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Extraction of Rare Earth Metals Using Liquid Surfactant Membranes Prepared by a Synthesized Surfactant

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ABSTRACT

Three surfactants, L-glutamic acid dioleyl ester ribitol (nonionic, $2C_{18}\Delta^9GE$), L-glutamic acid dioleyl ester quaternary ammonium chloride (cationic, $2C_{18}\Delta^9GEC_2QA$), and dioleyl dimethyl quaternary ammonium chloride (cationic, $2C_{18}\Delta^9QA$) were synthesized for potential use in liquid membrane operations. These surfactants have strongly hydrophobic, twin oleyl chains as the hydrophobic moiety. Using the synthesized surfactants, extraction of rare earth metals was carried out by liquid surfactant membranes in a stirred tank. The extraction behavior of 12 kinds of rare earth metals was systematically studied with 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (commercial name: PC-88A) as a carrier. Different surfactants having an identical hydrophobic moiety can have significantly different behaviors in rare earth extractions by liquid surfactant membranes, where extraction efficiency appears to be governed by the nature of the interfacial microenvironment between oil and water. An interfacial reaction model which takes into account the adsorption of a surfactant at the interface has been proposed to evaluate the permeation rate of rare earth metals by liquid surfactant membranes. It was found that a cationic surfactant strongly enhances the extraction rate of rare earth metals compared with the conventional surfactant, Span 80. The cationic surfactant $2C_{18}\Delta^9GEC_2QA$ appears to be one of the best surfactants currently available for rare earth extraction by liquid surfactant membranes.

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INTRODUCTION

An efficient separation process for rare earth metals has been actively studied for producing novel advanced materials for various electronic, optical, and magnetic devices (1). High technology using ultrapurified rare earth metals will be available for marketing in the near future. Conventional solvent extraction is well known to be an effective method for the separation and concentration of rare earth metals on an industrial scale. However, this process requires a large number of stages in a series of mixer-settlers, at a huge energy cost, to obtain high-purity products because these elements behave almost identically in their chemical reactions and their mutual separation is very difficult. Thus a new separation technique for rare earth metals is desirable to reduce the energy cost.

Recently, a separation technique using liquid surfactant membranes (henceforth LSMs) has been investigated as a novel method for separating and concentrating metal ions (2). The separation process can concentrate metal ions quickly to a high degree in fewer stages while maintaining the high selectivity of a solvent extraction. The liquid membrane usually consists of a surfactant, an extractant as a carrier of metal ions, and an organic solvent, and each component strongly affects the permeation rate of metal ions through an LSM (3). In particular, it is well known that the surfactant plays an important role in the LSM process, and the selection of the surfactant often decides the success of liquid membrane operations (4). The surfactant is usually used to stabilize W/O emulsions. However, the presence of surfactants often results in a decrease in the extraction rate in LSM operations because adsorbed surfactants at the interface inhibit the forward extraction of the complex between metal ions and a carrier on the surface of emulsion globules. Therefore, the presence of surfactants should be considered when the permeation rates of rare earth metals are evaluated in LSMs. Apart from the large amount of work on the extraction of base metal ions by LSMs, few studies have examined rare earth extraction (5, 6). Teramoto et al. proposed a well-designed permeation model, the ''multilayer shell model,'' for the extraction of rare earth metals using LSMs prepared with the commercial surfactant Span 80 (5). However, the effect of surfactants was not considered in their model, and the contribution of surfactants in the permeation model was implied in the rate constant of the forward extraction.

