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Determination of Selective Mass Transfer Rates across Liquid Membranes by Measurement of Permeation Coefficients

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Abstract

Permeation coefficients of urea and NH_4^+ across liquid membranes of glycerine esters were determined. The enzymatic hydrolysis of urea was chosen to show the selectivity of the membranes with respect to urea and ammonium ions. The mass transfer rate for urea was up to 15 times higher than for ammonium ions.

INTRODUCTION

The principle of the liquid membrane technique developed by Li (*1*) is based on forming liquid membrane capsules in such a way that the encapsulated phase is dispersed in the membrane phase and the resulting emulsion is dispersed again in a third liquid phase.

Asher et al. (*2*) showed that liquid membranes with a high share of glycerine monooleate (GMO) act as ion barriers so that great differences in permeation rates of ionogenic and non-ionogenic molecules can be obtained. This effect can be utilized in separation processes.

To describe a liquid membrane system quantitatively, knowledge of the permeation rates of the solutes is necessary. Up to now, only few quantitative data are available (e.g., Ref. *3*).

Large surface areas can be obtained by the liquid membrane technique. Therefore this technique is of great interest for the removal of toxic substances of low concentrations from a continuous phase. Following Asher et al. (*2*), urea was chosen as the model toxin. Urea is of special interest because of the ionogenic character of its hydrolysis product $NH_4{}^+$. From the difference in polarity of the substrate and the product, different transfer rates through a liquid membrane can be expected. By using urease within a liquid membrane capsule, it is possible to trap urea in the form of $NH_4{}^+$ in the capsule.

Permeation through a liquid membrane is a complex mass transfer process, consisting of the following steps:

(1) Diffusion through the boundary layer
(2) Sorption in the membrane phase
(3) Diffusion through the membrane
(4) Desorption from the membrane phase
(5) Diffusion through the boundary layer.

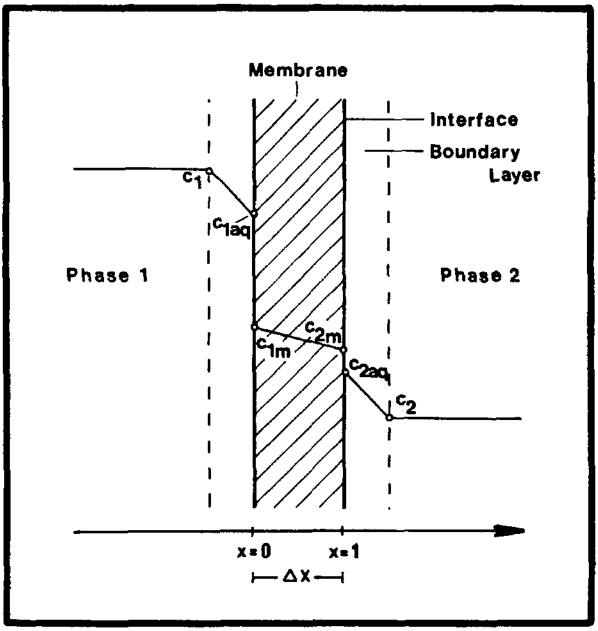

FIG. 1. Concentration profile across a membrane.

These processes are schematically shown in Fig. 1. Diffusion in the membrane phase and permeation through a membrane are specific for a membrane–solute combination.

Permeation coefficients (Q) can be obtained from mass transfer measurement according to Fick's first law. For two substances the ratio of the permeation coefficient measured at the same membrane is defined as the selectivity (σ) of the membrane with respect to the two substances.

EXPERIMENTAL

Materials and methods

For the determination of permeation coefficients according to Fick's first law, the transfer area and the concentration gradient must be known. Using solid supported liquid membranes instead of liquid membrane capsules, these data can easily be obtained. Membrane filters of known porosity were used as supporting material. Their effective pore length was obtained from diffusion measurements. with nonimpregnated membranes. Membrane filters (Sartorius, type SM 11307, D-3400 Göttingen, West Germany) with the following properties were used: porosity, 70 ± 3%; pore size, 0.2 μm; and effective length of pores, 165 μm.

