NOTE

A Computer Simulation Method to Calculate Concentration Profiles in Polymeric Membranes

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In an earlier article,[1] the results of sorption and diffusion for aldehydes and ketones through castor oil-based interpenetrating networks (IPNs) of polyurethane–polystyrene (PU–PS) were obtained in the temperature interval of 25–60°C. In that study, it was observed that diffusion coefficients calculated from the Fickian equation[2] were higher for aldehydes than for ketones. It is also realized from our previous studies[3–7] that the concentration profiles of the penetrating liquid molecules play an important role in the application of these membranes in diverse areas involving the exposure to such liquids. Therefore, in this note, an attempt was made to present computer-simulated results for the calculation of concentration profiles of liquids within the sheet (PU–PS) membranes.

To do this, we used Fick's second-order differential equation given in its most general form[2]:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{1}$$

where D is the diffusion coefficient (usually concentration independent), $\partial c/\partial x$ is the concentration gradient along the x direction, and ∂t is the time derivative. Equation (1) is solved using the following assumptions: (i) liquid diffusion into the membrane takes place in one direction only; (ii) sorption takes place under transient conditions with a constant diffusivity; (iii) during sorption, when the membrane is exposed to solvent, its concentration on the membrane surface reaches equilibrium immediately; (iv) the time required for the membrane to establish thermal equilibrium is negligible when compared to the time of sorption; and (v) changes in the membrane dimensions are negligible during the liquid exposure under the initial and boundary conditions, that is,

$$t = 0 \quad 0 \le x < h \quad C = 0 \tag{2}$$

$$t \ge 0 \quad x = 0, \quad x = h \quad C = C_\infty \tag{3}$$

$$\frac{\partial c}{\partial x} = 0 \quad x = 0, \quad t > 0 \tag{4}$$

to give 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), that is, the thickness of the membrane and time, t:

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

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Table I Diffusion Coefficients (D) of PU/PS IPN–Solvent Systems

Penetrants	Temperature (°C)	$D \times 10^7 \pm 0.004$ (cm^2/s) 90/10	75/25	60/40	50/50
Acetone	25	6.17	19.23	64.50	4.84
	40	8.05	14.43	19.75	8.84
	60	—	—	—	—
MEK	25	8.93	17.30	13.41	10.24
	40	7.51	20.10	15.25	10.74
	60	10.96	27.69	15.45	14.62
Cyclohexanone	25	1.05	3.14	8.06	2.06
	40	1.19	4.80	3.22	0.92
	60	1.79	7.25	12.90	4.70
Acetophenone	25	1.50	8.78	9.89	1.93
	40	1.58	6.21	4.16	1.30
	60	2.55	7.21	13.94	4.47
Acetaldehyde	25	2.25	8.28	8.33	0.90
	40	1.52	1.84	4.56	1.15
	60	1.45	11.96	6.86	3.76
Furfural	25	2.09	4.64	11.01	1.26
	40	7.12	4.78	4.26	1.22
	60	2.35	3.70	4.79	1.68
Benzaldehyde	25	2.20	7.74	10.31	2.15
	40	1.38	4.84	5.69	1.98
	60	3.09	7.36	15.45	6.90

In the above equation, the values of D used were calculated using the equation

$$D = \pi\left(\frac{h\theta}{4C_\infty}\right)^2 \tag{6}$$

where h is the thickness of the polymer sample, θ is the slope of the initial linear (<55% sorption) plot of sorption versus $t^{1/2}$, and C_∞ is the highest value of sorption calculated from the maximum asymptotic region of the equilibrium sorption curve. The values of the diffusion coefficients thus calculated are presented in Table I.

The profiles generated for a 50 : 50 PU : PS IPN for the high diffusing benzaldehyde at 25, 40, and 60°C are presented in Figure 1. It is observed that with increasing temperature, that is, from 25 to 60°C, the values of $C_{x,t}/C_\infty$ also increase, but the increase is more dramatic between 40 and 60°C rather than between 25 and 40°C. Thus, the simulation method appears to be a sensitive test protocol to predict the concentration profiles rather than mere calculation of the values of D. It may further be demonstrated that with an increasing immersion time the concentration profiles also increase dramatically.

As an example of the variation of composition of the IPNs, we compared the data in Figure 2 for benzaldehyde at 25°C for both 90/10 and 50/50 IPNs of PU/PS. We can observe a deviation between 90/10 and 50/50 IPN membranes and this variation is in accordance with the variation in D values presented in Table I. The data for cyclohexane diffusion through the 90/10 and 50/50 IPN membranes are presented in Figure 3, wherein it is found that the variations are quite drastic and these variations confirm that the D values in these systems exhibit considerable concentration dependency, a fact that has been a formidable problem in the literature[2,8] and especially more so in complicated systems such as the IPNs used in this study. At any rate, the present simulation method is convenient and helpful to predict the liquid concentration profiles, provided that the diffusion data of the liquid–polymer systems are available. Moreover, this method has been extensively adopted for other systems in the literature.[8,9]

