Effect of Membrane Morphology in Pervaporative Separation of Isopropyl Alcohol–Aromatic Mixtures— A Thermodynamic Approach to Membrane Selection

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ABSTRACT: Isopropyl alcohol (IPA)–benzene and IPA–toluene, which forms azeotropic mixtures, are commonly encountered in pharmaceutical industries. The present study deals with the use of pervaporation to separate these mixtures. For this purpose, several polymeric hydrophilic membranes with variation in solubility parameters such as regenerated cellulose or cellophane, poly(vinyl alcohol) (PVA), cellulose acetate (CA), cellulose diacetate (CDA), and cellulose triacetate (CTA) were studied. Some of these membranes gave a gradual shift of azeotropic point according to the variation of solubility parameter and interaction parameter values between solute and polymer matrix. Regenerated cellulose film gave the best pervaporation performance in terms of IPA selectivity and durability. PVA showed high selectivity with reasonable flux. Poly(dimethylsiloxane), which is hydrophobic, was also studied as an aromatic selective membrane. The experiments were carried out over the entire range of 0–100% at 30°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3912–3921, 2003

Key words: separation technique; pervaporation; cellulosic membranes; isopropyl alcohol; aromatic separation; interaction parameter; solubility parameter; hydroxyl group; membrane; morphology; selectivity; swelling

INTRODUCTION

In recent years, considerable interest has been evinced in the separation of alcohol–aromatic mixtures, especially in pharmaceutical, biotechnological, and water pollution fields. Separations of organic–organic mixtures represent the least developed and largest potential application[1,2] for pervaporation (PV). In our previous study,[3] methanol–benzene and methanol–toluene were considered, where we have studied methanol separation with different hydrophilic membranes and reproducible results were obtained in terms of both selectivity and flux. This separation encouraged us to separate the more difficult isopropyl alcohol (IPA)–aromatic system. As IPA is more hydrophobic than methanol, it was methanol that was not easy to separate, and in most of the cases, forms permazeotrope[4,5] with several membranes. In the conventional separation of IPA–benzene and IPA–toluene mixture, two steps, namely, (1) extraction with water and (2) extractive distillation, are required. In the first step, water is used to separate aromatic from IPA (as IPA is soluble in water), and in the next step, water–IPA separation further needs a two-column configuration. This three-step process increases the operational cost as well as fixed cost of the plant, and

therefore, a single-step separation process for aromatic–aliphatic alcohol[6,7,8] is desirable.

Most of the earlier work deals with the IPA–water system.[9–14] For this purpose, several authors used various types of hydrophilic[17–24] and hydrophobic[25–27] membranes and very few investigations considered the present type (alcohol–aromatic) system.[15,16] In this article, to investigate the permeation behavior, the PV separation of IPA–aromatic mixtures through hydrophilic and hydrophobic membranes was studied. It has been found that the mixtures, where two components are very close with respect to their solubility parameters,[28] form azeotrope[4,5] and create problems not only during separation through distillation, but also in membrane pervaporation. Therefore, a proper selection of membrane plays[29–31] the greatest role in giving a compromise between selectivity and flux, which are reasonable for industrial application.

THE ROLE OF HANSEN'S 3-D PARAMETER IN MEMBRANE SELECTION

Generally, in the condensed phase (solids, liquids), there exist[32–34] strong intermolecular forces of attraction. According to Hansen,[34] the total molar cohesive energy $(E_{coh})_{total}$ of a substance can be represented as the sum of contribution of interaction due to hydrogen bonding $(E_{coh})_h$, polar $(E_{coh})_p$, and dispersion forces $(E_{coh})_d$, or in other words

$$(E_{coh})_{total} = (E_{coh})_h + (E_{coh})_p + (E_{coh})_d \qquad (1)$$

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TABLE I
A Comparison of Different Δ Values for Cellulosic Materials

Membrane	$\Delta_{addition}$		Δ_{ratio}	
	IPA-Benzene	IPA-Toluene	IPA-Benzene	IPA-Toluene
Cellophane	614.332	614.974	5.44	5.66
CA	414.358	288.586	1.49	1.83
CTA	263.652	266.582	1.17	1.46

The solubility parameter value is the square root of cohesive energy density (CED), for instance,

$$\delta = (CED)^{1/2} = \{(E_{coh})_{total}/V\}^{1/2} \qquad (2)$$

The total solubility parameter (Δ) is generally represented on a 3-D plot with the three axes representing values for different forces similar to dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) in this way

$$\Delta_{1-2} = (\delta)^2_{1-2} = (\delta_d)^2_{1-2} + (\delta_p)^2_{1-2} + (\delta_h)^2_{1-2} \qquad (3)$$

The basis of the use of solubility parameter in predicting sorption selectivity lies in "The Regular Solution Theory." This theory, as originally developed by Scatchard and Hildebrand,[32] could be applied only for interactions between low molecular weight substances, which are nonpolar, non-hydrogen-bonded, and of similar molecular size. In the case of low molecular weight liquids, the physical significance of molar cohesive energy ($E_{coh})_{total}$ is composed of the energy required to vaporize the molecule and to expand the vapor to ideal gas state. For most of the polymers, however, the vaporization in the ideal state is not possible without degradation.

