

# Computer Simulation Method for Calculating Concentration Profiles in Polyurethane/Polystyrene Interpenetrating Polymer Network Membranes

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**ABSTRACT:** Interpenetrating polymer networks (IPNs) of polyurethane (PU) and polystyrene (PS; 90/10 and 75/25) were synthesized by the condensation reaction of castor oil with methylene diisocyanate and styrene, with benzoyl peroxide as an initiator. The IPN membranes were characterized for physicochemical, optical, and X-ray diffraction properties. Computer-simulated concentration profiles of aqueous salt solutions through PU/PS IPN membranes were

generated with Fick's second-order differential equation, and the results were examined in terms of diffusion anomalies. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 122–128, 2003

**Key words:** interpenetrating networks (IPNs); membranes; diffusion; simulation

## INTRODUCTION

Polyurethane (PU) and its interpenetrating polymer networks (IPNs) are used in numerous applications ranging from structural engineering to surface engineering and from biology to medical sciences. In addition, PU and its IPNs are widely used in ion-exchange resins,<sup>1</sup> controlled drug delivery,<sup>2</sup> dentistry,<sup>3</sup> coatings,<sup>4</sup> and adhesives.<sup>5</sup> However, membrane applications of polymers for aqueous salt solutions are important in marine engineering. Many researchers have reported the sorption behavior of aqueous salt solutions, organic liquids, and their mixtures through polymer membranes.<sup>6–9</sup> Some have studied the swelling behavior of IPNs with organic liquids to calculate the molar mass between crosslinks as well as the degree of crosslinking.<sup>10,11</sup> In our earlier studies, the sorption and diffusion of organic liquids through castor-oil-based PU IPNs and chain-extended PUs were reported.<sup>12–14</sup> Diffusion coefficient ( $D$ ) values were calculated from a Fickian equation,<sup>15</sup> which showed a dependence on the size, shape, viscosity, structure, and polarity of liquids as well as the morphology of the polymer membranes.<sup>16</sup> Even though extensive literature exists on the sorption and diffusion behavior of aqueous

salt solutions through different types of polymer membranes,<sup>17,18</sup> still there is a need for more literature data on PU-based IPNs. In this article, we report the computer-simulated results for the calculation of concentration profiles of aqueous salt solutions through PU/polystyrene (PS) IPN polymeric membranes. Concentration profiles of the migrating liquids for certain commercial membranes have been reported elsewhere.<sup>19–23</sup> This study is a continuation of these efforts.

## EXPERIMENTAL

Castor-oil-based (90/10 and 75/25 w/w) PU/PS IPNs were prepared according to a procedure reported elsewhere.<sup>12,24</sup> The obtained PU/PS sheets were tough and transparent. The IPNs were characterized according to the appropriate ASTM specifications. The density was determined by the displacement method according to ASTM D 792-86, and ASTM D 676-58J was used for Shore A hardness. The optical properties were measured with a Suga test instrument haze meter (Tokyo, Japan) with dust- and grease-free films of IPNs according to ASTM D 1003. X-ray diffraction data were collected on a Shimadzu XD-D1 X-ray powder diffractometer (Japan) with germanium monochromated Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation in a transmission mode, with a curved position-sensitive detector in the  $2\theta$  range of 5–40° at a scan rate of 4°/min. We used various equations reported elsewhere to calcu-

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late the microstructural parameters, such as the crystal size ( $\langle N \rangle$ ), lattice strain ( $g$ ), enthalpy for the formation of the crystal size ( $\alpha^*$ ), surface-weighted crystal size ( $D_{\text{sur}}$ ), and volume-weighted crystal size ( $D_{\text{vol}}$ ).<sup>25–27</sup>

