An assessment of chemical compatibility of bromobutyl rubber, chlorosulfonated polyethylene and epichlorohydrin membranes in the presence of some hazardous organic liquids

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Abstract

The present study addresses the currently available polymeric materials which are possibly used as liner materials in waste chemical ponds against hazardous organic liquids. To assess the chemical compatibility, bromobutyl rubber (BIIR), chlorosulfonated polyethylene and epichlorohydrin (ECO) are selected for exposure to chloroalkanes and non-chlorinated liquids. These solvents come under the category of hazardous liquids and protection from their contamination to ground water and other aquatics is an important hygienic requirement. One of the possible means of studying the chemical compatibility of the liner membranes against such liquids is to investigate their transport characteristics into the membrane matrices. Thus, results of sorption and diffusion of the above-mentioned systems in the temperature interval 25–60 °C are presented using the sorption gravimetric technique. These results are analyzed by using the Fickian equation. The dependence of transport coefficients on the size and shape of the liquid molecules is discussed. Transport results are greatly influenced by the type of the polymer–solvent interactions in addition to the size of the liquid molecules. The Arrhenius activation parameters are estimated from a temperature dependence of sorption, diffusion and permeation coefficients. Enthalpy and entropy of sorption for the polymer–solvent systems have also been studied. Computed parameters and experimental results are used to discuss the transport mechanism in terms of the type and nature of the polymer membranes and the solvent molecules. Volume dilation of the polymers in the presence of the chosen liquid media has been measured. BIIR and ECO membranes appeared to be reactive toward tetrahydrofuran at 60 °C.

1. Introduction

Polymeric liner materials of low permeability and high sensitivity to hostile environment are increasingly used in handling the hazardous chemicals [1–3]. The

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primary function of such barrier materials is to prevent the transport of leachate and liquid components from the waste. For a better performance, the material should act as an effective barrier for a prolonged period. In the absence of actual experiments on the long-term performance of polymeric liners, it would be necessary to use the predictive methods based on the accelerating test methods to estimate the service-life of the material. The materials used as protective liners may be subject to a variety of chemicals that may adversely affect their performances due to chemical degradation, swelling of the polymer or dimensional instability. These factors also influence the materials' mechanical properties and increase transport of the liquid or leachate.

The goal of the present program is to identify factors which limit the barrier performance of the materials. Various kinds of organics have been identified as the major hazardous constituents of leachate from municipal landfills [4, 5]. In the present paper, the compatibility of bromobutyl rubber (BIIR), chlorosulfonated polyethylene (CSM) and epichlorohydrin (ECO) polymeric membranes with some of the hazardous liquids from the class of chloroalkanes and non-chlorinated solvents has been investigated. This is studied in terms of sorption, diffusion and permeation of the liquids into the barrier materials.

The molecular transport of liquids through a given barrier material is dependent on the temperature, polymer morphology, thickness and compatibility of the material [6–8]. Pores, holes or other imperfections in the membrane will also affect the overall transport of liquids and confound the molecular transport measurement attempts. However, the liquid transport performance of liner materials may be predicted to a reasonable accuracy in certain instances [6] and in other cases, additional experiments may be necessary. Our earlier efforts in this area dealt with the molecular transport studies on BIIR, CSM and ECO membranes against a variety of organic solvents [9–14]. In continuation of this research, the present study is extended to include dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 2-methoxyethanol, 1,1,2,2-tetrachloroethane, cyclohexane, tetrahydrofuran, 1,4-dioxane, acetonitrile, dimethyl sulfoxide and N,N-dimethylformamide over the temperature interval 25–60 °C. The results of this study indicate the usefulness of the polymers as liner materials in the chosen solvent media.
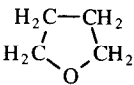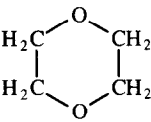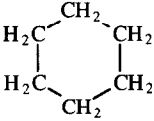
2. Experimental

2.1. Reagents and materials

Polymer sheets of BIIR, CSM and ECO in dimensions of 0.2 cm × 15 cm × 15 cm were molded at UTEX, Weimer, TX by Mr. Andy Kutac. During sample fabrication, a 30.5 cm laboratory mill was used to mix and prepare the rubber compounds for molding; the ECO polymer sheets were press-cured at 176 °C for 30 min, whereas CSM and BIIR membranes were press-cured, respectively, at 155 °C and 165 °C for 30 min. The compositions and some of the representative engineering properties of the membranes were given earlier [10]. The toxicity data [4, 5] of these solvents along with other physical properties [15] are given in Table 1.

Table 1
Molar volume, V_S (cm^3 mol^{-1}), solubility parameter, δ (J$^{1/2}$ cm$^{-3/2}$), dipole moment, μ and threshold limiting value (TLV) of the solvents

Name	Structure	V_S	δ	μ	TLV (ppm)
Acetonitrile	CH_3CN	52.9	24.8	3.53	40
Dichloromethane	CH_2Cl_2	65.5	20.2	1.14	500
Dimethyl sulfoxide	$CH_3-\overset{\overset{O}{\|\|}}{S}-CH_3$	71.3	24.5	4.06	a
Dimethylformamide	$H\overset{\overset{O}{\|\|}}{C}-N(CH_3)_2$	77.4	24.8	3.24	10[b]
2-Methoxyethanol	$CH_3O-(CH_2)_2-OH$	79.3	a	2.04	a
1,2-Dichloroethane	CH_2Cl-CH_2Cl	79.4	20.0	1.83	50
Trichloromethane	$CHCl_3$	80.7	19.4	1.15	50
Tetrahydrofuran	$\begin{matrix} H_2C-CH_2 \\ H_2C\diagdown{}_O\diagup CH_2 \end{matrix}$	81.8	20.3	1.63	200
1,4-Dioxane	$\begin{matrix} H_2C^{\diagup O\diagdown}CH_2 \\ H_2C_{\diagdown O\diagup}CH_2 \end{matrix}$	85.7	20.7	0.45	100[b]
Tetrachloromethane	CCl_4	97.1	17.5	0.00	10
1,1,2,2-Tetra-chloroethane	$CHCl_2-CHCl_2$	105.8	20.1	1.71	5[b]
Cyclohexane	$\begin{matrix} CH_2 \\ H_2C^{\diagup}{}^{\diagdown}CH_2 \\ H_2C_{\diagdown}{}_{\diagup}CH_2 \\ CH_2 \end{matrix}$	108.8	16.8	0.00	300

[a] Not available.
[b] For skin.

