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ORIGINAL CONTRIBUTION

INTERACTIONS OF CHLOROSULFONATED POLYETHYLENE GEOMEMBRANES WITH ALIPHATIC ESTERS: SORPTION AND DIFFUSION PHENOMENA

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ABSTRACT. The resistance of chlorosulfonated polyethylene geomembranes to nine aliphatic esters viz., methyl acetate, ethyl acetate, methyl acetoacetate, ethyl acetoacetate, *n*-butyl acetate, diethyl oxalate, *iso*-amyl acetate, diethyl malonate, and diethyl succinate was investigated in the temperature interval 25–60°C by measuring the liquid sorption using a gravimetric method. A Fickian diffusion equation was used to calculate the diffusion coefficients, and these data were dependent on the type of ester molecules and their interactions with the geomembrane, in addition to temperature and solvent concentration. The activation energy values for the diffusion process were in the range 18–41 kJ/mole and the heat of sorption varied from 0.61 to 18.50 kJ/mole. The sorption/swelling results were found to follow the first order kinetics. Solvent front velocities were calculated from the sorption data. The statistical error analysis has been presented in order to judge the reliability of the technique used. The experimental data and calculated parameters were used to discuss transport results in terms of membrane-solvent interactions. None of the esters showed any degradative effects on the geomembrane used.

INTRODUCTION

Contamination of ground water by spills of hazardous liquids, migration from landfills and leaking underground storage tanks are problems of great environmental concern. Hence, waste should be contained in low permeability liner system to prevent or reduce contamination of the environment below tolerable limits. The liner system must act as a barrier between the hazardous materials and the environment. The major technical demand on a liner system, that is, how to minimize pollutant escape/transport, has not been satisfactorily addressed. An evaluation of the effectiveness of a selected liner on the basis of time of future emission/transport is necessary. Mass transport equations that consider physical, chemical, and hydraulic phenomena can be used as mathematical tools to compute long-term transport.

Various types of geomembranes have been widely used in the hazardous waste management areas as protective barrier liners against toxic and aggressive waste chemicals (1–5). The proper selection of a barrier material requires accurate measurements and understanding of the permeation and diffusion coefficients, sorption kinetics, solvent penetration rates, polymer degradation and its morphology. Such an investigation requires both accurate and feasible test methods that may be performed routinely in laboratories.

The chlorosulfonated polyethylene geomembrane known as CSM, is a versatile engineering elastomer possessing good weather and ozone resistance. It is used as a material for inner layers of

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tubeless tires and blended with other elastomers for use in linings, belts, hoses, and seals. In these applications, the CSM geomembrane might come into contact with esters in addition to other hazardous liquids. In industrial sites, the CSM geomembrane was found to be useful liner for hazardous waste ponds (5–8). The esters used as flavoring agents or aromas in the perfume industries form a part of the waste chemicals. Therefore, an understanding of the molecular interactions of esters with the CSM geomembrane is important before we envisage the commercial application of CSM as a useful and effective fluid barrier. A gravimetric method has been used to assess the fluid uptake by the geomembrane as a function of time (9–18).

For membrane applications in hazardous waste containment facilities, both the chemical and physical effects of the geomembrane need to be considered (19). When the chemical degradative effects occur, they are likely to affect the geomembrane structure and ultimately lead to the destruction of the network. Physical effects refer to solvent migration into the membrane material, which contribute to diffusion, permeation, and swelling due to solvent sorption. Due to the nonavailability of database on molecular transport of aliphatic esters into CSM geomembranes and in view of the importance of CSM as useful liner material for hazardous chemical pond lining applications, in the present study, we have obtained the sorption and transport results for methyl acetate (MA), ethyl acetate (EA), methyl acetoacetate (MAA), ethyl acetoacetate (EAA), *n*-butyl acetate (BA), diethyl oxalate (DEO), *iso*-amyl acetate (AA), diethyl malonate (DEM), and diethyl succinate (DES) into CSM geomembranes. The sorption, S, diffusion coefficient, D, and permeability coefficient, P, over the temperature interval 25–60°C were evaluated. The Arrhenius parameters for different transport processes were estimated from a temperature dependence of these coefficients. The sorption results were analyzed using the first order kinetics. The experimental and calculated quantities were used to discuss the interactions of esters with CSM geomembranes.

EXPERIMENTAL

Materials and Reagents

Polymer sheets of CSM in dimensions of 0.2 cm × 15 cm × 15 cm were obtained from UTEX, Wiemer, TX (courtesy of Mr. Andrew Kutac). During sample fabrication, a 30 cm laboratory mill was used to mix and prepare the rubber compounds for molding. The geomembrane was press-cured at 165°C for 30 min. The elastomer compositions and typical engineering properties were given earlier (15). The polymer sheets were circularly cut (diameter = 1.96 cm) and dried for 24 h in a desiccator before use.

