

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Role of and Criterion for Sorption Selectivity in Pervaporative Removal of Trace Organics from Aqueous Solutions

Anantkumar R. Samdani^a; Sangita Mandal^a; Vishwas G. Pangarkar^a

^a Department of Chemical Technology, University of Mumbai, Matunga, Mumbai, India

Online publication date: 27 February 2003

To cite this Article Samdani, Anantkumar R. , Mandal, Sangita and Pangarkar, Vishwas G.(2003) 'Role of and Criterion for Sorption Selectivity in Pervaporative Removal of Trace Organics from Aqueous Solutions', Separation Science and Technology, 38: 5, 1069 – 1092

To link to this Article: DOI: 10.1081/SS-120018124

URL: <http://dx.doi.org/10.1081/SS-120018124>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 5, pp. 1069–1092, 2003

Role of and Criterion for Sorption Selectivity in Pervaporative Removal of Trace Organics from Aqueous Solutions

Anantkumar R. Samdani, Sangita Mandal,
and Vishwas G. Pangarkar*

Department of Chemical Technology, University of Mumbai,
Matunga, Mumbai, India

ABSTRACT

Pervaporative separation of trace organics from aqueous solutions was studied using poly(dimethyl siloxane) (PDMS) membrane at compositions up to saturation concentration of organics. The organics compounds studied were allyl isothiocyanate (AITC), 1-butanol, 2-phenyl ethyl alcohol (PEA), benzyl alcohol, aniline, benzaldehyde, nitrobenzene, and carbon tetrachloride. Except for AITC, all other compounds were found to yield high permeation selectivity. Effects of various approaches of solubility parameter approach were found to be most satisfactory in predicting permeation selectivity in terms of sorption behavior in the solute–solvent–polymer ternary system.

*Correspondence: Vishwas G. Pangarkar, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India; Fax: +91-22-4145614; E-mail: vgp@udct.ernet.in.

Key Words: Pervaporation; PDMS membrane; Solubility parameter; Organic removal; Permeation selectivity.

1. INTRODUCTION

Pervaporation (PV) is an emerging membrane separation process that makes possible the separation of liquid mixture by partly vaporizing it through a nonporous perm-selective membrane. The feed mixture is circulated in contact with the membrane, and the permeate is evolved in vapor state from the opposite side of the membrane, which is kept under vacuum by continuous pumping or swept with a stream of gas.^[1] High separation efficiency and potential savings in capital and energy costs have increased the importance of pervaporation in separation processes mainly for azeotropic, close-boiling mixtures and in separating temperature-sensitive compounds.

Pervaporative separation can be used to separate liquids in the following categories:

- 1) Removal of trace organics from an aqueous solution, e.g., chloro-hydrocarbons present in low concentration
- 2) Organic–organic separation, like (methanol–aromatics),
- 3) Dehydration of organics, such as ethanol, isopropyl alcohol, etc.

Lipnizki et al.^[3,4] have performed organophilic separation and recovery of organic compounds from wastewater. Several papers and reviews published on pervaporative separation, process design, application, economic, merit and drawback with discussion.

The removal of trace organics from aqueous solutions is usually carried out by adsorption or extraction. These methods need a subsequent regeneration unit and hence previously mentioned separation techniques are not economical. COD value of these organics is very high. For instance, one molecule of benzene requires 7.5 molecules of oxygen although the solubility of these organics in water is relatively low. In some special cases, with a highly selective pervaporative membrane a high selectivity can be obtained. Therefore, in the permeate, two distinct phases are obtained out of which the organic phase is removed and aqueous phase is recycled, making PV a closed-loop operation (Fig. 1). This process has two advantages: 1) COD value is drastically reduced and 2) recovered organics can be recycled.

Pervaporative Separation of Organics from Aqueous Solutions

1071

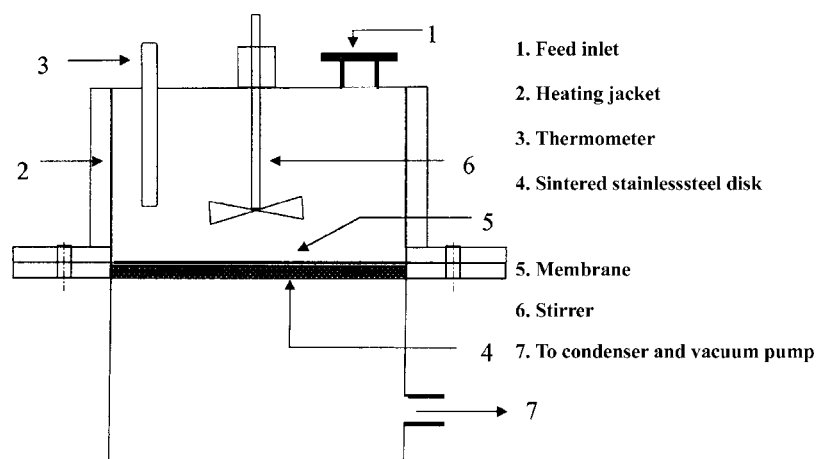


Figure 1. Experimental setup for pervaporative separation.

In view of these advantages, pervaporation with enhanced permeation of the organic components using hydrophobic membranes can be an effective method for significant reduction of the amount of the organics.^[5]

Removal of trace organics from aqueous solutions is needed in various practical situations like water treatment, water purification, bioprocesses and food process applications, recovery of valuable compounds from steam distillation condensates,^[6–8] etc. These organics are of varying properties and chemical structure. Some researchers have studied pervaporative separation of organics. Enrichment of ethyl acetate, 1,1,2-trichloroethane,^[9] pyridine,^[10] butanol,^[11] diacetyl and S-methylthiobutanoate,^[12] ethanol,^[13] picolines,^[14] chloroform,^[15] and essential oils^[6] through highly selective membranes was successfully carried out.

