Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kuo, Yue and Gregor, Harry P.(1983) 'Acetic Acid Extraction by Solvent Membrane', Separation Science and Technology, 18: 5, 421 — 440
To link to this Article: DOI: 10.1080/01496398308060285
URL: http://dx.doi.org/10.1080/01496398308060285

SEPARATION SCIENCE AND TECHNOLOGY, 18(5), pp. 421–440, 1983

Acetic Acid Extraction by Solvent Membrane

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Abstract

Solvent extraction of acetic acid at low concentrations from aqueous solutions was studied. Decalin was found to be the optimal solvent and trioctyl phosphine oxide an effective carrier species. Phase equilibrium constants were measured and the results agree with the theoretical equation in the low carrier concentration range. The polymer supported solvent membranes carrying the same solvent and carrier, under various physical and chemical conditions, were prepared and the apparent diffusion coefficients of acetic acid through these membranes were measured and the results were discussed. The apparent diffusion coefficient of acetic acid in these tests was not interfered with by the existence of hydrochloric acid in the feed stream.

INTRODUCTION

The solvent membrane process is one which combines the solvent extraction and stripping processes in a single step. Solvent membranes have a solvent which is contained within the pores of the membrane, wherein a solute from a feed solution is dissolved selectively in the membrane, in the solvent itself, or by combining with a carrier species to form a complex which carries out the transport process. The solute is then released at the other side of the membrane either by dissolution in a more dilute stream or by a stripping mechanism.

The original oil membranes of Harber (*1*) and Beutner (*2–4*) were thin film of an oil between two aqueous phases, wherein one or more of the solutes present was soluble in the oil and thus could diffuse across the oil phase in

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the presence of a concentration gradient. Beutner also studied systems wherein a component ordinarily insoluble in the oil phase but soluble in the aqueous adjacent phase could be transported across the membrane by forming an oil-soluble complex or a salt with an oil-soluble compound or ligand. This latter membrane process is termed facilitated transport and was studied extensively in recent years.

Facilitated transport through membranes probably takes place in life processes. Scholander (*5*), Wittenberg (*6*), and Wyman (*7*) described the facilitated diffusion of oxygen in systems containing proteins. Hladky (*8*) extended the theory to explain the transport of ions across lipid membranes. The experimental results from Ciani et al. (*9*) supported the accepted view that complexation between ions and the macrocyclic antibiotics occurs at the membrane surface.

This facilitated transport phenomena has attracted the attention of chemical engineers because of its highly selective characteristics. Schultz et al. (*10*) reviewed carrier mediated transport in membranes as a general, nonreactive process. By appropriately adjusting cation and anion concentrations on both sides of a membrane, liquid membranes containing a macrocyclic polyether can transport or pump a specific cation against its concentration gradient (*11–13*). Gaseous products, such as carbon dioxide, H_2S, and nitric oxide, were also transported through enzymatically active synthetic membranes (*14–18*). Smith et al. (*20*) developed approximate analytical solutions, corresponding to facilitative films. Smith and Quinn (*21*) presented a simple equation to predict the facilitation factor for reaction-augmented membrane transport. The solution agreed well with the transport of carbon dioxide in monoethanolamine solutions. The "near-equilibrium" reaction in membrane diffusion was evaluated and mathematically confirmed (*22*).

Table 1 lists the solvent or liquid membranes systems described in the literature. In modern terminology, solvent membranes are of two kinds: liquid surfactant membranes, and polymer-supported solvent membranes.

A liquid surfactant membrane is a film composed of a surface-active substance and an immiscible solvent in a solution phase. An original description of the separation of liquid mixtures by surface-active membranes can be found in Ref. *24*. Stelmaszek and Borkowska (*25*) used different surface-active compounds to separate a mixture of toluene and heptane with liquid membranes. They found that the following experimental conditions affected the liquid membrane process: the length of the hydraulic chain of the surface active compound, the mole fraction of toluene in the feed, the number of mixture revolutions in forming the feed emulsion in surface-active solution, and the volume ratio of solvent to feed. Casamatta et al. (*26*) used saponin in water to form the liquid membrane outside of the droplet of a