The polymer sheets were cut circularly (diameter = 1.96 cm) by means of a sharp-edged steel die; the samples were dried thoroughly in a vacuum desiccator over anhydrous calcium chloride before experimentation. The sample thicknesses were measured at several points with an accuracy of $\pm$ 0.001 cm by using a micrometer screw gauge. The average of several of these values was taken to be the initial thickness, h of the polymer samples.

For sorption measurements, dry specimens (W_0) were immersed in about 30 cm^3 of the respective solvents in screw-tight test bottles. They were periodically removed, the adhered liquid drops around the sample surfaces were blotted off quickly by using the

tissue roll papers and weighed immediately (W_t) using a Mettler digital balance (Model AE 240, Switzerland) having a stated precision of $\pm$ 0.01 mg. Repeat measures of the weight of the polymer samples vary generally within $\pm$ 0.05 mg, but this depends on the nature of the liquid chosen. For instance, with highly volatile liquids such as dichloromethane and trichloromethane, the errors in repeat measurements generally lie in the range 0.05–0.1 mg. However, the weighings are done quickly within 20–30 s in order to minimize the errors due to solvent evaporation from the membrane materials. After several days, the specimens approached a limiting weight (W_∞) which, within the precision of the balance, did not change significantly over the further period of a day or two. By convention, changes in weight were calculated as: $M_t = W_t - W_0$ and $M_\infty = W_\infty - W_0$. From these data, mol% uptake values, Q_t were calculated by using the molecular weight, M_s of the solvent as,

$$Q_t = \frac{M_t}{W_0} \times \frac{100}{M_s} . \tag{1}$$

3. Results

3.1. Diffusion behavior

The sorption results of the liquid–polymer systems are analyzed with reference to the theoretical equation for diffusion in a plane sheet geometry according to Fick's relation [16].

$$\frac{Q_t}{Q_\infty} = 1 - -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{h^2}\right), \tag{2}$$

where Q_t and Q_∞ are the mol% penetrant uptake at time t and infinite time, t_∞ respectively; h is the thickness of the sheet and D is the diffusion coefficient. The values of D were calculated by the iterative procedure considering the first 11 terms of Eq. (2), i.e., $n = 0$ to 10. The computed values of D are accurate to $\pm$ 0.005 units, but these are approximated to two decimal places (Table 2). Values of D were also calculated from the slopes of the initial portion of the Q_t versus $t^{1/2}$ plots determined by the method of least squares as given by Eq. (3):

$$\frac{Q_t}{Q_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{1/2}; \tag{3}$$

alternatively,

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

where θ is the slope of the initial portion of the Q_t versus $t^{1/2}$ curves. Eq. (2) is valid for large t, corresponding to Q_t/Q_∞ greater than 0.5, while the latter is a good approximation for small t, corresponding to Q_t/Q_∞ less than 0.5.

Table 2
Coefficients of sorption, S (mol%) and diffusion, D (cm^2 s^{-1}) at different temperatures

Solvent	S			$D \cdot 10^7$		
	25 °C	44 °C	60 °C	25 °C	44 °C	60 °C
BIIR						
Dichloromethane	1.53	—	—	5.79	—	—
1,2-Dichloroethane	0.39	0.56	0.84	1.96	3.31	3.80
Trichloromethane	2.96	3.23	3.04	5.00	6.37	10.00
Tetrahydrofuran	0.68	0.59	a	2.00	3.00	a
1.4-Dioxane	0.27	0.46	0.47	0.12	0.22	0.84
Tetrachloromethane	2.76	2.59	3.00	2.11	2.99	5.21
1,1,2,2-Tetrachloroethane	1.30	1.64	2.36	0.88	1.13	1.44
Cyclohexane	2.72	2.75	2.78	2.16	3.11	5.12
CSM						
Dichloromethane	1.58	—	—	11.95	—	—
1,2-Dichloroethane	1.12	1.12	1.21	4.00	6.17	7.45
Trichloromethane	1.45	1.39	1.38	6.76	9.75	11.36
Tetrahydrofuran	0.91	1.04	1.18	2.84	4.41	4.61
1,4-Dioxane	0.57	0.85	0.94	1.03	1.38	1.88
Tetrachloromethane	0.83	0.82	0.82	1.09	2.32	3.11
1,1,2,2-Tetrachloroethane	1.16	1.17	1.26	1.65	2.45	3.06
Cyclohexane	0.43	0.46	0.51	0.52	1.17	2.01
ECO						
Acetonitrile	2.07	2.05	1.91	8.00	10.98	13.85
Dichloromethane	3.82	—	—	16.44	—	—
Dimethyl sulfoxide	1.90	2.10	1.14	1.32	2.39	2.84
N,N-Dimethylformamide	2.16	2.33	1.68	3.63	6.05	4.70
2-Methoxyethanol	1.30	1.20	1.42	1.44	1.91	3.14
1,2-Dichloroethane	2.82	2.71	2.67	6.45	8.46	11.46
Trichloromethane	3.13	2.95	2.81	9.91	12.53	14.72
Tetrahydrofuran	2.94	2.87	b	5.66	6.93	b
1,4-Dioxane	2.37	2.41	2.37	2.95	4.95	6.54
Tetrachloromehane	0.58	0.71	0.75	1.39	2.15	3.15
1,1,2,2-Tetrachloroethane	2.65	2.56	2.61	2.45	3.60	4.83

[a] The polymer becomes sticky and degrades.

[b] The polymer dissolves.

A diffusion process which obeys Eq. (2) is said to be 'Fickian'. However, most generally, the liquid transport into elastomeric membranes above their glass transition temperatures, deviates slightly from the simple Fickian mechanism. Thus, the values of D obtained from Eq. (4) are good if the departure from the Fickian kinetics are much smaller. In cases, where deviations occur from the Fickian trend, it seems justifiable to use Eq. (2) to calculate the values of D because it calculates D at every point to the near-linear portion of the curves up to 55% of equilibrium sorption by the method of iteration [8].

