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Study of the Stability of W/O/W-Type Emulsion During the Extraction of Nickel via Emulsion Liquid Membrane

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ABSTRACT

Considerable effort has been directed toward describing the analysis of mass-transfer resistance for solute diffusion and reaction in an emulsion liquid membrane (ELM) system but very little attention has been paid to the loss of extraction efficiency often encountered in these systems due to rupture of the emulsion globules. In the present work, batch extraction of nickel(II) with ELM from a dilute sulfate solution by using di-(2-ethylhexyl) phosphoric acid (D2EHPA) as an extractant and hydrochloric acid as a stripping agent is reported. However, separation efficiency

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significantly decreases with breakage of the liquid membrane. Important variables affecting the stability of the emulsion, such as pH of the feed phase, speed of agitation, emulsion drops size per unit specific interfacial area, surfactant concentration, pH in inner aqueous phase, and the presence of different tracers, are systematically investigated during the extraction of nickel(II) ions.

Key Words: Emulsion liquid membrane; Nickel(II); Di-(2-ethylhexyl) phosphoric acid; Water-in-oil-in-water.

INTRODUCTION

A variety of separation problems have been investigated over the last two decades by using the emulsion liquid membrane (ELM) process. Compared with conventional processes, the ELM process has certainly some attractive features, e.g., simple operation, high efficiency of extraction and stripping in one stage, larger interfacial area, and scope of continuous operation.

Electroplating is one of the important processes involved in surface finishing and metal deposition for better life of articles and for decoration. Nickel, copper, and chromium are the three most commonly used metals for electroplating. Thus, the wastewater of such industries contains nickel(II). To date, there are numerous published works on the separation of nickel(II)[1–5] ions in the ELM process. An important problem in the practical application of the ELM process is the stability of the liquid membranes. The instability of liquid membrane leads to breakage and, hence, unselective release of already separated compounds. The swelling of a membrane is due to the transport of water from the aqueous feed phase to the aqueous strip phase. The swelling ultimately results in breakage of the membrane. So it is important to obtain information about the swelling, the breakup, and the coalescence of dispersed drops[6] in the success of the ELM process. However, it seems difficult to extract precise information about the breakup or the coalescence for the system in which both inner and outer water phases are distilled water.[7]

Since their development in 1968 ELM have shown tremendous promise in a wide variety of industrial separations. But the problem that inhibits the application of this technology in industrial equipment is the loss of extraction efficiencies that often occur in these systems due to a lack of stability of the emulsion globules.

Stability of double emulsions is generally understood as the resistance of the individual globules against coalescence. The breakdown of water-in--oil-in-water (W/O/W) type globule dispersions is described through several possible mechanisms,[8] which include: (i) coalescence of the internal aqueous droplets into larger internal droplets; (ii) coalescence of the emulsion globules suspended in the external continuous phase; (iii) expulsion of the internal droplets after rupture of the thin membrane film during interaction of the internal and the external continuous phases; and (iv) swelling or contraction due to water permeation through the oil membrane by diffusion in the case of W/O/W emulsion. Hou and Papadopoulos[8] microscopically studied the stability of a single W/O/W globule and found that under all experimental conditions that produced limited stability, the internal water droplets did not coalesce among themselves, and when the globule broke, it was because the internal water droplets coalesced with the external phase. Therefore, mechanism (iii) described above may be considered to be the most appropriate mechanism of breakdown of double emulsion globules. Kita et al.[9] measure the stability of multiple phase emulsion using viscometric method. Goto et al.[10] and Kasaini et al.[11] used the tracer technique to study emulsion stability. Wan et al.[12] studied the effect of carrier concentration on the stability of liquid membranes for extraction of phenol. The main drawback of the above studies is their limited applicability as they are useful only to the specific conditions under which the experiments were performed. Hou and Papadopoulos[8] have studied on stability of W/O/W types by bringing the internal water droplets in contact with each other and with the external interface between water and oil. Bandyopadhyaya et al.[13] have considered globule–globule interaction and leakage on batch extraction, utilising ELMs.

