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

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To cite this Article Abou-Nemeh, I. and Van Peteghem, A. P.(1994) 'Membrane Aging and Related Phenomena in Liquid Surfactant Membranes Process', Separation Science and Technology, 29: 6, 727 — 741

To link to this Article: DOI: 10.1080/01496399408005605

URL: http://dx.doi.org/10.1080/01496399408005605

SEPARATION SCIENCE AND TECHNOLOGY, 29(6), pp. 727–741, 1994

Membrane Aging and Related Phenomena in Liquid Surfactant Membranes Process

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ABSTRACT

The membrane aging phenomenon and its influences on the kinetics of cobalt(II) permeation by the liquid surfactant membranes (LSM) process has been studied. The experimental results showed that the emulsion formulated from the internal aqueous phase and the membrane (organic phase) of a certain age has far-reaching consequences on the kinetics of metal extraction and emulsion stability. The investigations have revealed that there exists an optimal age and composition of the membrane in which the highest extraction (synergism) and the lowest emulsion swelling are achieved. Analytical and instrumental examinations of the membrane phase during aging have shown various chemical and physical changes as a result of the surfactant decomposition, reaction products precipitation and self-association, and macroemulsion formation.

INTRODUCTION

Membrane separation processes, including reverse osmosis and electrodialysis, are now being used on an industrial scale. The liquid surfactant membranes (LSM) process, which was originally developed in the late sixties by Li (1) for hydrocarbons separation, has been hailed to have the potential to solve a number of challenging separation problems. For example, removing phenols and amines from wastewater (2, 3), and differ-

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ent metallic species such as copper (4–6), cobalt (7, 8), zinc (9–11), lanthanides (12), and uranium (13–15) from industrial, leaching, and mining waters. Despite the successful attempts to apply this process on an industrial scale (16), emulsion stability remains the major question among many others to be solved. No solution is visible in the near future.

Up till now, aging phenomenon has not been considered as a significant factor in emulsion stability. However, for many commercial emulsion products, tests (centrifugation, freezing, etc.) are systematically carried out to check their stability and lifetime, and the results are correlated to a certain lifetime of emulsion stability.

Aging of the interfacial film has been studied by a few researchers. Sherman (17) utilized a surface viscometer to study the interfacial film properties of sorbitan sesquioleate in a mineral oil/water interface for 2.5 and 10% of the surfactant solution. He observed an increase in the apparent interfacial viscosity, reaching a maximum followed by a gradual fall to a constant level. However, this maximum was shifted toward shorter aging times as the amount of the surfactant was increased to reach 170 and 120 hours, respectively. Moreover, the higher the surfactant concentration, the faster its approach to the culminating value of the interfacial viscosity. Criddle and Meader (18), in analogical attempts, measured the interfacial viscosity of sorbitan monooleate in mineral oil solution/water and observed a rapid development of the interfacial film for higher concentrations of the surfactant.

Summarizing previous research, it can be seen that none of the authors mentioned earlier has investigated the aging mechanism in the presence of an extractant in the oil phase. Therefore, it is difficult to extrapolate their interfacial findings to LSM because all commercial extractants are of an amphipathic nature which is responsible for their tendency to adsorb at the oil/water interface and, thus, to alter the interfacial viscosity and elasticity properties of the interfacial film, and hence, the emulsion stability.

Therefore, the results reported here deal with the membrane aging effect on the kinetics of metal permeation, water transport, the combined effect of the membrane composition by tri-*n*-butyl phosphate (TBP) variation, and aging on the extraction efficiency.

