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TRANSPORT OF ORGANIC ACIDS THROUGH A SUPPORTED LIQUID MEMBRANE

The transport of some di- and tribasic carboxylic acids from water solution through a supported liquid membrane (SLM) consisting of *n*-decanol or trioctylamine (TOA) solution in *n*-decanol adsorbed on a polytetrafluoroethylene film was studied. The influence of TOA as a carrier on the mass flux rate of different carboxylic acids was investigated. The experimental results have been quantitatively interpreted by mass transfer equations for carrier-facilitated and simple diffusional transport, taking into account the controlling transport resistance in the organic membrane phase.

Introduction

Both liquid membrane configurations, namely the supported liquid membrane (SLM) and the emulsion liquid membrane (ELM), have been used to extract several organic acids from their aqueous solutions. In most cases, ELM has been applied [1, 2, 3]. In spite of its relatively low mass transfer rate, SLM is a good tool for investigating the mechanism and kinetics of the chemical and mass transfer processes occurring in liquid membranes. Hikita et al. [4] have studied the separation and enrichment of fumaric, *L*-malic, and phthalic acids by SLM consisting of some organic solvents (incl. decanol) adsorbed on a polytetrafluoroethylene or cellulose ester film. In doing so, they have examined only a simple diffusional permeation in the membrane phase, without using any carriers. Other authors [2] have proposed the use of selective carriers (incl. TOA) for organic acid extraction by ELM. The facilitated nitric acid transport through SLM has been quantitatively described by Cianetti and Danesi [5]. The present study aims at:

- (1) examining the transport of di- and tribasic carboxylic acids, namely *o*-phthalic, succinic, and citric acids, through SLM consisting of *n*-decanol or the TOA solution in decanol adsorbed on the microporous polytetrafluoroethylene film;
- (2) determining the influence of the TOA carrier on the transport rate of the above-mentioned acids;
- (3) establishing possibilities of acid separation;
- (4) describing mathematically the mass transfer process of acids.

Experimental

All the reagents used were analar according to specifications of Sojuzreaktiv, USSR.

SLM consisted of the Vladipor microporous polytetrafluoroethylene membrane of MFF type No. 1, with a pore size of 0.15 μm and thickness 100 μm , on which *n*-decanol or TOA-decanol solution was adsorbed.

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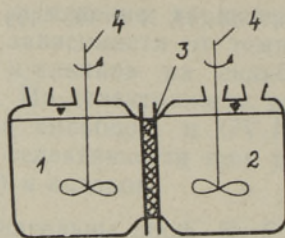


Fig. 1. Scheme of experimental apparatus. 1 — feed solution vessel, 2 — strip solution vessel, 3 — SLM, 4 — stirrer.

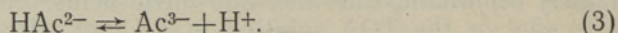
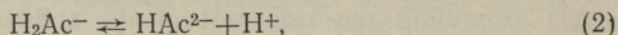
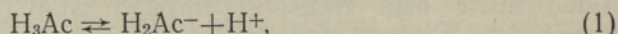
A scheme of the apparatus used is presented in Fig. 1. The apparatus consists of two 130 cm³ glass vessels for feed and strip solutions (1, 2). The two vessels are clamped together by two flanges facing each other, giving a cross-sectional area of 16.6 cm² where SLM (3) is positioned. Each vessel is provided with sampling and stirrer ports. The vessels are stirred by glass stirrers (4) driven by electric motors. The stirring speed was kept at 150 RPM in both the feed and strip solutions.

All the experiments were carried out at room temperature (20.0 ± 1.0°C). The acid concentration in the feed solution was determined potentiometrically using an EV-74 universal ionometer. The initial acid concentration in the feed solution was about 2 wt %. The strip phase consisted of 12% sodium carbonate solution, its concentration remaining practically constant in each run because of a large excess of Na₂CO₃ with respect to the low number of equivalents of the acid transported through the membrane. The carrier concentration in the liquid membrane phase was 50%.