The permeability coefficients, P have been calculated from the simple empirical relation: $P = DS$, where S (in g g^{-1}) is the sorption coefficient which is the maximum

saturation sorption value, Q_∞ (in mol%) as obtained from the plateau regions of the sorption curves. Permeability is thus a combination of diffusion (kinetic) and sorption (thermodynamic) processes. The calculated values of P are included in Table 3. In the calculation of P, the values of S are taken in the units of $g\,g^{-1}$ instead of mol%.

3.2. Sorption mechanism

As a further test to know the existence of Fickian or non-Fickian-type mechanisms in rubbery polymeric systems, Alfrey et al. [17] suggested the following empirical relation:

$$Q_t/Q_\infty = Kt^n, \tag{5}$$

Table 3
Coefficients of permeation, P ($cm^2\,s^{-1}$) and values of the exponent n of Eq. (5)

Solvent	$P \cdot 10^7$			n		
	25 °C	44 °C	60 °C	25 °C	44 °C	60 °C
BIIR						
Dichloromethane	7.52	—	—	0.56	—	—
1,2-Dichloroethane	0.75	1.82	3.17	0.51	0.53	0.55
Trichloromethane	17.66	24.57	36.24	0.65	0.66	0.65
Tetrahydrofuran	0.99	1.28	a	0.54	0.54	a
1,4-Dioxane	0.03	0.09	0.35	0.52	0.55	0.56
Tetrachloromethane	8.92	11.92	24.01	0.64	0.64	0.67
1,1,2,2-Tetrachloroethane	1.92	3.10	5.70	0.55	0.59	0.63
Cyclohexane	4.92	7.18	11.98	0.67	0.66	0.67
CSM						
Dichloromethane	16.01	—	—	0.66	—	—
1,2-Dichloroethane	4.45	6.86	8.93	0.64	0.62	0.62
Trichloromethane	11.69	16.18	18.74	0.67	0.67	0.67
Tetrahydrofuran	1.86	3.30	3.91	0.75	0.62	0.62
1,4-Dioxane	0.52	1.03	1.55	0.57	0.59	0.61
Tetrachloromethane	1.38	2.93	3.94	0.62	0.63	0.62
1,1,2,2-Tetrachloroethane	3.23	4.80	6.46	0.63	0.64	0.65
Cyclohexane	0.19	0.45	0.86	0.58	0.60	0.59
ECO						
Acetonitrile	6.79	9.23	10.84	0.59	0.61	0.61
Dichloromethane	53.26	—	—	0.72	—	—
Dimethyl sulfoxide	1.95	3.93	2.52	0.60	0.59	0.56
N,N-Dimethylformamide	5.73	10.30	5.78	0.63	0.63	0.57
2-Methoxyethanol	1.43	1.75	3.39	0.57	0.58	0.59
1,2-Dichloroethane	18.01	22.68	30.27	0.68	0.68	0.66
Trichloromethane	36.97	44.14	49.42	0.69	0.68	0.70
Tetrahydrofuran	11.98	14.34	b	0.66	0.67	b
1,4-Dioxane	6.16	10.49	13.63	0.65	0.64	0.65
Tetrachloromethane	1.23	2.35	3.65	0.54	0.58	0.54
1,1,2,2-Tetrachloroethane	10.89	15.44	21.12	0.66	0.66	0.66

[a] The polymer becomes sticky and degrades.
[b] The polymer dissolves.

where K and n are the characteristic system parameters which are evaluated from the least-squares procedure. The numerical values of the exponent n are suggestive of the type of transport phenomenon. For instance, if $n = 1/2$, the process is called 'Fickian' or Case I and this happens when the solvent concentration is low and polymer swelling is negligible or not important. If $n = 1$, the process is referred to as 'non-Fickian' or Case II; here, the solvent concentration is high and swelling becomes important so that the solvent front is sharp and moves at a constant velocity. When both the mechanisms are operative, the value of the exponent n varies between 1/2 and 1; under these conditions, the process is termed 'anomalous'. The estimated values of n for all the polymer–liquid systems are given in Table 3. Table values of n are accurate to ± 0.01 units.

3.3. Arrhenius parameters

With an increase in temperature, the average inter-chain distance between polymer segments is increased and hence, the molecular interactions between the neighboring polymer segments is minimized, thereby resulting in higher transport. Therefore, the temperature-dependent transport coefficients (D and P) have been analyzed by using the Arrhenius equation:

$$X = X_o \exp(-E_X/RT), \tag{6}$$

where X refers to D or P and X_o is the pre-exponential term D_o or P_o. The activation energy values, E_X, represent E_D or E_P for the process of diffusion or permeation, respectively; T is the temperature in Kelvin and R is the universal molar gas constant.

The heat of sorption is calculated from the difference: $\Delta H_S = E_P - E_D$. The quantity, ΔH_S is a composite parameter involving both the Henry's law and the Langmuir (hole-filling)-type sorption mechanisms. The Henry's law requires both the formation of a hole in the polymer matrix and the transport of the liquid molecule into that hole. The formation of such a hole requires an endothermic contribution. On the other hand, with the Langmuir mode, the holes already exist within the polymer matrix and consequently, sorption by hole filling gives exothermic heat of sorption giving negative values of ΔH_S.

Alternatively, it is also possible to obtain ΔH_S directly from a thermodynamic consideration i.e., by the use of van't Hoff equation from the thermodynamic equilibrium constant values, K_S for the sorption process as [18]

$$\ln K_S = \Delta S/R - \Delta H_S/RT. \tag{7}$$

The values of K_S are the sorption coefficients. The entropy of sorption, ΔS and enthalpy of sorption, ΔH_S are obtained from the least-squares estimations using Eq. (7).

