

Liquid Transport Through Membranes Prepared by Grafting of Polar Monomers Onto Poly(tetrafluoroethylene) Films. II. Some Factors Determining Pervaporation Rate and Selectivity

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Synopsis

The effect of some factors including temperature, pressure, film thickness, and grafting ratio on the fractionation of binary liquid mixtures has been investigated by pervaporation through poly(tetrafluoroethylene) films grafted with N-vinylpyrrolidone or 4-vinylpyridine. The purpose was to estimate the best conditions in which the pervaporation process must be carried out. It was concluded that the pervaporation rate is increased at roughly constant selectivity when the temperature of the liquid charge is higher or when the downstream vapor pressure or the film thickness are decreased. A pressure higher than 1 atmosphere above the liquid does not increase the rate. When the grafting ratio is increased, the rate shows a maximum, and for particular conditions, the selectivity becomes much higher.

INTRODUCTION

The purpose of this series of investigations is to study the separation of liquid mixtures using modified PTFE films by the pervaporation technique. In the previous paper,¹ data for fractionations of various liquid mixtures, including systems of chloroform-hydrocarbon or ethyl ether, water-alcohol, and water-nucleophilic organic solvent, were reported.

This second part is concerned with the effect of temperature, pressure, film thickness, and grafting ratio on the efficiency and the rate of separation. These factors are the most important for estimating the best conditions under which pervaporation must be carried out. Other characteristics such as chemical nature of membrane and composition of the mixture are not systematically studied. Several liquid mixtures have been studied to show general trends. In the third paper of this series,² results will be examined to supply a further insight into the theory of the pervaporation.

Briefly, the mechanism of the pervaporation process can be described as involving dissolution of the liquid into the membrane, transport through the membrane, and evaporation of the penetrant molecules from the downstream side of the screen. Solubility of the compounds into the polymer

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is a thermodynamic quantity related to the activity of a substance in the solution in contact with the membrane. Transport is a kinetic quantity related to the mobility of penetrant molecules within the polymeric chains. The physical and chemical properties of the compounds (penetrant and polymer) as well as the external conditions of temperature, pressure, and concentration will govern the ability of a substance to swell a membrane and to diffuse into it. In particular, it has been shown¹ that by grafting Lewis bases (N-vinylpyrrolidone or 4-vinylpyridine) onto poly(tetrafluoroethylene) films, membranes were obtained which allowed those compounds having the greatest affinity for the nucleophilic sites to be selectively transported. In the present study, the same type of membrane has been used.

EXPERIMENTAL

Membranes

The poly(tetrafluoroethylene) films (PTFE films), 17 μ in thickness, were du Pont's Teflon films obtained by multicoating from suspensions of grains about 0.3 μ in diameter ("multicoating Teflon").

PTFE films, 100 and 50 μ in thickness, as the asymmetrical films were supplied by the Société Ugine Kuhlmann (Soreflon films). The former were made from a massive cylinder obtained by sintering grains of about 35 μ in diameter (Soreflon déroulé). The latter were obtained by cumulative coating. To make the porous layers, poly(methyl methacrylate) is added to the Soreflon suspension and then eliminated by heating. The used PTFE grains were about 0.3 μ in length and 0.2 μ in width.

Poly(tetrafluoroethylene)-poly(4-vinylpyridine)- and poly(tetrafluoroethylene)-poly(N-vinylpyrrolidone)-grafted membranes (PTFE-P4VP and PTFE-PVP membranes) were prepared by direct radiation grafting of PTFE films according to a previously described technique.^{1,3,4} The grafting reactions were carried out in mixtures of 4-vinylpyridine (80 ml)-methanol (20 ml) at 21°C under a radiation intensity of 45 rads/min and in mixtures of N-vinylpyrrolidone (50 ml)-pyridine (50 ml) at 50°C under 380 rads/min.

The grafting ratio was expressed by the weight ratio:

$$G(\%) = \frac{W - W_0}{W_0} \times 100$$

where W is the weight of the grafted membrane and W_0 is the weight of the original PTFE film.

