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Pervaporation and Dialysis of Water–Ethanol Solutions Using Silicone Rubber Membranes

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Abstract

Ethanol–water solutions may be concentrated by pervaporation through silicone rubber and regenerated cellulose film. Using silicone, separation factors (SF) decrease as the ethanol concentration in the feed solution increases (SF = 6.5 using 12.9 w/w% ethanol and 1.4 using 83.2% ethanol at 30°C). The temperature effect on separation factors is negligible, but is appreciable on permeation rates.

Ethanol permeation rates in the dialysis mode are not linear with ethanol chemical potentials in solution; silicone swelling coefficients also increase noticeably with alcohol concentration in aqueous solutions, indicating that preferential ethanol sorption occurs and is responsible for the separation.

INTRODUCTION

Ethanol recovery from dilute aqueous solutions is an essential and energy-consuming part of current liquid fuel production processes from biomass. Established distillation methods are effective enough so that the overall process has a positive energy balance, but they have two definite problems: First, large volumes of vinasse (*1*), the aqueous by-product, are obtained. This is a corrosive, low pH, and high-salt content liquid, which has to be appropriately dealt with to avoid environmental problems. Second, corrosion caused by sugar cane "wine" in distillation equipment is a serious practical problem.

Polymer membranes could be useful in alcohol–water separation, provided selective and highly permeable systems could be found. Most published work on water–alcohol separation indicates preferential permeation of membranes by water (*2–5*).

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We have done some preliminary work to find a polymer suitable for water–ethanol separation, preferentially permeated by the alcohol. Silicone rubber was found to be adequate in both the dialysis and pervaporation modes. When this work was nearly completed, the paper by Hoover and Hwang on water–ethanol pervaporation through silicone rubber appeared (*6*), and for this reason we give only a short account of our work on this topic, together with data on dialysis using silicone and on pervaporation through regenerated cellulose.

EXPERIMENTAL

The silicone tubing used in this work was a general purpose tubing made from Dow Silastic resin. Infrared reflectance spectrophotometry showed this rubber to be predominantly poly(dimethylsiloxane) (*7*). Cellulose membranes were SIGMA 250-9U dialysis sacks. Cross-linked dextran from Pharmacia (G-25 Sephadex) and a food-grade corn starch were used.

Water–ethanol solution concentrations were determined by refractometry in a Bausch-Lomb Abbé type refractometer and by densimetry in a DMA 602 PAAR meter.

Liquid pumping was done using peristaltic pumps with Tygon tubing for which pervaporation rates of water and ethanol were found negligible.

RESULTS

Preliminary experiments were made to verify the differential sorption of water–ethanol solutions by two hydrophylic polymers, starch and cross-linked dextran. This was done by allowing the polymers to swell in solutions of various concentrations, removing the swollen polymers, and measuring the solution refractive indices before and after contact with the carbohydrates. Only small changes were observed, and therefore these polymers have not received further attention.

On the other hand, laboratory practice with silicone rubber tubing shows that evaporation of some volatile liquids from within these is rather fast. For example, by filling 1-m long pieces of silicone tubing (2.60 mm o.d. × 1.50 mm i.d.) with water–ethanol solutions and allowing them to hang in contact with room atmosphere, weight losses are easily detected, leading to a water-rich residue as shown in Table 1.

To examine this behavior more systematically, a pervaporation unit was set up as depicted in Fig. 1. By using this arrangement, permeate flow rates

TABLE 1
Weight Loss and Final Ethanol Concentration of Water–Ethanol Solutions Contained in Closed 1-m Long Silicone Tubing (2.60 mm o.d., 1.50 mm i.d.) in Contact with Room Air

Initial concentration (w%)	Final concentration (w%)	Weight loss (%)
0	0	8.7
4.0	0	12.4
7.8	1.2	17.3
23.8	1.8	35.4
41.8	4.2	45.6

