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Some Aromatic Amine Transport through Emulsion Liquid Membranes

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ABSTRACT

This paper reports the permeation of 10 aromatic amines through emulsion liquid membranes and estimates of the apparent diffusion coefficients and apparent moving rates.

INTRODUCTION

The technique of liquid membranes is astonishing if one considers its procedure simplicity. Both emulsion liquid membranes (ELM) and liquid supported ones are widely used in various fields: the concentration of metal ions from wastewaters (1–4), the elimination of radioactive metals from the waters of nuclear power plants (5, 6), the removal of organic (7, 8) and inorganic (9) pollutants from residual waters, the separation of hydrocarbons and gases (10), some medical techniques (11).

An emulsion liquid membrane consists of a liquid film which separates a continuous source phase and an internal discontinuous phase (Fig. 1). It may be achieved from a multiple emulsion of the W/O/W or O/W/O

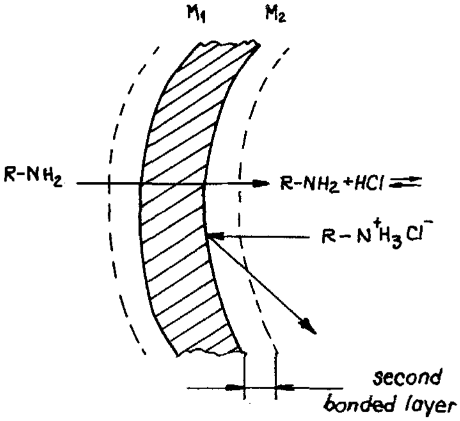

FIG. 1 Liquid membrane.

type. This separation technique exhibits the advantage of a very high transfer surface (10^6 m^2/m^3).

EXPERIMENTAL

Materials

We tested 10 aromatic primary amines from Fluka or Merck, purified by distillation or recrystallization. The membrane consisted of kerosene, *n*- and isoalkane fractions (carefully purified to eliminate any traces of aromatic hydrocarbons), and SPAN 80 emulsifier (Fluka). Analytical solutions of HCl (0.1 to 0.5 N) were used as the internal phase. $Na_2HPO_4 \cdot 12H_2O$ was used as the buffer (pH 8) when the samples were analyzed.

Analyses

The permeation process was followed by a UV-VIS spectrophotometer (M40 Carl Zeiss Jena) at pH 8 (pH-meter OP-205/1 Radelkis). The samples were analyzed (final concentration, after treating the source phase with ELM) at λ_{max} for each amine, and the concentrations were determined from specific calibration curves. The water content of the organic material was determined by the Karl-Fischer method.

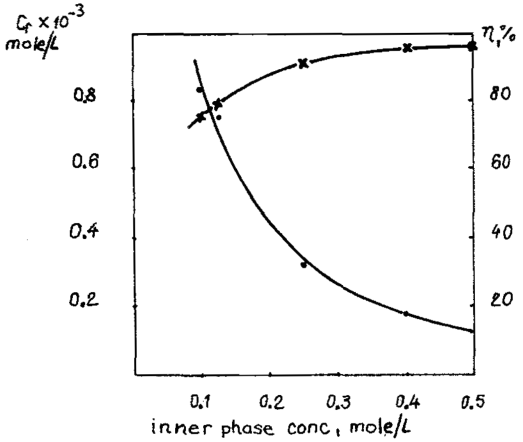

FIG. 2 Influence of membrane material/inner phase material ratio. (×) η = *f*(membrane material/inner phase ratio). (●) c_r = *f*(membrane material/inner phase ratio).

Procedure

Initially, some experiments for choosing the membrane material, the inner phase material/membrane material ratio, and inner phase concentration were performed (Figs. 2 and 3).

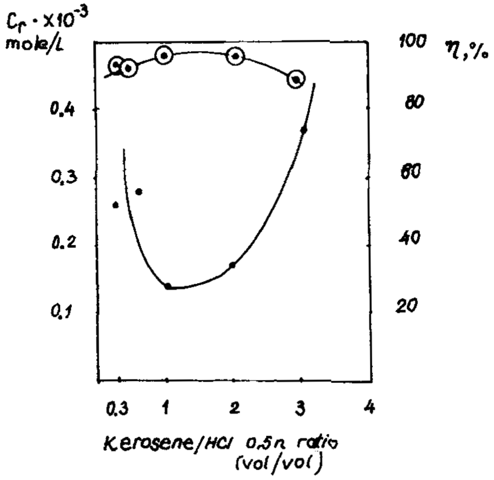

FIG. 3 Influence of inner phase concentration. (⊙) η = *f*(inner phase concentration). (●) c_r = *f*(inner phase concentration).

