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Microemulsion Liquid Membranes. II. Copper Ion Removal from Buffered and Unbuffered Aqueous Feed

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Abstract

A separation technique utilizing nonionic microemulsions as emulsion liquid membranes has been successfully applied to the removal of copper ion from both buffered and unbuffered aqueous feed. The reversible phase behavior of the microemulsion was utilized to demulsify the liquid membrane phase and recover the copper ion via a temperature change of approximately 40°C. Material balances closed to within 15%. Benzoylacetone posed no special problems when employed as a complexing reagent in buffered media but was not effective for copper removal from unbuffered solution. LIX 860 was found to be effective in unbuffered media if it was present in concentrations equal to or greater than the stabilizing surfactant.

INTRODUCTION

The microemulsion liquid membrane technique, an extension of techniques invented by Li (*1*), has proven to be effective for separating organics from aqueous solution (*2*). The process has high loading capacity, can easily concentrate solutes from parts per million to a few percent, has very fast rates of separation, and is energy efficient compared to classical thermal separations such as distillation. In an extension of earlier work (*2*), microemulsions have been utilized to separate an ionic species (Cu(II)) from aqueous solution utilizing a complexing reagent. As discussed below, microemulsions exhibit several advantages over coarse emulsions when used as liquid membranes including even faster rates of separation, low leakage, and ease of demulsification. To implement microemulsions as emulsion

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liquid membranes, a detailed understanding of the thermodynamic and kinetic behavior of microemulsions is needed. For example, pH buffering capacity of the feed solution has a dramatic impact of the efficacy of the separation method.

BACKGROUND

Microemulsions

A microemulsion may be defined as a thermodynamically stable dispersion of oil and water stabilized by surfactant. A microemulsion has a microstructure (typically droplets) with small oil and water domains (approximately 100 Å) separated by a monolayer of surfactant (*3*). The variables which affect the phase behavior and microstructure of microemulsions have recently been reviwed in several publications (*4–7*). Such variables include surfactant type and concentration, cosolvent type and concentration, temperature, and pH. Microemulsions can be water-continuous [lower phase or oil-in-water (o/w) type], bicontinuous (middle phase), or oil-continuous [upper phase or water-in-oil (w/o) type]. Microemulsions exhibit ultralow interfacial tensions (less than 0.01 dyn/cm) under appropriate conditions of temperature and salinity when three phases exist in equilibrium: a middle phase microemulsion, an excess oil phase, and an excess brine phase. In summary, microemulsions are thermodynamically stable while coarse emulsions are not.

Coarse Emulsion Liquid Membranes Employing Complexing Reagents

Coarse emulsion liquid membranes employ an immiscible liquid which separates two mutually miscible phase. The desired chemical species (referred to as the solute) is selectively transported from the feed phase across a thin liquid film of the immiscible phase and enriched in the receiving phase. The phases involved are stabilized by forming an emulsion of the membrane and one of the other phases (i.e., the feed phase, or as assumed in Fig. 1, the receiving phase). The emulsion is then dispersed as macrodrops (typical diameters of 0.1–5.0 mm) into the feed phase which contains the solute. The solute is transported across the thin membrane film to the internal receiving phase droplets (see Fig. 1). The membrane phase contains surfactant as a stabilizing agent and a solvent (e.g., hydrocarbon) and often complexing agents which help facilitate solubilization and mass transport of the solute across the membrane phase. The main advantage of emulsion liquid membranes over other separation techniques is the large surface area available for mass transfer, which results in a fast rate of

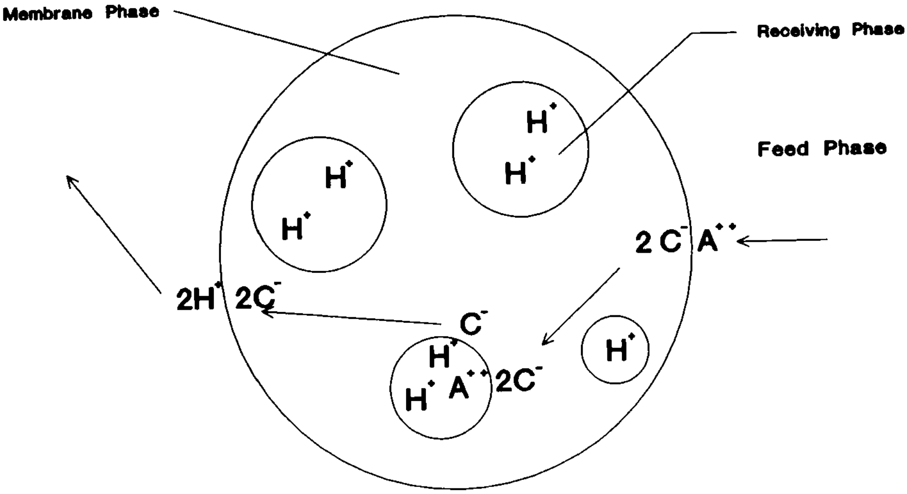

FIG. 1. A typical emulsion liquid membrane which employs a complexing reagent (C). The larger circle represents a macrodrop (typical diameters of 0.1 to 2.0 mm) which is dispersed into a feed solution containing the ionic solute (A). Microdrops which are encapsulated within the macrodrop contain an exchangeable ion such as hydrogen ions (H). The emulsion is stabilized by surfactant.