TABLE 1
Liquid Membrane Processes

Form	Liquid matrix	Solvent	Carrier	Material transferred	Feed/ stripping	Ref.
Liquid held between highly permeable membranes	None	Water	HCO_3^-	CO_2	Gas/gas	15
	None	Formamide	F_e^{2+}	NO	Gas/gas	14
Liquid in pores of matrix	Millipore filter	Water buffer	HCO_3^-	CO_2	Gas/gas	15
	Hydrophobic membrane, $\phi_p = 0.6–0.7$	Water	CO_3^{2-}	H_2S	Gas/gas Gas/aq	18
	Polypropylene, $\phi_p = 0.45$	Octanol	LIX-64 N, LIX-65 N	Cu^{2+}, Ni^{2+}	Aq/aq	19
	Millipore filter	Aq buffer	Hemoglobin	O_2	Gas/gas	23
Glass fiber paper between dialysis papers	Glass fiber paper	Octanol	Cholanic acid	K^+, Na^+	Aq/aq	12
		Tetrachloroethane	Monensindibenzo-18-crown-6	K^+	Aq/aq	11
Liquid microcapsules	None	Hexachloro-1,3-butadiene	LIX-64 N	Cu^{2+}	Aq/aq	19

mixture of toluene–*n*-heptane. An experimental, comparative analysis of the various factors involved in the separation of styrene–ethylbenzene mixtures by liquid membrane permeation was performed by Alessi et al. (*27*). Liquid surfactant membranes were used to extract copper (*19*) by feeding a dilute base copper stream into a mineral oil solvent containing LIX-64N.

Polymer-supported solvent membranes are made up of three groups. The first is a solvent clamped between two highly permeable membranes, with the solutes diffusing through one membrane, across the solvent, and then through the other membrane. The solvent layer between the two membranes should be as thin as possible to minimize the diffusion resistance, a difficult thing to accomplish. One method is to soak a glass fiber sheet in a solvent and mount it between two dialysis papers.

The second group consists of a porous polymer membrane with the solvent strongly adsorbed in the pores. Solutes diffuse through the pores of the membrane directly. In order to achieve a good membrane, two factors must be satisfied: the membrane must be strong enough to withstand an appreciable pressure difference between feed and stripping streams, and the membrane must hold sufficient solvent for an appreciable area for solute diffusion. However, to achieve a reasonable degree of mechanical strength, the polymer film may be slightly cross-linked to inhibit swelling and still be flexible.

The third class is that of membranes which sorb the immisible solvent, swell in the process, and thus form a gel phase. A preferred type is the interpolymer membrane, one consisting of two kinds of polymer, one which swells strongly in the solvent phase, and the second which is insoluble in the solvent phase and, as opposed to the first, is a film-forming polymer of high mechanical strength in the solvent. Interpolymer membranes have been investigated extensively by Gregor et al. (*28–32*). One example of facilitated transport was that of copper through a solvent membrane of the third type, investigated by Gregor and Brandlein (*33*). Here kerosene was sorbed by an interpolymer membrane composed of polyisobutylene and polyvinylidine fluoride. The carrier was a water-insoluble liquid ion exchange (LIX) material of the oxime kind, one which forms a strong and and selective complex with copper which is also kerosene soluble. In a continuous extraction-stripping process, copper was removed from a weakly acidic phase into a strongly acidic one. By properly controlling the pH values on both sides of the membrane, copper was extracted from the low concentration in the stream to the high concentration in the stripping stream.

Acetic acid is an important by-product of various processes, such as the pulping of wood, oxidation reactions, and coal conversion. It is quite commonly found in industrial wastewaters, in municial sewages, and in the wastes of fermentation processes. The conventional techniques used to recover acetic acid from water are distillation, solvent extraction, or a combination of both (*35*). Since the relative volativity of acetic acid to water is low and the concentration of acetic acid in wastewaters is generally low, a large number of equilibrium stages and a high reflux ratio are required to recover acetic acid by the distillation method. Solvent extraction of acetic acid from water has been widely investigated (*36–46*). Solvent extraction followed by fraction is employed for the recovery of acetic acid in the concentration range of 2 to 60% (*34*).

Recently, Grinstead (*47, 48*) found that the addition of phosphine oxides or amines to organic solvents increases the distribution coefficients of acetic acid between those organic and aqueous phases. Wardell and King (*49*) examined solvent equilibria for the extraction of carboxylic acids from water by the addition of alkoxy-substituted carbonyl and phosphoryl substances in the organic phase, and showed that in the same solvent, exchanging alkyl for alkoxy substituents into ligand increased its Lewis basicity through inductive effects and increased the distribution coefficients for acetic acid. The addition of valuable or notorious material in the solvent to facilitate the extraction of acid from aqueous solution was highly recommended in a review article on wastewater treatment by solvent extraction (*50*).