Skelland and Meng[14] found that conversion of membrane phase to suitable non-Newtonian will increase the stability of ELM without reducing the permeability of it. Osmotic swelling and leakage behavior of globules have been studied by Yan and Pal[15] and Wan and Zhang.[16] The osmotic swelling behavior of W/O/W-type ELMs has been investigated by Yan and Pal[15] by using an optical microscope equipped with a camera by creating a concentration difference of D-glucose between the internal and external aqueous phases. The concepts of apparent and actual swelling are proposed by Wan and Zhang[16] to illustrate the relationship between the emulsion swelling and membrane breakage.

There still exists some scope for better insight into swelling and breakage determination study during the recovery of metal ions from wastewater by the ELM process. In this paper, the important variables affecting the swelling and breakage of the ELM system, including pH of the feed phase, speed of agitation, emulsion drops size per unit specific interfacial area, surfactant concentration, pH in inner aqueous phase, and the presence of different tracers are systematically investigated during the extraction of nickel(II) ions.

Chemistry and Mechanism of Nickel(II) Solvent Extraction by Using ELM

The equations given below show the extraction and stripping reactions of nickel(II) occurring in the ELM process, where RH represents the protanated form of an extractant, which is used as carrier [di-(2-ethylhexyl) phosphoric acid (D2EHPA), in this study]. The carrier D2EHPA is known to dimerize in non-polar aliphatic solvents.
Formation of the complex:

$$\mathrm{Ni^{2+} + 2(HR)_2 = NiR_2(HR)_2 + 2H^+} \tag{1}$$

Stripping reaction:

$$\mathrm{NiR_2(HR)_2 + 2H^+ = Ni^{2+} + 2(HR)_2} \tag{2}$$

Equation (1) represents the complexation reaction, which occurs at the membrane–external phase interface, while Eq. (2) shows stripping at the membrane–internal aqueous phase interface. The overall reaction represents an ion exchange of nickel(II) for two hydrogen ions. A schematic presentation of the liquid membrane globule and simultaneous extraction and stripping mechanism in ELMs is exhibited in Fig. 1.

EXPERIMENTAL PROCEDURE

Chemicals

Simulated Feed

For the transport study of nickel(II) ions through the ELM, nickel sulfate (99.99% pure, Emerk make (Merck, Mumbai, India) was used.

Commercial kerosene of specific gravity 0.798 and boiling point range 145°C to 250°C was used as the membrane phase. The extractant used was di-(2-ethylhexyl) phosphoric acid, which is commercially known as D2EHPA [CAS No. 298-07-7], having 98.5% purity, Span 80 (Sorbitan mono-oleate) containing O_2 based moleties was used as the surfactant, *n*-heptane was used as a diluent or stabilizer for the membrane phase, and NaAc–HAc was used as a buffer (to maintain pH) for all the experiment.

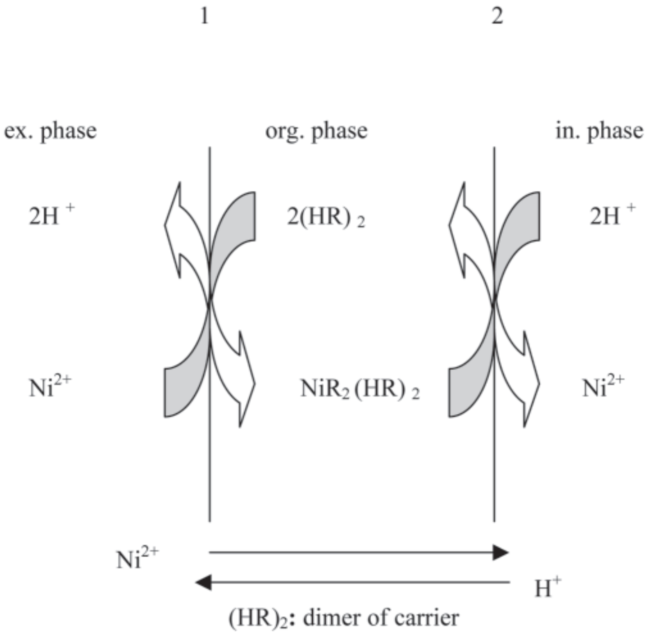

Figure 1. Simultaneous extraction and stripping mechanism in ELMs.