For successful implementation of this technique, it is necessary to know the solubility parameters of the polymer and the solute for both the data on solubility parameter values are available.[28] The Hansen's 3-D solubility parameter[34] method has been used in evaluating the separation potential. Another prediction of results using this technique for permeation in membranes was used by Gooding and Sferazza.[35] According to their study for ternary system (1-2-3), where 1 is weakly sorbed, 2 is strongly sorbed, and 3 represents the membrane, the following approaches have been considered

(1) The first approach involves the use of $\Delta_{addition}$

$$\Delta_{addition} = \Delta_{1-2} + \Delta_{1-3} + \Delta_{2-3} \qquad (4)$$

Here Δ_{1-2}, Δ_{1-3}, and Δ_{2-3} can be evaluated from eq. (3). A larger value of $\Delta_{addition}$ implies higher sorption selectivity for the solute.

(2) The second approach involves the use of the ratio (Δ_{ratio})

$$\Delta_{ratio} = \Delta_{1-3}/\Delta_{2-3} \qquad (5)$$

For high sorption selectivity of the desired solute, Δ_{ratio}, should be high.

A comparison of the two approaches have been given in Table I. Larger values of $\Delta_{addition}$ and Δ_{ratio} for the components of the IPA-aromatic mixtures (Table II) with cellophane than others (Table III) imply higher IPA sorption selectivity. Between the two mixtures, IPA–toluene is expected to give better IPA selectivity with hydrophilic membranes than IPA–benzene, as can be calculated from Table I.

EXPERIMENTAL

Materials

The poly(vinyl alcohol) (PVA) used, polynol 117, average molecular weight 75 kDa and 99% hydrolyzed, was kindly supplied by Polychem Ltd. (Mumbai, India). Cellulose diacetate (CDA, 52.8% acetyl content), cellulose triacetate (CTA, 59.6% acetyl content), and cellophane membranes were used. Elastosil LR 7660A and B solutions were kindly supplied by Wacker Chemie (Germany) to prepare poly(dimethylsiloxane) (PDMS) membrane. CDA (52.8% acetyl content) was kindly supplied by Ion Exchange Ltd. (Mumbai, India). Cellulose acetate (CA, 40% acetyl content) was supplied by Sigma-Aldrich (Bangalore, India). Dimethylformamide (DMF) was procured from S.D. Fine Chemicals (Mumbai, India). Analytical reagent-grade isopropyl alcohol and laboratory grade benzene and toluene were used for the studies.
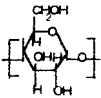
Membrane preparation

Membrane was prepared by dissolving polymer (such as CTA or PVA) in a suitable solvent (DMF and de-

TABLE II
Solubility Parameters, Molar Volume, and Nature of Interaction of Different Solutes

Compound	Solubility parameter $(MPa)^{1/2}$	Molar volume (Vm) (mL/mol)	Nature of interaction
Isopropanol	23.5	76.8	Polar
Benzene	18.8	89.4	Nonpolar
Toluene	18.2	106.8	Nonpolar

TABLE III
Structural Features and Related Properties of Polymeric Materials

Properties	PDMS	PVA	Cellophane	CA	CDA	CTA
Solubility parameter $(MPa)^{1/2}$	14.9	25.78	32.24	25.08	23.22	18.84
Selective sorption	Aromatic	Alcohol	Alcohol	Alcohol	Alcohol	Alcohol
Specific gravity	1.268	0.838	0.676	1.285	1.114	1.001
Expected T_g (°C)	−123	70	250–330	165	178	190
Polymeric backbone/ Repeat unit	$\left[\begin{smallmatrix} \vert \\ Si-O \\ \vert \end{smallmatrix}\right]$	$\left[\begin{smallmatrix} CH_2 CH \\ \vert \\ OH \end{smallmatrix}\right]$	(structure)	Same as cellophane	Same as cellophane	Same as cellophane
Side group/s	—CH$_3$	—OH	—OH and —CH$_2$OH	—OH, —CH$_2$OH, —OCOCH$_3$	—OCOCH$_3$ increases	—OCOCH$_3$ increases
Features of interest affeceting T_g	Flexible back bone	Polar interaction	Extensive polar polar interaction	Interchain interaction	Interplasticization	Stiff back bone

PDMS, poly(dimethylsiloxane); LLDPE, linear low-density polyethylene; PVA, poly(vinyl alcohol); Cellophane, regenerated cellulose; CA, cellulose acetate; CDA, cellulose diacetate; CTA, cellulose triacetate.

mineralized water, respectively) and casting on a glass plate, maintaining a certain thickness with a bar coater. Drying at a certain temperature (60 and 100°C, respectively) gave a stable membrane. CA and CDA were prepared in the same way as CTA. PDMS membrane was prepared by spreading a homogeneous mixture of matrix with crosslinking agent in the ratio of 9 : 1 and curing at 80°C for 6 h. Structural features and related properties of the polymers have been presented in Table III.

Pervaporation experiments

Experiments were carried out in a batch-stirred cell described (Fig. 1) elsewhere.[3] The permeation selectivity is defined as

$$\alpha = (Y_i/Y_j)/(X_i/X_j) \tag{6}$$

where X and Y represent the weight fraction of the corresponding solute in the feed and permeate, respectively. Subscript i refers to the desired component (whose selectivity is to be determined) and j refers to the second component.