4. Discussion

4.1. Bromobutyl rubber (BIIR)

The sorption results of BIIR with dichloromethane, trichloromethane, tetra-chloromethane, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane at 25 °C are given in

Fig. 1. The values of S at 25 °C, 44 °C and 60 °C as obtained from the plateau regions of the sorption curves are given in Table 2. Due to the low boiling point of dichloromethane, the sorption data at higher temperatures are not obtained. The experimental results of molecular interactions between the polymer chain segments and the permeating molecules may be satisfactorily explained in terms of the solubility instead of the size and nature of the permeating molecules. Solubility is more dependent on the compatibility of the functional groups, which make up the material and the permeating chemical, than merely on the size of the chemical. On the other hand, diffusion coefficient values are more dependent on the molecular size of the permeating chemical. However, there is an interaction between solubility and diffusivity, and in describing this interaction, the concentration dependence of D also must be considered. As the concentration of the permeant in the polymer increases, the average inter-chain distance between the polymer chain segments also increases thereby the molecular interactions between the neighboring polymer segments are minimized, resulting in a higher transport.

Keeping the above facts in mind, if we look at a series of chemicals that have similar functional groups (similar solubility in BIIR), then as the size of the molecule increases, the diffusion coefficient will decrease. If the permeating chemicals have widely differing solubility (but similar size) in the given polymer, then the chemical which is more soluble will swell the polymer more, thus increasing its transport, e.g., the trichloromethane is much more soluble than 1,2-dichloroethane in BIIR. Even though they have the same size, the trichloromethane has a higher D because the BIIR is swollen more. On the other hand, the di-, tri- and tetra-chloromethanes have the same functional groups, their molecular sizes determine the D. The larger the molecule in this series, the smaller the D. Thus, it appears that the transport results are not
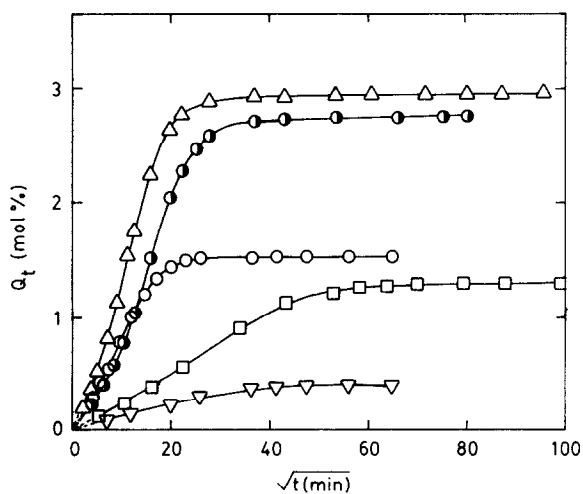

Fig. 1. Sorption plots for bromobutyl rubber with (○) dichloromethane, (△) trichloromethane, (●) tetra-chloromethane, (▽) 1,2-dichloroethane, and (□) 1,1,2,2-tetrachloroethane at 25 °C.

alone influenced by the penetrant size, but the polymer–penetrant interactions also play an important role. This is further indicative from the slight sigmoidal nature of the sorption curve for trichloromethane and tetrachloromethane presented in Fig. 1. The extent of sigmoidal shape decreases with a decrease in the solubility of the liquid in the BIIR membrane. Due to the structural similarity between tetrachloromethane and trichloromethane, the shapes of the sorption curves are also almost identical (Fig. 1). The slightly higher sorption for trichloromethane than tetrachloromethane may be due to its higher solubility parameter value.

The time to reach equilibrium sorption depends on the type of the penetrant molecule in the particular system. For instance, dichloromethane, trichloromethane and tetra-chloromethane with nearly spherical shapes exhibit almost identical times ($\sim$21 h) to attain the equilibrium saturation. On the other hand, elongated 1,1,2,2-tetra-chloroethane and 1,2-dichloroethane molecules require 74 and 54 h, respectively. The sorption of cyclohexane, tetrahydrofuran (THF) and 1,4-dioxane into BIIR at 25 °C are displayed in Fig. 2. Tetrahydrofuran at 60 °C tends to degrade the BIIR membrane and hence, the sorption experiments at this temperature were not performed. The sorption of 1,4-dioxane is extremely slow at 25 °C as it did not reach equilibrium even after 17 days of continuous immersion. However, at 44 °C and 60 °C, the approach to equilibrium sorption is considerably fast and saturation is achieved within 200 and 65 h respectively. Cyclohexane is a saturated molecule with an axis of symmetry about the center of the molecule very much like the point of symmetry about tetrachloromethane. The two solvents exhibit zero dipole moments and their solubility parameter values are 16.8 and 17.5 $J^{1/2}$ cm$^{-3/2}$, respectively. Thus, cyclohexane and tetrachloromethane have almost identical solubility and diffusivity; even the equilibrium saturation times for these pene-trants are nearly identical ($\sim$21 h). On the other hand, the time to attain equilibrium saturation with cyclohexane is quite shorter than required for THF or 1,4-dioxane (Fig. 2).
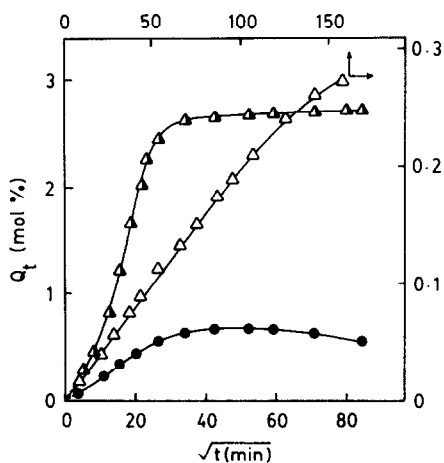

Fig. 2. Sorption plots for bromobutyl rubber with ($\bullet$) tetrahydrofuran, ($\triangle$) 1,4-dioxane and ($\blacktriangle$) cyclo-hexane at 25 °C.

From the temperature-dependent sorption data given in Table 2, we notice that sorption generally increases with increasing temperature but, in case of trichloromethane and THF, sorption decreases with increasing temperatures. This is attributed to two possibilities: one is that at 60 °C, the polar trichloromethane might interact with the BIIR chain segments more aggressively than at ambient temperature thereby extracting out the indigenous additive compounds resulting in a further weight loss of the polymer. The second effect (but not the remote possibility) is that the permeating chemicals plasticize the polymer, reducing the glass-transition temperature and thus reducing the crystallinity within the polymer [9, 19].