Apparatus and Procedure

Emulsion was prepared by emulsifying an aqueous solution of acid (strip phase) with an organic phase (membrane phase). The membrane consisted of varying proportions of non-ionic surfactant Span 80, a carrier reagent D2EHPA, and diluent (*n*-heptane). The mixer was stirred at 5000 rpm for 15 min by using a homogenizer (six-blade turbine impeller of 30-mm diameter) to form a uniform mixture. Then, the internal strip phase was added. The contents again were simultaneously stirred at 5000 rpm for 15 min. An excellent milky-white and stable emulsion was obtained. The emulsion was dispersed in the feed phase containing nickel ions from which nickel was to be extracted.

A six-blade paddle impeller of 50-mm diameter rotating at 400 rpm was used for stirring. For measuring speed of the agitator and homogenizer, a hand tachometer having a range of 0–10,000 rpm had been used.

Samples of about 5 mL were withdrawn from the extractor at different intervals of time and were filtered through a sintered glass plug to separate the emulsion and the aqueous feed phase. Samples of about 5 mL were withdrawn from the extractor at 1-min interval up to a total time period of 8 min, and, for breakage experiment, it continued for 20 min. It has been found from the previous studies[17] that emulsion swelling occurred at the start of a run and continued to progress with time, and the maximum extraction occurred, in most cases of the ELM process, within 8–10 min.

A tracer technique was used to study swelling and breakage of the emulsion. It involved determining the quantity of tracer, leaking out of the inner dispersed droplets into the continuous phase due to the breakup of emulsion drops. The tracers used were red dye solution, NaCl, NaSCN, and $CuSO_4$. Their concentrations in the continuous phase were being analyzed. All experimental runs were conducted at $25^\circ C \pm 0.5^\circ C$.

Analysis

Samples of aqueous feed phase, containing nickel (after extraction) and red dye solution (tracer, due to leakage of the emulsion), have been analyzed. Analysis of nickel(II) ion and the red dye solution is conducted by a spectrophotometer (CE1020, 1000 series manufactured by CECIL, U.K.). Analysis of nickel(II) ions had been carried out according to the standard methods.[18]

Samples of aqueous phase, containing NaCl, NaSCN, and $CuSO_4$ (tracers) had been analyzed on a conductivity meter (Orion, USA).

RESULTS AND DISCUSSION

Separation of Nickel(II) by ELMs

In earlier studies, we conducted[4,5,19,20] batch extraction of nickel(II) ions from an aqueous solution by ELM with D2EHPA as an extractant, sorbitan mono-oleate (Span 80) as a surfactant, kerosene as a membrane phase, and hydrochloric acid as a stripping solution (Table 1). A series of experiments was conducted to find out the effects of the initial solute (nickel) concentration in feed phase, the internal reagent concentration, the treat ratio, and the volume fraction of the internal phase on the extraction of nickel(II). The model had been derived from the advancing front model of Ho et al.[21] and neglected the external-phase mass-transfer resistance and the effect of membrane breakage. The rate of the solute diffusion in emulsion globules can be described based on the advancing front model in dimensionless form, following the work of Chakraboty et al.[4,19]

Table 1. Summary of experimental conditions for ELMs batch tests.

Membrane phase (oil)	
Volume	25 mL
Carrier (D2EHPA)	10% V/V
Diluent (*n*-heptane)	5% V/V
Surfactant Span 80	5% V/V
Kerosene	80% V/V
Exterior phase (water)	
Volume	450 mL
Ni(II)	100–300 ppm
pH	3.5
Buffer (NaAc–HAc)	0.05 mol/L
Interior phase (water)	
Volume	25 mL
Acidity	1 N (HCl)

Note: For preparation of aqueous solutions double-distilled water was used.