The present study deals with pervaporative separation of allyl isothiocyanate (AITC), 1-butanol, 2-phenyl ethyl alcohol (PEA), benzyl alcohol, aniline, benzaldehyde, nitrobenzene, and carbon tetrachloride from their aqueous solutions using poly(dimethyl siloxane) (PDMS) membrane. Solubility of these compounds in water is shown in Table 1. AITC is a major component in mustard oil obtained by steam distillation. Its condensate has 0.2% AITC dissolved in it.^[7] Butanol is present in dilute concentrations in by-product streams of various organic chemicals.^[11] PEA has potential use in food and fragrance industries and is obtained by fermentation and extraction.^[16] The other organics selected belong to the category where their removal/recovery is required on pollution/economic considerations. All

**Table 1.** General properties and δ values for the organics.

	B.P. °C	Density	Solubility in water, ppm	$c \text{ MPa}^{1/2}$	$\delta_d \text{ MPa}^{1/2}$	$\delta_p \text{ MPa}^{1/2}$	$\delta_h \text{ MPa}^{1/2}$	Molar volume
AITC ^a	150	1.01	2000	21.1	17.1	6.4	10.5	86.0
1-butanol	117	0.81	79000	23.1	16	5.7	15.8	91.5
PEA ^b	220	1.02	16000	23.7	19.2	4.5	13.2	113.6
Benzyl alcohol	205	1.05	36000	23.7	18.4	6.3	13.7	103.6
Aniline	184	1.02	40000	22.5	19.4	5.1	10.2	91.5
Benzaldehyde	180	1.05	4000	21.5	19.4	7.4	5.3	101.5
Nitrobenzene	211	1.05	1900	22.1	20.1	8.6	4.1	102.7
Carbon tetrachloride	77	1.59	800	17.8	17.8	0	0.6	97.1
Water	100	1.0	—	47.9	15.5	16	42.4	18.0
PDMS ^c	—	—	—	16.6	16.0	0.1	4.7	—

All other δ values are reported by Grulke.^[23]

^a δ values calculated by Hoy's group contribution method.^[23]

^b δ values calculated by van Krevelin's group contribution method.^[23]

^c δ values reported by Mulder.^[18]

**Pervaporative Separation of Organics from Aqueous Solutions****1073**

the compounds used are hydrophobic in nature and should be readily sorbed by the hydrophobic PDMS membrane. However, they have different diffusional cross sections, and hence their membrane phase diffusivities would be different.

2. THEORY

The transport of the permeate through the dense membrane involves three successive steps^[2]:

- 1) Upstream portioning of the feed components between the flowing liquid mixtures and the swollen upstream layer of the membrane (sorption).
- 2) Diffusion of the penetrants through the permselective membrane barrier (diffusion).
- 3) Permeate desorption, which takes place at the downstream side of the membrane (evaporation).

This multistage process is very complex as compared to the single vaporization step, and hence the composition of permeates is quite different from VLE.^[17] In this three-step process, generally step 1 or 2 is important. Therefore, separation in pervaporation is based on differences in solubility (sorption) and diffusion.

2.1. Sorption

An ideal membrane is sorption selective for one of the components in the feed mixture. Thus, a particular component is preferentially sorbed by the membrane surface. The preferential sorption occurs when the compositions of binary liquid mixture inside the polymer and in the liquid feed mixture are different.^[18] This represents the sorption selectivity. Various intermolecular forces are necessary for sorption to occur. These are solubility-determining forces. If the solubility of membrane material is high in the desired component of binary liquid feed, then its sorption selectivity for this component is also higher. The sorption of a membrane depends on the presence of functional groups and the free volume to accommodate the sorbed species.

2.1.1. Interactions/Forces

These interactions/forces contributing to potential energy of the molecule are^[19]:

A) Dispersion Forces:

These arise from the fluctuating atomic dipole caused by the presence of a positive nucleus with electrons rotating about it.

B) Polar Forces:

These arise from i) the interaction of permanent dipoles in the interacting molecules and ii) the induction of dipole in other molecules by the permanent dipoles and thus creating a relatively weak interaction.

C) Hydrogen Bonds:

These exist in compounds having hydroxyl or amino groups (water, alcohol, acid). These act as hydrogen donor and form bonds with hydrogen acceptor.

2.1.2. Solubility Parameter

It is calculated as the square root of cohesive energy density (CED).^[20]

$$\delta = (\text{CED})^{1/2} \quad (1)$$

CED is the ratio of energy of vaporization (potential energy) to the molar volume of the solute.

$$\delta = (\Delta E/V_m)^{1/2} \quad (2)$$

The use of this solubility parameter for predicting the sorption selectivity was described by the regular solution theory proposed by Schatchard and Hildebrand.^[18]

I) Regular Solution Theory^[21]

This theory is based on following assumptions:

- a) Entropy of mixing is ideal.
- b) No change of volume on mixing at constant pressure.

**Pervaporative Separation of Organics from Aqueous Solutions****1075**

The enthalpy of mixing is given by:

$$\Delta H_m = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (3)$$

We can write free energy change for mixing as:

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (4)$$

For mixing to occur ΔG_m must be negative.

As ΔS_m is always positive, ΔH_m must be reduced as much as possible in order to ensure negative ΔG_m .

$$\Delta H_m \text{ is minimum (zero) when } \delta_1 = \delta_2 \quad (5)$$

Per regular solution theory, solubility parameter of the two materials involved should be close to each other for mixing/sorption to occur. This regular solution theory has some limitations for predicting sorption behavior.

Limitations of Regular Solution Theory

It does not consider contribution of polar and hydrogen bonding forces toward cohesive energy.

To overcome the previously mentioned limitation, Hansen^[19] proposed the 3-dimensional solubility parameter approach.

II) Hansen's 3-D Solubility Parameter

The cohesive energy is the sum of its contributions due to dispersion, polar, and hydrogen bonding forces^[19]

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h \quad (6)$$

Dividing by molar volume V_m ,

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (7)$$

For many compounds, δ value and its contributions are not available. However, considering the various groups forming that compound (such as $-\text{CH}_3$, $-\text{CH}_2-$, and $-\text{OH}$ for butanol), δ value can be calculated by group contribution method. Group contribution methods given by Hoy as well as van Krevelen are useful for calculating solubility parameter with its contributions.^[23]

According to this theory, preferential sorption will occur if the difference in the individual contributions of the solubility parameter for solute and

polymer are less.

$$\Delta_{1-2} = (\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \quad (8)$$

But this approach is restricted to a binary system only.