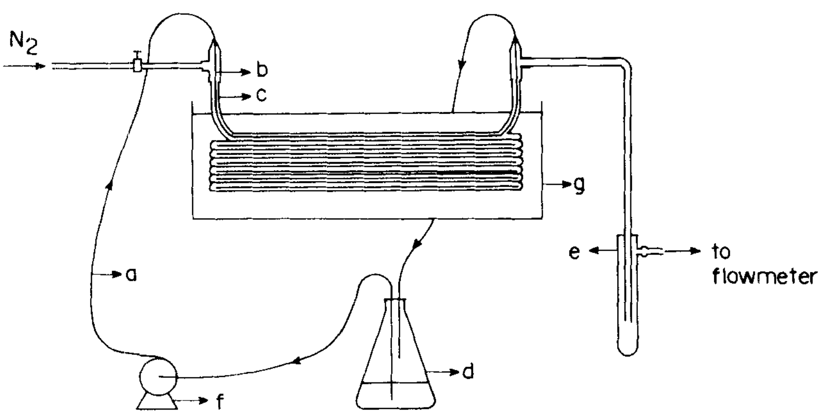

FIG. 1. Pervaporation apparatus using silicone tubing. (a) Tygon tubing, (b) silicone tubing, (c) copper tubing, (d) feed solution reservoir, (e) condensation trap, (f) peristaltic pump, (g) thermostated bath.

and composition were determined. Permeation rates and separation factors were calculated using the following expressions (*8*):

$$SF_j^i = \frac{J_i}{J_j} \times \frac{C_j}{C_i} \tag{1}$$

$$\text{Permeation rate} = \frac{\text{permeate mass}}{\text{time} \times \text{area}} \tag{2}$$

where J_i is the flux of component i in the vapor phase and C_i is the molar concentration of this component in the liquid phase.

The results are given in Figs. 2 and 3, together with data obtained using regenerated cellulose as the pervaporation membrane, in the apparatus

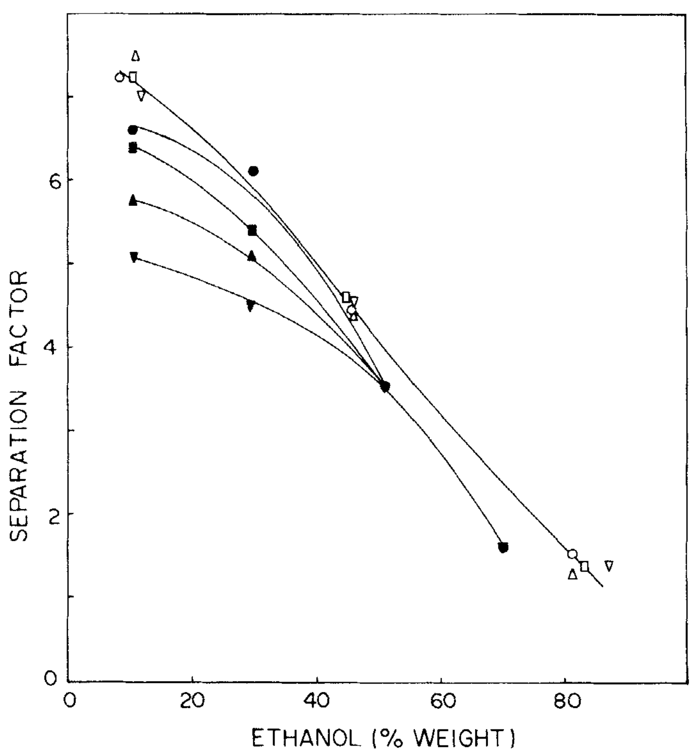

FIG. 2. Separation factor of silicone rubber (open symbols) and cellulose (filled symbols) to water–ethanol pervaporate at various temperatures: (○, ●) 30°C; (□, ■) 40°C; (△, ▲) 50°C; (▽, ▼) 60°C.

