curves for $s_0 N_{Re}^{-1} = 0.01$, $a_0 \approx 0.8$, and for $s_0 N_{Re}^{-1} = 0.05$, $a_0 \approx 0.5$. The error in the present model, applied to particle flow, is therefore less than should be expected from its crudeness as an approximation to the inlet flow as indicated by Figure 2, especially since the additional resistance introduced by the particles will be proportional to the area under the f curve in Figure 5, from $s_0 N_{Re}^{-1}$ to the appropriate value of $s_1 N_{Re}^{-1}$.

On the other hand, Figure 5 shows that the error may still be appreciable for particles that nearly fill the tube, being less the smaller the particle. The model is only valid for particles on the axis, however, and this probably puts a lower limit on the particle size, since Segré and Silberberg (7) have shown that small particles migrate from the axis.

NOTATION

a = dimensionless radius of core
a_0 = dimensionless radius of particle
a_1 = dimensionless radius at core intersection
c = volume concentration of particles
f_1 = dimensionless friction force $\frac{F_1}{8\pi\mu U_0 R}$, according to Schiller's model
f_2 = dimensionless friction force $\frac{F_2}{8\pi\mu U_0 R}$, according to present model
F_1 = friction force per unit length in inlet flow, Schiller's model
F_2 = friction force per unit length in inlet flow, present model
$I_0^* = \int_{s_0}^{s^*} \frac{1}{1-a^4}\, ds$
$I_0^1 = \int_{s_0}^{s_1} \frac{1}{1-a^4}\, ds$
$J(a) = -\int \frac{1}{1-a^4} \frac{(1-a^2)\left(1-\frac{a^2}{3}\right)}{(1+a^2)^2}\, a\,da$
L = length of tube
n = number of particles in tube length L
N_{Re} = tube Reynolds number $\frac{\rho U_0 R}{\mu}$
p = pressure
Δp = pressure drop over L with particles in tube
Δp_0 = pressure drop over L without particles
δp = pressure drop associated with each particle
q = dimensionless core velocity U/U_0
r = dimensionless radial coordinate
R = radius of tube
s = dimensionless axial coordinate x/R
s^* = dimensionless coordinate of core apex
s_0 = dimensionless coordinate of section where core and particle radii are equal
s_1 = dimensionless coordinate of core intersection
u = axial velocity, function of r and s
U = axial velocity in the core, function of s
U_0 = axial flux velocity, constant
x = axial coordinate

Greek Letters

ρ = fluid density
μ = dynamic viscosity
μ^* = apparent dynamic viscosity

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Permeation Through Liquid Surfactant Membranes

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A novel separation technique based on the selectivity of a liquid membrane composed of surfactants and water is described. The permeation mechanism is discussed in terms of surfactant concentration, surfactant structure and chain length, the nature of permeate, and the solubility of permeate in water.

A novel separation technique using liquid surfactant membranes has been discovered (*1*) which is effective in separating hydrocarbons of different kinds, including those similar in their physical and chemical properties.

A liquid surfactant membrane, or abbreviated as liquid membrane, is a film composed of surfactants and their solvent. When water-soluble surfactants are used, the film consists of water and one or more water-soluble surfactants. This kind of film serves two purposes in a process of separating hydrocarbons. First, it permits selective permeation by one or more components of the feed. Second, it keeps the hydrocarbon feed from mixing with a hydrocarbon solvent used to carry away the permeates.

An actual separation scheme is illustrated in Figure 1 with key steps indicated by letters. The key steps consist of dispersing the solution to be separated in the form of droplets in a surfactant solution on the bottom of a diffusion column (*A*). Membranes composed of surfactant and water form almost instantly at the surface of the hydrocarbon droplets. The droplets then pass up into an organic solvent phase, which is chosen to be heavier than the dispersed phase, where the selective permeation through the surfactant water membrane takes place (*B*). The droplets, thus enriched with the nonpermeating compounds, gradually rise out of the solvent phase and coalesce to form a separate phase (*C*). Several stages can be used to achieve additional enrichment of the nonpermeating compounds in the raffinate phase and increase the total permeate yield from all the stages. The solvent can be any hydrocarbon boiling well outside the range of the permeate because the permeate can then be easily removed by flash distillation. In all the experiments discussed in this paper, the solvents used had no significant selectivity for any of the feed components. In this way, the separations obtained were entirely due to membrane selectivity. The function of the solvent was merely to provide a medium for receiving the permeates. This means the solvents were completely miscible with all the feed components.