The PTFE-P4VP membranes were treated with 0.1*N* KOH to ensure that 4 VP groups were in a nonionic state.

Chemicals

All the organic liquids used in the pervaporation process were Prolabo Co. compounds.

Apparatus

The pervaporation apparatus has been previously described.¹ Briefly, it consists of a pervaporation cell which holds the membrane and the liquid, a circulation pump to agitate the mixture, and traps to condense the pervaporate removed from the membrane by means of a vacuum pump. A heating jacket surrounding the cell allows temperature changes of the liquid charge. An inert gas pressure was used to increase the upstream pressure.

The following procedure was used to study the effect of the downstream pressure: traps were maintained at a given temperature; the pressure was the vapor pressure of the pervaporate at this temperature under these conditions.

Analysis of Binary Mixtures

The composition of the samples collected in the traps was determined with a universal refractometer OPL or with a Carl Zeiss precision refractometer. The low water concentrations were determined by a Karl Fisher apparatus (Metrohm).

Representation of Pervaporation Results

To describe the characteristic data of a pervaporation test, two factors were selected: (1) the pervaporation rate, represented by Φ and expressed in kilograms (or liters) per hour per square meter,

$$\Phi \text{ (kg or l./hr-m}^2\text{)}$$

and (2) the selectivity factor α , defined as the concentration ratio y_A/y_B in the pervaporate, divided by the ratio x_A/x_B in the pervaporant,

$$\alpha = \frac{y_A/y_B}{x_A/x_B}$$

where A is the species which is preferentially pervaporated.

The composition of the liquid mixture was kept constant in order to determine average values of Φ and α . The errors on Φ are less than 5%. The error on x and y are less than 0.5%, but the dispersion on the α values depends also on both compositions of the liquid mixture and the pervaporation rate. That is, for a mixture with $x_A = x_B$, the relative errors in α are, respectively, 15%, 10%, and 5% for selectivity values of 20, 10, and 5. For very efficient separations, there is no significant difference between selectivity values such as 50, 100, or more.

Other parameters have been used when the purpose is the full elimination of one of the components of the mixture. If V , V_A , and V_B are, respectively, the total initial volume and the partial initial volumes of A and B of the liquid mixture and if Σ_v , Σ_{v_A} , and Σ_{v_B} are, respectively, the total volume and the partial volumes of A and B which have been pervap-

orated since time zero, the volume fractions X , Y_A , and Y_B can be calculated:

$$X = \frac{\Sigma v}{V}, Y_A = \frac{\Sigma v_A}{V_A}, Y_B = \frac{\Sigma v_B}{V_B}.$$

The total fractionation of the A-B mixture can be analysed if Y_A and Y_B are plotted versus X .

Swelling Ratio

A piece of membrane after drying to constant weight (W) is immersed in the liquid at constant temperature. When the sorption equilibrium is reached, the piece is rapidly taken out of the bath, blotted free of surface liquid, and weighed (W_1). The swelling ratio is defined by

$$S\% = \frac{W_1 - W}{W} \times 100.$$

The precision is about 5%.

The effect of the membrane thickness on the pervaporation data needs the use of a stack of identical membranes as a model for a single, thicker membrane. The samples, having been equilibrated in the pervaporant, are put one on another and clamped together in the cell. The pressure gradient between the two sides of the stack makes good physical contact between the membranes.

Membrane Thickness

The membrane thickness at swelling equilibrium, l , was determined with a Mauser micrometer (applied pressure 20 g). The precision was about 5%.

RESULTS AND DISCUSSION

Pervaporation tests of various pure compounds and binary mixtures were carried out at different temperatures through PTFE-P4VP membranes (Table I) and PTFE-PVP membranes (Fig. 1). For each series of experiments, all variables except temperature of the liquid charge were kept constant. It was found that the results could be expressed by an Arrhenius relation:

$$\Phi = \Phi_0 e^{-E_\Phi/RT}$$

where E_Φ is the activation energy for pervaporation equal to the sum of the activation energy for diffusion and of the heat of solution.⁵

The activation energies for mixtures as for pure liquids are generally low (Fig. 1, Table I). This is in agreement with the relatively fast rate of the transport at room temperature.