Over the past several years we have been developing many new surfactants for the extraction of metal ions using LSMs (4), and we have found that a specially designed surfactant can promote the extraction rate of metal ions through an LSM (7–9). In a previous paper we developed a new cationic surfactant for rare earth extraction by LSMs, and a kinetic model that takes into account the effect of surfactants on extraction was proposed to evaluate the extraction rates for three light rare earth metals, La, Pr, and Nd (6). The objectives of the present study are (i) to improve the previously proposed reaction model to determine the permeation behavior for whole rare earth metals with LSMs, and (ii) to obtain useful information on the design of appropriate surfactants for rare earth extraction by LSMs. Because the difference in extraction rate with the extractant PC-88A is more than 4 orders between light rare earth metals (such as La, Pr, and Nd) and heavy rare earth metals (such as Er, Tm, and Yb) (10), the permeation mechanism of both groups of rare earth elements in LSM operations is deduced to be different under the same experimental conditions. To study this difference, we have synthesized two new cationic surfactants containing two long oleyl chains in the hydrophobic moiety, and have investigated the extraction behavior of 12 rare earth metals (Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb) using LSMs containing PC-88A as a carrier for comparison with conventional Span 80 surfactant LSM systems.

EXPERIMENTAL

Reagents

The extractant PC-88A, which is also a carrier for rare earth metals by LSMs, was kindly supplied by Daihachi Chemical Industry Co., Ltd., and used without further purification. The surfactants L-glutamic acid dioleyl ester ribitol (abbreviated $2C_{18}\Delta^9GE$), dioleyl dimethyl quaternary ammonium chloride (abbreviated $2C_{18}\Delta^9QA$), and L-glutamic acid dioleyl ester quaternary ammonium chloride (abbreviated $2C_{18}\Delta^9GEC_2QA$) were synthesized according to procedures described in previous papers (7, 11). The hydrophilic structure in $2C_{18}\Delta^9GEC_2QA$ is a little different from the previously synthesized cationic surfactant. Both chloride and bromide anions were used as the counterion of the two cationic surfactants. The final products were purified by recrystallization and were identified by IR, ^{1}H-NMR, and elementary analysis. The commercially available surfactant sorbitan monooleate (commercial name: Span 80) was purchased from Kishida Chemical Co., Ltd. (Japan), and used as received. Figure 1 shows the structures of the surfactants along with their abbreviations. Rare earth metals were used as their lanthanide chlorides, and the purity was more than 99.9%. Analytical grade *n*-heptane was used as an organic solvent in liquid membrane operation. Other reagents were of commercially available grades.

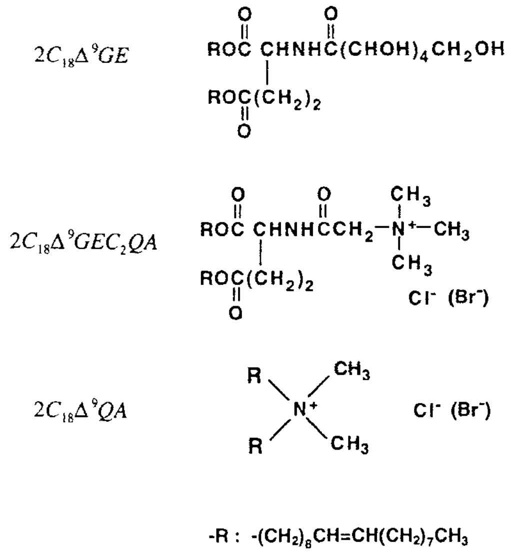

FIG. 1 Molecular structure and abbreviations of synthesized surfactants.