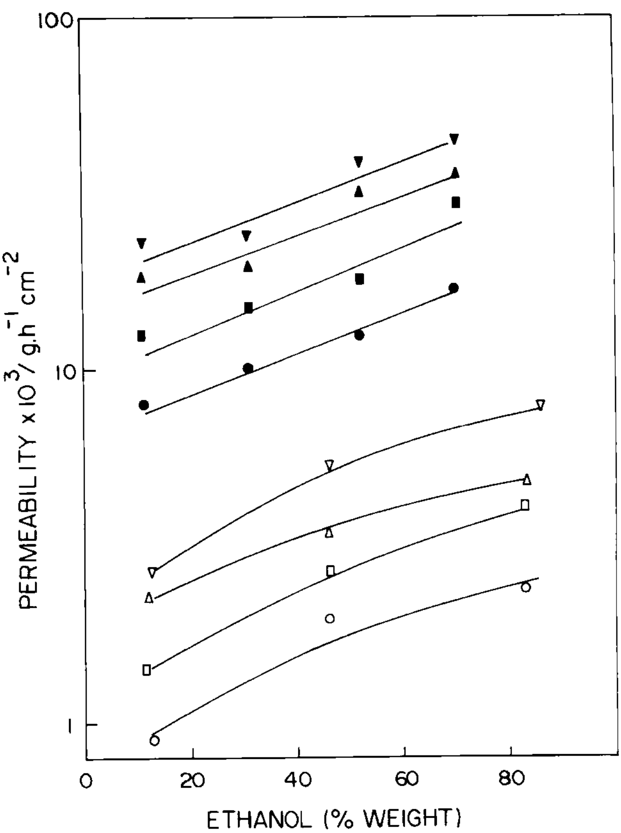

FIG. 3. Permeability of silicone rubber (open symbols) and cellulose (filled symbols) to water–ethanol pervaporate at various temperatures: (○, ●) 30°C; (□, ■) 40°C; (△, ▲) 50°C; (▽, ▼) 60°C.

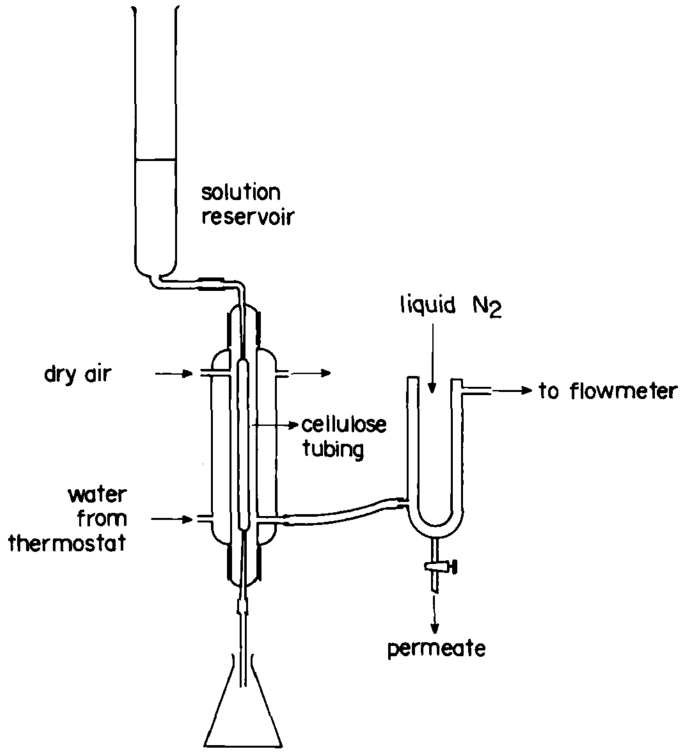

FIG. 4. Pervaporation apparatus using cellulose tubing.

described in Fig. 4. It is clear that permeability of the thinner cellulose film is much higher although selectivity is lower.