The reagent grade methyl acetate, ethyl acetate, methyl acetoacetate, ethyl acetoacetate, *n*-butyl acetate, diethyl oxalate, *iso*-amyl acetate, diethyl malonate, and diethyl succinate were double distilled before use. Their measured physical properties such as density and refractive index at 25°C agreed well with the literature values (20). Some important physical properties of the esters used as penetrants are given in Table 1.

Sorption Experiments

Sorption experiments were performed on circularly cut polymer samples by immersing them in 30–40 ml of the respective solvent contained in airtight, closed test bottles maintained at the desired temperature in an electric oven (Memmert, Germany). The experimental details are the same as described earlier (21). The output from a sorption experiment is the mol % uptake versus $t^{1/2}/\bar{h}$ profile, where $\bar{h}$ is the average thickness of the geomembrane samples, taken from the initial and swollen thicknesses. After complete sorption, the final dimensional changes (i.e., thickness and diameter) of the samples were also monitored. The thickness changes were measured by means of a micrometer screw gauge to an accuracy of ±0.001 cm while the changes in diameter were monitored to an accuracy of ±0.01 cm by using a vernier caliper. In all the sorption plots the symbols represent the average experimental values of the set of measurements, and the solid lines are the smoothed curves within experimental points.

RESULTS AND DISCUSSION

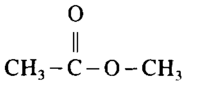
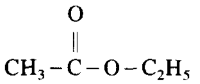
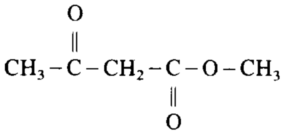
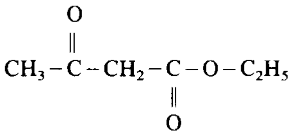
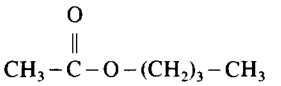
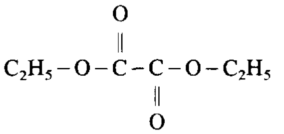
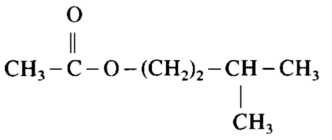
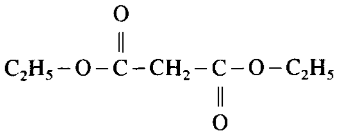
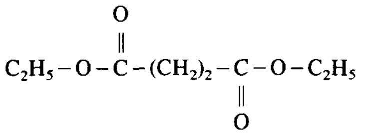
Sorption Mechanism

In semicrystalline polymers, sorption is thought to be confined to amorphous regions where the diffusion is controlled by the simple Fickian mode. However, the degree of crystallinity and polymer morphology also exert an effect on the overall transport behavior. The dynamic sorption results before the attainment of 55% equilibrium sorption were fitted to the empirical equation:

$$\frac{Q_t}{Q_\infty} = Kt^n, \qquad [1]$$

where Q_t and Q_∞ are the values of the mol % solvent uptake by the geomembrane at time t and at equilibrium time, respectively; K is a characteristic constant of the geomembrane-ester system. The value

TABLE 1
Esters Used as Probe Penetrants and Some of Their Representative Properties at 25°C

Ester	Structure	Molecular Volume (Å^3)	B.P. (°C)	η (mPa.s)	ρ (g/cm^3)
Methyl acetate (MA)	 $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$	133	56.9	0.364	0.928
Ethyl acetate (EA)	 $CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$	164	77.1	0.426	0.895
Methyl acetoacetate (MAA)	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3$	180	171.7	1.568	1.072
Ethyl acetoacetate (EAA)	 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5$	212	180.8	1.508	1.021
n-Butyl acetate (BA)	 $CH_3-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-CH_3$	220	126.1	0.691	0.876
Diethyl oxalate (DEO)	 $C_2H_5-O-\overset{O}{\overset{\|}{C}}-\underset{\underset{O}{\|}}{C}-O-C_2H_5$	226	185.4	1.849	1.073
iso-Amyl acetate (AA)	 $CH_3-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$	250	142.0	0.872^a	0.865
Diethyl malonate (DEM)	 $C_2H_5-O-\overset{O}{\overset{\|}{C}}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5$	254	199.3	1.940	1.048
Diethyl succinate (DES)	 $C_2H_5-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5$	278	216.5	2.466	1.035

[a] Compared at 19.91°C.

of the exponent *n* indicates the type of the transport mechanism. If *n* takes the value of 0.5, then the transport mechanism follows the Fickian mode, and this occurs when the rate of diffusion is much less than the rate of polymer relaxation. If $n = 1.0$, then a nonFickian transport is observed, in which case diffusion is very rapid compared to the polymer relaxation process. In several instances, the values of *n* fall between 0.5 and 1.0 suggesting the anomalous behavior (9–18). This is observed when diffusion and relaxation rates are comparable.