For tetrachloromethane, the S values at 44 °C are lower than at 25 °C but, at 60 °C, these increase further; one possible explanation for this effect is that the morphology of the polymer film were such that imperfections such as microvoids and irregularities within the polymer might have resulted in the reduced effectiveness of the sample drying technique. The other possibility is extraction of the additives from the polymer as stated before and, this was also verified from the desorption experiments. Among the penetrants considered for BIIR, trichloromethane shows the highest solubility, while 1,4-dioxane exhibits the least; however, the long-term sorption data of the latter are not available to justify this statement. The increase in S with temperature for other systems follows the conventional wisdom that free volume of the system increases with temperature, thereby absorbing larger quantities of the liquids within the available free volume spaces. A typical plot of the temperature dependence of sorption is shown in Fig. 3 for BIIR with 1,2-dichloroethane and 1,4-dioxane.

The permeability results are given in Table 3. Due to the large differences in the sorption values of dichloromethane and trichloromethane, the permeability coefficients, P of the latter are quite higher than the former. Similarly, the permeability coefficients of 1,2-dichloroethane are quite smaller than 1,1,2,2-tetrachloroethane for the same reasons. Thus, the trend in the variation of P values is not identical to those of D in case of di-, tri- and tetra-chloroalkanes. The values of P for all liquids increase with increasing temperature. The values of n vary from a minimum of 0.51 to a maximum of 0.67 indicating that the molecular transport mechanism deviates slightly from the simple Fickian mode, but is still close to the Fickian mode. Based on the earlier arguments [6–14], the transport mechanism is classified to be of anomalous-type.

4.2. Chlorosulfonated polyethylene (CSM)

The sorption results of CSM membrane with chloroalkanes at 25 °C are presented in Fig. 4. It is obvious that the shape and the size of the liquids have no significant effect on the sorption. The varied trends of sorption and diffusion of chloroalkanes by CSM may be attributed to the combined effect of size, shape and polarity of the solvents; each of these factors contributing toward the extent of liquid–membrane interaction. The 1,2-dichloroethane and 1,1,2,2-tetrachloroethane have almost identical solubility parameter values and hence, their solubilities in CSM are also similar (Fig. 4). The sorption curve for 1,1,2,2,-tetrachloroethane is slightly more sigmoidal when compared to 1,2-dichloroethane; thus, D is more concentration dependent in this case.
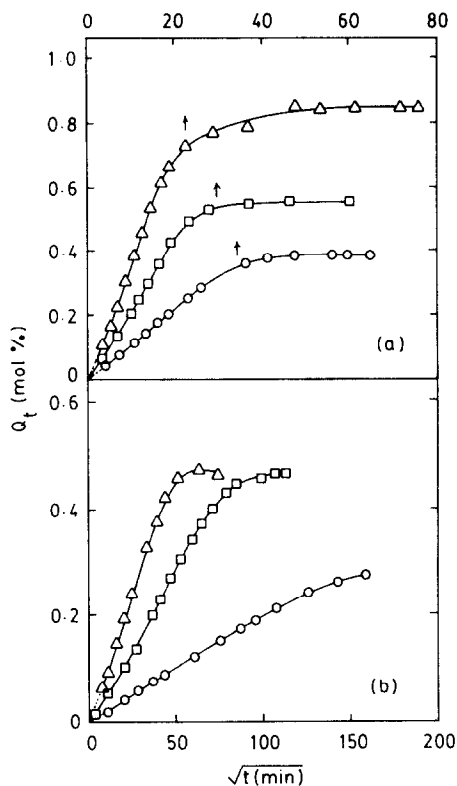
Fig. 3. Sorption plots for bromobutyl rubber with (a) 1,2-dichloroethane and (b) 1,4-dioxane at (○) 25 °C, (□) 44 °C and (△) 60 °C.

The diffusion coefficients of 1,1,2,2-tetrachloroethane are quite smaller than 1,2-dichloroethane. Dichloromethane, the smallest of all the chloroalkanes, exhibits high sorption and diffusion coefficients. However, trichloromethane has a higher D than 1,2-dichloroethane. The 1,2-dichloroethane due to its elongated shape, moves slower than trichloromethane (comparatively a spherical molecule). Tetrachloromethane and cyclohexane, due to their low solubility parameter values, also exhibit lower sorption than other liquids. The diffusion coefficient values of di-, tri- and tetra-chloroalkanes decrease with their increasing molecular sizes. The times required to reach equilibrium sorption also vary depending on the nature of the penetrant molecules.

The sorption results of tetrahydrofuran, 1,4-dioxane and cyclohexane at 25 °C are presented in Fig. 5. It is observed that for tetrahydrofuran, sorption decreases after attaining equilibrium saturation which is attributed to the highly interactive nature of THF with the CSM chain segments and thereby, also extracting out the additives from the polymer at longer immersion times. The sorption of cyclohexane is lower than 1,4-dioxane probably due to its lower solubility parameter value, but their diffusivity trends are dependent on the molecular sizes except at 60 °C. With an increase in temperature, the sorption of trichloromethane and tetrachloromethane
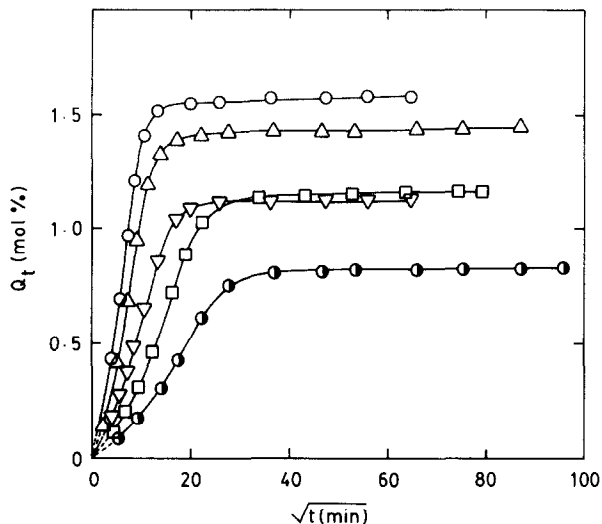
Fig. 4. Sorption plots for chlorosulfonated polyethylene with chloroalkanes at 25 °C (with the solvent symbols as shown in Fig. 1).
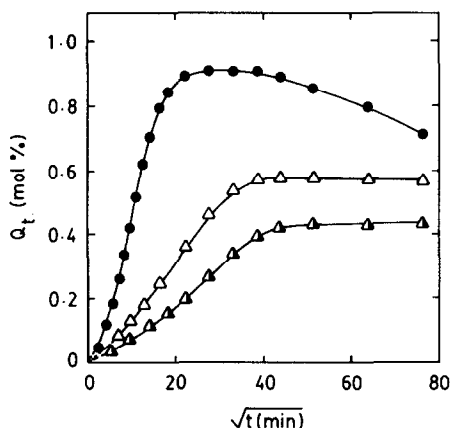

Fig. 5. Sorption plots for chlorosulfonated polyethylene with non-chlorinated liquids at 25 °C (with the solvent symbols as shown in Fig. 2).

with the CSM membrane decreases. However, with other liquids, the S values increase with increasing temperature.