Dialysis of Water–Ethanol Solutions through Silicone Rubber

Ethanol may be transferred from an aqueous solution to another more dilute one through silicone rubber. This was done using the arrangement depicted in Fig. 5. Results of experimental runs demonstrating ethanol transfer to the more dilute solution are given in Fig. 6, and permeabilities calculated from these data are given in Table 2.

Another set-up was used for the same purpose; this is shown in Fig. 7. By using it, transfer rates of ethanol from solutions of various concentrations to

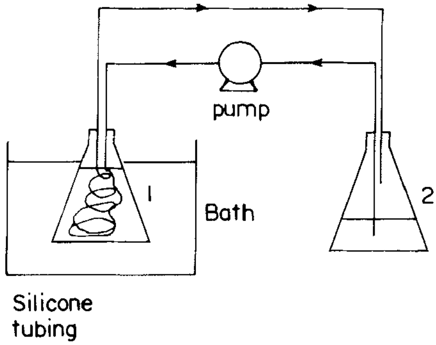

FIG. 5. Dialysis apparatus using silicone tubing. (1) Solution, (2) Water. Initial volumes: solution, 0.55 L; water, 0.1 L.

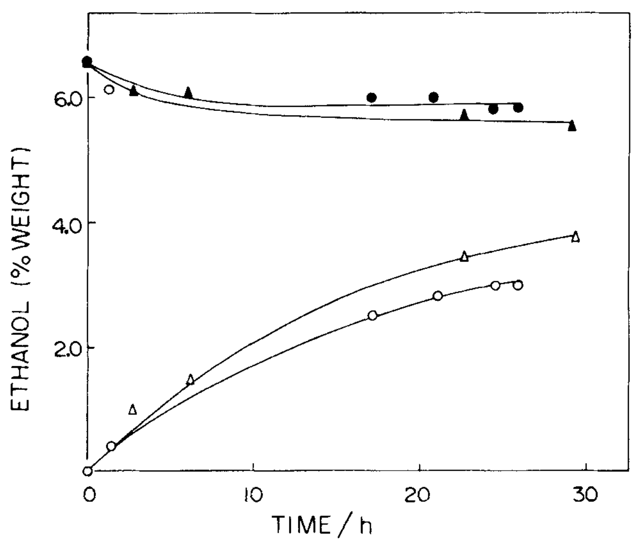

FIG. 6. Dialysis of aqueous ethanol against water: (●, ○) 45°C; (▲, △) 60°C. Open symbols: solution undergoing dialysis. Filled symbols: dialysate.

TABLE 2
Permeation Rates of Ethanol through Silicone Rubber Tubing Calculated from the Dialysis Experiment in Fig. 6

Time (h)	$t = 45°C$, permeation rate $\times 10^4$ g/h·cm^2	Time (h)	$t = 60°C$, permeation rate $\times 10^4$ g/h·cm^2
0		0	
1.33	3.14	2.83	3.87
17.3	1.51	6.17	2.44
21.0	1.39	22.8	1.56
24.3	1.29	29.2	1.34
26.0	1.16		

pure water were determined. These are given in Fig. 8, from which we can observe that ethanol transfer rates are not a linear function of ethanol chemical potential in solution (*9*). Permeability coefficients increase noticeably at higher ethanol concentrations, which is probably due to increased swelling of silicone with ethanol concentration. This was determined independently by weighing and is shown in Fig. 9.

An independent assessment on water transfer through silicone in dialysis experiments was determined by using pure water and 1 *M* aqueous glucose solution. Under these conditions, the water permeation rate is 4×10^{-9} cm/s, which is much lower than the figures obtained for ethanol.

DISCUSSION

Silicone rubbers are interesting media for making membranes because dissolved gases (and probably vapors, too) have high diffusion coefficients. Sorption data given in this paper show that ethanol swells poly(dimethylsiloxane) more than water, indicating that it should also have higher permeation coefficients.

