Sorption/Desorption, Diffusion, and Swelling Characteristics of Geomembranes in the Presence of Halo-Organic Liquids

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ABSTRACT: Sorption/desorption results of halogen-containing liquids into high-density polyethylene, linear low-density polyethylene, very low-density polyethylene, and polypropylene geomembranes are presented at 25, 50, and 70°C. Sorption results are obtained by a gravimetric method, and diffusion coefficients have been calculated by using Fick's equation from the initial linear portions of the sorption/desorption curves. Swelling of the geomembranes was studied from a measurement of the increase in volume, thickness, and diameter. From a temperature dependence of sorption and diffusion coefficients, the Arrhenius parameters have been calculated. Liquid concentration profiles have been computed using Fick's equation for the appropriate initial and boundary conditions. The results of this study may have relevance in selecting the suitable geomembrane for a specific application in hazardous waste chemical ponds and other similar situations. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 349–359, 1999

Key words: geomembrane; sorption; diffusion; swelling

INTRODUCTION

Geomembranes are the highly specialized polymeric materials that find applications in a variety of underground applications including solid and liquid containment facilities such as hazardous waste landfills and caps, ponds, lagoons and reservoirs, mining heap, beach pads, failings, impoundments, solution channels, industrial sites, floating covers, etc. These are nonporous materials that are impermeable to organic waste liquids and leachates containing acids, bases, and other hazardous compounds.^{1–7} Geomembranes are used as liners for the containment of hazardous or municipal wastes in conjunction with geotextiles

or mesh underliners that reinforce or protect the more flexible geomembrane, and at the same time serves as an escape route for gases and leachates generated in certain waste ponds.

The geomembrane products and their applications have expanded rapidly over the past decade. Selecting a liner geomembrane requires the knowledge of the site, length of storage, and hazardous waste to be contained. Failure of the performance of the geomembrane might occur due to aggressive chemical attack. However, before the successful field applications of such materials it is important to study their resistance to chemicals. One approach would be to investigate their sorption/desorption and diffusion properties with respect to aggressive chemicals.⁷ Due to the wide differences in chemical structure, crosslinking, morphological set up, etc., geomembranes resist differently to the chemicals. In an effort to study this effect, we have chosen the interactions of halogenated liquids with respect to the widely

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used geomembranes developed by National Seal Company (Galesburg, IL). These include highdensity polyethylene (HDPE), linear low-density polyethylene (LLDPE), very low density polyethylene (VLDPE), and polypropylene (PP). Among these, HDPE is one of the most widely used geomembranes for tank linings and sludge ponds, as it provides good chemical resistance, impermeability, and exceptional UV resistance, with a good mechanical strength. The LLDPE and VLDPE geomembranes have also been used frequently. The successful uses of these geomembranes as effective barriers between the organic pollutants and the fertile soil require an accurate determination of sorption/desorption and diffusion parameters.

Over the past decade, we have been investigating the molecular transport of liquids into polymeric membrane materials.⁸⁻¹⁴ In continuation of this program of research, we now present useful experimental data on the resistivity of HDPE. LLDPE, VLDPE, and PP geomembranes to halocompounds that are frequently found in landfill and impoundment sites. Sorption results at 25, 50, and 70°C and the desorption data at 25°C have been obtained by the gravimetric sorption technique. From the sorption and desorption data, diffusion coefficients have been calculated using Fick's equation.¹⁵ From a temperature dependence of sorption and diffusion coefficients, we have estimated the Arrhenius activation parameters. Also, the concentration profiles of liquids into the selected geomembranes have been calculated from a solution of Fick's equation. This database would be useful to the liner manufacturers, vendors, purchasers, and reviewers of permit applications to select the proper geomembrane for a given waste site.

EXPERIMENTAL

Chemicals

The liquids employed in this research are: chloroform, carbon tetrachloride, trichloroethane, tetrachloroethane, trichloroethylene, tetrachloroethylene, bromobenzene, and bromoform (all were of analytical reagent grade samples supplied from s.d. fine Chemicals, Mumbai, India).

