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TRANSPORT PROCESSES IN LIQUID MEMBRANES: DOUBLE EMULSION SEPARATION SYSTEMS

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INTRODUCTION

The field of membrane technology is currently undergoing a rapid expansion of the areas of both research and industrial separation techniques. Developments in membrane technology have been guided by the need to develop relatively simple but highly selective separation techniques that are economically attractive when compared to other separation processes. An area of current interest is the use of liquid membranes to separate species or to control mass transfer rates. Liquid membranes can be manipulated to selectively separate a specific solute from a mixture, and even to extract a solute against its concentration gradient by coupling its flux to the flux of another solute or by coupling to another external force across the membrane such as an electrical field.

The advantage of using a liquid membrane over a solid polymer membrane is that the diffusion rates of species in a liquid are considerably larger than those found in solids, and further, the solubility properties of liquids offer a wider range of possibilities than normally found with solids. A disadvantage is that liquid membranes are inherently less stable to mechanical forces than solid-type membranes. In general, liquid membranes are either supported or unsupported.

Supported liquid membranes can be held in a porous structure or bounded on either side by two thin polymeric films. The former method of support is more common and the porous structure can be a porous polymer membrane or filter paper. The liquid membrane can be either in the form of a flat plate or in tubular shell geometry as is shown in Figure 1. Ward and Robb[1] were probably the first investigators who applied liquid membranes containing carriers to possible industrial separation processes.

Unsupported liquid membranes are usually in the form of double emulsion drops. The addition of surfactants is necessary to stabilize the drops. Figure 1 shows an example of a water/oil/water (W/O/W) system. For the W/O/W system it is the immiscible oil phase, separating the two aqueous phases, which is the liquid membrane across which selective diffusion takes place. For a O/W/O system, the liquid membrane is the immiscible water phase which separates the two oil phases. It is in principle possible to devise other systems such as W/O/O if the two oil phases are immiscible. The subdrops contained in the larger drop of the membrane phase can also be substituted by a solid phase. However, such systems have not yet been studied.

The phase contained in the subdrops is often referred to as the encapsulated phase. Its primary purpose is to serve either as a sink or source solution. In separation processes it serves primarily as a sink for the removal of species from the continuous phase. In certain controlled release applications, e.g., controlled release of drugs, the encapsulated phase can serve as a source.

The use of double emulsion drops as separation media was first proposed by Li.[2,3,4] The advantages of the unsupported form of liquid membranes is that the surface area to volume ratio can be made large by using smaller drops. Further, the reagent phase contained in the subdrops can be made into sinks by the introduction of reactants which combine irreversibly with the species to be separated from the

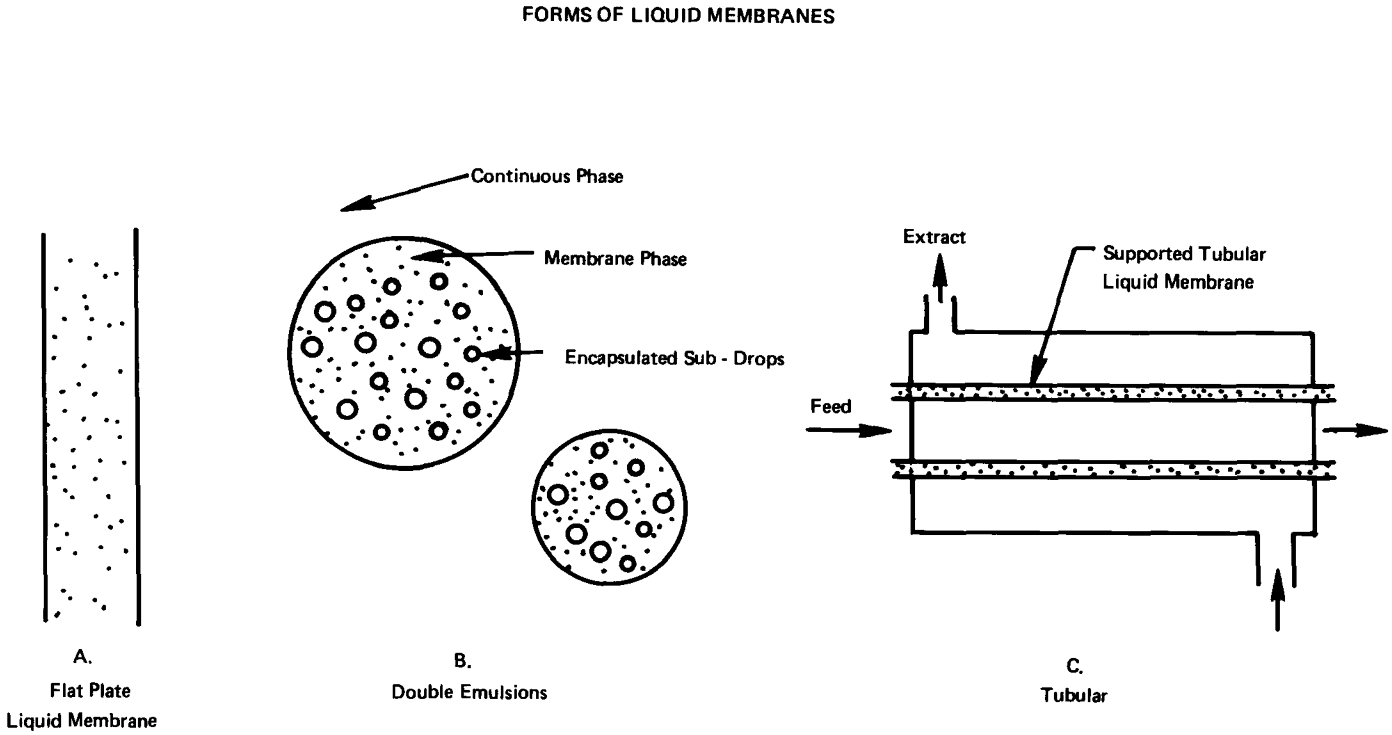


Figure 1: Schematic diagram of the different types of liquid membranes: A) Supported liquid membrane in a porous structure separating two compartments. B) Double emulsion drops of unsupported liquid membrane phase containing subdrops of encapsulated phase. The double emulsion drops are dispersed in the continuous phase. The drop diameter can be from approximately 20 µm to several mm. C) Supported liquid membrane in a tubular shell of a porous structure.

continuous phase. The reaction is chosen in such a manner that the product is retained in the reagent phase due to poor solubility and low diffusion rates in the liquid membrane phase. The irreversible reaction, if kinetically fast compared to diffusion rates, causes the concentration of the diffusing species inside the subdrops to be low, effectively maximizing the concentration gradient across the liquid membrane.

In either form of liquid membrane, supported or unsupported, the addition of reversible carrier compounds into the liquid membranes, which are constrained to remain within the membrane phase, can considerably increase the mass transfer rate of a particular species. In addition to the requirement that the carrier compound complexes reversibly, selectively and rapidly with the species to be separated, other desirable characteristics are that the carrier and its complex have a large diffusivity, and that the carrier can be dissolved in large concentrations in the membrane phase while it is insoluble in the adjoining phases. Considerable work has been reported on using carriers in facilitated transport,[5] co-transport,[6] and counter-transport systems.[7] It is the use of carriers which has made the industrial utilization of liquid membranes more attractive.

Transport processes in supported liquid membranes have been succinctly discussed in a number of papers, for example by Smith et al.[9] and Way et al.[10] In this article the problem of transport processes occurring in unsupported membranes will be addressed. In particular, the effect of drag forces on the stability of double emulsion drops and the modelling of mass transfer in double emulsions will be dealt with.

HYDRODYNAMIC STABILITY

The problem that is inhibiting the application of double emulsions in industrial equipment is the stability of the drops in contacting equipment, i.e. mixers, pumps, etc. At present, the widespread use of double emulsions as a separation system in industrial processes has not yet been possible due to problems of stability.[11] An understanding of the hydrodynamic stability of double emulsion drops is necessary to logically set operating conditions for contacting equipment.