On the other hand, temperature had no marked effect on selectivity (Table I). This result is in keeping with those of other membranes (i.e.,

TABLE I
Effect of Temperature on Pervaporation Data of Some Mixtures
and Pure Compounds Through PTFE-P4VP Membrane^a

Liquid charge (A or A plus B)	Temp., °C	Pervapora- tion rate Φ , l./hr-m ²	Selectivity α	Activation energy E_{Φ} kcal/mole
Pure water	21	0.29		
	41	0.38		2.9
	61	0.59		
	83	0.70		
Pure N,N-dimethylacetamide	20	0.38		
	40	0.72		5.7
	60	1.26		
	81	2.00		
Water (70 ml) plus N,N-dimethyl- acetamide (30 ml)	20	0.49	∞	
	60	1.45	∞	4.6
	85	1.60	∞	
Water (16.3 ml) plus N,N-di- methylacetamide (83.7 ml)	20	0.06	24	
	40	0.25	18	12.6
	64	0.79	15	
	72	1.38	15	
Water (50 ml) plus sulfolane (50 ml)	20	0.28	250	
	60	0.65	250	
Water (50 ml) plus N,N-dimethyl- formamide (50 ml)	20	0.45	45	4.3
	55	1.00	45	
Chloroform (50 ml) plus pentane (50 ml)	20	0.20	4.3	
	30	0.45	4.3	3.5
	40	0.51	5.0	

^a PTFE thickness, 50 μ ; 200% grafting.

polyethylene,⁶ polypropylene,^{7,8} cellulose⁹) but not with the systems water/*n*-propanol/cellophane or poly(vinyl alcohol).¹⁰

The fact that the selectivity is almost constant and the rate is higher when the charge liquid temperature is increased is of great practical importance for applications of this process.

We may note a large increase of E_{Φ} for the system water/N,N-dimethylacetamide/PTFE-P4VP (Table I) when the water content of the mixture decreases. This result may be due to associations between water and N,N-dimethylacetamide which are stronger in the more concentrated amide mixture.¹¹

Effect of Upstream Pressure

The data for the system water/N,N-dimethylformamide/PTFE-P4VP are listed in Table II. In these experiments, all variables except the upstream pressure were maintained constant.

As the upstream pressure was increased, the selectivity remained constant and the pervaporation rate did not increase. This last result cannot be explained by a Poiseuille-type flow through continuous pores but agrees well with a diffusional-type flow. The slight decrease of the rate may be

TABLE II
Effect of Upstream Pressure on Pervaporation Data^a

Upstream pressure, bar	Pervaporation rate Φ , kg/hr-m ²	Selectivity α
1	0.37	16
5	0.28	16
10	0.24	16

^a Liquid charge mixture, water (50 ml) plus N,N-dimethylformamide (50 ml); membrane, PTFE-P4VP 21% grafting; PTFE thickness, 50 μ ; temperature, 20°C; downstream pressure, 10⁻² mm Hg.