Experimental Apparatus and Procedure

In a preliminary experiment to select an acid as the receiving phase in liquid membrane operation, we investigated the effect of three kinds of acids (nitric, hydrochloric, and sulfuric acids) on the extraction efficiency of rare earth metals by an LSM. Sulfuric acid was chosen as the internal aqueous phase of emulsions. The internal aqueous solution was prepared by dissolving nickel nitrate and magnesium nitrate in 0.5 M sulfuric acid as a tracer to measure the degree of break-up of emulsions and as a controller of ionic strength to prevent shrinking of emulsions, respectively. The organic phase, which would be a liquid membrane, was prepared by dissolving a surfactant and the extractant PC-88A in *n*-heptane. An ordinary W/O emulsion was made from equal volumes (50 mL) of the organic and aqueous solutions by stirring at 1000 rpm under ultrasonic irradiation for 5 minutes (Branson Sonifier 250). The external feed aqueous phase contained three rare earth metals (La, Pr, and Nd; or Sm, Eu, and Gd; or Dy, Ho, and Tm; or Y, Er, and Yb), and the initial pH was adjusted to 2, which is a common value for a leaching metal solution in a solvent extraction process, using 0.1 M acetic acid and 0.1 M hydrochloric acid for adjustment. For the extraction experiments by LSMs, 100 mL prepared emulsion was dispersed in 700 mL aqueous feed solution, giving a feed

TABLE 1
Standard Experimental Conditions for Metal Extraction by LSMs

Internal aqueous phase	$V_i = 50$ mL
	H_2SO_4 (1000 mol/m^3)
Organic phase	$V_{org} = 50$ mL
	n-Heptane
External aqueous phase	$V_i = 700$ mL
	pH 2.0
	$C_M^0 = 0.5$ mol/m^3
Stirring speed	5 s^{-1} (300 rpm)
Carrier	PC-88A ($C_{HR} = 5$–100 mol/m^3)
Surfactants[a]	Span 80 ($C_S = 50$ mol/m^3)
	$2C_{18}\Delta^9GE$ ($C_S = 20$ mol/m^3)
	$2C_{18}\Delta^9QA$ ($C_S = 20$ mol/m^3)
	$2C_{18}\Delta^9GEC_2QA$ ($C_S = 20$–60 mol/m^3)
Break-up tracer	$Ni(NO_3)_2$, $C_{Ni} = 5$ mol/m^3

[a] The surfactants were used in the range greater than the critical surfactant concentrations (7, 11).

to emulsion volume ratio of 7. The two phases were mixed in a standard cylindrical mixer (9.2 cm diameter and 15 cm depth) with four vertical baffles and a turbine impeller having six flat blades. Extraction runs were conducted at a mixing rate of 300 rpm, and the temperature was kept at 303 K with a thermostated water bath. Samples of the external phase were removed periodically during the course of a run. After separating the emulsion phase and the external aqueous phase, the concentration of nickel in the aqueous phase, caused by break-up of the LSM, was measured by atomic absorption spectrochemical analysis (Seiko, Model SAS-760). The concentration changes of rare earth metals in the feed solution were determined by ICP atomic emission spectroscopy (Shimadzu, ICPS-5000). The standard experimental conditions are listed in Table 1.

RESULTS AND DISCUSSION

Permeation Kinetics of Rare Earth Metals by LSMs

The permeation of rare earth metals is assumed to consist of four steps as shown in Fig. 2: (I) diffusion of metal ions to the external interface of the emulsion globules; (II) interfacial reaction between metal ions and the carrier at the external interface; (III) diffusion of the metal complex into the emulsion globules; (IV) stripping reaction at the interface of internal droplets. However, since Steps (III) and (IV) can be assumed to be very fast under the present experimental conditions (12), we used Steps (I) and

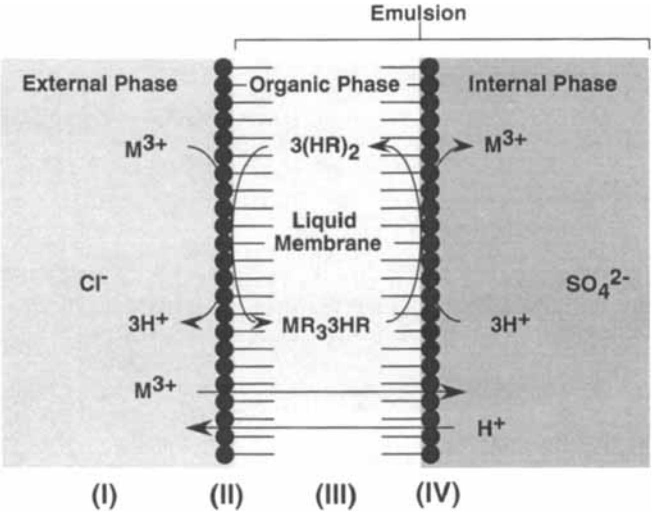

FIG. 2 Permeation mechanism of rare earth metals using liquid surfactant membranes.