Actually the stability of double emulsions can be of at least two types: thermodynamic and hydrodynamic. In reality, no emulsion is thermodynamically stable. The emulsion drops always tend to coalesce so as to reduce the total interfacial area. The surfactant that is added to the membrane phase in the preparation of these emulsions can substantially, though not completely, reduce the coalescence rate. The residence time of these emulsions in the mixing equipment is short enough so that the thermodynamic stability is not the crucial factor in the design of equipment.

On the other hand, the hydrodynamic stability can play a vital role in the design of equipment used with double emulsions. Hydrodynamic stability is a measure of the resistance offered by the emulsion drops to the viscous and inertial drag forces acting on them due to the motion of the continuous phase. When these drag forces exceed the resisting forces (mainly surface tension forces), the drop breaks. The consequence of the breaking of double emulsion drops is the liberation of some of the encapsulated solution into the continuous phase which leads to a reduction in the extraction efficiency and extraction rate. An understanding of the stability of double emulsions when subjected to hydrodynamic forces is necessary to set the correct operating conditions for equipment.

The first study on stability was done experimentally by Hochhauser and Cussler.[8,12] The liquid membrane systems used in this study were made up in the following way:

i. encapsulated phase - 0.1 M sodium dichromate solution.

ii. membrane phase - solution of Span 80 in an organic solvent.

iii. continuous phase - water.

The solubility of sodium dichromate in this membrane is negligibly small, and any dichromate found in the water phase is due to the breakage of the membranes. They expressed their results in the form of a percentage breakup defined as the ratio of chromium present in the water phase to the total amount present in the system. Stirring of the double emulsion drops in a container with the continuous phase was accomplished with a 2-inch, 3-vane, marine type propeller with a 50° pitch.

The stirring rate and the concentration of sodium dichromate were found to have no effect on the breakup. Rapid breakup during an initial period with no further breakup was observed. Hochhauser and Cussler explained their results by postulating the existence of two types of liquid membranes, one which is easily and rapidly breakable and another which is stable for longer times. Another plausible explanation for this time dependency can be that the emulsion drops, at the end of this initial period, have reached a size at which drag forces trying to rupture the drops could not overcome the surface tension forces holding the drops together (σ/a).

The variables that showed pronounced influence on the stability were viscosity of the membrane solution, volume fraction of the subdrops within the emulsion drop, and the concentration of the surfactant. A 50% reduction of the membrane rupture required either a 1500% increment in the viscosity of the membrane solution or a 25% reduction in the volume fraction of the subdrops or a 0.2 wt% increment in the surfactant concentration (Fig. 2). The results for the volume fraction of subdrops is surprising. In general, an increase of the volume fraction of the subdrops increases the viscosity of the emulsion drop and so one would expect a positive effect on the stability of the emulsion.

Martin and Davies[13] performed some stability studies along with their mass transfer studies on the extraction of copper from

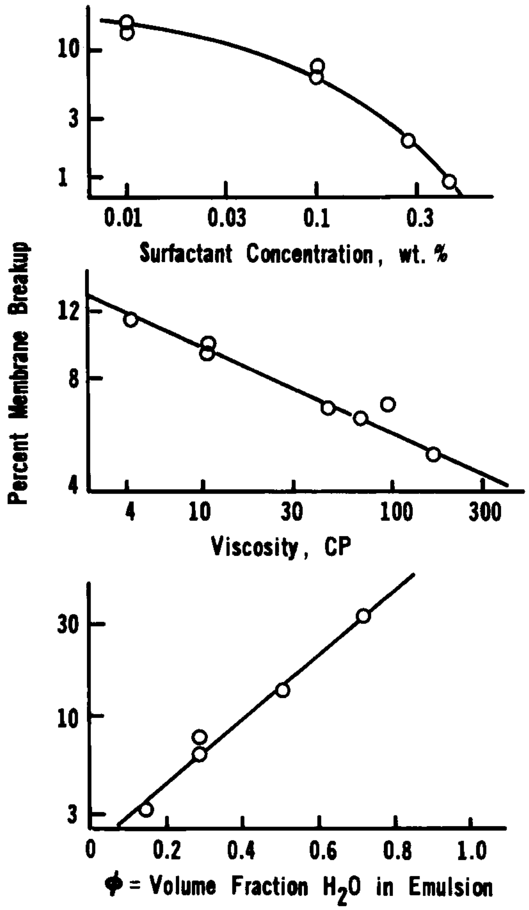


Figure 2: Effect of surfactant concentration, membrane viscosity and volume fraction of the encapsulated phase on the percent of membrane breakage (100 ξ). Redrawn from Hochhauser and Cussler.

aqueous feed solution through a membrane phase consisting of a commercial chelating agent (LIX 64N), an organic diluent, and a nonionic surfactant. The encapsulated phase used was H_2SO_4 solution. The emulsion breakup was estimated by measuring the concentration of hydrogen ion in the continuous phase in excess of what should actually be present (each copper ion results in a counter transfer of two H^+ ions).

Martin and Davies reported that the emulsion breakup depends on the following:

i. the size of the subdrops
ii. the operating conditions in the mixing device
iii. the type of surfactant used.

The smaller the size of the subdrops, the greater was the stability. The size of the subdrops depended on the type of mixing device used in the initial formation of the W/O emulsion before introduction into the continuous phase. They further observed a dependence of the % breakdown on the impeller speed in a mixing vessel, as shown in Fig. 3. Breakage was found to increase linearly with time in almost all cases. This is in contrast with the findings of Hochhauser and Cussler.[8] Use of sorbitan mono-laurate gave greater breakage than sorbitan mono-oleate. Presumably the interfacial tension with sorbitan mono-laurate was lower but those values were not reported.

Recent investigations on the stability of emulsion drops are those of Takahasi et al.,[14] Kita et al.,[15] Tanaka et al.[16] and Kondo et al.[17] In general stability was also measured using a tracer technique. Release of the tracer (usually a salt) from the subdrops was a direct measure of the breakage of double emulsion drops since the tracer transport through the liquid membrane was negligible.

Breakage was measured in terms of the factor ξ defined as the ratio of moles of tracer in the continuous phase to the total amount of tracer initially present in the subdrops. The effects of the following variables were studied:

i. tracer or salt concentration
ii. agitation time
iii. size of the emulsion drops
iv. concentration of emulsifying agent
v. pH of the subdrops

Similar to the studies of Hochhauser and Cussler[8] and Martin and

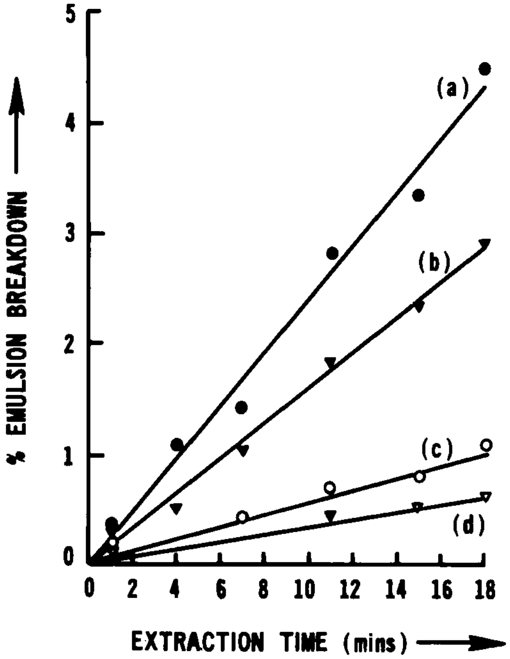


Figure 3: Influence of the type of surfactant and mixing speed on percent of membrane breakage (100 ξ):

A) Sorbitan mono-laurate, mixer speed 300 rpm;

B) Sorbitan mono-laurate, mixer speed 250 rpm;

C) Sorbitan mono-oleate, mixer speed 300 rpm;

D) Sorbitan mono-oleate, mixer speed 250 rpm.

Redrawn from Martin and Davies.

Davies,[13] the parameter ξ is an indication of the amount of subdrops expelled into the continuous phase. The mechanism of this process is not entirely clear although it presumably occurs when double emulsion drops break up into two or more drops when hydrodynamic forces are exerted on the drops. The breakup process apparently releases some subdrops into the continuous phase.