III) Sfferaza's approach:

Sfferaza^[24] used two types of approaches for predicting sorption selectivity in a ternary system based on Hansen's 3-D solubility parameter.

1) Addition-type approach:

$$\Delta = \Delta_{3-2} + \Delta_{3-1} + \Delta_{1-2} \quad (9)$$

2) Ratio-type approach:

$$\Delta = \Delta_{3-2}/\Delta_{1-2} \quad (10)$$

For preferential sorption of solute, each Δ should be very high.

2.2. Diffusion

The sorbed component diffuses across the membrane under an activity gradient. Generally, size of the molecule dominates the diffusion phenomenon.^[25] Diffusion coefficient depends on:

- a) Size of diffusing molecule,
- b) Temperature,
- c) Concentration,
- d) Nature of membrane material.

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 "micro-cavities" or "minute holes" that exist in the polymer matrix, which are generally created by the segmental motion of the side group, can be considered as a factor responsible for accommodation of the penetrant. In this stage, some segmental chains are flexible enough to move/bend in such a way as to create a passage for

**Pervaporative Separation of Organics from Aqueous Solutions****1077**

the penetrant. Cooperation of the neighboring polymer segments is necessary for the penetrant to diffuse.

Generally two types^[26] of membranes are available, hydrophilic and hydrophobic. The latter type such as PDMS is more suitable for selective organophilic separation. The difference is due to structural properties. In rubbery polymers the polymer chains exhibit a high degree of hydrophobicity. This allows ready redistribution of the free volume, which is essential for rapid diffusion. Thus, rubbery polymers not only exhibit high sorption selectivity for organics because of organophilicity, but they also afford high diffusion coefficient.

2.2.1. Selectivity

Selectivity for pervaporation, i.e., permeation selectivity, is defined as the ratio of desired component in the permeate to that in the feed.

$$\alpha = Y_i/Y_j/X_i/X_j \quad (11)$$

where X and Y represent the weight fraction of corresponding solute in feed and in permeate, respectively. Subscript i refers to the desired component (whose selectivity is to be determined). It incorporates both sorption as well as diffusion selectivity.

The ideal membrane permeation selectivity S_{ij}^o and the real permeation selectivity S_{ij} for a binary mixture are defined as^[27,28]

$$S_{ij}^o = P_i^o/P_j^o \quad (12)$$

$$S_{ij} = P_i/P_j = S_{ij}^{\text{diff}} \times S_{ij}^{\text{sol}} \quad (13)$$

where P^o refers to the permeability of the pure components, P is the permeability of the components in the mixture, S_{ij}^{diff} is the diffusion selectivity, and S_{ij}^{sol} is the sorption selectivity. Furthermore:

$$S_{ij}^{\text{diff}} = D_i/D_j \quad (14)$$

$$S_{ij}^{\text{sol}} = K_i/K_j \quad (15)$$



3. EXPERIMENTAL

3.1. Materials

Elastosil LR 7600 A and B solutions were kindly supplied by Wacker Chemie, Germany, to prepare poly(dimethyl siloxane) membrane. Iso-octane, benzaldehyde, benzyl alcohol, aniline, and butanol were procured from S.D. Fine Chemicals, Mumbai, India. Nishant Aromas, India, kindly supplied phenyl ethyl alcohol. Allyl isothiocyanate (AITC) steam distillation condensate water was obtained from Kancor Flavours and Extracts, India.^[7]

3.2. Membrane Preparation

Elastosil LR 7600 A and B were mixed in 9:1 proportion and 10% solution of this in iso-octane was prepared. It was then spread on a glass plate and then cured at 80°C for 6 hrs.^[14] This procedure yielded a stable PDMS membrane of thickness about 100 microns. [As the membrane was hand cast (with a bar coater) slight variation of thickness was observed (from 98–103 μm). Thus, the thickness of the membrane was taken as 100 μm (average). The flux values reported in the revised manuscript are normalized for a 10- μm -thick membrane.]

3.3. Permeation Studies

Pervaporation experiments were carried out in a batch-stirred cell operated under vacuum.^[29] The downstream pressure was maintained at 1 mm Hg. The cell had 2-flanged compartments. The upper compartment, containing liquid feed, had a capacity of 550 cc and was provided with an outer jacket for temperature control. The membrane was supported on a porous stainless steel sintered disc and sealed with a rubber O-ring. Effective membrane separation area was 19.65 sq. cm. The permeate was collected in traps cooled by liquid nitrogen.

3.4. Analysis of Permeants

The feed and permeate concentrations of all the mixtures were analyzed by measuring the absorbance of UV light in these solutions by Chemito 2100 UV Spectrophotometer at corresponding wavelengths (Table 2).

A two-phase mixture was obtained as the Permeate. This mixture was diluted further with water, to obtain a homogeneous mixture. The permeate was

Table 2. The corresponding wavelength values for the compounds.

Compound	Wavelength, nm
1-butanol	245
2-phenyl ethyl alcohol (PEA)	260
Benzyl alcohol	257
Aniline	283
Benzaldehyde	252
Nitrobenzene	272
Carbon tetrachloride	268
AITC	242

then analyzed and the concentration was obtained from the calibration curve concentration (in ppm) vs. absorbance for the diluted mixture. The original permeate organic concentration was then calculated using the known dilution factor used.

4. RESULTS AND DISCUSSION

In pervaporation of organic compounds from their dilute solutions, concentration polarization in the liquid film can develop. Under these conditions the true membrane permeation behavior is masked by the external diffusion (concentration polarization) resistance. In the present case, the upper liquid feed compartment of the cell used was provided with a downflow turbine. Preliminary experiments were carried out at varying speeds of agitation and the flux values were determined. It was found that starting with a low speed (1 rev/s) the flux values increased and then became constant at and above 4 rev/s for the 100- μ m-thick membrane used. In the experimental data reported in this work all the experiments were carried out at 5 rev/s.