Results and discussion

The facilitated transport of di- and tribasic carboxylic acids through SLM represents a set of chemical reactions and diffusion processes.

The dissociation of acid in an aqueous feed solution, for example, in case of a tribasic (citric) acid, may be expressed as follows:



The equilibrium constants of these reactions are given by

$$K_{1A} = [\text{H}_2\text{Ac}^-][\text{H}^+]/[\text{H}_3\text{Ac}], \quad (4)$$

$$K_{2A} = [\text{HAc}^{2-}][\text{H}^+]/[\text{H}_2\text{Ac}^-], \quad (5)$$

$$K_{3A} = [\text{Ac}^{3-}][\text{H}^+]/[\text{HAc}^{2-}]. \quad (6)$$

Thus, the total (analytical) concentration of citric acid $[\text{H}_3\text{Ac}]_T$ is a sum of molecular concentrations of undissociated acid $[\text{H}_3\text{Ac}]$ and dissociated anions $[\text{H}_2\text{Ac}^-]$, $[\text{HAc}^{2-}]$, and $[\text{Ac}^{3-}]$:

$$[\text{H}_3\text{Ac}]_T = [\text{H}_3\text{Ac}] + [\text{H}_2\text{Ac}^-] + [\text{HAc}^{2-}] + [\text{Ac}^{3-}]. \quad (7)$$

The dissociation constant values K_{1A} , K_{2A} , and K_{3A} for phthalic, succinic, and citric acids are available in literature [6, 7]. In the observed concentration interval of acids the undissociated part of the acid remains practically constant, being in all cases higher than 0.85. The concentrations of products of the second and third diffusion steps were negligible.

The concentration equilibrium of undissociated acid at the membrane-feed interface is given by the distribution or partition coefficient

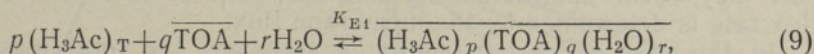
$$K_p = \frac{[\overline{\text{H}_3\text{Ac}}]}{[\text{H}_3\text{Ac}]}, \quad (8)$$

where $[\overline{\text{H}_3\text{Ac}}]$ is the concentration of undissociated acid in *n*-decanol. The partition coefficient was measured by the conventional method, while the concentration of undissociated acid was calculated from Eqs. (4)–(7). The K_p values obtained are given in the Table.

Partition coefficients of acids and permeabilities of SLM at 20 °C

| Acid | K_p | P_D , m/s | P_F , m/s |
|--------------------|--------|----------------------|----------------------|
| <i>o</i> -Phthalic | 1.8415 | $0.93 \cdot 10^{-6}$ | $3.0 \cdot 10^{-6}$ |
| Succinic | 0.1053 | $0.36 \cdot 10^{-6}$ | $0.37 \cdot 10^{-6}$ |
| Citric | 0.0071 | $0.23 \cdot 10^{-6}$ | $0.14 \cdot 10^{-6}$ |

The chemical acid-TOA equilibria at the membrane-feed interface can be described by the following equations:

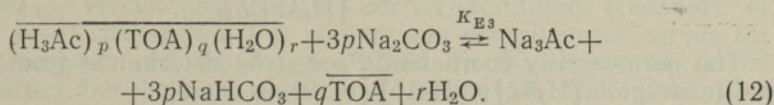
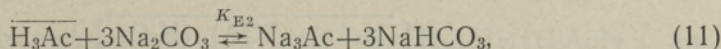


$$\begin{aligned} [\overline{\text{TOA}}]_T &= [\overline{\text{TOA}}]_e + q [(\overline{\text{H}_3\text{Ac}})_p (\overline{\text{TOA}})_q (\overline{\text{H}_2\text{O}})_r] = \\ &= [\overline{\text{TOA}}]_e + q K_{E1} [\text{H}_3\text{Ac}]_T^p [\overline{\text{TOA}}]_T^q [\text{H}_2\text{O}]_T^r, \end{aligned} \quad (10)$$

