Separation of Volatile Organic Compounds by Pervaporation for a Binary Compound Combination: Trichloroethylene and 1,1,1-Trichloroethane

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This study evaluates the behavior of sweeping air pervaporation when used to separate trichloroethylene (TCE) and 1,1,1-trichloroethane (TCEthane) from wastewater. Selectivity and membrane preference are studied. Models for binary compounds are studied to evaluate the extent of cross influence on TCE flux due to the presence of another volatile organic compound, TCEthane. Using the models, the integral dry diffusion coefficient for TCEthane is evaluated. Results indicate that the membrane exhibits a preference for TCE over TCEthane. However, the values of the diffusion rates are found to be comparable. Selectivity values are found to be independent of the air flow rate but dependent on the relative concentration of the compounds in the feed solution. It is found that, due to the presence of TCEthane, the flux of TCE decreased. Further, it is found that the ratio of the integral dry diffusion coefficients of the compounds is inversely proportional to the ratio of their molecular weights.

Introduction

Conventional technologies like air stripping, activated carbon adsorption, chemical oxidation, incineration, etc., are found to be only partially successful (Brown et al., 1993) for treatment of volatile organic compounds (VOCs), especially when the concentration of the VOCs is very low in a contaminated stream and the quantity of wastewater is large. Interest has therefore been shifted to explore other forms of technology as well. Pervaporation, which is a technology predominantly used in chemical engineering for dehydration of alcohols and breaking of azeotropic mixtures, seems to be an emerging substitute to the conventional treatment processes.

VOCs have long being held as a potential threat to biosphere, and most of these compounds are classified as priority pollutants. Of the commonly occurring VOCs, trichloroethylene (TCE; CAS No. 79-01-6) and 1,1,1-trichloroethane (TCEthane; CAS No. 71-55-6) are found abundantly and in the highest concentrations (Love and Eilers, 1982). These compounds are used in industry predominantly as solvents for cleaning, metal degreasing, and various other activities. The tendency to volatilize within a very short time once these compounds come into contact with the atmosphere has augmented the problem of treatment. An uncontrolled volatilization is not at all desirable due to the risk of subsequent air pollution. Out of the different possible treatment pathways, one may be to remove the solvents by an in-line stripper from the wastewater and put it to the final treatment by incineration, catalytic combustion, chemical oxidation, etc., i.e., those technologies which are better known. The VOC can be either caught in a vacuum as in the case of vacuum-aided pervaporation or in a gas/air stream as in the case of sweeping gas/air pervaporation. One advantage of using in-line stripping first is to eliminate chances of uncontrolled

volatilization and improve the performance of the conventional techniques due to a higher concentration of VOCs in a small amount of gas/air. Also, elaborate arrangements for treating the wastewater are eliminated.

We have undertaken a study to understand the behavior of pervaporation in separating the VOCs from a synthetic wastewater. Sweeping air pervaporation or air perstripping (Acda and Mora, 1992) was chosen because handling of air compared to vacuum may be more suitable for practical implementation of the system. Well-proven air-handling equipment is already available, is commonly used, and involves a lesser degree of complication in installation, operation, and maintenance.

The results obtained for a binary compound combination (TCE and TCEthane) are discussed. Additional references to the results obtained from single-compound (TCE) pervaporation are provided wherever deemed necessary. These results, when integrated with more results on the subject, will form the basis of evaluating the suitability of pervaporation as a stripping technology.

Theoretical Considerations

In order to evaluate the performance of pervaporation, two parameters, flux and selectivity, are commonly used. Flux is defined as the amount (mass or mole) of the target compound in the permeate and is given by

$$J_i = Q_i/At \qquad (1)$$

Selectivity can be defined as the relative separation achieved, between the compounds, due to the difference in the transport rate of the permeants through the membrane, which reflects the interaction of the permeate with the membrane polymer. It is also an indirect measure of the preferential sorption, as it is found that the compound that is preferentially sorbed also permeates preferentially (Mulders and Smolders, 1991). Math-

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ematically, selectivity can be expressed [in line with Spitzen (1988)] as the ratio of the fluxes of two compounds for unit concentration of each in the feed.