Analysis of permeates

The feed and permeate concentration of all the mixtures were analyzed by measuring the refractive indices of these solutions by a Bausch and Lomb Refractometer by use of a calibration curve. The precision of this method was ±0.05 wt %.
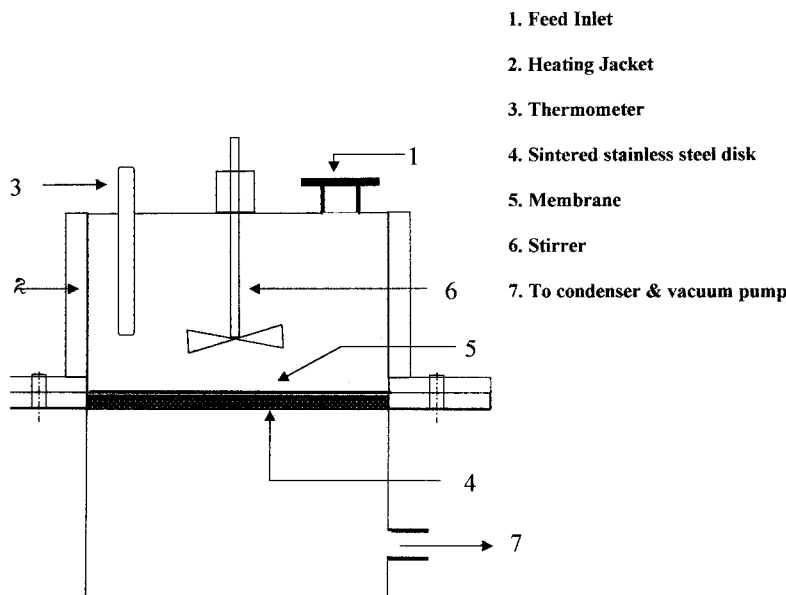
1. Feed Inlet

2. Heating Jacket

3. Thermometer

4. Sintered stainless steel disk

5. Membrane

6. Stirrer

7. To condenser & vacuum pump

Figure 1 Experimental set up for pervaporative separation.

Polymer membrane	Isopropanol	Benzene	Toluene
CA	0.87	1.64	1.72
CDA	1.023	1.38	1.41
CTA	1.11	1.15	1.19
PVA	1.58	2.98	3.84
Cellophane	0.782	1.84	2.04
PDMS	1.16	0.72	0.64

Determination of interaction parameter

Samples of dry membranes of known weight were immersed in pure solvent and were allowed to equilibrate for 72 h. These membranes were taken out from the solvent and the superfluous liquid was wiped off with tissue paper. Then the swollen membrane was weighed. In the case of equilibrium sorption of a pure solvent in a polymer, the binary interaction parameter χ_{ip} can be calculated[7,29] from the following equation

$$\chi_{ip} = -(\ln\phi_s + \phi_p)/(\phi_p)^2 \qquad (7)$$

where φ_s is the volume fraction of solute in the polymer and φ_p is the volume fraction of polymer.

RESULTS AND DISCUSSION

The results discussed below pertain to experiments that were frequently checked for their reproducibility, which was found to be ±2%.

Interpretation based on interaction parameters

The interaction parameters[29,36] for various solute–polymer systems are given in Table IV. The lower the interaction parameter value, the higher the interaction or affinity of solvent is for that membrane. The sorption[37] of a membrane depends (1) on the presence of functional groups and (2) the free volume to accommodate the sorbed species. The selection of a membrane for pervaporative separation is usually decided by the inherent sorption characteristics of the membrane material. In general, the more the polar groups in the polymer matrix, the higher will be its sorption affinity toward IPA. However, the accessibility of these groups, the degree of crystallinity of the matrix, and the relative strengths of IPA–IPA and IPA–polymer bonds are also important factors. The sorption capacity depends not only on the nature of the group but also on its position and stereospecific/tactic distribution (Fig. 2) in the polymer chain.

A comparison of interaction of CA, CDA, and CTA

Interaction with membranes of cellulose triacetate

The interaction parameter[3,38-40] of IPA for CTA is 1.11, which is quite low, suggesting a good interaction with this membrane. The values for benzene (1.15) and toluene (1.19) show a considerably close affinity with CTA. CTA contains a significant amount of acetyl groups (59.6%) and remaining are hydroxyl groups; therefore, it shows amphoteric affinity.

Interaction with CDA membrane

From Table IV, it is found that the affinity of IPA with CDA ($\chi = 1.023$) is higher than benzene/toluene ($\chi_{Bz} = 1.38/\chi_{tol} = 1.41$), and it creates a better difference in interaction than CTA. Because CDA (52.8% acetylated) contains a smalller amount of substitution than CTA (59.6% acetylated), this suggests a more hydrophilic nature of CDA than CTA. This hydrophilicity explains the polar–polar attraction. The solubility parameter value of CDA ($\delta = 23.22$ MPa$^{1/2}$) is greater than its triderivative (18.84 MPa$^{1/2}$) and IPA ($\delta = 23.5$ MPa$^{1/2}$) is very close to CDA. Toluene shows less affinity than benzene as it has high molecular diameter to accommodate within the membrane matrix and lower solubility parameter [$\delta = 18.2$ (MPa)$^{1/2}$].