The material balances for the solute in the membrane phase:

$$\frac{\partial g}{\partial \tau} = \frac{1}{(1-\phi)\eta^2}\frac{\partial}{\partial \eta}\left(\eta^2 \frac{\partial g}{\partial \eta}\right) \quad \text{at } (\chi < \eta < 1,\ \tau > 0) \tag{3}$$

$$\tau = 0, \quad g = 0, \quad (\eta \le 1) \tag{4}$$

$$\eta = \chi, \quad g = 0, \quad (\tau \ge 0) \tag{5}$$

$$\eta = 1 \quad \text{then } g = C_D h \quad \text{at } (\tau = 0) \tag{6}$$

The material balance equation in the external phase:

$$\frac{dh}{d\tau} = -E \frac{\partial g}{\partial \eta}\Big|_{\eta=1} \tag{7}$$

$$\tau = 0, \quad h = 1 \tag{8}$$

The material balance equation at the reaction front is as follows:

$$-\frac{d\chi}{d\tau} = \frac{1}{\phi m}\frac{\partial g}{\partial \eta}\Big|_{\eta=\chi} \tag{9}$$

$$\tau = 0, \quad \chi = 1 \tag{10}$$

The coupled Eqs. (3), (7), and (9) have been solved by numerical computation with an implicit finite difference technique. A central difference scheme had been used for integration along the dimensionless radial distance. The grid sizes in τ and χ directions had been chosen by trial and error to obtain good convergence. To calculate dimensionless time [$\tau = (D_e^t/R^2)$], the value of effective diffusivity of the D2EHPA–Nickel complex in the membrane phase was determined by the correlation of Willke and Chang,[22] Jefferson and Witzell[23] and was found to be $0.7832 \times 10^{-10}\,\mathrm{m^2/sec}$. The sauter mean diameter was found to be 0.1 cm.[24]

It is found, from Fig. 2, that the fraction of solute [nickel(II)] extracted (at pH 3.5) is higher with a lower initial external phase solute concentration. This is due to a higher distribution coefficient for a lower initial external phase solute concentration. As leakage of the internal phase to the external phase was not considered in the advancing front model, Fig. 2 shows that initially experimental and simulated data are superimposing but along with the time deviation is observed due to this leakage problem only. Membrane breakage starts initially and continues to progress with time. For the variation of other parameters, i.e., internal reagent concentration, treat ratio, and volume fraction of internal phase, the same trend has been observed.[4]

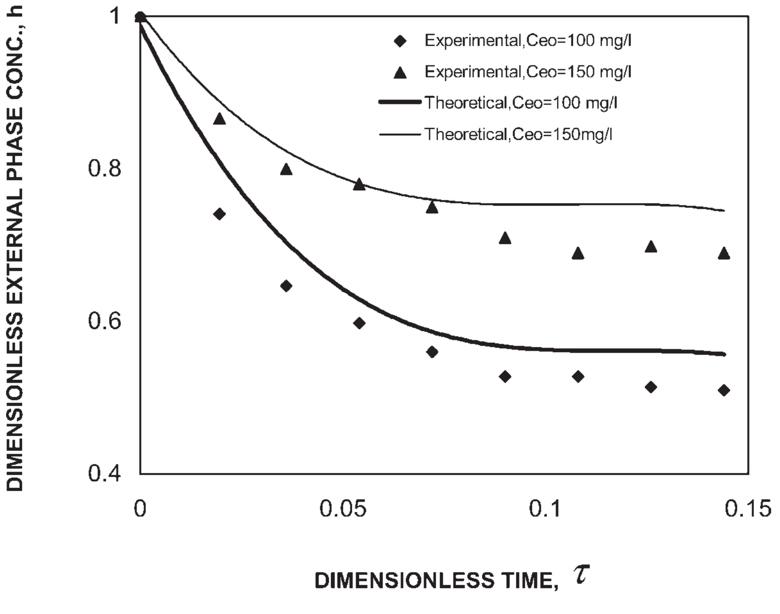

Figure 2. Variation of external phase nickel ion concentration with initial external phase nickel concentration.