The values of the exponent n of Eq. (5) given in Table 3 fall between 0.57 and 0.75, indicating the anomalous-type sorption transport. The Arrhenius parameters, i.e. $(E_D, E_P, \Delta H_S$ and $\Delta S)$ given in Table 4 do not follow any systematic trend with the size or shape of the liquid molecules. The values of E_D and E_P vary almost in an identical manner for the liquid–CSM systems. The ΔH_S values of trichloromethane and

Table 4

Activation parameters for diffusion and permeation (E_D and E_P in kJ mol^{-1}), enthalpy of sorption (ΔH_S in kJ mol^{-1}) and entropy of sorption (ΔS in J deg^{-1} mol^{-1})

Solvent	E_D	E_P	ΔH_S	ΔS
BIIR				
1,2-Dichloroethane	15.88	34.09	18.21	14.72
Trichloromethane	16.03	16.80	0.77	− 26.52
1,4-Dioxane	44.92	58.34	13.42	− 3.69
Tetrachloromethane	21.04	22.78	1.73	− 24.31
1,1,2,2-Tetrachloroethane	11.66	24.45	13.79	9.89
Cyclohexane	20.18	20.72	0.54	− 28.18
CSM				
1,2-Dichloroethane	14.88	16.53	1.66	− 1.85
Trichloromethane	12.41	11.27	− 1.14	− 39.06
Tetrahydrofuran	11.80	17.90	6.10	− 18.67
1,4-Dioxane	14.14	25.97	11.83	− 2.96
Tetrachloromethane	25.15	25.03	− 0.11	− 40.27
1,1,2,2-Tetrachloroethane	14.64	16.39	1.75	− 31.27
Cyclohexane	32.23	35.91	3.69	− 32.99
ECO				
Acetonitrile	12.97	11.12	− 1.85	− 38.35
Dimethyl sulfoxide	18.51	7.32	− 11.19	− 69.60
N,N-Dimethylformamide	6.89	1.47	− 5.42	− 49.55
2-Methoxyethanol	18.07	19.73	1.65	− 30.84
1,2-Dichloroethane	13.44	12.11	− 1.33	− 34.16
Trichloromethane	9.37	6.88	− 2.49	− 37.15
1,4-Dioxane	18.94	18.93	− 0.02	− 31.12
Tetrachloromethane	19.33	25.73	6.40	− 21.25
1,1,2,2-Tetrachloroethane	16.07	15.56	− 0.51	− 31.74

tetrachloromethane are negative while, for the remaining liquids, these are positive. The entropy results are negative for all the liquids.

4.3. Epichlorohydrin membrane (ECO)

The sorption results of ECO membrane with chloroalkanes at 25 °C are presented in Fig. 6. Among the chloroalkanes considered, dichloromethane at 25 °C exhibits the highest sorption while, the tetrachloromethane shows the least. The solubility of trichloromethane is higher than 1,1,2,2-tetrachloroethane and 1,2-dichloroethane. The time needed to attain the equilibrium sorption follows the sequence: $CCl_4 > CHCl_2CHCl_2 > CH_2ClCH_2Cl > CHCl_3 > CH_2Cl_2$. For the chloroalkanes used, the values of S decrease with increasing temperature except for tetrachloromethane and 1,1,2,2-tetrachloroethane. The sorption results of THF, 1,4-dioxane, 2-methoxyethanol, acetonitrile, dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) are presented in Fig. 7. The 2-methoxyethanol and DMF seem to interact with the chain segments of ECO membrane at 25 °C as evidenced by a slight
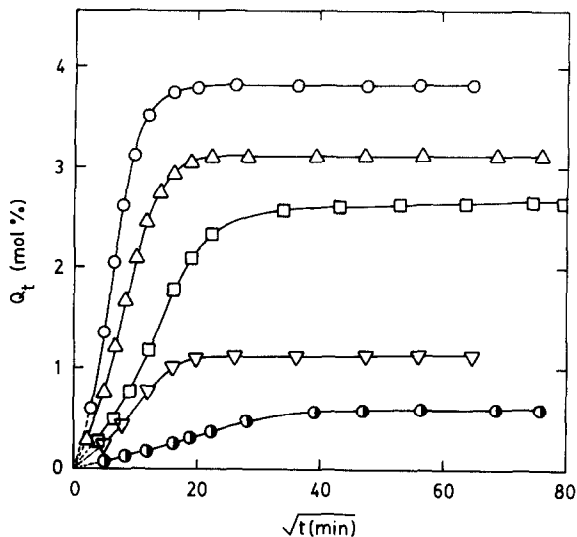
Fig. 6. Sorption plots for epichlorohydrin with chloroalkanes at 25 °C (with the solvent symbols as shown in Fig. 1).
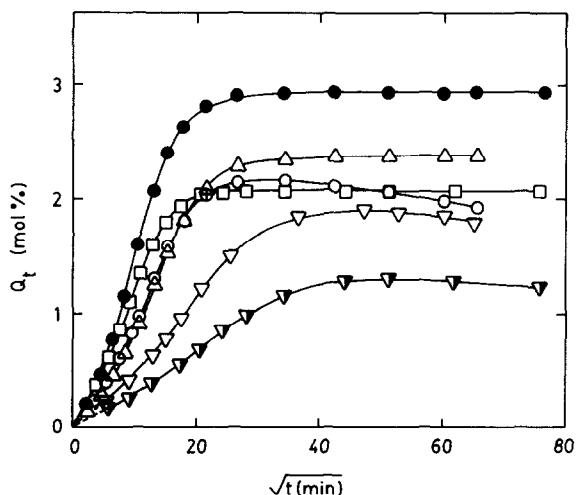

Fig. 7. Sorption plots for epichlorohydrin with (□) acetonitrile, (▽) dimethyl sulfoxide, (○) N,N-dimethylformamide, (▼) 2-methoxyethanol, (●) tetrahydrofuran and (△) 1,4-dioxane at 25 °C.

decrease in the sample weight after equilibrium saturation; similarly, for THF, the sorption experiments at 60 °C are not performed due to its high interaction with ECO segments.