Trioctyl phosphine oxide (TOPO) is a white crystaline solid at room temperature, soluble in organic solvents and insoluble in water. It is particularly useful in the extraction of uranium, thorium, plutonium(IV) and (VI), and americium (*51*). Laskoin et al. (*52*) attributed the weaker basicity of TOPO compared to trioctylamine oxide and trioctylarsine oxide to conjugation of the unshared electrons on the oxygen atom with the vacant orbitals on P. In CCl_4 at ambient temperatures a strong hydrogen bond (P—O . . . H) was demonstrated by IR absorption. The reaction of TOPO with HCl formed TOPO-HCl (*53*). The extraction of $Ph(CH_2)_3COOH$ and salicyclic acid from water into $CHCl_3$ or hexane was aided by the addition of TOPO which formed 1:1 H-bounded adducts with those acids (*55*). Also, C_2–C_4 carboxylic acids were recovered by passing an aqueous solution of these materials through membranes of composite cellulose, cellophane, or curophane into organic liquids containing TOPO (55). Schmidt and Rybakov (*56*) determined equilibrium constants for the extraction of acetic and other acids from aqueous solutions into solutions of TOPO and amines in $CHCl_3$. TOPO is considered to be a nulceophilic extracting agent, according to its mechanism. Grinstead used hydrocarbon solvents containing TOPO at various concentrations to extract acetic acid from its aqueous solutions at low concentrations such as 0.025 *M* (*47, 48, 57*). The distribution coefficient of acetic acid is highly dependent upon the solvent used in the extraction process. With TOPO in a mixture of heptane and hexanol, because of complicated interactions among solvent, additive, and acid, the distribution coefficient reached a maximum value at an intermediate composition. The phosphine oxides may form micelles or other aggregates at higher concentrations, which could reduce their effective concentration (*48*).

The research objective of this paper was to investigate 1) solvent extraction of acetic acid with the complex formation in the solvent phase, and 2) facilitated transport of acetic acid through polymer-supported solvent membranes.

EXPERIMENTAL

Determination of Equilibrium Constants in Solvent Extraction

Trioctyl phosphine oxide (TOPO), reagent grade from Eastman Kodak, was dissolved in organic solvents to the required concentrations. Acetic acid solutions were prepared from reagent grade glacial acetic acid (Fisher Scientific, 99.7% min). Equal volumes (10 mL) of the aqueous acetic acid solution and pure organic solvent with or without TOPO were shaken in a closed vial for at least 2 h. The system reached equilibrium in a few minutes. The two phases were separated and the acid content in the aqueous phase was titrated with standard sodium hydroxide solution before and after extraction. A Corning Scientific Instrument Model 5 pH meter was used, with the equivalent point taken at pH 8.73 (*58*). For the extraction of a mixture of acetic acid and hydrochloric acid, the procedures were the same, with total acid content also determined by titration. The hydrochloric acid concentration was determined by Mohr's chloride titration method (*58*).

Solvent Membranes

The membranes used in this study were supplied by the polymer synthesis group. They were prepared by selecting a polymer, high soluble in the solvent of choice (decalin), and containing side chains capable of effecting a postcross-linking reaction. The membranes were prepared by impregnating a nonwoven spun-bonded nylon fabric (Xerex, Monsanto Co.) with a solution of the polymer in a suitable solvent and cross-linking agents, and then effecting the cross-linking reaction *in situ*. In order to be sure that there were no effects or pinholes, a small amount of polymer solution was spreaded onto the preformed membrane and recross-linked so that a pinhole-free and coherent material resulted. The nylon matrix gave the system substantial mechanical strength.

Each membrane was characterized by its thickness and volume fraction of solvent within the membrane. All membranes were washed thoroughly with the solvent before use and to remove any traces of soluble materials and cross-linking agents, and the final polymer membrane was quite inert and not capable of reacting with any of the low molecular weight constituents used in these experiments.

These membranes had a very low hydraulic permeability. When a pressure difference as high as 1 atm was imposed across the membrane, there was no apparent transport of organic solvent either into or out of the membrane itself.

Table 2 lists the properties of the four membranes of this study. The membranes selected were particularly robust to withstand the conditions imposed by the use in these tests.

Measurement of Rate of Transport

All experiments were performed in plastic cells of the design of Fig. 1. Cells were constructed of Lucite. Each cell held the membrane firmly clamped between gaskets with stirrers mounted in each of the compartments and rotating within a few millimeters of the membrane surfaces. The rate of rotation was measured directly by a strobe meter. A fine stainless steel heat exchanger was introduced into each compartment of the cell to maintain the temperature constant to within 0.2°C.

In the experiments conducted, mixtures of acids or acetic acid itself were on one side of the membrane and a solution of sodium hydroxide on the other side. If there were any pinholes in the membrane or leaks in the cell

TABLE 2
Properties of the Four Membranes Used

Membrane	A	B	C	D
Cross-linking agent	High MW	High MW	Low MW	Low MW
Vacuum	Yes	Yes	Yes	No
ϕ_p	0.418	0.647	0.369	0.314
L (microns)	365	514	434	255
T_t (g/mL soln)	4/60	8/50	4/60	4/60

