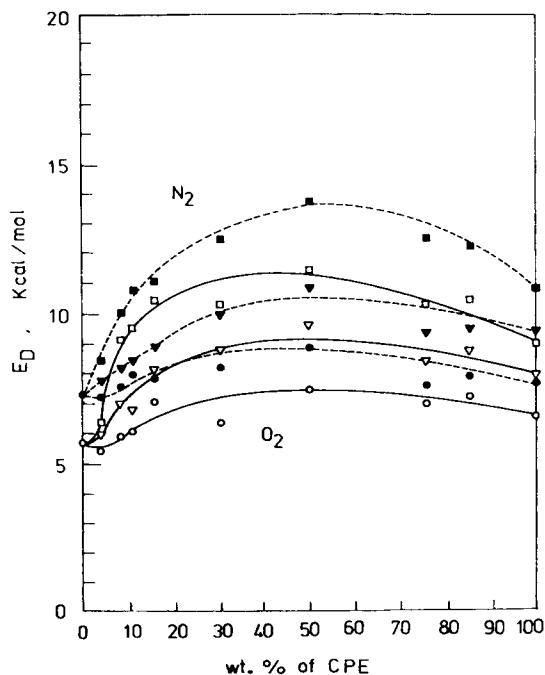


Fig. 9. Activation energy of diffusion for  $O_2$  and  $N_2$  vs. polymer blend composition.  $E_D$  of  $O_2$ : (○) in PVC/CPE-1 blends; (▽) in PVC/CPE-2 blends; (□) in PVC/CPE-3 blends.  $E_D$  of  $N_2$ : (●) in PVC/CPE-1 blends; (▼) in PVC/CPE-2 blends; (■) in PVC/CPE-3 blends.

from Fickian diffusion will introduce serious errors in the interpretation of sorption behavior of systems where the dual sorption process occurs. The initial transition period in the time-lag experiment will delay the reaching of a steady state because permeant molecules are immobilized. The resulting apparent diffusivities will be lower than the ideal values from Fick's law. On the other hand, this leads to larger apparent solubilities than the true values. Another factor of uncertainty may be gradual changes in the hole adsorption mode of the blends as suggested by Stannett et al.<sup>30</sup>

As shown in Table IV, the solubilities of inert gases (He,  $N_2$ , and  $O_2$ ) in the 50/50 blends decreased with increasing Cl content in CPE of the blends, whereas those of  $CO_2$  increased.

If blend components are incompatible and the adsorption modes of the components in the blend are not changed by blending, the overall solubilities of gases in the blend,  $S_m$ , are expressed in terms of solubilities of PVC,  $S_1$ , and CPE,  $S_2$ , and volume fraction of PVC,  $V_1$ , in the blends:<sup>31,32</sup>

$$S_m = S_1 V_1 + S_2 (1 - V_1) \quad (6)$$

However, the  $S_m$  values of the 50/50 blends as determined from eq. (6) and the experimental values do not agree. The deviations are systematic and probably not due to uncertainties in the determination of sorption values. More likely, they are due to changes of the sorption process due to interaction between the two polymers in the blends and/or to changes in adsorption mode due to changes in hole statistics by blending the two polymers. In particular, the differences between the values calculated according to eq. (6) and

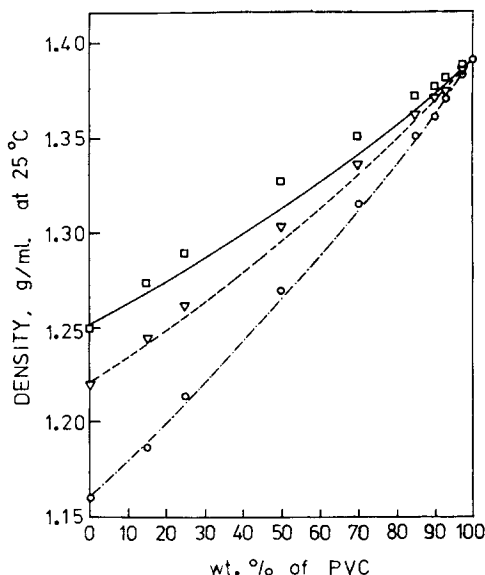


Fig. 10. Experimental and calculated densities vs. polymer blend composition. Experimental values: (O) for PVC/CPE-1 blends; ( $\nabla$ ) for PVC/CPE-2 blends; ( $\square$ ) for PVC/CPE-3 blends. Calculated values: (---) for PVC/CPE-1 blends; (---) for PVC/CPE-2 blends; (---) for PVC/CPE-3 blends.

the experimental values are larger for  $\text{CO}_2$  than for He,  $\text{O}_2$ , and  $\text{N}_2$ . This indicates that the sorption process of large and/or polar permeants like  $\text{CO}_2$  is more complex than for small and/or nonpolar permeant molecules and that several sorption processes may be operative.