Geomembranes

The PP, LLDPE, VLDPE, and HDPE geomembranes used were supplied from the NSC Research Center, Galesburg, IL, in sheets with dimensions of $28 \times 22 \times 0.110$ cm, $35 \times 30 \times 0.106$ cm, $35 \times 30 \times 0.109$ cm, and $35 \times 30 \times 0.160$ cm, respectively (courtesy of J. Siebken and J. Donaldson). Some typical properties of the geomembranes are given in Table I.

Sorption/Desorption Measurements

In our experimental protocol, the uniformly cut geomembrane samples were exposed to the challenge chemical for a definite period of time and the changes in mass as well as dimensions of the samples were measured. These polymers absorb the liquids, depending upon the network structure. Thus, the mass gain or loss due to sorption or desorption respectively as well as swelling of the geomembranes could be monitored accurately with sample's immersion time. Such data are useful to compute diffusion and sorption coefficients of the migrating chemicals inside the geomembrane.⁸⁻¹⁴

Sorption experiments were performed at 25, 50, and 70°C using an electronically controlled oven (WTB Binder, Germany) maintained at the desired temperature within the accuracy of ± 0.5 °C. The circularly cut disc-shaped geomembrane samples with a diameter of ≈ 2.00 cm were placed in vacuum oven at 30°C for 48 h before start of the experiments. These samples were then exposed to the liquids (20-30 cm³) by placing them inside the screw-tight test bottles maintained at the desired temperature within an accuracy of ± 0.5 °C. The test bottles were placed inside the oven that was calibrated previously with a quartz thermometer for the precise control of temperature. The mass measurements were taken at precisely selected times by removing the samples and wiping with the smooth filter paper wraps. The samples were later placed on a toploading single pan digital Mettler balance (Model AE 240, Switzerland) sensitive to ± 0.01 mg and their masses were measured.

Total time spent by the geomembrane outside the test bottles was kept within 20–30 s to minimize the possible experimental error. This error was negligible due to a negligible time spent (30 s or even less) by the geomembrane outside the test bottle while weighing. The desorption runs were performed by keeping the already sorbed samples in a vacuum-controlled oven at 25°C under atmospheric pressure. The mass loss of the samples was monitored at regular intervals of time by removing them from the oven and weighing in the

				Geomembranes			
Property	Method	Units	PP	VLDPE	LLDPE	HDPE	
Thickness	ASTM D 751, NSF mod.	mm	1.085	1.06	1.08	1.59	
Density	ASTM D 1505	g/cm ³	0.91	0.922	0.928	0.948	
Carbon black content Tensile properties	ASTM D 1603 ASTM D 638	%	2.3	2.5	2.3	2.35	
Stress at vield		MPa	_	11.6	_	17.6	
Stress at break		MPa	18.8	32.6	35.2	33.4	
Strain at yield	1.3" gauge length (NSF)	%	—	20.5	—	16.9	
Strain at break	2.0" gauge or extensometer	%	—	1000	—	890	
Modulus of elasticity	ASTM D 638	MPa		571		931	
100% Secant modulus		MPa	10.8				
Dimensional stability	ASTM D 1204, NSF mod.	%	0.4	1.1	0.6	0.4	
Tear resistance	ASTM D 1004	N/cm	692	1505	1243	1050	
Puncture resistance	ASTM D 4833	N/cm	2058	3542	4098	3728	
Water absorption	ASTM D 570 at 23°C	%	—	0.04		0.05	
Water vapor transmission	ASTM E 96	g/day m ²		0.174	—	0.009	

Table I Some Typical Properties of Geomembranes Used

same manner as was done in sorption experiments. When the samples attained equilibrium sorption or desorption, no more mass gain or loss occurred, and this did not change significantly by keeping the samples inside the containers for a further period of 1 or 2 days.

The weight % increase C_t , as a function of time, t was calculated as:

$$C_t = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \tag{1}$$

where W_o is initial weight of the sample and W_t is its weight at time t, for the immersion period. These data are given in Table II. The wt % decrease for desorption was calculated similarly using eq. (1).