where the bar indicates the organic (membrane) phase species, $[\overline{\text{TOA}}]_T$ is the total (analytical) TOA molecular concentration, $[\overline{\text{TOA}}]_e$ — the concentration of TOA not bound to acid, $[(\overline{\text{H}_3\text{Ac}})_p (\overline{\text{TOA}})_q (\overline{\text{H}_2\text{O}})_r]$ — the concentration of the acid-TOA complex. The summary equilibrium constant K_{E1} takes into account both the acid dissociation and reaction of dissociated species with TOA.

The values of p , q , and r depend on the system used and are given in the literature [6, 7, 8, 9]. The hydration of the complex with $p\text{H}_2\text{O}$ has been established for citric acid only. Moreover, in case of a low concentration of the acid, $[\text{H}_2\text{O}]$ might be considered constant. Solvation of acid molecules with decanol is also possible.

At the strip side of the membrane the diffused acid and the acid-TOA complex react with sodium carbonate



The mass flux from the feed to the strip phase depends on the diffusion velocity of the acid and the reaction products through the aqueous boundary layers in the feed and strip phases, through the membrane, as well as on the rate of reactions (9), (11), and (12). All these processes are not rate-determining. As in our case the diffusion resistance

of the membrane is very high and the stirring speed of the feed and strip solutions is sufficient (150 RPM), there is no doubt that the diffusion resistance of both the feed and strip aqueous boundary layers is negligible. Therefore we can take the concentrations of undissociated acid and dissociated species at the feed-membrane interface equal to those in the feed bulk.

The rate of reactions (9), (11), and (12) is high enough for the reaction kinetics to be taken instantaneous. At the feed side of the membrane the chemical equilibrium of reactions (9) is always valid. The composition of the strip solution is such that equilibria (11) and (12) are completely directed to the right and are localized at the membrane-aqueous strip interface. The volume of the organic membrane phase is negligible as compared to that of the feed and if the acid concentration is high enough, the major part of TOA at the feed-membrane interface is bound to the acid-TOA complex. So, $[\text{TOA}]_e$ is negligible as compared to $[(\text{H}_3\text{Ac})_p(\text{TOA})_q(\text{H}_2\text{O})_r]_f$ and we can take

$$[\text{TOA}]_{T,f} \approx q [(\text{H}_3\text{Ac})_p(\text{TOA})_q(\text{H}_2\text{O})_r]_f \approx \text{const}, \quad (13)$$

where f indicates the feed-membrane interface.

On the basis of the foregoing, we can describe two different mass transfer mechanisms: one for the carrier-facilitated transport and the other for the simple diffusional permeation. Both kinds of mass transport may occur simultaneously and for both of them the total mass flux rate is determined by the membrane flux.

In the case of carrier-facilitated transport the total mass flux I_F is equal to

$$I_F = -V_f \frac{d[\text{H}_3\text{Ac}]_T}{dt} = Q \frac{D_M}{\delta_M} [(\text{H}_3\text{Ac})_p(\text{TOA})_q(\text{H}_2\text{O})_r]_f, \quad (14)$$

where V_f is the aqueous feed volume, Q is the membrane area, D_M is the effective diffusion coefficient of the complex in the membrane, δ_M is the membrane thickness, t is the residence time.