Hochhauser and Cussler did not observe a significant effect on salt concentration. Kita et al.[15] reported a decrease in ξ with increasing salt (NaCl) concentration in the range of 0.3 - 0.5 wt%. Takahasi et al.[14] observed very little effect up to a concentration of 2 wt%, above which ξ increased with increasing concentration of tracer. Stability was found to decrease with increasing salt concentration in the continuous phase.

According to Hochhauser and Cussler,[8,12] emulsion drops broke up to a certain time, beyond which there was no further breakup. They did not report any relation between ξ and time. Martin and Davies[13] observed a linear relationship between ξ and time. Takahasi et al.[14] reported that an initial nonlinear behavior precedes a constant rate period.

Takahasi et al.[14] showed that the double emulsion is more stable when the drop size of the emulsion is smaller. Obviously for smaller drops the surface tension force, which holds the drop together, is more significant than that for larger drops.

Most of the studies on the effect of the surfactant concentration (in the liquid membrane phase, C_s) on the breakage indicated that ξ decreased with increasing C_s. Kondo et al.[17] reported a sudden decrease in ξ at about 1.0 wt% of surfactant. Takahasi et al.[14] observed ξ to depend on C_s raised to the -1.5 power. It is difficult to compare such results since the double emulsion systems were different in each case. Although addition of surfactant should lower the interfacial tension between liquid membrane and continuous phase giving rise to a reduced resistance of the surface tension force to hydrodynamic forces, addition of surfactants appears to be beneficial in preventing the subdrops to be expelled in the continuous phase when the double emulsion drops break into smaller fragments.

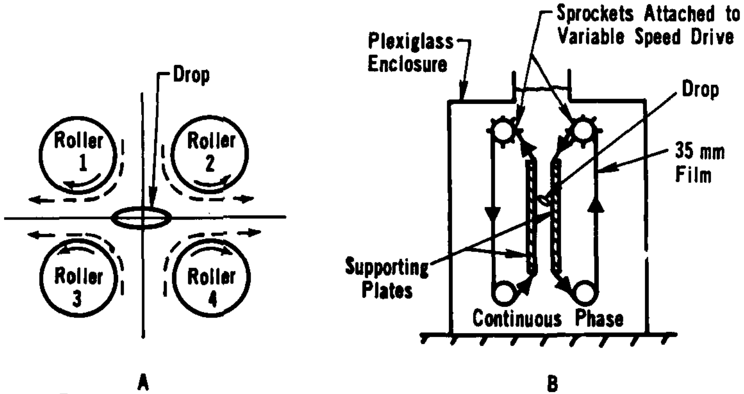
Takahasi et al.[14] also studied the effect of pH on ξ. The emulsions were more stable for pH values between 3 and 11.5. Outside this range the emulsion breakage was substantial, possibly due to the increase of either hydrogen or hydroxyl ion as was found with increased salt concentration.

The main drawback of the above studies is their limited applicability. The studies are useful only to the specific conditions under which the experiments were performed. Many of the systems were different and mixing of the double emulsion drops in the continuous phase was only controlled by fixing the rpm of the stirrer. Obviously, shear rates in the mixer were radically different from point to point. Drops were exerted to varying degrees of inertial and viscous forces. Details of the experimental conditions were often not fully specified. A way by which the drawback can be surmounted is by correlating the breakup data in terms of dimensionless quantities that can be used irrespective of the experimental conditions and materials. Such an approach has been made by Stroeve et al.,[18,19] who have studied the effect of viscous forces on double emulsions. The basis of this work is the classical work of Taylor.[20]

Taylor[20] was the first investigator who studied both experimentally and theoretically the deformation and breakup of a drop of a Newtonian liquid suspended in another immiscible Newtonian liquid undergoing definable fields of flow (simple shear and plane hyperbolic flows). Thereafter numerous researchers became interested in this subject. Of particular importance are the experimental works of Rumscheidt and Mason,[21] Karam and Bellinger,[22] Torza, Cox and Mason[23] and finally of Grace,[24] whose experiments cover a large range of p from 10^{-6} to 10^{3} (p is the ratio of the viscosity of the dispersed phase to the viscosity of the continuous phase).

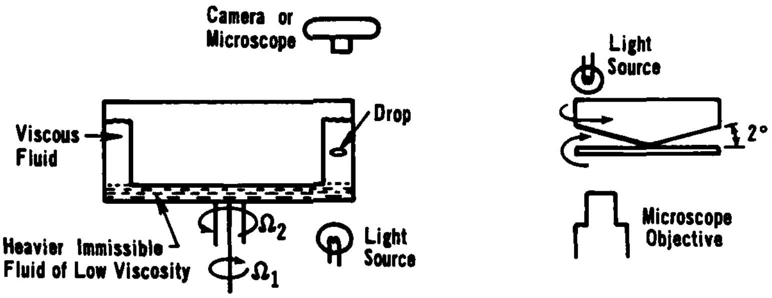
Neglecting significant deviations of the drop from sphericity, the theoretical problem of breakup was tackled first by Taylor[20] and then by Chaffey and Brenner[25] and Cox[26], and finally by Barthès-Biesel and Acrivos.[27] These theories are known as small deformation theories, and are successful in the high-viscosity ratio range where the drops deform only by a small amount before they break, usually into two smaller drops. On the other hand, the drops are observed to become very long and slender before breakup into several smaller drops when the viscosity ratio, p, is much smaller than unity. To represent this behavior, it is necessary to have a theory that takes advantage of the slenderness of the drop rather than extending the small deformation theories which basically involve constructing a solution by using perturbation expansions of the appropriate variables in terms of a deformation parameter ε $(= \frac{G\mu_c a}{\sigma})$. This parameter is a measure of the ratio of viscous forces to surface tension forces. Taylor[28] was the first one to use such a technique to determine the maximum value of $\varepsilon = \varepsilon_B$ for which a long slender drop can exist in the system before breakup for the case of axisymmetric straining flow. This theory was later extended for other flow situations by Buckmaster,[29,30] Acrivos,[31] Hinch and Acrivos,[32,33] and by Hinch.[34] These theories give excellent predictions of drop breakup for low values of p. Recently, Rallison and Acrivos[35,36] developed a numerical scheme that is applicable over the entire range of p. The studies mentioned above were all concerned with the dispersions of Newtonian drops in Newtonian liquids. Studies on the behavior of viscoelastic drops and threads in Newtonian and viscoelastic media have been done by Gauthier et al.,[37] by Flumerfelt,[38,39] and by Middleman.[40] Chin and Han[41,42] studied the deformation of drops in nonuniform flows.

Most of the above-mentioned experimental studies are restricted to either plane hyperbolic flow or simple shear flow. These can be achieved by choosing an appropriate apparatus amongst the four shown in Fig. 4. The four-roller apparatus produces plane hyperbolic flow while any of the other three produces simple shear flow. Stroeve et al.[18,19] used a counter-rotating cone and plate viscometer to study the deformation and breakup of both homogeneous Newtonian drops and double emulsion drops. The angle of the cone used was 2°, a value low enough for the shear rate to be constant through-



A
Four-Roller Device

B
Parallel-Band Device
(as Modified by Flumerfelt)



C
Couette Device

D
Cone and Plate Device

Figure 4: Types of devices used to study the behavior of drops in plane hyperbolic (A) and simple shear flow (B,C,D).

out the viscometer. The dilute dispersion was observed through an inverted microscope over which the viscometer is mounted. The cone and plate rotated at equal but opposite speeds. The double emulsions studied were of W/O/W type and the continous phases were corn syrups of different viscosities. For better contrast, methylene blue dye was added to the subdrops so that size analysis could be performed. The diameter of the subdrops ranged from 1 μm to 7 μm with a number average of 2.5 μm. The surfactant used to stabilize the membrane phase was Span 80 (sorbitan mono-oleate) and it