The primary emulsion (internal phase/organic phase) was achieved using a seven-branched stirrer RW 47 (with continuous adjustable rotation) as follows:

Membrane material, cm^3	20
Internal phase, cm^3	20
SPAN 80 emulsifier, %	8
Stirring time, minutes	15
Stirring speed, rpm	1200

The particle size lies between 2 and 5 μm.

The ELMs were obtained by dispersing the primary emulsion in the source phase at different ratios (Fig. 4):

Primary emulsion/source phase ratio	1:5 ÷ 1:15
Contacting time, minutes	0.25–10
Stirrer speed, rpm	150
Temperature, °C	20 ± 2
Diameter of globules, mm	0.5 ÷ 3

The initial concentration of the amines (Table 1) in the source phase was 3.5×10^{-3} mol/L. It was chosen according to the solubility limit of certain amines and the possibility of comparing the transfer phenomena.

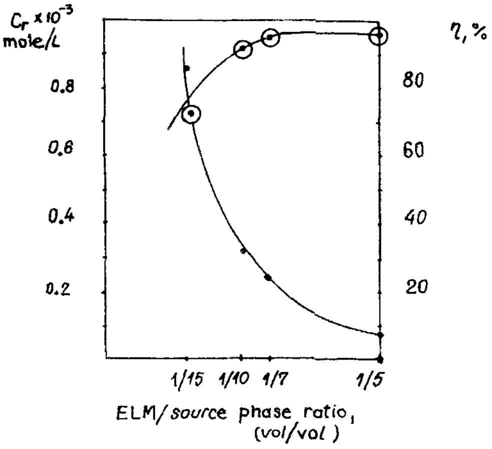

FIG. 4 Influence of ELM/source phase ratio. (⊙) η = *f*(ELM/source phase ratio). (●) c_r = *f*(ELM/source phase ratio).

TABLE 1
Aromatic Amines[a]

Amine	K_b	Permeation yield (η%)	σ*	E_s	D' (min^{-1})	n' (J/mol·min)
Aniline	4.1×10^{-10}	99	+0.087	1.24	0.3707	1.522×10^{-4}
o-Nitroaniline	1×10^{-14}	44.3	−0.069	—	0.0506	2.077×10^{-5}
m-Nitroaniline	2.88×10^{-12}	96	−0.170	—	0.1544	6.338×10^{-5}
p-Nitroaniline	1×10^{-13}	28.9	0.710	—	0.0306	1.256×10^{-5}
o-Toluidine	2.45×10^{-10}	99.2	1.460	—	0.2638	1.083×10^{-4}
m-Toluidine	4.90×10^{-10}	99.1	0.00	0	0.4177	1.715×10^{-4}
p-Toluidine	1.26×10^{-9}	99.1	−0.10	−0.07	0.2382	9.777×10^{-5}
o-Cl-aniline	4.50×10^{-12}	96.7	0.37	0.18	0.1556	6.387×10^{-5}
o-Br-aniline	3.39×10^{-12}	95.3	0.38	0.00	0.2302	9.449×10^{-5}
o-Ethylaniline	2.34×10^{-10}	99.0	1.39	−0.75	0.1617	6.638×10^{-5}

[a] The K_b values are taken from Ref. 13. $\eta = \frac{c_{in} - c_r}{c_{in}} \times 100$.

RESULTS AND DISCUSSION

The permeation of the amines is achieved by simple diffusion coupled with chemical reaction in the internal phase. The ionic species of the aryl ammonium chloride are insoluble in the organic membrane; the permeation is uni-directional.

Considering the diffusion coefficient D, the transfer area A, and the thickness of liquid membranes are difficult to determinate, the first law of Fick may be expressed as (12):

$$\ln \frac{c_{in}}{c_r} = D' \left(\frac{V_{em}}{V_{sph}}\right) \cdot \theta \qquad (1)$$

where c_{in} = initial concentration of source phase (mol/L)
c_r = final concentration of source phase (mol/L)
D' = apparent diffusion coefficient (min^{-1})
V_{em} = primary emulsion volume (cm^3)
V_{sph} = source phase volume (cm^3)
θ = treatment time (minutes)

The apparent diffusion coefficient calculation allows for the computation of n' for the species.

The transport yields are high for very low permeation times (Fig. 5). This means that diffusion through the membrane is not the rate-determining step.