To generate the computer-simulated results of the concentration profiles of liquids within the PU/PS membranes, we used Fick's second-order differential equation in its most general form:<sup>23</sup>

$$\partial C / \partial t = D(\partial^2 C / \partial x^2) \quad (1)$$

where  $D$  is concentration-independent,  $t$  is the sorption time,  $C$  is the liquid concentration within the membrane material, and  $\partial C / \partial x$  is the concentration gradient along the  $x$  direction. Equation (1) is solved under the following assumptions: (1) liquid diffusion into the membrane takes place in one direction only; (2) sorption takes place under transient conditions with a constant diffusivity; (3) during sorption, when the membrane is exposed to the solvent, its concentration on the membrane surface reaches equilibrium immediately; (4) the time required for the membrane to establish thermal equilibrium is negligible in comparison with the time of sorption; and (5) changes in membrane dimensions are negligible during liquid exposure under the initial and boundary conditions:

$$t = 0 \quad 0 \leq x < h \quad C = 0 \quad (2)$$

$$t \geq 0 \quad x = 0, \quad x = h \quad C = C_\infty \quad (3)$$

$$\partial C / \partial x = 0, \quad x = 0, \quad t > 0 \quad (4)$$

This gives the concentration profile [ $C_{(x,t)}/C_\infty$ ] of the liquids within the polymer membrane as a function of the penetration depth (i.e., distance  $x$ ), and the thickness of the membrane at time  $t$ :

$$C_{(x,t)}/C_\infty = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \times \exp[-D(2m+1)^2 \pi^2 t / h^2] \sin[(2m+1)\pi x / h] \quad (5)$$

In eq. (5), the values of  $D$  were calculated as follows:

$$D = \pi[h\theta/4C_\infty]^2 \quad (6)$$

**TABLE I**  
Optical Properties of PU/PS IPNs

Composition of IPNs (PU/PS)	Diffuse (%)	Transmittance (%)	Haze (%)
90/10	20.5	81	42
75/25	17.9	84	37

**TABLE II**  
Microstructure Parameters of PU/PS IPNs

Composition of (PU/PS)	$\langle N \rangle$	$g$ (%)	$\alpha^*$	$D_{\text{sur}}$ (Å)	$D_{\text{vol}}$ (Å)
90/10	$6.2 \pm 0.1$	$3.83 \pm 0.06$	0.152	19.56	30.66
75/25	$6.1 \pm 0.1$	$2.76 \pm 0.04$	0.144	19.75	30.96

where  $h$  is the thickness of the polymer sample,  $\theta$  is the slope of the initial linear plot (before <55% sorption) of sorption versus square root of sorption time,  $t^{1/2}$ , and  $C_\infty$  is the equilibrium value of sorption calculated from the maximum asymptotic region of the equilibrium sorption curve.