EXPERIMENTAL

Emulsification Unit and Procedure

The emulsion used for metals permeation and water transfer study was formulated by adding the internal aqueous phase reagent (2 M H_2SO_4)

dropwise to the membrane (organic phase) of a certain age. The membrane contained 5.5 vol% bis(2-ethylhexyl) phosphoric acid (D2EHPA) of 98.6 or 97% purity (Lot 31291608 purchased from Johnson Matthey Ltd. or Ventron GMBH, respectively) and 3 vol% Span 80 (Lot V-3106, kindly supplied by ICI Essen, Germany). Tri-*n*-butyl phosphate (TBP) of 99 or 97% purity purchased from Aldrich or Union Chimique Belge (UCB), respectively, was added; its concentration varied from 0.5 to 2.7 vol%. A paraffinic and isoparaffinic kerosene (Shellsol T) purchased from Shell-Belgium was used as a matrix of the membrane. All chemicals were used without further purification or treatment. This mixture was stirred vigorously in an ultraspeed homogenizer (Ultra-Turrax T-45) laboratory type for 10 minutes total mixing time. The stirring was conducted at a fixed impeller speed of 10,000 min^{-1}. Cooling of the emulsion was maintained during emulsification to avoid heating up the mixture due to the high-shearing stress.

Permeation Unit and Procedure

Cobalt cation (Co^{2+}) from acetate solution was chosen as a model metallic contamination of a real wastewater (19). In this manner, $Co(CH_3COO)_2 \cdot 4H_2O$, a reagent-grade compound purchased from Union Chimique Belge (UCB), was dissolved in distilled water. The initial pH (see Table 1) of the solution was adjusted by adding acetic acid of 99.4% purity.

The permeation experiments were carried out in a cylindrical bench-scale reactor with an active volume of 0.7 L (19, 20). The internal construction resembles a compartment of an Old–Shue–Rushton column. The dimensions (diameter, height, distribution, thickness, width, material, etc.) of the buffles and the impeller blades were designed to meet the requirements of polydispersed systems. The advantage of such construction is to avoid the "creaming phenomenon" and ensure homogeneous distribution of the emulsion globules in the agitated vessel. Additionally, the reactor was maintained with temperature and pH sensors interfaced to a microprocessor WTW 3000 pH-meter type for continuous measuring of the raffinate temperature and acidity. Moreover, a sampling port was installed inside the reactor and connected to the sampling system developed at the Laboratory for Non-Ferrous Metallurgy (LNFM) (20). Mixing of the emulsion and the feed was performed by an Ika-Ruhr-Werke RW-20 stirrer at a fixed impeller speed of 250 min^{-1} and was controlled by a digital Speed Counter RW-20 DZM1 type. The reaction zone was thermostated, and the temperature was maintained at 20°C and regulated to within ±0.1°C.

TABLE 1
Operating Conditions for Permeation Experiments

Parameter	Value
Emulsification:	
Membrane Composition (vol%):	
1. D2EHPA	5.5
2. Span 80	3.0
3. TBP	0–3
4. Shellsol T	Remainder
Internal aqueous phase	2 M H_2SO_4
Stirring speed (emulsion preparation)	10,000 min^{-1}
Total stirring time	10 minutes
Emulsion volume	70 mL
Phase ratio (membrane/internal aqueous phase)	2/1
Metal extraction:	
Temperature	20°C
Mixing speed	250 min^{-1}
Treat ratio (emulsion/feed)	1/5 mL/mL
Feed volume	350 mL
Feed initial pH	2.9–3.1
Emulsion flow rate	7 mL/min
Cobalt initial concentration	1.0–1.1 g/L
Acetic acid concentration	2.4–2.6 M
Emulsion residence time	20–60 minutes
ac electric field strength	1250 V/cm
Frequency range	900 Hz

Permeation Experiment

Emulsion prepared in this manner was fed to the reactor already filled with the treated solution by means of a membrane pump (Prominent E type). A fixed treat ratio (the emulsion volume to that of the feed) of 1/5 has been applied throughout this study. During metal permeation, the profile of the raffinate was traced by analyzing samples periodically withdrawn from the reactor. Early samples were diluted by means of an electronic diluter Hamilton Micro Lab.1000 and analyzed for metal contents by means of an atomic absorption spectrophotometer of Perkin-Elmer type. The concentration of cobalt in the internal aqueous and the membrane after emulsion splitting in an electric field was also determined.

RESULTS AND DISCUSSION

The extraction efficiency is defined as the ratio of cobalt concentration at time *t* to its initial one substracted from unity. This can be represented by

$$\text{Extraction (\%)} = (1 - C_{e,t}/C_{e,0}) \times 100 \quad (1)$$

The experimental results displayed in Figs. 1, 2, 5, and 6 were reproduced in triplicate, and the points represent average values.

