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COMMUNICATION

Stabilizing Emulsion Liquid Membranes

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ABSTRACT

A novel method of stabilizing emulsions used in liquid membrane extractors is considered. The method is based on modification and control of the rheological properties of the organic membrane phase. Data presented are used to compare the proposed method with traditional emulsion liquid membranes stabilized by surfactants. The proposed technique is shown to have similar rates of extraction with the advantage of easy and reversible stabilization and destabilization of the membrane for recovery of the internal phase and thus has potential advantages. The rheological properties of the stabilized membrane investigated are shown to be affected during the production of the emulsion, possibly due to the production of a fine stable dispersion of the internal phase in the membrane phase. Thus careful design of the mixing vessel is required to increase the stability of the membrane to ensure the membrane material can be reused.

INTRODUCTION

Nearly twenty years have passed since the first use of surfactant-stabilized liquid membranes were reported (1); during this period several pilot plants for the recovery of uranium, copper, chromium, mercury, and zinc (1–5) have demonstrated the technical feasibility of this process. The process consists of forming an emulsion of small aqueous droplets, the internal phase, in an organic liquid, the membrane phase. This emulsion is usually stabilized by the addition of surfactants, such as Span 80 for exam-

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ple. The surfactants' charge stabilizes the emulsion, and as a result a thermodynamically stable emulsion can be formed. The emulsion is then dispersed in a second aqueous phase, the external phase (refer to Fig. 1). The conditions of the internal and external phase are adjusted to promote transfer of the desired solute from the external phase to the internal phase or vice versa. The process can be made selective by the addition of phase-transfer catalyst to the membrane phase, and a significant increase in the concentration of the solute can be obtained because the ratio of the external phase to the internal phase is usually of the order of ten to one; such a phase ratio is difficult to achieve in a mixer-settler without recycle.

The addition of surfactant required to stabilize the emulsion have, in some cases, been found to influence the rate of mass transfer (6), and requires complex or expensive destabilization processes such as electrostatic coalescence (7). In addition, the surfactant has a finite solubility in the external aqueous phase, which can result in significant losses of surfactant to the process.

In this paper an alternative method of stabilizing the emulsion is proposed based on a modification of the rheological properties of the membrane phase. This will not produce a thermodynamically stable emulsion but will slow the drainage of the film between coalescing drops and so increase the stability of the membrane. Thus this mechanism is fundamentally different from the surfactant-stabilized systems. This has the advantage that the rheological properties are temperature sensitive and so relatively small changes in temperature can be used to stabilize and destabilize the emulsion; further, as none of the additives are soluble in the aqueous

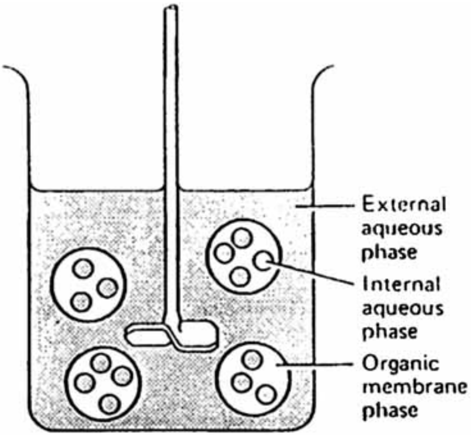

FIG. 1 Schematic diagram of liquid membrane extraction processes.

phase, the membrane could in principle be reused. The aim of this work is to compare the performance of the surfactant-stabilized membrane systems with the membrane stabilization system proposed herein.

Rheology of the Membrane Phase

The proposed membrane relies on a marked reduction in the coalescence rate of droplets in a viscoelastic fluid as the degree of elasticity is increased, as observed by Dekee et al. (8). One possible explanation of this is that the coalescence process is controlled by film drainage which is essentially a contracting or squeezing flow. The apparent viscosity of viscoelastic fluids is much greater in contracting flow than in shearing flow, thus the rate of coalescence is significantly reduced in comparison with a Newtonian fluid of similar steady-shear viscosity.