Equation (14) can be integrated to

$$\begin{aligned} \frac{[\text{H}_3\text{Ac}]_T}{[\text{H}_3\text{Ac}]_{0,T}} &= 1 - \frac{Q [(\text{H}_3\text{Ac})_p(\text{TOA})_q(\text{H}_2\text{O})_r] D_M t}{[\text{H}_3\text{Ac}]_0 \delta_M V_f} \\ &= 1 - P_F \frac{Q}{V_f} t, \end{aligned} \quad (15)$$

where $[\text{H}_3\text{Ac}]_0$ is the initial acid concentration. The time-independent membrane permeability coefficient for facilitated transport, P_F , is given by

$$P_F = \frac{[(\text{H}_3\text{Ac})_p(\text{TOA})_q(\text{H}_2\text{O})_r] D_M}{[\text{H}_3\text{Ac}]_0 \delta_M}. \quad (16)$$

The permeability coefficient P_F can be determined from the slope of the linear plot $[\text{H}_3\text{Ac}]_T/[\text{H}_3\text{Ac}]_{0,T}$ versus time.

In the case of simple diffusional permeation (unfacilitated transport) the total mass flux I_D is also determined by the membrane resistance and given by

$$I_D = -V \frac{d[\text{H}_3\text{Ac}]}{dt} = Q \frac{D_M}{\delta_M} K_p [\text{H}_3\text{Ac}]. \quad (17)$$

Integration of Eq. (17) gives

$$\ln \frac{[\text{H}_3\text{Ac}]}{[\text{H}_3\text{Ac}]_0} = -\frac{D_M}{\delta_M} K_p \frac{Q}{V_f} t = -P_D \frac{Q}{V_f} t. \quad (18)$$

Here D_M is the effective membrane diffusivity of acid and the permeability coefficient for diffusional transport, P_D , equals

$$P_D = \frac{D_M \cdot K_p}{\delta_M}. \quad (19)$$

Fig. 2 shows experimental data and linear plots of $\ln([\text{H}_3\text{Ac}]/[\text{H}_3\text{Ac}]_0)$ and $\ln([\text{H}_2\text{Ac}]/[\text{H}_2\text{Ac}]_0)$ versus time for unfacilitated diffusional permeation of acids. The mass transfer rate of citric and succinic acids is considerably lower than that of phthalic acid. The permeability coefficient values, P_D , were determined from the slope of the linear plots. The results are presented in the Table.

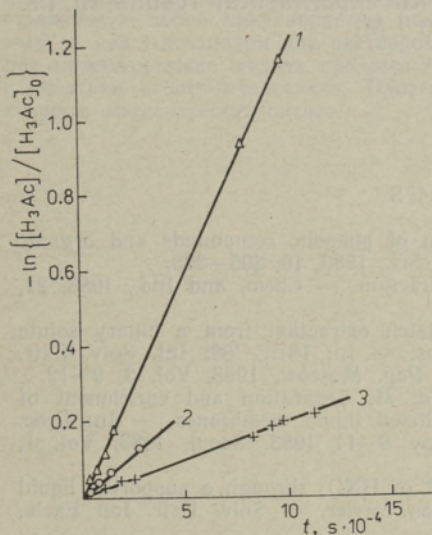


Fig. 2. Dependence of $\ln\{[\text{H}_3\text{Ac}]/[\text{H}_3\text{Ac}]_0\}$ on time, t , for unfacilitated diffusional permeation. Temp. 20°C, acid concentration 0.03–0.1 M. 1 — *o*-phthalic acid, 2 — succinic acid, 3 — citric acid.

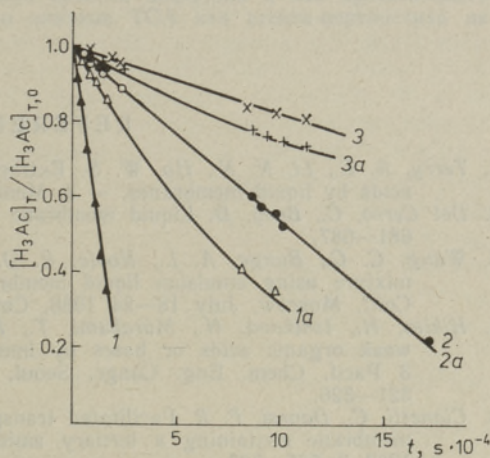


Fig. 3. Dependence of $[\text{H}_3\text{Ac}]_T/[\text{H}_3\text{Ac}]_{T,0}$ on time, t , for carrier-facilitated transport. Temp. 20°C, acid concentration 0.03–0.1 M. 1 — *o*-phthalic acid, 2 — succinic acid, 3 — citric acid, 1a, 2a, 3a — the same for unfacilitated transport.