Table IV shows that the solubilities of He,  $\text{O}_2$ , and  $\text{N}_2$  in the blends decrease, but that the solubility of  $\text{CO}_2$  increases with increasing Cl content of the CPE in the blends. This suggests that the sorption can be described as a Kwei-Arnheim's sorption process. The sites to accommodate the penetrant molecules (He,  $\text{O}_2$ , and  $\text{N}_2$ ) decrease with increasing Cl content of CPE in the blends. Increasing Cl content will provide decreasing fractional free volume in the CPE component of the blends, partly due to increased mutual interaction between PVC and CPE. For  $\text{CO}_2$ , it appears from the solubility that the

TABLE IV  
Solubility Parameters of He,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  for 50/50 Blends of PVC and CPE<sup>a</sup>

Gas	$\epsilon/k$ , $^{\circ}\text{K}$	$S_{\text{exp.}}^{\text{b}}$			$S_{\text{calc.}}^{\text{c}}$			$\Delta H_s^{\text{d}}$		
		A	B	C	A	B	C	A	B	C
He	10	1.67	1.08	0.92	1.22	1.18	1.16	1.02	1.24	1.63
$\text{N}_2$	95	7.96	5.59	3.20	5.41	5.05	4.83	-1.41	-1.20	-0.86
$\text{O}_2$	118	10.80	9.77	7.39	8.80	8.58	8.27	-1.67	-2.02	-1.84
$\text{CO}_2$	229	93.48	157.80	218.82	74.76	77.92	82.19	-2.63	-4.08	-4.87

<sup>a</sup> Blend A = PVC/CPE-1; blend B = PVC/CPE-2; blend C = PVC/CPE-3.

<sup>b</sup>  $S \times 10^{-4}$ , cc (S.T.P.)/cc (polymer) cm Hg, obtained from  $P/D$  ratio.

<sup>c</sup>  $S \times 10^{-4}$ , cc (S.T.P.)/cc (polymer) cm Hg, obtained from eq. (6).

<sup>d</sup> kcal/mole.

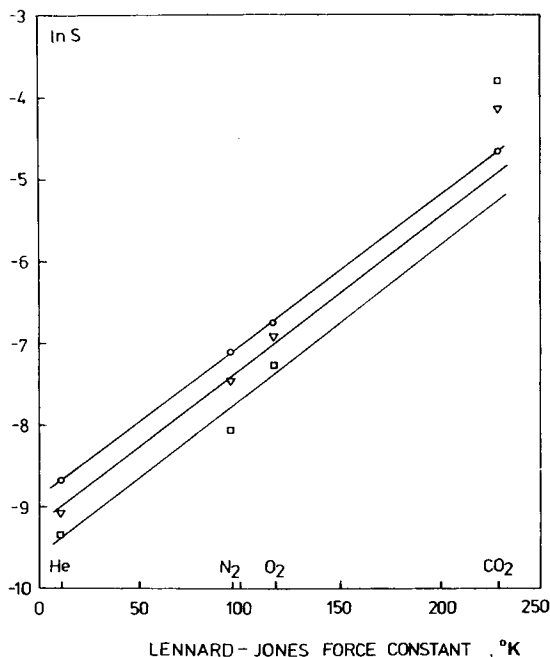


Fig. 11. Solubility of gases ( $\ln S$ ) vs. gas force constant ( $\epsilon/\kappa$ ) for the 50/50 blends: (O) for PVC/CPE-1 blend; ( $\nabla$ ) for PVC/CPE-2 blend; ( $\square$ ) for PVC/CPE-3 blend.

polar interaction of CO<sub>2</sub> with the polymer molecules increases with increasing Cl content of CPE. This may mean that the effect of decreasing free volume on the sorption process is exceeded by the effect of increased polar interaction with increasing Cl content in CPE of the blends.

The enthalpies of solution ( $\Delta H_s$ ) for He are endothermic for all blends (see Table IV), while all other gases exhibited exothermic solution processes. This suggests that the sorption process for He may involve formation of holes in the polymer to accommodate the permeant molecules. For all other gases with larger molecules than He, the sorption seems to proceed by a dissolution process. The exothermic heat of sorption for these gases arises from the interaction of gas molecules with the polymer molecules at the sorption sites. These interactions between permeant and polymer molecules are probably of the van der Waals type. A general trend of increasing heat of solution with increasing gas force constant ( $\epsilon/\kappa$ ) supports this view.<sup>33-37</sup>

The relationship between  $\epsilon/\kappa$  and  $\ln S$  is plotted in Figure 11. All gases except CO<sub>2</sub> fit well to a linear relationship between these two functions. A similar deviation of CO<sub>2</sub> has previously been observed for poly(ethylene terephthalate).<sup>25</sup> The deviation from linearity of  $\epsilon/\kappa$  versus  $\ln S$  becomes larger with increasing Cl content in the CPE components of the blends. This is probably due to increasing the specific polar interaction of CO<sub>2</sub> with the polymer molecules of the blends with increasing Cl content. The data in Table IV also show a trend of increasing exothermicity with increasing  $\epsilon/\kappa$ . This is good agreement with the linear and positive correlation between  $\Delta H_s$  and  $\epsilon/\kappa$ , as found for several polymer-permeant systems.<sup>25,26,35-38</sup>