## RESULTS AND DISCUSSION

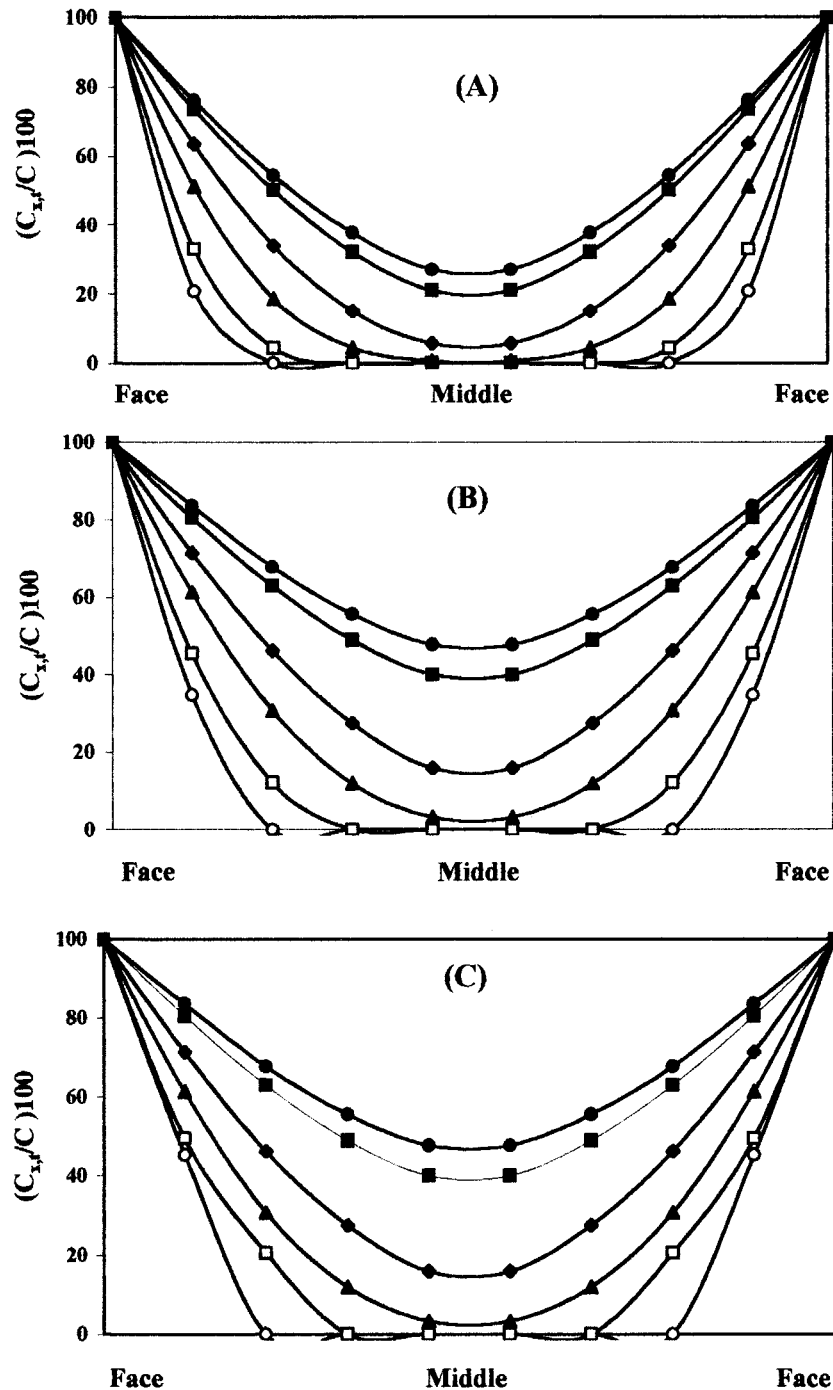
In our earlier communications,<sup>28,29</sup> we reported on the engineering properties, such as the tensile strength, tensile modulus, and percentage of the elongation at break, and the microcrystalline parameters of PU/PS systems. Some of the typical properties, such as the tensile strength and percentage of the elongation at break for 90/10 and 75/25 PU/PS IPNs are 1.8 and 2.0 MPa and 129 and 108, respectively. The density and surface hardness of the PU/PS membranes are 0.960–0.980 g/cm<sup>3</sup> and 80–82 Shore A, respectively. From these results, it can be concluded that the tensile strength, tensile modulus, and surface hardness in-

**TABLE III**  
 $D$  Value of 90/10 and 75/25 PU/PS IPNs at Different Concentrations of Aqueous Salt Solutions

Liquid solutions	Temperature (°C)	$D \times 10^7$ cm <sup>2</sup> /s			
		0.15M <sup>a</sup>		0.5M <sup>a</sup>	
		90/10 <sup>b</sup>	75/25 <sup>b</sup>	90/10 <sup>b</sup>	75/25 <sup>b</sup>
BaCl <sub>2</sub>	25	30.38	38.84	35.31	40.50
	40	32.75	64.80	44.32	68.80
	60	68.23	97.00	83.80	99.05
SrCl <sub>2</sub>	25	28.14	34.70	37.52	44.10
	40	38.22	48.70	43.54	55.54
	60	52.60	83.70	56.53	88.30
MgSO <sub>4</sub>	25	33.11	28.50	42.33	46.10
	40	47.14	47.60	53.23	58.30
	60	59.90	54.20	109.00	93.34
K <sub>2</sub> CO <sub>3</sub>	25	36.50	41.52	70.42	55.66
	40	47.14	53.00	91.90	62.90
	60	59.90	72.80	117.00	95.70
K <sub>2</sub> CrO <sub>4</sub>	25	43.51	22.90	43.91	34.93
	40	52.73	30.26	69.78	52.73
	60	73.34	66.43	93.89	93.84
KI	25	32.01	32.00	33.21	34.15
	40	42.03	59.00	44.33	67.54
	60	59.92	98.00	62.40	112.00

<sup>a</sup> Concentration of salt solutions.