separation. Two disadvantages of the technique have been: 1) the lack of stability of the emulsion which allows leakage of the solute and unreacted internal reagent back into the feed phase, and 2) swelling of the internal microdrops with water from the feed phase. Both of these effects result in reduced separation efficiency.

Microemulsion Liquid Membranes Employing Complexing Reagents

A microemulsion suitable for use as a liquid membrane must fulfill several constraints. The microemulsion must be oil-continuous if utilized to separate species from an aqueous feed phase. The receiving phase should constitute a significant volume fraction of the microemulsion in order to allow for high separation capacity. The microemulsion should be tolerant to large pH changes because pH is often used as the driving force for separation. Therefore, nonionic surfactants are ideal candidates for this application due to low sensitivity to pH. Finally, the microemulsion should not contain components which easily partition into the aqueous feed phase. This requirement limits the use of cosurfactants to those which are water immiscible. Finding a microemulsion which fulfills all of the above constraints is nontrivial. Coarse emulsions can be formulated to contain any concentration of the various constituents. Microemulsions, on the other hand, attain a thermodynamic equilibrium which often limits the amount of receiving phase which may be incorporated into the microemulsion. Phase behavior studies have been conducted and used to optimize the microemulsion formulations (*8*, *9*). Such studies are necessary in view of the thermodynamic constraints on solubilization in microemulsions. The use of surface-active complexing reagents, such as LIX 860, further complicates the formulation of microemulsions with sufficient internal aqueous phase.

Advantages of Microemulsion Liquid Membranes

The advantages afforded by replacing coarse emulsions with microemulsions include:

1. The low interfacial tensions which are characteristic of microemulsions will lead to smaller macrodrops which implies faster mass transfer rates due to increased surface area per unit volume.
2. The microdrops dispersed in a coarse emulsion will coalesce over time and phase separate. Such phase separation will undesirably result in leakage of the receiving phase into the feed phase. Microemulsions do not show such phase separation due to their thermodynamic stability and may offer a more stable liquid membrane.
3. Another key advantage is the ease of both emulsification and demulsification provided by the microemulsion system. A simple adjustment of temperature can cause spontaneous emulsification or demulsification of the microemulsion. Formation of the microemulsion requires no special mixing; however, gentle mixing is usually provided in order to minimize the time required for the microemulsion to form spontaneously.

Previously presented experimental results support all of these claims (*2*).

Related Work

There are several techniques for copper removal from aqueous solution by extraction. The classical equilibrium-staged techniques are typically reported by the manufacturer of the extractant (*10*). Recently, equilibrium-based extraction has been conducted in surfactant solutions which are formulated to form a microemulsion during separation. The idea of utilizing the large surface area to volume ratio present in microemulsions as a means to enhance separation was first suggested by Robbins (*11*). More recently, Bauer and Komornicki (*12*) utilized the large surface area per unit volume available in microemulsion phases to increase the rate of germanium extraction from aqueous solution into an organic, microemulsion-forming phase. Others, including Harada and coworkers (*13*) as well as Paatero and coworkers (*14*), extended this technology to copper separations. Vijayalakshmi, Gulari, and Annapragada (*15*, *16*) modeled the equilibrium behavior of copper partitioning in such microemulsion systems based on a Stern double layer model. The model accounts for the "enhanced" partitioning of the copper into the microemulsion phase due to electrostatic attraction of the copper cation with the anionic surfactants (Aerosol OT) which are typically used in these systems. Although partition coefficients can be increased in such systems compared to surfactant-free systems, such separation techniques will always be limited by equilibrium. Liquid membranes offer a means of simultaneous extraction and stripping; thus, liquid membrane separations are limited only by the amount of stripping reagent.

Liquid membranes can be classified into two major categories, supported liquid membranes (SLM) and emulsion liquid membranes (ELM). Supported liquid membranes utilize a porous solid support such as a polymeric membrane to stabilize the extractant between the feed phase and the stripping phase. Emulsion liquid membranes utilize a multiple emulsion to stabilize the phases. Supported liquid membranes have been the subject of many investigations and it is beyond the scope of this paper to thoroughly review the SLM literature. Recent investigations of copper removal via SLMs include that of Miyoshi and coworkers (*17*), Schneider and Rintelen (*18*), and Loiacono and coworkers (*19*, *20*). Cahn and Li of the Exxon Corporation were issued a patent on the use of coarse emulsion liquid membranes for the separation of copper from aqueous solution in 1978 (*21*). They followed this patent with a paper printed in the open literature in 1981 (*22*). Since that time, investigators in China (*23*, *24*) and in Europe (*25*, *26*) have investigated continuous processes utilizing this technology. Enhancements to the basic technology continue to be investigated. Gu, Wasan, and Li (*27*) employed ligands such as acetate ions which enhance the rates of separation. More recently, Wodzki, Wyszynska, and Narebska (*28*) utilized a charged macromolecule which not only stabilizes the emulsion but simultaneously serves as the ion-carrier.