The solubility parameter values of the liquids do not seem to be the controlling factors in determining their transport behaviors with the polar ECO membrane. For

instance, DMF and DMSO having almost identical values of solubility parameters ($\delta \cong 25$ J$^{1/2}$ cm$^{-3/2}$) exhibit different values of S and D. The higher values of S and D for DMF than DMSO is probably attributed to its chemical interactions. The DMF seems to extract out the indigenous additives from the ECO membrane as is indicated by a decrease in the sorption after complete saturation, thus exhibiting its aggressiveness towards ECO membrane. However, DMSO transports much slower than the other liquids and its saturation time is ~ 37 h. The sorption and diffusion of dichloromethane is higher than acetonitrile; but, their solubility parameter values are also quite different (see Table 1). The DMF, 2-methoxyethanol, 1,2-dichloroethane, trichloromethane and THF have the molar volumes ranging from 77 to 82 cm^3 mol^{-1}, but these liquids exhibit quite different diffusion coefficients; this is again attributed to the differences in chemical interactions between these liquids and the polar ECO membrane.

The affinity of the polar ECO membrane towards the cyclic ethers, viz., tetrahydrofuran and 1,4-dioxane as indicated in Fig. 7 is different and the diffusion data of these liquids is dependent on their sizes. However, the negligible chemical interactions of 2-methoxyethanol with ECO membrane leads to smaller values of S and D. Moreover, 2-methoxyethanol requires $\cong 40$ h to attain equilibrium sorption, while acetonitrile attains saturation at ~ 10 h. Initially, DMF and 1,4-dioxane exhibit almost identical sorption pattern (see Fig. 7) probably because both are cyclic molecules with negligible molecular size differences. The values of D show a systematic increase with temperature for all the solvents with ECO membrane except DMF for which a reverse tendency is observed at 60 °C. A dependence of D on the molecular size is observed only in case of dichloromethane, trichloromethane and tetrachloromethane. The results of permeability coefficient follow a different trend than those of the diffusivity, because of differences in solubility of permeants.

The activation parameter values given in Table 4 do not follow any systematic trend with the molar volumes of the liquids. However, ΔH_S values are positive for ECO with 2-methoxyethanol and tetrachloromethane suggesting Henry's-type sorption. For the remaining solvents, ΔH_S values are negative suggesting the Langmuir-type sorption. The estimated values of ΔS are negative for all the solvent–polymer systems.

4.4. Concentration dependence of diffusivity

Solvent transport into polymer membranes is governed by the structure of both the liquid molecules and the membrane materials. Diffusivity is dependent on concentration in the polymer due mainly to swelling. The results of D versus concentration (C) at 25 °C for the BIIR and CSM membranes with the haloalkanes are presented in Fig. 8 ((a) and (b), respectively). It is noticed that for high swelling liquids like di-, tri- and tetra-chloroalkanes, the D increases exponentially up to 55 wt% of liquid concentration showing a considerable dependence of D on concentration. For the elongated 1,2-dichloroethane and 1,1,2,2-tetrachloroethane molecules, the dependence of D on C is not considerable (Fig. 8(a)). The exponential increase of D with concentration for some liquid–polymer systems is further confirmed by the slightly sigmoidal shapes of
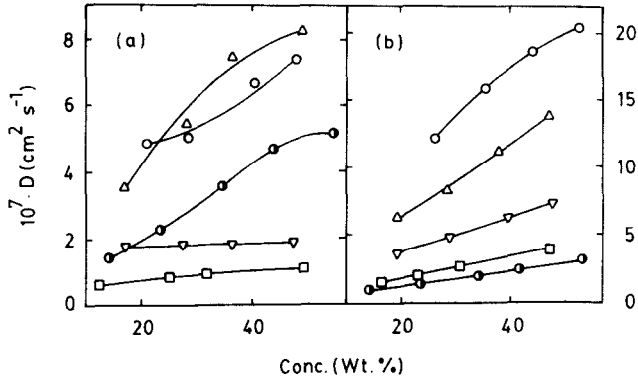
Fig. 8. Concentration dependence of diffusivity at 25 °C for (a) BIIR with chloroalkanes, (b) CSM with chloroalkanes. Symbols same as in Fig. 1.
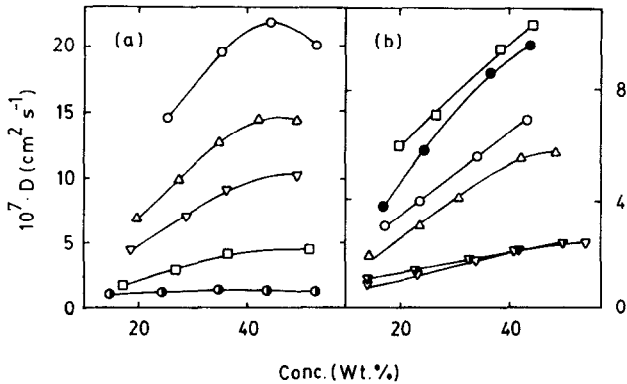

Fig. 9. Concentration dependence of diffusivity at 25 °C for ECO with (a) chloroalkanes (with solvent symbols as shown in Fig. 1) and (b) non-chlorinated liquids (with the solvent symbols as shown in Fig. 7).

the sorption curves. This trend is slightly reversed when the barrier material is changed to CSM as shown in Fig. 8(b) wherein, we see a lesser dependence of D on C for tetrachloromethane and 1,1,2,2-tetrachloroethane. However, a considerable dependency is observed for dichloromethane and trichloromethane.