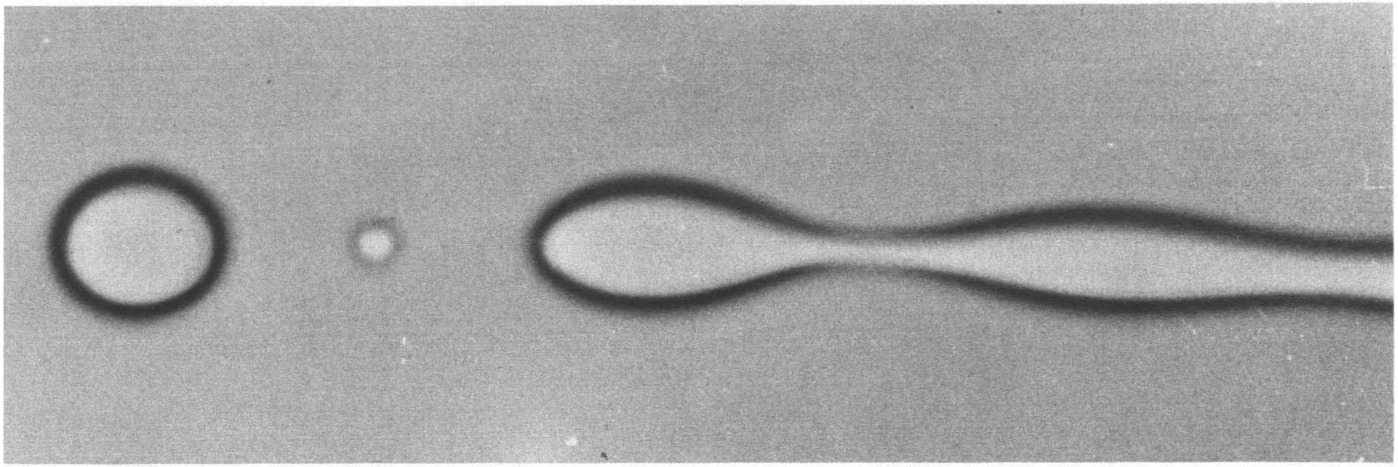


Figure 5: Breakup of Newtonian homogeneous drop due to viscous forces from simple shear flow. The drop deformed first into a long slender body before a Rayleigh instability wave appeared on the surface. The thinning of the nodal regions leads to breakage. The small satellite drop came from the final breakage of the nodal region.

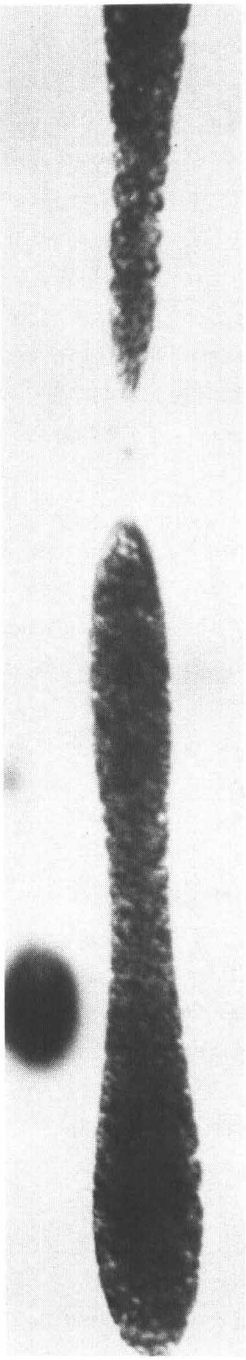


Figure 6: Breakup of a double emulsion drop (W/O/W) due to viscous forces from simple shear flow.

amounted to about 10% of the total membrane phase. The size of the initial emulsion drops were about 80-100 μ.

Figures 5 and 6 show photographs of the breakup of both Newtonian and double emulsion drops as observed by Stroeve et al.[18,19] It is interesting to note that the double emulsion drops break up in the same way that Newtonian drops do. Upon reaching a maximum deformation from sphericity, a Rayleigh instability wave appears on the drop's surface. The nodal regions of the wave then thin, eventually breaking, so that the drop breaks into main fragments. The thinning of the nodal regions often leads to the generation of small drops between the main fragments, and these small drops are known as satellite drops.

When Newtonian drops are suspended in another Newtonian liquid, it can be shown that breakup, in the case of negligible inertial forces, can be represented by the two main dimensionless groups, namely, the deformation parameter at breakup, ε_B, and the viscosity ratio p. Since the mechanism of breakup of liquid membranes is similar to Newtonian drops, it is reasonable to correlate the breakup data of double emulsion drops in terms of these same dimensionless groups.

Figures 7 and 8 show the breakup data of both Newtonian drops and double emulsion drops containing different volume fractions of subdrops. Breakup is correlated in terms of ε_B as a function of p. Accounting for the differences in the types of apparatus used and the size of droplets studied, the breakup data for Newtonian drops agree reasonably well with those obtained by the researchers.[18,22,23,24] Except for the results of Karam and Bellinger,[22] the minimum value of ε_B for Newtonian drops is around 0.3 - 0.75. According to Grace,[24] Karam and Bellinger[22] used the equilibrium surface tension, which caused the minimum value of ε_B to be higher. All the above studies indicate that drops cannot be broken upfor $p > 4.0$. The second asymptote observed by Karam and Bellinger[22] is possibly due to equipment limitations, as discussed by Grace.[24]

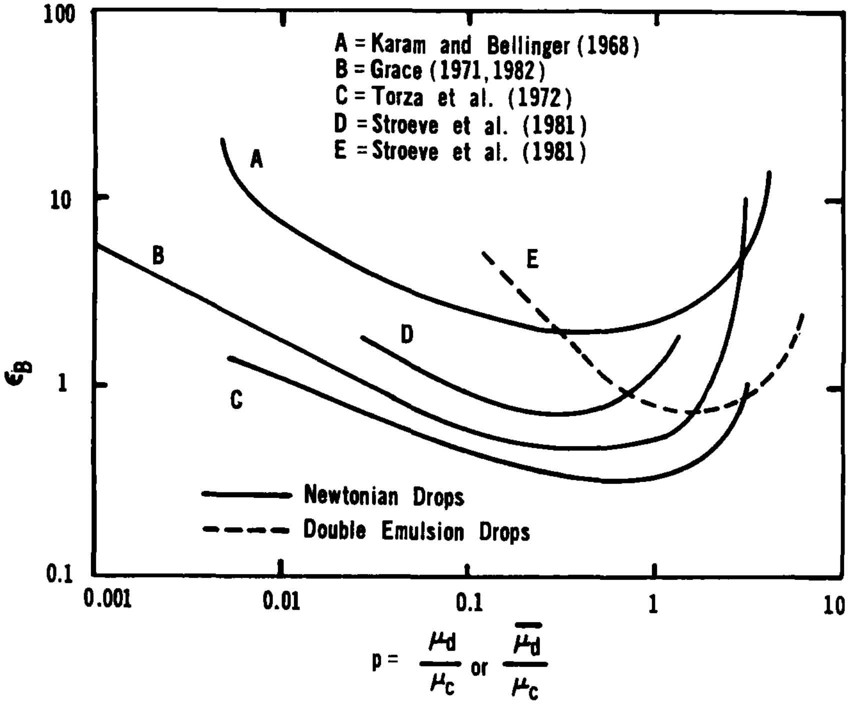


Figure 7: Experimental results for drop breakup. Results for curves A, B, C, and D are for homogeneous Newtonian drops suspended in a Newtonian phase. Curve E is for double emulsion drops suspended in a Newtonian phase (W/O/W). ε_B is the value of the breakup parameter ε at drop breakage.

