Experimental and Simulation Studies on Molecular Transport of Substituted Monocyclic Aromatic Liquids into Fluoropolymer Sheet Membranes: Liquid Structure–Diffusion, –Sorption, and –Permeation Relationships

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ABSTRACT: The present study reports an investigation on the molecular transport of 10 monocyclic aromatic liquids (benzene, chlorobenzene, 1,2-dichlorobenzene, bromobenzene, toluene, *p*-xylene, trimethylbenzene, ethylbenzene, methoxybenzene, and ethoxybenzene) at 40 and 50°C through sheet polymeric membranes (FLS-2650) using a sorption gravimetric technique. Diffusion and permeation coefficients of these liquids were calculated from the sorption data using Fick's diffusion equation. Sorption results were analyzed typically in the case of benzene and chlorobenzene to compute the concentration profiles at different depths along the thickness direction of the sheet membranes and at different time intervals by solving the Fick's equation under appropriate boundary conditions, based on the numerical simulation method developed in "C" language using a finite-difference method. Transport results were analyzed to establish the relationships between the penetrating liquid structures with diffusion, permeation, and sorption data. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 991–996, 2004

Key words: diffusion; sorption; Fick's law; concentration profiles; simulation

INTRODUCTION

Molecular transport of organic liquids into polymeric sheet membranes has been the subject of increasing practical utility in petrochemical and process engineering areas.[1–4] The resistivity of a polymeric membrane under specified applications can be judged from its sorption/permeation characteristics toward hostile environments constituting organic liquids.[5] Commercial sheet membranes available presently in the market are mainly developed by the Du Pont and 3M companies for a variety of applications. However, before seeking their end applications, it is important to understand their interactions with the aggressive aromatic organic liquids to study their chemical resistivity and dimensional stability in the presence of such media. The organic media chosen in this study included monocyclic aromatics, such as benzene, chlorobenzene, 1,2-dichlorobenzene, bromobenzene, toluene, *p*-xylene, trimethylbenzene, ethylbenzene,

methoxybenzene, and ethoxybenzene, because these are the most widely used solvents in petrochemical industries.

The commercially available fluoropolymer (Fluorel™, FLS-2650) membrane developed by 3M Company (St. Paul, MN) exhibits a unique combination of high temperature and both chemical and electrical resistance properties. These elastomers are designed for use in molded goods and extruded shapes where compression-set resistance as well as gas (e.g., nitrogen and carbon dioxide) blistering and antiextrusion resistance is important. These polymers are used as O-rings, seals in hydraulic and brake systems, jet engines, cable clamps, hoses, and pipeline patches. Their good property retention and moderate volume swell prompted us to undertake their resistivity toward the chosen organic media.

In previous studies from this laboratory,[4–15] we reported different aspects of diffusion anomalies for several polymer/solvent systems. In continuation of these studies, we present here sorption (*S*), diffusion (*D*), and permeation (*P*) characteristics of these liquids at 40 and 50°C to understand the structure–diffusion, –sorption, and –permeation relationships through the Fluorel™ FLS-2650 membrane, which is a terpolymer derived from tetrafluoroethylene, propylene, and difluoromethylene (developed by the 3M Company). In previous literature, no such data are available on these

membranes and thus the present study was undertaken. The concentration-independent diffusion coefficients were calculated from Fick's equation using the experimentally obtained sorption results. Furthermore, Fick's equation was solved under the suitable boundary conditions to compute the concentration profiles in the case of only two typical liquids (benzene and chlorobenzene) based on the finite-difference method[16] as a function of liquid penetration distance (depth) and immersion time. The simulation program was developed in "C" language. The program is of a general nature and can also be used for other liquids.

EXPERIMENTAL

Materials

Fluorel™ FLS-2650 in powder form was mixed with curatives, fillers, and other compounding ingredients on a conventional two-roll mill or by internal mixing methods. In a typical formulation, peroxide and coagent are preblended with dry powders before being added to FLS-2650. Care should be taken to avoid mixing temperatures above 121°C. After mixing, the stock solution should be cooled rapidly by either air or water-cooling technique. Mixed catalyzed compound (cure-incorporated) should be stored in a cool and dry place before use. Polymer compositions along with some of their representative physical/mechanical properties were previously published.[12]