Fig. 9(a) and (b) presents the concentration dependence of diffusivity results at 25 °C in case of ECO with chloroalkanes (Fig. 9(a)) and non-chlorinated liquids (Fig. 9(b)). In Fig. 9(a), the magnitude of concentration dependency with diffusivity varies in the order: dichloromethane > tichloromethane > 1,2-dichloroethane > 1,1,2,2-tetrachloroethane > tetrachloromethane. However, with the other liquids, except 2-methoxyethanol and DMSO, the dependence is quite sharp (Fig. 9(b)). These dependencies are consistent with the swelling behaviors of the liquid–polymer systems.

4.5. Volume dilation, interaction parameter and molar mass between cross-links

In view of the observed polymer swelling in the presence of some solvents, the percent volume dilations, $\Delta V\%$ of the polymers were calculated [8] and these results are given in Table 5. It is observed that cyclohexane shows the highest swelling i.e., $\Delta V\% \cong 309$ and 245, respectively, for BIIR and CSM membranes. However, in case of ECO membrane, 1,1,2,2-tetrachloroethane shows the highest swelling ($\Delta V\% \cong 411$). The least swelling is seen in case of 1,4-dioxane with BIIR and CSM membranes, whereas for ECO membrane, tetrachloromethane shows the least swelling. The intermediate swelling values are observed for all the remaining solvents. These volume dilation data are also in consistence with the sigmoidal shapes of the sorption curves, i.e., a more sigmoidal shape is observed for those solvents which exhibit the

Table 5
Percent volume increase, $\Delta V\%$, interaction parameter, χ and molar mass between crosslinks, $\bar{M}_C$ for polymer + liquid systems at 25 °C

Solvent	$\Delta V\%$	χ	$\bar{M}_C$
BIIR $[\delta_p = 17.5 (\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2})]$			
Dichloromethane	108	0.532	1175
1,2-Dichloroethane	35	0.542	258
Trichloromethane	253	0.461	5293
Tetrahydrofuran	51	—	—
1,4-Dioxane	28	—	—
Tetrachloromethane	287	0.340	4257
1,1,2,2,-Tetrachloroethane	152	0.620	8560
Cyclohexane	310	—	—
CSM $[\delta_p = 20.1 (\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2})]$			
Dichloromethane	140	0.341	1174
1,2-Dichloroethane	129	0.340	1192
Trichloromethane	165	0.353	1873
Tetrahydrofuran	77	—	—
1,4-Dioxane	67	—	—
Tetrachloromethane	106	0.597	3471
1,1,2,2,-Tetrachloroethane	181	0.340	2552
Cyclohexane	245	—	—
ECO $[\delta_p = 20.1 (\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2})]$			
Acetonitrile	156	—	—
Dichloromethane	330	0.341	4679
Dimethyl sulfoxide	185	—	—
N,N-Dimethylformamide	174	—	—
2-Methoxyethanol	131	—	—
1,2-Dichloroethane	318	0.340	4932
Trichloromethane	346	0.353	6414
Tetrahydrofuran	284	—	—
1,4-Dioxane	276	—	—
Tetrachloromethane	81	0.597	1641
1,1,2,2-Tetrachloroethane	411	0.340	9479

highest $\Delta V\%$ value and these in turn, also exhibit considerable concentration dependency.

Realizing the fact that sorption is influenced by the polymer morphology in addition to other experimental variables mentioned before, attempts have been made to estimate the molar mass between cross-links, $\bar{M}_C$ from the swelling results. The interaction parameter, χ needed in the estimation of $\bar{M}_C$ has been calculated as [20].

$$\chi = \beta + \frac{V_S}{RT}(\delta_S - \delta_p)^2, \tag{8}$$

where V_S and δ_S are, respectively, the molar volume and solubility parameter of the solvents, β is a lattice constant whose value is taken to be 0.34 and RT is the energy term. To calculate χ, the solubility parameter of the polymer, δ_p needs to be estimated and this was calculated by the procedure suggested by Gee [21] and Takahashi [22]. The values of δ_p were obtained by this procedure which were used in the calculation of $\bar{M}_C$ from the Flory and Rehner theory [23]. The values of χ and $\bar{M}_C$ obtained by this procedure are given in Table 5.

Generally, the values of $\bar{M}_C$ show an increasing trend with the increasing size of the chloroalkanes with a few exceptions. Because the nature of the cross-linked system is understood either in terms of $\bar{M}_C$ or in terms of its reciprocal value, which will be indicative of the cross-link density, it is evident that the cross-link density decreases with an increase in the size of the penetrant molecules. The calculated $\bar{M}_C$ values for BIIR and CSM membranes with dichloromethane are almost equal (1175). On the whole, the $\bar{M}_C$ values are in the range 258–8560 for BIIR, 1174–3471 for CSM and 1641–9479 for ECO. The values of $\bar{M}_C$ for the non-chlorinated liquids are not reported due to the difficulty in calculating the χ values for these liquids by the method of Gee [21]. It may be noted that the cross-link density of a polymer is an intrinsic property, in which case it should remain constant. However, in the present case, we are referring to the chain-entanglement-cross-link which would generally decrease with increasing penetrant size. At any rate, the estimation of $\bar{M}_C$ values from the Flory–Rehner theory has limited applications and the values presented here may be regarded as approximate.

5. Conclusions

The present paper addresses the usefulness of a sorption gravimetric technique to assess of the chemical compatibility of bromobutyl rubber, chlorosulfonated polyethylene and epichlorohydrin memberanes against some selected hazardous liquid media. The sorption, diffusion and permeation coefficients have been determined for the polymer–liquid systems. The diffusivity data of the systems have shown the dependence on the size of the penetrant molecules. While this information is important in predicting the behavior of the polymer membranes, it does not provide practical information for selecting the appropriate barrier membranes in field conditions where there are complex mixtures of hazardous liquids.

The results of the present study might primarily help the manufacturers of rubbers to determine the performance of suitable candidate materials as membranes against organic liquids utilizing the Fickian diffusion relationships and the Arrhenius temperature behavior. Environmental sensitivity of the candidate material must be assessed under conditions of temperature, hostile solvent media and polymer morphology that simulate the actual field usage. Failure of a material in this context can severely limit the range of applicability of a membrane material that otherwise has outstanding properties. More research in the practical utility of these membranes in actual field conditions is necessary.

Acknowledgements

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