$$\alpha \text{ (selectivity)} = \frac{J_i/C_{if}}{J_j/C_{jf}} \qquad (2)$$

Model for Single-Compound Permeation. Out of the different mathematical models used so far for estimating the flux of a compound beforehand, the solution–diffusion (S–D) model is used widely and can be derived (Mulder and Smolders, 1991) from Fick's law of diffusion, the final form of which can be expressed as

$$J_i = \frac{D_{oi}}{Y_i \delta}[\exp(Y_i C_{if}) - 1] \qquad (3)$$

where D_{oi} is the dry diffusion coefficient at zero swelling condition and is independent of the feed side concentration. The above equation can be further simplified (by expanding the exponential series) to

$$J_i = D_{oi}(C_{if}/\delta) \qquad (4)$$

Replacing D_{oi}/δ by K_{oi}, which can be defined as the dry diffusion coefficient per unit membrane thickness or the integral dry diffusion coefficient, the above equation can be written as

$$J_i = K_{oi} C_{if} \qquad (5)$$

The most important assumptions underlying the above derivation are the following:
(i) diffusion of a compound through the membrane is the rate-limiting step,
(ii) the gas phase concentration of a permeant in the permeate is negligible compared to that of the liquid phase, and
(iii) the integral dry diffusion coefficient, K_{oi}, is independent of the concentration of the permeant in the liquid phase.

It is found from eq 5 that flux depends on the feed concentration of the target compound, and therefore, the total quantity of flux depends on the initial feed concentration. In order to compare the different values of flux (for a close range of initial feed concentrations), the concept of normalized flux has been used. Normalized flux is calculated as the average flux over the log-mean concentration of the compound in the feed, i.e., it is the flux per unit concentration of the compound in the feed. Comparison of the normalized flux thus eliminates the variance of initial feed concentration. In this study, log-mean concentration has been used instead of arithmetic average between two different points of time, in line with the log-mean drive commonly used for a chemical diffusion process. Log-mean concentration has been calculated as

$$\text{log-mean } C_i = \ln \frac{C_{i1} - C_{i2}}{C_{i1}/C_{i2}} \qquad (6)$$

Model on Binary Compound Permeation. The S–D model is valid only for a single-compound permeation. However, in cases of more than one compound, the prediction of flux cannot be done so simply and more complex relationships are required. The most important factor in these models is the estimation of the mutual

coupling effect. The mutual coupling effect gives an idea of the amount of cross influence on the diffusion of one compound by any other compound(s). The extent of such a mutual coupling effect is not only difficult to measure quantitatively but also difficult to estimate beforehand (Mulder and Smolders, 1991).

Of the various models that have been proposed by different researchers, a simple one was presented by Kadem (1989). In the present study, this model has been used to investigate the nature of mutual coupling effect.

The derivation of the model is not dealt with here; however, some important assumptions and terms are explained here for convenience.

The final form of the model as proposed by KADEM, can be expressed as

$$J_i = P_i p_{if} \frac{QJ_j}{1 - \exp(-QJ_j)} \qquad (7)$$

and

$$J_j = P_j p_{jf} \frac{QJ_i}{1 - \exp(-QJ_i)} \qquad (8)$$

Q is defined as the drag coefficient, and it is the parameter which gives an idea of the mutual coupling effect. It is termed the drag coefficient to indicate a drag on the flux of one compound due to the presence of additional compound(s).

The major assumption in the derivation of the model was that Q and the permeability coefficients (P_i, P_j) are independent of the concentration of the target compounds. However $P_i p_{if}$ and $P_j p_{jf}$ can be replaced by $D_i C_{if}$ and $D_j C_{jf}$, respectively, using Henry's law given by

$$P_{ij} = H_{ij} D_{ij} \qquad (9)$$

and

$$p_{ij} = C_{ij}/H_{ij} \qquad (10)$$

D_i is, however, not independent of the concentration and can be given as (Mulders and Smolders, 1991) $D_i = D_{oi} \exp(Y_i C_{if})$. For very low values of C_{if} (the case normally encountered with real wastewater), $\exp(Y_i C_{if})$ tends to unity and $D_i \approx K_{oi}$ for unit membrane thickness. Thus eqs 7 and 8 can be written as