TBP Effect on Cobalt Extraction

The commercial use of organophosphorous compounds such as TBP or tri-*n*-octyl phosphine oxide (TOPO) is reflected in raw material processing and nuclear fuel reprocessing. In the LSM process the application of TBP or TOPO has always been in combination with an ion-exchanger; otherwise, the coupled mechanism of mass transport is not satisfied. In this manner, Bock et al. (13), Hayworth et al. (14), and Yoo et al. (15) applied the extracting mixture D2EHPA and TOPO for uranium extraction. Abou-Nemeh and Van Peteghem (8, 19, 21) recently used D2EHPA and TBP extensively for different metals permeations from simulated and industrial effluents. It is well known that by the use of D2EHPA in combination with TBP or TOPO under well-defined experimental conditions, enhanced extraction for a number of metals can be obtained.

A series of experimental runs was conducted in this manner to elucidate the effect of TBP addition to the membrane phase containing D2EHPA on the kinetics of cobalt extraction. The TBP concentration range was scanned from 0 to 2 vol%. As seen in Fig. 1, the metal uptake is decisively better for the membrane containing TBP within the concentration range from 0.5 to 0.75 vol% than that without TBP. However, any increase beyond 0.75 vol% results in a drastic inhibition in metal permeation. For the 1.6–2 vol% range of TBP concentration, a dominant emulsion instability is observed. The steadily increasing linear part of the curves is a typical symptom of emulsion breakage in LSM. These findings are consistent with previous ones (22) where the kinetics of emulsion breakage upon using TBP for metals extraction has revealed excessive emulsion destabilization and a leaking out of the internal aqueous phase to the external phase. To evaluate the extent of leakage, the tracer technique (22) was used. The emulsion breakage constant (k_b) was estimated from the modified breakage model proposed by Boyadzhiev et al. (23), which can be represented by

$$d\beta/dt = -k_b(1 - \beta) \quad (2)$$

where

$$\beta = C_{iT,e}V_{e,t}/C_{iT,0}V_{i,0} \quad (3)$$

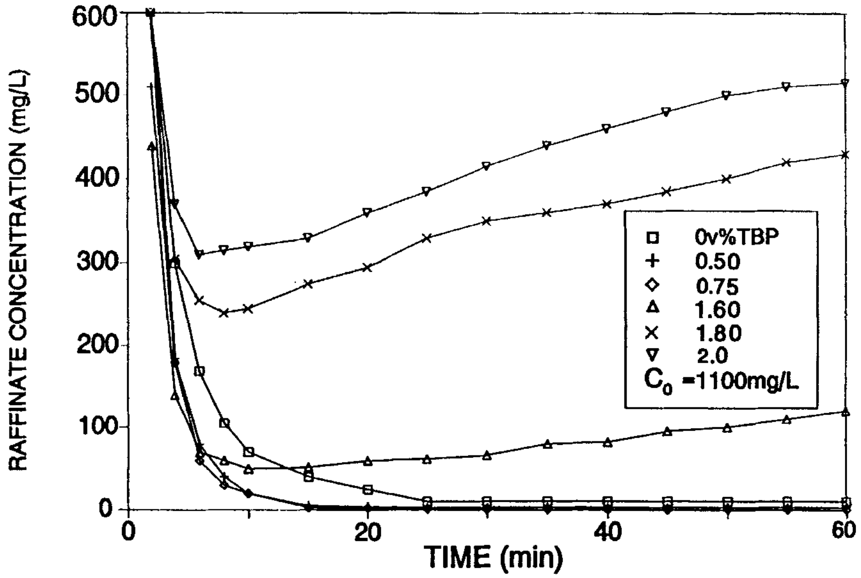

FIG. 1 The effect of TBP addition on the kinetics of cobalt permeation (initial feed pH = 3.1; fresh membrane).