Figures 2–9 show the variation of organic flux and selectivity with feed concentration. Flux was found to increase with increasing feed concentration. It led to enhanced organic flux. At the same time, selectivity decreased at higher concentration.

In the present study, sizes of all the organic molecules are higher than the water molecule. Generally, diffusion process tends to be selective for the smaller size molecule. But due to the ‘surface selective flow,’ such high permeation selectivity for bigger organic molecules, which are preferentially

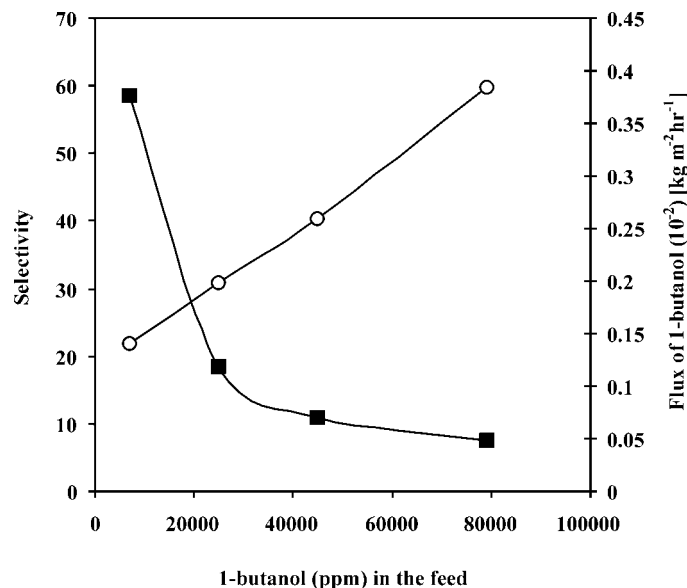


Figure 2. Variation of flux and selectivity of 1-butanol with its feed concentration using PDMS membrane.

sorbed, has been observed.^[30] Surface of the membrane sorbs the organics selectively regardless of their sizes at its active sites. Subsequent diffusion of that selectively sorbed organic molecule in the free volume created yields high permeation selectivity. This surface selective flow has been observed in the permeation of the organics studied.

Solubility parameters of the organics were close to PDMS. But different selectivities for these organics were obtained. Table 3 shows selectivity at saturation concentration (solubility limit) with various approaches of solubility parameters. Surface selective flow relates sorption as the dominant parameter in the permeation process. Hence, different approaches of solubility parameter were tried for correlating with the permeation selectivity.

4.1. Solubility Parameter of Solute Only

PDMS is nonpolar membrane ($\delta_p = 0.1$). Also there is less possibility of hydrogen bonding with PDMS membrane ($\delta_h = 4.7$). Hence, dispersive

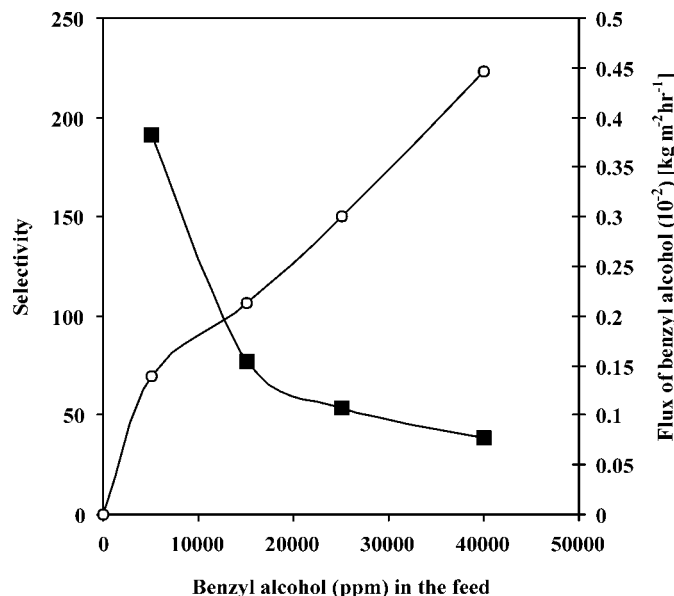


Figure 3. Variation of flux and selectivity of benzyl alcohol with its feed concentration using PDMS membrane.

contribution of solubility parameter δ_d should be dominant for separation. The ratio (δ_d/δ) should be close to one for high selectivity. But poor correlation was observed in order to relate δ_d/δ as the governing factor for selectivity. Similarly, for the ratio of polar contribution (δ_p/δ) , no particular trend was observed. But for hydrogen bonding (δ_h/δ) , a clear trend showed increase in selectivity as the ratio δ_h/δ decrease was observed. As the value of δ_h is low, the hydrophobicity of the solute is more (i.e., less solubility in water, Table 1). This shows that value of δ_h should be low for better permeation of organics through the PDMS (nonpolar, nonhydrogen-bonding) membrane.

This criterion does not consider the membrane characteristics (δ_d , δ_p , δ_h for the membrane). In the case of membranes having strong/moderate hydrogen-bonding capacity, the trend observed might be different. Hence, the generalization of this behavior is not correct in every case. Therefore, it was concluded that these factors alone were insufficient for explaining the permeation selectivity observed.

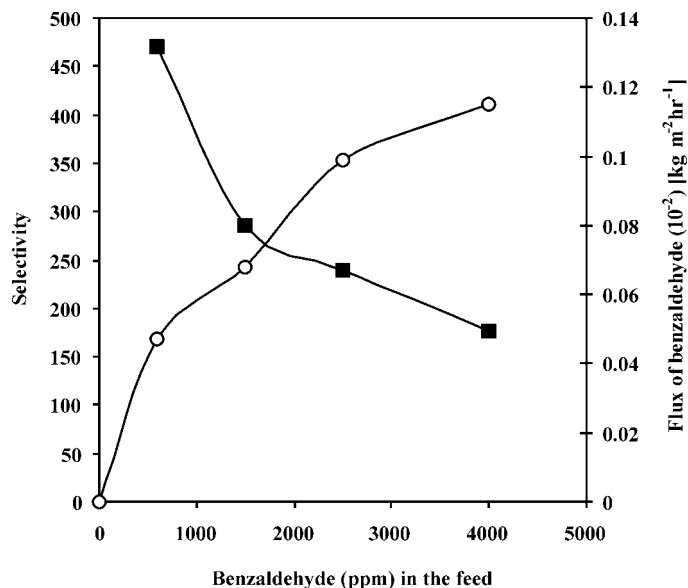


Figure 4. Variation of flux and selectivity of benzaldehyde with its feed concentration using PDMS membrane.