The rate of diffusion in Newtonian fluids is inversely proportional to the viscosity to the power 0.6. However, for elastic fluids Metzner (9) reported that the rate of diffusion is proportional to the solvent viscosity, in this case kerosene and Hyvis, and only slightly influenced by the addition of the polymer such as polyisobutylene, which imparts the elasticity. Wickramasinghe et al. (10) showed a slight increase in the rate of diffusion as the extent of elasticity is increased. Thus in the design of the membrane phase there is a need to keep the solvent viscosity low to ensure that high mass transfer rates are maintained and to maximize the amount of dissolved polymer to increase the degree of elasticity and so stabilize the emulsion. The membrane used in this investigation was composed of 0.2% polyisobutylene (PIB) supplied by Exxon (Vistanex MMl-140, MWT = 1.5×10^6) dissolved in 10% Shellsol 2046, supplied by the Shell Chemical Co. (kerosene) and 89.8% HYVIS 3 supplied by BP Chemicals (polybutene). The rheological properties of the membrane are presented in Table 1. The data in Table 1 were obtained by mixing the membrane and

TABLE 1
Rheological Properties of the Membrane Phase

PIB content (%)	Mixing time (min)	Temperature (°C)	Steady shear viscosity (Pa·S)	Normal stress coefficient (Pa·S^2)
0.2	0	21	1.86	0.224
0.2	30	21	1.33	0.0093
0.2	60	21	1.29	0.0093
0.0	0	21	1.15	0.0
0.0	20	21	0.88	0.0

internal phase for the specified time. The resultant emulsion was then heated to destabilize it, and then the membrane phase was separated and its rheological properties measured.

Most of the change in the elastic nature of the material, as measured by the normal stress coefficient, occurs within the first few minutes of mixing, as shown in Table 1; however, the steady shear viscosity continues to decline as the fluid is sheared. It was this feature that made it impossible to reuse this particular membrane for further extraction. This reduction in the viscosity is due to the formation of a very fine and stable dispersion of the aqueous phase in the organic membrane phase. Improved design of the mixing vessels could overcome this limitation, allowing the membrane to be reused.

EXPERIMENTAL

A set of extraction experiments were carried out with the membrane described above under conditions as close as possible to those described by Hochhauser and Cussler (11), using membranes stabilized by surfactants to permit a comparison of the relative performance of the two stabilization techniques. See Table 2.

In these experiments the membrane phase forms a barrier to bulk flow but allows transfer of chromium and hydrogen ions between an external acidic solution containing chromium and the internal basic solution, as shown in Fig. 1. The mechanism of transport across the membrane is shown in Fig. 2, and was described by Hochhauser and Cussler (11). In summary, a molecule of chromic acid forms a complex with two molecules of tertiary amine according to Eq. (1).

$$\underset{\substack{\text{external}\\ \text{phase}}}{H_2Cr_2O_7} + \underset{\substack{\text{membrane}\\ \text{phase}}}{2[CH_3(CH_2)_{11}]_3N} \leftrightharpoons \underset{\substack{\text{membrane}\\ \text{phase}}}{\text{Complex}} \qquad (1)$$

The complex diffuses through the organic membrane and reacts with the excess hydroxyl groups in the internal phase, releasing the chromate ion into the internal phase and the amine to diffuse back according to Eq. (2).

$$\underset{\substack{\text{membrane}\\ \text{phase}}}{\text{Complex}} + \underset{\substack{\text{internal}\\ \text{phase}}}{4OH} \leftrightharpoons \underset{\substack{\text{internal}\\ \text{phase}}}{3H_2O + 2CrO_4^{2-}} + \underset{\substack{\text{membrane}\\ \text{phase}}}{2[CH_3(CH_2)_{11}]_3N} \qquad (2)$$

The net result is a flux of hydrogen ions and chromium ions from the external phase across the membrane to the internal phase. This is driven by the difference in hydrogen ion concentration between the internal and external phases.

TABLE 2
Experimental Conditions for the Extraction of Chromium

	Present system	Hochhauser and Cussler (11)
Initial chromium concentration ($C_{eA,0}$)	0.000962 N $K_2Cr_2O_7$ (100 ppm Cr^{6+})	100 ppm Cr^{6+}
Initial NaOH concentration ($C_{ir,0}$)	0.25 N	0.20 N
pH in the external phase (adjusted with H_2SO_4)	1.6	1.6
Initial volume of external phase ($V_{i,0}$)	40 mL	—
Volume of membrane phase (V_m)	100 mL	—
Initial volume of external phase ($V_{e,0}$)	400 mL	—
Emulsion $[V_{i,0}/(V_m + V_{i,0})]$	0.286	0.286
Treat ratio $[V_{e,0}/(v_m + V_{i,0})]$	2.86	2.86
Complexing carrier	0.05 M Alamine 336	2% tridodecylamine
Liquid membrane	89.8% HYVIS 3	2% sorbitan monooleate (SPAN 80)
	10% Shellsol 2046	19% hexachloro butadiene
	0.2% PIB	75% polybutadiene (viscosity = 0.184 Pa·s)
Temperature	20–24°C (unless indicated otherwise)	Ambient