EXPERIMENTAL PROCEDURE

Copper Separations from Buffered Feed

The microemulsion formulation contained 65.5% v/v decane, 6.5% v/v nonionic surfactant (Emery DNP-8), 1.6% w/v benzoylacetone (Sigma Chemical), and 26.4% v/v H_2SO_4 (30% solution by weight in water). Benzoylacetone is the complexing reagent in this case. Benzoylacetone tended to cause the formation of liquid crystals in some microemulsions as evidenced by birefringence observed through polarized light. The particular formulation outlined above was chosen because it did not display such birefringence. The feed solution contained 1000 ppm $CuSO_4$ buffered to a pH of 6 by the addition of 1 g sodium acetate and 1 mL glacial acetic acid. All experiments and solutions were maintained at 21.5°C except as noted.

All separations were conducted in 2-L resin flask using a marine-type impeller for agitation. The feed phase (aqueous solution of buffered $CuSO_4$ solution) was first placed in the flask, and the impeller speed was calibrated by using a phototachometer. The mixer was stopped after calibration, and the microemulsion liquid membrane was added. As soon as the membrane was added, the mixer and a stopwatch were started. Samples were taken over time through a stopcock located in the bottom of the flask. The number of samples was kept to a minimum in order to minimize the change in feed volume. Sample size was approximately 10 mL. These samples were immediately centrifuged to remove any residual microemulsion liquid membrane. All copper concentrations were determined by atomic absorption spectroscopy.

A coarse emulsion was prepared and run under conditions similar to the microemulsion system. The coarse emulsion contained 77% v/v decane, 3% w/v polyamine surfactant (Exxon ECA 5025), 2.0% w/v benzoylacetone, and 18% v/v H_2SO_4 (30% solution by weight in water). The polyamine surfactant was chosen in view of its reported success in coarse emulsion liquid membrane formulations (*22*). The above constituents were sonicated for 2 min to provide a stable coarse emulsion.

Copper Separations from Unbuffered Feed: The Effect of Surfactant on Interfacial Reactions

All experiments employed an ethoxylated nonylphenol surfactant (BASF Igepal C0210) with an HLB of 4.6. This surfactant is very soluble in oil and essentially insoluble in water. Heptane (Humphrey Chemicals) was used as the oil phase, and 1000 ppm $CuSO_4$ solution (no buffer) was used as the aqueous feed phase. LIX 860 was used in view of its fast complexation kinetics. A typical experiment involved contacting 400 g of the $CuSO_4$ solution with 80 g of the oil phase. The oil phase contained varying amounts of surfactant and LIX 860. Contacting was carried out at 21.5°C, with the impeller speed at 300 rpm for 20 min.

Ultimately, these experiments suggested a new microemulsion formulation employing equal amounts of surfactant and complexing reagent. The oil phase of this microemulsion contained 79.92 w/w % hexadecane (Humphrey Chemical), 9.98 w/w % Emery DNP-8 surfactant, and 10.1 w/w % LIX 860. This oil phase was equilibrated with an aqueous phase containing 30 w/w % H_2SO_4. The resulting microemulsion contained a water volume fraction of 0.06 as determined by Karl Fisher titration.

RESULTS AND DISCUSSION

Copper Ion Removal from Buffered Aqueous Feed

The mechanism of cation separation is depicted in Fig. 1. Such a mechanism has been utilized to carry out copper separations from water. This mechanism has also been previously employed for the coarse emulsion case (*21*, *22*). In contrast to acetic acid, copper is not soluble in the organic liquid membrane phase. For this reason, a complexing agent (C^-) is used to couple the cation (A^{2+}), in this case copper, at the membrane/feed phase interface. The copper complex is soluble in the organic phase and diffuses toward the globule center. Upon encountering an internal droplet, the copper is decoupled from the complexing agent by a reversible reaction with hydrogen ions present in the internal droplets. The complexing agent is now free to diffuse back to the membrane/feed interface to perform the same process over again. The reaction at the interfaces (i.e., feed phase/membrane phase and membrane phase/receiving phase) may be crudely represented as:

$$C_2A + 2H^+ \leftrightarrow 2CH + A^{2+}$$

The reaction equilibrium is governed by the concentration of hydrogen ions. For this reason, the pH of the external phase must be buffered at a high enough level (i.e., low concentration of H^+) to allow the complexation reaction to occur.