<sup>b</sup> Composition of PU/PS IPNs.

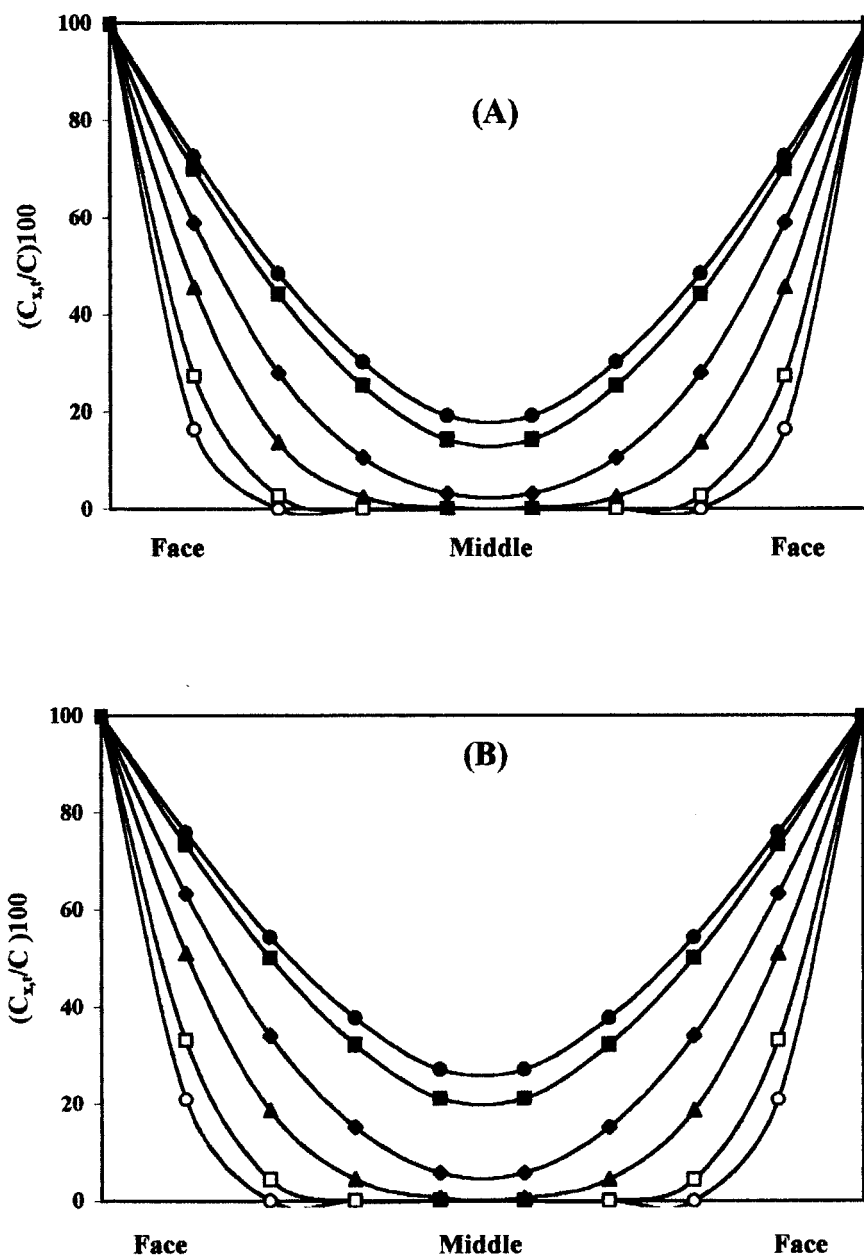


**Figure 1** Concentration profiles calculated from eq. (5) for 0.15M BaCl<sub>2</sub> at (○) 5, (□) 10, (▲) 25, (◆) 50, (■) 100, and (●) 120 min with 75/25 PU/PS IPNs at (A) 25, (B) 40, and (C) 60°C.

crease with an increase in the plastic phase (PS) of the membrane.