The least-squares estimations of *n* and *K* as obtained from Eq. 1 are listed along with error analysis in Table 2. The values of *n* for dicarbonyls were in the range of 0.50–0.55, and for monocarbonyls, 0.54–0.61, suggesting the diffusion to be somewhat closer to the Fickian behavior. The values of *n* were less affected by the temperature. On the other hand,

TABLE 2
Analysis of Sorption Data for Chlorosulfonated Polyethylene Geomembrane With Esters at Different Temperatures Along With the Estimated Average Errors [σ]

	n				Log *K*			
Ester	25°C	44°C	60°C	$10^2 \cdot \sigma$	25°C	44°C	60°C	$10^2 \cdot \sigma$
MA[a]	0.55	0.54	0.54	±0.72	−1.48	−1.30	−1.22	±1.01
EA	0.57	0.58	0.55	±1.18	−1.50	−1.39	−1.29	±1.69
MAA	0.50	0.50	0.51	±0.42	−1.73	−1.71	−1.65	±0.97
EAA	0.50	0.50	0.50	±0.40	−1.76	−1.72	−1.69	±1.03
BA	0.60	0.59	0.60	±0.81	−1.71	−1.53	−1.48	±1.32
DEO	0.50	0.52	0.53	±0.93	−1.74	−1.84	−1.74	±2.21
AA	0.59	0.60	0.61	±0.72	−1.69	−1.56	−1.49	±1.17
DEM	0.50	0.51	0.52	±0.70	−1.85	−1.75	−1.65	±1.65
DES	0.50	0.54	0.55	±0.95	−1.99	−1.97	−1.82	±2.22

[a] The values for methyl acetate are obtained at 40°C and 50°C instead at 44°C and 60°C, respectively.

K increased with an increase in temperature, and the dependence of *K* on the size of esters was observed. The highest value of *K* was observed for the smallest penetrant (methyl acetate) and the lowest value for the largest diethyl succinate.

Sorption or diffusion, being a function of structure of both the geomembrane and the migrating liquid molecule, can be used to understand the type of molecular interactions between esters and the geomembranes. The reduced plots of mol % sorption, Q_t or S, versus $t^{1/2}/h$ at 25°C for CSM + esters are given in Fig. 1. The results of mol % sorption given in Table 3, and the time required to attain equilibrium sorption, showed a dependence on the nature and structure of the ester molecules. For instance, in the case of methyl acetoacetate and ethyl acetoacetate, the sorption values were quite small, that is, they ranged from 0.06 to 0.14 mol %. Similarly, for diethyl oxalate, diethyl malonate, and diethyl succinate, smaller values of S were observed; however, these values were slightly higher than methyl acetoacetate and ethyl acetoacetate. On the other hand, for ethyl acetate, *n*-butyl acetate, and *iso*-amyl acetate, the values of S were high, that is, ranging between 0.4 to 0.5 mol %. Thus, the sorption results did not seem to depend on the size of the esters but, mainly on their structural characteristics.

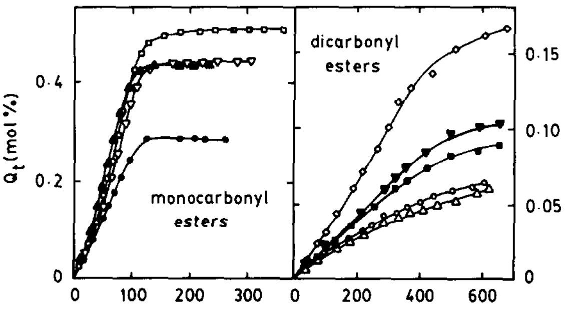


FIGURE 1. Reduced plots of sorption for CSM geomembrane with monocarbonyl esters: (●), methyl acetate; (▲), ethyl acetate; (□), *n*-butyl acetate; (▽), *iso*-amyl acetate; (○), methyl acetoacetate; (△), ethyl acetoacetate; (■), diethyl oxalate; (▼), diethyl malonate and (◇), diethyl succinate at 25°C.

The initial slopes of Q_t versus $t^{1/2}/h$ plots for ethyl acetate, *n*-butyl acetate, and *iso*-amyl acetate shown in Fig. 1 were almost identical, but the slope for methyl acetate was quite different. Similarly, the S values for *iso*-amyl acetate and ethyl acetate were quite identical whereas, for methyl acetate and *n*-butyl acetate, they varied somewhat; the latter showed higher sorption (approximately, 0.5 mol %) than the former for which S varied between 0.29–0.41 mol %. The times for attainment of equilibrium sorption were almost identical for CSM + monocarbonyl esters (viz., methyl acetate, ethyl acetate, *n*-butyl acetate and *iso*-amyl acetate). The sorption results of CSM with dicarbonyl esters (viz., methyl acetoacetate, ethyl acetoacetate, diethyl oxalate, diethyl malonate and diethyl succinate) presented in Fig. 1 showed that the shapes and the initial slopes of the curves were identical for diethyl malonate and diethyl oxalate, ethyl acetoacetate, and methyl acetoacetate. However, for diethyl succinate, sorption was higher than for the other dicarbonyl esters. Also, the time required to attain equilibrium saturation was higher (12 to 13 days at 25°C) with dicarbonyl esters when compared to monocarbonyl esters. Thus, sorption was dependent on the nature and type of the ester molecules rather than their sizes. The shapes of the sorption curves were somewhat sigmoidal for some lower esters viz., methyl acetate, ethyl acetate, *n*-butyl acetate and *iso*-amyl acetate (Fig. 1), suggesting a slight deviation from the Fickian transport phenomenon for these molecules.