$$J_i = K_{oi} C_{if} \frac{QJ_j}{1 - \exp(-QJ_j)} \qquad (11)$$

and

$$J_j = K_{oj} C_{jf} \frac{QJ_i}{1 - \exp(-QJ_i)} \qquad (12)$$

Or

$$J_i = K_{oi} C_{if} \psi_j \qquad (13)$$

and

$$J_j = K_{oj} C_{jf} \psi_i \qquad (14)$$

where

$$\psi_i = \frac{QJ_j}{1 - \exp(-QJ_j)} \qquad (15)$$

Table 1. Experimental Organization

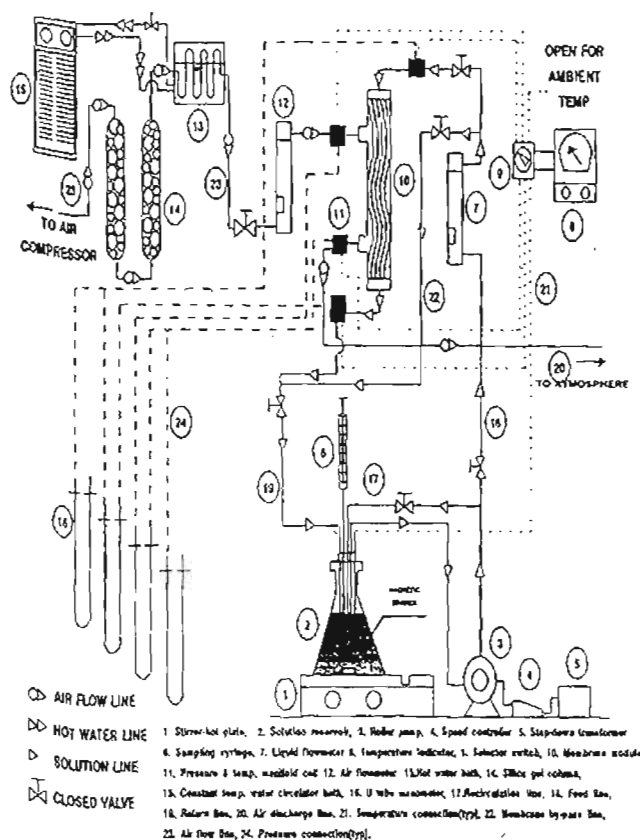| compound used	concn ranges (ppm, w/w)	air flow rate (L/min)	other conditions
trichloroethylene and distilled water	1000–800, 800–600, 600–400, below 400	10, 12, 14, 16, 18, 20	feed flow 0.5 L/min
1,1,1-trichloroethane, trichloroethylene, and distilled water	for TCEthane: 800–600, 600–400, 400–300, below 300	10, 12, 14, 16, 18, 20	feed flow 0.5 L/min, TCE concn 600–400 ppm (w/w)

Figure 1. Schematic arrangement for experimental apparatus.

and

$$\psi_j = \frac{QJ_i}{1 - \exp(-QJ_i)} \tag{16}$$

If eq 13 is compared with eq 5, ψ_j can be interpreted as a factor by which flux of compound i will reduce due to the presence of another compound j compared to when used singly.

Experimental Section

Experimental Procedures. Figure 1 shows the layout of the experimental setup for the cocurrent flow mode; i.e., the air and solution flow in the same direction parallel to each other. It was found from the previous study with air perstripping (Castillo et al., 1994) that cold trapping of the permeate vapor (for measuring the concentration of VOC in permeate), using liquid nitrogen, was not effective and reliable. This was due to the shortage of capacity of the trapping devices used. Instead, depletion of concentration can be measured directly from the feed solution to estimate the efficiency of stripping.

Depletion of VOCs was monitored by sampling, at definite time intervals, directly from the feed reservoir. The depletion was converted first to VOC amount and then to VOC flux. Water flux was measured similarly, by noting the loss of water from the feed reservoir with
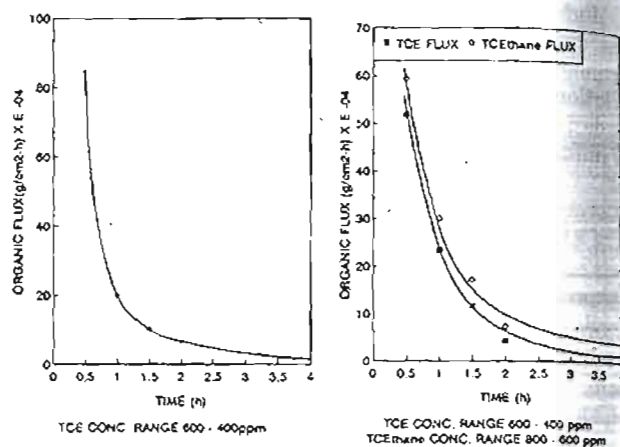

Figure 2. Time decay of organic flux.

the help of a level scale attached on the outer surface of the volummetric flask (feed reservoir).