4.2. Hansen's 3-D Solubility Parameter

Hansen's 3-D solubility parameter for solute membrane (Δ_{1-2}) was plotted against permeation selectivity (Fig. 10). But it was not found to be a good criterion for predicting the selectivities observed.

4.3. Sfferaza's Approach

This approach considers all the possible interactions in the ternary organic–water–membrane polymer system. Therefore, it was thought that apart from the individual contributions of solubility parameter and solute–membrane solubility parameter value (Δ_{1-2}), other interactions (Δ_{3-2} and Δ_{3-1}) must have an impact on the separation performance. In view of this the two approaches proposed by Sfferaza^[24] (addition and ratio type of approaches for Δ values, Eqs. (9) and (10), respectively) were used. Figure 11 shows the plot of selectivity at saturation concentration with ratio type of Δ value Eq. (10) and Fig. 12 shows the relation of addition type of Δ value Eq. (9) with

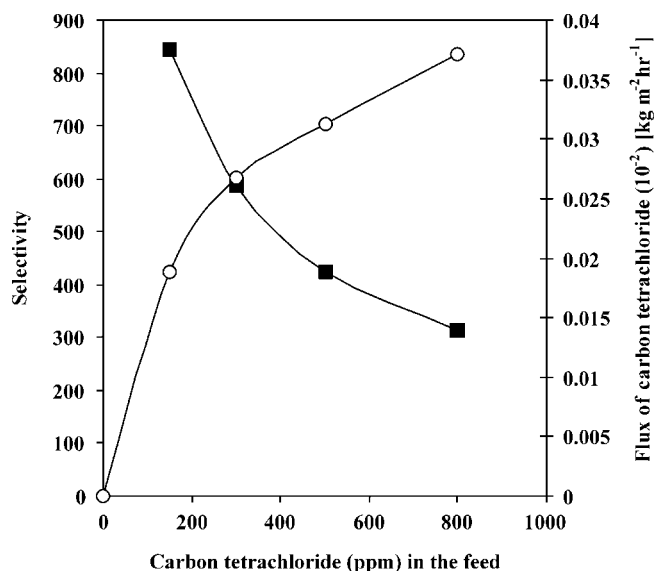


Figure 5. Variation of flux and selectivity of carbon tetrachloride with its feed concentration using PDMS membrane.

selectivity. No correlation was observed with the ratio type of solubility parameter approach for predicting the selectivities. As the Δ value by addition type of approach increases, the permeation selectivities also increase. Thus, the sorption (and hence pervaporation) is found to be explained satisfactorily by Sfferaza's addition type of approach. Also from Table 1, it can be seen that as the hydrophobicity of organics increases (as its solubility in water decreases), selectivity increases.

Figures 11 and 12 include the independent data of Bennett et al.^[31] for pyridine, methylisobutyl ketone (MIBK), phenol, and chloroform for plain (unmodified) PDMS membrane. It is evident that except for chloroform (separation factor 8510, not shown in the figures due to very high value) the other components fit in the trend of data of present work plotted using Sfferaza's addition type approach. This is further supporting evidence in favor of the addition type approach.

A different trend was observed for AITC. Here, selectivity less than one was obtained. AITC has reactive $\text{N}=\text{C}=\text{S}$ group. PDMS (RTV grade) membrane has some vinyl groups for crosslinking. Crosslinker is mixed in the proportion of 9:1, which is sufficient for the membrane preparation. Therefore, some unreacted vinyl groups might be present in the membrane. Hence, there

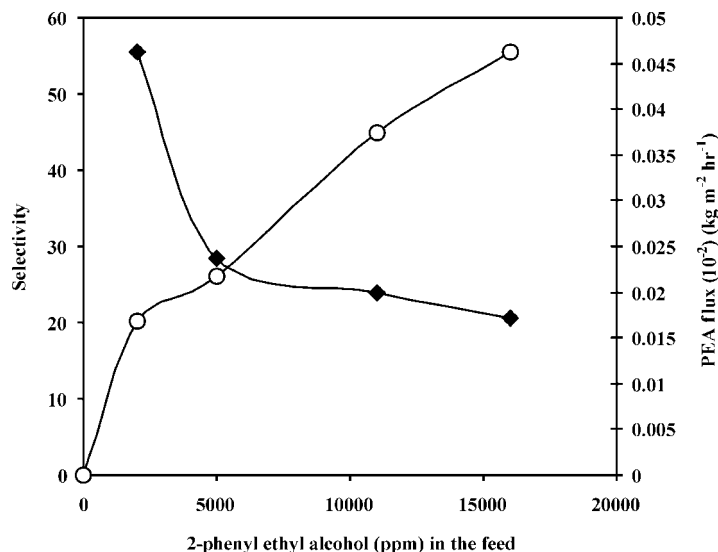


Figure 6. Variation of flux and selectivity of 2-phenyl ethyl alcohol with its feed concentration using PDMS membrane.

is the probability of reaction between these groups and $\text{N}=\text{C}=\text{S}$ group of AITC during the experiment. Bennett et al. in Ref.^[31] their work have shown the effect of different allyl reactive groups e.g., allyl cyanide, allyl benzene with PDMS in presence of platinum catalyst and their performances in separating phenol, chloroform, pyridine, and methylisobutylketone (MIBK). From their work it has been found that such reactive allyl groups react with PDMS and get attached with membrane matrix. Phenol transport was significantly facilitated by the incorporation of basic groups into the membrane structure. For pyridine, chloroform, and MIBK separations from water, selectivity toward organic component was greatly enhanced^[31] by the incorporation of these groups. From this experimental support, it can be confirmed that some reaction between AITC and PDMS matrix occurs.