The estimated breakage constant was almost doubled [from (4.18 ± 0.1) × 10^{-5} to (7.64 ± 0.53) × 10^{-5} s^{-1}] for the membrane without and with 4 vol% TBP, respectively. This fact might be sound justification for the relatively high concentration of surfactant (5 vol% Span 80) used by Yoo et al. (15) to stabilize the emulsion used for uranium extraction.

Synergism Identification

The enhancement of metal extraction from aqueous solutions by a mixture of an acidic extractant (D2EHPA) and a neutral organophosphorous compound (TBP), the extraction being better than by either constituent alone, is called synergism (24). However, above a certain concentration of the ester, synergism no longer exists and, as a result, antisynergism is obtained.

The extraction of divalent metals by dimerized acidic organophosphorous compounds can be represented by (25):

$$M^{2+} + nH_2X_2 \rightleftarrows M(HX_2)_2(H_2X_2)_{n-2} + 2H^+ \qquad (4)$$

The experimental results of cobalt permeation by the combined mixture (D2EHPA + TBP) for a wide range of TBP concentrations are depicted in Fig. 2. The results clearly indicate the presence of metal extraction enhancement of more than 4% for a 0.75 vol% TBP concentration in the membrane phase. However, on further TBP addition, inhibition in the metal uptake was observed. The previous phenomenon was identified with synergism, while the latter was identified with antagonism, which is the result of an excessive interaction between TBP (S) and D2EHPA (HX) through hydrogen bonding. This can be represented by the following reactions (26–28):

$$(HX)_2 + 2S \rightleftarrows 2HX{\cdot}S \tag{5}$$

$$HX + S \rightleftarrows HX{\cdot}S \tag{6}$$

$$HX + 2S \rightleftarrows HX{\cdot}S_2 \tag{7}$$

$$(HX)_2 + S \rightleftarrows (HX)_2{\cdot}S \tag{8}$$

These associates are believed to be relatively strong and stable. Such interactions will compete with the "free" acidic extractant molecule for the metallic cation and, as a result, exert an inhibiting effect on metal extraction.

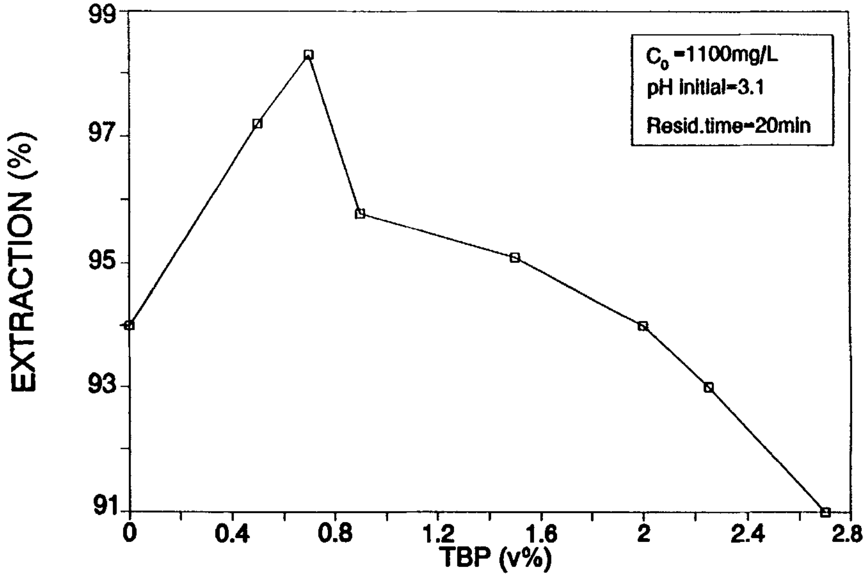

FIG. 2 The synergic effect of TBP addition on cobalt permeation.

Chemical and Physical Characterization of the Membrane

Water Analysis

The chemical and physical nature of the membrane phase is rather complicated due to the continuous dynamic change and the formation of a multiphase system in the membrane itself. The chemical composition of the organic phase, which consists of Span 80, D2EHPA, TBP, water, and kerosene, is rather impure. The water is mainly from Span 80 and partially from TBP. Water concentration in the organic phase was determined by the Carl-Fisher technique. Its concentration was estimated to be 0.015–0.017 M for the membrane compositions investigated.