The goals of this research were: 1) to prove that microemulsion liquid membranes may be utilized to separate copper from aqueous solution, 2) to directly compare microemulsion separation with coarse emulsion separation, and 3) to investigate the effects of mixing intensity and treat ratio on separation kinetics.

Microemulsion vs Coarse Emulsion

As indicated in Fig. 2, the separation of copper using the microemulsion liquid membrane was completed within 1 min and no leakage was detected up to 60 min. With the coarse emulsion, the same separation took roughly 10 min. As expected, the globule size for the microemulsion system was observed to be much smaller than for the coarse emulsion system. The

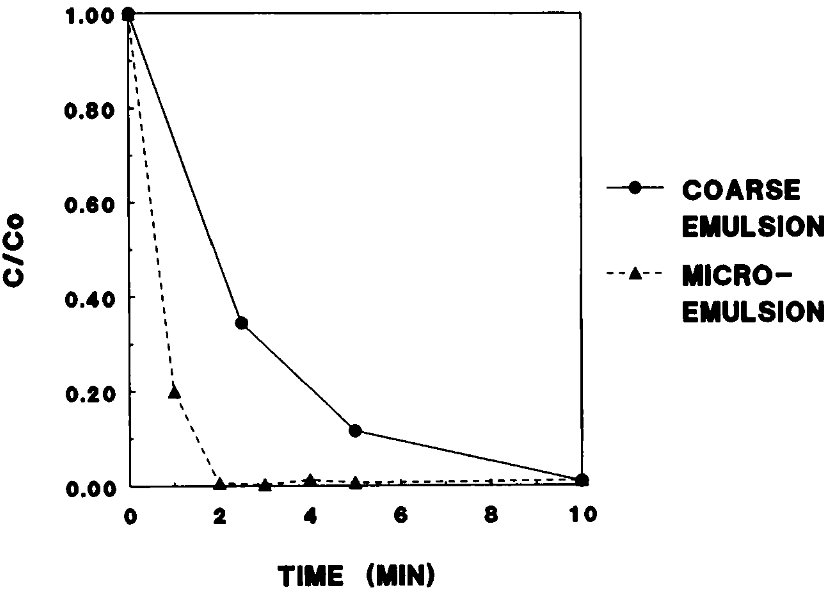

FIG. 2. Separation of copper from buffered media via microemulsion and coarse emulsion liquid membranes. Experimental conditions: Treat ratio (volume of liquid membrane : volume of feed solution) of 1:5 and a mixing speed of 300 rpm.

globules for the microemulsion case were on the order of 0.1 mm in diameter vs 1–2 mm (determined by photography) for the coarse emulsion case. Some undesirable partitioning of the surfactant into the aqueous feed phase was observed for separations utilizing microemulsions. This problem can be circumvented by choosing a surfactant of slightly lower HLB (i.e., a less water-soluble surfactant). The partitioned surfactant is easily recovered by contacting the residual aqueous stream with carbon tetrachloride.

Upon spontaneous demulsification of the microemulsion by raising the temperature to 60°C, the receiving phase was recovered and analyzed for copper. The copper was concentrated to 6500 ppm and the material balance agreed to within 15%. The presence of the copper in the receiving phase is evidence that the copper was being stripped into the receiving phase and was not accumulating in the membrane phase.

Effect of Mixing Intensity

Increased rates of mixing (higher impeller rpm) cause an increase in the rate of copper separation from water (see Fig. 3). This trend indicates that

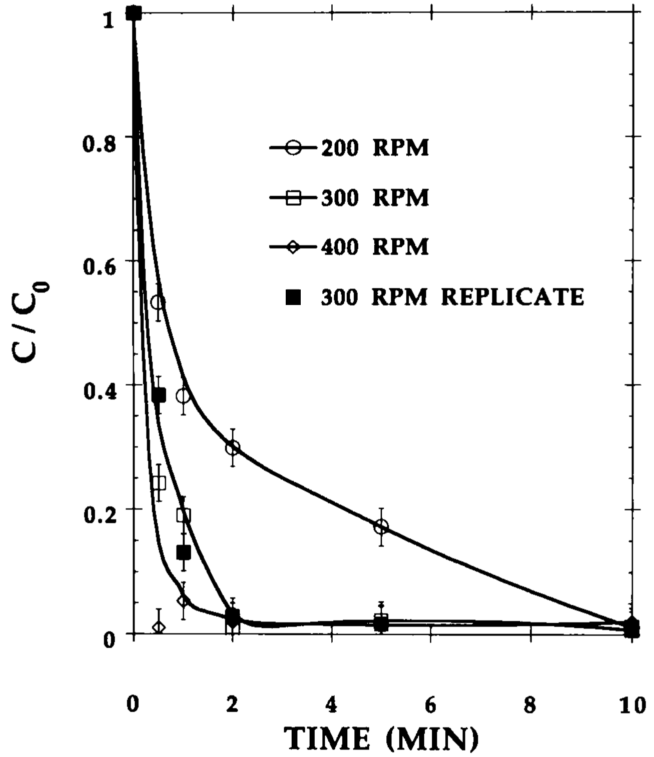

FIG. 3. Effect of mixing speed on separation kinetics for the microemulsion liquid membrane with benzoylacetone as complexing agent. Experimental conditions: Treat ratio (volume of liquid membrane: volume of feed solution) of 1:5 and a feed phase of 1000 ppm $CuSO_4$ buffered to a pH of 6.0.