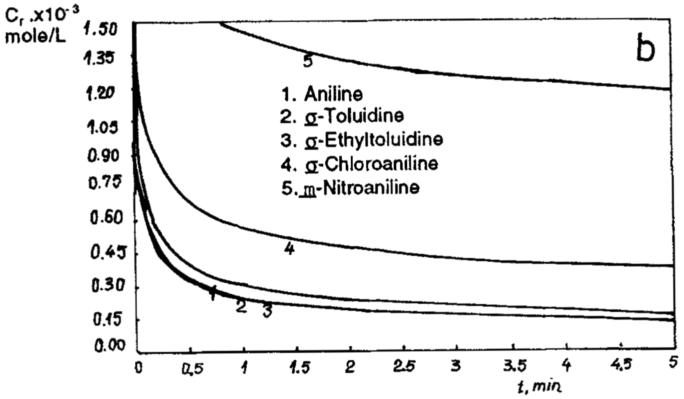

FIG. 5 Variation of amines concentration vs time.

Changes in membrane thickness, which may be achieved by changes of the emulsifier concentration, the phases ratio of the primary emulsion, or the stirring speed, do not result in significant changes of the transportation yield. This indicates the remarkable mobility of the amines studied.

It is known (13) that

$$D = n \times RT \tag{2}$$

where D is the diffusion coefficient and n is the species moving rate.

One may assume that Eq. (2) is similar to Eq. (3):

$$D' = n' \times RT \tag{3}$$

where D' is the apparent diffusion coefficient and n' is the apparent moving rate of the specie (Table 1).

As can be seen from Table 1, the apparent diffusion coefficients D' and the corresponding apparent moving rates n' are poorly related to the K_b values of the amines. This means that the permeation process is practically insensitive to the basicity of amines and that the rate-determining step is not the chemical reaction in the internal phase, i.e., protonation of the amines. It follows that the rate-determining step should be one of the two diffusion processes; diffusion of amine molecules through the liquid membrane or diffusion of the arylammonium ions from the liquid membrane–internal phase interface.

In order to establish a simple linear free energy relationship between the permeation rates (expressed by the apparent diffusion coefficients D') and the steric and polar substituent effects, linear correlations with the

E_s and σ^* Taft substituent constants (14) were attempted. A plot of log $D'x/DCH_3$ values versus steric substituent constants E_s for ortho-substituted anilines (Fig. 6) gave a small correlation coefficient ($r = 0.8325$), suggesting that the steric interaction mechanism is different from that of the acid-catalyzed hydrolysis of esters, which is the standard reaction for defining E_s–Taft values.

One may also to assume that steric hindrance is of little importance for the permeation process of amines through the membrane.

A better correlation seems to exist with the polar substituent constants. A plot of log $D'x/D'$ versus the σ^* Taft substituent constants (for ortho-substituted derivatives) and the σ-Hammett constants (15) (for meta- and para-substituted anilines) gives a correlation coefficient of 0.89 and a slope of −0.494 (Fig. 7). Since the absolute value of the slope is small, one may assume that the influence of polar effects on the rate of diffusion through the liquid membrane is of little importance. The negative value of the slope indicates that permeation through the liquid membrane is facilitated by electron-withdrawing substituents.

Consider the two diffusion processes assumed to control the permeation of amines. The former, that is, the diffusion of amine molecules through the liquid membrane should be more sensitive to electronic and particularly steric effects than the results from the slopes of the Taft correlations indicate. The latter is the diffusion of the arylammonium cations (the internal phase is a 0.1–0.5 N HCl solution) from the membrane–internal phase interface determined mainly by the solvation of the cations, which is much

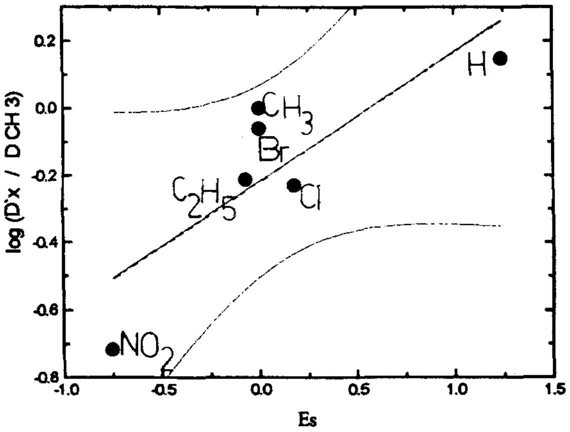

FIG. 6 log $(D'x/DCH_3) = f(E_s)$.

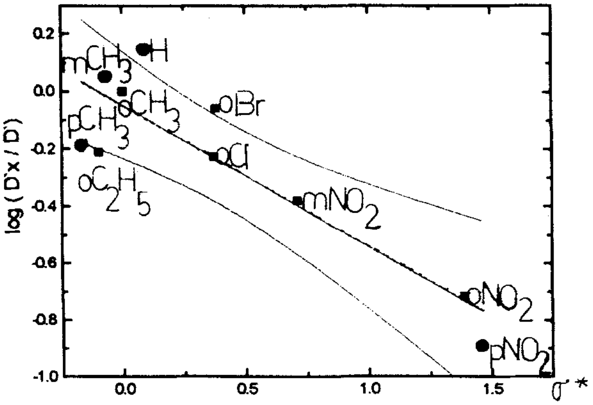

FIG. 7 $\log(D'x/D') = f(\sigma)$.