Some typical sorption plots for the temperature dependence of uptake values versus $t^{1/2}/h$ are given

TABLE 3

Sorption [S], Diffusion Coefficient [D], Permeability Coefficient [P], Penetration Velocity [v], and First-Order Kinetic Rate Constant [k_1] at Different Temperatures and Maximum Percent Volume Changes [ΔV_∞] at 25°C for Chlorosulfonated Polyethylene Geomembranes With Esters Along With the Estimated Average Errors [σ]

Ester	Temp. (°C)	$10 \cdot S$ (mol %)		$10^7 \cdot D$ (cm^2s^{-1})	$10^8 \cdot P$ (cm^2s^{-1})	$10^4 \cdot v$ ($cm \cdot s^{-1}$)	$10^3 \cdot k_1$ (min^{-1})	ΔV_∞ (%)
MA	25	2.88		2.50	5.33	2.58	4.42	30
	40	3.96		5.42	15.88	4.80	8.78	
	50	4.13		7.15	21.89	6.62	12.28	
			σ	±0.18	±0.55	±0.36	±0.36	
EA	25	4.32		2.79	10.60	2.66	4.99	60
	44	4.68		4.72	19.47	4.22	8.03	
	60	4.92		5.99	25.95	5.34	9.96	
			σ	±0.21	±0.87	±0.24	±0.22	
MAA	25	0.64		0.26	0.19	0.15	0.25	11
	44	0.96		0.56	0.62	0.51	0.80	
	60	1.41		0.74	1.21	0.86	1.41	
			σ	±0.01	±0.02	±0.05	±0.05	
EAA	25	0.60		0.23	0.18	0.15	0.24	12
	44	0.85		0.56	0.62	0.49	0.83	
	60	1.23		0.87	1.39	0.76	1.26	
			σ	±0.01	±0.02	±0.04	±0.04	
BA	25	5.05		1.63	9.59	1.60	2.97	98
	44	5.03		3.03	17.69	2.77	5.46	
	60	5.20		3.84	23.18	3.58	7.07	
			σ	±0.19	±1.10	±0.11	±0.07	
DEO	25	0.88		0.22	0.28	0.15	0.25	17
	44	1.49		0.38	0.83	0.47	0.72	
	60	1.91		0.65	1.80	0.83	1.32	
			σ	±0.02	±0.05	±0.04	±0.04	
AA	25	4.41		1.74	9.97	1.54	2.97	96
	44	4.50		2.99	17.52	2.68	5.18	
	60	4.55		3.74	22.14	3.58	7.02	
			σ	±0.18	±1.06	±0.10	±0.06	
DEM	25	1.02		0.17	0.27	0.14	0.22	21
	44	1.27		0.52	1.06	0.56	0.92	
	60	1.52		0.93	2.27	0.95	1.69	
			σ	±0.02	±0.04	±0.04	±0.04	
DES	25	1.66		0.14	0.40	0.14	0.24	41
	44	2.40		0.30	1.24	0.33	0.59	
	60	2.72		0.58	2.75	0.74	1.26	
			σ	±0.02	±0.08	±0.03	±0.02	

in Fig. 2 for ethyl acetate and methyl acetoacetate. This dependence was systematic, that is, S increased with an increase in temperature for all the esters suggesting increased molecular mobility of the CSM chain segments. For *n*-butyl acetate at 25° and 44°C, the sorption values were nearly identical and in all cases, before the attainment of 55% equilibrium sorption, the initial portion of the curves were steeper with increasing temperature.

Diffusion Coefficients From Solvent Uptake Data

Due to the initial near-linearity in the reduced sorption plots, Fick's second law of diffusion was used to calculate the solvent diffusivity into the geomembrane matrix:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right). \qquad [2]$$

Here, x is the penetrant transport depth into the geomembrane, and C is the penetrant concentration. The average values of D considered as a constant and taken over a range of concentration intervals were calculated by using Eq. 3 for a thin sheet geometry of a polymer sample (22,23):

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{h^2}\right). \qquad [3]$$

The values of D were computed by the iterative procedure considering the first 11 terms, that is, $n = 0$ to 10 using the standard algorithm. The com-