The depletion of the surfactant solution is very small in this separation process not only because the water-soluble surfactant can always be chosen to have a dominating hydrophilic part so that its solubility in hydrocarbons is negligibly small (*2* to *4*), but also because the process contains a surfactant recovery system described as follows.

The coalescence of oil drops in the top section of the diffusion column can occur automatically if the drop size is not too small. For example, a drop size of 0.5 cm. in diameter used in this work was suitable to induce automatic coalescence of the drops. This results in surfactant and water being rejected first to the interface between the coalesced drop phase and the solvent phase. From there they gradually form small droplets, which, being heavier than the solvent, fall back to the aqueous phase.

The important steps in the surfactant functioning cycle in a diffusion column therefore are:

1. Water-soluble surfactant molecules stick to oil feed droplets.
2. Surfactant and water molecules form a surface membrane through which selective permeation occurs when the drops are in the solvent phase.
3. Oil droplets coalesce after leaving the solvent phase, pushing water and surfactant molecules to the interface between the coalesced drop phase and the solvent phase.
4. Water molecules form droplets at the interface carrying surfactants back to the aqueous phase.
5. The recovered surfactant molecules are available for forming new membranes.

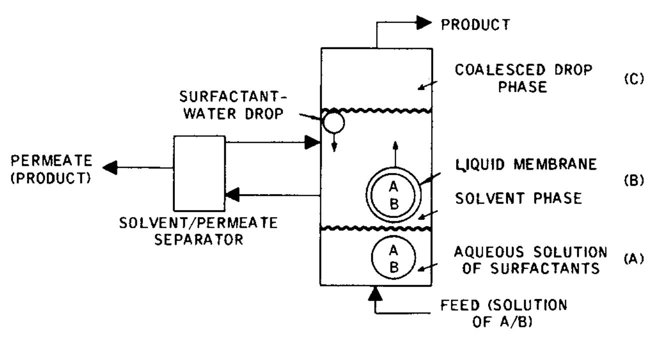


Fig. 1. Schematic diagram of a diffusion column operation.

Depending on the surfactants used, some of the drops might break up in the solvent phase due to the rupture of weak membranes. This results in the entire content inside these drops dissolved in the solvent phase. The overall separation factor therefore will be lowered. To minimize drop breakup, very small emulsion size droplets may be used. As shown in Table 1, a decrease of drop diameter from 0.5 to 10^{-4} cm. stabilized greatly the droplets. It also improved tremendously the permeation rate because of the greatly increased total surface area for mass transfer. The emulsion size droplets, however, do not coalesce automatically and some means of demulsification, such as heating or use of an electrostatic coalescer, must be used.

TABLE 1. EFFECT OF DROP SIZE ON SEPARATION

Surfactant: Igepal
Solvent: Solvent 100 Neutral
Temperature: 25°C.
Feed: Heptane/toluene (42% nC_7)

	Final conc. (one stage)	Drop breakup	Diffusion rate, ΔC/min.
Large drops ($d \geq 0.5$ cm.)	43.5	30%	2.6
Emulsion ($d \sim 10^{-4}$ cm.)	70.5	Small (<10%)	43.2

In comparison to solid polymeric membranes, liquid surfactant membranes do not develop pin holes because of the surface-tension effect associated with a surface film of liquid surfactant, and do not have to be replaced or repaired. They also do not require mechanical support. In addition, it is possible to provide much greater surface area for mass transfer within a given process volume with liquid membranes than would be possible with solid membranes. The liquid membranes are much thinner than the commonly available solid polymeric membranes. This means higher transfer rates. Also, there is no film life problem, because the liquid membranes form almost instantly on the surfaces of the droplets and are recovered after use.

EXPERIMENTAL APPARATUS AND PROCEDURE

Most of the results presented in this paper were obtained from the single-drop runs in a small glass tube. The rest were from the multiple-drop runs in a large diffusion column.