FLS-2650 grade fluoroelastomer membranes (550 × 300-mm slabs) with the initial thickness ranging from 0.218 to 0.245 cm were obtained from 3M Industrial Chemical Products Division (St. Paul, MN; a generous gift from Nena McCallum). Circular disc-shape samples (diameter: 19.80 mm) were cut from large sheets using a sharp-edge carbon-tip steel die. The cut samples were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for at least 24 h before use. The samples were then soaked in screw-tight test bottles containing 15–20 cm^3 of the liquids maintained at the desired temperature (±0.5°C) in an electronically controlled hot-air incubator (WTB Binder, Tuttilgen, Germany). Polymer samples were removed periodically, the solvent drops adhering to the surface were wiped off using filter paper wraps, and samples weighed immediately on a digital Mettler balance (Model AE 240; Mettler, Greifensee, Switzerland) within the accuracy of ±0.01 mg. Other experimental details are the same as published earlier.[4–15] Reagent-grade benzene, chlorobenzene, 1,2-dichlorobenzene, bromobenzene, toluene, p-xylene, trimethylbenzene, ethylbenzene, methoxybenzene, and ethoxybenzene were procured from S.D. Fine Chemicals (Mumbai, India).

Sorption experiments

The initial mass of the cut polymer sample was taken on a single-pan digital microbalance (model AE 240,

Mettler) sensitive to ±0.01 mg. Polymer samples were placed inside the specially designed airtight test bottles containing 20 cm^3 of the test solvent. Test bottles were placed inside the oven maintained at the constant desired temperature. Mass of the samples was determined at selected time intervals by removing them from the test bottles and wiping the surface-adhering liquid droplets by gently pressing in between filter paper wraps; samples were again placed back into the oven. To minimize solvent evaporation losses, this step was completed within 15–20 s. All the samples reached equilibrium sorption within 48 h, which remained steady over an extended period of 1 or 2 days. After the completion of sorption experiments, percentage mass uptake M_t of the samples at time t was calculated using the experimental gravimetric sorption data as

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

where W_t is mass of the membrane at different time intervals and W_0 is the initial dry mass of the sample. Results of sorption (in mass %) obtained gravimetrically at 40 and 50°C are presented in Table I.

RESULTS AND DISCUSSION

Sorption kinetics

A fundamental understanding of the interactions between penetrating liquid molecules and the polymer membrane material is necessary to judge the end utility of the polymer in adverse industrial applications. Sorption increases with increasing temperature in all cases. To understand the nature of the sorption mechanism, we fitted the experimental mass uptake data (M_t/M_∞) of the liquids to the following equation[4–15]:

$$\frac{M_t}{M_\infty} = kt^n \qquad (2)$$

where M_∞ represents the equilibrium mass uptake by the membrane, k is a parameter that represents the nature of interactions between the membrane polymer and the liquid molecules, whereas the exponent value n indicates the nature of the transport mechanism. For Fickian transport, $n = 0.5$, whereas $n = 1.0$ for non-Fickian transport. The values of M_∞ in mass % were converted into mol % by taking the asymptotic (saturation) region of the sorption curves. These values were fitted to eq. (2) to estimate the values of k and n by the least-squares method. It was found that n values at both temperatures for all the liquids vary between 0.50 and 0.55, indicating the Fickian mode of diffusion. The results of k increase with increasing temperature in all cases, suggesting the increased in-

TABLE I
Transport Data on Liquids–Fluorel^{TM} (9FLS-2650) Membrane at 40° and 50°C

Liquid	V (cm^3/mol)	S (mol %)		$D \times 10^6$ (cm^2/s)		$P \times 10^6$ (cm^2/s)	
		40°C	50°C	40°C	50°C	40°C	50°C
Benzene	89.4	0.39	0.46	2.46	2.62	0.959	1.205
Chlorobenzene	102.2	0.37	0.44	1.94	2.20	0.718	0.968
Bromobenzene	106.1	0.36	0.45	1.86	2.48	0.669	1.116
Toluene	106.9	0.34	0.41	2.01	2.52	0.683	1.033
1,2-Dichlorobenzene	108.1	0.35	0.43	1.80	1.92	0.630	0.825
Methoxybenzene	110.2	0.35	0.42	1.82	1.91	0.637	0.802
Ethylbenzene	123.5	0.29	0.35	1.79	1.58	0.519	0.553
p-Xylene	123.9	0.28	0.34	1.32	1.52	0.369	0.516
Ethoxybenzene	127.3	0.28	0.35	1.21	1.42	0.338	0.497
Trimethylbenzene	139.6	0.25	0.32	0.91	1.13	0.227	0.362

teractions at higher temperature; however, these do not exhibit any systematic trends with the nature of the liquid molecules.