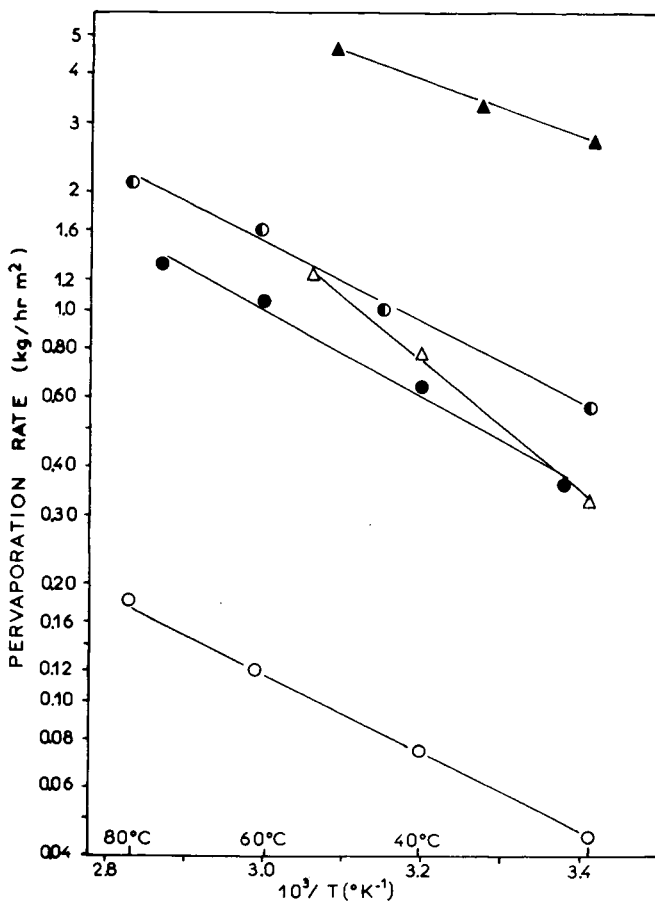


Fig. 1. Arrhenius plots for pervaporation through a PTFE-PVP membrane (PTFE thickness, 50 μ ; 38% grafting): (○) dioxane, $E_{\Phi} = 4.6$ kcal/mole; (●) water, $E_{\Phi} = 4.6$ kcal/mole; (●) water (17.6 ml)-dioxane (82.7 ml), $E_{\Phi} = 4.9$ kcal/mole; (▲) chloroform, $E_{\Phi} = 3.3$ kcal/mole; (△) propanol, $E_{\Phi} = 10.7$ kcal/mole.

due to a compacting effect in the membrane. In some cases it may contribute to an enhancement of the selectivity as observed by Featherstone and Cox.⁸

Effect of Downstream Pressure

When the downstream vapor pressure was increased, rate and selectivity decreased, as is shown in Table III for the system methyl alcohol/methyl acetate/PTFE-PVP. The same behavior was observed with other systems such as water/N,N-dimethylformamide/PTFE-PVP,¹² water/ethanol/PTFE-PVP,¹² and benzene/cyclohexane/polypropylene.⁷ However, for other systems such as acetone/water/polypropylene⁸ or water/caprolactam/cellophane,¹³ the selectivity increases with the downstream pressure. It is difficult to give a complete interpretation because, from the published data, we do not know if the downstream pressure is solely the vapor pressure of the pervaporate. However, if we assume that the driving force in the pervaporation process is the difference between the activity (or

TABLE III
Effect of Downstream Vapor Pressure on Pervaporation Data^a

Condensation temp. of pervaporate °C	Downstream pressure of pervaporate, mm Hg	Pervaporation rate Φ , kg/hr-m ²	Selectivity α
Liquid air	0.01	4.1	3.3
-10	38	4.0	2.8
0	70	3.7	2.4
+10	110	2.8	2.1

^a Liquid charge mixture, methyl alcohol (20 g) plus methyl acetate (80 g); membrane, PTFE-PVP 70% grafting; PTFE thickness, 50 μ ; temperature, 27°C.

concentration) of the compound at each face of the membrane,² it is obvious that with higher downstream vapor pressure, the driving force and then the rate are lower. But for a mixture, it is possible that the increase of the activity of each component in the downstream side of the membrane may contribute to an increase or a decrease in selectivity.

For practical purposes, these results show that it is not advantageous to carry out pervaporation at high upstream pressure, and in most cases the condensation temperature of the pervaporate must be relatively low to obtain a good efficiency of fractionation and a compromise must be found between the best efficiency and the lower cost.

Effect of Film Thickness and Structure

Very few results have been published on the effect of film thickness on the fractionation by pervaporation. The most complete study⁹ showed that the rate is inversely proportional to the thickness and the selectivity is constant in the range of 20–50 microns.