ESTIMATION OF SOLVENT DIFFUSION COEFFICIENTS

The resistivity of a geomembrane to the liquid chemical is related to its ability to perform the intended function during or after contact with a liquid. If no change occurs in its ability to function as designed after its chemical exposure, it is said to be resistant to the chemical. In the present research, we have used Fick's diffusion equation to estimate the diffusion coefficient:¹⁵

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{2}$$

where C = C(x, t) is liquid uptake in wt %, *D* is diffusion coefficient in cm²/s, and *x* is sample thickness in cm. Equation (2) can be solved for concentration-independent diffusivity, *D* as:¹⁵

$$D = \pi \left(\frac{h\theta}{4C_{\infty}}\right)^2 \tag{3}$$

where C_{∞} is equilibrium weight uptake at $t \rightarrow \infty$, θ is slope of the initial linear portion of the sorption/ desorption curves; h is membrane thickness. The sorption/desorption data initially vary linearly with time up to about 50–55% attainment of equilibrium saturation. However, for a successful application of the geomembranes it is important to know the liquid concentration profiles of the migrating chemicals. This was done by solving the one-dimensional Fick's diffusion equation under appropriate initial and boundary conditions.¹⁶

The final solution of eq. (2) for solvent uptake, $C_{(x,t)}$ inside the geomembrane sheet of thickness h, at time, t and distance, x is then written as:¹⁶

$$\begin{aligned} \frac{C_{(x,t)}}{C_{\infty}} &= 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \\ &\times \exp\left[-\frac{D(2m+1)^2 \pi^2 t}{h^2}\right] \sin\left[\frac{(2m+1)\pi x}{h}\right] \end{aligned} (4)$$

where m is an integer. Solving eq. (4), we obtain concentration profiles of the migrating liquids inside the geomembrane. These data are useful to study the liquid migration as a function of time and penetration depth of the liquid from face to the middle of the geomembranes along the thickness direction.

RESULTS AND DISCUSSION

Sorption/Desorption Kinetics

The dynamic sorption results for the PP geomembrane expressed in wt % units at 25, 50, and 70°C as well as desorption data at 25°C are presented in Figure 1. The smoothed best lines are drawn from the experimental points. It is observed that at all temperatures, the sorption of bromoform, tetrachloroethane, and bromobenzene increase linearly with time as well as temperature, but the time to reach equilibrium sorption decreases with temperature. However, with chloroform, carbon tetrachloride, trichloroethane, trichloroethylene, and tetrachloroethylene, the sorption values at 25°C though increase with time initially, later show slight sigmoidal trends. Sigmoidal shapes of the C_t vs. $t^{1/2}$ curves are indicative of the deviation of the sorption mechanism from the Fickian trend. In such cases, the polymer segments move much slower when compared to the transport of liquids within the free volume spaces of the samples, thereby inducing a slow relaxation of the segments. After attainment of equilibrium saturation, these liquids show a decrease in sorption. This type of decrease becomes more significant at higher temperatures (50 and 70°C) than at 25°C. At 70°C, the sorption results of chloroform were not obtained due to its low boiling nature. At all



Figure 1 Sorption curves, i.e., wt % uptake (C_t) vs. square root of time $(t^{1/2})$ for PP geomembrane with (\bigcirc) chloroform, (\triangle) carbon tetrachloride, (\Box) trichloroethane, (\bigtriangledown) tetrachloroethane, (\bullet) trichloroethylene, (\blacktriangle) tetrachloroethylene, (\blacksquare) bromobenzene, and (\blacktriangledown) bromoform at (A) 25°C, (B) 50°C, (C) 70°C, and (D) desorption curves at 25°C.

the temperatures, sorption values are lowest for bromoform and highest for carbon tetrachloride, but the intermediary values are observed for the remaining liquids. The desorption curves at 25°C for all the liquids show a rapid but systematic decline. However, the general tendency is that those liquids that exhibit lower sorption desorb much slower and vice versa.