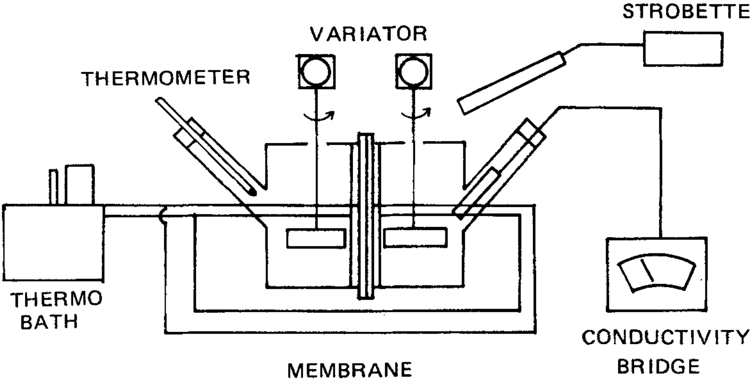

FIG. 1. Experimental set-up.

assembly, the leakage of base across the membrane caused a sharp increase in the conductivity of the acetic acid solution. A dipping conductivity meter was kept immersed in the acid side to monitor the effectiveness of the experimental procedures.

Rate experiments were carried out as follows. First, the dry membrane was soaked in the solvent of choice (decalin) with or without TOPO for several days at room temperature. Then the membrane was removed from the solvent and excess solvent was allowed to drain off; the membrane was then weighed to determine the volume fraction of solvent within the membrane. Following this, this membrane was clamped between the two half cells, the two ambient solutions were placed on either side of the membrane, the stirring rate adjusted as was the temperature control, and the experiment was continued with the samples taken from the acid side. In every case conductivity measurements were taken to insure the absence of any pinhole leaks in the membrane itself.

It was not necessary to make any corrections for the boundary resistances in the ambient solutions in these studies. This was because evaluation of the various magnitudes of the different resistance terms involved revealed the boundary layer of resistances to be negligible compared to those in the membrane itself. The rate of stirring was such that a boundary layer thickness in the acid solution of about 20 μm was usually anticipated, and this value was only 5% of the overall membrane thickness. Also, since the diffusion coefficient of acid in aqueous solution is very much greater than in the oil membrane itself, it is evident that the error which is introduced by ignoring the aqueous solution boundary layer resistance is of the order of a few percent at most. In the basic solution side, the concentration of acetic acid is so small that resistance is indeed negligible.

As pointed out in Ref. *63*, decalin is termed "insoluble" in water. This usually means that the solubility is less than a few ppm. Since the volume of the membrane was approximately 2.5 mL on the average and these contained about 1 mL of decalin, and since about 700 mL of solution was used in each experiment, the total solubility of decalin would be of the order of a few ppm. Thus, only when large volumes of ambient solution were employed would an appreciable loss of decalin from the membrane phase be expected, and this could be readily corrected by saturating the feed stream with this particular solvent.

RESULTS AND DISCUSSION

Selection of Solvent

A solvent for solvent membranes must possess certain characteristics. It must be quite insoluble in water. It is contained in a thin film of large surface area in contact with large volumes of feed and stripping solutions. Even a slight solubility in water would deswell the membrane. With a solvent virtually insoluble in water, the loss of solvent is minimal so the solvent can be quite expensive.

The solvent must be strongly sorbed by the polymer of the membrane, and held in pores of molecular dimensions so the pressure gradients between the feed and stripping streams which prevail will not press it out of the membrane. The sorption of solvent by the polymer making up the membrane must be strong enough so that the mole fraction of the solvent is high and the available area for diffusion is large.

The solvent should be of low volatility and of low toxicity. Some solvent loss to the process stream is unavoidable. One application of solvent membrane is to extract acetic acid from the fermentation broths, then recycle the broth to the fermentor. If the solvent inhibits microorganisms, the process cannot be employed.

Six solvents were examined for their ability to extract acetic acid from aqueous solutions. The same, original acid feed concentrations were used with the solvents with or without TOPO dissolved in them (Table 3).

Except for decalin and diethylsuccinate, the usual solvents employed in conventional solvent extraction were tested. All of the distribution coefficients measured were approximately the same with the same concentrations of TOPO in the solvents. Toluene has a higher distribution coefficient, but

TABLE 3

Distribution Coefficients of Acetic Acid between Organic Solvents with or without TOPO and Water (27°C)[a]

Solvent	$K_{o,w}$ without TOPO	$K_{o,w}$ with 0.209 M TOPO
Hexane	nd[b]	1.24
Toluene	nd	1.84
Decalin	0.024	1.06
Diethylsuccinate	nd	1.19
Kerosene	nd	1.14
Ethyl acetate	0.50	0.92

[a] The initial acetic acid concentration is 0.0893 M.