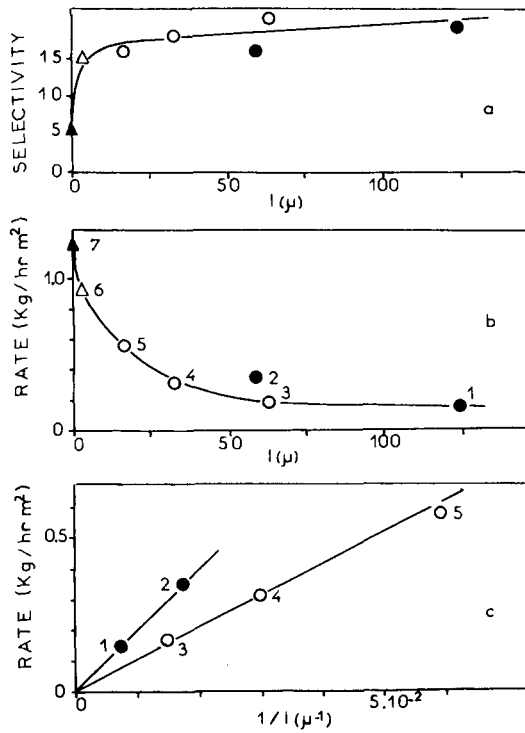


Fig. 2. Effect of membrane structure and thickness (l) on pervaporation rate and selectivity. Mixture, water (17.4 ml)-dioxane (82.6 ml); temperature, 25°C; PTFE-PVP membranes, 35% grafting:

Essay	1	2	3	4	5	6	7
PTFE thickness, μ	100	50	4×17	2×17	17	dense layer, 3 porous layer, 12	14
PTFE nature	"Soréflon déroulé"		multicoating Teflon			asymmetrical multi-coating Soreflon	porous Soreflon

Having PTFE films of different structures, it was interesting to study this factor, especially to see if films composed with a fine dense skin and a thicker porous part could be used efficiently in pervaporation.

Several PTFE-PVP films with similar grafting ratio were chosen. The results obtained with a water-dioxane mixture are shown in Figure 2, where pervaporation rate and selectivity are plotted versus membrane thickness, l , at the equilibrium swelling in the mixture. First, it can be seen that the pervaporation rate is greatly increased when a film with a dense layer 3 μ in thickness is used (essay 6, Fig. 2b), while the selectivity is not affected by the membrane thickness (Fig. 2a). Moreover, essay 7 shows that through a porous membrane, the selectivity of the fractionation is very low (Fig. 2a).

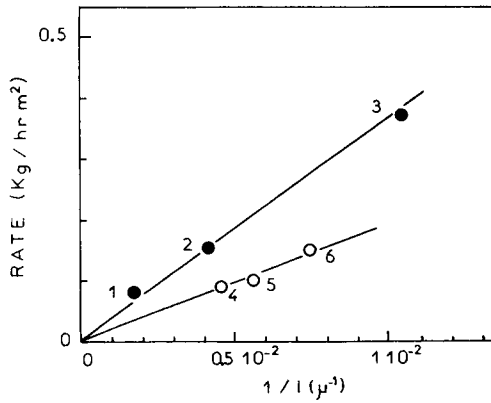


Fig. 3. Effect of membrane structure and thickness (l) on pervaporation rate. Mixture, water (50 ml)-N,N-dimethylformamide (50 ml); temperature, 25°C; PTFE-P4VP membranes, 150% grafting:

Essay	1	2	3	4	5	6
PTFE thickness, μ	5×50	2×50	50	5×17	4×17	3×17
Pervaporate DMF content, vol-%	4	4	6	1	2	4
PTFE nature	"Soréflon déroulé"			Multicoating Teflon		