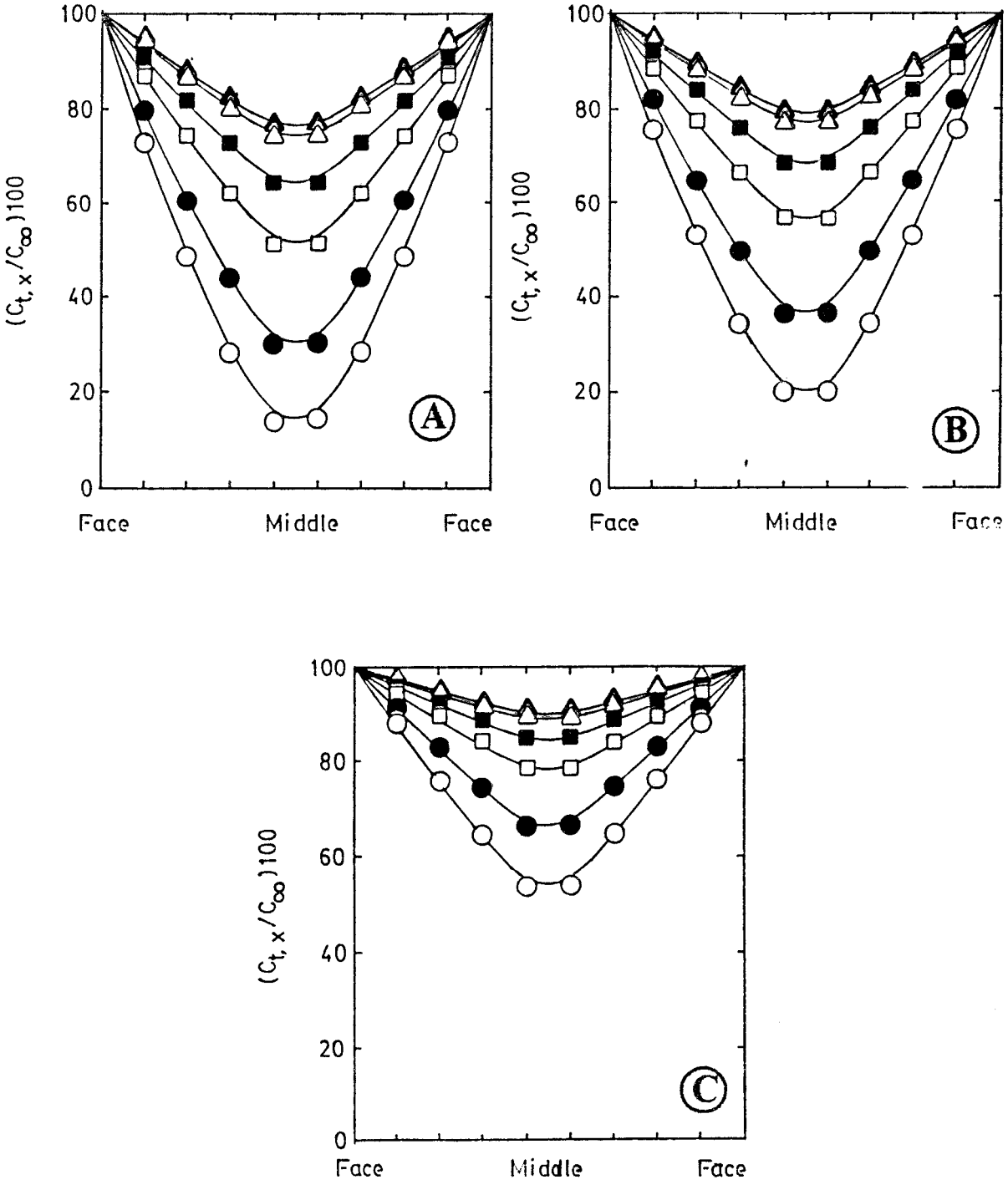
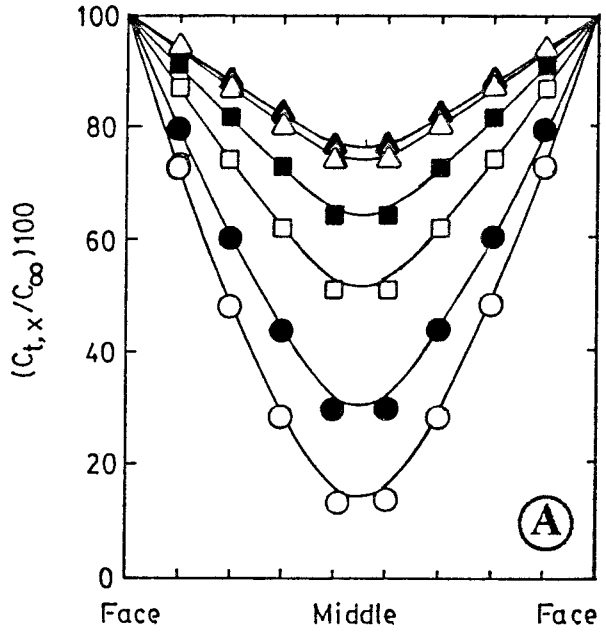


Figure 1 Concentration profiles calculated from eq. (5) for benzaldehyde at (○) 5 min, (●) 10 min, (□) 25 min, (■) 50 min, (△) 100 min, and (▲) 120 min with 50/50 PU/PS IPNs at (A) 25°C, (B) 40°C, and (C) 60°C.