For double emulsion drops, the smaller the volume fraction of the subdrops, the lesser is the shift of the breakup curve along the horizontal axis, relative to the breakup curves of the homogeneous Newtonian drops. The 15 vol% emulsion drops approach the breakup behavior of Newtonian drops. As Fig. 9 shows, the viscosity behavior of this double emulsion is Newtonian while the other emulsions ($\bar{\mu}_d$) were non-Newtonian. The minimum in the value of the breakup parameter is smaller for 15 and 39 compared to that for 62 vol%. Note that the apparent viscosity of the double emulsion $\bar{\mu}_d$ is that at the shear rate prevailing in the continuous phase. The utility of

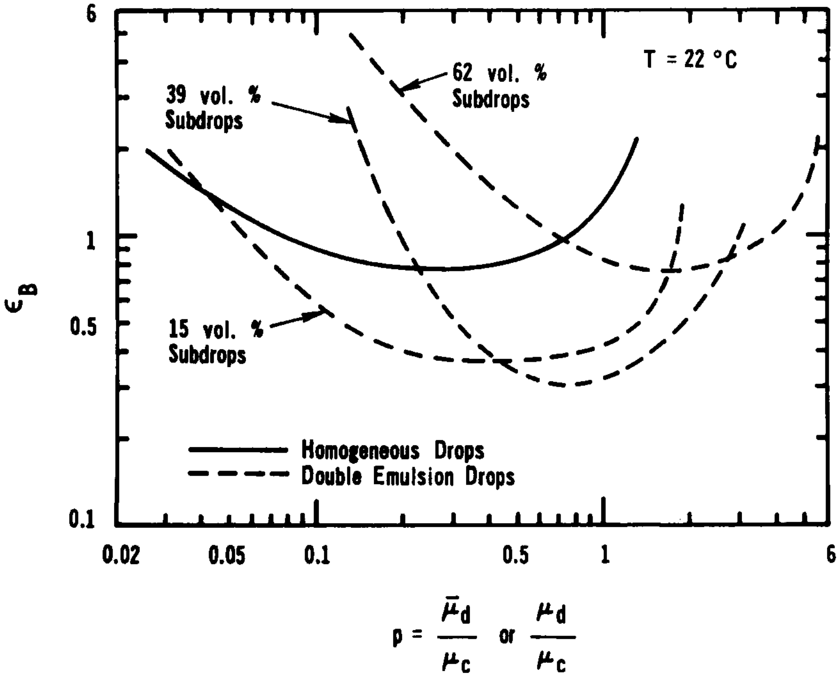


Figure 8: Experimental results for the breakage of double emulsion drops with different volume fractions of subdrops. The solid curve is for homogeneous Newtonian drops and corresponds to curve D in Figure 7. The 62 vol% subdrop curve is identical to curve E in Figure 7.

these breakup curves is that if one knows the largest drop size of the double emulsion, one can find the maximum shear rate that can be applied without breaking the drops.

There are several possible explanations for the shift in the breakup curves and the variation of the minimum of the breakup parameter. The decrease in the minimum of the ϵ_B may possibly be due to the heterogeneity of the double emulsion drops. At lower volume fractions, the subdrops tend to form aggregates, a process that might affect the internal circulation. This effect on the internal circulation may reduce the stability. (The degree of stress generated

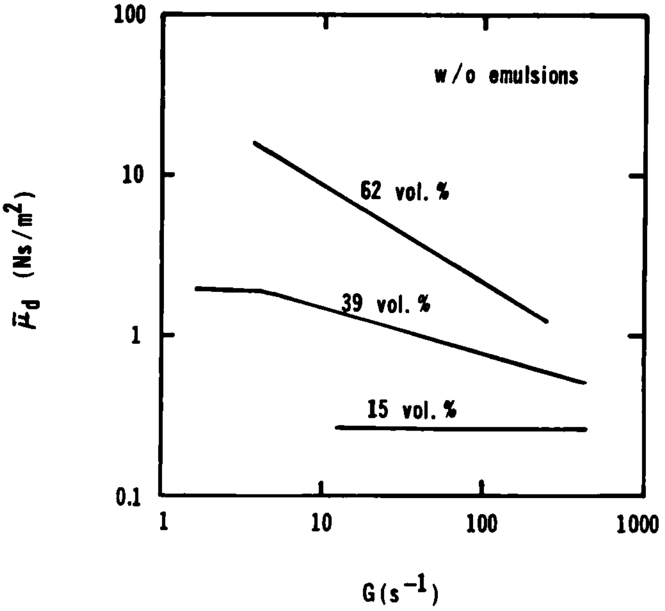


Figure 9: Apparent viscosity of the water in oil emulsions as a function of shear rate and the volume fraction of subdrops (encapsulated phase).

within the drop depends on the circulation inside the drop. The drop breaks up only when the difference in the external and internal stresses exceeds the surface tension force.) The elastic nature of the 62 vol% emulsion may be the cause of the higher values of ε_B. Elastic forces may aid the surface tension forces in resisting the viscous drag forces, thereby increasing the shear rate necessary to break up the drop.

Another explanation is based on the cohesion of the drop phase. At low volume fractions, the cohesion of the drop is not likely to be affected but, as soon as the drop is drawn out into a long thread, the thickness of the liquid thread obviously cannot become less than the average size of the subdrops, so ε_B is lower. When the drop is completely packed (62 vol%), the cohesive forces among the subdrops increase the cohesion of the overall drop, thereby increasing ε_B.

As mentioned earlier, $\overline{\mu_d}$ is calculated at the shear rate prevailing in the continuous phase. Obviously this is not the true shear rate within the drop. Since the internal subdrops undergo rotary flow inside the main drop and in addition may spin around their axes, this shear rate could be larger compared to the shear rate prevailing in the continuous phase. Since the emulsion is shear thinning, its viscosity would be lower at higher shear rates and this would cause the curves to shift back to lower values of p.

The results shown in Figures 7 and 8 are consistent with the notion that smaller double emulsion drops are more stable in a given shear rate than large drops. Also the lower the interfacial tension between drop and continuous phase (σ), the smaller the surface tension force σ/a. Apparently no studies have been conducted on the effect of inertial forces on the stability of double emulsion drops. The results for viscous forces are valid for low Reynolds number flow for the drops. It is possible that in contacting equipment the drop Reynolds number is sufficiently large that inertial forces play an important role.

In none of the previous studies has the mechanism(s) by which subdrops are expelled into the continuous phase during double emulsion breakup been identified. Stroeve et al.[18,19] have observed a decrease in the volume fraction of subdrops contained in the smaller double emulsion drop fragments but the actual release of subdrops could not be observed. The drop breakup becomes a very rapid process once the nodal regions start necking. Subdrops contained in this region most likely escape into the continuous phase when the nodal region is pulled into a liquid thread because the much smaller satellite drops between the main drop fragments often are devoid of subdrops.

The problem of double emulsion breakup due to swelling in the presence of an osmotic pressure gradient into the double emulsion drop has not been adequately studied. This phenomenon may have been important in some of the previous studies on the stability of double emulsions in mixing vessels (e.g., the effect of salt concentration). The double emulsions of Stroeve et al.[18,19] were osmotically balanced and stable over hours when no shear was present. Another stability problem arises when the double emulsion drops collide with vessel walls or the air/water interface. Due to the relatively low interfacial tension of the continuous and the liquid membrane interphase, the spreading coefficient of the double emulsion is positive. Contact with a surface with a high surface tension causes the drops to spread rapidly and to be pulled apart. Although these stability problems are different from the hydrodynamic stability, they deserve further study.

MASS TRANSFER PROCESSES

In dealing with mass transfer into double emulsion drops, it is advantageous to simplify the double emulsion drop to the spherical shell model as shown in Fig. 10. For a motionless double emulsion drop, the subdrops are assumed to form one large coalesced subdrop with the liquid membrane phase forming a spherical shell of thickness δ^* around the encapsulated phase. Stroeve et al.[18,19] have observed that when the double emulsion drops are exposed to shear flow, the subdrops undergo rotary flow inside the deformed double emulsion drop. When rotary flow takes place the assumption of the spherical shell model is still applicable, except that (according to the stagnant film approach of Whitman) the layer thickness would be reduced to a value δ. The spherical shell model has met with success in approximate theoretical modelling of transport processes,[43,44,45] and appears to be a reasonable physical approximation. In the spherical shell model, under flow conditions, the concept of the summation of resistances can be applied. In one simple model, the resistance to mass transfer from the continuous