[b] nd = too low to determine, $K_{o,w} < 0.001$.

because of its toxicity it is not considered to be a good solvent. Hexane is a good solvent on the basis of its distribution coefficient alone. However, its boiling point is low (68.95°C). Kerosene is widely used as a solvent because of its low price and stability, but it is slightly soluble in water and not appropriate for this system. Diethylsuccinate is a good solvent for many polymers, but it did not swell the polymer membranes supplied.

Decalin was selected as the best solvent for the polymer membrane employed. It is quite insoluble in water (*59*), the polymer membrane swelled well in it, and its distribution coefficient for acetic acid is comparable with other solvents. Its boiling point is 195.65°C for the cis and 187.25°C for the trans form. On all basis, it was appropriate for this system.

Decalin (decahydronaphthalene) is $C_{10}H_{18}$ and occurs in cis and trans forms. The commercial product is virtually all *trans*-decalin or a mixture containing up to 60% *cis* decalin.

Determination of Distribution and Dimerization Constants

By assuming 1) the organic solvent and water are totally immiscible, 2) the carrier T (TOPO) and the carrier-acid complex (TA) dissolve only in the solvent phase, 3) the carrier concentration is not too high to form micelles or aggregates, 4) the carrier does not form a complex with the acid dimer if the acid dimer exists in the organic solvent phase, the equilibrium distribution coefficient of acetic acid between the organic solvent and aqueous phases can be expressed as (*60*)

$$K_{o,w} = K_1 + 2K_1^2K_2A + K_1K_3T_t/(1 + K_1K_3A) \qquad (1)$$

where $K_{o,w}$ is the ratio of acid concentration in the solvent phase to acid concentration in the aqueous phase. K_1 is the equilibrium constant of acid between solvent and aqueous phases. K_2 is the acid dimer formation in the solvent phase ($2A_{org}=A_{2_{org}}$, $K_2 = A_{2_{org}}/A_{org}^2$). K_3 is the carrier-acid complex formation in the solvent phase ($A_{org} + T=TA$, $K_3 = TA/(A_{org}T)$). T_t is the original carrier concentration in the solvent phase before solvent extraction. A, A_{org}, $A_{2_{org}}$, T, and TA are the acid concentration in the aqueous phase, acid concentration in the solvent phase, acid dimer concentration in the solvent phase, and carrier concentration and carrier-acid complex concentration both in the solvent phase, respectively.

Table 4 shows the distribution coefficients for acetic acid between pure decalin and the aqueous phase at different initial acid concentrations. Since the volume of the two phases was the same, the equilibrium concentrations in the aqueous phase were lower by about 2–3%. In the absence of TOPO in the solvent phase, the distribution coefficient of acid could be a linear function of acid concentration in the aqueous solution and of slope $2K_1^2K_2$ if dimerization took place. Since the slope was essentially zero, there was no appreciable dimerization of acetic acid in decalin. The average distribution coefficient measured at 27°C was 0.024, so $K_1 = 0.024$ and $K_2 = 0.00$.

Determination of K_3

Figure 2 shows the distribution coefficient of acetic acid in water and in decalin containing 0.259 and 0.1295 *M* TOPO. The TOPO concentration was kept constant and the initial aqueous acid concentration was changed.

TABLE 4
The Distribution Coefficient of Acetic Acid between Decalin and Water at Different Initial Acid Concentrations (27°C)[a]

Initial acid conc (*M*)	$K_{o,w}$
0.400	0.0236
0.133	0.0207
0.0866	0.0264
0.0674	0.0271

[a] Average $K_{o,w} = 0.024 \pm 0.0015$.

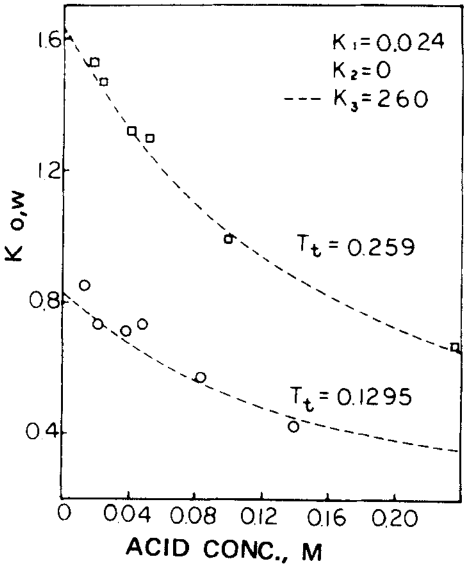

FIG. 2. $K_{o,w}$ changes with acid concentration at different T_t.

The distribution coefficients decreased with increasing acid concentration. From the fit of data to Eq. (1), the equilibrium constant was $K_3 = 260$.