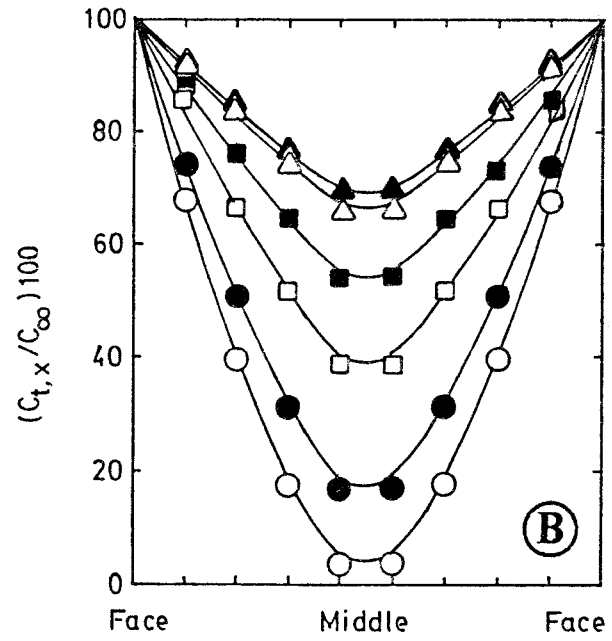
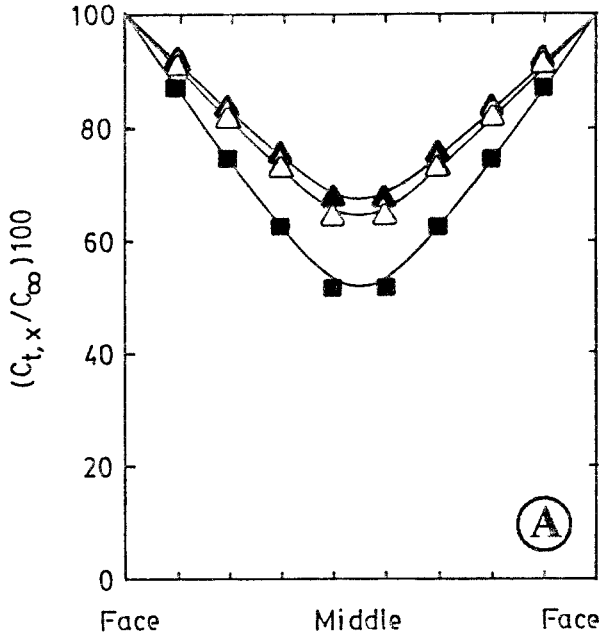


Figure 2 Concentration profiles calculated from eq. (5) for benzaldehyde with (A) 90/10 and (B) 50/50 PU/PS IPN membranes for the same time intervals as in Figure 1 at 25°C.



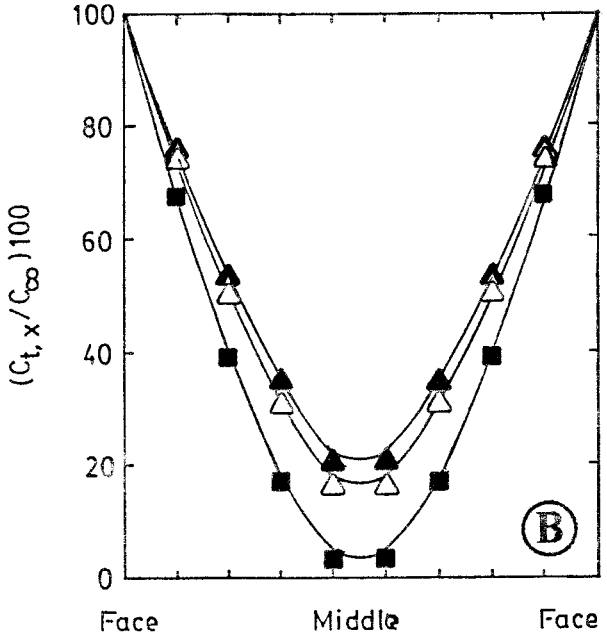


Figure 3 Concentration profiles calculated from eq. (5) for cyclohexanone with (A) 90/10 and (B) 50/50 PU/PS IPNs for (■) 50 min, (△) 100 min, and (▲) 120 min at 25°C.

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