

Semipermeable Membranes of Cellulose Acetate for Desalination in the Process of Reverse Osmosis.

IV. Transport Phenomena Involving Aqueous Solutions of Organic Compounds

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Synopsis

Transport of a solute through semipermeable membranes of secondary cellulose acetate is dependent both upon its capacity for hydrogen bonding with bound water and upon steric factors. The rate of transport of water is influenced by Gibbs adsorption of solute.

INTRODUCTION

Material transport across semipermeable membranes can be divided into two pure mechanisms: Poiseuille (viscous) flow through pores and diffusive flow as a result of the migration of a substance under the influence of a difference in chemical potential. In the case of normal¹ Poiseuille flow, semipermeability is due to a physical sieving action which depends on the respective sizes of the permeant species and membrane pores. In transport by diffusion, on the other hand, separation occurs as a result of differences in migrating tendencies of solvent and solute. Solution transport is a special case of diffusion wherein separation is attributable to the existence of low-energy sites on the membrane for which the permeating species possesses some affinity. In practice, hybrid mechanisms in which transport occurs partly by diffusion and partly by Poiseuille flow are often encountered. An example of the latter is the permeation of cellophane membranes by liquids described by Ticknor.²

There is a growing body of evidence in support of the general solution-diffusion theory of material transport across the cellulose acetate membrane used for desalination. Reid³ calculated a negative entropy of activation for water transport in a range indicative of an "alignment-type" mechanism. Kesting et al.⁴ observed a sudden increase in the slope of a plot of water transport rate versus membrane water content and interpreted this on the basis of transition from a diffusion to a hybrid transport mechanism as more highly swollen membranes were employed. The membranes of

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interest for desalination of sea water possessed swelling ratios corresponding to pure diffusion transport.

In one of the few papers to treat anomalous transport phenomena, Shuler et al.⁵ observed that the permeation constants for water depended upon the solute used. According to their view, a diffusing solute molecule passes from one equilibrium position to the next by pushing aside neighboring molecules which have to adjust their positions in order to allow a molecule to move. The rate of diffusion of water will therefore depend not only upon its own nature, but on that of the solute species present in solution.

In the present study two facets of transport phenomena involving two component solutions are considered: the nature of the diffusion transport of various organic solutes and the dependence of water permeation upon the nature of the solute. Diffusion of a solute is shown to depend both upon its capacity for hydrogen bonding with membranous bound water and upon its steric configuration. Anomalous water permeation, on the other hand, appears to be partially related to Gibbs adsorption of solute at the membrane-solution interface.

EXPERIMENTAL

Transport Rates

The transport rates of the various organic solutes were established by allowing dilute aqueous solutions (0.1*M* in the case of the glycerine-triacetin series and 1% by weight for the other compounds) to impinge upon a membrane at 102 atmospheres pressure in a cell of a type previously described.⁴ Solute transport is most often described in terms of semipermeability (solute concentration in product divided by solute concentration in feed). However, although semipermeability adequately describes effluent composition, it does not describe effluent quantity. To describe transport situations quantitatively it is expedient to distinguish between transport rates of water (from a pure water feed) J_0 , of water (from a solution) J_1 , and of solute J_2 . The three rates may be normalized with respect to J_0 by division therewith, hence J_1/J_0 and J_2/J_0 (the normalized transport rates of the aqueous and solute components of a solution, respectively) equal fractions less than unity.

Hydrogen-Bonding Index

The wavelength of the third water band (in millimicrons) when 1% of water is dissolved in a given permeant species has been designated as the hydrogen-bonding index of this species. This index is a measure of the capacities of the various solutes for hydrogen bonding with water.

Gibbs Adsorption

The adsorption of various solutes at the membrane-solution interface was established by surface-tension measurements employing a direct reading Du Noüy tensiometer.

EXPERIMENTAL RESULTS AND DISCUSSION

Solute Transport by Hydrogen Bonding to Membranous Bound Water

The cellulose acetate membrane consists of a swollen⁶ polymer gel. Water is an integral part of the membrane gel structure and consists of two types: bound and capillary.⁷ There is some difference of opinion regarding the nature of the polymer groups to which water is bound, since Reid and Koppers³ favor the acetate and Kesting et al.,^{4,7} the hydroxyl. Although the latter represent sites of lower energy inasmuch as the heat of wetting of cellulose acetate increases with hydroxyl content,⁸ the nature of the groups which adsorb the primary bound waters may be of minor importance insofar as solute transport is concerned. Of greater importance are the capacities

TABLE I
Hydrogen-Bonding Indices and Normalized Transport Rates for C₃ and C₄ Linear Compounds

Permeant species	Semi-permeability, solute concentration in effluent/solute concentration in feed ^a	Normalized water transport rate, J_1/J_0^b	Normalized solute transport rate, J_2/J_0^b	Hydrogen-bonding index, $m\mu^c$
Propionic acid	0.776	0.843	0.655	1468
<i>n</i> -Propylamide	0.623	0.813	0.506	1468
<i>n</i> -Propanol	0.604	0.843	0.491	1462
Propionaldehyde	0.490	0.843	0.414	1426
Propionitrile	0.833	0.750	0.625	1421
1-Nitropropane	0.870	0.125	0.110	1414
<i>n</i> -Butyric acid	0.780	0.843	0.658	1470
<i>n</i> -Butylamine	0.690	0.813	0.560	1470
<i>n</i> -Butanol	0.683	0.780	0.534	1454
Butyronitrile	0.689	0.500	0.345	1421
Butyraldehyde	0.320	0.344	0.110	1418

^a Feed concentration = 1% by weight of solute in water.

