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Solute Separations from Water by Dialysis.
I. The Separation of Aniline

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Summary

The dialytic transport of aniline from dilute water solutions through polymeric membranes was investigated. The activity gradient caused by neutralization of the base was used to drive the process. A number of membranes suitable for such separations were identified.

INTRODUCTION

The use of dialysis for the separation of two or more solutes from a common solvent generally relies for its driving force on the difference in chemical potential between the solution and the receiving dialysate. For example, the recovery of NaOH from alkaline solutions containing both NaOH and hemicelluloses is effected by dialyzing the above solution against fresh water using parchment membranes; the diffusional transport of the NaOH through the membrane coupled with the inability of the hemicelluloses to permeate the same membrane leads to a hemicellulose free solution. An original solution of approximately 20% NaOH in the feed stream yields a dilute dialysate free of hemicellulose and containing 4–5% caustic. Similarly, the separation of sulfuric acid from copper and other metals by dialysis represents a separation based on differences in chemical potential coupled with differences in rates of diffusion. A solution containing both acid and metal is dialyzed against fresh water, with the acid diffusing more rapidly than the metal salt. The retained feed stream is enriched in metal and recycled. The driving force for both the acid and metal transport is their respective difference in chemical potential with respect to the dialysate. The separation achieved is the result of this potential and the differences in the mass transport rates of the species through the separating membrane.

A number of other examples of both laboratory and industrial scale dialysis processes have been reported (*1*, *1a*), and in each case the driving force is based on the presence of a chemical potential across the membrane. The simplest cases represent a solution containing a permeating species separated from an equal volume of pure solvent by a permeable membrane. The solute is transferred from one compartment to the other by diffusion until its activity is the same in both compartments. If the solute is ionic, and other ionic, nondiffusible species are also present, then the Donnan equilibrium constraints will govern the final ratios of the concentrations of solutes in each compartment. However, the concentration in the dialysate compartment will always be lower than the initial concentration of diffusing species.

Thus to employ dialysis for the removal of small quantities of noxious solutes from water, and at the same time to concentrate the solute, requires that the chemical potential must be manipulated in some manner. This paper describes experiments designed to explore the feasibility of achieving such separations for the purpose of purifying effluent waters at the unit operation site in chemical plants. The processes to be reported will examine the coupling of the following two effects:

(a) Control of solute permeability by proper membrane selection.
(b) Facilitation of membrane diffusion by maintaining large chemical potential gradients.

In this report the separation of aniline from water will be examined. The concentration of aniline is taken to be less than the saturation concentration, and a prior assumption is made that there will exist a polymeric membrane which will allow aniline to permeate, but which will not allow anilinium ion or anions to permeate, and whose water permeability is significantly lower than the aniline permeability. These assumptions are verified in the experiments.

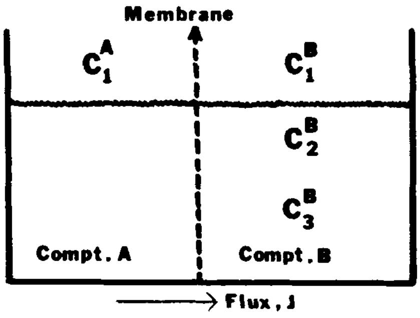

FIG. 1. Diagrammatic representation of dialysis.

In Fig. 1 is shown the schematic of the dialysis situation, ignoring solution boundary layers for the present. Compartment A contains water and aniline solution. It is separated from Compartment B by a polymeric membrane which has a very low hydraulic conductivity; i.e. convective transport by a pressure gradient is very low. Compartment B contains water and an excess of acid over that required to establish the equilibrium.

The concentrations are designated as C_1^A = concentration of aniline in A, C_1^B = concentration of aniline in B, C_2^B = concentration of acid in B, and C_3^B = concentration of anilinium ion in B. The flux of aniline from A to B is given by

$$J_1 = -P(C_1^B - C_1^A) \tag{1}$$

where J_1 is the steady-state flux, C_1^A and C_1^B are the bulk concentrations under zero boundary layer conditions, P is a membrane permeability constant, A is the membrane area, and l is its thickness.