Diffusion and permeation

Molecular transport of liquids through polymeric membranes depends on the membrane structure, its history (such as method of preparation, polymer morphology, etc.), and the nature of the interacting molecule.[4–15] In the present study, sorption kinetics, liquid permeation rate, and diffusion anomalies of the substituted benzenes were investigated for the Fluorel (FLS-2650) membrane in an effort to establish the migrating liquid structure–diffusion, –sorption, and –permeation relationships. Thus, the concentration-dependent diffusion coefficients D were calculated using Fick's equation[17]:

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left[\frac{Dt}{\pi}\right]^{1/2} \qquad (3)$$

where h is the thickness of the membrane and M_∞ is the equilibrium mass uptake (actually the S values). Values of D calculated using eq. (3) from the initial mass uptake data (i.e., before reaching 60% of equilibrium saturation) are also included in Table I. These data follow the conventional wisdom that diffusion increases with increasing temperature. The same dependency is observed for permeability coefficients (also presented in Table I) calculated from the relationship, $P = DS$. Permeability values follow the same trends as those of diffusion and sorption values for all the liquids. Thus, a clearcut linear relationship exists between the molar volumes of liquids with sorption, diffusion, and permeation coefficients, as shown in Figure 1 at 40 and 50°C. The values of S, D, and P decrease systematically with increasing molar volumes of the liquids at both temperatures.

Simulation of concentration profiles of liquids

For the successful use of FLS-2650 membranes in engineering areas, it is essential to compute the liquid

concentration profiles of the transporting molecules across the barrier membrane. This was done by solving[5,6,16] the Fick's second-order differential equation using the appropriate boundary conditions to obtain eq. (5) to calculate the solvent uptake $C_{(x,t)}$ inside the membrane of thickness h as a function of time t and distance x using the following equation:
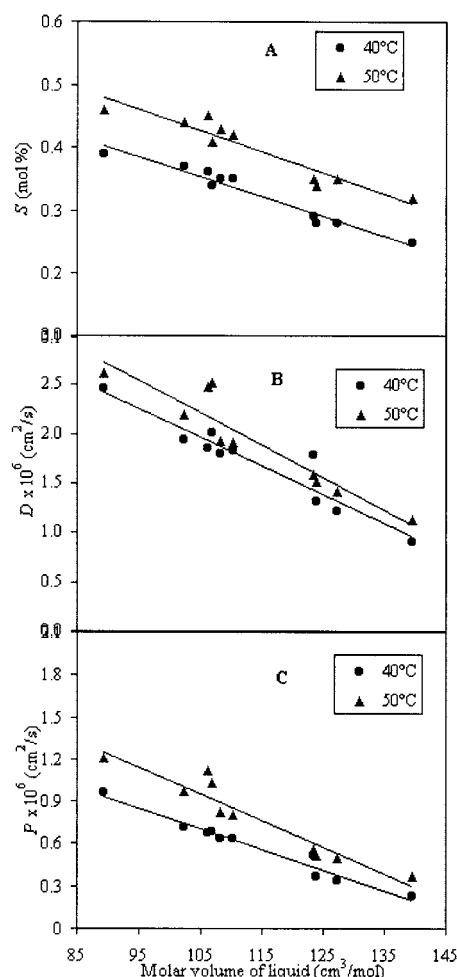

Figure 1 Molar volume of the liquids versus (A) sorption, (B) diffusion, and (C) permeation through the membrane. Symbols: (●) 40°C and (▲) 50°C.

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \quad (4)$$

$$\left(\frac{C(x,t)}{C_\infty}\right) = 1 - \frac{4}{\pi}\sum_{m=0}^{\infty}\frac{1}{(2m-1)}\exp$$

$$\left[-\frac{D(2m-1)^2\pi^2 t}{h^2}\right]\sin\left[\frac{(2m-1)\pi x}{h}\right] \quad (5)$$

In eq. (5), m is an integer and D is the diffusion coefficient (assumed to be constant) computed from eq. (3). To solve eq. (4) to obtain eq. (5), several assumptions were made[5,6,16]: (1) when a membrane is soaked in liquid media, its concentration on both sides of the membrane surface immediately reaches equilibrium; (2) the time required to attain thermal equilibrium for the membrane is negligible when compared to sorption (immersion) time; and (3) changes in membrane dimensions are negligible (i.e., negligible swelling) during the entire period of liquid immersion test. Then, by using the following boundary conditions

$$t = 0 \quad 0 < x < h \quad C = 0$$

$$t > 0 \quad x = 0, \quad x = h \quad C = C_x \quad (6)$$

we have generated the concentration profile curves typically in the case of benzene and chlorobenzene at 40 and 50°C at different exposure times for the imaginarily varying depths of liquid penetration into the membranes. Profiles of concentration were simulated using the "C" program written from the theory proposed by Vergnaud.[16]