Pervaporation data given in this article may be compared to Hoover and Hwang's data (*6*). From Table 2 in Ref. *6* we know that pervaporation at 28°C of a 73% ethanol feed solution gives SF's (as defined in this paper) of 2.3 and 2.1 at different reflux ratios. Interpolating from our data, we obtain a SF equal to 2.4 under the same conditions. Using a lower concentration in the feed (18%) and 26°C, the SF calculated from their data is 4.9, and interpolation from our results yields 6.4.

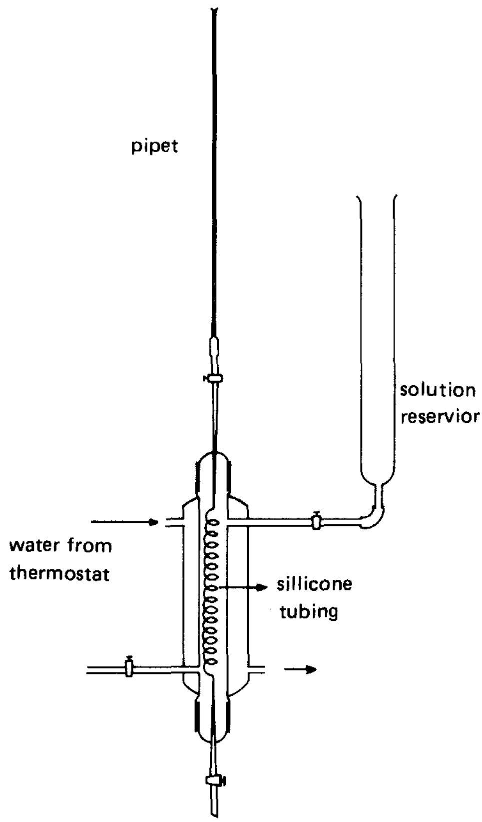

FIG. 7. Apparatus for the determination of ethanol permeation through silicone rubber under dialysis. Silicone tubing is initially filled with water.

The flow rates are also similar: using a 73% feed at 36°C and a reflux ratio of 8.5, they obtained 9.1×10^{-4} g/h·cm^2 (ethanol); interpolating from our data, we obtain 2×10^{-3} g/h·cm^2. The small differences observed are probably due to differences in the actual tubing used.

In this regard, we have observed that miscibility of low molecular weight liquids with silicones may be highly dependent on the composition of these. For instance, the solubility of ethanol in a silicone oil (Dow Corning 704), which was identified by us as a poly(phenylmethylsiloxane), is much lower than in the rubber used in this work.

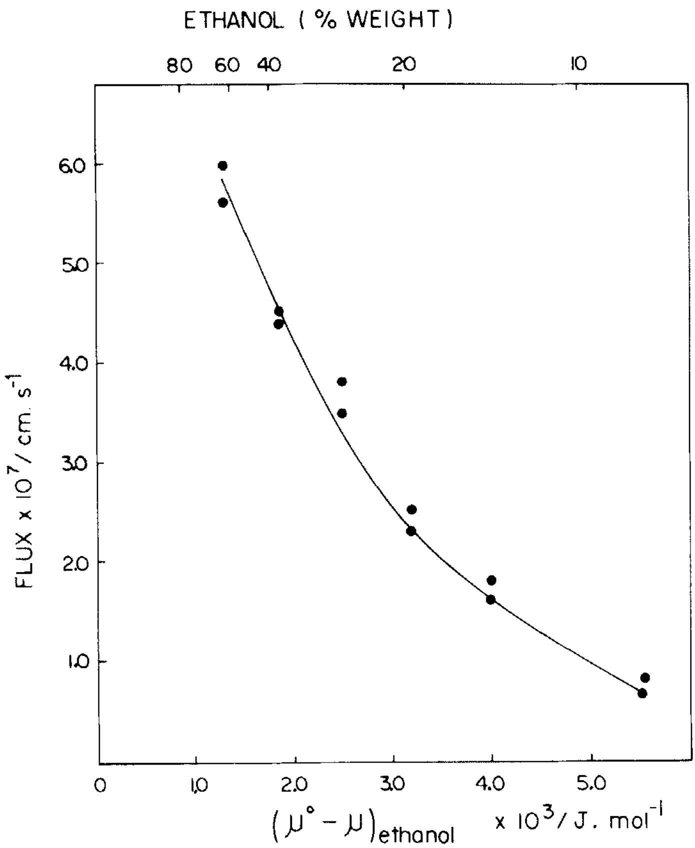

FIG. 8. Ethanol transfer from solution to water through silicone rubber as a function of ethanol chemical potential within the solution. $t = 25°C$.