In conclusion, the sorption of He, O<sub>2</sub>, and N<sub>2</sub> in PVC/CPE blends seems

primarily to be related to the free volume, while the sorption of CO<sub>2</sub> is more significantly affected by the interaction between permeant and polymer molecules. As also noticed in previous work,<sup>2</sup> the changes of permeant solubility in the blends (obtained from the  $P/D$  ratio) are irregular with changing the blend compositions. This may be due (a) to the less reliable sorption values obtained by the time-lag method when applied to heterogeneous polymer blends, (b) to the variation of hole adsorption process by changing the hole statistics in the blends, and/or (c) to the interaction between the two polymers forming the blend. A solution of this problem requires, first of all, direct measurements of solubility and a better understanding of the blend morphology.

Thanks are due to the Swedish Polymer Research Foundation for the financial support of this work and to KemaNord AB, Sweden, for preparing the samples and providing valuable information about them.

### References

1. Y. J. Shur and B. Rånby, *J. Appl. Polym. Sci.*, **19**, 1337 (1975).
2. Y. J. Shur and B. Rånby, *J. Appl. Polym. Sci.*, **19**, 2143 (1975).
3. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
4. F. Bueche, *Physical Properties of Polymers*, Interscience, London, 1962.
5. C. E. Rogers, V. Stannett, and M. Szwarc, *J. Polym. Sci.*, **45**, 62 (1960).
6. S. Prager and F. A. Long, *J. Amer. Chem. Soc.*, **73**, 4072 (1951).
7. C. A. Kumins and T. K. Kwei, *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic Press, London, 1968, Chap. 4.
8. T. K. Kwei and W. Arnheim, *J. Polym. Sci.*, **A2**, 1873 (1964).
9. P. Meares, *Polymers: Structure and Bulk Properties*, Van Norstrand, London, 1965.
10. M. L. Williams, R. F. Landel, and M. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
11. R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
12. A. Eisenberg and S. Saito, *J. Chem. Phys.*, **45**, 1673 (1966).
13. H.-C. Draibach, D. Jeschke, and H. A. Stuart, *Z. Naturforsch.*, **17a**, 447 (1962).
14. P. Meares, *J. Amer. Chem. Soc.*, **76**, 3415 (1954).
15. P. Meares, *Trans. Faraday Soc.*, **53**, 101 (1957).
16. P. Meares, *Trans. Faraday Soc.*, **54**, 40 (1958).
17. W. H. Burgess, H. B. Hopfenberg, and V. Stannett, *J. Macromol. Sci.*, **B5**, 23 (1971).
18. A. Peterlin, *ACS Div. Coatings Plastics Prepr.*, **34** (1), 429 (1974).
19. J. Petersen and B. Rånby, *Makromol. Chem.*, **133**, 251 (1970).
20. C. N. Burnell and R. H. Parry, *Appl. Polym. Symp.*, **11**, 95 (1969).
21. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **13**, 202 (1973).
22. C. E. Locke and D. R. Paul, *Polym. Eng. Sci.*, **13**, 308 (1973).
23. J. Zelinger, *J. Polym. Sci. C*, **16**, 4259 (1969).
24. W. I. Higuchi and T. Higuchi, *J. Amer. Pharm. Assoc. Sci.*, **49**, 598 (1960).
25. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
26. W. R. Vieth, P. M. Tam, and A. S. Michaels, *J. Colloid Interface. Sci.*, **22**, 360 (1966).
27. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 13 (1963).
28. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
29. D. R. Paul and D. R. Kemp, *J. Polym. Sci. C*, **41**, 79 (1973).
30. R. L. Stallings, H. B. Hopfenberg, and V. Stannett, *J. Polym. Sci. Symp.*, **No. 41**, 23 (1973).
31. S. Sternberg and C. E. Rogers, *J. Appl. Polym. Sci.*, **12**, 1017 (1968).
32. C. M. Peterson, *J. Appl. Polym. Sci.*, **12**, 2649 (1968).
33. P. Y. Hsieh, *J. Appl. Polym. Sci.*, **7**, 1743 (1963).
34. W. R. Vieth, H. H. Alcalay, and A. J. Frabetti, *J. Appl. Polym. Sci.*, **8**, 2125 (1964).

35. J. E. Jolly and J. A. Hildebrand, *J. Amer. Chem. Soc.*, **80**, 1050 (1958).
36. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).
37. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 313 (1961).
38. C. E. Rogers, *Engineering Design For Plastics*, Chap. 9, E. Baer, Ed., Reinhold, New York, 1964, p. 609.

Received November 3, 1975

Revised December 30, 1975