Numerical solutions of eq. (5) are approximate. However, in the present study, the finite-difference method[16] was used wherein partial differential equations are converted into algebraic equations (more accurately, difference equations). Instead of using the continuous variable x, we selected a discrete set of points $\{x_j\}$, and instead of time t we selected the set $\{t_i\}$. Likewise, the concentrations become $C_{i,j}$ and the derivatives are given as follows:

$$\frac{\partial C}{\partial t} \simeq \frac{C_{i+1,j} - C_{i,j}}{\Delta t} \quad (7)$$

and

$$\frac{\partial^2 C}{\partial x^2} \simeq \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{(\Delta x)^2} \quad (8)$$

In eqs. (7) and (8), higher-order terms are negligible and are thus eliminated. Upon inserting eqs. (7) and (8) into eq. (4) and rearranging, we obtain

$$C_{i+1,j} = C_{i,j} + \frac{D(\Delta t)}{(\Delta x)^2} + (C_{i,j+1} - 2C_{i,j} + C_{i,j+1}) \quad (9)$$

where the increments $\Delta t = t_{i+1} - t_i$ and $\Delta x = x_{j+1} - x_j$ are constants. If the initial concentration profiles $C_{i,j}$ are known, then eq. (9) provides a means of moving up in time to $C_{i+1,j}$ (upward curve). Such iterations are continued until the numerical approximation to equilibrium or steady state is achieved (minima). The values of Δt are considered in the numerical analysis and the barrier membrane is divided into a number of equal finite slices of thickness, Δx by the concentration difference planes. The computer program in "C" language was written to solve these equations (see Appendix).

Concentration profiles for all liquids follow the trends that are the same as those of sorption, diffusion, and permeation. However, such curves for other liquids are not displayed graphically to avoid the overcrowding of the curves. An important observation to make here is that as long as the diffusion is Fickian, an effective constant diffusivity can be used to mimic the sorption process. It can be understood from Figure 2 that this holds good even under severe conditions. When diffusivity is considered to be constant, the concentration profiles change smoothly within the membrane matrix. When D increases with concentration, then a sharp solvent front is observed because, for the same concentration gradient, flux increases. This results in a parabolic nature of the concentration profiles as shown in Figure 2. The minimum is observed at the center of the membrane thickness. It may be noted that during desorption, the fraction of liquid molecules desorbed is equal to the fractional mass uptake when D is constant. Therefore, sorption and desorption curves shown in Figure 2 are symmetrical in nature on either side of the membrane.

It is observed that the profile values show minima in the middle of the barrier membranes for both benzene and chlorobenzene. However, decreasing and increasing tendencies of the profile curves are observed at the face as well as at the bottom sides of the membrane, indicating the validity of the model used while calculating concentration profiles. All the curves show a systematic variation with temperature, that is, with an increase in temperature the concentration profiles also increase, suggesting a relationship of the variation in concentration profiles with transport data (sorption, diffusion, and permeation).

CONCLUSIONS

In this report, sorption data were obtained at 40 and 50°C for different substituted structures of monocyclic aromatic liquids of industrial importance. Using these data, diffusion and permeation coefficients of liquids through the Fluorel™ FLS-2650 membrane were calculated using Fick's equation. Such data are useful in
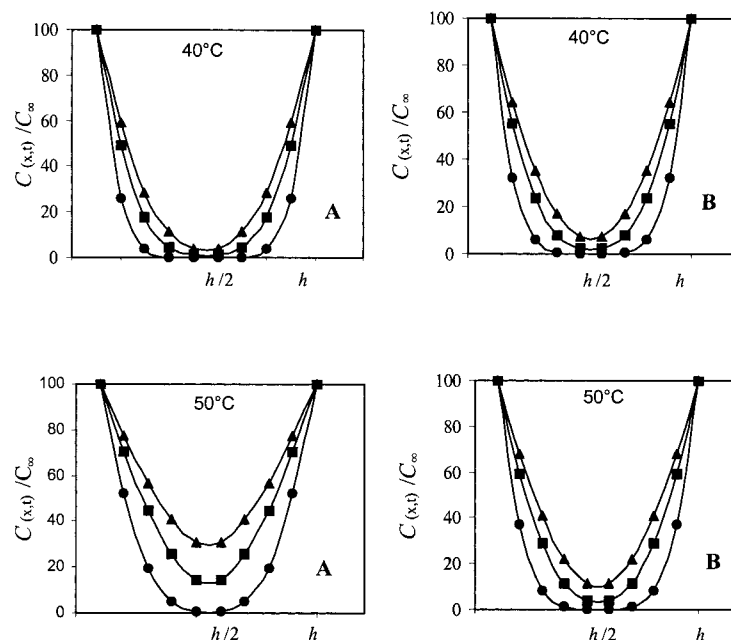
Figure 2 Concentration profiles calculated from eq. (9) for Fluorel™ FLS-2650 membrane in (A) benzene and (B) chlorobenzene. Symbols: (●) 30 min, (■) 90 min, and (▲) 150 min.