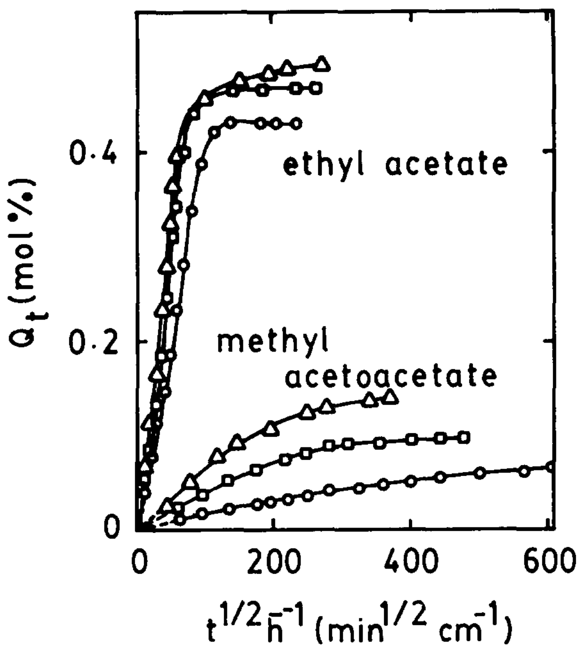


FIGURE 2. Temperature dependence of sorption for CSM geomembrane with ethyl acetate and methyl acetoacetate at (○), 25°C; (□), 44°C and (△), 60°C.

puted values of D are included in Table 3. The average deviations estimated in the calculation of D are also included.

Another solution to Eq. 2 before 55% of equilibrium sorption was also used to calculate the average values of D (considered to be independent of penetrant concentration) using the initial slope, θ, of the sorption curve as:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2. \qquad [4]$$

A diffusion process obeying Eq. 4 is referred to as 'Fickian'. It may be noted that in cases where the sorption curves were sigmoidal initially, the diffusion coefficients calculated from Eq. 4 differed slightly from those calculated from Eq. 3. However, the latter values were regarded to be more reliable because using Eq. 3, the D values were calculated at several points of the sorption curve taking due account of the slight sigmoidal deviation of the curves up to 55% (11).

In order to estimate the extent of deviation from the Fickian mechanism for those penetrants exhibiting sigmoidal shapes, we have used the average values of D (calculated from Eq. 3) into Eq. 3 and simulated the long-term theoretical sorption curve. Some typical data for methyl acetate, *n*-butyl acetate and diethyl malonate are presented in Fig. 3. It is observed that the theoretical and experimental sorption curves for diethyl malonate were identical because of the insignificant swelling of CSM geomembrane in the presence of diethyl malonate. However, slight deviations between the experimental and theoretical sorption curves were observed for methyl acetate and *n*-butyl acetate. This further supported the suggestion that molecular transport of these esters (and others whose curves are not shown) is not much different from the Fickian diffusion.

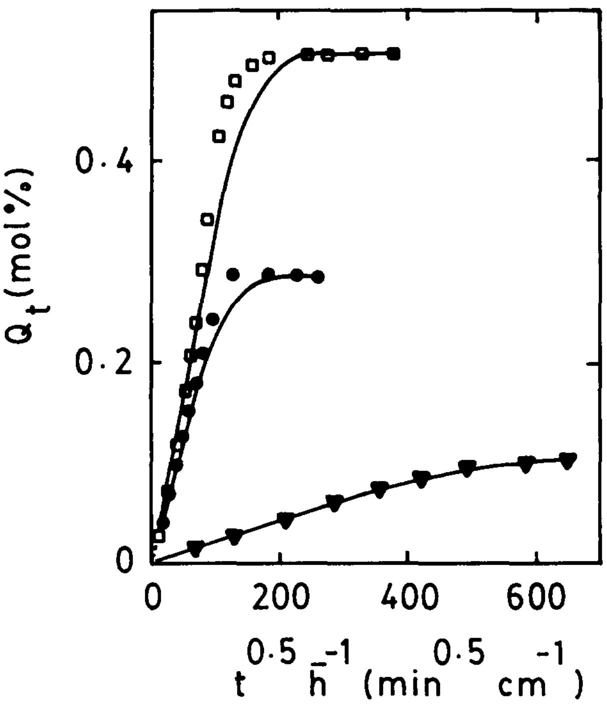


FIGURE 3. Comparison of experimental (points) and theoretically simulated (solid line) reduced sorption plots for CSM geomembrane with methyl acetate, *n*-butyl acetate and diethyl malonate at 25°C. Symbols have the same meanings as in Fig. 1.

Results given in Table 3 indicated that the diffusion coefficients were not dependent on the molecular size of esters; on the other hand, these were influenced by their chemical nature. For instance, dicarbonyl esters like methyl acetoacetate, ethyl acetoacetate, diethyl malonate, diethyl oxalate, and diethyl succinate, have diffusion coefficients an order of magnitude lower than the monocarbonyl esters viz., methyl acetate, ethyl acetate, *n*-butyl acetate and *iso*-amyl acetate. The D values at 25°C followed the trend: DES < DEM < DEO < EAA < MAA < BA < AA < MA < EA. This trend varied slightly at higher temperatures. The observed smaller values of D for methyl acetoactetate, ethyl acetoacetate, diethyl oxalate, diethyl malonate, and diethyl succinate are attributed to their molecular interactions with the CSM chain segments and also with the molecular sizes and shapes of the esters. In addition, viscosity, η, of the solvents showed a dependence on diffusivity (24) as shown in Fig. 4, that is, the values of D decreased with an increase in solvent viscosity, η.