Generally thiozoles, such as mercaptobenzothiozole (MBT), dibenzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), or sulphenamide, types of compounds containing sulfur in their reactive parts, are used for rubber vulcanization. During the experiment, it was noticed that the membrane acquired a distinct yellow color probably due to the attack of AITC. This is likely to be due to the fact that the AITC gets attacked, which indicated the presence of both sulfur (1.1%) and nitrogen (2.5%) in bound form

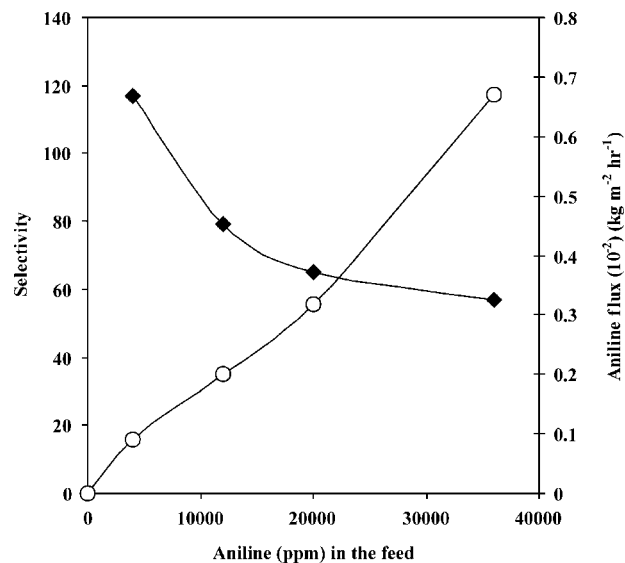
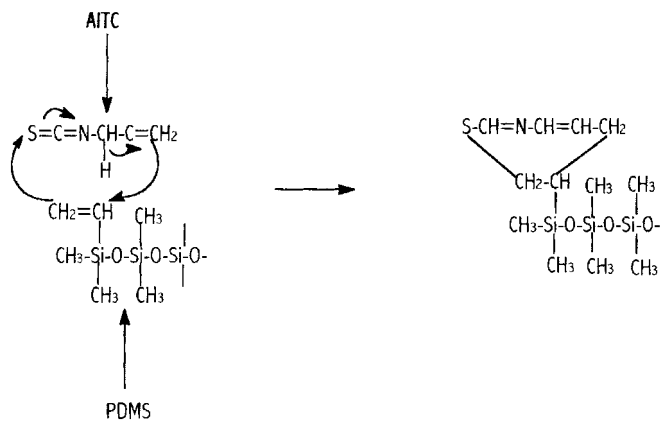


Figure 7. Variation of flux and selectivity of aniline with its feed concentration using PDMS membrane.

(not elemental sulfur or nitrogen). Virgin PDMS does not have any nitrogen or sulfur species. Thus, it could be concluded that the bound sulfur and nitrogen must have come from a reaction between AITC and vinyl groups of PDMS.

Proposed reaction mechanism is as shown:



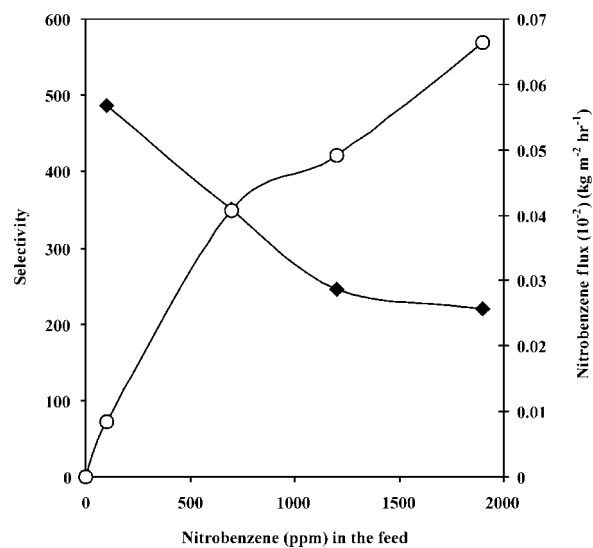


Figure 8. Variation of flux and selectivity of nitrobenzene with its feed concentration using PDMS membrane.

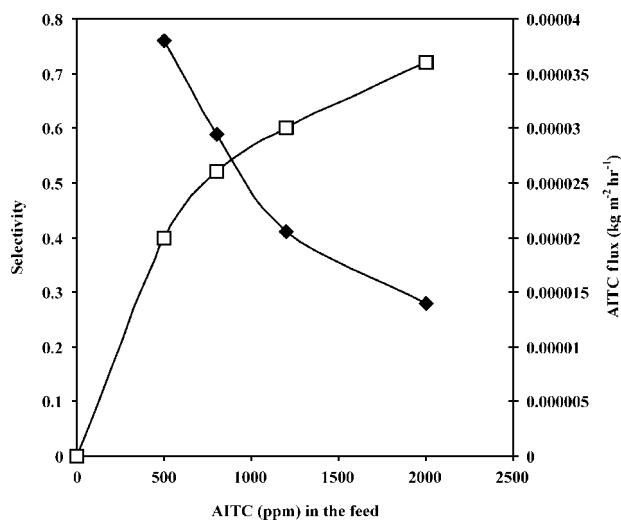


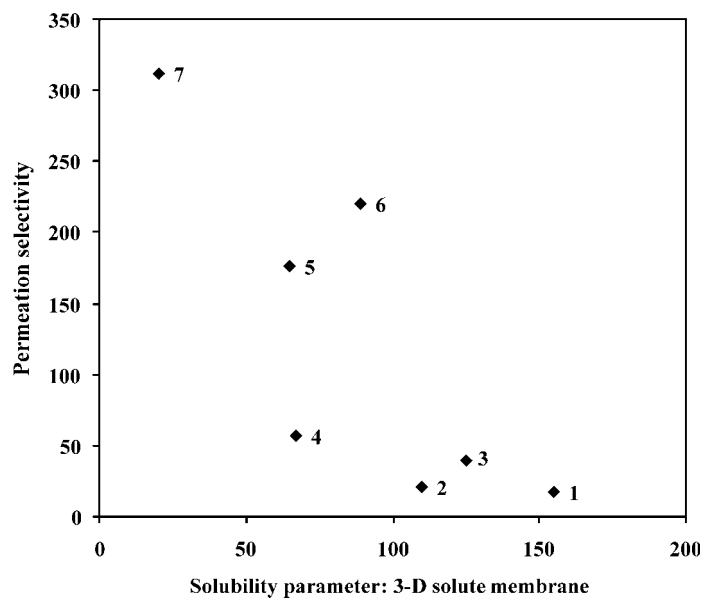
Figure 9. Variation of flux and selectivity of AITC with its feed concentration using PDMS membrane.