at the higher rates of mixing, the globules are more finely dispersed, which leads to increased surface area for mass transfer. Note that the 300 rpm experiment was repeated. The error bars represent the standard deviation of the analytical analysis.

Effect of Treat Ratio

Increasing the treat ratio (membrane to feed volume ratio) causes an increase in the rate of copper separation (see Fig. 4). As for the acetic acid case, this increased separation rate is due to the increased surface area available for mass transfer but is not as dramatic as in the case of acetic acid.

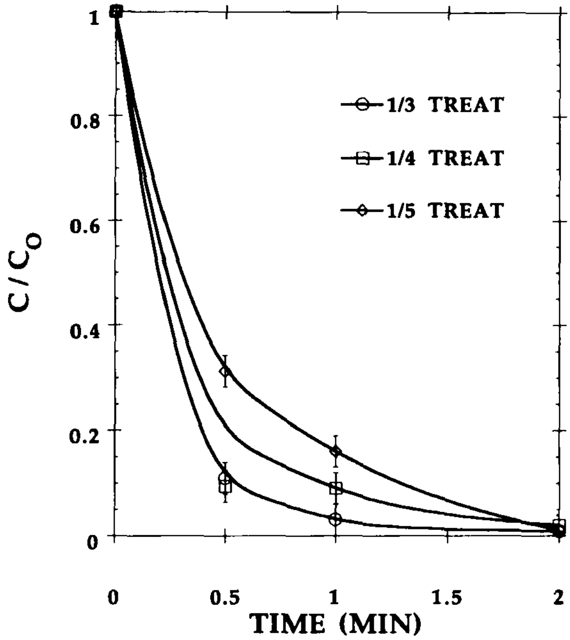

FIG. 4. The effect of treat ratio (volume of liquid membrane : volume of feed solution) on separation kinetics for the microemulsion liquid membrane with benzoylacetone as complexing agent. Experimental conditions: Mixing speed of 300 rpm and a feed phase of 1000 ppm $CuSO_4$ buffered to a pH of 6.0.

Copper Removal from Unbuffered Aqueous Feed

As mentioned earlier, pH affects the complexation equilibrium at the interfaces. Low pH results in the release of the cation in favor of a hydrogen ion complexation. Unfortunately, most industrial process streams are not buffered as in the above experiments. If no buffer is added to the feed phase, there is a dramatic decrease in separation capacity and rates as shown in Fig. 5.

The heart of the problem lies in the complexing agent employed. Complexing agents are commercially available which are effective in unbuffered media. For example, LIX reagents produced by Henkel Corporation are utilized to separate copper ions from unbuffered media. Formulations employing LIX reagents at concentrations similar to the benzoylacetone employed above did not give appreciable separation of the copper from water. In order to gain a clearer understanding of this phenomenon, the effect of surfactant on the complexation kinetics was investigated. Ultimately this investigation clarified the interaction between surfactant and complexing

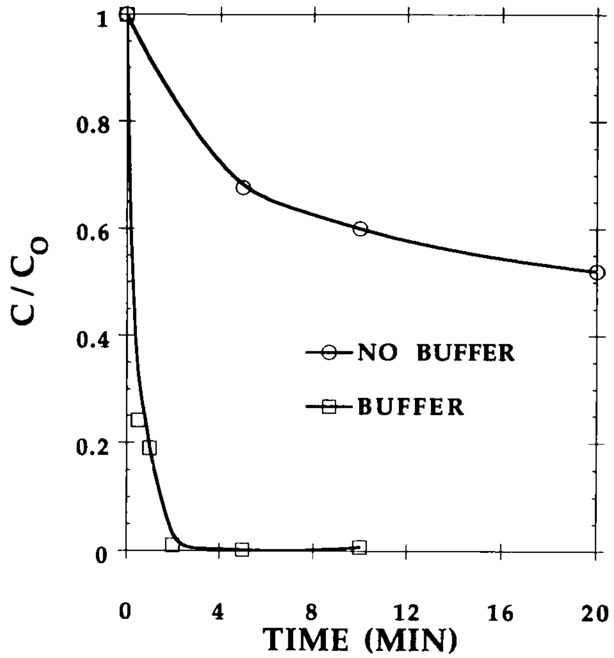

FIG. 5. The effect of buffering on separation capacity and kinetics for the microemulsion liquid membrane containing benzoylacetone as complexing agent. Experimental conditions: Mixing speed of 300 rpm, treat ratio (volume of liquid membrane:volume of feed solution) of 1:5, and a feed phase of 1000 ppm $CuSO_4$.

reagent, and allowed for the formulation of a microemulsion which could be used to carry out copper separations from unbuffered aqueous feed phases.