The sorption results at 25 and 50°C, for VLDPE geomembrane increase systematically with time for all the liquids. However, we could observe some differences in the variations of the sorption values between 25 and 50°C. At 25°C, sorptions of carbon tetrachloride and tetrachloroethylene vary almost identically, but at 50°C, tetrachloroethylene shows higher values than carbon tetrachloride. On the other hand, at 70°C a decrease in sorption is observed for trichloroethylene, tetrachloroethylene, and carbon tetrachloride. The sorption data of chloroform at 70°C were not obtained. The sigmoidal trends are more prev-

Liquids	Temp (°C)	PP	VLDPE	LLDPE	HDPE
Chloroform	25	491.1	47.6	36.9	17.7
	50	711.2	82.2	66.2	25.9
		(84.5)	(32.4)	(27.2)	(15.0)
Carbon tetrachloride	25	726.9	73.7	53.5	23.3
	50	995.5	129.4	97.6	34.7
	70	1425.6	422.7	170.2	61.3
		(89.9)	(42.5)	(35.6)	(18.5)
1,1,1-Trichloroethane	25	442.1	40.0	31.2	14.5
	50	600.2	60.1	55.4	21.4
		(84.0)	(28.9)	(24.2)	(12.7)
1,1,2,2-Tetrachloroethane	25	148.6	22.7	19.6	11.2
	50	294.3	39.7	35.1	16.1
	70	479.5	100.3	60.7	27.0
		(61.7)	(18.8)	(17.1)	(8.0)
Trichloroethylene	25	623.2	66.1	49.9	21.5
·	50	857.7	116.9	88.5	32.2
	70	1285.4	376.1	161.9	53.4
		(88.4)	(40.0)	(33.2)	(18.2)
Tetrachloroethylene	25	643.7	71.8	54.5	23.3
-	50	920.2	152.8	99.4	36.5
	70	1330.9	456.6	185.2	58.9
		(88.6)	(42.6)	(35.1)	(19.2)
Bromobenzene	25	240.4	35.1	29.6	14.5
	50	403.4	71.6	53.6	22.5
	70	597.7	166.1	101.3	34.1
		(72.6)	(26.4)	(22.3)	(13.4)
Bromoform	25	94.5	31.2	28.9	16.7
	50	174.4	61.4	50.4	26.1
	70	271.6	115.5	93.6	38.7
		(48.8)	(23.87)	(21.7)	(14.0)

Table II Sorption Coefficients (S in wt %) of Geomembranes with Liquids at Different Temperatures

Values in the parantheses are for desorption runs at 25°C.

alent at 25 and 50°C than at 70°C for all the liquids with the VLDPE geomembrane. The same reasons could be attributed to such a behavior as explained before for the PP geomembrane. As for desorption is concerned, tetrachloroethylene and carbon tetrachloride desorb much faster, while tetrachloroethane desorbs slower than all the liquids.

The sorption results of LLDPE geomembrane at all temperatures also increase with time. For carbon tetrachloride and tetrachloroethylene both at 25 and 50°C, sorption data vary almost identically. Similarly, for trichloroethane, bromobenzene, and bromoform, the sorption data vary almost identically. At 70°C, only slight decrease in sorption takes place in the case of carbon tetrachloride, tetrachloroethylene, and trichloroethylene after attaining equilibrium saturation. For the LLDPE geomembrane, tetrachloroethane shows the lowest value of sorption, whereas highest sorption is observed for tetrachloroethylene. The desorption data at 25°C is fastest for tetrachloroethylene, while it is slowest for tetrachloroethane.

For HDPE, the sorption data at all the temperatures show more sigmoidal trends than the other geomembranes, and also, no decrease in sorption after attainment of equilibrium saturation is observed. The observed sigmoidal shapes indicate a slight deviation of transport from the Fickian trend. At 25°C, tetrachloroethylene and carbon tetrachloride exhibit almost identical sorption values, as does trichloroethane and bromobenzene. However, at 50 and 70°C, we find that no two liquids exhibit similar sorption equilibrium values. In general, the lowest sorption is observed for tetrachloroethane and the highest value is shown by tetrachloroethylene except at 70°C, at which carbon tetrachloride exhibits the highest sorption. Regarding the desorption data, it is