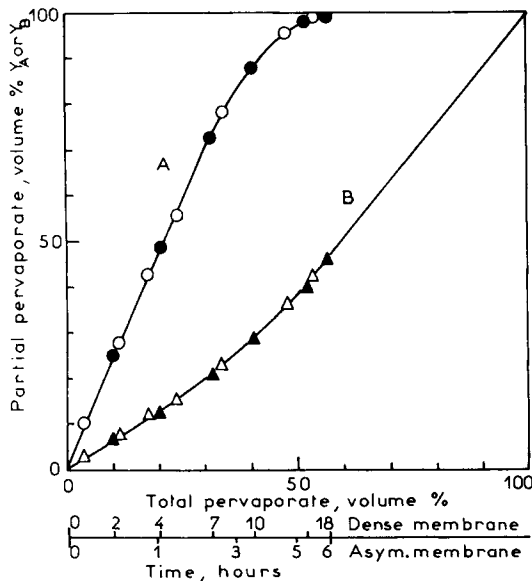


Fig. 4. Graphic representation of pervaporation. Mixture of methyl alcohol (20 ml) (A) and methyl acetate (80 ml) (B); temperature, 25°C: (O, Δ) PTFE-PVP asymmetric membrane (dense layer, 3 μ ; porous layer, 12 μ) 74% grafting; (\bullet , \blacktriangle) PTFE-PVP dense membrane (50 μ); 65% grafting.

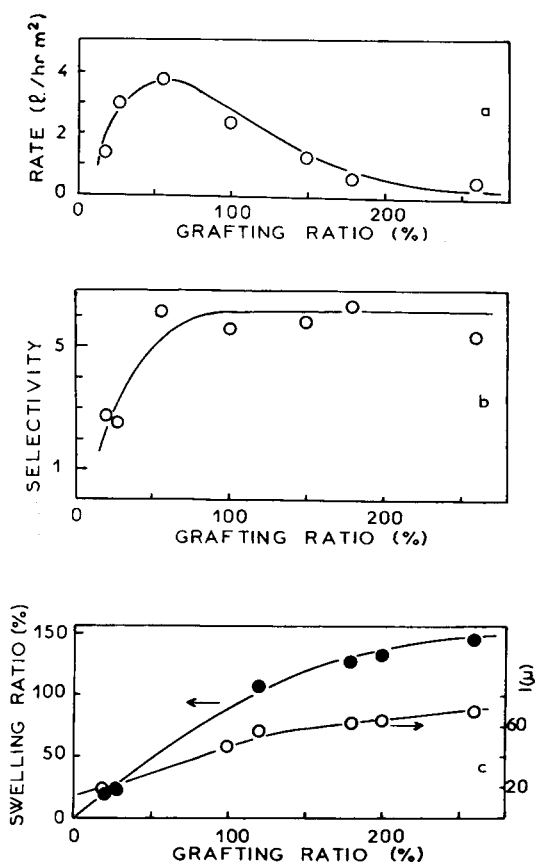


Fig. 5. Effect of per cent grafting on pervaporation data (a and b), on swelling ratio and on membrane thickness (c). Mixture, chloroform (50 ml)-pentane (50 ml); PTFE-P4VP membranes; PTFE thickness, 17 μ ; temperature, 20°C.

The same data were plotted as Φ versus $1/l$ (Fig. 2c). The experimental points are on two straight lines, according to the initial PTFE film structure. In order to show that essays 3, 4, and 5, which were carried out with a stack of membranes, are characteristic of the structure, another series of experiments was made by using stacks of two types of PTFE-P4VP membranes (Fig. 3). Inasmuch as the same difference was observed, it is fully proved that the method of preparing the films is of chief importance. Another conclusion is that the transport mechanism is the same through a stack of membranes as through a single membrane of similar thickness.

In Figure 4 we have plotted a graph showing the total fractionation of a mixture of methyl alcohol-methyl acetate through a dense and an asymmetrical membrane. Through the latter, the selectivity is unchanged, but pure methyl acetate is obtained more quickly (the dense 50 μ membrane being prepared by grafting onto "Soreflon dérovlé").

Effect of Grafting Conditions

The modification of the properties of polymer films by radiation graft copolymerization have been extensively studied, but few data are available on the effect of grafting on the transport properties of polymer films. Huang and Fels^{14,15} reported results on the effect of styrene grafting on the pervaporation of binary hydrocarbon liquids through polyethylene membranes. It was concluded that in some cases, the permeation rate can increase about three times when the grafting ratio changes from 0% to 26%, but the selectivity is only increased by 25%.