(II) to determine the permeation behavior of metal ions by LSMs. In liquid–liquid extraction of rare earth metals with the extractant PC-88A, the extraction kinetics has been elucidated and the extraction mechanism is expressed as follows (10, 13):

$$(HR)_{2\,org} = (HR)_{2\,ad} \qquad K_{(HR)_2} \qquad (1)$$

$$M^{3+}_{aq} + (HR)_{2\,ad} = MR_{2\,ad}^{+} + 2H^{+} \qquad K_1 \qquad (2)$$

$$MR_{2\,ad}^{+} + (HR)_{2\,org} = MR_3HR^{+}_{ad} + H^{+} \qquad K_2 \qquad (3)$$

$$MR_3HR^{+}_{ad} + (HR)_{2\,org} = MR_33HR_{org} \qquad k_f/k_r \qquad (4)$$

where $K_{(HR)_2}$ is the adsorption equilibrium constant of the dimeric extractant and the subscript "ad" indicates the adsorbed state at the interface. K_1 and K_2 are the equilibrium constants of Eqs. (2) and (3), respectively, and subscripts "aq" and "org" denote the aqueous and organic species. However, we have to take into account the existence of surfactants on the surface in the permeation mechanism of metal ions by LSMs because such a surfactant is always more interfacially active than a metal carrier

(6). Assuming that Eq. (4) is the rate-determining step, and further taking into account the adsorption of surfactants at the interface, the interfacial reaction rate between rare earth metal ions and the carrier, R_M, is expressed as follows (6, 10, 13, 14):

$$R_M = k'_{fM}(C^*_M/a^3_{H,e}) \tag{5}$$

$$k'_{fM} = \frac{k_{fM}C^3_{(HR)_2org}}{(1 + K_{(HR)_2}C_{(HR)_2org} + K_S C_{S\,org})} \tag{6}$$

where k'_{fM} is the apparent interfacial reaction rate constant for each metal M. C_S is the surfactant concentration, K_S is the interfacial adsorption equilibrium constant of surfactant, and superscript * denotes the aqueous or organic solution adjacent to the interface.

The concentration of rare earth metals adjacent to the external interface is obtained from the following relation, in which the interfacial reaction rate should equal the mass transfer rate at steady state.

$$R_M = k_m(C_M - C^*_M) \tag{7}$$

where k_m is the mass transfer coefficient of rare earth metals. Equation (8) is obtained by eliminating C^*_M from Eqs. (5) and (7).

$$R_M = k_o C_M \tag{8}$$

$$k_o = \frac{1}{k_m} + \frac{1}{k'_{fM}/a^3_H} \tag{9}$$

The concentration change of rare earth metals in a stirred tank with time can be shown by the following equation:

$$-V_e\left(\frac{dC_M}{dt}\right) = AR_M \tag{10}$$

where A ($= 6V_E/d_E$) is the interfacial area and V_e is the volume of the external aqueous solution. The diameter of W/O emulsion globules in the stirred tank was around 0.28 mm in the surfactant concentration range (6). Furthermore, in order to take into account the break-up of emulsions, a break-up rate constant, k_b, is defined by Eq. (11) according to a previous paper (11).