Stability of an Emulsion Drop

Breakage

The breakage/leakage due to swelling of internal phase was estimated by using the following formula:

$$\%\text{breakage} = \frac{C_{\mathrm{e,f}} V_{\mathrm{e,f}}}{C_{\mathrm{i,o}} V_{\mathrm{i,o}}} \times 100$$

Measuring the tracers concentration in the external and internal phase at time *t* and 0, we can easily calculate %breakage of the emulsion. Figures 3–8 are plotted as %breakage vs. different parameters, which are responsible for the water transport to the internal phase, causing it to increase the breakage by making the emulsion increasingly unstable.

Effect of pH

In a series of our experiments with various external phase pH, the values of %breakage are varied according to the Fig. 3. From Fig. 3, it is found that

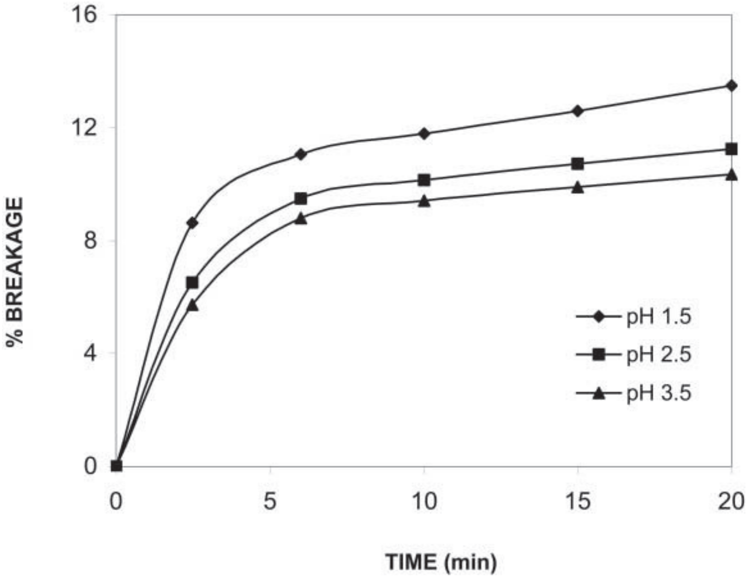

Figure 3. Effect of external phase pH on membrane breakage.

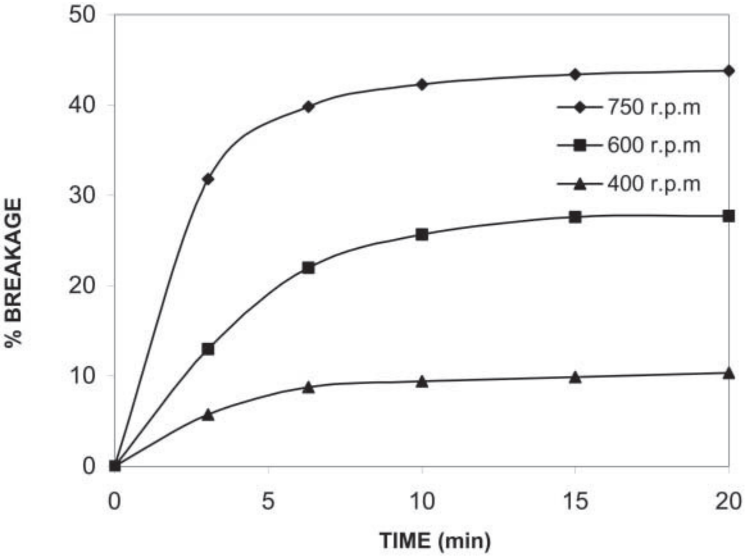

Figure 4. Effect of agitation on membrane breakage.

