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Analysis of pervaporation of methanol–MTBE mixtures through cellulose acetate and cellulose triacetate membranes

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Experiments were performed on pervaporation of methanol–MTBE mixtures through cellulose acetate (CA) and triacetate (CTA) membranes. The total flux for CA was lower than for CTA, whereas the selectivity for CA was higher than for CTA. For CA, the permeation of methanol seems to be unaffected by MTBE, whereas the permeation of MTBE is apparently affected by methanol through the plasticizing effect. For CTA however, both methanol and MTBE show complex coupling phenomena. These phenomena are successfully explained by the Flory–Huggins theory and the solution-diffusion model. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: pervaporation; cellulose acetate membranes; methanol–MTBE mixtures)

INTRODUCTION

Pervaporation[1,2] is a separation process in which a liquid mixture is in direct contact with the feed side of a membrane and in which the permeate is removed from the other side as a vapour. The mass flux is driven by maintaining the downstream partial pressure lower than the saturation pressure. Transport of liquids through membranes for pervaporation differs from other membrane processes using dense membranes such as gas separation, because permeants in pervaporation usually show high solubility in polymeric membranes. The high permeant concentrations in membranes often have a significant influence on the diffusion coefficients of the permeants. In case of glassy polymers such as cellulose acetate and cellulose triacetate, the mobility of the chains may increase due to the so-called plasticizing effect of small penetrants. No satisfactory theory exists that properly describes the transport of liquid mixtures with a plasticizing effect[3–5]. When a liquid mixture permeates through a membrane, coupling phenomena occur. The flux of one component of a binary mixture is influenced by the other component. In a binary mixture, both components will exert a plasticizing effect on segmental motions of glassy polymers, and the mobility of both permeants will be enhanced by the combined plasticizing action.

Methyl *tert*-butyl ether (MTBE) has been used as an octane booster in gasoline and produced by the reaction of methanol with isobutylene. It is often desired to add methanol in up to 20% excess to improve the reaction conversion. However, the use of excess methanol causes a purification problem because methanol forms a minimum-boiling azeotrope with MTBE at a composition of 14.3 wt% methanol at atmospheric pressure. Pervaporation has therefore been used to break this azeotrope[6,7].

In this work, based on the solution model[8] and Flory–Huggins thermodynamics[9], the pervaporation of methanol and MTBE through CA and CTA membranes is analysed, and the mechansim of pervaporation through CTA is compared with that through CA in terms of the degree of acetylation.

EXPERIMENTAL

Materials and membrane preparation

Cellulose acetate (CA) with degree of substitution 2.45 and cellulose triacetate (CTA) were obtained from Eastman and Fluka respectively. Methanol and MTBE were obtained from James Burrough and Yukong respectively, and used without further purification.

Membranes were prepared by the solvent casting method. About 1 g of polymer was dissolved in a 30 mL of DMF for CA and in methylene chloride for CTA. This solution was cast on a glass plate, then allowed to evaporate at 70°C for CA and at 20°C in a glove box for CTA for 1 day. Finally, the membrane was removed from the glass plate and dried in a vacuum oven at 80°C for 3 days. The resulting membranes were completely transparent and were dense, with a thickness of $\sim 20\ \mu m$.

Swelling measurements and pervaporation experiments

Swelling measurements were performed to calculate binary interaction parameters between liquids and membrane and to determine the composition of liquid mixtures in the membrane. First, membranes were dried in vacuum for 1 day and weighed. These membranes were immersed in liquid mixtures with different compositions at 40°C. After 3 days of immersion, the membranes were removed, pressed between tissue paper and then weighed. The weight

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difference before and after immersion was used for calculating the swelling ratio and the volume fraction of polymer in a swollen membrane.

The feed temperature was kept at 40°C under continuous magnetic stirring to prevent the concentration polarization effect. The permeate was collected by a trap in liquid nitrogen. The fluxes for membranes with different thickness were normalized to a membrane of 20 μm thickness. It is noteworthy that the film thickness is used directly for the thickness of active layer because the membranes prepared in this study were dense membranes. The composition of the permeate was analysed by gas chromatography.