At equilibrium, the relationship between the three components in Compartment B is given by

$$K_{eq} = \frac{(C_3^B)}{(C_1^B)(C_2^B)} \tag{2}$$

The boundary conditions for the experiments to be described are

$$(C_1^B)^0 = (C_3^B)^0 = 0 \quad \text{at} \quad t = 0 \tag{3}$$

$$(C_2^B)^0 \neq 0; \quad (C_2^B) \ggg (C_3^B)$$

The zero superscripts denote the values refer to the beginning of the experiment. The rate equations relating the changes in concentration in two compartments having volumes V_a and V_b (separated by membrane of area A), and containing an excess of acid in Compartment B, are given by

$$\frac{dC_1{}^{\mathrm{A}}}{dt} = \frac{AP}{V_a l} (C_1{}^{\mathrm{B}} - C_1{}^{\mathrm{A}}) \tag{4}$$

$$\frac{dC_1{}^{\mathrm{B}}}{dt} = \frac{-AP(C_1{}^{\mathrm{B}} - C_1{}^{\mathrm{A}})}{V_b l} - \frac{dC_3{}^{\mathrm{B}}}{dt}$$

$$= \frac{-AP}{V_b l} (C_1{}^{\mathrm{B}} - C_1{}^{\mathrm{A}}) - K_{\mathrm{eq}} C_2{}^{\mathrm{B}} \frac{dC_1{}^{\mathrm{B}}}{dt} \tag{5}$$

We assume that equilibrium is attained in Compartment B as rapidly as 1 diffuses into the compartment. With the boundary conditions cited, this leads to a discrete expression for the permeability constant in terms of the measurable experimental variables as follows:

$$P = \frac{V_A(1 + K_{\mathrm{eq}} C_2{}^0) l}{At(1 + K_{\mathrm{eq}} C_2{}^{\mathrm{B}} + V_a/V_b)} \ln \frac{(C_1{}^{\mathrm{A}})^0}{(C_1{}^{\mathrm{A}} - C_1{}^{\mathrm{B}})} \tag{6}$$

Since the equilibrium constant for aniline is known, the experimental data allow the calculation of the permeability constant P. The form of Eq. (6) is most useful for application to measurements with a rotating batch dialyzer characterized in an earlier report (*2*).

EXPERIMENTAL

Membrane Preparation

Membranes were obtained commercially as films, or prepared by solvent casting on clean glass plates in a controlled environment. Commercially available polymers were used to make casting solutions. The resulting membrane thickness was measured by a simple interference method (*3*).

Commercial Films

Polyethylene A	Handiwrap, showed presence of plasticizer in IR.
Polyethylene B	Commercial bag film, showed no plasticizer.
Saran	A household polyvinylidene copolymer.

Cast Films

Kraton 101	A styrene–butadiene–styrene block copolymer from Shell Chemical Co. was cast from methyl isobutyl ketone solutions.
XD-7	A polycarbonate–polysiloxane copolymer from G.E. was cast from methylene chloride solutions.

Permeability Measurements

The water transmission rate of the membranes was determined at 25°C using the ASTM 96-66 method. For solute permeabilities, the rotating batch dialyzer characterized earlier (*2*) was used. For the purposes of screening membrane performance, the contributions of boundary resistance were not evaluated. Rotational speed was kept constant at 90 rpm. Thus the absolute error in the reported values could be as large as 20%, but the relative errors between membranes are kept to a minimum. The direction of the error is such that a more efficient dialyzer can lead to larger transport rates. With the less permeable membranes the error due to the boundary layer resistance is of course minimal, since the membrane resistance is larger than the boundary resistance by a factor of 10 or more.

The transport measurements were carried out using a 0.32 *M* initial concentration of aniline, and a 2.0 *N* sulfuric acid concentration in the receiving side. The two compartments were each filled with 35.0 cc, the rotation started, and after preselected time intervals the contents of each compartment were drained rapidly. Analyses of the contents of the compartments were carried out by UV absorbance measurements after neutralization to a common pH. Dilutions of the sample were necessary to bring the concentration to the levels suitable for analysis at 281 nm.

The use of Eq. (6) requires a knowledge of the concentration of the free aniline base in Compartment B. This was calculated from the analysis for total aniline, and a knowledge of the acid concentration and the equilibrium constant. The K_{eq} as designated in Eq. (2) is 1.9×10^4, so that (C_1^B) is approximately equal to $(C_3^B)(C_2^B) \times 10^{-4}$, which is much smaller than C_1^A. If the product $K_{eq}(C_2^B) \rangle\rangle\rangle 1$, then the coefficient for the logarithm term of Eq. (6) can be simplified to

$$P = \frac{V_a l}{At} \ln \frac{(C_1^A)^0}{(C_1^A - C_1^B)} \tag{7}$$

In our experiments (C_1^B) was maintained much lower than (C_1^A), so that the final expression contained only the term ln $[(C_1^A)^0/(C_1^A)]$.