Liquids	Temp (°C)	PP	VLDPE	LLDPE	HDPE
Chloroform	25	4.59	4.09	4.34	1.87
	50	6.54	7.21	7.17	2.63
		(12.13)	(10.39)	(10.09)	(3.67)
Carbon tetrachloride	25	3.35	3.06	2.69	1.12
	50	5.13	5.02	4.68	2.11
	70	5.91	5.44	4.96	2.90
		(9.29)	(7.29)	(7.18)	(2.68)
1,1,1-Trichloroethane	25	3.09	2.41	2.24	1.02
	50	5.63	4.98	4.61	1.46
		(8.15)	(4.99)	(4.88)	(1.91)
1,1,2,2-Tetrachloroethane	25	2.76	2.41	1.82	0.94
	50	3.18	3.55	3.48	1.34
	70	4.07	6.90	3.64	2.37
		(2.52)	(3.00)	(2.53)	(1.31)
Trichloroethylene	25	6.49	6.58	6.23	2.72
·	50	8.48	8.10	7.88	3.46
	70	9.79	9.29	8.53	5.13
		(4.26)	(8.98)	(8.40)	(3.90)
Tetrachloroethylene	25	4.39	5.17	3.99	1.68
-	50	5.90	4.72	5.99	2.26
	70	8.10	7.98	7.12	3.19
		(2.00)	(8.91)	(7.90)	(3.89)
Bromobenzene	25	4.56	4.45	3.66	1.96
	50	4.95	4.95	5.84	2.44
	70	6.14	8.19	7.18	3.18
		(0.72)	(5.40)	(3.78)	(2.51)
Bromoform	25	3.44	2.82	2.57	1.51
	50	4.26	3.16	4.00	2.05
	70	6.48	6.13	5.89	2.00
		(3.20)	(3.48)	(3.66)	(1.75)

Table III	Results of Parameter K ×	10 ² (in	$g/g (min)^n$	of eq. (5)	for Geomembranes
at Differen	nt Temperatures				

Values in the parantheses are for desorption runs at 25°C.

found that desorption is fastest in the case of tetrachloroethylene and slowest for tetrachloroethane.

The values of sorption coefficients, *S*, calculated from the equilibrium, uptake values in wt % units and the desorption data are presented in Table II. As discussed before, these data show a dependence on the nature of the geomembrane and the liquid molecules. For instance, HDPE has the least sorptivity, whereas LLDPE and VLDPE show higher sorption than HDPE. In the case of PP geomembrane, sorption is higher than all the polyethylene-based geomembranes (HDPE, LLDPE, and VLDPE). Also, we find that the equilibrium sorption results decrease with increasing density of the geomembranes. The temperature effect on sorption is more significant with the PP, VLDPE, and LLDPE than with the HDPE

geomembrane. These values vary according to the sequence: PP > VLDPE > LLDPE > HDPE for all the liquids.

The sorption data before the completion of 50-55% of equilibrium have been fitted to the empirical relationship.^{17,18}

$$\frac{M_t}{M_{\infty}} = Kt^n \tag{5}$$

The parameter, K, represents the extent of interaction between the liquids and geomembranes, while the exponent value of n indicates the type of transport mechanism. The values of K and n have been calculated using the least-squares procedures, but only the results of K are presented in Table III. It may be noted that the values of K also

Liquids	Temp (°C)	PP	VLDPE	LLDPE	HDPE
Chloroform	25	2.46	1.84	1.62	0.72
	50	3.82	2.91	2.89	1.47
		(40.04)	(2.75)	(2.35)	(0.72)
Carbon tetrachloride	25	1.32	0.91	0.82	0.30
	50	2.67	1.50	1.46	0.72
	70	5.35	3.19	2.45	1.73
		(34.07)	(1.91)	(1.31)	(0.37)
1,1,1-Trichloroethane	25	1.04	0.65	0.51	0.18
	50	2.31	1.55	1.15	0.66
		(21.95)	(0.96)	(0.82)	(0.19)
1,1,2,2-Tetrachloroethane	25	0.38	0.30	0.26	0.08
	50	0.91	0.86	0.80	0.39
	70	1.52	1.37	1.29	0.87
		(1.49)	(0.38)	(0.30)	(0.09)
Trichloroethylene	25	3.20	2.65	2.55	1.31
-	50	6.12	4.75	4.55	2.59
	70	9.50	6.95	5.56	4.24
		(57.83)	(5.96)	(6.09)	(1.44)
Tetrachloroethylene	25	1.87	1.69	1.51	0.53
-	50	3.04	2.35	2.28	1.32
	70	5.66	3.89	3.42	1.83
		(17.49)	(2.59)	(2.03)	(0.60)
Bromobenzene	25	1.18	1.13	1.11	0.36
	50	1.95	1.87	1.81	1.18
	70	2.93	2.85	2.75	1.89
		(3.90)	(1.25)	(1.27)	(0.36)
Bromoform	25	0.40	0.36	0.34	0.10
	50	0.89	0.87	0.84	0.41
	70	1.75	1.64	1.57	1.00
		(0.45)	(0.35)	(0.34)	(0.11)