Inverse gas chromatography

To calculate the diffusion coefficients of permeants at zero concentration, inverse gas chromatography (i.g.c.) experiments were performed on an SRI gas chromatograph equipped with a flame ionization detector. Nitrogen was used as carrier gas and propane gas as a marker for retention time. The polymers were coated on to the inert support (Chromosorb W, 60–80 mesh) by the soaking method[10]. The polymer loading (polymer/inert support) was set at 7 wt%. The probes were injected with a 0.5 μL Hamilton syringe. Three consecutive injections were made for each set of measurements.

RESULTS AND DISCUSSION

Sorption

Figure 1 shows that the amount of total sorption does not vary significantly with the volume fraction of methanol in the liquid mixture. At first glance this seems to be unusual, because it is known that methanol has a better affinity with both CA and CTA than does MTBE, as discussed later. This phenomenon may be analysed by the theory proposed by Mulder and co-workers[11,12]. At a given volume fraction of penetrant in the feed, v_i, the volume fraction in the membrane, ϕ_i, can be calculated by following equation:

$$\ln\frac{\phi_1}{\phi_2} - \ln\frac{v_1}{v_2} = (r-1)\ln\frac{\phi_1}{v_2} - g_{12}(\phi_2 - \phi_1) - g_{12}(v_1 - v_2) - \phi_3(\chi_{13} - r\chi_{23}) + u_1\phi_2\frac{\partial g_{12}}{\partial u_1} - v_1 v_2\frac{\partial g_{12}}{\partial v_2} \quad (1)$$

where g is a concentration-dependent binary interaction parameter, χ is a concentration-independent binary interaction parameter, r is the ratio of molar volumes of methanol and MTBE (V_1/V_2), u_i is the relative volume fraction of component i, and subscripts 1, 2 and 3 represent methanol, MTBE and polymer respectively. Before equation (1) is solved for ϕ_i, the values of parameters χ_{13}, χ_{23} and g_{12} are determined by the following procedure. First, binary interaction parameters between penetrant and polymer, χ_{13} and χ_{23}, are assumed to be concentration-independent because this is a polymer–non-solvent system. In this case, the membrane is considered as a swollen gel and expressed by the Flory–Rehner theory[9]. Then χ_{13} and χ_{23} can be calculated from swelling measurements by:

$$\chi_{i3} = -\frac{[\ln(1-\phi_3) + \phi_3]}{\phi_3^2} \quad (2)$$

It seems reasonable to speculate that methanol has a strong capacity to form hydrogen bonding with pendent groups of CA and CTA, whereas MTBE has little capacity because the oxygen atom in MTBE is surrounded by its own bulky methyl groups. Thus methanol is expected to have a better affinity than MTBE has. This speculation is confirmed by swelling experiments, as shown in *Table 1*. The values of

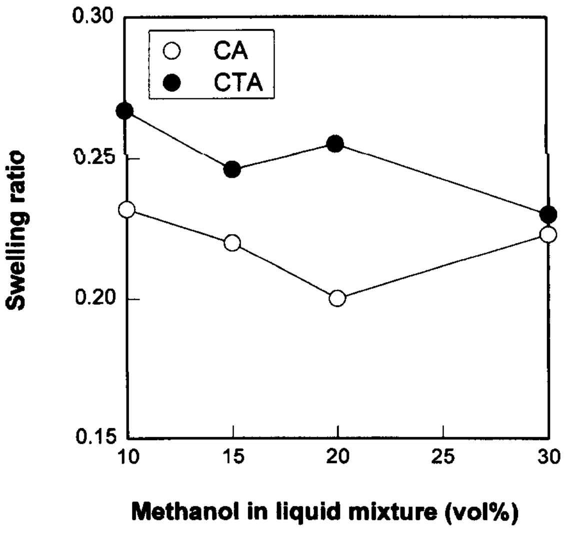

Figure 1 Effect of methanol in liquid mixture on swelling ratio

Table 1 Sorption values and binary interaction parameters between liquids and polymers