Microscopical Investigations

During membrane aging, a change in the physical appearance from a transparent amber color to a misty turbid one was observed after 30 minutes. Moreover, the rate of change was faster the higher the concentration of D2EHPA and TBP. This process was continued and traced for several days and even to weeks for some samples. After 4 days a clear separation of phases was obtained. Samples were withdrawn to analyze the chemical and physical compositions of both phases. A microscope (Ultraphot II Carl Zeiss type) with a high resolving power was used; a sample between two glass plates was magnified 1000 times. The investigations revealed a macroemulsion and solid precipitate formation in the membrane phase as shown in Fig. 3.

Infrared Spectral Analysis

Infrared instrumental analysis of the membrane showed the existence of sorbitol alongside the other membrane components. Samples were systematically withdrawn for 55 hours from two flasks containing aged membranes of different compositions. The infrared spectra of the carbonyl group (C═O) are shown in Fig. 4. This peak, which appears at wavenumber 1750 cm^{-1}, is characteristic for esters, and therefore was traced versus time. As can be seen from this figure, a diminishing tendency in the size of the carbonyl group peak was observed for both membrane compositions. This suggests the disappearance of ester during aging according to the following equation:

$$\mathrm{R'COOR_{(o)}} + \mathrm{H_2O} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{R'OH_{(s)}} + \mathrm{RCOOH_{(o)}} \tag{9}$$

It was reported earlier by Abou-Nemeh and Van Peteghem (29) that the kinetics of ester decomposition is faster for a membrane without TBP than with TBP.

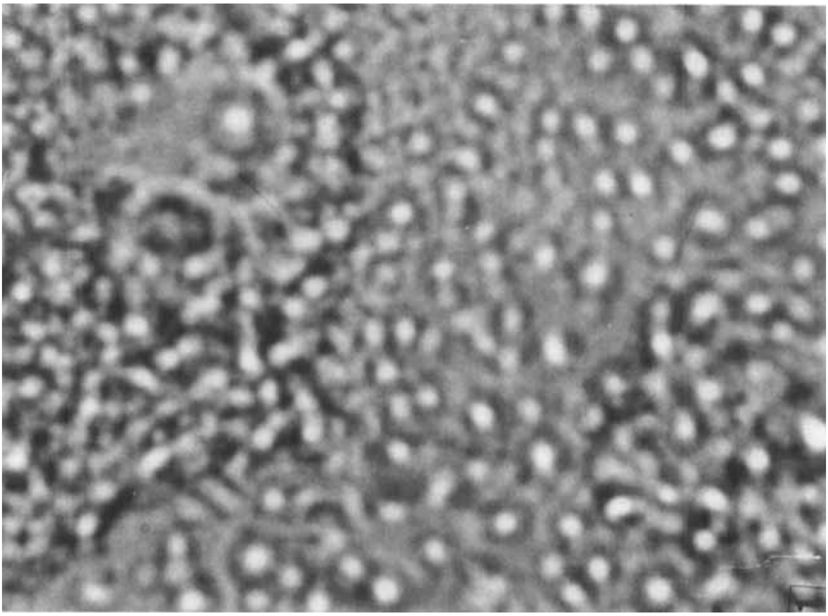

FIG. 3 Microphotograph (1000×) of the macroemulsion and sorbitol formed in the membrane phase during membrane aging.