The single-drop runs were made in a glass tube of 1 in. in diameter and 2 in. in length. A single feed drop was injected into the bottom surfactant solution by a hypodermic needle where a thin liquid membrane formed around the drop. The solvent on top of the surfactant solution, unlike the solvents used in the diffusion columns, was selected to be lighter than the feed so that the feed drop was submerged entirely in the solvent phase after rising out of the surfactant solution. The solvent phase was stirred to ensure its uniformity of composition and was sampled from time to time for analysis of the concentration of the permeates. The surface area of the drop was calculated from the lengths of the major and minor axes of the drop measured with a cathetometer.

The diffusion column runs were made with a column having a size of 1 in. in diameter and 7 ft long. The surfactant solution occupied a section of 1 ft in height on the bottom, whereas the solvent phase, which was chosen to be heavier than the feed and completely miscible with it, occupied a section of 4 ft in height immediately above the surfactant solution. The rest of the column was for the raffinate phase formed by the coalescence of the feed drops arising out of the solvent phase. The column operation has been described in the previous section.

RESULTS AND DISCUSSION

Determination of Membrane Selectivity

Membrane selectivity, or separation factor, is the most critical characteristic of a separation process because it sets an upper limit on yield. The selectivity is commonly defined as the concentration ratio of the permeate to a reference compound in the solvent phase to the ratio in the raffinate phase.

$$S = \left(\frac{C_{d1}}{C_{d2}}\right) \Big/ \left(\frac{C_{r1}}{C_{r2}}\right) \qquad (1)$$

The selectivity of liquid membrane was found to be very high for many hydrocarbons in both the single-drop experiments and the diffusion column runs (Tables 2 and 3).

In a diffusion column, the amount of permeate in the solvent cannot be directly determined by measuring the permeate concentrations in the solvent phase since the concentration obtained represents a combined effect of membrane permeation and drop breakup. A dye tracer technique was therefore developed for determining the membrane selectivity. It measures quantitatively the ratio of material transferred into the solvent phase by diffusion to that transferred by drop breakup. The technique involves injecting a trace of dye into the feed. The large and bulky dye molecules do not diffuse through the membrane; therefore a colorimetric determination of the extent to which the dye is concentrated in the product shows the magnitude of diffusion of feed.

TABLE 2. MEMBRANE SELECTIVITIES DETERMINED BY THE DYE TRACER TECHNIQUE

Dye used: "Brilliant Oil Blue" (1-butyl-amino, 4-methyl amino anthraquinone) manufactured by Allied Chemical Corp.
Temperature: 25°C.
Membrane selectivity [By Equation (1)]: >100 for the following surfactants tested for column runs

Hydrocarbon mixture	Surfactant	Surfactant solution concentration (wt. %)	Perferentially permeating compound
nC_6/Benzene	Saponin	5.0	Benzene
nC_7/Toluene	Saponin	5.0	Toluene
	Saponin	0.5	Toluene
	Igepal-850	0.5	Toluene
	Sodium dodecyl sulfate	0.25	Toluene
nC_8/iC_8*	Igepal-710	0.5	i-C_8

*iC_8 = Trimethyl pentane.

TABLE 3. EFFECT OF WATER SOLUBILITY ON THE SELECTIVITY OF LIQUID MEMBRANE

Surfactant: Saponin
Temperature: 25°C.

Mixture	Solubility ratio	Separation factor determined in single-drop runs
A_6/nC_6	187.5	106
A_7/iC_7	127.0	36
A_7/nC_6	54.2	7.2
$nC_6^{==}/nC_6$	17.8	5.7
cyclo C_6/nC_6	5.8	3.2
$nC_6^{=}/nC_6$	5.3	2.9

A_6 = Benzene, A_7 = Toluene, iC_7 = 2,4 Dimethyl pentane.