Polymer	ϕ_3	χ_{13}	ϕ_3	χ_{23}
CA	0.771	1.18	0.973	2.79
CTA	0.776	1.20	0.813	1.31

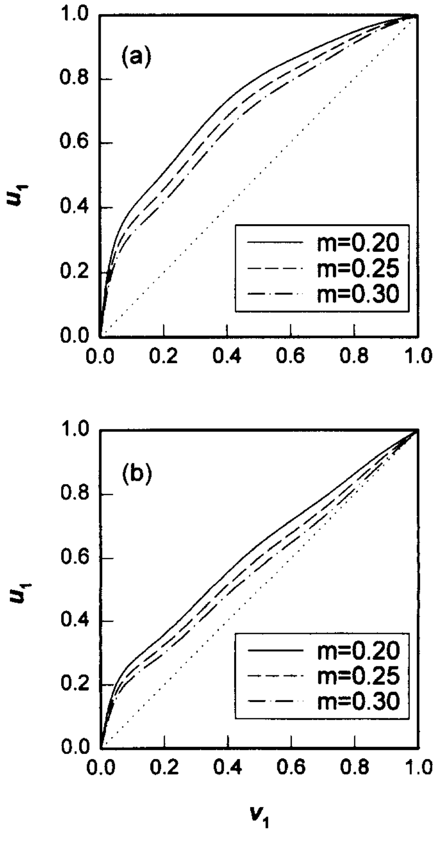

Figure 2 Relative volume fraction of methanol, u_1, in (a) CA and (b) CTA, calculated from equation (1)

χ_{13} are smaller than those of χ_{23}, indicating that methanol is more soluble in both CA and CTA than MTBE is.

Second, the concentration-dependent interaction parameter, g_{12}, can be determined by Flory–Huggins thermodynamics[9]. For a binary system the activity a_1 is given by:

$$\ln a_1 = \ln \nu_1 + \left(1 - \frac{V_1}{V_2}\right)\nu_2 + g_{12}\nu_2^2 \qquad (3)$$

The activity a_1 is determined by the UNIFAC (universal quasi-chemical functional group activity coefficients) method[13,14], which allows a substantial reduction of experimentally determined activity data to obtain parameters characterizing interactions between pairs of structural groups. Using this method, the dependence of g_{12} on ν_2 can be expressed by the following fourth-order polynomial relation, and then the value of g_{12} is calculated at a given ν_2:

$$g_{12} = 0.375 - 0.341\nu_2 + 3.612\nu_2^2 - 6.782\nu_2^3 + 4.774\nu_2^4 \qquad (4)$$

Finally, ϕ_1 and ϕ_2 can be determined by substituting the values of χ_{13}, χ_{23} and g_{12} calculated from equations (2)–(4) into equation (1). *Figure 2* shows the degree of preferential sorption of methanol on to CA and CTA at a given swelling ratio, m ($= \phi_1 + \phi_2$). It is clear that both CA and CTA have sorption selectivity for methanol, but the degree of preferential sorption is greater in CA than in CTA. *Figure 3* shows the results of analysis of the swelling measurements by equation (1). The volume fraction of methanol in membrane increases with ν_1 whereas that of MTBE decreases with increasing ν_1 for both CA and CTA. These two opposite dependences make the swelling ratio independent of the volume fraction of methanol, as shown in *Figure 1*.