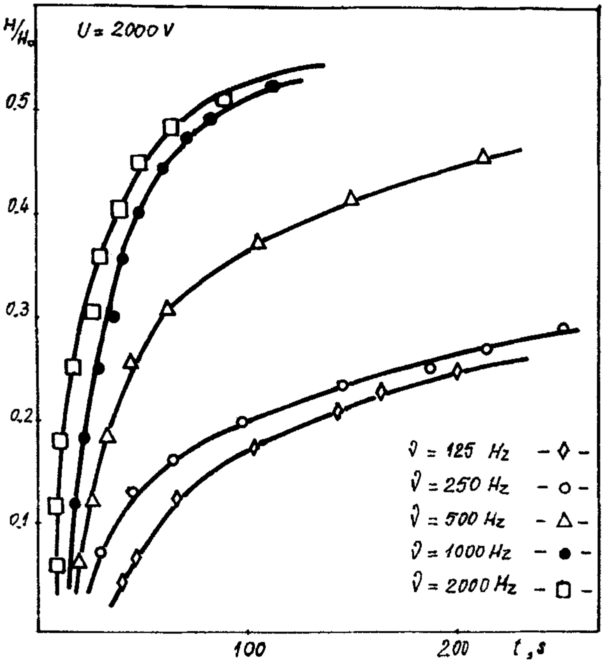

FIG. 8 Electrical breakup at $U = 2000$ V.

less influenced by electronic or steric effects. It follows that the rate-determining step of permeation is probably the diffusion of arylammonium cations from the membrane–internal phase interface. This is known as the "polarization of concentration" phenomenon and has also been observed for certain other species studied.

The liquid membrane experiments did not exhibit strong effects of swelling or breaking up.

The exhausted ELMs were electrically broken up (16–18) in a cylindrical cell provided with a vertical isolated central electrode and a cell-embracing second one at voltages (U) of 1000–4000 V and frequencies (ν) of 100–2000 Hz. The breaking-up process was followed by measuring the amount of separated water with respect to the total amount of emulsion. The data were processed using a Simplex optimized nonlinear regression program (IBM/PC/XP computer):

$$H/H_0 = b_1 + b_2 \cdot e^{-b_3 t} \tag{4}$$

where H = the height of the separated water layer (mm)

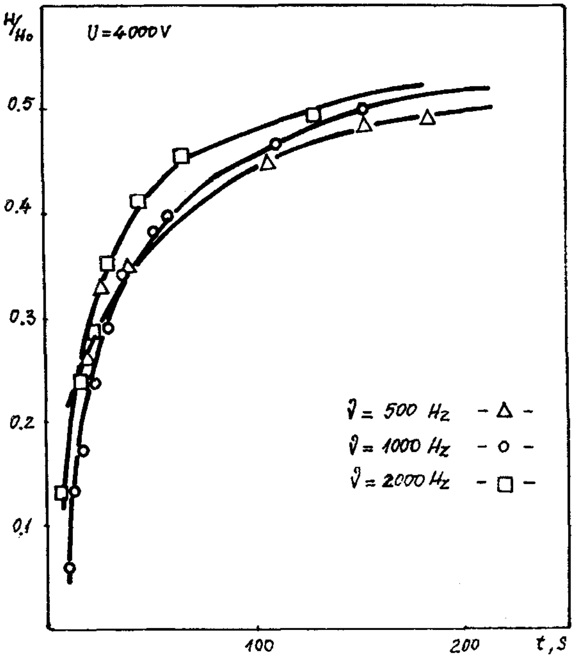

FIG. 9 Electrical breakup at U = 4000 V.

H_0 = the initial height of the emulsion layer (mm)
t = time (seconds)
b_1, b_2, b_3 = parameters

It may be observed that at lower voltages the influence of the frequency is more pronounced; at higher voltages the frequency effect is less important (Figs. 8 and 9).

The breaking up of the exhausted emulsion by this procedure is not complete (maximum separation extent $H/H_0 = 0.7$). The organic material retains between 0.8 and 1.81% water (determined by the Karl-Fischer method).

CONCLUSIONS

The ELM method allows for the separation and concentration with good yields of aromatic amines from wastewater by simple diffusion coupled with chemical reaction in the receiving phase. The exhausted membrane was best broken up by using an alternative electric field of 4000 V and 2000 Hz with promising results. The apparent diffusion coefficients and the apparent moving rates for the amines studied have been estimated.

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