Interaction with CA

Cellulose acetate shows higher affinity toward IPA ($\chi_{IPA} = 0.87$) than benzene ($\chi_{Bz} = 1.64$) and toluene ($\chi_{IPA} = 1.72$). Cellulose acetate (40% acetylated) contains a significant number of hydroxyl groups, which exhibit very good interaction with IPA. In contrast, toluene shows a lower affinity for CA than benzene, which might be due to higher molecular diameter of the former. Besides, the solubility parameter value of CA [$\delta = 25.08$ (MPa)$^{1/2}$] is most suitably selective for IPA [$\delta = 23.5$ (MPa)$^{1/2}$] than toluene [$\delta = 18.2$ (MPa)$^{1/2}$].

Interaction with PVA membrane

The much lower interaction value of IPA (1.58) with PVA compared to benzene (2.98) and toluene (3.84) suggests that IPA has much better affinity compared to the aromatic. PVA contains one hydroxyl group on each —CH$_2$—CH— moiety. The presence of highly polar group in a sufficient amount converts this membrane into a strongly hydrophilic membrane, which is able to break the azeotropic character. The high interaction value of benzene and toluene reveals less affinity of the aromatics toward PVA.
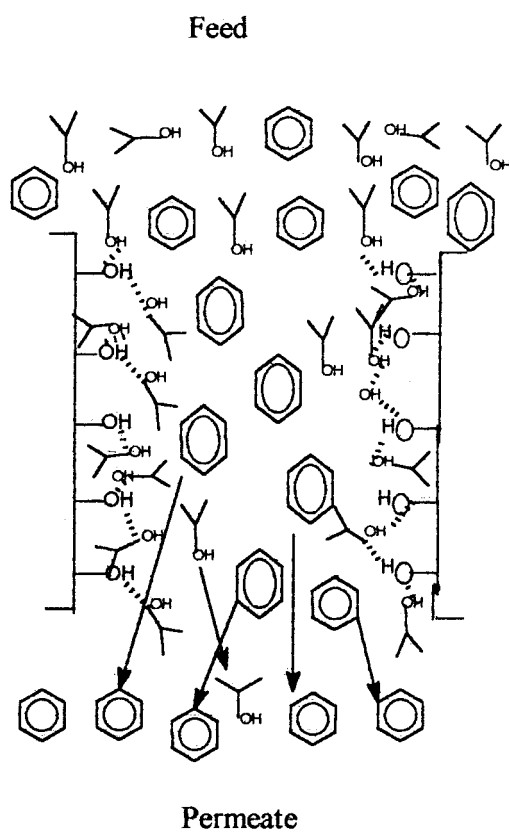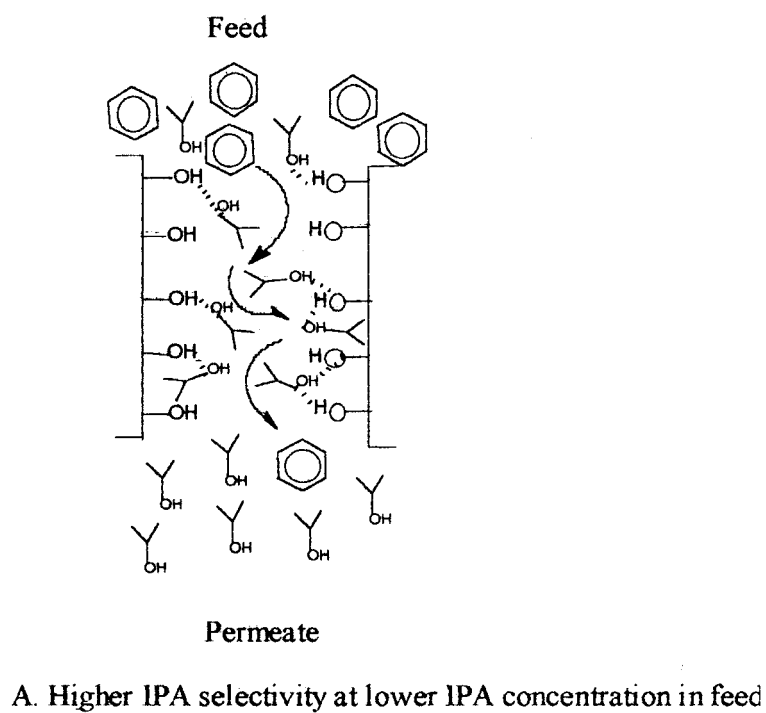
Feed

Permeate

A. Higher IPA selectivity at lower IPA concentration in feed

Feed

Permeate

B. Lower IPA selectivity at higher IPA concentration in feed

Figure 2   Effect of plasticization on permeation of IPA through hydrophilic polymeric membranes.

Interaction with cellophane membrane

The interaction parameter values of IPA ($\chi = 0.782$), benzene ($\chi = 1.84$), and toluene ($\chi = 2.04$) suggest that cellophane is an excellent hydrophilic membrane. For the IPA–toluene system, the χ value of IPA shows much more of a difference with χ_{tol} than χ_{ben}. This observation can be explained on the basis of molecular structures. Each monomer moiety of cellophane contains[3] two hydroxyl groups, one —CH_2OH group, as well as one —C—O—C— linkage in between each monomer unit, where each six-membered cyclic repeating unit contains another oxygen atom. Thus, cellophane is the most hydrophilic among all the membranes mentioned above.