Membrane filters were impregnated with a liquid membrane phase in vacuo (0.1 Torr) to achieve uniform penetration of the filters with the impregnation fluid.

In Fig. 2 the permeation apparatus is shown schematically. It consists of a permeation cell (1–5), measuring cells (6), peristaltic pumps (7), and flowmeters (8). The permeation cell is made from Plexiglas and consists of two identical cylindrical sections (2) with diameters of 8 cm and depths of 0.3 cm.

The compartments are divided by the membrane (1). The pressures in them are measured by the liquid manometer (5). The peristaltic pumps are regulated by these pressures and by means of the light gates (4) to avoid convection across the membrane due to the unequal pressure in the compartments.

One of the sections of the permeation apparatus was filled with 48 ml of an equimolar urea–NH_4Cl solution (each 1 M), and the other one with 48 ml of distilled water. The flow rates were 15 cm^3/min and the temperature was 25°C. The increase of urea and NH_4Cl concentration was measured in the part of the permeation apparatus filled with distilled water.

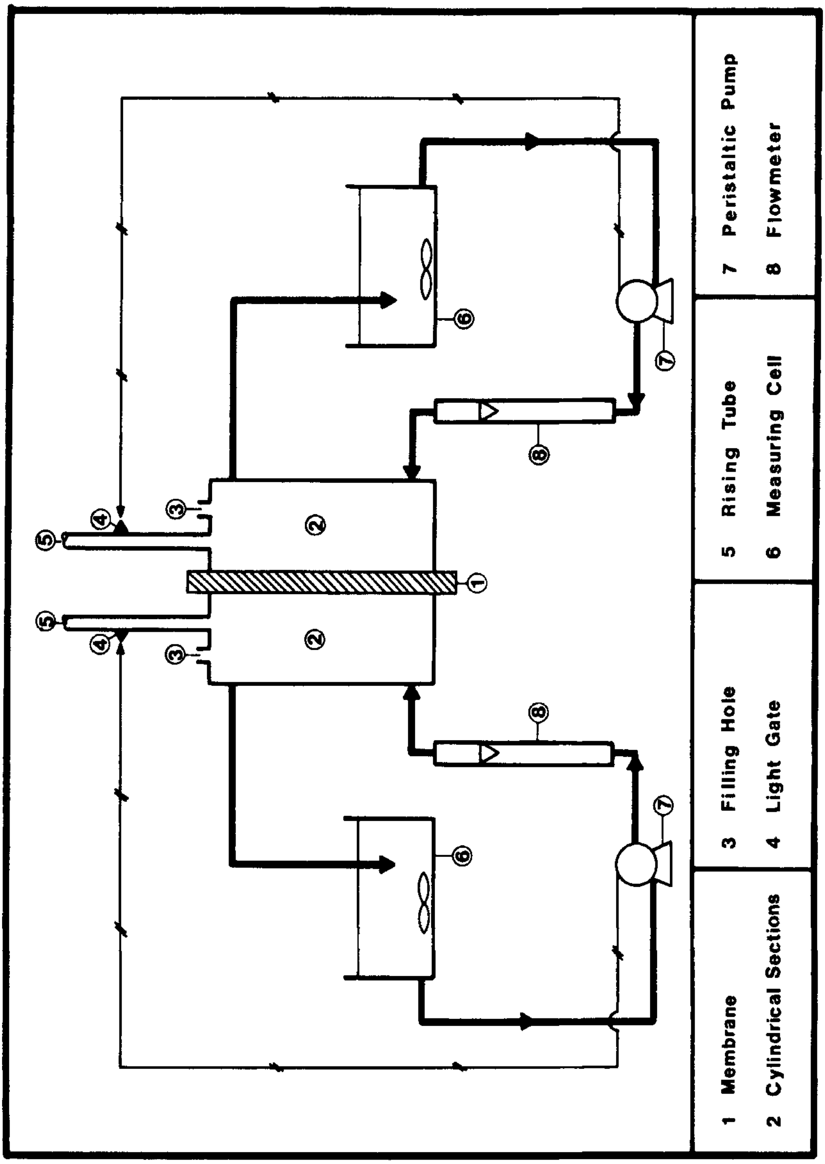

FIG. 2. Schematic diagram of permeation apparatus.