Pervaporation

Figure 4 shows that the fluxes of both methanol and MTBE are greater for CTA than for CA. This phenomenon can be explained as follows. There are three types of interaction between the CA pendent groups (hydroxyl and acetyl groups): strong hydroxyl–hydroxyl (hydrogen bonding), strong hydroxyl–acetyl (hydrogen bonding), and weak acetyl–acetyl (dipole–dipole) interactions[15–17]. Since the CTA has very few if any hydroxyl groups, the CTA has only weak dipole–dipole interactions, whereas the CA, which has both hydroxyl and acetyl groups, has strong hydrogen bonding as well as dipole–dipole interactions. Thus the CTA may have a looser structure than the CA. As a result, the CTA may have higher permeability than the CA has. In contrast, the CA has better selectivity than the CTA, as shown in *Figure 5*. This phenomenon is widely accepted in pervaporation, i.e. the lower-permeable membrane yields the better selectivity. It is also noteworthy from *Figures 4 and 5* that the flux increases whereas the selectivity decreases with increasing volume fraction of methanol in the feed. This seems to arise from the plasticizing effect of methanol. In other words, the membranes become more plasticized as the amount of methanol increases. Consequently the loose structure may give higher permeability and at the same time lower selectivity.

It is also desirable to predict theoretically the flux of each

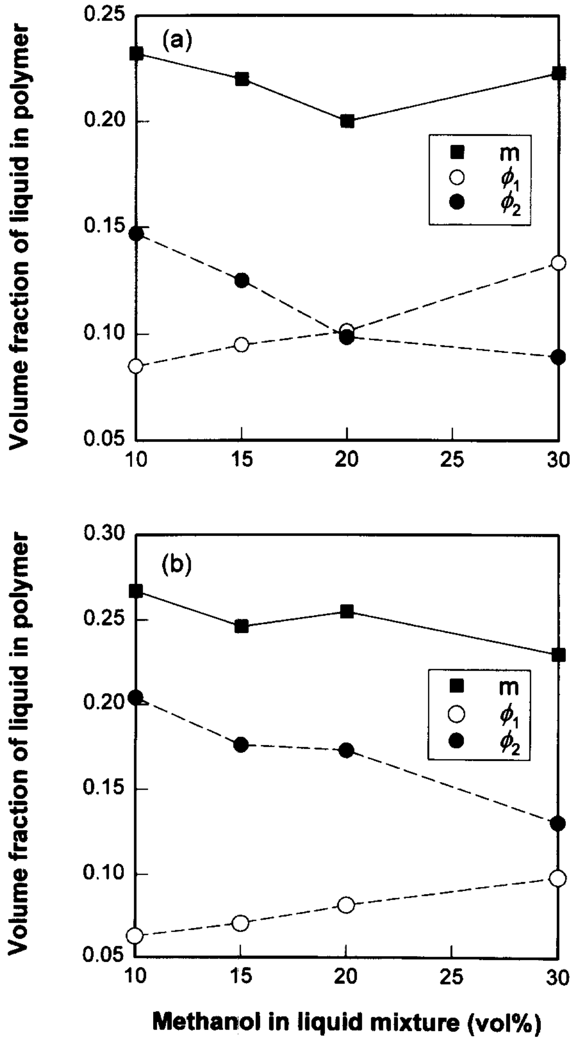

Figure 3 Effect of methanol in liquid mixture on volume fraction of liquid in (a) CA and (b) CTA