Some tests were carried out with modified PTFE films of different grafting ratios to compare them with the above results and to fit the grafting conditions in order to obtain the best pervaporation efficiency.

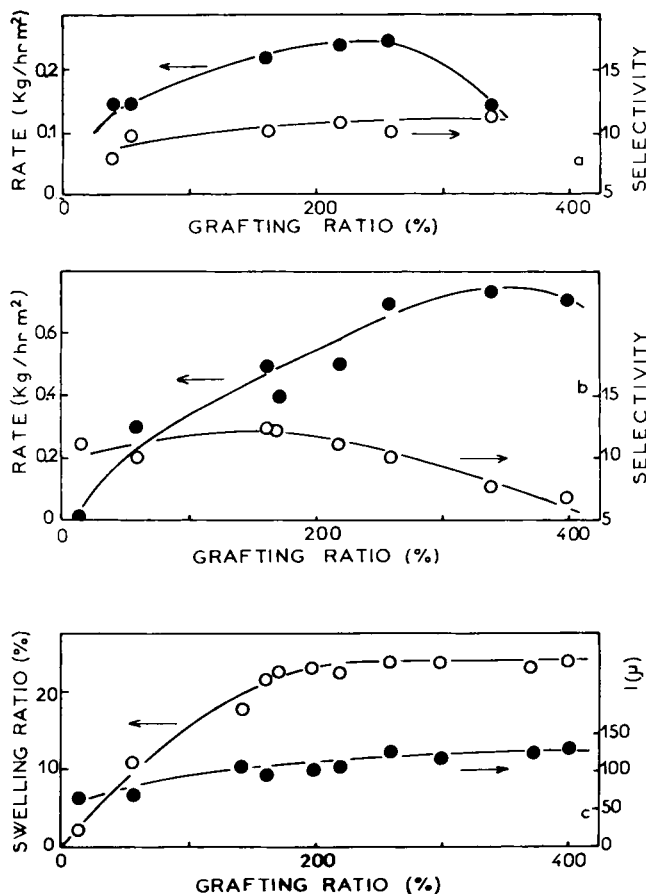


Fig. 6. Effect of per cent grafting on pervaporation data for mixtures of water (30 ml)-N,N-dimethylformamide (70 ml) (a) and water (17.6 ml)-dioxane (82.4 ml) (b) and on swelling ratio in water and on membrane thickness (c). PTFE-P4VP membranes; PTFE thickness, 50 μ ; temperature, 20°C.

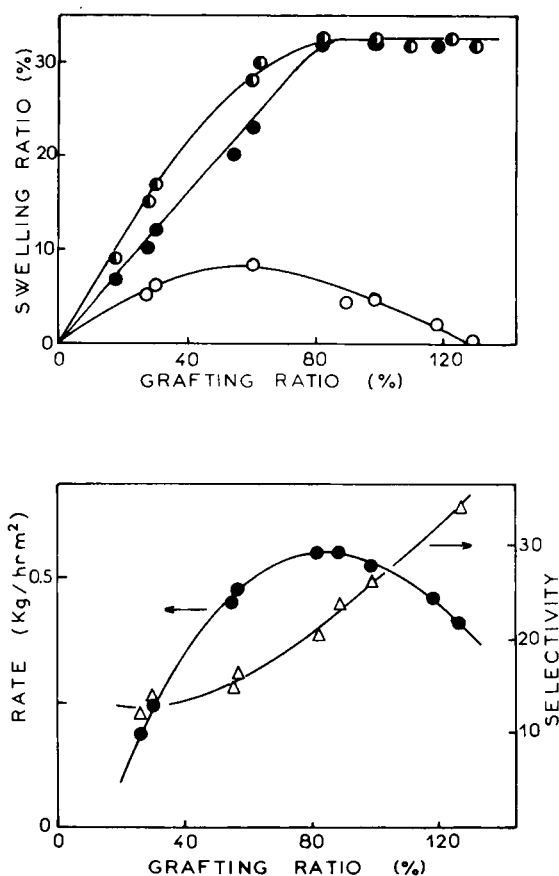


Fig. 7. Effect of per cent grafting on pervaporation data (b) and on swelling ratio (a) in water (●), in dioxane (○), and in the pervaporant mixture of water (17.4 ml)-dioxane (82.6 ml) (●). PTFE-PVP membranes; PTFE thickness, 50 μ ; temperature, 25°C.