^b At 102 atm. applied pressure, J_0 = fresh water transport rate (128 ml./cm.²/day), J_1 = transport rate of water from solution, J_2 = transport rate of solute from a solution.

^c Hydrogen-bonding index = wavelength of maximum adsorption of the third water band (in millimicrons) when 1% by weight of water is dissolved in permeant species. The wavelength of the maximum of this band for pure water is 1475 $m\mu$.

TABLE II
Solute Densities and Normalized Transport Rates for the Isomeric Butanols and Butylamines

Solute species	Semi-permeability, solute concentration in effluent/solute concentration in feed ^a	Normalized water transport rate, J_1/J_0^b	Normalized solute transport rate, J_2/J_0^b	Specific gravity (20°C.)
<i>n</i> -Butanol	0.683	0.781	0.534	0.810
<i>sec</i> -Butanol	0.489	0.812	0.397	0.808
Isobutanol	0.290	0.750	0.218	0.801
<i>tert</i> -Butanol	0.074	0.844	0.062	0.789
<i>n</i> -Butylamine	0.690	0.813	0.560	0.740
<i>sec</i> -Butylamine	0.604	0.813	0.489	0.724
Isobutylamine	0.526	0.719	0.378	0.736
<i>tert</i> -Butylamine	0.228	0.843	0.192	0.696

^a Feed concentration 0.135*M*.

^b Transport at 102 atm. pressure.

of the various solutes for dissolving in the membranous bound water structure. In this study the solution effect in diffusion transport was determined by establishing the hydrogen-bonding capacities of a number of C₃ and C₄ compounds with different functional groups and relating these capacities to their respective J_2/J_0 values (Table I). The relative hydrogen-bonding capacities of various organic solutes were established by determining the position of the second water OH overtone of a small amount of water in a large excess of organic substance, the hydrogen-bonding index. Those materials with a high capacity for hydrogen bonding effected either a slight blue shift (compared to the position of the band in pure water) or a shift to the red (indicating an enhancement of the hydrogen-bonding capacity of the solution beyond that exhibited by pure water). Those materials with a low capacity for hydrogen bonding caused a substantial blue shift of the OH overtone. It was anticipated and subsequently established that the farther to the red the maximum of the water OH band in a given solute, the greater the solute's J_2/J_0 value. Thus both J_2/J_0 values and hydrogen-bonding indices decrease from the acid to the nitroparaffin. The lability of the acid hydrogen renders the carboxyl group highly polar and accounts for its great hydrogen-bonding capacity according to the electrostatic model of the hydrogen bond. The primary amines rank higher than the alcohols,

which is probably attributable to their two H atoms, each of which may participate in hydrogen bonding. The aldehydes, butyronitrile (but not propionitrile), the nitroparaffins, and the acetins also exhibited the expected relationship. It is therefore considered that the correlation existing between J_2/J_0 values and hydrogen bonding indices constitutes evidence for the existence of solution effects in the transport of solutes across the membrane by diffusion. However, this statement does not imply that steric effects are of no importance. In the case of the isomeric butanols and butylamines, e.g., there is a good correlation between solute specific gravity (and hence partial molal volume) and J_2/J_0 values (Table II). The one apparent discrepancy, involving the secondary and isobutylamines, might be the result of an inversion of the assumed specific gravity-partial molal volume relationship for these two compounds.

The Gibbs Adsorption Concept Applied to the Dependence of Water Transport Rate upon the Nature of the Solute

Although solution transport by hydrogen bonding appeared to account satisfactorily for the rates of solute transport for sterically matched solutes, and sieving for separations within an isomeric series, the very striking differences apparent among the J_1/J_0 values remained anomalous (Tables I, II, and III). It will be recalled that Shuler et al.⁵ have attributed differences in water permeability coefficients to solute effects upon water mobility during the diffusion process. However, although reduction of solvent flow by virtue of obstruction by solute appears quite reasonable it is not the only

TABLE III
Relationship between Solution Surface Tension and Normalized Transport Rates

Permeant species	Surface tension 25°C. of aqueous solution at 0.1 <i>M</i> concentration, dyne/cm.	Normalized water transport rate, J_1/J_0^a	Normalized solute transport rate, J_2/J_0^a
Water ($J_1 = J_0$) ^b	72.0	1.00	—
Glycerine	71.9	0.906 (0.1 <i>M</i>)	0.170
Monoacetin	63.8	0.718 (0.1 <i>M</i>)	0.060
Diacetin	63.0	0.656 (0.1 <i>M</i>)	0.046
Triacetin	55.4	0.344 (0.1 <i>M</i>)	0.023
<i>tert</i> -Butyl alcohol	61.0	0.844 (0.135 <i>M</i>)	0.062
<i>sec</i> -Butyl alcohol	59.6	0.812 (0.135 <i>M</i>)	0.397
<i>n</i> -Butyl alcohol	59.2	0.781 (0.135 <i>M</i>)	0.534
Isobutyl alcohol	58.0	0.750 (0.135 <i>M</i>)	0.218

^a At 102 atm. pressure and given solute concentration.