Table IV Diffusion Coefficients $(D.10^7 \text{ cm}^2/\text{s})$ of Liquids into Geomembranes at Different Temperatures

Values in the parantheses are for desorption runs at 25°C.

exhibit the trends similar to sorption results, i.e., these results in general vary according to the sequence: HDPE < LLDPE < VLDPE < PP. The values of *K* increase systematically with increasing temperature. The values of *n* (not included in Table III) for the present liquid–geomembrane systems show variations from 0.50 to 0.61, suggesting that transport is of Fickian type in majority of systems, but slightly deviate from such a behavior only in a few cases. For instance, the values of *n* for HDPE geomembrane range between 0.50–0.57; for LLDPE, *n* varies between 0.50–0.59; for VLDPE, it is 0.50–0.59, whereas for PP, *n* values are in the range 0.50–0.61.

Diffusion

Diffusion coefficients, D calculated from eq. (3) are given in Table IV. The values of D vary, de-

pending upon the nature of the liquids. For instance, tetrachloroethane and bromoform exhibit lower values of D than tetrachloroethylene and chloroform. Similarly, the D values for carbon tetrachloride are higher than trichloroethane, probably because carbon tetrachloride is more of a globular molecule than trichloroethane. On the other hand, trichloroethylene exhibits the highest values of D for all the geomembranes at all the temperatures. In general, diffusion data also support the fact that HDPE is the most resistive of all the geomembranes studied. Values of K and D for desorption experiments at 25°C are also included in Tables III and IV. When these data are compared with the results obtained from sorption experiments, it is observed that the values obtained from desorption experiments are higher than those obtained from sorption data for all the liquids.



Figure 2 Concentration profiles calculated from eq. (4) for carbon tetrachloride with PP (\bigcirc); VLDPE (\bigcirc); LLDPE (\square); and HDPE (\blacksquare); at (A) 25°C, (B) 50°C, and (C) 70°C for 25-min immersion.

Concentration Profiles

The calculated concentration profiles from eq. (4)for the high diffusing carbon tetrachloride and the low diffusing tetrachloroethane with all the geomembranes at 25, 50, and 70°C are displayed in Figures 2 and 3, respectively. In general, concentration profiles increase systematically with increasing temperature and these profiles depend on the type of geomembrane and show similar variations to those exhibited by S and D values. While calculating the theoretical curves it was not possible to use the same initial times so as to facilitate a comparison of the curves under identical conditions, and hence, different times were chosen for different membranes. However, it is gratifying to note that different shapes and different values of the profiles are observed, depending upon the nature of the geomembrane. For the remaining liquids, intermediary values are observed, but these are not displayed graphically to avoid redundancy. It is further found that higher values of concentration profiles are observed for the PP geomembrane than all the other geomembranes.

Swelling

Dimensional response of the geomembranes has been investigated from a calculation of the volume changes of the samples due to swelling. The changes in thickness and diameter of the geomembranes were calculated at different times while sorption experiments were in progress. The thickness of the samples were measured (± 0.001 cm) using a micrometer screw gauge, while vernier calipers was used to measure the diameter (± 0.001 cm). The values of *D* based on volume expansion of the samples have been calculated as per the procedures published earlier:^{19,20}

$$D_v = \pi \left(\frac{\theta h}{4\Delta V_m}\right)^2 \tag{6}$$

where $\Delta V_m = \Delta V_{\infty}/V_0$, and θ is slope of the $\Delta V_t/V_0$ vs. $t^{1/2}$ plots.