Membrane and Module. Commercial composite (SEM-PVG-G3) of dense silicone permselective active layer, supported over a relatively thick poly(ether sulfone) layer, was used as membranes (Sempas Membrantechnik GmbH, Germany). Fifteen capillary fibers of ~150 cm² total effective area potted/fixed in a glass tube ~360 mm long and 20 mm in diameter were used.

Analysis. Headspace analysis (Dietz and Singley, 1979) was performed to determine the concentration of VOCs in the sample. Samples of 10 mL were taken from the feed reservoir and stored in 120 mL serum bottles capped with Teflon-lined rubber septa and Teflon sheets. Samples were kept inside a rotary-shaker incubator at 25 °C and 60 rpm for at least 4 h prior to any analysis. Headspace gas (0.25 mL) was withdrawn from the serum bottle with the help of a precision airtight glass syringe and then injected into the gas chromatograph (GC) machine. All concentrations were measured using a Shimadzu CR14A GC, with a 2 m long stainless steel column packed with 1% SP-1000 on Carbopack B 60/80 mesh. The carrier gas was nitrogen at a head pressure of 196.2 kPa. The injector temperature was 210 °C, the oven was held isothermally at 190 °C, and the flame ionization detector at 230 °C.

Wastewater Preparation. Reagent-grade chemicals were used to prepare synthetic wastewater in the laboratory. The chemicals were dissolved in 2% (v/v) methanol solution. The feed solution and air temperature were kept constant at 40 ± 2 and 30 ± 4 °C, respectively, for all experiments.

Experimental Organization. The experimental organization is shown in Table 1.

Results and Discussion

Figure 2 shows the comparison of the time decay of flux for the single-compound (TCE) and for the binary compound combination (TCE and TCEthane). The trend of the curve clearly shows that the nature of the relationship is the same irrespective of the number of compounds in the solution. The initial higher rate of permeation is due to the availability of a large concen-
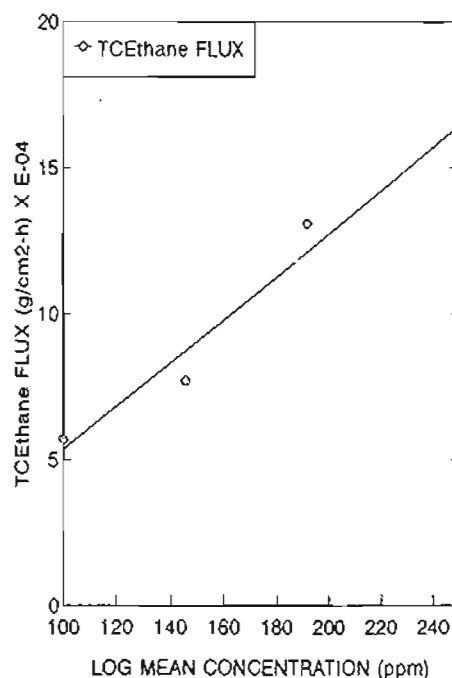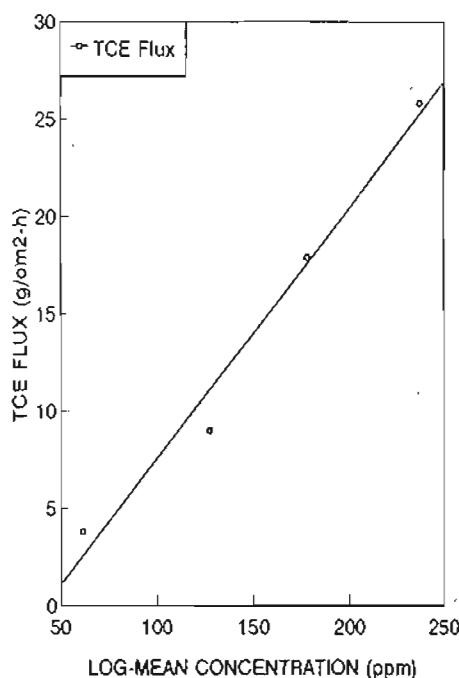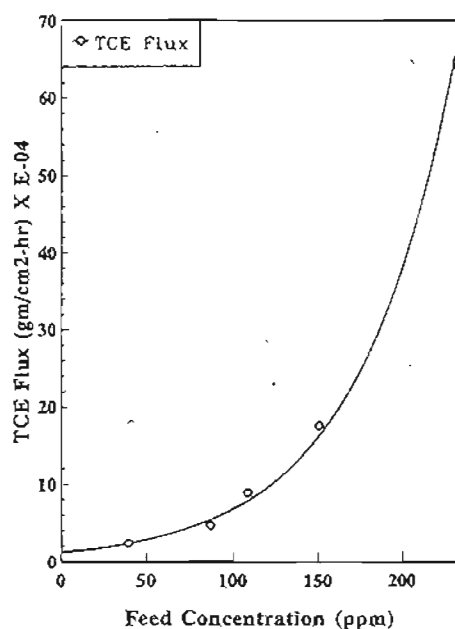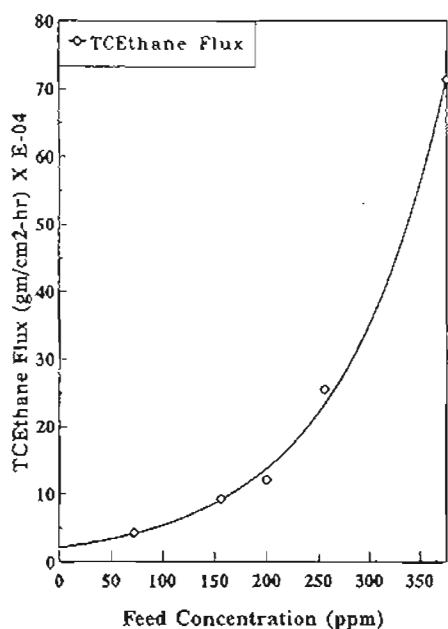
Figure 3. (a, top) Variation of flux with feed concentration. (b, bottom) Variation of flux with log-mean concentration.