$$\ln(1 - \epsilon) = -k_b t \tag{11}$$

$$\epsilon = (V_e C_{Ni,e})/(V^0_i C^0_{Ni,i}) \tag{12}$$

where ϵ is the break-up ratio of LSM, V_i is the volume of the internal aqueous solution, and C_{Ni} is the concentration of Ni(II) as a break-up tracer. The subscripts "e" and "i" denote the external and the internal aqueous solutions, respectively, and the superscript "0" denotes the initial value. The change of hydrogen-ion activity with time is expressed as follows:

$$\frac{da_{\mathrm{H,e}}}{dt} = -3\sum_{n=1}^{m}\left(\frac{dC_{\mathrm{M}}}{dt}\right) + \frac{a_{\mathrm{H,i}}V_{\mathrm{i}}}{V_{\mathrm{e}}}\left(\frac{d\epsilon}{dt}\right) \tag{13}$$

The improvements in the present permeation model are consideration of the diffusion of metal ions to the external surface of emulsion globules and the account taken of the break-up of emulsions. We discuss verification of the model in more detailed in the next section. Figure 3 shows a typical result of rare earth metal extractions by LSMs. The order in the permeation rates of rare earth metals by LSMs is similar to the results in liquid–liquid extraction (10), and it followed the molecular weights of the rare earth metals. The overall rate constants, k_o, for each metal could be evaluated by fitting the experimental results with Eqs. (8)–(13) using the Runge–Kutta–Gill method.

Verification of Permeation Model

Figures 4 and 5 show the relation between the overall mass transfer coefficients, k_o, and the extractant dimer concentration, $C_{(\mathrm{HR})_2}$, or the surfactant concentration, C_{S}, with synthesized cationic surfactant, $2C_{18}\Delta^9GEC_2QA$. On the basis of the results in Fig. 4, we found that an increase in the concentration of the carrier is effective for enhancing the extraction rate of such light rare earth metals as La and Nd but not very effective for such heavy rare earth metals as Yb because the rate-determin-

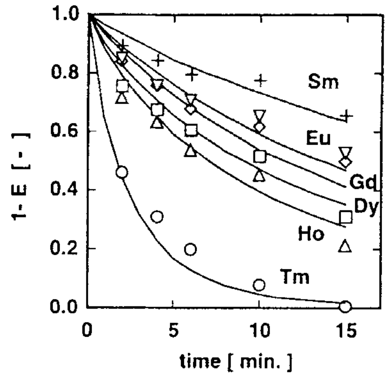

FIG. 3 Extraction of rare earth metals with liquid surfactant membranes.

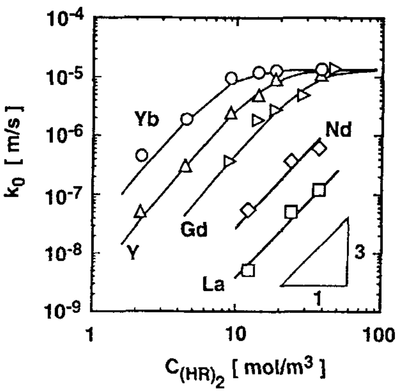

FIG. 4 Relation between extraction rate and dimer concentration of carrier for each metal (C_S = 20 mol/m^3).

ing step for heavy rare earth metals shifts from the interfacial reaction step (Step II) to the diffusion step of metal ions to the external interface (Step I) with increasing concentration of the carrier. Therefore, the distribution of Step (I) to the permeation behavior of metal ions is important with increasing molecular weight of rare earth metals. The k_o values in Fig. 4 lie on the calculated line, which has a slope of about 3 at a low dimer concentration as predicted from Eq. (6) and approaches the mass transfer coefficient k_m in the high concentration range. The obtained value of k_m, which is 1.2×10^{-5} m/s, is close to the value reported previously

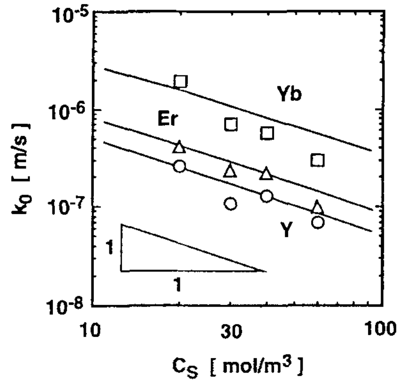

FIG. 5 Relation between extraction rate and surfactant concentration for each metal ($C_{(HR)_2}$ = 4.72 mol/m^3).