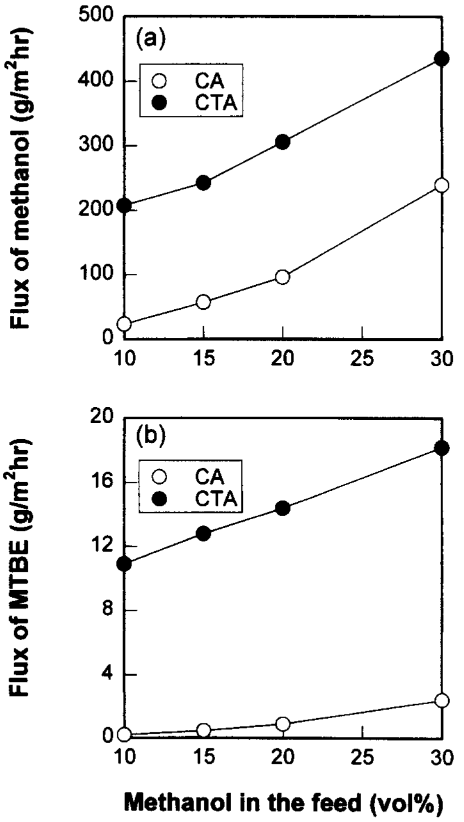

Figure 4 Effect of methanol in feed on pervaporation flux of (a) methanol and (b) MTBE

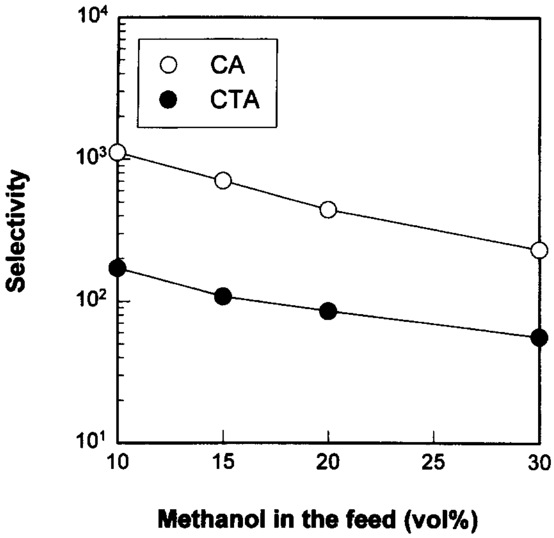

Figure 5 Effect of methanol in feed on pervaporation selectivity

component. For this purpose, we adopt the solution-diffusion model[4]. According to the model, the flux J_i for component i can be described by:

$$J_i = \frac{\rho_i}{l}\int_0^{\phi_{i0}} D_i \, \mathrm{d}\phi_i = \frac{\rho_i}{l}\int_0^{\phi_{i0}} (D_T)_i \frac{\partial \ln a_i}{\partial \ln \phi_i} \mathrm{d}\phi_i \qquad (5)$$

where ρ is the density, l is the membrane thickness, D_T is the thermodynamic diffusion coefficient, a is the activity and ϕ_0 is the volume fraction on the feed side. To calculate the flux J_i from equation (5), the values of ($\partial \ln a_i/\partial \ln \phi_i$) and $(D_T)_i$ must be determined. The activity of methanol and MTBE in the membrane can be obtained by differentiating the Gibbs free energy with respect to n_1 and n_2, and then the gradient of activity coefficient with concentration, ($\partial \ln a_i/\partial \ln \phi_i$), may be obtained differentiating the activity with respect to $\ln \phi_i$[12]:

$$\begin{aligned}\frac{\partial \ln a_1}{\partial \ln \phi_1} = \phi_1 \Bigg\{ & \frac{1}{\phi_1} - \left(1 - \frac{V_1}{V_3}\right) - g_{12}\phi_2 \\ & + \frac{V_1}{V_2}\phi_2\chi_{23} - \chi_{13}(2 - 2\phi_1 - \phi_2) \\ & - \frac{\phi_2^2(1-\phi_1)}{(1-\phi_3)^2}\frac{\partial g_{12}}{\partial u_2} + u_2^2(1-2u_2)\frac{\partial g_{12}}{\partial u_2} \\ & + u_2^3(1-u_2)\frac{\partial^2 g_{12}}{\partial u_2^2}\Bigg\} \end{aligned} \qquad (6)$$