^b Distilled water at 102 atm. pressure.

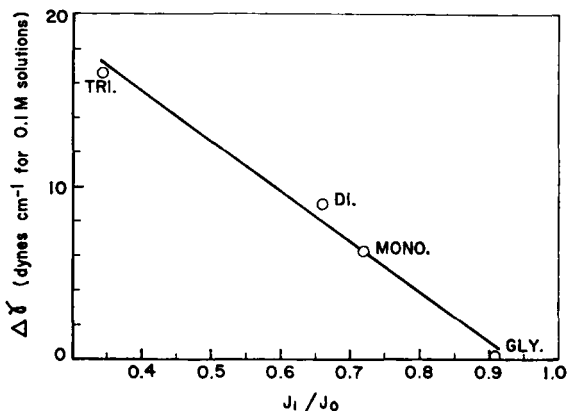


Fig. 1. Decrease in surface tension vs. J_1/J_0 values for glycerol acetates.

possible explanation for this phenomenon. An alternative explanation is offered by the Gibbs adsorption of solute at the membrane-solution interface.

Expressed quantitatively, the Gibbs adsorption isotherm states that

$$\mu = -(1/RT) (\partial\gamma/\partial\alpha)_{T,A} \quad (1)$$

where μ is the quantity of solute adsorbed in excess of that in the bulk solution, R is the gas constant, T is absolute temperature, γ is the surface tension of the solution, α is the activity of the solute, and A is the area of the surface of the solution.

Assuming that eq. (1) is linear and that α does not differ significantly for equal concentrations of the organic solutes involved, then

$$\mu \approx -(1/RT)\Delta\gamma \quad (2)$$

where $\Delta\gamma$ is the difference in surface tension between pure water and solution. Insofar as the adsorption of matter onto the membrane will cover sites otherwise available for water transport, J_1/J_0 is inversely proportional to the amount of solute adsorbed and hence can be substituted for μ in equation (2). It follows that a plot of J_1/J_0 versus $\Delta\gamma$ for a series of solutes, where J_2/J_0 is low, should yield a straight line with negative slope. Support for the contention that solute adsorption is a contributing factor regarding the effects of solute nature upon J_1/J_0 is given by the results from both the isomeric butanols and the glycerine-triacetin series (Fig. 1 and Table III). Admittedly the fact that triacetin causes the greatest decrease in the value of J_1/J_0 and glycerine the least correlates well with both J_2/J_0 and solution surface tension values (Table III). However, in the case of the isomeric butanols, the correlation between solution surface tension and J_1/J_0 is apparent whereas steric effects cause a breakdown in the J_2/J_0 versus J_1/J_0 relationship. It may be therefore, that the adsorption of solute at the membrane-solution interface should not be neglected in any considerations of anomalous decreases in the rate of solvent transport.

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References

1. J. D. Ferry, *Chem. Rev.*, **18**, 373 (1936).
2. L. Ticknor, *J. Phys. Chem.*, **62**, 1483 (1958).
3. D. Reid and J. Kuppers, *J. Appl. Polymer Sci.*, **2**, 264 (1959).
4. R. E. Kesting, M. Barsh, and A. Vincent, *J. Appl. Polymer Sci.*, **9**, 1873 (1965).
5. K. Shuler, C. Dames, and K. Laidler, *J. Chem. Phys.*, **17**, 860 (1949).
6. R. E. Kesting, *J. Appl. Polymer Sci.*, **9**, 663 (1965).
7. A. L. Vincent, M. Barsh, and R. E. Kesting, *J. Appl. Polymer Sci.*, **9**, 2363 (1965).
8. P. Newsome and S. Sheppard, *J. Phys. Chem.*, **36**, 930 (1932).

Résumé

Le transport de matière dissolvée à travers les membranes, semipermeables d'acétate secondaire de cellulose dépend de la capacité pour liaison hydrogène de la structure aqueuse liée et des facteurs stériques. La vitesse due transport d'eau c'est influencé pour l'adsorption Gibbs de matière dissolvée.

Zusammenfassung

Der Transport von aufgelöstem Material durch halbdurchlässige Membrane von Cellulose Diacetat hängt von der Kapazität des Materials mit verbundenen Wasser Wasserstoffbrücke zu bilden und auch von sterischen Faktoren ab. Die Geschwindigkeit des Wassertransportes wird von der Gibbschen Adsorbierung des aufgelösten Materials beeinflusst

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