For $T_t = 0.259$ *M*, if the equilibrium free-acid concentration in the solvent phase is 0.01 *M* (K_1A), the carrier-acid concentration is 2.6/3.6 of T_t, and more than two-thirds of the TOPO present is in complex form in the solvent. If the equilibrium free-acid concentration in the solvent phase is 0.001 *M*, the carrier-acid concentration is 0.26/1.26 of T_t, and about 20% of the total TOPO becomes the complex. For $T_t = 0.1295$ *M*, the same ratio of TOPO exists in the complex form. Thus the complex concentration in decalin was higher than the free acid in the same solvent. The high complex formation constant greatly increased the ease of extraction of acetic acid by the solvent phase.

Figure 3 shows the distribution coefficients of acetic acid with a fixed, initial concentration (0.0893 *M*) with changes in TOPO concentration in decalin from 0 to 0.52 *M*. As the TOPO concentration increased, the distribution coefficient increased up to T_t of 0.2 *M* with the experimental results fitting Eq. (1) well. This follows the basic postulates of the solvent extraction theory employed, which required that there was no specific effect among solvent, carrier, and carrier-acid complex. When T_t exceeded 0.2 *M*,

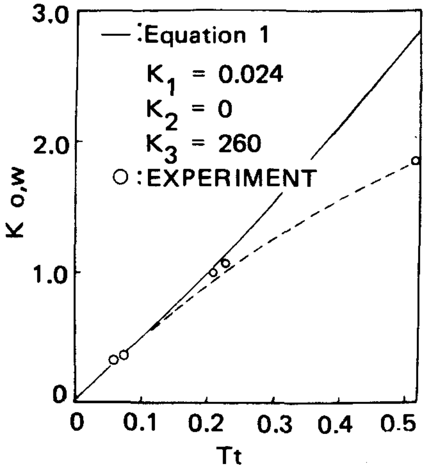

FIG. 3. Distribution coefficient as a function of T_t.

the slope of the distribution coefficient function deviated from Eq. (1), as expected. At high TOPO concentrations, association or micellization of TOPO is known to yield deviations from ideal behavior. At a TOPO concentration of 0.5 *M*, the system appeared to be nearly saturated because prolonged stirring of some hours was required to dissolve the solute.

An aqueous solution of HCl (0.05 *N*) was extracted with decalin. The distribution coefficient was 0.055. When TOPO was added to decalin at a concentration of 0.234 *M*, the equilibrium distribution coefficient increased to 0.064. If now a solution containing 0.05 *M* acetic acid and 0.05 *N* HCl were extracted with decalin with 0.234 *M* TOPO, the equilibrium distribution coefficient of HCl would be 0.064 and that of acetic acid would be 1.25. From Fig. 2, the $K_{o,w}$ value of acetic acid in water alone was about 1.25. So, if HCl exists in the acetic acid aqueous solution, the extraction of acetic acid by the decalin-TOPO phase would not be affected greatly.

Rate Processes

The half cell, containing the acid solution, is taken as a constant stirred homogeneous reactor.

The acid diffuses out of the reactor, with no acid input and no acid accumulation. The material balance is

$$\begin{array}{ccc} \text{input} - \text{output} & = & \text{accumulation} \\ 0 \quad - J\mathbf{A}\,dt & = & V\,dC \end{array} \tag{2}$$

where J is the flux of acid through the membrane, **A** is the membrane area, t is the time, and V is the volume of the acid solution. We let C be the acid concentration at time t in the reactor.

For a fixed solvent membrane system, the constants K_1, K_2, and K_3 are fixed. Then, if the entire membrane is taken as a black box, acid enters and leaves the membrane. Fick's law of diffusion can be expressed as:

$$J = -\bar{D}(\Delta C/\Delta x)\phi_p K_1 \tag{3}$$

where $\bar{D}$ is the apparent diffusivity of acid in the membrane. $(\Delta C/\Delta x)$ is the acid concentration gradient across the solvent membrane. $\bar{D}$ is a function of the acid concentration at the boundaries and the concentration of the carrier TOPO. The experimental conditions were set such that the acid concentration change in the reactor was small (about 10%) during each experiment. The total carrier concentration was fixed and much larger than the acid concentration in the membrane. Under these conditions, the apparent diffusion coefficient $\bar{D}$ is quite constant. Then, we take ΔC as the concentration difference in the solutions at the two sides of the membrane and its thickness as L, so $(\Delta C/\Delta x)$ can be replaced by $(C_{\text{in base}} - C_{\text{in acid}})/L$. In this system the acid concentration on the base side is zero, and Eq. (2) becomes

$$-\bar{D}(C/L)\phi_p K_1 \mathbf{A}\, dt = V\, dC \tag{4}$$

$$\int (1/C)\, dC = -\int \bar{D}(\mathrm{A}/L)\phi_p K_1(1/V)\, dt \tag{5}$$

Since the volume V is constant,

$$\ln C = -\bar{D}(\mathbf{A}/L)\phi_p K_1(1/V)t + \text{constant} \tag{6}$$

$$C = C_0 \exp\left(-\bar{D}(\mathbf{A}/L)\phi_p K_1(1/V)t\right) \tag{7}$$

Thus, the acid concentration varies exponentially with time.