$$\begin{aligned}\frac{\partial \ln a_2}{\partial \ln \phi_2} = \phi_2 \Bigg\{ & \frac{1}{\phi_2} - \left(1 - \frac{V_2}{V_3}\right) - \frac{V_2}{V_1}g_{12}\phi_1 \\ & + \frac{V_2}{V_1}\nu_{13}\phi_1 + \nu_{23}(2\phi_2 + \phi_1 - 2) \\ & + \frac{V_2}{V_1}(1-\phi_2)\frac{\phi_1^2}{(1-\phi_3)^2}\frac{\partial g_{12}}{\partial u_2} \\ & + \frac{V_2}{V_1}u_1^2(1-2u_2)\frac{\partial g_{12}}{\partial u_2} + \frac{V_2}{V_1}u_1^3(1-u_1)\frac{\partial^2 g_{12}}{\partial u_2^2}\Bigg\} \end{aligned} \qquad (7)$$

The thermodynamic diffusion coefficient of component i, $(D_T)_i$, can be considered as a function of ϕ_1 and ϕ_2 at constant temperature. Thus, in general, D_T for methanol and MTBE are expressed by:

$$(D_T)_1 = D_1^0 f(\phi_1, \phi_2) \qquad (8)$$

$$(D_T)_2 = D_2^0 g(\phi_1, \phi_2) \qquad (9)$$

where D^0 is the diffusion coefficient at zero concentration and f and g are functional forms which represent the plasticizing effect of penetrants on D_T. The diffusion coefficient at zero concentration of species i, D_i^0, can be determined by inverse gas chromatography[18,19]. With a packed chromatographic column, diffusion coefficients are determined from an analysis of the variation of the theoretical plate height, H, with the average gas velocity, p, by use of the van Deemter equation[20]:

$$H = A + \frac{B}{p} + Cp \qquad (10)$$

The constant C accounts for mass transfer in the stationary polymer phase and is related to the diffusion coefficient D as follows:

$$C = \frac{8kf_m^2}{\pi^2(1+k)^2 D^0} \qquad (11)$$

where f_m is the film thickness at its deepest point and k is the mass distribution ratio of the solute between the gaseous and liquid phases. At high flow rates, the second term in equation (10), representing diffusion in the gas phase, becomes negligible and the constant C can be determined from the slope of a plot of H *versus* p as seen in *Figure 6*. Finally, D^0 can be calculated by equation (11). *Table 2* lists diffusion coefficients at zero concentration of methanol and MTBE determined by the above procedure. When the pervaporation mechanism for CA is compared with that

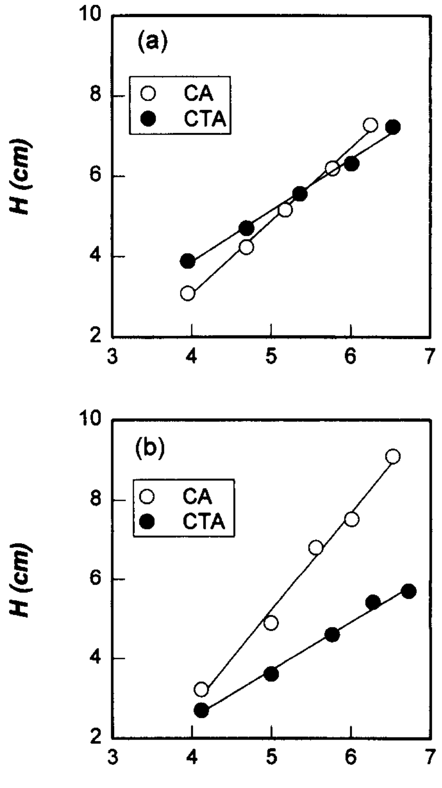

Figure 6 Effect of velocity of carrier gas, p, on theoretical plate height, H, for (a) methanol and (b) MTBE

for CTA in *Figure 4*, the permeation of methanol for CA seems to be unaffected by MTBE, whereas the permeation of MTBE is apparently influenced by the plasticizing effect of methanol. Thus both *f* and *g* in equations (8) and (9) for CA can be set as functions of only ϕ_1. For CTA, both *f* and *g* in equations (8) and (9) must be set as functions of both ϕ_1 and ϕ_2, since both methanol and MTBE show complex coupling phenomena. These functions may be set as exponential forms whose parameters can be determined by the best fit with flux data. The resulting diffusion coefficients of methanol and MTBE for CA and CTA are as follows:For CA:

$$(D_T)_1 = D_1^0 \exp(26.3\phi_1^{1/2}) \qquad (12)$$

$$(D_T)_2 = D_2^0 \exp(588\phi_1^2) \qquad (13)$$

For CTA:

$$(D_T)_1 = D_1^0 \exp(23\phi_1^{1/2} + 8.5\phi_2^{1/2}) \qquad (14)$$

$$(D_T)_2 = D_2^0 \exp(675\phi_1^2 + 115\phi_2^2) \qquad (15)$$

From the above procedures, we can estimate the thermodynamic diffusion coefficient $(D_T)_i$ and the gradient of activity coefficient with concentration $(\partial \ln a_i / \partial \ln \phi_i)$, from which we can calculate the flux by use of equation (5). *Figure 7* shows the comparison of experimental data with theoretical calculations for the fluxes of methanol and MTBE. The theoretical predictions agree well with the experimental data, indicating that the solution-diffusion model can successfully explain pervaporation as long as the proper methods are used for estimating the parameters.

Table 2 Diffusion coefficients (10^{-11} cm^{2}s^{-1}) at zero concentration of methanol and MTBE in CA and CTA membranes

Membrane	D_1	D_2
CA	7.01	2.59
CTA	9.33	4.73

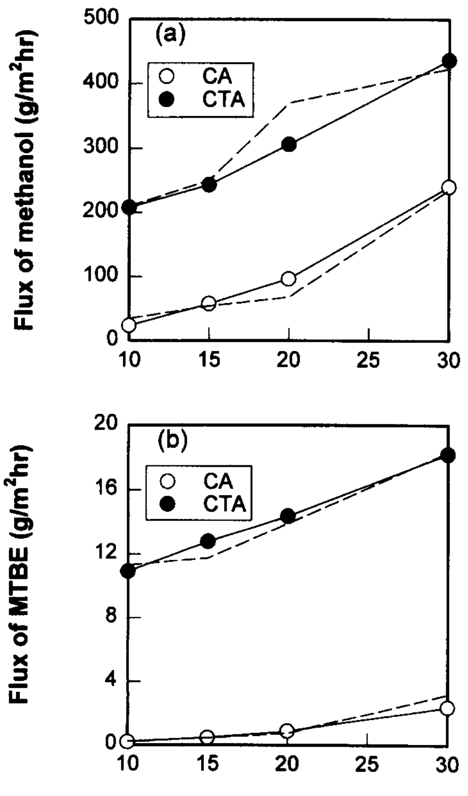

Figure 7 Comparison of experimental flux with theoretical predictions for (a) methanol and (b) MTBE. The dashed lines represent theoretical predictions calculated by the solution-diffusion model, equation (5)

CONCLUSIONS

The pervaporation of methanol–MTBE mixtures through CTA has been compared with that through CA. In sorption experiments, it was observed that the amount of total sorption does not vary significantly with the volume fraction of methanol in the liquid mixture. This seemed unusual, because methanol has a better affinity with both CA and CTA than MTBE has. This abnormality was successfully analysed by adopting a model based on Flory–Huggins theory. In pervaporation experiments, both methanol and MTBE showed a higher flux with CTA than with CA, whereas the selectivity with CTA was lower than with CA. This is probably due to a looser structure of CTA, which has bulkier side groups and a relatively weak dipole–dipole interaction without hydrogen bonding as compared with CA. It was also possible to predict properly the flux of methanol and MTBE for both CTA and CA by using the solution-diffusion model, in which the diffusion coefficients of methanol and MTBE were assumed to be concentration-dependent, i.e. for CA the diffusion coefficients depend on the concentration of methanol, while for CTA they depend on the concentrations of both methanol and MTBE.

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