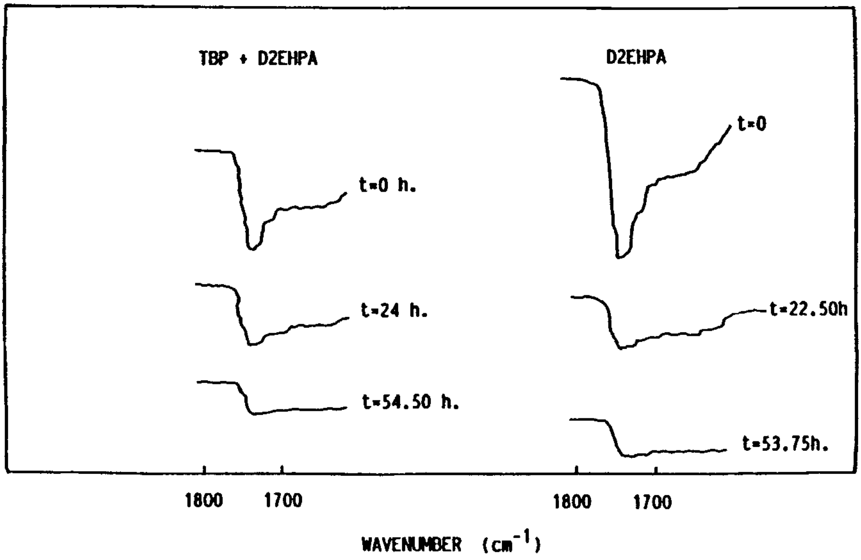

FIG. 4 Infrared spectra of the carbonyl group of Span 80 esters during membrane aging. Membrane composition: 5.5 vol% D2EHPA and/without 1 vol% TBP, 3 vol% Span 80, and *n*-decane. Thin film on NaCl.

Oleic Acid and D2EHPA Identification

To reveal the identity of the second decomposition product, i.e., oleic acid, the potentiometric titration technique (29) has been extensively applied to trace the presence of acids in the membrane. The titrant (sodium ethoxide) was prepared by dissolving reagent-grade sodium hydroxide in absolute ethanol. Samples of the membrane were added to acetone as a medium. Two well defined peaks representing D2EHPA and oleic acid were observed. Oleic acid was found to be strongly self-associated, and the degree of self-association was determined to be from 3.5 to 1.5 for a wide range of oleic acid concentrations from 0.003 to 0.013 M, respectively.

Summarizing previous thoughts, it can be seen that apart from molecular interactions between TBP and D2EHPA and the formation of various associates (see Eqs. 5–8), surfactant hydrolysis due to the presence of D2EHPA, sorbitol precipitation (a strongly hydrophilic product in a hydrophobic medium), macroemulsion formation, microemulsion, and oleic acid self-association are significant additional factors which, to a great extent, affect the nature of the interfacial film and, thus, emulsion performance and stability.

Estimation of Water Transport

The volume of the water transferred at the end of the trial was estimated from the mass balance of the solute (cobalt). This can be represented by

$$V_{e,0}(C_{e,0} - C_{e,t}) = V_{i,t}(C_{i,t} - C_{i,0}) + V_m(C_{m,t} - C_{m,0}) \qquad (10)$$

However, this approach is only valid under the following conditions.

1. No water accumulation in the organic phase. Thus, the water is entirely transferred to the internal aqueous phase. Consequently, the volume of the membrane is constant: V_m = constant.

2. Cobalt concentration in the membrane phase is practically negligible. This has been experimentally verified because the membrane contained almost no solute (0.5–1.5 ppm) after 60 minutes residence time, and thus $C_{m,t} = 0$.

3. The emulsion breakage is relatively small. This has also been verified, and the rate constant of breakage (k_b) was found to be in the range from 1.42×10^{-5} to $4.16 \times 10^{-5}\ s^{-1}$ for TBP concentrations from 0.5 to 2 vol%, respectively.

Therefore, the internal phase leakage will not significantly affect the real amount of transported water. The initial conditions of cobalt are as follows:

$$\text{at } t = 0,\ C_{i,0} = C_{m,0};\ C_e = C_{e,0} \qquad (11)$$

which implies that no cobalt was present in the internal aqueous phase and the membrane at $t = 0$. Solving for $V_{i,t}$ from Eq. (10) yields

$$V_{i,t} = V_{e,0}[(C_{e,0} - C_{e,t})/C_i, t] \tag{12}$$

and hence, the volume of transferred water is

$$V_t = V_{i,t} - V_{i,0} \tag{13}$$

To check the mass balance of water in the system, the final volume of the emulsion and the feed was measured, and hence:

$$V_t = V_{e,0} - V_{e,t} \tag{14}$$

$$V_t = V_{em,t} - V_{em,0} \tag{15}$$

Membrane Aging and Composition Effect on Osmosis

A series of experimental runs was carried out to investigate the impact of membrane age on water transfer, and thus the emulsion swelling due to osmosis. The main principle relies on emulsifying the membrane of a certain shelf-life with the internal aqueous phase. Such an emulsion was used for metal permeation experiments and water transport evaluation. The experimental results of water transport for a spectrum of TBP concentrations and a wide range of ages are presented in Fig. 5. As can be seen