The equations for evaluating selectivity are derived as follows:

A material balance for the entire system is

$$F = R + D + B \qquad (2)$$

A material balance for component 1 is

$$FC_{f1} = RC_{r1} + DC_{d1} + BC_{f1} \qquad (3)$$

The ratio of the color intensity in the product to that in the feed, I, can be expressed in terms of D and R:

$$I = 1 + \frac{D}{R} \qquad (4)$$

Substituting Equations (3) and (4) into (2), we obtain

$$C_{d1} = \frac{IC_{f1} - C_{r1}}{I - 1} \qquad (5)$$

The membrane selectivity can also be determined in single-drop experiments. The concentrations of permeates in the solvent phase can be readily measured and the concentration of the permeating compounds in the raffinate phase can be obtained by sampling the content inside the drop or calculated by material balance. The permeate concentration in solvent versus time curve, such as the ones for the single drops of pure toluene, pure heptane, and a 1/1 by weight of toluene and heptane mixture as shown in Figure 2, can also be used to calculate the permeation rate.

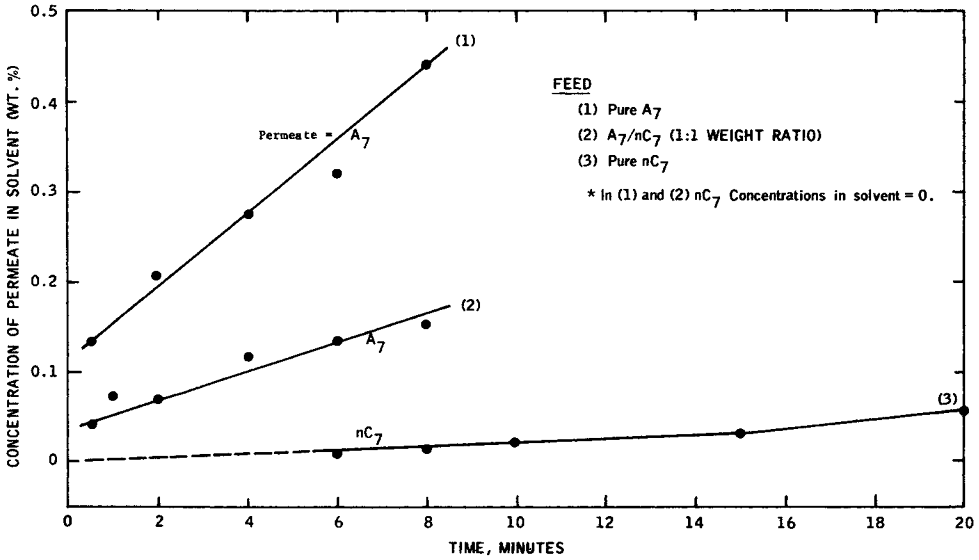


Fig. 2. Permeation of toluene/heptane mixture through Igepal membranes.

In the case of a toluene and heptane mixture, no appreciable concentration of heptane could be measured during the 8 min. time studied.

The selectivities obtained in single-drop experiments should be in general higher than those obtained by the tracer technique in the diffusion column runs. This is due to the difference in the degree of film thinning in these two cases. In the single-drop experiment the feed drop is stationary in the solvent phase, whereas in a diffusion column all the feed droplets are constantly in motion. Membrane thinning rate in the former case therefore is much smaller than in the latter. This also means that the membrane in the former case contains much more water for the same period of drop life than the membrane in the latter. As discussed later, thicker membrane, including thicker water layer in the membrane, gives higher membrane selectivity.

Effect of Surfactant Concentration on Membrane Selectivity

The separation of hydrocarbons was found to be independent of surfactant concentrations in the range investigated—from 0.001 to 0.1 wt. %, including the critical micelle concentration (Table 4). This indicates strongly that the liquid membrane around a hydrocarbon drop is composed of a fixed number of layers of surfactant and water. Most likely it is composed of one surfactant layer and one water layer when the drop carrying the liquid membrane is in the surfactant solution, and is composed of two surfactant layers with one water layer in between when the drop is in the organic solvent.

TABLE 4. EFFECT OF SURFACTANT CONCENTRATION ON MEMBRANE SELECTIVITY

Feed: Heptane (C_7)/Hexadecane (C_{16})(1:1 by wt.)