Pervaporative Separation of Organics from Aqueous Solutions

1087

Table 3. Selectivity at saturation concentration and criteria using various approaches of solubility parameter.

	δ_d/δ	δ_d/δ	δ_d/δ	Δ_{1-2}	Δ_{Ratio}	Δ_{addition}	Selectivity at sat. conc.
AITC	0.81	0.31	0.50	75	22.32	2711	0.28
1-butanol	0.69	0.25	0.68	155	10.80	2333	17.5
PEA	0.81	0.19	0.56	110	20.90	2369	20.5
Benzyl alcohol	0.78	0.27	0.58	125	13.39	2475	39
Aniline	0.86	0.23	0.45	67	25	2778	57
Benzaldehyde	90	0.34	0.25	65	25.75	3075	176
Nitrobenzene	0.91	0.39	0.19	89	18.8	3128	220
Carbon tetrachloride	1.0	0.00	0.03	20	83.70	3663	312

**Figure 10.** Plot of permeation selectivity with Hansen's 3-D solubility parameter for solute polymer (Δ_{1-2}) of organics. 1) 1-butanol, 2) phenyl ethyl alcohol, 3) benzyl alcohol, 4) aniline, 5) benzaldehyde, 6) nitrobenzene, 7) carbon tetrachloride.

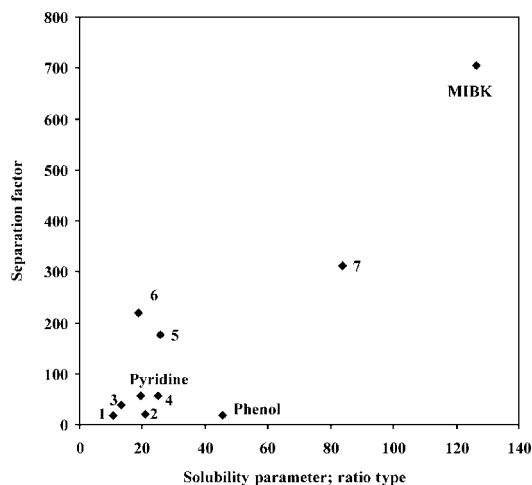


Figure 11. Plot of permeation selectivity with Sfferaza's ratio type of solubility parameter (Δ_{ratio}) [includes the data of MIBK, pyridine, and phenol from Bennett et al.^[31] 1) 1-butanol, 2) phenyl ethyl alcohol, 3) benzyl alcohol, 4) aniline, 5) benzaldehyde, 6) nitrobenzene, 7) carbon tetrachloride.

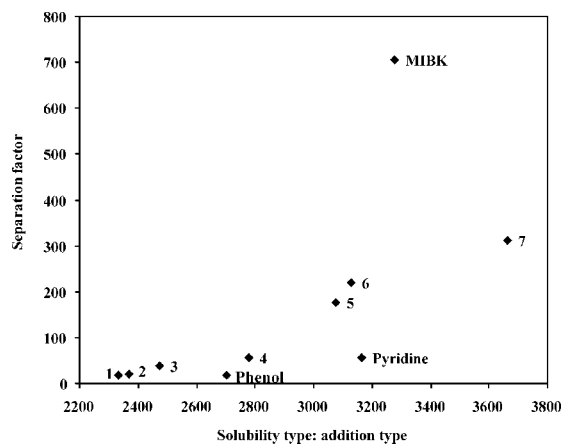


Figure 12. Plot of permeation selectivity with Sfferaza's addition type of solubility parameter (Δ_{addition}) [includes the data of MIBK, pyridine, and phenol from Bennett et al.^[31] 1) 1-butanol, 2) phenyl ethyl alcohol, 3) benzyl alcohol, 4) aniline, 5) benzaldehyde, 6) nitrobenzene, 7) carbon tetrachloride.



Therefore, an elastomeric membrane containing a double bond cannot be used for efficient recovery of AITC by pervaporation.

5. CONCLUSION

PDMS membrane yielded good selectivity for the trace organics removal. Selectivity was found to increase with the hydrophobicity of organics. For the nonpolar membrane like PDMS, value of δ_h of the organic should be low in order to achieve good selectivity. Among the various approaches for predicting sorption selectivity, Sfferaza's addition type of approach using 3-D solubility parameter was found to be most satisfactory for predicting permeation selectivity.

NOTATION

T	absolute temperature (K)
ΔE	total energy of vaporization
ΔG_m	Gibbs free energy change on mixing
ΔH_m	enthalpy change on mixing
ΔS_m	entropy change during mixing
V_m	molar volume of the mixture
X	weight fraction in feed
Y	weight fraction in permeate
ϕ	volume fraction in the mixture
δ	solubility parameter, (MPa ^{1/2})
α	selectivity

Subscript

1	organic
2	membrane
3	water
d	dispersive
p	polar
h	hydrogen bonding
i	desired component