Interaction with PDMS membrane

PDMS shows a reverse trend in attraction. As it is a hydrophobic membrane, it gives a selective sorption of the aromatic. From Table IV, it is seen that the affinity for apolar toluene toward PDMS ($\chi = 0.64$) is more than benzene ($\chi = 0.72$) and IPA ($\chi = 1.16$). This sorption depends on the solubility parameter value of a pure solvent in the membrane, for example, PDMS [$\delta = 14.9$ $(MPa)^{1/2}$] will attract toluene [$\delta = 18.2$ $(MPa)^{1/2}$] more than benzene [$\delta = 18.8$ $(MPa)^{1/2}$]. Although it shows very little difference, it indicates the likelihood of interaction between the pendant —CH_3 group on membrane[3] and the same group of toluene.

HYDROPHILIC MEMBRANES

Effect of feed concentration on permeation

Cellulose acetate, cellulose diacetate, and cellulose triacetate

Figures 3 and 4 present a comparison of permeation behavior with the variation of concentration of IPA in
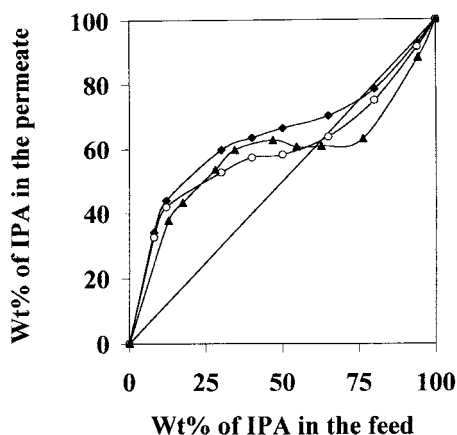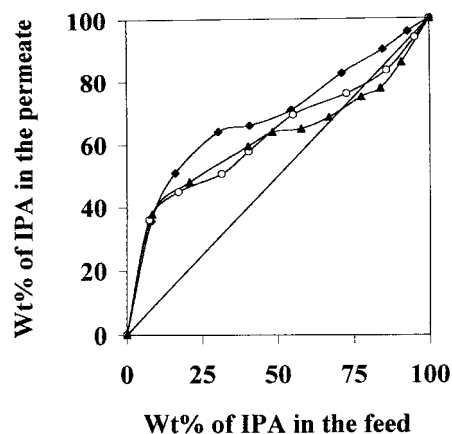
Figure 4 Variation of concentration of IPA in the permeate with its feed concentration for IPA–toluene system with cellulose derivatives. ◆, CA; ▲, CDA; ○, CTA.

the feed for IPA–benzene and IPA–toluene, respectively. These figures show the effect of degree of acetylation on permeation. From CA (40%) to CDA (52.8%), and CTA (59.6%), substitution increases. As a result, hydrophilicity decreases, and second, free space increases, due to which IPA sorption decreases and aromatic permeation increases. Thus, these cellulosic membranes form permazeotrope (in Fig. 3) with IPA–benzene, but with IPA–toluene, first permazeotrope disappeared for CA membrane. Between toluene and benzene, toluene possesses less affinity (Table IV), lower solubility (Table III), and higher molar volume (Table III) than benzene. Therefore, it is expected that toluene will be sorbed less, and in contrast, IPA will be permeated more. Thus, with CA permazeotrope was not observed for IPA–toluene system (Fig. 4), in contrast to IPA–benzene (Fig. 3).

PVA and cellophane membranes

Figure 5 shows the weight percentage of IPA in the permeate against the same in the feed for PVA and cellophane membranes. It is worth mentioning that none of the systems form a permazeotrope with these membranes. Among these two systems, IPA–toluene shows a better IPA separation than IPA–benzene. When the two membranes are compared, cellophane gives the best separation for both the systems as compared to PVA. The large number of hydroxyl groups in cellophane (as mentioned earlier) than PVA exhibit much greater polar–polar attraction. For membranes such as PVA and cellophane, specific interactions, such as hydrogen bonding, play an important role in determining permeation. Because of limited polymer chain mobility, comparable penetrant molecular size, and shape, the secondary bonding decides the sorption and diffusion of alcohol (Fig. 2). The —OH groups of the membrane and alcohol exhibit a natural simi-

Figure 3 Variation of concentration of IPA in the permeate with its feed concentration for IPA–benzene system with cellulose derivatives. ◆, CA; ▲, CDA; ○, CTA.
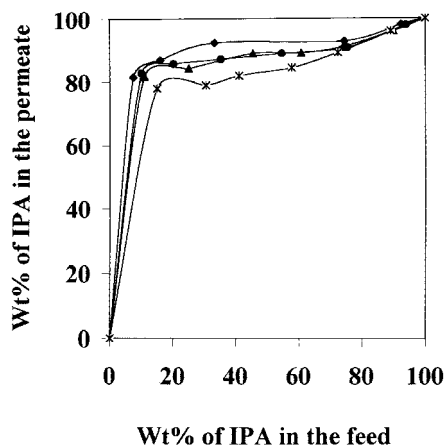
Figure 5 Variation of concentration of IPA in the permeate with its feed concentration for IPA–aromatic system with PVA and cellophane membrane. ♦, IPA–toluene system with cellophane; ●, IPA–benzene system with cellophane; ▲, IPA–toluene system with PVA; ×, IPA–benzene system with cellophane.

larity in stark contrast to the aromatic moiety of either benzene or toluene. The compact nature of the membranes restricts the passage of the nonpolar larger sized aromatics. Therefore, the sorption and diffusion of IPA is favored. Between these two aromatics, toluene is more bulky, less soluble, and shows lower affinity than benzene. Thus, IPA–toluene gives better separation for IPA than IPA–benzene.