Characterization of Complexation Kinetics

In order to get a quantitative measure of the kinetics of complexation, data were collected on classical liquid–liquid extraction in simple oil/water systems (i.e., no internal receiving phase). The data were fit to a simple first-order rate equation:

$$C/C_0 = \exp(-kt)$$

where C is the time-dependent concentration of $CuSO_4$ in solution, C_0 is the initial concentration of $CuSO_4$, t is time, and k is the rate constant which characterizes the complexation kinetics. Some typical fits are shown in Fig. 6.

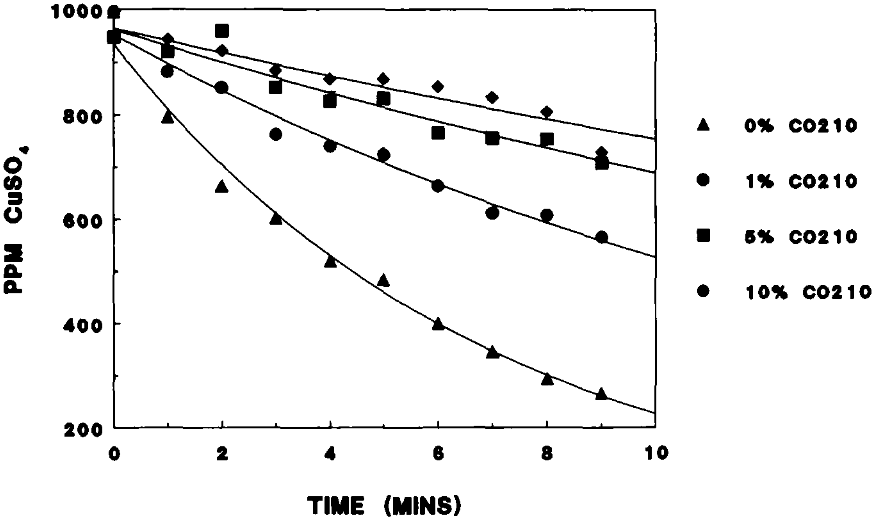

FIG. 6. The effect of a nonionic surfactant (Igepal CO210) on liquid–liquid extraction kinetics (i.e., no internal receiving phase). Experimental conditions: 40 g oil phase contacted with 200 g unbuffered 1000 ppm CuSO$_4$ solution. The oil phase contained 10 w/w % LIX 860, the noted amount of CO210 (w/w %), and the remainder decane. Mixing speed was maintained at 300 rpm.

The variable of interest for this investigation was the ratio of surfactant concentration to LIX 860 concentration. The data are summarized in Table 1. Since the rate of extraction is influenced by the amount of LIX 860 in the oil phase, the kinetic rate constants are normalized by the value of the rate constant at the same LIX 860 concentration in the absence of surfactant (k_0).

Interpretation of Results

The rate constant, k, will depend not only on the inherent complexation kinetics but also on the relative volumes of the two phases as well as the droplet sizes. The relative volumes of the two phases were held constant, leaving only droplet size and inherent complexation kinetics as variables affecting the rate constant. In Fig. 7 the normalized rate constant (k/k_0) is plotted as a function of the ratio of surfactant to LIX 860 concentration. At a concentration ratio of zero, there is no surfactant in the system and, by definition, the normalized rate constant is 1. Up to a concentration ratio of 1.0, the rates are enhanced dramatically (up to 4 times). This enhancement is ascribed to the decreased droplet sizes and the corresponding increase in surface area for mass transfer. Above a concentration ratio of 1.0, the rates fall off dramatically and approach zero. At these higher concentration ratios there is much more surfactant in the system than LIX

TABLE 1

A Summary of the Rate Constants at Various Levels of Surfactant (Igepal CO210) and LIX 860 Concentrations. All Experiments Were Conducted at 300 rpm, with 40 g Decane Phase Dispersed in 200 g Unbuffered 1000 ppm $CuSO_4$ Solution

Surfactant concentration (w/w %)	LIX 860 concentration (w/w %)	*k* (1/min)
0.0	0.5	0.0092
0.0	1.0	0.0175
0.0	2.5	0.0353
0.0	10.0	0.0648
5.0	0.5	0.0000
5.0	1.0	0.0028
5.0	2.5	0.0068
0.1	10.0	0.1105
0.5	10.0	0.0805
1.0	10.0	0.2630
5.0	10.0	0.2426