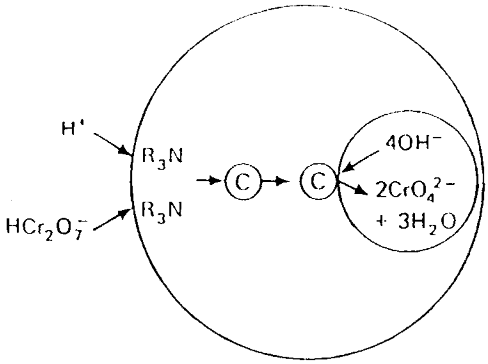

FIG. 2 Mechanism for chromium transport from the external phase across the liquid membrane to the internal phase.

The mass transfer performance of the proposed membranes was determined from the following experiments. The internal phase was added to the membrane phase and mixed at 250 rpm for 5 minutes in a 1-L beaker. The mixing rate was increased to 600 rpm for 30 minutes, resulting in the internal phase being dispersed in the membrane phase with a mean drop size of 0.5 mm. The extraction was started by the addition of the external phase. The mixing rate was kept constant at 100 rpm throughout the run. During the run the external phase was sampled, and at the end of the run the emulsion was decanted and placed in a water bath at 50°C with gentle agitation to enhance phase disengagement. The volumes of the internal and membrane phases were noted, and the concentration of chromium was measured by atomic adsorption spectrophotometry. The results are presented in Fig. 3.

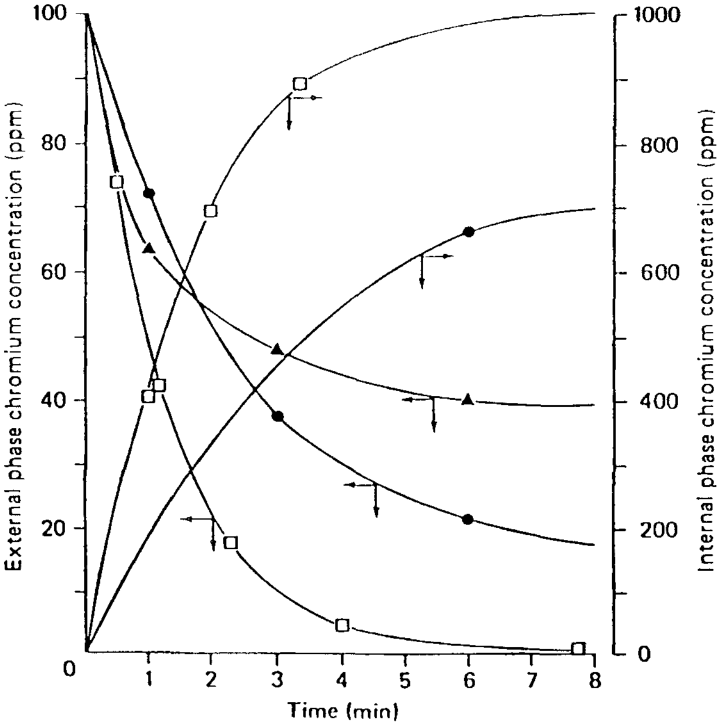

FIG. 3 Concentration in the internal and external phases as a function of time. (□) Surfactant-stabilized membrane (11); (●) rheological-stabilized membrane (0.2% PIB); (▲) inelastic viscous membrane (0.0% PIB).