EFFECT OF FEED CONCENTRATION ON SELECTIVITY AND FLUX

At lower concentration of IPA in the feed, its selectivity is very high. In this case, initially the solute (IPA) is sorbed preferentially at specific sites and a little perturbation of the matrix swells the upper layer. This layer immediately exerts an expansion force for the next unswollen matrix layer and gradually the upstream part of the membrane becomes swollen with solute. In this solution, IPA is present in much higher concentration than the counterpart (aromatics). The hydrogen-bonding capability (as discussed earlier) of IPA and its linear structure helps in its accommodation within the polymer matrix. Thus, IPA selectivity is highest in this region. However, with increasing concentration of the solute in the feed, all these specific sites get exhausted (Fig. 2) and membrane plasticization takes place because of excessive swelling. By that time, free volume of the membrane matrix increases, which increases aromatic flux and reduces IPA selectivity drastically. Sorption[37] is only the first step but in the second step (diffusion) the different nature of the functional groups or pendant moieties (such as —OCOCH$_3$ groups with increasing amount

of substitution in cellulosic derivatives) change the overall permeation performance of the membrane.

The "microcavities" or "minute holes," which exist in the polymer[31] matrix, are generally created by the segmental motion of the side groups and can be considered as a factor responsible for accommodation (as explained earlier) of the penetrant. Even the microcavity population may gradually change in the presence of solute. In this stage, some segmental chains are flexible enough to move/bend in such a way as to create a passage for the penetrant. Cooperation of the neighboring polymer segments is necessary[39] for the penetrant to diffuse. Thus, during sorption, redistribution of free volume caused by random fluctuations in local density creates some void space leading to tortuous path for diffusion as a next step. The membrane morphology, the chemical nature of the groups, and number of hydrophilic moiety has a profound influence on sorption[3] and the crystalline/amorphous nature of polymer determines[39] the amount of diffusion.

CA, CDA, CTA membranes

IPA–benzene

Figure 6 shows how permeation selectivity and flux of IPA decreases with increasing alcohol concentration in the feed with these membranes. As already mentioned, CA (40% acetylated) contains more hydroxyl groups than CDA (52.8% acetylated) and CTA (59.6% acetylated). Thus, CA affords stronger polar–polar attraction with alcohol and selectively sorbs IPA. CDA contains a smaller number of —OH groups; hence, IPA affinity is lower than CA. CTA contains more
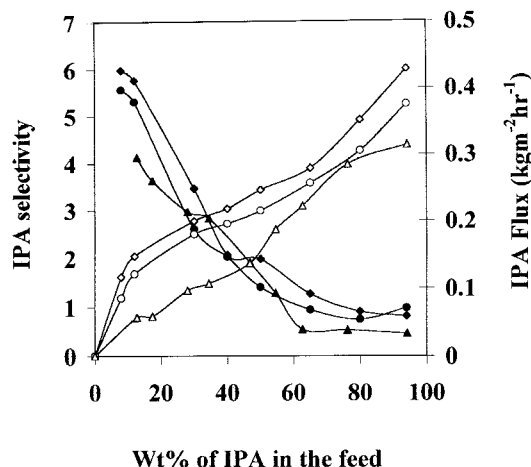

Figure 6 Variation of IPA selectivity and flux for IPA–benzene system with its feed concentration and cellulosic derivatives. (i) Permeation IPA selectivity versus feed concentration: ♦, CA; ●, CDA; ▲, CTA. (ii) IPA flux versus feed concentration: ◇, CA; ○, CDA; △, CTA.
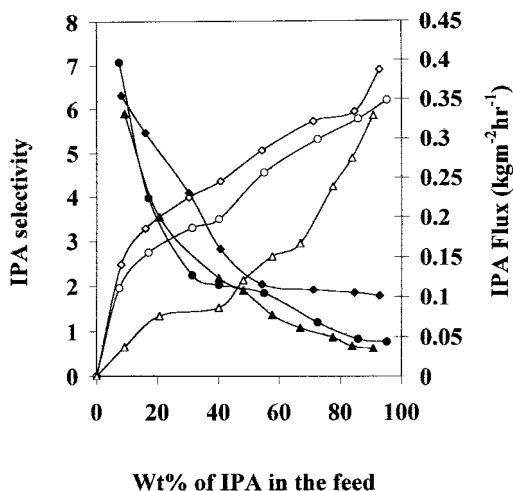
Figure 7 Variation of IPA selectivity and flux for IPA–toluene system with its feed concentration and cellulosic derivatives. (i) Permeation IPA selectivity versus feed concentration: ●, CA; ♦, CDA; ▲, CTA. (ii) IPA flux versus feed concentration: ◇, CA; ○, CDA; △, CTA.

acetyl groups, and therefore, interaction is least. Thus, IPA selectivity follows this order CA > CDA > CTA.