As stated before, the D values obtained from Eq. 3 or 4 represent the average values over a range of concentrations. In order to see this effect, at least in few cases like methyl acetate, ethyl acetate, *n*-butyl acetate and *iso*-amyl acetate, an effort has been made to show the dependence of D on concentration for these penetrants (Fig. 5). The experimental data points before 100% of equilibrium sorption were arbitrarily divided into several concentration intervals, and average D was calculated for each of these intervals for an average value of concentration. With other solvents, the variation of D with concentration was not significant, and, hence, the results are not displayed graphically.

Permeability coefficients, P, were calculated from the relation: $P = D \cdot S$ by taking the values of S expressed in g/g units and the values of D were taken from Eq. 3. These results are also included in Table 3 along with the estimated errors. The values of P followed a different trend when compared to the values of D in the investigated range of temperatures. This may be due to the differences in their solubilities. However, the trends in P with all the esters at higher temperatures remained the same.

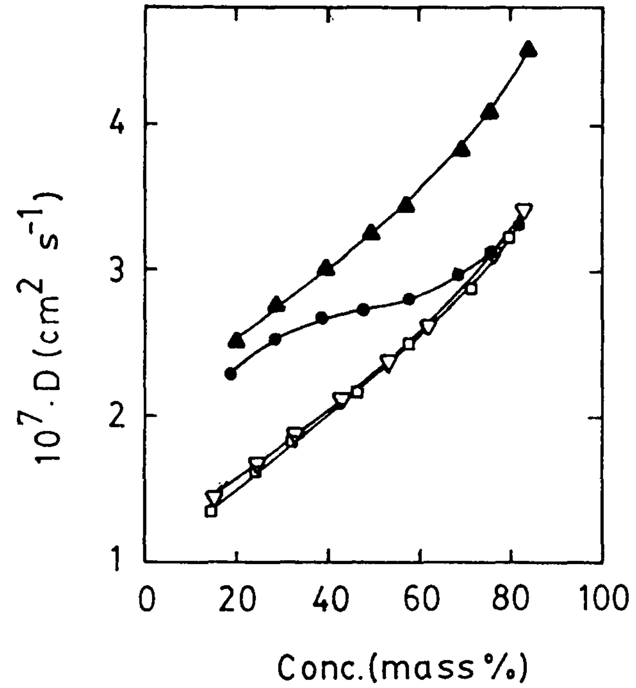


FIGURE 5. Dependence of diffusion coefficient on solvent concentration (mass %) for CSM geomembrane with methyl acetate, ethyl acetate, *n*-butyl acetate and *iso*-amyl acetate at 25°C. Symbols have the same meanings as in Fig. 1.

Volume Dilation Data

In actual field applications, the dimensional response of the geomembrane is extremely important to assess its solvent resistivity. Whenever a geomembrane is brought into contact with the liquid environment, the solvent ingresses and occupies the free volume spaces within the matrix. Sometimes, extensive swelling occurs due to interactions of the solvent molecules with the polymer chain segments, resulting in volume dilations of the matrix material. These results were calculated from the changes in thickness and diameter of the circular-shaped geomembrane samples. The dimensional response data are compiled in Table 3. The percent volume changes, ΔV_∞, for dicarbonyl esters, with comparatively smaller values of S, D or P were also small; this was consistent with their swelling tendencies. The highest value of $\Delta V_\infty = 98\%$ for *n*-butyl acetate and the smallest value of $\Delta V_\infty = 11\%$, were observed for methyl acetoacetate. For the remaining esters the intermediate values were observed.

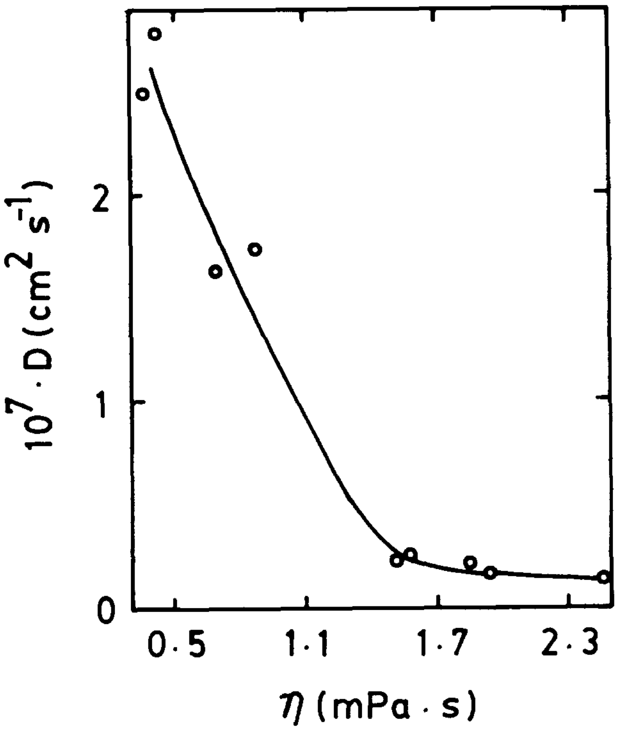


FIGURE 4. Dependence of diffusion coefficient on viscosity of the esters at 25°C.