tration gradient of the permeating compounds between the feed side and the vapor side, as well as more empty space or free volume in the virgin polymer network. With time, the concentration gradient reduces (as the experiments were operated in a recycled batch mode) and more and more saturation is achieved due to the residual permeating molecules inside the network. After a sufficient time, the permeation rate reduces significantly and the rate of change is practically negligible. At this stage the number of molecules entering the membrane and leaving it should be very nearly equal and the membrane may have attained a full swelling condition.

Had it been that only the operating mode is the single cause of this phenomenon one could have expected an almost linear decay of the flux instead of the exponential one as obtained. This suggests that the saturation of membrane free volume must have played a prominent role. However, attainment of a dynamic equilibrium is hinted by almost quasi-flattening of the flux lines (at the later part) but cannot be firmly established due to constant depletion of molecules (for batch-mode experimentation) in the feed side. Operation in a continuous mode will probably clarify the doubts regarding the attainment of the dynamic equilibrium.

The variation of flux with the feed and log-mean concentration is shown in Figure 3. It can be noted that the variation of flux with the log-mean concentration is a straight line relationship. From these experimental results, it is found that in eq 5 substitution of log-mean concentration may be more appropriate. Otherwise it may be more suitable to use eq 3 after values of K_{oi} and Y_i are obtained. It is also found that the relationship is same for both the compounds used, which means that usage of the log-mean concentration in eqs 13 and 14 may be also permitted.

Values of α (from a set of 24 experiments, selectivity values are found to lie between 1.096 and 1.205) are
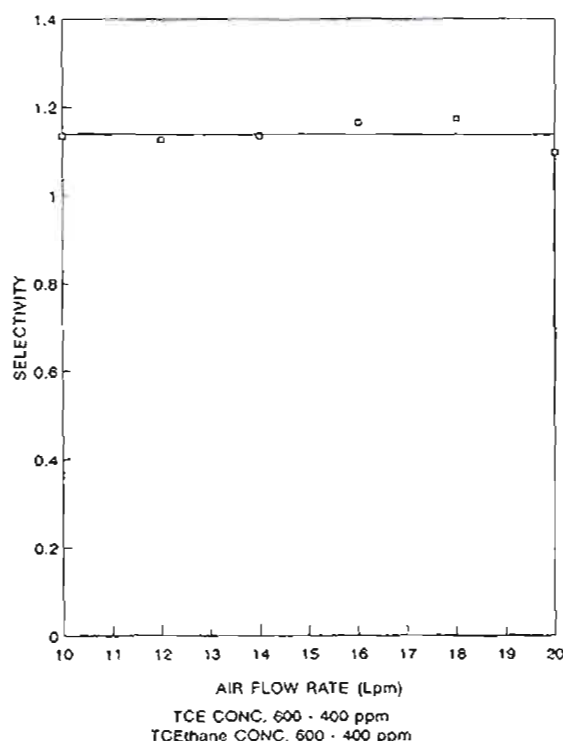
Figure 4. Effect of air flow rate on selectivity.