IPA–toluene

Figure 7 gives the change in permeation selectivity versus flux for the IPA–toluene system with IPA concentration in the feed. The decreasing trend in selectivity obeys the same order as followed in IPA–benzene system (i.e., CA > CDA > CTA), although the selectivity is comparatively better for the IPA–toluene system. The smaller interaction parameter value of toluene suggests that it possesses lesser affinity compared to benzene. Because of the self-steric hindrance factor, toluene sorption is reduced. At a higher concentration of IPA in the feed, almost all the membrane hydroxyl groups are exhausted [according to the content of —OH group in cellulosic derivatives (CA > CDA > CTA)]. The interaction nature indicates an interplasticization effect. Plasticization increases the interstitial spaces, provides accommodation for nonpolar compounds, and thus, helps in aromatic diffusion[21] (as shown in Fig. 2). Thus, IPA selectivity decreases with increasing IPA concentration in the feed.

PVA and cellophane membranes

Figure 8 indicates that the "trade-off relationship" between selectivity and flux of IPA for PVA and cellophane decreases with increasing concentration of IPA in the feed for both the systems. Permeation selectivity is a cumulative effect of sorption and diffusion. These two steps depend[29] on polar–polar interaction, size of the penetrant, and free volume of the membrane. Figure 8

shows the best IPA selectivity with cellophane membrane. A large number of polar hydroxyl groups present on the backbone of glucose ring make cellophane the best hydrophilic membrane among all the membranes used for this system. PVA contains a comparatively lower number of polar groups and hence is less hydrophilic than cellophane. In addition, cellophane contains (as discussed earlier) a polar oxygen atom within the heterocyclic ring of monomer and also another oxygen atom attached as a linkage between the two-monomer moieties. Thus, cellophane is a better IPA selective membrane than PVA.

Figure 8 shows the IPA flux with varying concentrations in the feed for both the systems, which is considerably high for industrial implementation.

HYDROPHOBIC MEMBRANE

PDMS is a very effective membrane[3,38] for the removal of comparatively nonpolar component, even present in trace amount. It has a solubility value[28] of 14.9 $(MPa)^{1/2}$ and possesses a highly hydrophobic nature. Inorganic polymers such as PDMS contain —O—Si—O— skeleton, which is longer than the —C—C— bond, found in organic membranes as a counterpart. These inorganic polymers are much less "congested," and as a consequence, much more stable and flexible.

Effect of feed composition on permeation

Figure 9 shows the variation in permeation behavior of aromatics with PDMS for IPA–benzene and IPA–
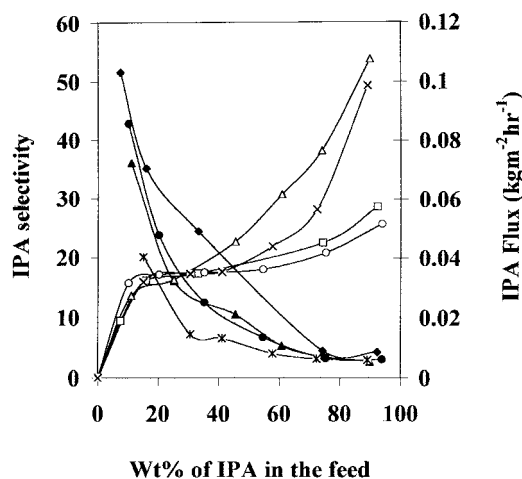

Figure 8 Variation of IPA selectivity and flux for IPA–aromatic system with its feed concentration; PVA and cellophane membranes. (i) Permeation selectivity versus feed concentration: ♦, IPA–toluene system with cellophane; ●, IPA–benzene system with cellophane; ▲, IPA–toluene system with PVA; ×, IPA–benzene system with PVA. (ii) IPA flux versus feed concentration: ◇, IPA–toluene system with cellophane; ○, IPA–benzene system with cellophane; △, IPA–toluene system with PVA; ×, IPA–benzene system with PVA.
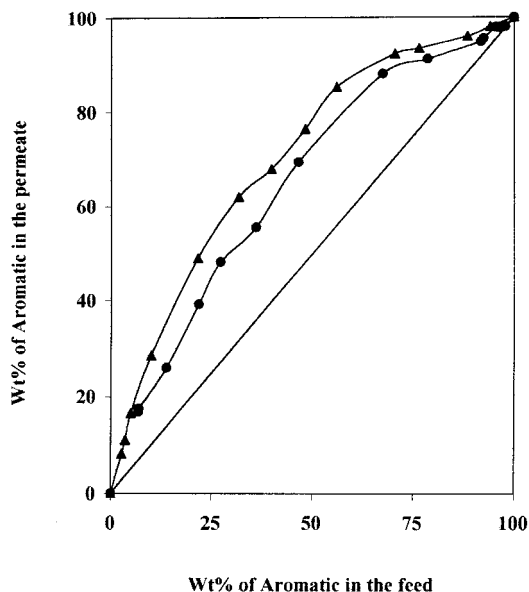
Figure 9 Variation of concentration of aromatic in the permeate with its feed concentration for IPA–aromatic system with PDMS membrane. ▲, IPA–toluene system with PDMS; ●, IPA–benzene system with PDMS.

toluene. As PDMS is a hydrophobic membrane, all the curves were drawn for the aromatic separation only. From the curves, it is clear that toluene permeates more than benzene for any particular concentration of the respective component from mixture with IPA. The interaction value of toluene (0.64) with PDMS suggests that it interacts more with this membrane than benzene ($\chi = 0.72$). However, the separation is not so good as found with methanol[3] instead of IPA.