ELM is less stable at pH 1.5 than with pH 2.5 and 3.5. Hydrolysis of Span 80 will actually be responsible for this emulsion breakage. It has been reported by Nemeh and Peteghem[25] that Span 80, which is a mixture of different esters (mono-, di-, tri-, and tetra-oleate; oleic acid; and sorbitol) is chemically unstable and undergoes the reaction of hydrolysis in moderate acidic and basic media. It is observed that at pH 1.5, the rate of Span 80 hydrolysis is faster than that at pH 2.5 and 3.5. In view of the practical applications of liquid membrane separation by using the W/O/W-emulsion system, the %breakages of emulsion are measured over a wide range of pH not only when using the red dye solution as a tracer but also when using copper sulfate, sodium thiocyanate, and sodium chloride as tracers. In all other remaining experiments, external feed phase pH are maintained at 3.5.

Effect of Agitation

It is observed from the graph that %breakage has a positive correlation with degree of agitation. Such breakage of membranes does not result from the direct impact of agitation. This result may be explained on the basis of the fact that at a high stirrer speed, the hydrodynamic force exceeds the surface tension force and, thus, the breakage increases, which makes the

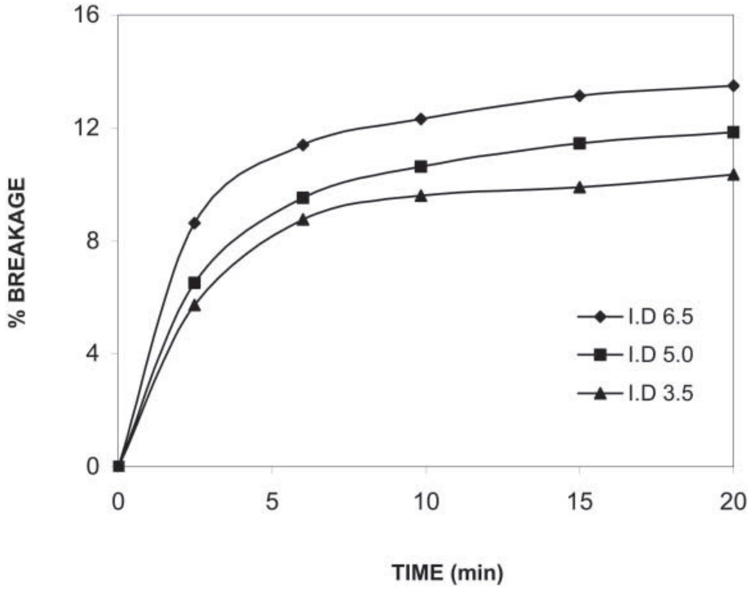

Figure 5. Effect of emulsion drops size per unit specific interfacial area on membrane breakage.

membrane less stable. It has been found that different stirrer speeds show the different %breakage at 20 min of stirring.

From Fig. 4, it is found that with an increase of intensity of agitation and time, %breakage will be increased. The initial positive impact of agitation on permeation rate may be ascribed to the reduced external phase mass-transfer resistance due to enhanced agitation. The adverse effect of agitation in this case arises from membrane rupture due to agitation-induced shear. On rupture of the membrane, internal phase spills out to the external continuous phase.

Effect of Emulsion Drops Size per Unit Specific Interfacial Area

The results are shown in Fig. 5 as a plot of %breakage vs. time. As the microdroplets (provide larger specific interfacial area) are more stable compared with macrodroplets, smaller emulsion drops, which will form stirring with an impeller of internal diameter 3.5 cm, are more stable than the emulsion drops formed with impeller diameters 5 and 6.5 cm.