The results for the diffused light, total transmittance of light, and haze measurements are given in Table I.<sup>28</sup> From these data, it can be observed that the values of the total percentage of transmittance for the 90/10 and 75/25 PU/PS IPNs are 81 and 84, respectively.

Data obtained from X-ray diffractograms, such as  $\langle N \rangle$ ,  $g$ ,  $\alpha^*$ ,  $D_{sur}$  and  $D_{vol}$  are given in Table II. Both  $\alpha^*$  and the crystal size increased with an increase in the percentage of PS because of the reordering of molecules within these samples. The X-ray study confirms that these IPNs are semicrystalline in nature.<sup>29</sup> Independent physical, optical, and X-ray studies of PU films in the presence of additional PS



**Figure 2** Concentration profiles calculated from eq. (5) for 0.15M BaCl<sub>2</sub> with (A) 90/10 and (B) 75/25 PU/PS IPN membranes for the same time intervals used in Figure 1 at 25°C.

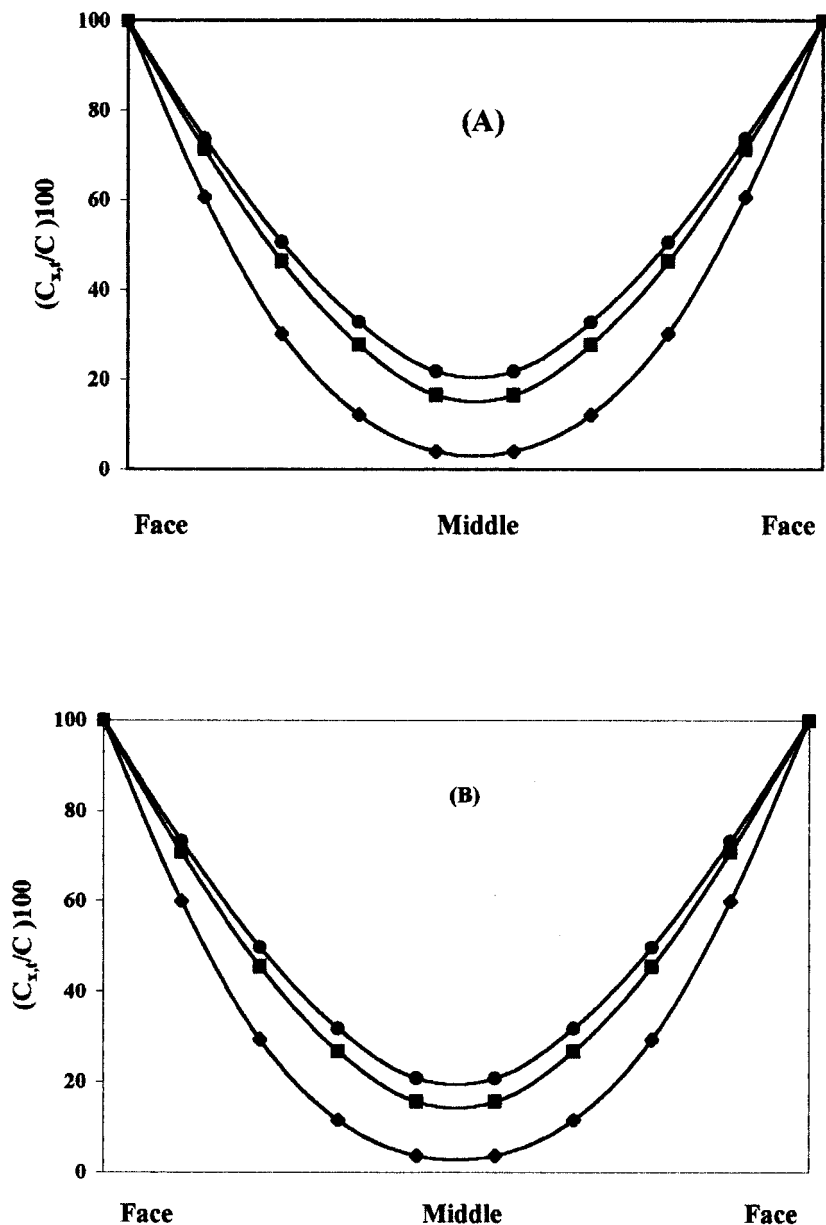
gave consistent results. The increase in the transparency and hardness was due to an increase in the crystal size and an increase in  $g$  in these samples.