Swelling curves for PP, VLDPE, and LLDPE geomembranes at 25°C are presented in Figure 4. From these curves, the maximum percent increase in volume, ΔV_m were obtained, which were



Figure 3 Concentration profiles calculated from eq. (4) for Tetrachloroethane with PP (\bigcirc); VLDPE (\bigcirc); LLDPE (\square), and HDPE (\blacksquare) at (A) 25°C, (B) 50°C, and (C) 70°C for 25-min sorption.



Figure 4 Percentage increase in volume (ΔV_m) vs. square root of time $(t^{1/2})$ for (A) PP, (B) VLDPE, and (C) LLDPE geomembranes at 25°C for the same solvents as given in Figure 1.

used to compute D_v using eq. (6). Another useful parameter, i.e., swelling index, α , has also been calculated using:

$$\alpha = \frac{\Delta h_{\infty} d_0}{\Delta d_{\infty} h_0} \tag{7}$$

where h_0 and h_∞ are the original and final thicknesses of the samples while d_0 and d_{∞} refer to the original and final values of diameter of the disc shaped samples. The ΔV_m and θ values presented in Table V vary as: PP > VLDPE > LLDPE for all the liquids. Swelling is generally smaller for bromoform than for chloroform. The D_v values, also presented in Table V, are generally higher for PP geomembrane, and these data show a decreasing trend towards VLDPE and LLDPE geomembranes. However, these D_v data are smaller than those obtained from the sorption/desorption experiments. This may be explained in terms of free volume considerations. If the available free volume spaces between polymer segments are bigger than the solvent molecule, then the liquid entering into these spaces may not cause significant change in volume. On the other hand, when the solvent molecules do not enter into the already available free volume, then the polymer segments tend to relax and thereby contribute toward swelling. In the absence of any such interactions between the polymer segments and solvent molecules at any time t, the mass uptake by the geomembrane may not be equivalent to the corresponding volume gain. This further results in a decrease in the values of volume gain when compared to mass gain results. Therefore, the diffusion coefficients calculated from mass gain measurements are higher than those obtained from dimensional response measurements.

Arrhenius Activation Parameters

Diffusivity values show an increase with increasing temperature. This prompted us to calculate the energy of activation for diffusion, E_D from the Arrhenius equation. A representative plot of log D vs. 1/T is shown in Figure 5. These data exhibit

Table V Percent Maximum Increase in Volume ($\Delta V_{\omega}/V_0$), Diffusivity for Volume Change, D_{v} (10⁷ cm²/s), and Swelling Index, α (cm³/g) at Equilibrium

		PP		VLDPE			LLDPE		
Liquids	ΔV_m	D_v	α	ΔV_m	D_v	α	ΔV_m	D_v	α
Chloroform	2.69	1.74	7.51	0.27	0.96	1.19	0.23	1.13	1.06
Carbon tetrachloride	3.91	0.81	7.04	0.38	0.65	1.04	0.32	0.73	1.10
1,1,2,2-Tetrachloroethane	0.72	0.53	9.07	0.13	0.29	1.08	0.13	0.43	1.47
Tetrachloroethylene	3.83	1.75	6.94	0.40	1.37	1.14	0.34	1.21	1.24
Bromobenzene	1.51	1.90	8.77	0.22	0.72	1.04	0.21	0.68	1.33
Bromoform	0.32	0.36	7.41	0.11	0.44	1.38	0.11	1.00	1.38



Figure 5 Arrhenius plots of $\log D$ vs. 1/T for (A) PP, (B) VLDPE, (C) LLDPE, and (D) HDPE geomembranes for the same solvents as given in Figure 1.