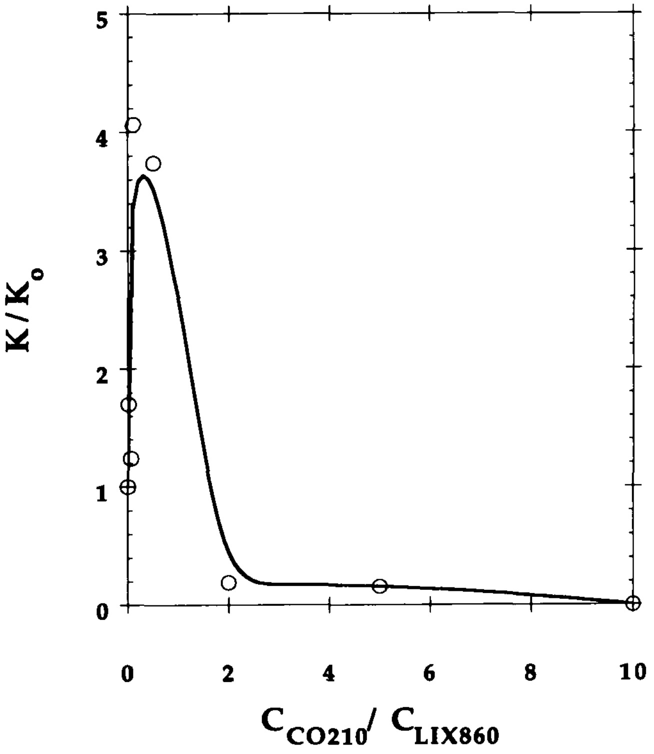

FIG. 7. The effect of surfactant on the relative rate constant.

860. The LIX 860 is unable to adsorb at the interface at these higher surfactant concentrations. This displacement from the interface isolates the complexing reagent from the copper, and the rates are greatly diminished. These observations are consistent with the results of Mikucki and Osseo-Asare (*29*) who report the same phenomenon for a coarse emulsion liquid membrane system containing LIX 65N and Span 80 surfactant.

Improved Microemulsion Formulation

Realizing that the ratio of the surfactant and LIX 860 concentration should be nearer to unity, a microemulsion was formulated containing LIX 860 at substantially higher concentrations.

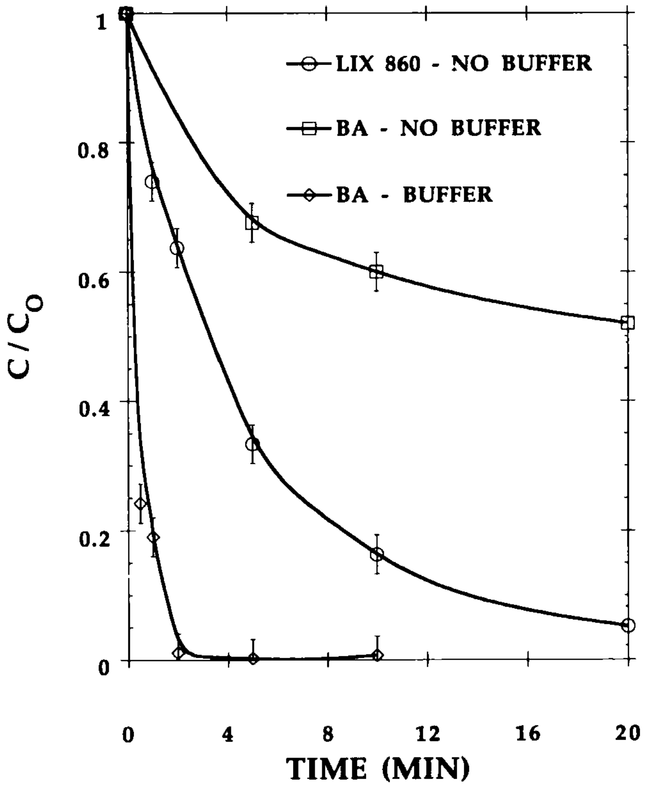

FIG. 8. A comparison of separation capacity and kinetics for microemulsions employing benzoylacetone and LIX 860 in buffered and unbuffered media. The LIX 860 microemulsion liquid membrane is able to separate copper from unbuffered media, but at rates slower than copper separation from buffered media when employing the benzoylacetone-containing microemulsion liquid membrane. Experimental conditions: Mixing speed of 300 rpm, treat ratio (volume of liquid membrane: volume of feed solution) of 1:5, and a feed phase of 1000 ppm $CuSO_4$.

This microemulsion was used to carry out the separation of copper ion from an unbuffered aqueous feed phase. The rate of separation for the unbuffered feed solution is not as fast as the formulations used with buffered feed. However, the rate is significantly faster than the previous formulation with an unbuffered feed solution (see Fig. 8). This observation suggests that the kinetics of copper separation is largely governed by the interfacial complexation. Indeed, the normalized rate constant for the microemulsion is estimated to be 2.4 at a concentration ratio of approximately 1.0. This value is coincident with the value interpolated from Fig. 7. This supports the hypothesis that the interfacial complexation kinetics is the rate-limiting step for copper separation.