Analytical

The concentrations of urea and NH_4^+ ions were determined enzymatically (*4*):

$$\text{Urea} + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2 \tag{1}$$

$$2\alpha\text{-ketoglutarate} + 2NADH + 2NH_4^+ \xrightarrow{\text{GlDH}} 2\text{L-glutamate} + 2NAD^+ + 2H_2O \tag{2}$$

The decrease of NADH was measured by the change of extinction at 340 nm. It is proportional to the amount of NH_4^+. It is possible to determine urea and NH_4^+ quantitatively from one sample by first recording NH_4^+ (Eq. 2) and then urea by the addition of urease (Eqs. 1 + 2). The total concentration of NH_4^+ in the sample should not be higher than 1 mmole/l when using 1 cm cuvettes. Mono-, di-, and triglycerides of the oleic acid were used as membrane phases:

(1) Monoglyceride of the 12-hydroxy oleic acid (GMRO) [Henkel, Dusseldorf, West Germany, glycerine monoricineoleate (Rilanit GMRO)]
(2) Diglyceride of the oleic acid (GDO) [Henkel, Dusseldorf, West Germany, glycerinedioleate (Rilanit GDO)]
(3) Triglyceride of the oleic acid (GTO) [Roth, Karlsruhe, West Germany, glycerinetrioleate (Triolein purum)]

RESULTS

Figure 3 shows some typical results of the permeation measurements. In the upper half the transported amount of urea and in the lower half the transported amount of NH_4^+ are plotted as functions of the time. The parameter is the composition of the liquid membranes. The ratio of the slopes (for identical membrane liquids) is the previously defined selectivity σ. The experimental data are summarized in Table 1. From the abscissa intersections of the curves in Fig. 3 the so-called "time lags" t_l can be obtained by extrapolation. By using these time lags, the diffusion coefficients D can be calculated (*5*):

$$t_l = \frac{(\Delta x)^2}{6D} \tag{3}$$

The resulting diffusion coefficients are given in Table 2 together with the diffusion coefficients in water for comparison.

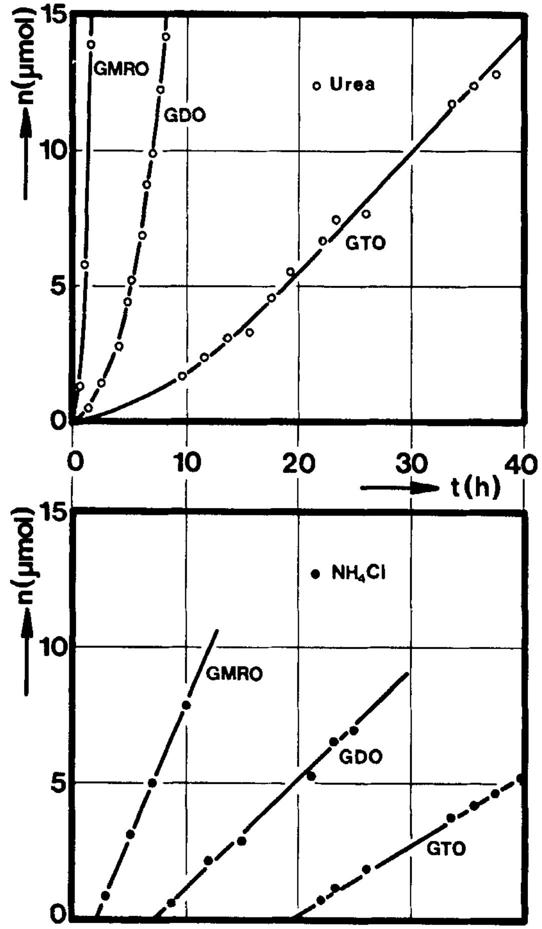

FIG. 3. Permeation of urea and ammonium chloride through solid supported liquid membranes. Ordinate: moles permeated. Abscissa: time.