calculated using eq 2, where i stands for TCE and j for TCEthane. The values of selectivity greater than unity indicates that the membrane "prefers" TCE to TCEthane. The cause can be explained by considering the molecular structure of the two compounds. Because of the presence of a double bond between the two carbon atoms in a TCE molecule, it is spatially less voluminous compared to a TCEthane molecule that has a single bond between the two carbon atoms. Thus, a TCE molecule is less "spread" (spatially or is more "planer"), and resistance to its diffusion through the membrane network may therefore also be less. Moreover, TCE is less polar than TCEthane (dipole moment of TCE, 1.01; TCEthane, 1.78), which can also be accounted for its higher permeability. The lower the polarity the higher is the sorption and the permeability. Both the above phenomena were also observed by Dotremont et al., (1993). However, from the selectivity values, a marked difference cannot be identified because it is found that for volatile compounds the rate of diffusion is primarily controlled by the bulk liquid phase transport (Psaume et.al, 1988). The diffusion coefficient of TCE in water is ~1.1 times that of TCEthane, which might have played an important role in the selectivity values.

From the above discussion it is found that the membrane selects a less polar molecule (TCE) compared to a high polar molecule (TCEthane), which indicates that the membrane will reject water (which is highly polar) relatively more compared to an organic solvent. This is a prime requirement for separating organic compounds from industrial wastewater. However, under all ordinary circumstances, the concentration of VOC is very low and therefore appreciable water flux will be produced along with high VOC flux.

Selectivity is found to be independent of the air flow rate, as shown in Figure 4. It is seen from the figure that an increase of air flow rate will not enhance or diminish the sorption and diffusion characteristics of a compound relative to the other, unless the air flow rate is diminished to an extent that proper sweeping is

affected. In other words, a change of air flow rate will have virtually no effect on the value of α as long as proper sweeping takes place. This indicates that selectivity is a property that depends on the polymer-penetrant relationship and the relative concentration of the compounds used and not on the downstream conditions.

Figure 5 shows the relationship of selectivity with concentration of the organic compounds. It is seen that, with the increase of TCEthane concentration in the feed, the selectivity value decreases and approaches unity. A higher concentration of TCEthane in the feed for a fixed concentration of TCE produces a higher TCEthane flux. Further, it will be found that when the TCEthane concentration is increased the flux of TCE is reduced due to the mutual coupling effect. Therefore, the value of the numerator of eq 2 is lowered and the value of selectivity is lowered. On the other hand, a higher concentration of TCE in the feed means a higher diffusion rate of TCE and higher selectivity values. Thus, it is found that selectivity depends upon the relative concentration of the compounds. Mulder and Smolders (1991) also found that the interaction parameters for preferential sorption are concentration dependent, which is in line with the results obtained here.

Model Study. The average value of K_{oi} is evaluated from the first set of experiments with TCE alone. This value of K_{oi} for TCE is then introduced in eq 11 to calculate the drag coefficient Q, using values of J_i, J_j, and C_{if} as obtained from the second set of experimental data with binary compounds. The values of Q as obtained are mostly negative (ranging from -0.00537 to -0.0544), indicating that there is a flux reduction. From these values of Q, values of ψ_j are calculated. ψ_j comes out to be in the range of $0.65-0.97$. Thus, there is a reduction in the TCE flux due to the presence of TCEthane. Somewhat similar results were obtained by Huang and Feng (1992) in their study with water/ ethanol, where they observed that the water flux decreases with increase of the ethanol concentration in the feed. The probability of such a phenomenon was indicated by Nguyen (1986). A major cause of such a reduction may be due to the competition among the compounds (that are somewhat similar in nature) for occupation of the free volume in the membrane network, or repulsive interaction between them, or both. The repulsive action can be important due to the basic similarity in the nature of the compounds used. The sharing of sites in the membrane matrix by the two compounds and/or their repulsive interaction will therefore allow each of the compounds to diffuse in a lower quantity than they could have done if present singly. However, with the present sets of experimental results, it is not possible to investigate whether diffusion of the compounds through the liquid and gaseous phases is also modified due to the repulsive interaction between the interfering compounds. No reported study could be found on this subject. Even if there is any modification in the bulk liquid phase, any change in the bulk gaseous phase can be ruled out due to the very negligible influence of this over the whole diffusion process.