In Fig. 3 experimental data and plots of $[\text{H}_3\text{Ac}]_T/[\text{H}_3\text{Ac}]_{T,0}$ and $[\text{H}_2\text{Ac}]_T/[\text{H}_2\text{Ac}]_{T,0}$ versus time for the carrier-facilitated transport of acids (curves 1–3) are shown. For comparison experimental curves for unfacilitated transport (1a, 2a, 3a) are given. In the region where the acid concentration lies between $3 \cdot 10^{-2}$ and $2 \cdot 10^{-1}$ M the plots give straight lines of different slope for all the acids observed. The values of P_F calculated from the slopes of straight lines 1–3 are presented in the Table. As appears from the experimental data in Fig. 3, the rate of the carrier-facilitated transport of phthalic acid is considerably higher than those of succinic and citric acids.

It is important to point out that the addition of the TOA-carrier to *n*-decanol increases the mass transfer rate of phthalic acid approximately four times. In the case of succinic acid, the difference between the facilitated and unfacilitated transport is not noticeable. Moreover, for citric acid the influence of the carrier is even negative. This phenomenon might open a new possibility for effective separation of acid mixtures.

Conclusion

The transport rate of di- and tribasic carboxylic acids from the aqueous feed solution to that of sodium carbonate through SLM consisting of a porous polytetrafluoroethylene film on which *n*-decanol is adsorbed is in case of sufficient mixing of the feed and strip solutions controlled by the membrane diffusion only. The use of TOA-carrier increases the transport rate of phthalic acid approximately four times, but does not accelerate the permeation of succinic and citric acids. Equations describing the carrier-facilitated and simple diffusion transport of acids are in good agreement with experimental results in the range of acid concentration $3 \cdot 10^{-2}$ to $2 \cdot 10^{-1}$ M.

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ORGAANILISTE HAPETE TRANSPORT LÄBI IMMOBILISEERITUD VEDELIKMEMBRAANI

On uuritud mõnede kahe- ja kolmealuseliste orgaaniliste hapete (ftaal-, merevaik- ja sidrunhape) massiülekannet vesilahusest läbi hüdrofoobse vedelikmembraani, mis koosnes mikropoorsest polütetrafluoroetüleenkilest ning sellele adsorbeeritud 1-dekanoolist või trioktülamiini (TOA) ja dekanooli lahusest. On kontrollitud TOA kui kandeagendi mõju hapete massiülekanne kiirusele. Hapete massiülekanne on kirjeldatud matemaatilisel ning võrreldud lihtdifusioonülekanne kandeagendi osavõtul toimunud protsessiga.

Гуйдо РАЯЛО, Надежда ЛИВАНЦОВА, Марье АРРО

ТРАНСПОРТ ОРГАНИЧЕСКИХ КИСЛОТ ЧЕРЕЗ ИММОБИЛИЗОВАННУЮ ЖИДКУЮ МЕМБРАНУ

Изучен массоперенос некоторых ди- и трикарбоновых кислот (фталевой, янтарной и лимонной) из водных растворов через гидрофобную жидкую мембрану, представляющую собой микропористую политетрафторэтиленовую пленку с адсорбированным на ней 1-деканолом или раствором триоктиламина (ТОА) в деканоле. Построены две математические модели процесса — как простой диффузии и как протекающего с участием агента-переносчика. Проверено влияние ТОА как агента-переносчика на скорость массопереноса кислот.