TABLE 1

Permeation Coefficients of Urea and NH_4Cl and Selctivity

	GMRO	GDO	GTO
T, °C	25	25	25
A, cm^2	35.18	35.18	35.18
Δc, moles/l	1	1	1
Δx, μm	165	165	165
$\dot{n}_{Ur}$, mole/sec	4.46×10^{-9}	7.52×10^{-10}	1.15×10^{-10}
$\dot{n}_{NH_4Cl}$, mole/sec	2.92×10^{-10}	1.13×10^{-10}	5.47×10^{-11}
Q_{Ur}, cm^2/sec	2.09×10^{-9}	3.53×10^{-10}	5.39×10^{-11}
Q_{NH_4Cl}, cm^2/sec	1.37×10^{-10}	5.30×10^{-11}	2.56×10^{-11}
$\sigma = Q_{Ur}/Q_{NH_4Cl}$	15.26	6.66	2.11

TABLE 2

Diffusion Coefficients of Urea and NH_4Cl

	H_2O	GMRO	GDO	GTO
D_{Ur} cm^2/sec	1.38×10^{-5}	2.14×10^{-8}	0.394×10^{-8}	0.199×10^{-8}
D_{NH_4Cl}, cm^2/sec	1.838×10^{-5}	0.546×10^{-8}	0.172×10^{-8}	0.066×10^{-8}

The data in Table 1 show that the monoglyceride has the best selectivity and therefore GMRO was used to form liquid membrane capsules. To improve the stability of these capsules, 3% (in weight) of a tenside [Baker, Deventer, Netherlands, sorbitanmonooleate (Span 80)] was added to the membrane phase. The permeation rates were not influenced by this addition.

To check whether the selectivity of the liquid membrane capsules made of GMRO is equal to the selectivity measured with the solid supported liquid membrane and to estimate the transfer rates attainable by the liquid membrane technique, 2 ml of an equimolar urea–NH_4Cl solution (each 0.05 *M*) was added dropwise to 3 ml of the membrane-forming solution with vigorous agitation. The resulting emulsion was washed with distilled water and added dropwise to 50 ml of water, this time with moderate agitation. The increase of concentration in the continuous aqueous phase was recorded. The results are shown in Fig. 4. The transported amounts of urea and NH_4^+ are plotted as functions of the time. Because of the large surface area compared with the solid supported liquid membranes, the concentration gradient cannot be regarded as constant during the entire experiment. This is obvious from the decreasing mass transfer rate of urea.