Penetration Velocity

The phenomenon of solvent transport into geomembranes was also understood by calculating the penetration velocity, v, as (25):

$$v = \frac{1}{2\rho_p A M_\infty}\left(\frac{dM_t}{dt}\right), \qquad [5]$$

where the uptakes M_t and M_∞ were expressed in grams of solvent sorbed per gram of the geomembrane at time t and at infinite time as opposed to Q_t used in Eqs. 1 and 3, which referred to mol % uptake, ρ_p is the density of the polymer; A is the area of one face of the disc-shaped membrane, and the factor 2 accounts for liquid migration through both faces; the area of the edges of the circular disc was also accounted while computing the total area of the geomembrane exposed to the solvent media. The values of the penetration velocity along with their estimated errors are also included in Table 3. In general, these data followed the same pattern as those of the permeability coefficients discussed before. The values of v increased with an increase in temperature and showed a systematic decrease with the molecular size of the monocarbonyl esters with the exception of ethyl acetate. However, no systematic trend was observed for the dicarbonyl esters.

Kinetics of Sorption

Evaluation of kinetic rate constants, k_1, from the sorption data was found to be useful in assessing the solvent transport characteristics of a membrane (21,26). The first order kinetics of sorption was used to calculate the kinetic rate constants using:

$$k_1 t = \ln\,[C_\infty/(C_\infty - C_t)] \qquad [6]$$

where C_t and C_∞ are, respectively, the penetrant concentrations at time t and at infinite time (i.e., at equilibrium saturation), and these quantities have the same meanings as Q_t and Q_∞ discussed before. As long as the increase in sample thickness is not substantial, the first-order rate was applicable to the diffusion-controlled sorption. This was further confirmed by the straight line plots of $\log(C_\infty - C_t)$ versus t as shown in Fig. 6. The calculated values of k_1 along with the estimated errors are tabulated in Table 3.

For long sorption times, the higher terms with $n \geqslant 1$ and $\ln(8/\pi^2)$ can be ignored from Eq. 3 to give:

$$\ln\left(\frac{C_\infty}{C_\infty - C_t}\right) \cong \frac{\pi^2 D t}{\bar{h}^2}. \qquad [7]$$

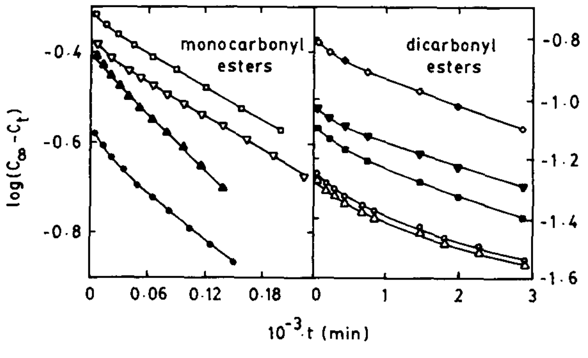


FIGURE 6. Kinetic plots of log $(C_\infty - C_t)$ versus time for CSM geomembrane with monocarbonyl esters and dicarbonyl esters at 25°C. Symbols have the same meanings as in Fig. 1.

Equation 7 is identical to Eq. 6 when:

$$k_1 = \frac{\pi^2 D}{\bar{h}^2}. \qquad [8]$$

Thus, in the present work, the values of k_1 followed the same trends as those of D.

Arrhenius Parameters

The diffusivity results given in Table 3 suggested a dependence on temperature. At higher temperatures, due to an increase in polymer segmental motion, solvent diffusivity also increased. The Arrhenius plots of log D versus $1/T$ given in Fig. 7 exhibited a slight curvature dependence over the investigated range of temperatures. The activation energy, E_D, for the process of diffusion, was calculated from the least-squares analysis using:

$$D = D_0 \exp\,(-E_D/RT), \qquad [9]$$

where D_o is the pre-exponential factor. The values of E_D, along with the estimated errors included in Table 4, did not show any systematic dependence on the penetrant size. Other studies in the literature also support this conjecture (27,28).

The plots of log P on $1/T$, displayed in Fig. 7 showed a similar pattern to those of diffusion coefficients. The activation energy, E_P, for permeation was calculated from a least-squares fit of the log P and $1/T$ (see Table 4). The results of ΔH_S, that is, enthalpy of sorption, being indicative of the sorption process (endothermic or exothermic) were calculated as: $\Delta H_S = E_P - E_D$. The quantity of ΔH_S involves both Henry's law and the Langmuir (hole filling) type sorption mechanisms (endothermic contribution). With the Langmuir mode, the exothermic heat of sorption are to be observed. The ΔH_S values of this work were positive and varied from 0.6 to 18.5 kJ/mol showing an endothermic sorption followed by Henry's law.