linearity suggesting that the values of E_D are roughly constant over the temperature interval studied. Similarly, the heats of sorption, ΔH_S have been obtained from a plot of log S vs. 1/T (not displayed graphically to avoid redundancy). The estimated values E_D and ΔH_S were obtained from the least-squares procedure by fitting the data to the general type of equation:

$$\ln X = \ln X_0 - \frac{E_X}{RT} \tag{8}$$

where *X* is *D* or *S* and X_0 is D_0 or S_0 ; E_X gives the values of E_D or ΔH_S as constants, T is absolute temperature, and R is gas constant. These values are compiled in Table VI. In the case of the PP geomembrane, the E_D values increase from 17.1 to 27.9 kJ/mol for bromobenzene to bromoform, whereas for VLDPE, the E_D values range from 15.4 to 29.4 kJ/mol for tetrachloroethylene to tetrachloroethane. For LLDPE geomembrane, the E_D increases from 15.0 to 30.4 kJ/mol for trichloroethylene to tetrachloroethane. The E_D values for HDPE range from 22.1 to 45.3 kJ/mol for trichloroethylene to tetrachloroethane. The results of ΔH_S are highest in the case of VLDPE geomembrane when compared to the remaining geomembranes. The heat of sorption being positive in all the cases, suggests that sorption in the present systems follows an endothermic process.

CONCLUSIONS

Before the intended field applications of geomembranes, it is important to study their sorption/ desorption and diffusion characteristics with respect to aggressive organic liquids. The geomembranes with high resistivity to liquids are useful as liners in hazardous waste ponds to prevent the transport of leachates or liquids in the wastes and

Table VI Activation Energy for Diffusion (E_D in kJ/mol) and Heat of Sorption (ΔH_S in kJ/mol) for Geomembranes with Liquids

Liquids	Property	PP	VLDPE	LLDPE	HDPE
Carbon tetrachloride	E_D	$26.1~\pm~2.7$	$23.1~\pm~5.2$	$20.5~\pm~1.5$	$32.8~\pm~3.5$
	ΔH_S	$12.6~\pm~1.8$	$32.0~\pm~10.1$	$21.7~\pm~1.8$	17.9 ± 3.7
1,1,2,2-Tetrachloroethane	E_D	$26.5~\pm~1.2$	29.4 ± 3.6	30.4 ± 3.8	$45.3~\pm~3.8$
	ΔH_S	22.1 ± 0.2	27.4 ± 6.9	21.2 ± 1.8	16.2 ± 3.4
Trichlorothylene	E_D	$20.6~\pm~0.1$	18.3 ± 0.2	$15.0~\pm~2.6$	$22.1~\pm~0.3$
	ΔH_{S}	$13.4~\pm~2.3$	31.8 ± 9.8	$22.0~\pm~2.6$	16.9 ± 2.9
Tetrachloroethylene	E_D	$20.6~\pm~3.6$	$15.4~\pm~3.5$	$15.3~\pm~1.5$	$23.8~\pm~4.0$
	ΔH_S	$13.6~\pm~1.5$	$34.2~\pm~7.3$	$22.9~\pm~2.6$	$17.3~\pm~2.1$
Bromobenzene	E_D	$17.1~\pm~0.8$	$17.4~\pm~0.9$	$17.1~\pm~1.0$	$31.5~\pm~4.7$
	ΔH_S	$17.2~\pm~0.4$	$28.9~\pm~4.4$	$22.9~\pm~2.9$	$16.1~\pm~1.5$
Bromoform	E_D	$27.9~\pm~1.4$	$28.6~\pm~0.3$	$29.0~\pm~0.3$	$43.2 ~\pm~ 1.2$
	$\Delta \overline{H}_S$	$19.9~\pm~0.2$	$24.5~\pm~2.1$	$21.9~\pm~3.0$	$15.8~\pm~1.0$

thereby to minimize or avoid the pollution of ground water. In the absence of actual field experience on long-term performance of geomembranes, preliminary laboratory test data of the kind presented here are useful. From the results presented in this article we find that HDPE shows the highest resistivity towards halo-organics employed. The least resistivity is observed by PP geomembrane. However, the LLDPE and VLDPE geomembranes are found to be the materials of choice that behave intermediary to those of HDPE and PP geomembranes. It may be concluded that the chemical resistivity of a geomembrane depends upon the base polymer structure, its molecular weight, crystallinity, and degree of crosslinking. Chemical compatibility testing of these materials must be performed both to meet the designers need to support the material selection decision and to provide documentation for the facility operating permit application. Our present results indicate that HDPE is the best candidate geomembrane in field applications involving exposure to the halo-organics studied here.

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