The values of  $D$  calculated for 75/25 and 90/10 PU/PS membranes for 0.15 and 0.5M aqueous salt solutions at 25, 40, and 60°C are presented in Table III. From these data, it can be noticed that higher  $D$  values are observed for 0.5M barium chloride solutions than for 0.15M barium chloride in both IPNs. In other words, the higher the concentration of the liquid solution, the higher  $D$  is, as expected.

The concentration profiles generated for a PU/PS (90/10) IPN for barium chloride at 25, 40, and 60°C are

shown in Figure 1. With the temperature increasing from 25 to 60°C, the values of  $C_{(x,t)}/C_{\infty}$  increase, and such an increase is more drastic between 40 and 60°C than between 25 and 40°C. This is due to an increase in the free volume of the membrane, which enhances the diffusion of liquid molecules. The simulation method performs a sensitive test<sup>17</sup> to predict concentration profiles. With increasing immersion time, concentration profiles also increase.

As an example of the composition variation of IPNs, we compare the diffusion data in Figure 2 for barium chloride (0.15M) at 25°C for both 90/10 and 75/25 PU/PS membranes. We find a deviation be-



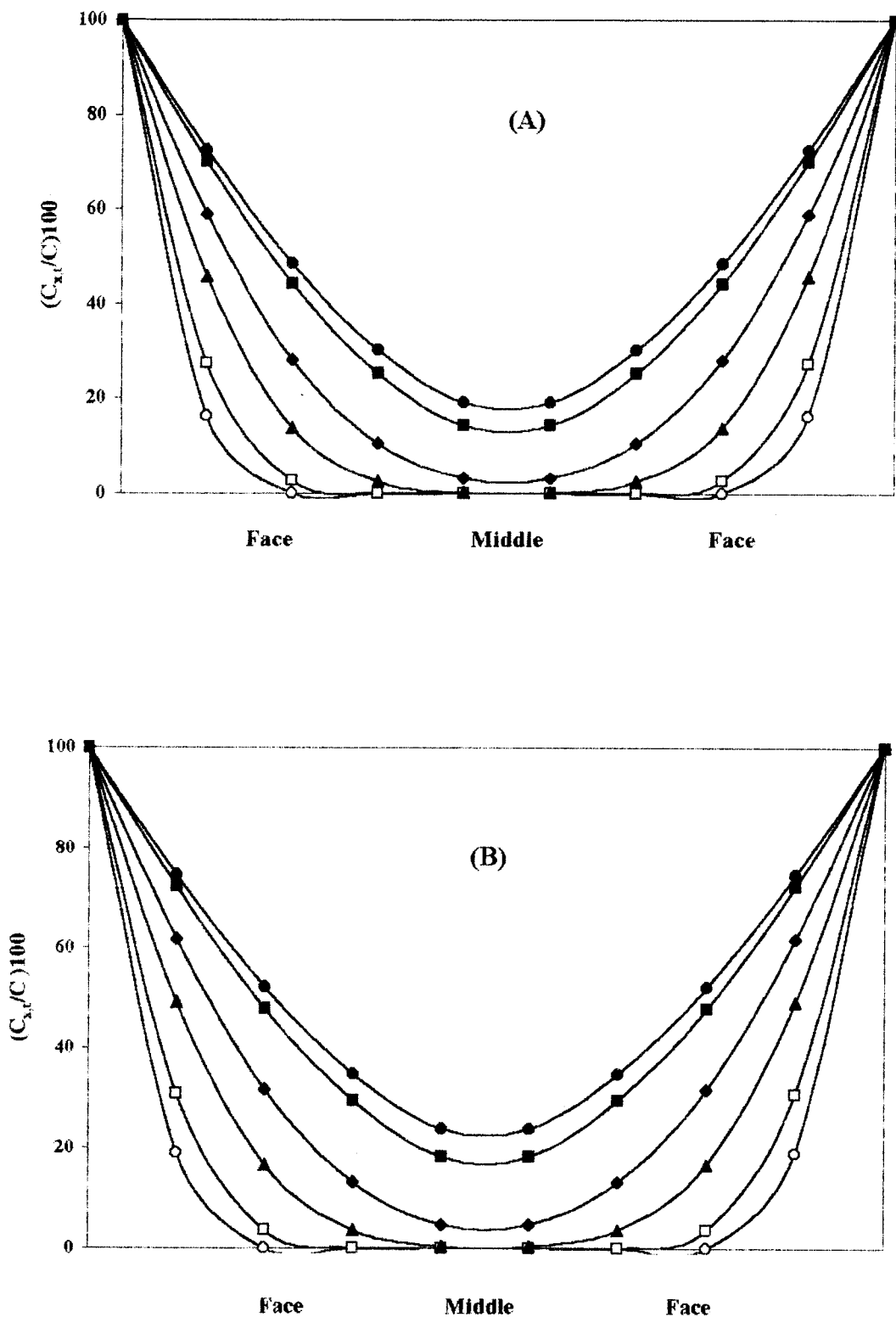
**Figure 3** Concentration profiles calculated from eq. (5) for 0.15M KI with (A) 90/10 and (B) 75/25 PU/PS IPNs at (◆) 50, (■) 100, and (●) 120 min at 25°C.

tween 90/10 and 75/25 IPN membranes, and this variation agrees with the variation in the  $D$  values of the liquid solutions, as presented in Table III. A slight increase in  $D$  values or concentration profiles can be noticed for the 75/25 PU/PS system in