industrial/engineering applications of the membrane in the chosen media. Analytical solutions of Fick's equation under suitable boundary conditions yielded the concentration profiles of liquids into the Fluorel sheet membranes at different times along the thickness (x-direction). A computer-simulation technique was used based on the finite-difference method by developing programs in "C" language. Concentration profiles were calculated typically only in the case of benzene and chlorobenzene; however, similar profiles can also be easily reproduced for other liquids. The present study was an effort toward the basic understanding of the transport phenomena (sorption, permeation, and diffusion) through the chosen fluoropolymer membrane. Transport parameters are systematically influenced by the size, nature, and shape

of the solvent molecules as well as the temperature. Systematic structure, diffusion, sorption, and permeation relationships were observed. Molecular transport followed the anomalous-type behavior. The polymer when used as a barrier membrane did not degrade under the experimental conditions used.

Appendix

'C' Program to find concentration profiles for liquid mixtures and solvents

```
#include <stdio.h>
main()
{
    char s[]="System=Water + Acetic Acid at 30, 40, 50 deg C";
    float h,d,cn,h1,dx,dx2,m;
    int dt,n1,j,j1,n=0;
    static float c[100][100];
    FILE *fp;
    fp=fopen("sftk.txt","w");
    clrscr();
    printf("Enter the values for h,d,cn,dt,n1 and j1 ");
    scanf("%f%e%e%d%d%d",&h,&d,&cn,&dt,&n1,&j1);
    printf("%s\n",s);
    printf("h = %7.4f cm D=%.2e cm ^ 2/s Cn=%f mol\%\n",h,d,cn);
    printf("\tt\tPlane\t1\t2\t3\t4\t5\n");
```

```
h1=h/n1;
printf("(min)=%7.4f\t%7.4fcm\t%7.4fcm\t%7.4fcm\t%7.4fcm\n",h1,2*h1,3*h1,4*h1,
5*h1);
dx=h1;
dx2=h1*h1;
m=dx2/(60*dt*d);
for(j=0;j<=j1;j++)
{
   if(n==0)
     c[n][j]=cn;
   if(n==n1)
     c[n][j]=cn;
}
for(n=1;n<=n − 1;n++)
{
   if(j==0)
     c[n][j]=0;
}
for(j=1;j<=j1;j++)
{
   printf("%d",j*dt);
   for(n=1;n<= ((n1/2)−1);n++)
   {
     c[n][j]=(1.0/m)*(c[n+1][j − 1]+(m − 2)*c[n][j − 1]+c[n − 1][j −
1]);
     printf("%.4e\t",c[n][j]);
   }
   c[n][j]=(1.0/m)*((m − 2)*c[n][j − 1]+2*c[n − 1][j − 1]);
   printf("%.4e\n",c[n][j]);
}
printf("press a key");
getch();
printf("\n(100xCt/Cn) works out the following\n");
for(j=1;j<=j1;j++)
{
   printf("%d\t",j*dt);
   for(n=1;n<=((n1/2)−1);n++)
   {
     c[n][j]=(1/m)*(c[n+1][j − 1] + (m − 2) * c[n][j − 1] + c[n − 1][j −
1]);
     printf("%6.3f",100*c[n][j]/cn);
   }
   c[n][j]=(1/m)*((m − 2) * c[n][j − 1] + 2 * c[n − 1][j − 1]);
   printf("%7.3f\n",100*c[n][j]/cn);
}
fclose(fp);
}
```

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