Generally it is found that the lowest values of ψ_j are obtained when the concentrations of TCEthane are highest while the highest values of ψ_j are obtained for the lowest concentrations of TCEthane. Figure 6 shows is relationship (the intermediate gap is due to the absence of any experimental data in this range). It may be concluded that, for higher concentrations of one
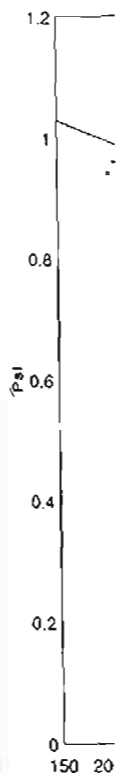
Figure 5. Va

Figure 6. V

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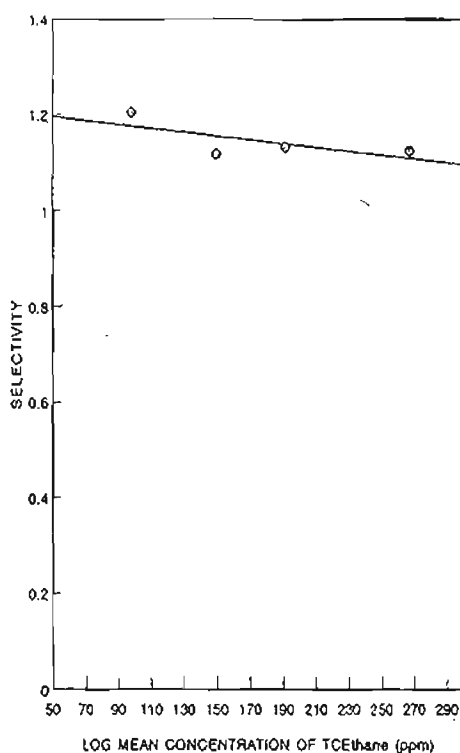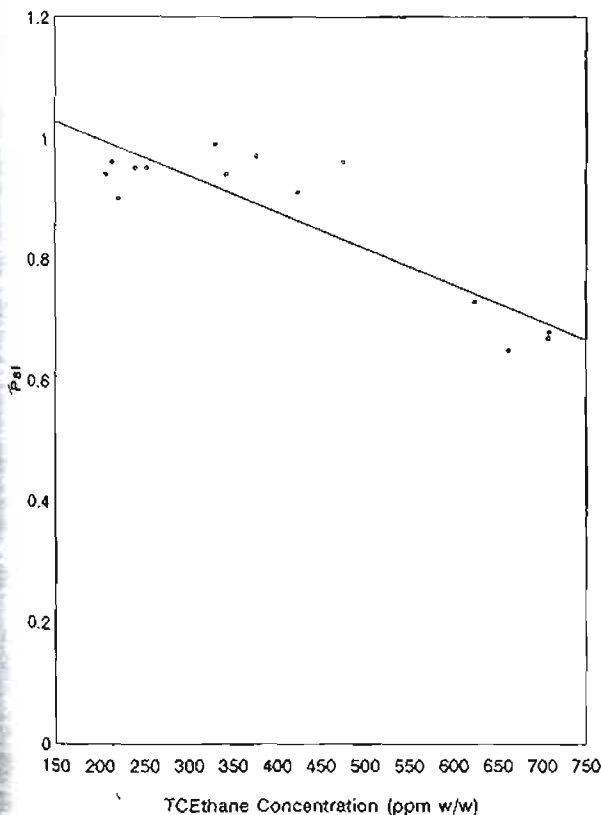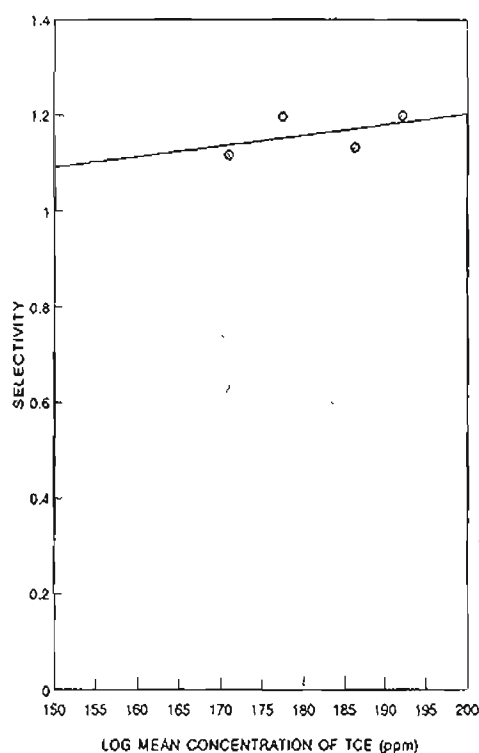
Figure 5. Variation of selectivity with log-mean concentration.