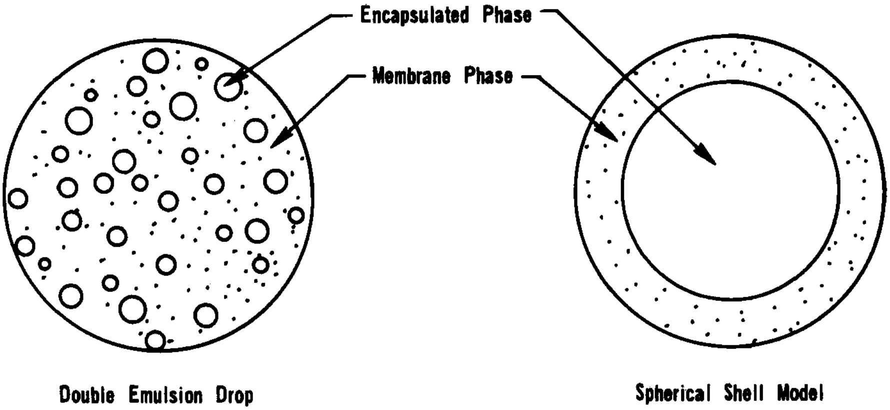
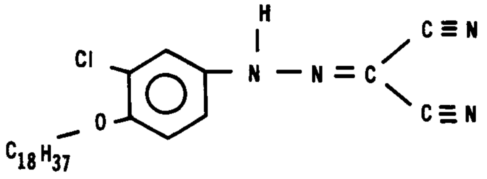


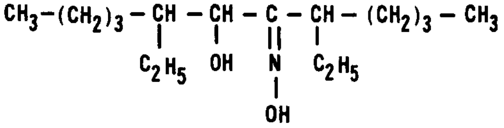
Figure 10: Simple spherical shell model of a double emulsion drop.

phase to the liquid membrane interface is governed by one mass transfer coefficient and the mass transfer from the continuous/ liquid membrane interface into the encapsulated phase by another mass transfer coefficient that is related to the thickness δ. The overall resistance can be measured by monitoring the flux of a passive diffusant into the double emulsion drop.

As mentioned in the introduction, the use of reversible carriers in the liquid membrane phase, with the presence of reactants in the encapsulated phase that irreversibly consume the diffusing species, has made double emulsions desirable as separation systems. Examples of carrier compounds are shown in Fig. 11. Other carriers have been described by Kobuke et al.,[46] Wong et al.,[47] Kopolow et al.,[48] Christensen et al.,[49] Strzelbicki and Bartsch,[50] and Volkel et al.,[51] among others. The first carrier compound shown in Figure 11, p-octadecyloxy-m-chlorophenylhydrazonemesoxalonitrile or OCPH, is known to combine selectively and reversibly with hydrogen ions.[52] The next two compounds have been used extensively in copper ion extraction,[51] and the last compound is known to complex with a variety of cations.[50] It is obvious from Fig. 11 that the selectivity

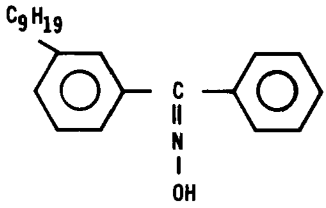


p – octadecyloxy – m – chlorophenyl – hydrazonemesoxalonitrile



$$CH_3-(CH_2)_3-\underset{C_2H_5}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{\underset{OH}{\underset{|}{N}}}{\underset{\|}{C}}-\underset{C_2H_5}{\underset{|}{CH}}-(CH_2)_3-CH_3$$

LIX 63



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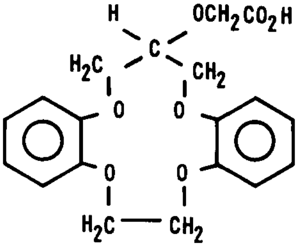
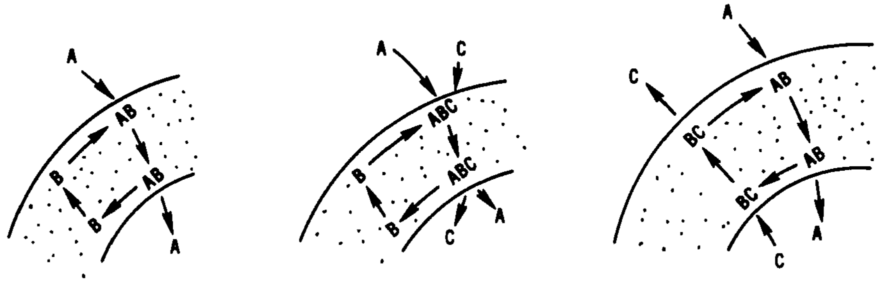


sym – Dibenzo – 13 – crown – 4 – oxyacetic acid

Figure 11: Examples of carrier compounds.

of the carrier compound depends to a large extent on the complexity of its chemical structure.

The introduction of carriers into the liquid membrane offers the possibility of carrier-facilitated transport, co-transport, or counter-transport mechanisms to play a role. Fig. 12 shows schem-



Facilitated Transport **Co – Transport** **Counter – Transport**

Figure 12: Schematic example of facilitated, co- and counter-transport occurring in the liquid membrane.

atic representations of these transport processes occurring in the model of spherical shells for the liquid membranes with thickness δ. It is assumed that the interior concentration of the diffusing species C_A^{δ} is uniform, due to internal mixing and/or rapid irreversible reaction inside the encapsulated phase.

In the case of very rapid reversible chemical reaction rates relative to diffusion rates, the chemical reaction in the liquid membrane phase can be assumed to be at equilibrium. If a mobile carrier B is present within the membrane phase and if the carrier reacts reversibly with the diffusing species

$$A + B \rightleftarrows AB, \qquad K_1 \tag{1}$$

The total transport of A at steady state can be given by[53]

$$J = D_A k_A \left(\frac{C_A^{o} - C_A^{\delta}}{\delta} \right) + D_{AB} \frac{K_1 C_T k_A}{(1 + K_1 k_A C_A^{o})(1 + K_1 k_A C_A^{\delta})} \frac{C_A^{o} - C_A^{\delta}}{\delta} \tag{2}$$

(where the membrane thickness is either δ or δ^*).

Eq. 2 is an example of carrier-facilitated transport. Several assumptions were made in arriving at Eq. 2, including the assumption of equal diffusivities for the carrier and the complex, and that δ is much smaller than the radius (a) of the double emulsion. In the latter assumption, the problem can be simplified by using a planar geometry. A similar simple expression can be obtained for co-transport when, for example, the reaction

$$A + C + B \rightleftarrows ACB, \quad K_2 \tag{3}$$

can be assumed to be at equilibrium. The total flux of solute A at steady state is given by[54]

$$J = D_A k_A \left(\frac{C_A{}^o - C_A{}^\delta}{\delta} \right)$$

$$+ \frac{D_{ABC} K_2 C_T k_A k_C}{(1 + K_2 k_A k_C C_A{}^o C_C{}^o)(1 + K_2 k_A k_C C_A{}^\delta C_C{}^\delta)} \left(\frac{C_A{}^o C_C{}^o - C_A{}^\delta C_C{}^\delta}{\delta} \right) \tag{4}$$

Again the assumptions of equal diffusivity for carrier and complex species, and planar geometry ($\delta << a$) have been made to obtain Eq. 4. For the case of counter transport as shown in Fig. 11 with the reactions[55]

$$A + B \rightleftarrows AB, \quad K_A \tag{5}$$

$$C + B \rightleftarrows CB, \quad K_C \tag{6}$$

the steady-state flux of A is

$$J = D_A k_A \frac{C_A{}^o - C_A{}^\delta}{\delta} + D_{AB} R k_A \frac{C_A{}^o - C_A{}^\delta}{\delta} +$$

$$+ D_{AB} K_C R k_A k_C \frac{C_A{}^o C_C{}^\delta - C_A{}^\delta C_C{}^o}{\delta} \tag{7}$$

where

$$R = \frac{K_A C_T}{(k_A C_A{}^o K_A + k_C C_C{}^o K_C + 1)(k_A C_A{}^\delta K_A + k_C C_C{}^\delta K_C + 1)}$$

and

$$D_B = D_{AB} = D_{CB}$$

The determination of the flux of the species A for facilitated or coupled transport systems is simple if chemical equilibrium can be assumed. In general, these are problems of diffusion with chemical reaction. The flux is obtained by solving the differential mass balances for all species involved in the diffusion process subject to the appropriate boundary conditions. In many diffusion-chemical reaction problems, equilibrium can be safely assumed if the chemical reaction rates are fast relative to diffusion rates. This situation is often encountered with ionic association-dissociation reactions,which are very fast. When chemical reaction rates are slow, the simple equilibrium solutions are not applicable. Also when the liquid membrane film becomes very thin, as for fully packed double emulsion drops or double emulsion drops undergoing shear, the assumption of chemical reaction equilibrium may become tenuous due to large diffusion rates. The more difficult problem of diffusion with non-equilibrium chemical reaction needs then to be considered.