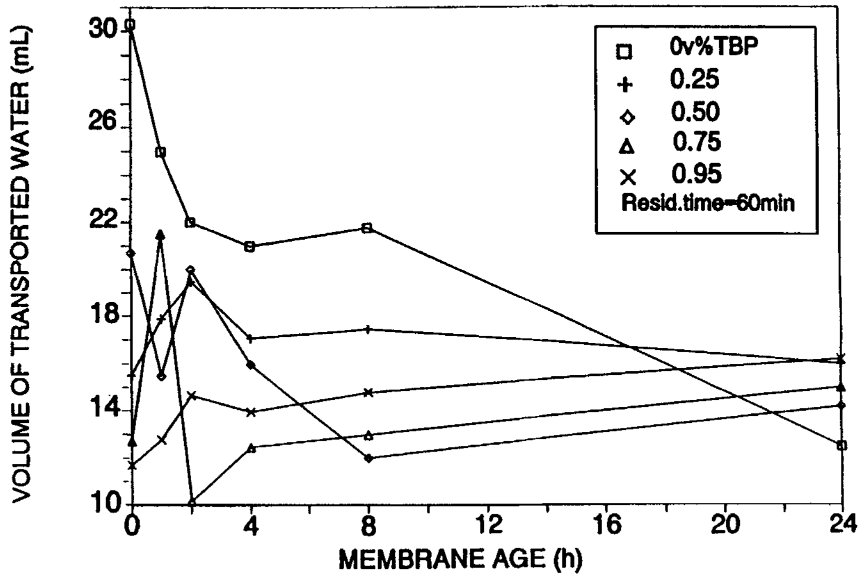

FIG. 5 The influence of membrane aging and composition on water transfer (initial feed pH = 2.9).

from this figure, the presence of TBP in the membrane phase dramatically influences water transport, particularly for short membrane ages. The highest emulsion swelling (nearly 130%) of the initial internal phase ($V_{i,0}$ = 23.3 mL) was observed for a freshly prepared emulsion of the membrane without TBP. This tendency continued for even longer ages; however, the older the membrane, the lower the water transport. The most characteristic feature in Fig. 5 is the effect of TBP on osmosis. At 2 hours, all the curves except those for 0 and 0.75 vol% TBP show a local maximum and a steady increase in emulsion swelling for longer ages. On the other hand, the membrane containing 0.75 vol% TBP shows the lowest water transfer. After 24 hours, almost no effect of TBP on osmosis was observed. All compositions of the membrane show a "leveling off" effect of emulsion swelling. This fact suggests the attainment of a dynamic equilibrium of interactions between the different species in the membrane phase. Moreover, despite the shear applied later to emulsify the aged organic phase, some of the molecular associates or self-associates seem to be stable enough so that the shearing forces have a minor effect on the molecular structure of the monolayer interfacial film.

TBP and Membrane Aging Effects on Metal Extraction

The other aspect within the scope of this study is the effect of membrane aging and its composition (by varying the TBP content) on the kinetics