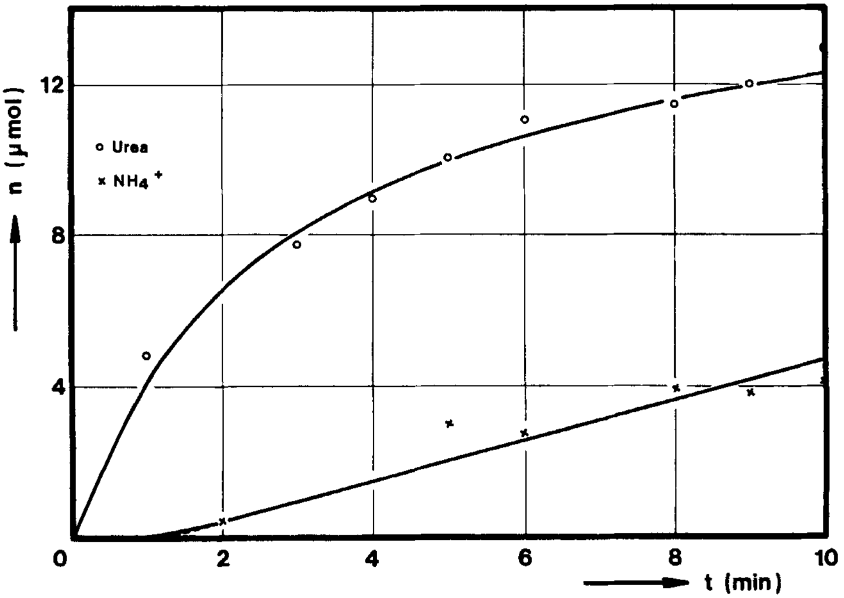

FIG. 4. Permeation of urea and ammonium chloride through GMRO-liquid membrane capsules. Ordinate: moles permeated. Abscissa: time.

The selectivity obtained ($\sigma = 9.04$), which is similar to that found in experiments with solid supported liquid membranes ($\sigma = 15.26$), shows a small leakage of the liquid membrane capsules.

By using the time-lag method (Eq. 3), the average membrane thickness Δx can be estimated from known diffusion coefficients D (Table 2) and known time lags of the NH_4^+ curve (Fig. 4). With the resulting membrane thickness (16 μm) and known permeation coefficients (Table 1), the surface area can be determined from the slope of the same curve. It amounts to 2040 cm^2. The average radius r of the capsules can be estimated by the ratio of the volume of the inner phase V to the surface area A, neglecting the membrane thickness in comparison to the radius of the capsules:

$$\frac{V}{A} = \frac{N\frac{4}{3}r^3\pi}{N4r^2\pi} \tag{4}$$

with N = number of capsules.

The average radius is found to be 176 μm, which justifies the upper approximation.

DISCUSSION

One can recognize from Table 1 that selectivity increases with the number of free hydroxy groups of the glyceride. The extent of the selectivity depends on two factors: (a) on the different mobilities (expressed by diffusion coefficients) of the two species in the membrane phase, and (b) on their distribution coefficients with regard to the membrane and aqueous phase. These distribution coefficients can be estimated by the ratio of permeation coefficients to diffusion coefficients. The resulting data are shown in Table 3. The selectivity can also be expressed by

$$\sigma = \frac{k_{\mathrm{Ur}} D_{\mathrm{Ur}}}{k_{\mathrm{NH_4Cl}} D_{\mathrm{NH_4Cl}}} \tag{5}$$

Equation (5) shows the effect of the two main factors on the selectivity. A high selectivity can only be achieved by small mass transfer coefficients. By the liquid membrane technique, however, large exchange areas are produced, so that in spite of these small coefficients, remarkably high transfer rates can be obtained (Fig. 4).

TABLE 3

Distribution Coefficients of Urea and NH_4Cl

	GMRO	GDO	GTO
$k_{\mathrm{Ur}} = Q_{\mathrm{Ur}}/D_{\mathrm{Ur}}$	9.77×10^{-2}	8.96×10^{-2}	2.71×10^{-2}
$k_{\mathrm{NH_4Cl}} = Q_{\mathrm{NH_4Cl}}/D_{\mathrm{NH_4Cl}}$	2.51×10^{-2}	3.08×10^{-2}	3.90×10^{-2}

The transport parameters found can be used to estimate geometric data of liquid membranes when mass transfer rates are known. If the geometric data are known by means of another method (e.g., photographic measurement), the transport parameters can be used to predict the rates.

From the measurements reported here, a transfer area of 1 m^2/15 ml membrane phase results. This ratio can be increased by increasing the agitation speed during formation of the liquid membrane capsules.

SYMBOLS

A	mass transfer area, cm^2
c	concentration, mole/l
D	diffusion coefficient, cm^2/sec
k	distribution coefficient
n	mole number, μmole

$\dot{n}$	molar flow, mole/sec
Q	permeation coefficient, cm^2/sec
T	temperature, °C
t	time (min or hr)
t_1	time lag (min or hr)
Δx	thickness of liquid membrane (μm)
σ	selectivity

Subscripts

1	phase 1
2	phase 2
m	in the membrane phase
aq	in the aqueous phase
Ur	urea
NH_4Cl	ammonium chloride

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