Theoretical difficulties also arise when the geometry is no longer planar and when the unsteady state problem becomes important. Each of these problems will be considered individually. Reference will be made to the case of facilitated transport but the discussion is applicable to coupled transport.

When chemical reaction rates are not many orders of magnitude larger than diffusion rates, the reversible chemical reaction can no longer be assumed to be at equilibrium throughout the liquid membrane. Consider as an example the reaction given by Eq. 1 which for finite reaction rates is

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB, \qquad K_1 = \frac{k_1}{k_2} \tag{8}$$

This reaction is chosen to be illustrative and it is assumed to follow the kinetics suggested by stochiometry. Again the carrier species B and the complex species AB are constrained to remain in the liquid membrane. For the steady state case the overall reaction is globally zero and the problem is to predict the flux of A. The differential mass balances are

$$D_A k_A \frac{d^2C_A}{dx^2} = D_B \frac{d^2C_B}{dx^2} = -D_{AB} \frac{d^2C_{AB}}{dx^2} = k_1 k_A C_A C_B - k_2 C_{AB} \tag{9}$$

The boundary conditions are the imposed concentrations of A at each side of the membrane, and the impermeability to carrier and complex species. Solution of Eq. 9 is simple if chemical reaction equilibrium exists since the left-hand side reduces to the equilibrium relationship. For finite kinetics, the differential mass balances are non-linear and difficult to solve unless approximations are made. In the case of equal diffusivities for the carrier and complex species the total steady state flux of A is

$$J = -D_A k_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} \tag{10}$$

Integration of Eq. 10 between x = 0 and x = δ yields

$$J = D_A k_A \frac{C_A{}^o - C_A{}^\delta}{\delta} + D_{AB} \frac{C_{AB}{}^o - C_{AB}{}^\delta}{\delta} \tag{11}$$

In the case of very fast kinetics or very slow diffusion rates (which is equivalent to thick membranes), the reaction approaches equilibrium. The concentration of the complex species can therefore be related to the concentration of A (expressed here in terms of the aqueous phases: continuous or encapsulated) by using the equilibrium relationship to yield Eq. 2. This equation can be rewritten as

$$J = D_A k_A \frac{C_A{}^o - C_A{}^\delta}{\delta} (1 + F_{eq}) \tag{12}$$

where F is called the facilitation factor. F is a maximum when the reaction is at equilibrium:

$$F = F_{eq} = \frac{D_{AB} C_T K_1}{D_A(1 + K_1 k_A C_A{}^o)(1 + K_1 k_A C_A{}^\delta)} \tag{13}$$

When the reaction deviates from equilibrium within the liquid membrane, the facilitation factor F is less than F_{eq}. An exact solution of Eq. 9 is not possible, but several approximate solutions of high accuracy are available in the literature. It is not the purpose of this article to review developments in non-equilibrium facilitated transport since many excellent treatises are available,[56,57,58,59] but a brief synopsis will be given. Approximate analytical solutions have been given for the two extreme regimes: i) the near-diffusion regime or thin liquid membrane, and ii) the near-equilibrium regime or thick liquid membrane. The usual parameters that distinguish these two regimes are either the Damköhler number, γ, or the modified Thiele modulus, ϕ,

$$\gamma = \phi^2 = \frac{\theta\delta^2}{CD} = \left(\frac{\delta}{\lambda}\right)^2 \tag{14}$$

where θ is the typical reaction rate. The characteristic length is a reaction-diffusion length scale[60] and is given by

$$\lambda = \frac{CD}{\theta} \tag{15}$$

A large Damköhler number characterizes the near-equilibrium regime where the chemical reaction rates are much greater than diffusion rates ("thick film") and the total flux of species A approaches its maximum value corresponding to chemical reaction equilibrium (Eq. 12). A small Damköhler number characterizes the near-diffusion regime ("thin film") where the diffusion rates are much greater than chemical reaction rates. Consequently, in the limit of $\gamma \rightarrow 0$, the facilitation factor F approaches zero (no reaction) and in the limit of $\gamma \rightarrow \infty$ the facilitation factor F approaches F_{eq} (equilibrium reaction). Analytical solutions for Eq. 9 are often given in terms of F and solutions are available for small Damköhler numbers[61,62,63] and large Damköhler numbers.[62,64,65,66,67] The steady state flux of A is then given simply by

$$J = D_A k_A \frac{C_A{}^o - C_A{}^\delta}{\delta} (1 + F) \tag{16}$$

However, the intermediate range of Damköhler numbers is often important and the above solutions for F are then not capable of giving accurate predictions.

Recently Hoofd and Kreuzer[68,69,70] presented a new solution consisting of the sum of the separate solutions for both thin and thick membranes. Hoofd and Kreuzer called the two separate solutions the "small Damköhler number solution" and the "large Damköhler number solution". Their new solution is known as the "combined Damköhler number solution", and they have shown that it can give accurate predictions of the facilitation factor over the whole range of Damköhler numbers ($0 \leq \gamma \leq \infty$). The solution is algebraically relatively simple so that with its accuracy it is the method of choice for reaction-diffusion problems. As yet it has not been applied to non-equilibrium situations of co- or counter-transport, nor to liquid membrane separations in general.

The combined Damköhler number solution can be derived for the case of the reaction given by Eq. 8. The variation of the concentration of species A is given by

$$k_A C_A = e(C_B) + f(x) \tag{17}$$

where e is the carrier-dependent part and f(x) is the position-dependent part. The function f serves as a correction for the large Damköhler number solution, and it is solved over the entire thickness of the membrane. The function e is solved as if f = 0, and f is solved for the condition near the boundaries, where

$$\frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \qquad \text{for } x = 0,\delta \tag{17}$$

since the carrier is constrained to remain in the membrane. The solutions for e and f are of the form

$$e(C_B) = \frac{k_2 C_{AB}}{k_1 C_B} \tag{18}$$

$$f(x) = -\frac{J\lambda}{D_A} \frac{\sinh\left(\left(\frac{1}{2}\delta - x\right)/\lambda\right)}{\cosh\left(\frac{1}{2}\delta/\lambda\right)} \tag{19}$$

where

$$\frac{1}{\lambda^2} = \frac{k_1 C_B}{D_A} + \frac{k_2}{D_{AB}} + \frac{k_2 C_{AB}}{D_B C_B} \tag{20}$$

The flux is given by Eq. 11. For each situation of fixed concentrations C_A^o and C_A^δ, a unique solution for Eqs. 17 through 20 and Eq. 11 exists, which can be found by a trial-and-error solution. It is obvious that when J is known, the facilitation factor can be obtained from Eq. 16.

Most of the solutions for non-equilibrium-facilitated transport have been given for planar geometry, and consequently facilitation factors are for flat membranes. Double emulsions are spherical instagnant media and ellipsoidal when distorted by uniform shear. When the liquid membrane thickness, δ or δ^*, becomes significant relative to drop radius, a, the appropriate geometry has to be taken into account. Stroeve and Eagle,[71] who considered the problem of facilitated transport in heterogeneous media, have given non-equilibrium facilitation factors for reactive spheres and cylinders placed in a field of unidirectional flux. The technique of single-point linearization[72] was used to obtain the facilitation factors. Since the spheres and cylinders were in a field of unidirectional flux, the species concentrations at the surfaces of these shapes are not uniform. For double emulsions, the drops experience a uniform concentration C_A^o, which therefore gives rise to a different boundary condition. Noble[73] has analyzed the problem of shape factors for spherical and cylindrical liquid membranes. A reaction of the form given by Eq. 8 was considered for reaction equilibrium and the near-diffusion regime. Hoofd and Kreuzer[70] have applied the combined Damköhler technique to the case of a vesicle embedded in a continuum with uniform distribution of species A. The vesicle geometry was analogous to the spherical shell model for a double emulsion drop. The reaction considered to occur in the spherical shell was of the form

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \tag{21}$$

An example of this reaction is where species B is produced by binding of A to a very abundant mobile carrier. Species B cannot diffuse through the boundaries of the membrane. An irreversible reaction occurred inside the encapsulated phase so that C_A could be taken as constant. For spherical geometry, and the reaction given by Eq. 21, Eq. 17 becomes

$$k_A C_A = e(C_B) + f(r) \tag{22}$$

Solutions for e and f were given by Hoofd and Kreuzer as

$$e(C_B) = \frac{k_2}{k_1} C_B \tag{23}$$

$$f(r) = \frac{1}{r}\left(A_1 e^{r/\lambda} + A_2 e^{-r/\lambda}\right) \tag{24}$$

with

$$\lambda = \left(\frac{k_2}{D_B} + \frac{k_1}{D_A}\right)^{-\frac{1}{2}}$$

The constants A_1 and A_2 are integration constants. The concentrations of the carrier and complex species in the liquid membrane are

$$k_A C_A = k_2\left\{A_3 + \frac{A_4}{r}\right\} + \frac{k_1 \lambda^2}{D_A} f(r) \tag{26}$$

$$C_B = k_1\left\{A_3 + \frac{A_4}{r} - \frac{\lambda^2}{D_B} f(r)\right\} \tag{27}$$

where A_3 and A_4 are again integration constants which are determined by the boundary conditions associated with the problem. Since C_A and C_B are known the flux can be calculated.