comparison with the 90/10 membrane, and this is due to the increase in the disorder of the molecular arrangement of 75/25 PU/PS due to an increase in the nonpolar nature of the PS phase. Such variations in  $D$  values may also be due to the complicated chemical structure and morphology of IPNs.

The effects of different aqueous salt solutions through the membranes have been studied. The concentration profiles for potassium iodide (0.15M)

through 90/10 and 75/25 PU/PS membranes are shown in Figure 3. There is a change in the extent of diffusion that may be due to the molecular volume, the ionic character of the salt solution, and the chemical properties of the aqueous salt solutions.

An attempt has been made to compare the effects of the concentration of barium chloride on PU/PS (90/10) IPNs at 25°C in Figure 4(A) and 4(B). From these plots, it is evident that as the concentration of the barium chloride solution increases,  $C_{(x,t)}/C_{\infty}$  also increases. These variations further confirm that the  $D$  values in these systems exhibit a considerable concentration dependency.<sup>16,30</sup>



**Figure 4** Concentration profiles calculated from eq. (5) with 90/10 PU/PS IPNs for (A) 0.15 and (B) 0.5M BaCl<sub>2</sub> at 25°C at (○) 5, (□) 10, (▲) 25, (◆) 50, (■) 100, and (●) 120 min.

### CONCLUSIONS

This simulation method is convenient and helpful for predicting liquid concentration profiles, as long as the

diffusion data for the liquid-polymer systems are available. Moreover, this method has extensively been adopted for other systems in the literature.<sup>30,31</sup>

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