Surfactant concentration (Igepal wt. %)	C_7/C_{16} in solvent phase	C_7/C_{16} in raffinate phase
0.001	1.45	0.89
0.01 CMC*	1.48	0.88
0.1	1.46	0.86

*Critical micelle concentration.

Effect of Permeate Solubility in Water on Separation Factor

Since the liquid membrane is composed of both water and surfactants, the permeate's solubility in water appears to have an important effect on membrane selectivity and rate. An examination of the permeate's solubility in water (5) shows that the compound that has a higher solubility in water is the preferentially diffusing compound as shown in Table 3. The separation factor also increases in magnitude with the increasing solubility ratio. This indicates clearly that selectivity is a function of the solubility of permeate in water as well as of the diffusivity of the permeate through the surfactant and water layers.

Determination of Mass Transfer Rate

The mass transfer rate of a permeate can be determined by measuring the increase of its concentration in the solvent phase for a single feed drop. Some typical rate curves are shown in Figure 2. Although the rate is usually expressed in the unit of grams per square centimeter per second, in certain cases where a comparison of rates is involved, it may suffice to express the rate simply as the change of permeate's concentration in the solvent phase per unit time.

The mass transfer rates of hydrocarbons through liquid membranes are in general higher than the rates of the same compounds through 1-mil thick polymeric films (6). For example, the permeation rate of toluene through Saponin membrane is 12.1 g./(hr.)(100 sq. cm.) measured 10 min. after membrane formation, whereas the permeation rate of toluene through a 1-mil polypropylene film is about 4.7 g./(hr.)(100 sq. cm.).

Effect of Surfactant Structure on Permeation Rate

Permeation rate varies with different kinds of surfactants. The diffusion rates of toluene through various surfactant membranes were measured as the change of the permeate concentration in the solvent with time in the single-drop experiments (Table 5).

TABLE 5. TOLUENE DIFFUSION RATE THROUGH THE SURFACTANT FILM ON A SINGLE FEED DROP

Surfactant concentration: 0.1% in water
Feed: 1/1 Toluene/heptane

Surfactant	Diffusion rate,* g./(hr.)(100 sq. cm)
Tween (polyoxyethylene Sorbitan Monolaurate)	10.2
Igepal [Nonylphenoxy-poly (ethyleneoxy) ethanol]	10.3
Saponin	12.1
Polyvinyl alcohol	16.6
Dodecyl trimethyl ammonium chloride	26.5
Sodium dodecyl sulfate	30.2

*Measured 10 min. after membrane formation.

Sodium dodecyl sulfate and dodecyl trimethyl ammonium chloride were found to give much higher rates than did the other membranes. Since these two surfactants are ionic and all the others are nonionic, or very weakly ionic, it appears that the strongly ionic membranes have a higher rate than nonionic membranes.

Effect of Surfactant Chain Length on Permeation Rate

The diffusion rates of toluene through four Igepal and five Pluronic membranes with different hydrophilic chain lengths were measured (Table 6). Although both surfactants have a straight-chain molecular structure, an Igepal molecule is composed of only a hydrophilic and a hydrophobic section, whereas a Pluronic molecule is composed of a hydrophobic section connected at both ends to two hydrophilic sections. The toluene diffusion rates were

TABLE 6. EFFECT OF SURFACTANT STRUCTURE ON PERMEATION RATE

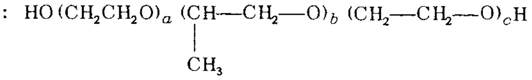
Permeate: Toluene

(1) Igepal: $C_9H_{19}—\phi—O—(CH_3CH_2O)_{n-1}\,CH_2CH_2OH$

ϕ: Benzene ring

Igepals	n	Rate (ΔC%/min.) 0.01% Igepal	0.1% Igepal	0.2% Igepal
CO-710	10	0.017	0.018	0.011
CO-730	15		0.023	
CO-850	20		0.042	
CO-880	30	0.066	0.051	0.059

(2) Pluronic:



$HO(CH_2CH_2O)_a\,(\underset{\displaystyle CH_3}{CH}—CH_2—O)_b\,(CH_2—CH_2—O)_cH$