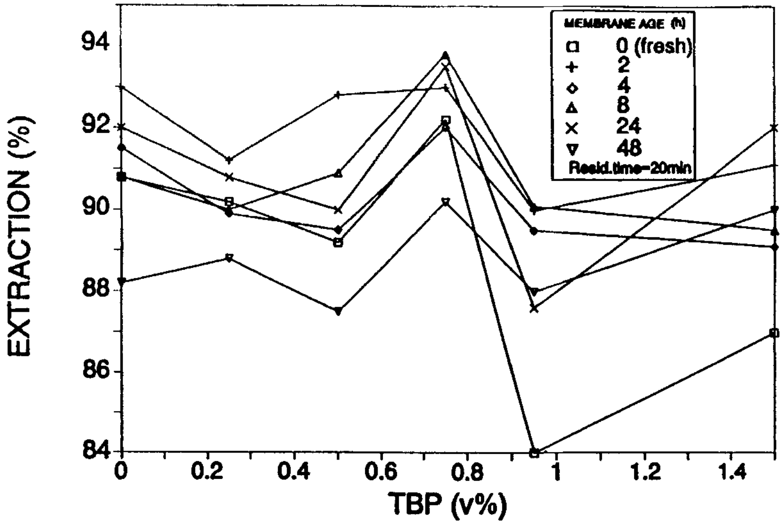

FIG. 6 The effect of TBP on cobalt extraction for different membrane ages (initial feed pH = 2.9).

of cobalt permeation. The extraction percentage of cobalt as a function of TBP concentration for various aging times is shown in Fig. 6. As can be seen, the most characteristic feature is the maximum at 0.75 vol% TBP regardless of the age of the organic phase. For 0.25 and 0.5 vol% TBP in the membrane, there is a declining tendency in metal extraction for all ages of the membrane except at 2 hours. Moreover, any further increase in TBP results in a sharp peak in metal permeation for 0.75 vol% TBP. Nonetheless, when the TBP concentration reached 0.95 vol%, a steep decline in metal uptake was observed, particularly for a fresh membrane. This decline was partially eliminated when more TBP was added. The other interesting phenomenon is that the highest extraction of cobalt was noted when the membrane was 2 hours old, regardless of the membrane composition.

CONCLUSIONS

In this study the experimental results of the aging phenomenon of the membrane phase and its composition on water transfer and metal extraction have been presented. The following conclusions can be drawn.

1. It has been found that there exists an optimal membrane composition (0.75 vol% TBP + 5.5 vol% D2EHPA) at which a maximum of cobalt extraction is achieved. However, any increase in TBP beyond this concentration results in excessive emulsion breakage and instability.
2. An optimal membrane age of 2 hours has been found to enhance the kinetics of metal permeation compared with a fresh one.
3. The optimal composition of a membrane was found to inhibit water transport, and the lowest emulsion swelling was noted for a membrane of 2 hours age.
4. Water transport decreased with the age of a membrane, and particularly for a membrane without TBP. All membrane compositions show nearly the same water transport value at a membrane age of 24 hours.
5. A membrane without TBP has enhanced water transfer. It was the highest regardless of membrane age.
6. During membrane aging, the surfactant undergoes hydrolysis and one of the reaction products, sorbitol, which is strongly hydrophilic, precipitates from the hydrophobic medium. The other product, oleic acid, forms self-associates.

These results leave little doubt about the complexity and importance of the phenomenon and its consequences for the LSM process, particularly when membrane storage and recycling become economic and technological necessities.

SYMBOLS

$C_{e,0}$, $C_{e,t}$	initial cobalt concentration and at time t in the feed, respectively (mol/L)
$C_{i,0}$, $C_{i,t}$	initial cobalt concentration and at time t in the internal aqueous phase, respectively (mol/L)
$C_{m,0}$, $C_{m,t}$	initial cobalt concentration and at time t in the membrane phase, respectively (mol/L)
$C_{iT,0}$	initial tracer (lithium sulfate) concentration in the internal aqueous phase (mol/L)
$C_{iT,e}$	tracer concentration in the external phase (feed) (mol/L)
$E\%$	extraction percentage
k_b	breakage rate constant (s^{-1})
$V_{e,0}$	initial feed volume (L)
$V_{e,t}$	feed volume at time t (L)
$V_{em,0}$, $V_{em,t}$	initial volume of the emulsion and at time t, respectively (L)
$V_{i,0}$, $V_{i,t}$	initial volume of the internal aqueous phase and at time t, respectively (L)
V_m	volume of the membrane phase (L)
V_t	volume of transported water to the internal aqueous phase (L)

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Received by editor August 31, 1992
Revised June 30, 1993