To measure the apparent diffusion coefficient $\bar{D}$ of the acid, samples of the acid side were taken at different times. Figure 4 shows experimental results with four different membranes. The least-square method was used to obtain the slope of ln C vs t plots. The apparent diffusion coefficients thus obtained are 26.7×10^{-6} cm^2/s for Membrane A, 36.1×10^{-6} cm^2/s for Membrane

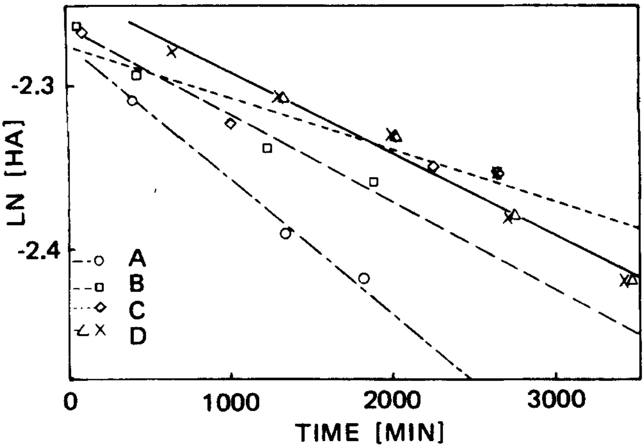

FIG. 4. Acid concentration change with time.

B, 20.6 × 10^{-6} cm^2/s for Membrane C, and 21.8 × 10^{-6} cm^2/s for Membrane D.

In the experiments performed, membranes made using different formulations were examined under the same conditions of total carrier concentration in the case of three systems and under increased carrier concentration in another case using an identical membrane. Runs with Membranes A, C, and D were the same in all respects except the membranes were prepared by somewhat different procedures. Membrane A employed a cross-linking agent having a higher molecular weight than in the case of Membranes C and D where the same, identical cross-linking agent of lower molecular weight was employed. In general, cross-linked polymer gels prepared with crossing the agents of greater length lead to higher diffusion coefficients and a more open structure, other things being equal. This can be well documented from the polymer literature and is well illustrated in the work of Gregor and Greff (*61*), who showed that polymer systems using the same polyelectrolyte cross-linked with different agents led to markedly different swelling properties. Thus, the fact that the apparent diffusion coefficients with Membrane A was 26.7 × 10^{-6} cm^2/s compared to 20.6 × 10^{-6} cm^2/s and 21.8 × 10^{-6} cm^2/s for Membranes C and D shows that the effect of the length of the cross-linking agent is appreciable, but not very strong. It is significant to note that Membranes C and D prepared by rather different procedures but with the same chemical cross-linking system were virtually identical in apparent diffusion coefficients.

The effect of different TOPO concentrations is shown when comparing the results with Runs A and B, which were the same but where the apparent diffusion coefficients were in the ratio 36.1/27.6 or 1.32; 2.4 was the relative, initial TOPO concentration. Runs A and B were performed by membranes under the same conditions, except the carrier concentrations were different. From Ref. *60*, the apparent diffusion coefficients in A and B were 82.08×10^{-6} cm^2/s and 142.9×10^{-6} cm^2/s, and the ratio of B to A is 142.9/82.08 or 1.74. It is clear that the measured diffusion coefficients are about one-third those theoretically derived. The theory neglected the tortuosity factor in the membrane; it is usually 3. Therefore, when the apparent diffusion coefficients are corrected by this tortuosity factor, the results fit the theory reasonably well.

Mixed Acids Effect

A mixture of acetic and hydrochloric acids was extracted with the TOPO-decalin membrane. Figure 5 shows concentration changes for acetic and hydrochloric acids with time. The initial TOPO concentration in Membrane D was 4 g/60 mL. Here the initial concentrations of each acid were 0.1 *M*. The measured apparent diffusion coefficient of acetic acid was 20.4×10^{-6} cm^2/s and of hydrochloric acid 7.49×10^{-6} cm^2/s. Thus the flux of hydrochloric acid was about one-third that of acetic acid. Comparing the apparent diffusion coefficient of acetic acid from the acid mixture with that from a solution containing only acetic acid, with the same membrane