CONCLUSIONS

Protection of the environment against contamination from hazardous waste landfill transport is an important engineering challenge. Realizing the limited amount of the chemical resistance data for CSM geomembranes and its importance as an useful liner material, the present study was undertaken to investigate its suitability in the environment con-

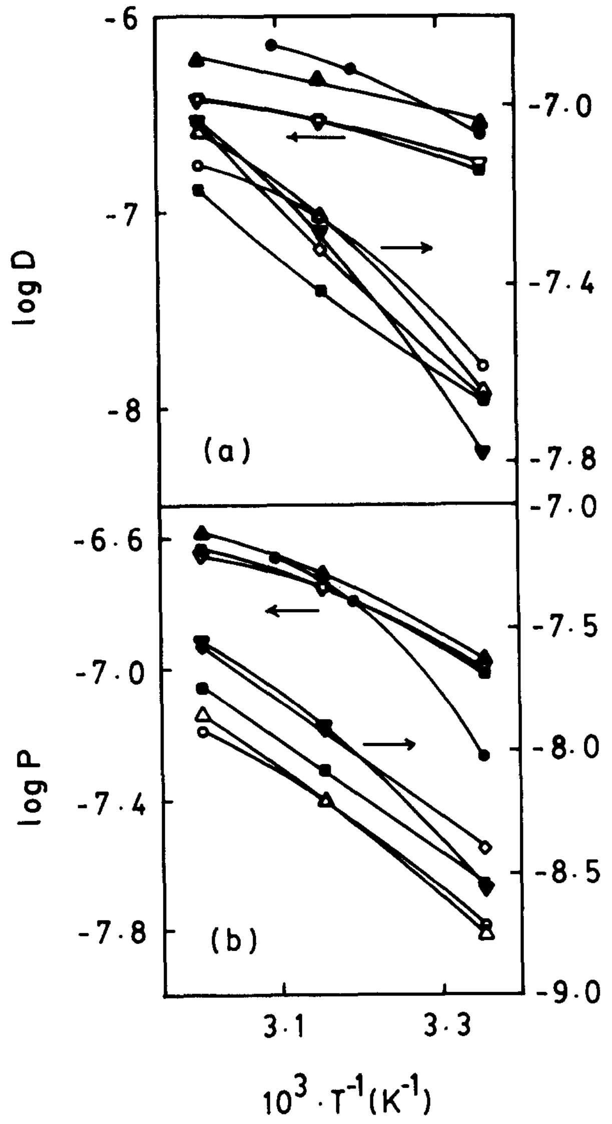


FIGURE 7. Arrhenius plots of (a) log D versus $1/T$ and (b) log P versus $1/T$. Symbols have the same meanings as in Fig. 1.

taining aliphatic esters. The transport (sorption, diffusion, and permeation) results of nine aliphatic esters with reference to CSM geomembrane were presented to test its potential use as a liner/barrier material in hazardous waste containment facilities. However, proper use of the data for a specific application may require additional information such as polymer morphology, mechanical testing of the untreated and treated samples.

TABLE 4
Activation Parameters [E_D and E_P in kJ/mol] and Heat of Sorption [ΔH_S in kJ/mol] for CSM + Esters Along With the Estimated Errors

Ester	E_D	E_P	ΔH_S
MA	34.27 ± 4.46	46.36 ± 1.93	12.08 ± 3.43
EA	18.23 ± 2.44	21.34 ± 2.22	3.10 ± 0.19
MAA	25.19 ± 4.67	43.69 ± 4.96	18.50 ± 1.21
EAA	32.05 ± 3.78	49.02 ± 7.87	16.97 ± 1.55
BA	20.45 ± 3.50	21.06 ± 3.11	0.61 ± 0.56
DEO	25.64 ± 1.50	44.07 ± 3.00	18.43 ± 2.34
AA	18.30 ± 2.86	19.06 ± 1.79	0.76 ± 0.07
DEM	41.18 ± 4.48	50.54 ± 7.24	9.37 ± 0.34
DES	33.78 ± 1.37	45.57 ± 1.17	11.79 ± 2.38

The general Fickian mass transport equation that incorporates terms for sorption and diffusion was used as a mathematical tool to compute the diffusion coefficients of CSM geomembrane for different landfill geometries. For the interpretation of transport data, physical state of the polymer, the type of the challenge chemical, experimental details for the test method, temperature of the system, and minimum detectable levels of uptake for the measurement, in addition to the knowledge of surface area and thickness of the membrane material are important. The high quality CSM liner used in this research showed extremely low levels of solvent transport. However, the transport coefficients did not correlate well with the size of the ester molecules, but the results were explained using the first order sorption kinetics.

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