% Hydrophilic unit in pluronic molecules	Molecular weight of hydrophobic base	Rate (ΔC%/min.) 0.01% Pluronic	0.1% Pluronic
10	1,750		0.063
20	1,750	0.050	0.045
40	1,750		0.015
80	1,750	0.009	0.006
40	3,250		0.022

found to increase with the increasing hydrophilic chain length of Igepals and with the decreasing hydrophilic chain length of Pluronics. The rates measured appear to be the net result of two counteracting effects, the extent of the surfactant chain entanglement and the thickness of the water layer with the chain entanglement effect favoring higher permeation rate. The chain entanglement effect can be enhanced by lengthening hydrophilic section of a surfactant molecule. This can be done by complexing the surfactant with colloids, as discussed elsewhere (*7*, *8*).

Permeability and Rate Equation

Permeability has been calculated from the data obtained in the single-drop experiments. It is defined by the following equation:

$$N = P(\bar{C} - C) \tag{6}$$

This equation is similar to the commonly used mass transfer equation with the permeability P equivalent to the overall mass transfer coefficient K_L. It should be noted that similar rate equations have been used to describe transfer through monolayer of surfactant at liquid-gas interface (*9* to *16*) or through a stirred oil layer (*17*). Analysis of the mass transfer coefficient (or permeability) gave valuable additional information on the mechanism of permeation through liquid membranes as discussed below.

Membrane structure is a function of the nature of feed as illustrated by the data in Table 7. When the feed was changed from 1/1 toluene/heptane to pure toluene, the permeability decreased, whereas the permeation rate increased. Since toluene was the only permeate detectable in the solvent phase during the period of sampling in both cases, the change in permeability should be due to the change in membrane structure and strength, whereas the change in permeation rate is a result of the change of the overall concentration difference. The variation of membrane structure and strength as a function of the nature of the feed is further evidenced by the fact that when the feed was changed from 1/1 toluene/heptane to pure toluene, the stability of the Saponin membrane formed on a single feed drop, expressed in terms of membrane life, was increased from 10 min. to 1 hr. This is probably due to the increase of compatibility between the surfactant and the feed. Saponin, which contains many aromatic rings in its hydrophobic molecular section, is more compatible with toluene than with heptane.

TABLE 7. PERMEABILITY OF LIQUID MEMBRANE

	Surfactant solution = 0.1% Saponin		
Feed	Permeation rate × 10^6 g./(sq.cm.)(sec.)	Permeability × 10^4, cm./sec.	Sampling time, min.
1/1 Toluene/ heptane	18.6	11.4	6
	32.9	21.2	10
Toluene	29.9	5.72	6
	58.8	11.8	10
Heptane	0.168	0.075	10
	0.396	0.115	18

When the feed was heptane, both the permeability and the permeation rate were smaller than those for pure toluene feed. The ratio of the permeability of toluene to that of heptane is very close to the separation factor obtained in separating a mixture of these two compounds. This suggests that prediction of separation factor as a general case may be made from the ratio of permeabilities of the compounds involved.

SUMMARY

A novel separation technique involving selective permeation of hydrocarbon through liquid-liquid interfaces has been developed. A film consisting of water and a water-soluble surfactant is used as a liquid membrane which shows nearly perfect membrane selectivity for many hydrocarbons. Because the membrane is only of a few molecules thick, the permeation is fast enough to make practical separations possible. The permeation mechanism is analyzed in terms of the effects of surfactant concentration, surfactant structure and chain length, the nature of permeate and the solubility of permeate in water on membrane selectivity, and permeation rate. A permeability parameter is suggested to estimate the separation factors for different separation systems.

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NOTATION

B = weight of the feed lost to the solvent due to drop breakup
C = concentration of a feed component
$\bar{C}$ = equilibrium concentration of a feed component in the solvent phase
D = total weight of permeates in the solvent phase
F = total weight of feed
I = color intensity as defined by Equation (4)
N = permeation rate of a feed component, g./(sec.)(sq. cm.)
P = membrane permeability, cm./sec., as defined by Equation (6)
R = total weight of the raffinate phase
S = separation factor

Subscripts

1, 2 = feed components 1 and 2
d = in the solvent phase
f = in the feed
r = in the raffinate phase

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