Figure 6. Variation of ψ with TCEthane concentration.

value very close to the inverse of the ratio of their molecular weights, i.e., 1.02. Since the molecular weight reflects the molecular structure in many cases, it may be said that the lower the molecular weight of a compound the more is the probability of a higher diffusion rate. However, the influence of molecular structure, steric arrangement of atoms, polarity, chemical properties, membrane penetrant relationship, etc., should be investigated additionally using different combination of compounds, before further conclusions are made.

Conclusions

From the above discussion it can be concluded that the rate of permeation reduces exponentially with time for both the compounds studied. Indications are obtained from the experimental curves that the system may tend to attain a dynamic equilibrium, but these have to be confirmed by experiments in a continuous mode of operation. From the flux concentration curves, usage of log-mean concentration instead of the arithmetic average concentration in the simplified (using a straight line relationship) models is found to be justified.

Selectivity values show that TCE has a higher diffusion rate than TCEthane due to its less molecular spread (spatially) and lower polarity. However, since diffusion through the bulk liquid phase controls the permeation process, selectivity values are found to be close to the ratio of the diffusion rates of the compounds through water. It is also found that the membrane exhibits an affinity for less polar compounds.

The value of the drag coefficient as determined from the model for binary compounds indicates that the flux of one organic compound is reduced due to the presence of another compound. It is also found that, with the increase in concentration of one compound in the feed solution, the flux of the other compound decreases. The value of the integral dry diffusion coefficient of TCEthane

compound, the drag will be higher and the flux will be lower for the other compound(s). In other words, it can be said that the amount of flux reduction of a compound is proportional to the concentration of other compound(s) in the solution.

The values of the drag coefficients are substituted in eq 12 to calculate the average value of the integral dry diffusion coefficient of TCEthane. The ratio of the dry diffusion coefficients of TCE to TCEthane is 1.03, a

and TCE indicates that the ratio of the values is inversely proportional to the ratio of their molecular weights.

Acknowledgment

Nomenclature

α: separation factor or selectivity

δ: thickness of the membrane

ψ_i: flux reduction factor for a compound j due to presence of a compound i

ψ_j: flux reduction factor for a compound i due to presence of a compound j

A: area of the membrane

C_{iC}: log-mean average concentration of a compound i in the feed

C_{jC}: log-mean average concentration of a compound j in the feed

C_{i1}: actual concentration of a compound i in the feed at a particular time 1

C_{i2}: actual concentration of a compound i in the feed at a particular time 2

C_{iij}: actual concentration of compound i or j

D_i: overall diffusion coefficient of a compound i

D_j: overall diffusion coefficient of a compound j

D_{oi}: dry diffusion coefficient of a compound i

D_{oj}: dry diffusion coefficient of a compound j

D_{uj}: dry diffusion coefficient of compound i or j

H_i: Henry's constant for a compound i

H_j: Henry's constant for a compound j

H_{uj}: Henry's constant for compound i or j

J_i: average flux of a compound i

J_j: average flux of a compound j

K_{oi}: integral dry diffusion coefficient of a compound i

K_{oj}: integral dry diffusion coefficient of a compound j

P_i: integral permeability coefficient of a compound i

P_j: integral permeability coefficient of a compound j

p_{if}: partial vapor pressure of a compound i in the feed

p_{jf}: partial vapor pressure of a compound j in the feed

p_{uj}: partial vapor pressure of compound i or j

Q: local drag coefficient

Q_i: quantity of VOC obtained in the permeate or escaping feed

t: time of sampling

Y_i: plasticizing constant of a compound i

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