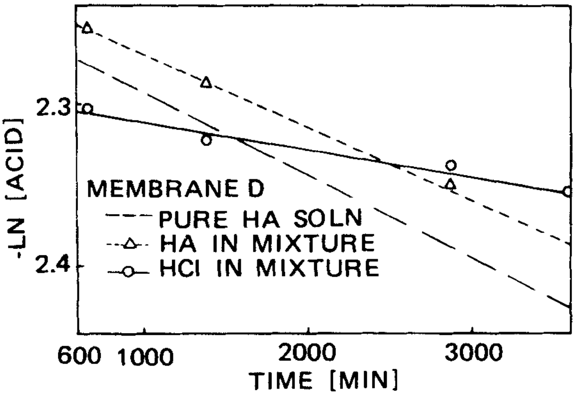

FIG. 5. Acid concentration change with time.

carrying the same concentration of TOPO, it was found that the two fluxes of acetic acid were nearly the same. This means that the presence of hydrochloric acid in the acetic acid feed solution did not decrease the transport rate of acetic acid. Besides, in the membrane phase most of the acetic acid exists in the TOPO-acetic acid complex form and most hydrochloric acid exists in the free HCl form, and the flux ratio of acetic acid to hydrochloric acid is

$$\begin{aligned}\frac{J_{\mathrm{HA}}}{J_{\mathrm{HCl}}} &= \frac{D_{\mathrm{TA}}C_{\mathrm{HA}}(K_{\mathrm{o,w}})/L}{D_{\mathrm{HCl}}C_{\mathrm{HCl}}(K_{\mathrm{o,w}})_{\mathrm{HCl}}/L}\\ &= \frac{D_{\mathrm{TA}}}{D_{\mathrm{HCl}}}\,\frac{(K_{\mathrm{o,w}})_{\mathrm{HA}}}{(K_{\mathrm{o,w}})_{\mathrm{HCl}}}\\ &= \frac{2.58\times10^{-6}}{16.88\times10^{-6}}\times\frac{1.25}{0.064}\\ &= 2.94\end{aligned}$$

where D_{TA} and D_{HCl} are calculated from the Wilke and Chang equation (*62*). So, theoretically the flux ratio of acetic acid to hydrochloric acid is 2.94. The experimental results are quite reasonable.

CONCLUSION

Solvent extraction of low concentration acetic acid from water was studied with decalin selected as the solvent and TOPO as the carrier of choice. The equilibrium distribution constant of acetic acid between decalin and water was 0.024. No appreciable dimerization of acetic acid in decalin was observed. The equilibrium constant of the TOPO-acetic acid reaction was 260 at low, initial acid concentrations. When the initial carrier was higher than 0.2 *M*, the complex formation was a function of the initial carrier concentration.

The apparent diffusion coefficient of acid through the solvent membrane was calculated from concentration vs time data. Four different kinds of membranes were tested. The measured apparent diffusion coefficients fitted the theoretical value if a tortuosity factor of 3 was included. If the cross-linking agents employed were the same, the apparent diffusion coefficients were almost the same. The higher the molecular weight of the cross-linking agent, the larger the apparent diffusion coefficient. The presence of hydrochloric acid in acetic acid aqueous solution did not appreciably affect the diffusion of acetic acid through the membrane.

SYMBOLS

A	concentration of acid in aqueous phase
$\mathbf{A}$	membrane area
A_{org}	concentration of acid in solvent phase
$A_{2_{\text{org}}}$	concentration of acid dimer in solvent phase
C	concentration of acid in feed stream at time t
C_{HA}	concentration of acetic acid in feed stream
C_{HCl}	concentration of hydrochloric acid in feed stream
C_0	arbitrary constant
$\bar{D}$	apparent diffusion coefficient of acid through the membrane
D_{TA}, D_{HCl}	diffusion coefficients of carrier–acetic acid complex and hydrochloric acid in solvent phase calculated by Wilke-Chang equation
J	flux of acid through the membrane
J_{HA}	flux of acetic acid through the membrane
J_{HCl}	flux of hydrochloric acid through the membrane
K_1	equilibrium constant of acetic acid between solvent and aqueous phases
K_2	acetic acid dimer formation constant in solvent phase ($2A_{\text{org}} = A_{2_{\text{org}}}$, $K_2 = A_{2_{\text{org}}}/A_{\text{org}}^2$)
K_3	carrier-acetic acid complex formation constant in solvent phase ($A_{\text{org}} + T = \text{TA}$, $K_3 = \text{TA}/(A_{\text{org}}T)$)
$K_{\text{o,w}}$	ratio of total acetic acid concentration in solvent phase to acetic acid concentration in aqueous phase
L	thickness of the membrane
TA	concentration of carrier–acid complex in solvent phase
T	concentration of free carrier in solvent phase
T_t	total carrier concentration in solvent phase before extraction
t	time of diffusion
V	volume of the acid solution
x	distance in the membrane ($x = 0$ is at the feed side, $x = L$ is at the stripping side)
ϕ_p	fraction of solvent in the membrane

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Received by editor October 19, 1982