Effect of feed composition on selectivity and flux

Figure 10 shows the trade-off relationship between selectivity and flux for aromatic with PDMS for IPA–toluene and IPA–benzene systems. With an increase in aromatic concentration in feed, flux increases but selectivity decreases. In the absence of any defects, the selectivity is a function of the material's property at the operating conditions. Unlike hydrophilic pervaporation, the selectivity of rubbery organophilic membranes[41] is often related to the preferential sorption of the solutes and less to the preferential diffusion. Here also the aromatics obey the solubility rule "like dissolves like" and show the "surface selective sorption" due to the nonpolar nature of PDMS membrane. The interaction parameters of aromatics suggest that benzene and toluene will be sorbed more than IPA. Thus, at a lower aromatic concentration in feed, the membrane tries to sorb a maximum amount of strongly sorbing component, and the selectivity is high. However, at higher aromatic concentration in feed, plasti-

cization increases and IPA permeates easily. Therefore, aromatic selectivity decreases.

It has also been observed that toluene selectivity and flux is more than benzene–IPA. However, at lower concentrations of aromatic in the feed, benzene shows better flux than toluene, probably because of the smaller size of the former. After 70 wt % concentration of toluene in the feed, however, its flux suddenly increases. It was found that toluene ($\chi = 0.64$) interacts more than benzene ($\chi = 0.72$) at a higher concentration (>70 wt %); at higher feed concentration, the affinity toward toluene becomes more effective. The chemical similarity of the —CH_3 group of toluene and side groups in PDMS, higher affinity of toluene than benzene, and membrane swelling help to give a better performance at higher aromatic concentration for toluene in terms of both the criteria (selectivity and flux) as compared to benzene.

CONCLUSION

A systematic study of interaction and permeation of IPA–benzene and IPA–toluene has been carried out by using different types of membranes starting from hydrophobic [$\delta = 14.9$ (MPa)$^{1/2}$] to hydrophilic [$\delta = 32.08$ (MPa)$^{1/2}$]. A difference in solubility or interaction parameter values causes a difference in sorption. Membranes such as CA, CDA, and CTA produce permazeotrope for IPA–aromatic systems. Among these, the monotony in permazeotrope formation was first found to break for IPA–toluene with CA. PVA shows a reasonable IPA flux and selectivity for both the mixtures. The higher value of solubility parameter of cellophane [32.08 (MPa)$^{1/2}$] than PVA yields the
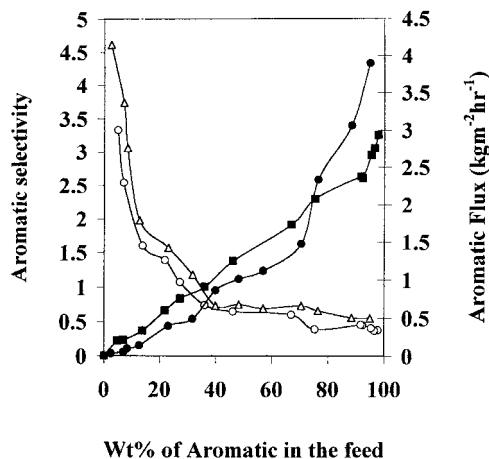

Figure 10 Variation of aromatic selectivity and flux for methanol–aromatic system with its feed concentration and PDMS membrane. (i) Permeation selectivity versus feed concentration; △, IPA–toluene system with PDMS; ○, IPA–benzene system with PDMS. (ii) IPA flux versus feed concentration: ●, IPA–toluene system with PDMS; ■, IPA–benzene system with PDMS.

best performance in selective permeation of IPA. The IPA selectivity performance can be summarized as follows: cellophane > PVA > CA > CDA > CTA.

PDMS membrane has durability, resistance to the adverse nature of huge number of chemicals, and a very appreciable aromatic selectivity in terms of flux and selectivity. Despite very close solubility, and kinetic diameter of IPA, with benzene and toluene, PDMS proves itself reasonably effective for aromatic separation. The similarity in —CH$_3$ groups present in both toluene and polymeric side chain helps in better toluene permeation than benzene. Under the experimental conditions, all these membranes were stable and no changes in the properties of the membranes were observed.

NOMENCLATURE

δ = Solubility parameter value (MPa$^{1/2}$)

V = Molar volume of the mixture (mL/mol)

φ_s = Volume fraction of solute in the polymer (—)

φ_p = Volume fraction of the polymer (—)

χ_{ip} = Interaction parameter for the ith component with polymer p (—)

$(E_{coh})_h$ = Cohesive energy contribution due to hydrogen bonding (J mol^{-1})

$(E_{coh})_p$ = Cohesive energy contribution due to polarity (J$^{1/2}$ cm$^{3/2}$ mol^{-1})

$(E_{coh})_d$ = Cohesive energy contribution due to dispersion forces (J$^{1/2}$ cm$^{3/2}$ mol^{-1})

α = Permeation selectivity (—)

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