A first series of data was obtained with PTFE-P4VP membranes for three different mixtures: chloroform-pentane (Fig. 5), water-N,N-dimethylformamide (Fig. 6a), and water-dioxane (Fig. 6b).

No mass transport occurs through the initial PTFE films. As more 4-vinylpyridine is grafted, the pervaporation rate shows an initial increase due to an enhancement of the solubility of the compounds in the membrane. But, although the swelling ratio always increases or remains constant, the rate begins to decrease. We may assume that the formation of the grafted poly(4-vinylpyridine) chains occurs with a volume extension of the film, but when the elasticity limit of the PTFE backbone is reached, the free volume of the membrane begins to decrease; the swelling did not increase linearly with the per cent grafting, and the rate of diffusion decreased.

In contrast, grafting has no marked effect on selectivity: for the three mixtures, selectivity is almost constant in a wide range of grafting ratios,

from 50% to 250% (Figs. 5b, 6a, 6b). This means that the length and the number of the graft chains do not disturb the specific interactions or the effects of preferential sorption which occurs in the ternary system solvent A/solvent B/membrane.

A detailed study of the relation between grafting conditions and pervaporation results has been published for PTFE-PVP membranes.⁴ The general conclusions are in agreement with the above trends. However, a particularity appears when the grafting of N-vinylpyrrolidone is carried out in pyridine medium. As shown in Figure 7, with such a medium it is possible to obtain a very high selectivity compared with the preceding results.

It can be concluded that, in general, as observed by Huang and Fels, the per cent grafting acts more specifically on the pervaporation rate and only very slightly on the selectivity. But it has been shown that a primary study of the grafting conditions is necessary to establish the best method for enhancing the selectivity with only a slight rate decrease.

CONCLUSIONS

In order to approach the best conditions in which the fractionation is optimal, it is necessary to study the different factors which affect the rate and the selectivity of the pervaporation process of a mixture through a membrane grafted with a chosen monomer.

The general trends are: the higher the liquid charge temperature and the smaller the membrane thickness and the downstream vapor pressure, the higher the pervaporation rate is, whatever the liquid charge pressure may be. An enhancement of the selectivity cannot be obtained by variation of these factors. It has been established that the initial structure of the PTFE films was an important parameter.

References

1. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **16**, 1061 (1972).
2. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, to be published.
3. A. Chapiro, A. M. Jendrychowska-Bonamour, G. Morel, and R. Oppelt, *Eur. Polym. J.*, **9**, 847 (1973).
4. P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, and J. Neel, *Eur. Polym. J.*, **9**, 877 (1973).
5. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, New York, 1968; K. Kummerle, *Chem.-Ing. Tech.*, **36**, 916 (1964).
6. R. Y. M. Huang and V. J. C. Lin, *J. Appl. Polym. Sci.*, **12**, 2615 (1968).
7. M. Kucharsky and J. Stelmaszek, *Przm. Chem.*, **3**, 156 (1967).
8. W. Featherstone and T. Cox, *Brit. Chem. Eng. Proc. Techn.*, **16**, 817 (1971).
9. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, **53**, 47 (1961).
10. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
11. R. C. Petersen, *J. Phys. Chem.*, **64**, 184 (1960).

12. P. Aptel, N. Challard, and J. Cuny, unpublished results.
13. J. Kubica, M. Kucharski, and J. Stelmaszek, *Przm. Chem.*, **6**, 353 (1967).
14. R. Y. M. Huang and M. Fels, *Chem. Eng. Progr. Symp. Series*, **65**, 52 (1968).
15. M. Fels and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 537 (1970).

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