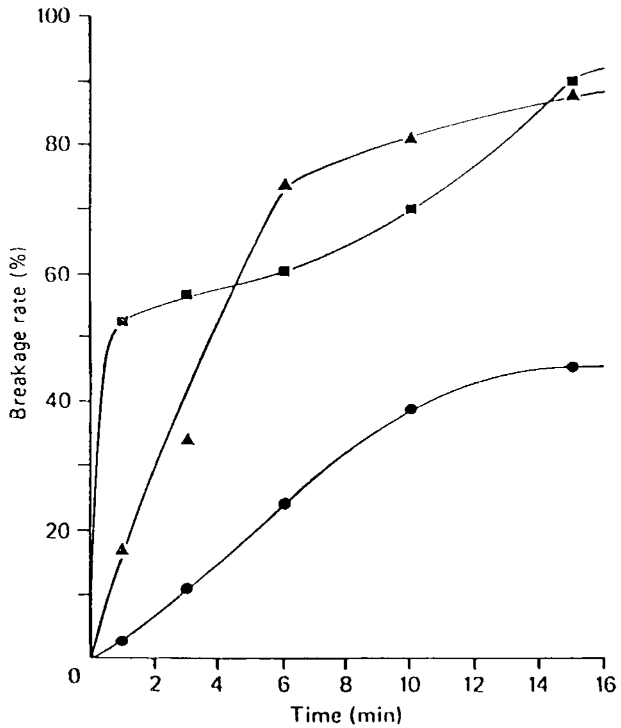

FIG. 4 Liquid membrane breakage rates. (■) No stabilization; (▲) 0.2% PIB at 50°C; (●) 0.2% PIB at 20°C.

The stability of the membrane was determined by coloring the internal phase with methylene blue, which is insoluble in the membrane phase, and performing the experiments as described above without the addition of chromium. By measuring the concentration of methylene blue in the external phase as a function of time, the stability of the membrane or the breakage rate was determined. The results are presented in Fig. 4.

DISCUSSION

A comparison of the rate of extraction using the proposed elastic membranes with surfactant-stabilized membranes is shown in Fig. 3. For example, after 6 minutes, 80% of the chromium was extracted from the external phase using the current membranes compared with 97% reported by Hochhauser and Cussler (11). This can be compared with the case of an inelastic viscous liquid membrane where 60% of the chromium is extracted after 6 minutes (Fig. 3). Thus there is a significant increase in the amount of material extracted in the case of the elastic membrane. The reduced extraction rate relative to the surfactant-stabilized membrane is primarily due to the lower stability of the particular membrane tested (refer to Fig. 4). It is envisaged that with improved design of the liquid membrane a range of stabilities could be obtained depending on the requirements of the process.

Destabilization of the membrane was easily carried out at 50°C where 75% of the internal phase was disengaged after 6 minutes and 90% after 14 minutes. The membrane stability is controlled by the degree of elasticity and the steady shear viscosity, both of which are temperature-sensitive. As the temperature is increased, the viscosity and elasticity are decreased, thus reducing the stability of the membrane as shown in Fig. 4. To increase the membrane stability it is necessary to increase the elasticity as an increase in steady shear viscosity will increase the resistance to mass transfer through the film. However, increasing the elasticity beyond the level proposed greatly hinders the dispersion of internal phase in the membrane and reduces the area available for mass transfer unless the stirring rate is increased, when more energy is required for drop breakup. No attempt was made to optimize the hydrodynamic conditions during the emulsion formation or the extraction. The conditions were kept as close as possible to those reported by Hochhauser and Cussler (11) for comparison purposes. This resulted in a larger drop-size distribution with drops up to 1 mm in diameter, compared to 1 to 10 μm (12) for surfactant-stabilized membranes, and contributes significantly to the reduced stability of the proposed membranes as the larger droplets would tend to settle out of the emulsion faster. In order to achieve a more stable emulsion it would be necessary to control the drop-size distribution and to reduce the mean size to the range 1 to 10 μm. Under the conditions of the experiments, the membrane material could not be reused, probably because of the large drop-size range produced in the initial emulsion formation. The smaller drops, less than 0.1 μm, did not settle out during the destabilization process, causing a change in composition of the recycled membrane and a consequent reduction in apparent viscosity and elasticity. Better control of drop size in the emulsion would overcome this problem.

CONCLUSIONS

It has been shown that a viscoelastic fluid can be used to form a stable emulsion for use in the liquid membrane extraction process and obtain rates of extraction comparable to surfactant-stabilized processes. These membranes have the advantage that emulsion stabilization is controlled by temperature, and thus forming and breaking the emulsion is an easily reversible process, unlike the traditional surfactant-stabilized process. Control of the drop size of the internal phase was found to be vitally important in the overall performance of the process.

NOTATION

$C_{eA,0}$	initial concentration of solute A in the external phase
$C_{ir,0}$	initial concentration of the reagent in the internal phase
$V_{e,0}$	initial total volume of the external phase
$V_{i,0}$	initial total volume of the internal phase
V_m	total volume of the membrane phase

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