REFERENCES

1. Binning, R.C.; Lee, R.J.; Jennings, J.F.; Martin, E.C. Separation of liquid mixtures by permeation. *Ind. Eng. Chem.* **1961**, *53* (1), 45.
2. Neel, J. Introduction to pervaporation. In *Pervaporative Membrane Separation Processes*; Huang, R.Y.M., Ed.; Elsevier: Amsterdam, 1991; 1.
3. Lipnizki, F.; Field, R.W.; Ten, P.-K. Pervaporation-based hybrid process, a review of process design, applications and economics. *J. Membr. Sci.* **1999**, *153* (2), 183–210.
4. Lipnizki, F.; Hausmanns, S.; Ten, P.K.; Field, R.W.; Laufenberg, G. Organophilic pervaporation—prospects and performance. *Chem. Eng. J.* **1999**, *73* (2), 113–129.
5. Netke, S.A.; Sawant, S.B.; Joshi, J.B.; Pangarkar, V.G. Comparative study of membranes for pervaporation of trace organics from aqueous solutions. In *Proc. of Euro-membrane-95 Conf.*; Bowen, W.R., Field, R.W., Howell, J.A., Eds.; Europ. Soc. for Membrane Sci. & Technol.; 1995; Vol. 2, 116.
6. Machale, K.W.; Niranjan, K.; Pangarkar, V.G. Recovery of dissolved essential oils from condensate water of Basil and Mentha arvensis distillation. *J. Chem. Technol. Biotechnol.* **1997**, *69*, 362.
7. Joagdeo, D.A.; Niranjan, K.; Pangarkar, V.G. Recovery of dissolved allyl isothiocyanate from mustard essential oil steam distillation condensate. *J. Chem. Technol. Biotechnol.* **2000**, *75*, 673.
8. Bohra, P.M.; Vaze, A.S.; Pangarkar, V.G.; Taskar, A. Adsorptive recovery of waster soluble essential oil components. **1994**, *60*, 97.
9. Blume, I.; Wijmans, J.G.; Baker, R.W. The separation of dissolved organics from water by pervaporation. *J. Membr. Sci.* **1990**, *49*, 253.
10. Joyce, P.C.; Devine, K.M.; Slater, C.S. Separation of pyridine/water solutions using pervaporation. *Sep. Sci. Technol.* **1995**, *30* (10), 2145.
11. Hickey, P.J.; Slater, C.S. Pervaporation of dilute ethanol solution through hydrophobic membrane. *Proceedings of 4th Int. conf. on pervaporation processes in chemical industries*; Bakish, R., Ed.; B.M.C.: New Jersey, 1989; 579.
12. Baudot, A.; Marin, M. Dairy aroma compounds recovery by pervaporation. *J. Membr. Sci.* **1996**, *120*, 207.
13. Hennepe, H.J.C.; Bargemen, D.; Mulder, M.H.V.; Smolder, C.A. Pervaporation with zeolite filled silicone rubber membrane. *Proceedings of 2nd Int. conf. on pervaporation processes in chemical industries*; Bakish, R., Ed.; B.M.C.: New Jersey, 1987; 71.



Pervaporative Separation of Organics from Aqueous Solutions

1091

14. Netke, S.A.; Sawant, S.B.; Joshi, J.B.; Pangarkar, V.G. Sorption and permeation of aqueous picolines in elastomeric membranes. *J. Membr. Sci.* **1994**, *91*, 163.
15. Lee, Y.M.; Bourgeois, D.; Belfort, G. Selection of polymer membrane material for pervaporation. Proceedings of 2nd Int. conf. on pervaporation processes in chemical industries; Bakish, R., Ed.; B.M.C.: New Jersey, 1987.
16. Fabre, C.E.; Blanc, P.J.; Marty, A.; Goma, G.; Souchon, I.; Voilley, A. Extraction of 2-phenyl ethyl alcohol. *Perfum. Flavor.* **1996**, *21*, 27.
17. Ten, P.-K.; Field, R.W. Organophilic pervaporation: an engineering science analysis of component transport and the classification of behaviour with reference to the effect of permeate pressure. *J. Chem. Eng. Sci.* **2000**, *55*, 1425–1445.
18. Mulder, M.H.V. Thermodynamic principles of pervaporation. In *Pervaporative Membrane Separation Processes*; Huang, R.Y.M., Ed.; Elsevier: Amsterdam, 1991; 225.
19. Hansen, C.M. The three dimensional solubility parameter—key to paint components affinities. I. Solvents, plasticizers, polymers and resins. *J. Paint Tech.* **1967**, *39* (505), 104.
20. Hildebrandt, J.H.; Scott, R.L. *Solubility of non-electrolytes*; Reinhold Publishing Corporation: U.S.A., 1950; Chap. 7, 119.
21. Hildebrandt, J.H.; Scott, R.L. *Regular Solutions*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1962.
22. Kirk Othmer's, Encyclopedia of Chemical Technology. **1997**, *22*, 534.
23. Grulke, E.A. Solubility parameter values in Bandrup. In *Polymer Handbook*; Immergat, J., Ed.; Wiley Interscience Publications: U.S.A., 1975; 675.
24. Sfferaza, A.R. PhD Dissertation, Chem. Eng. Dept., Clemson Univ., Clemson, USA, 1988.
25. Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic Publishers: London, 1996; Chap. 5, 210.
26. Bell, C.M.; Gerner, F.J.; Strathmann, H. Selection of polymers for pervaporation membranes. *J. Membr. Sci.* **1988**, *36*, 315–329.
27. Boddeker, K.W. Terminology in pervaporation. *J. Membr. Sci.* **1990**, *51*, 259–272.
28. Wojciech, K. Membrane selectivity in pervaporation. *Sep. Sci. Technol.* **1996**, *31* (11), 1555–1571.
29. Bhat, A.A.; Pangarkar, V.G. Methanol selective membranes for pervaporative separation of methanol–toluene mixtures. *J. Membr. Sci.* **2000**, *167*, 187.



1092

Samdani, Mandal, and Pangarkar

30. Koros, W.J.; Mahajan, R., Pushing the limits on possibilities for large scale gas separation: which strategies? *J. Membr. Sci.* **2000**, *175* (2), 181–196.
31. Bennett, M.; Brisdon, B.J.; England, R.; Field, R.W. Performance of PDMS and organo-functionalised PDMS membranes for the pervaporative recovery of organics from aqueous streams. *J. Membr. Sci.* **1997**, *137*, 63–88.

Received October 2001

Revised July 2002