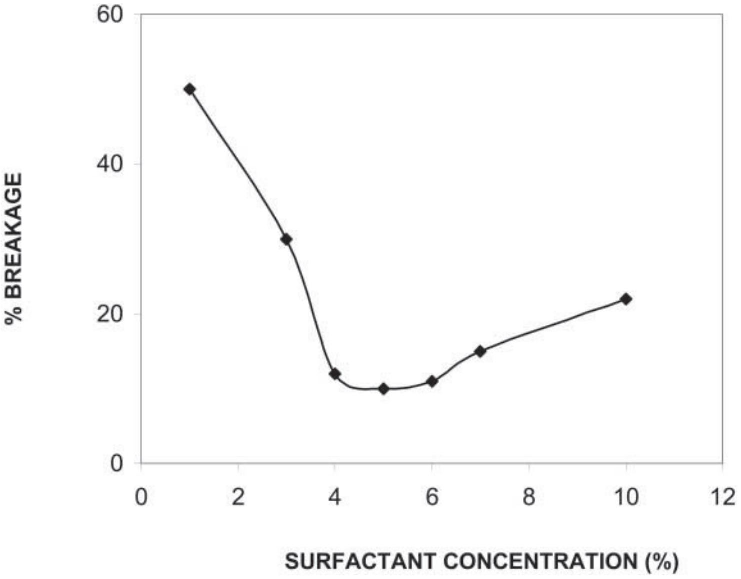

Figure 6. Effect of surfactant concentration on membrane breakage.

Effect of Surfactant

While studying the effect of surfactant concentration on membrane breakage, only surfactant concentration is changed, keeping all other parameters constant. Figure 6 shows that %breakage decreases with an increase of surfactant concentration up to a certain level but then it takes a U-turn. A higher surfactant concentration lowers the interfacial tension in the macrodroplet surface, and it appears at first sight that an increase in surfactant concentration should result in more breakage because a lower surface tension means easier rupture of the macrodrops. But contrary to this expectation, initially, %breakage decreases with an increase in surfactant concentration. This may be ascribed to the fact that initially surfactant concentration imparts higher stability to the membranes because of an increase in the number of surfactant monolayers adsorbed onto the macrodroplet interface. An increase in these layer results in increased stability of the droplet up to a limiting value, till the droplet surface gets saturated with surfactant monolayer. However, beyond this limiting value, higher surfactant concentration fails to further increase membranes stability, rather it weakens membranes probably due to hydrolysis of Span 80.

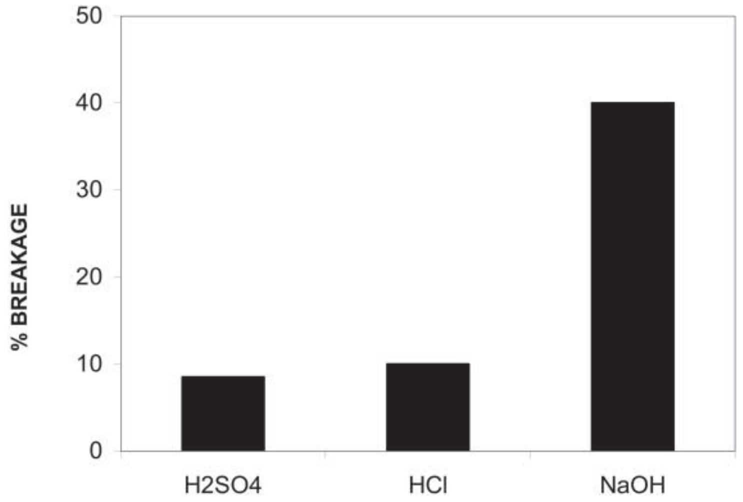

Figure 7. Effect of inner aqueous phase pH on membrane breakage.

Effect of pH in Inner Aqueous Phase

Figure 7 shows the results obtained for the inner aqueous solutions of sulfuric acid, hydrochloric acid, and sodium hydroxide. In the case of the aqueous solution of NaOH as an internal aqueous phase, nickel(II) extraction is not possible and the %breakage becomes very large. It is found that when internal NaOH concentration is 1 N, the greater part of the inner dispersed phase leaks out of the emulsion drops. On the other hand, using the acid solutions as the inner dispersed phase, %breakage with H_2SO_4 is lower than with HCl. This fact suggests that %breakage of the W/O/W-emulsion system is affected not only by the hydrogen ion concentration but also by the presence of associated anions (sulfate and chloride ions).