Distribution Coefficients

To determine the distribution coefficient of aniline between an aqueous solution and the membrane phase, a gas chromatographic method was used. A small sample of the membrane was equilibrated in a solution of aniline in water overnight. The membrane was blotted to remove surface liquids and then placed into the injection port of a gas chromatograph equipped with a flame ionization detector. The column packing used was a 10% OV-17 silicone on Chromosorb. The method has been published by Dupuy and Fore (*4*). After the injection port is closed, the carrier gas sweeps the membrane sample free of aniline. At the completion of the run the membrane is retrieved and weighed on a microbalance. With the same sensitivity and attentuation settings a 2.0 μl sample of the equilibrating aniline solution is also analyzed. The ratios of peak areas are then used to calculate the distribution coefficient, with allowances incorporated for the relative densities of the solution and the polymer. The final distribution coefficient is dimensionless; i.e., $(\mathrm{g/cc})_{\mathrm{pol}}/(\mathrm{g/cc})_{\mathrm{sol}}$.

RESULTS

The permeability constants for aniline and water are shown in Table 1 together with the distribution coefficients found for the concentration range of concern. The thickness of each membrane is reported, since the assumption in the derivation is made that the rate of transport is independent of the thickness of the specimen. The permeability constants are thus specific constants.

The permeability rate of the aniline through the organic polymer is surprisingly high. For comparison, the permeability of glucose through uncoated cellophane has been reported to be 6×10^{-7} cm²/sec, using the same techniques, but correcting for boundary layer effects (*2*). This is only 50% faster than the transport of aniline through the polysiloxane copolymer, thus there is some basis on which to project the possibility of applying dialysis as a process to separate trace organic chemicals from water.

The diffusion coefficients of aniline in the membrane can be estimated from the relationship

$$P = DK_d$$

TABLE 1

Permeability Coefficients at 25°C for Transport of Aniline and Water through Polymer Membranes

Polymer	Thickness	Permeability (cm²/sec) Water	Aniline	K_d[a]
Polyethylene A	20.0	1.16×10^{-10}	0.44×10^{-7}	
Polyethylene B	13.6	2.32×10^{-11}	0.15×10^{-7}	0.13
Saran	11.9	[b]	0.19×10^{-7}	1.44
Kraton 1101	35.7	3.8×10^{-8}	2.5×10^{-7}	0.765
XD-7	68.3	1.19×10^{-9}	3.9×10^{-7}	2.69

[a] Distribution coefficient:

$$K_d = \frac{\text{g of solute per unit volume of swollen polymer}}{\text{g of solute per unit volume of solution}}$$

[b] Transport was so low that the method was not applicable. Estimated to be less than 10^{-12}.

where D is an integral coefficient, since the concentration in the membrane ranges from C_1^A to C_1^B. These values are shown in Table 2.

Solution temperature may be used to advantage in this process. The effect of increasing temperature on membranes operating under a poretype mechanism is primarily to increase the diffusion rate of the solute in water filled pores. For diffusive membranes, such as reported here, the effect is both to increase the diffusion rate in the membrane and to alter the membrane structure. A review of the relationships between the permeability at some experimental temperature and the glass transition temperature is beyond the scope of the present report. For temperature responses of other polymers, an excellent review has been prepared by Fujita (*5*). His conclusions appear to be applicable to the present work, since the same generalizations can be deduced between the observed transport rates and the difference between experimental and glass transition temperatures. The plasticized polyethylene, which can be expected to have the lower T_g, has a greater permeability than the unplasticized membrane. The polysiloxane copolymer, whose blocks have a T_g of approximately −122°C, is the most permeable membrane. The butadiene copolymer, with blocks having a T_g of approximately

TABLE 2

Average Diffusion Coefficients for Aniline in Polymer

Polymer	D (cm^2/sec)
Polyethylene	1.0×10^{-7}
Saran	1.3×10^{-8}
Kraton	3.27×10^{-7}
XD-7	1.45×10^{-7}

−112°C, is the second most permeable membrane. From these data we can expect that both the Kraton and the polysiloxane copolymer will increase in permeability up to the temperature where mechanical structure of the membrane begins to fail. The advantage of the block copolymer is their ability to form large rubbery domains, in contrast to cross-linked elastomers, which have relatively short chains between cross-links.

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