SUMMARY

The separation of copper ions from buffered aqueous feed phases was successfully achieved and compared to coarse emulsion liquid membrane separation. The microemulsion displayed faster rates of separation due to decreased globule size (or increased surface area per unit volume). Neither system displayed leakage over the course of the experiment. Unlike the acetic acid case which is a diffusion-limited process, the kinetics of copper separation from unbuffered feed is apparently controlled by the interfacial complexation reaction for systems employing LIX 860. At high concentrations of surfactant, the LIX 860 is unable to adsorb at the feed phase/microemulsion interface. This displacement from the interface isolates the complexing reagent from the copper, and the rates are greatly diminished. Increasing the LIX 860 to a concentration comparable to the microemulsion-stabilizing surfactant results in an effective microemulsion liquid membrane which may be utilzied in unbuffered media.

Acknowledgments

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REFERENCES

1. N. N. Li, U.S. Patent 3,410,794 (1968).
2. J. M. Wiencek and S. Qutubuddin, *Sep. Sci. Technol.*, *27*, 1211 (1992).
3. B. P. Binks, J. Meunier, O. Abillon, and D. Langevin, *Langmuir*, *5*, 415 (1989).
4. C. A. Miller and Qutubuddin, S., in *Interfacial Phenomena in Non-Aqueous Media* (H. F. Eicke and G. D. Parfitt, eds.), Dekker, New York, Chap. 4.
5. K. Shinoda and B. Lindman, *Langmuir*, *3*, 135 (1987).
6. S. E. Friberg, *J. Dispersion Sci. Technol.*, *6*, 317 (1985).
7. A. M. Bellocq, J. Biais, P. Bothorel, B. Clin, G. Fourche, P. Lalanne, B. Lemaire, B. Lemanceau, and D. Roux, *Adv. Colloid Interface Sci.*, *20*, 167 (1984).

8. J. M. Wiencek and S. Qutubuddin, *Colloids Surfaces, 29,* 119 (1988).

9. J. M. Wiencek and S. Qutubuddin, *Ibid., 54,* 1 (1991).

10. G. A. Kordosky (ed.), *The Chemistry of Metals Recovery Using LIX Reagents,* Henkel Corporation, 1984.

11. M. L. Robbins, U.S. Patent 3,641,181 (1972).

12. D. Bauer and J. Komornicki, *International Solvent Extraction Conference,* 1983, p. 315.

13. M. Harada, N. Shinbara, M. Adachi, and Y. Miyake, *J. Chem. Eng. Jpn., 23,* 50 (1990).

14. E. Paatero, J. Sjoeblom, and S. K. Datta, *J. Colloid Interface Sci., 138,* 388 (1990).

15. C. S. Vijayalakshmi and E. Gulari, *Sep. Sci. Technol., 26,* 291 (1991).

16. C. S. Vijayalakshmi, E. Gulari, and A. V. Annapragada, *Ibid., 25,* 711 (1990).

17. H. Miyoshi, M. Yamagami, T. Kataoka, and T. Nishiki, *Chem. Express, 4,* 749 (1989).

18. K. Schneider and T. H. Rintelen, *Schriftenr. GDMB, 53,* 352 (1989).

19. O. Loiacono, E. Drioli, and R. Molinari, *J. Membr. Sci., 28,* 123 (1986).

20. O. Loiacono U. Fedele, G. DeMunno, and E. Driolo, *Chim. Ind. (Milan), 66,* 597 (1984).

21. R. P. Cahn and N. N. Li, U.S. Patent 4,086,163 (1978).

22. J. W. Frankenfeld, R. P. Cahn, and N. N. Li, *Sep. Sci. Technol., 4,* 385 (1981).

23. G. Liu, T. Ji, H. Xia, and J. Xu, *Mo Kexue Yu Jishu, 9,* 36 (1989).

24. Y. Liu, R. Su, Y. Zhang, G. Zhang, Z. Tao, P. Tong, and X. Zhang, *Mo Fenli Kexue Yu Jishu, 3,* 37 (1983).

25. M. Ruppert, J. Draxler, and R. Marr, *Sep. Sci. Technol., 23,* 1659 (1988).

26. K. Schuegerl, A. Mohrmann, W. Gutknecht, and H. B. Hauertmann, *Desalination, 53,* 197 (1985).

27. Z. M. Gu, D. T. Wasan, and N. N. Li, *J. Membr. Sci., 26,* 129 (1986).

28. R. Wodzki, A. Wyszynska, and A. Narebska, *Sep. Sci. Technol., 25,* 1175 (1990).

29. B. A. Mikucki and K. Osseo-Asare, *Solv. Extr. Ion Exch., 4,* 503 1986).

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