Recently Hoofd[74] has also solved the problem for the reaction given by Eq. 8 occurring in the spherical shell exposed to a uniform concentration C_A^{∞} at $r = \infty$. The situation is schematically depicted in Figure 13, Species A arrives at the continuous phase/liquid membrane interface by diffusion. The species is consumed inside the encapsulated phase so that $C_A^{\delta} = 0$ (note: δ or δ^* is equal to R_2 minus R_1). The solutions for e and λ are identical to Eqs. 18 and 20, while the solution for f is

$$f(r) = \frac{J}{D_A}\,\frac{\sinh\left(\frac{R_2 - r}{\lambda}\right) + \sinh\left(\frac{r - R_1}{\lambda}\right) - \frac{R_2}{\lambda}\cosh\left(\frac{R_2 - r}{\lambda}\right) + \frac{R_1}{\lambda}\cosh\left(\frac{r - R_1}{\lambda}\right)}{\left\{\frac{\delta^*}{\lambda}\cosh\frac{\delta^*}{\lambda} + \left(\frac{R_1R_2}{\lambda^2} - 1\right)\sinh\frac{\delta^*}{\lambda}\right\} r} \tag{28}$$

The total steady state flux of A is obtained from

$$D_A k_A C_A + D_{AB} C_{AB} = A_1 - \frac{J}{r} \tag{29}$$

where A_1 is an integration constant. The problem is now reduced to finding boundary values for C_A and C_{AB} so that $C_A^{\delta} = 0$ at $r = R_1$, $C_A^{o} = C_A^{\infty} - J/D_A{*}R_2$ at $r = R_2$, and the mean value of $C_B + C_{AB}$ is equal to C_T. Presumably the same approach as described by Hoofd can be taken if the continuous phase is stirred. The mass transfer rate of A arriving at the spherical shell is then governed by the mass transfer coefficient on the continuous phase side. If internal rotation takes place inside the drop the thickness δ^* is substituted by δ which is related to the internal mass transfer coefficient in the liquid membrane. Such theoretical studies have not yet been conducted and they need experimental verification.

Folkner and Noble[75] have considered the transient response of facilitated transport membrane. The transient flux of the permeant spe-

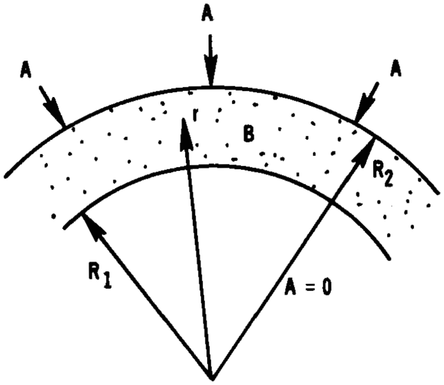


Figure 13: Schematic diagram of one-dimensional spherical coordinates for facilitated transport.

cies was determined for flat plate, spherical, and cylindrical geometries. The reaction scheme given by Eq. 8 was considered. Computer solutions of the differential mass balances were obtained and the flux J and facilitation factor F determined from the concentration profiles. The facilitation factor F was plotted as a function of time and the Damköhler number. Use of the charts allows for the determination of the time to reach the steady state value of F when the boundary conditions remain fixed. At present no analytical solutions are available to predict unsteady facilitated transport in liquid membrane systems.

SUMMARY

In the last decade considerable information has been obtained on transport processes in unsupported liquid membranes. However, the use of double emulsions as separation systems in industrial processes will require that additional fundamental studies be made on the transport characteristics of these systems. In particular, theoretical models on the hydrodynamic stability of double emulsion drops to viscous and inertial forces are lacking. Experimental data are necessary to confirm the use of such models for predictive applications in mixing equipment. Mass transport processes for flat supported membranes are reasonably well understood. For double emulsion separation systems the influence of stirring rates, volume fraction of subdrops, the kinetics of the irreversible reaction, interfacial tension and viscosity parameters on transport in the presence of chemical reactions is not known. Some authors contend that the stagnant liquid membrane film was the controlling resistance to mass transfer in their studies.[44] Nor is it known if the conclusion applies generally to all systems. Approximate values for the thickness of the liquid membrane have been given[45,76] but these values are probably applicable only to the particular double emulsion systems studied. Most of the studies have assumed that chemical equilibrium existed for the reversible chemical reactions in the liquid membrane phase. Although this assumption is often valid for ionic association-dissociation reactions, non-equilibrium effects may be very important in other reaction systems. The combined Damköhler technique appears to be most promising in the application to the problems in transport with chemical reaction in double emulsion separation systems.

NOMENCLATURE

A_i	Constants of integration (i = 1 to 4)
a	Radius of double emulsion drop $a = R_2$
C	Concentration
C_A	Concentration of species A expressed relative to an aqueous phase, i.e. the continuous and the encapsulated phases
C_T	Total carrier-plus-complex concentration in the liquid membrane
D	Diffusivity of species in the liquid membrane
D_A^*	Diffusivity of species A in the continuous phase
e	Carrier-dependent function
F	Facilitation factor

F_{eq}	Equilibrium facilitation factor
f	Position-dependent function
G	Shear rate
J	Flux of species A
K_1	Equilibrium constant for chemical reaction
K_2	Equilibrium constant for chemical reaction
K_A	Equilibrium constant for chemical reaction
K_C	Equilibrium constant for chemical reaction
k_A	Equilibrium distribution coefficient for species A between liquid membrane phase and aqueous phase (continuous or encapsulated): $k_A = \left.\frac{C_A \text{ (liquid membrane)}}{C_A \text{ (aqueous phase)}}\right\|_{\text{equilibrium}}$
k_C	Equilibrium distribution coefficient for species C
k_1	Forward kinetic rate constant
k_2	Backward kinetic rate constant
p	Viscosity ratio of dispersed phase to continuous phase
R	Function defined below equation 7
R_1	Radius of single subdrop of coalesced encapsulated phase, or radius of internal region which is assumed to be well-mixed due to rotary flow.
R_2	Radius of double emulsion drop
r	Radial coordinate
x	Cartesian coordinate

Greek Symbols

γ	Damköhler number
δ	Thickness of hypothetical liquid membrane film adjacent to interface

δ^*	Thickness of liquid membrane film $\delta^* = R_2 - R_1$
ε	Ratio of applied viscous force to surface tension force, or breakup parameter, $\varepsilon = (G\mu_c a)/\sigma$
ε_B	Breakup parameter for drop to burst
ξ	Ratio of moles of tracer species in the continuous phase to the total amount initially in the encapsulated phase (due to liquid membrane breakage)
θ	Reaction rate
λ	Characteristic length or reaction-diffusion length scale
μ_c	Viscosity of the continuous phase
μ_d	Viscosity of the dispersed phase
$\bar{\mu}_d$	Apparent viscosity of the W/O emulsion
σ	Interfacial tension between continuous phase and liquid membrane phase

Subscripts

A	Species A
AB	Species AB
B	Species B
BC	Species BC
C	Species C (expressed relative to an aqueous phase)

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