Effect of Tracers

In all experiments, we used a red dye solution (100 ppm) as a tracer to find the %breakage of ELM system. Instead of dye solution, copper sulfate, sodium thiocyanate, and sodium chloride also can be used as a tracer. Figure 8 shows that %breakage of emulsion drop is different when we are using different tracers (copper sulfate, sodium thiocyanate, and sodium chloride) as internal phase. It can be concluded that the stability of the W/O/W-emulsion system is not only dependent on inner phase pH but

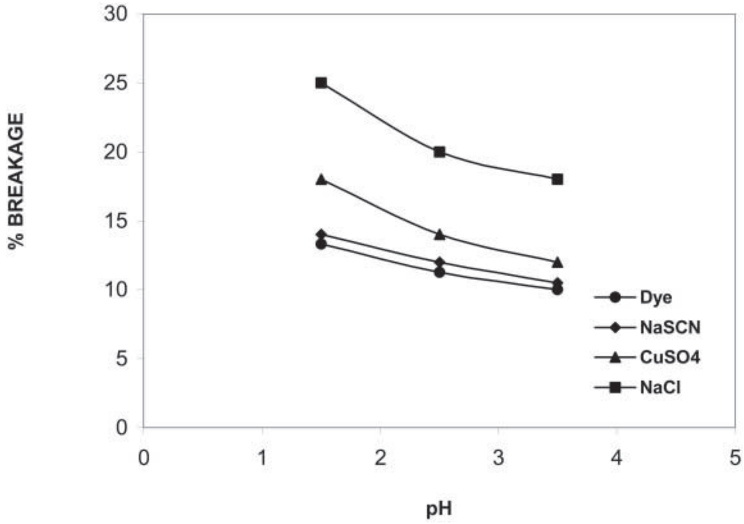

Figure 8. Effect of tracers concentration on membrane breakage.

also it depends on the ionic species and its concentration in the inner aqueous phase.

CONCLUSION

The stability of membrane is an important criterion in emulsion membrane extraction processes. The effects of different variables, such as pH of the feed phase, speed of agitation, emulsion drops size per unit specific interfacial area, surfactant concentration, pH in inner aqueous phase, and the presence of different tracers, are systematically investigated during the extraction of nickel(II) ions. The leakage phenomena, which reflect the stability, are found to be influenced by the external phase pH, and direct correlation between the %breakage and the external phase pH has been observed. There exists a trade-off between speed of agitation of the feed phase and hydrodynamic stability of membrane phase. In addition, little effect of drop size on stability is observed in the range studied. The stability of the W/O/W-emulsion system depends on the pH of the inner aqueous phase, ionic species (associated anions and tracers containing ions) and its concentration in the inner aqueous phase also.

NOMENCLATURE

C_{e}	Tracer concentration in external phase (mg/L).
C_{i}	Tracer concentration in internal phase (mg/L).
C_{D}	Distribution coefficient of the solute (nickel) between membrane and external phase.
D_{e}	Effective diffusivity of metal ion in saturated zone of emulsion globules ($\mathrm{m}^2/\mathrm{sec}$).
V	Total volume of emulsion phase (L).
V_{e}	Volume of external phase (L).
r	Radial coordinate in emulsion globules (m).
R	Radius of emulsion globules (m).
R_{f}	Reaction front position (m).
t	Time (min).
$g = C/C_{\mathrm{eo}}$	Dimensionless metal ions (nickel) concentration in saturated zone of emulsion globule.
$h = C_{\mathrm{e}}/C_{\mathrm{eo}}$	Dimensionless metal ions concentration in external phase.
$m = C_{\mathrm{i}}/C_{\mathrm{eo}}$	Dimensionless initial internal reagent concentration in internal phase.
$E = 3V/V_{\mathrm{e}}$	3 × total volume of emulsion phase/volume of external phase
0	Initial
f	Final.

Greek Letters

$\eta = r/R$	Dimensionless radial coordinate in emulsion globule.
$\chi = R_{\mathrm{f}}/R$	Dimensionless reaction front position.
$\tau = D_{\mathrm{e}}^{t}/R^2$	Dimensionless time.
ϕ	Volume fraction of internal aqueous phase in the emulsion.

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