The results of the dialysis experiments reported here indicate that silicone rubbers may also be useful dialysis membranes, but the flow rates are too low. The need to develop supported membranes having a thickness in the 1-μm range is obvious.

Regarding pervaporation experiments using cellophane, published work (*2, 3*) shows that water permeates the membrane preferentially to alcohols; moreover, permeation rates increase with the water content of the solutions. Results presented in this work are at variance with previous information; we believe that the major factor leading to this discrepancy is that in our pervaporation experiments, the vapor is driven by a current of (initially) dry air instead of a pressure gradient. Under the present circumstances, the external wall of the cellophane membrane is kept moist and plasticized during the experiments. Considering the model proposed by Misra and Kroesser, in the present case there would be no nonporous region in the membrane, and the solution would have free access to the polymer gel–gas interface. It is interesting to note that at a given temperature the composition of permeate obtained from a given feed solution is not too different from the composition of vapor in equilibrium with this liquid (*9*).

Another factor whose importance cannot be assessed at this time is the selectivity induced by the adsorbed material and by the interfacial properties of the membranes, as studied by Heisler. Further work will be necessary to elucidate this point.

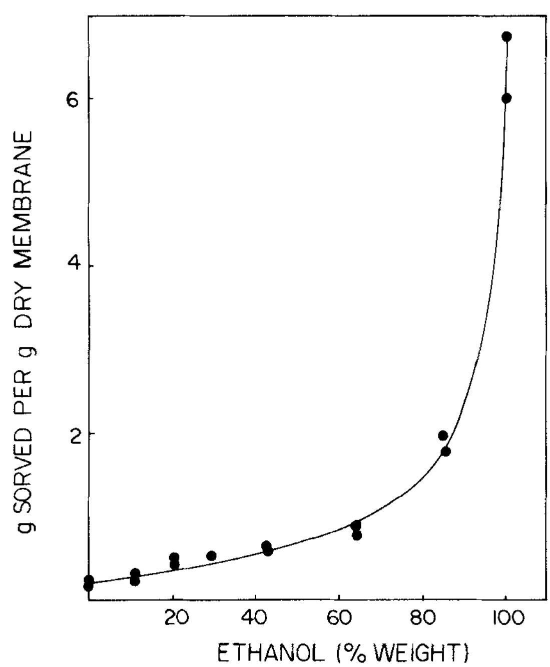

FIG. 9. Sorption coefficients of aqueous ethanol in silicone rubber. $t = 25°C$.

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REFERENCES

1. J. D. Camhi, *Bras. Açucareiro, 2,* 34 (1979).
2. A. Misra and F. W. Kroesser, *J. Polym. Sci., Polym. Chem. Ed., 41,* 145 (1973).
3. E. Nagy, O. Borlai, and A. Ujhidy, *J. Membr. Sci., 7,* 109 (1980).
4. E. G. Heisler and A. S. Hunter, *Science, 124,* 77 (1956).
5. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Membr. Sci., 1,* 271 (1976).
6. K. C. Hoover and S. T. Hwang, *Ibid., 10,* 253 (1982).
7. A. L. Smith, *Analysis of Silicones,* Wiley, New York, 1974.
8. C. H. Lee, *J. Appl. Polym. Sci., 19,* 83 (1975).
9. J. A. Larkin and R. C. Pemberton, *Nat. Phys. Lab. (U.K.), Div. Chem. Stand., Rep., 43,* (1976).

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