in the liquid–liquid extraction of rare earth metals (15). Clearly, the result in Fig. 5 suggests that the surfactant somewhat interrupts the permeation rate of metals due to the adsorption of surfactants at the outer surfaces of emulsion globules. In the present concentration range of surfactants, although W/O emulsions were very stable (6) and the degree of break-up is always less than 1% after 15 minutes of operation, the contribution of break-up appears at a degree of extraction of more than 95%. The values of k_b in this work were around $5 \times 10^{-7}\ s^{-1}$. The k_o values in Fig. 5 also lie on the calculated line, which is inversely proportional to the surfactant concentration as predicted from Eq. (6). These results support the validity of the permeation model proposed in this study.

Figure 6 shows the effect of $C_{(HR)_2}$ in the liquid membrane and the pH in the feed aqueous solution on the separation factor between Yb and Y, $\beta_{Yb/Y}$, with $2C_{18}\Delta^9GEC_2QA$. The separation factors are found to be strongly influenced by the two operational parameters pH and carrier concentration, and these results are reflected in the permeation mechanism of the rare earth metals by LSMs. A high separation factor can be obtained under conditions in which the interfacial reaction (Step II) governs the permeation process of metal ions. As the extraction rate is considerable small under such conditions, we have to determine the optimum conditions by taking into account the extraction rate of metal ions along with the separation efficiency. Since the calculated results agree with the experimental data, we can obtain the appropriate operational conditions for the separation of rare earth metals by calculating with the proposed model.

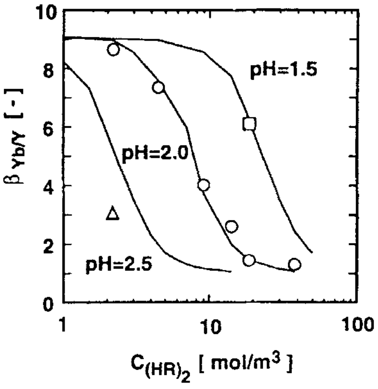

FIG. 6 Effect of dimer concentration of carrier and pH in the feed solution on the separation factor between Yb and Y.

Effect of Surfactant

Figure 7 shows a representative result of extraction by LSMs using four surfactants. The extraction rate was strongly influenced by the structure of the surfactant used, and it was accelerated by using the new cationic surfactant, $2C_{18}\Delta^9GEC_2QA$, as previously reported (6). Although the effect of the counterion of the cationic surfactant was investigated, there was no difference in the extraction behavior between chloride and bromide anions. As previously described, we can deduce that the higher the interfacial activity is, the lower the extraction rate is. However, $2C_{18}\Delta^9GEC_2QA$ has the highest interfacial activity and the highest extraction rate among surfactants used in this study. In a previous study (6) it was considered that the acceleration effect in the extraction of rare earth metals is due to the concentration of the anionic carrier dialkyl phosphoric acid to the reaction interface by the electric interaction between the cationic surfactant and the anionic carrier. For the cationic surfactant $2C_{18}\Delta^9QA$, however, the acceleration was not remarkable. This result means that different surfactants having identical electric properties can have significantly different behaviors in liquid membrane operation, and that the extraction rate of metals by LSMs is governed not only by the electric environment but also by the nature of the microenvironment, e.g., the microviscosity and local pH at the oil–water interface. Therefore, to design a surfactant suitable for LSM operations, we have to pay attention to not only the hydrophilic part of a surfactant but also to the hydrophobic part. It is surprising that small changes in the structure of a surfactant can cause quite different extraction results, and that the selection of a surfactant is

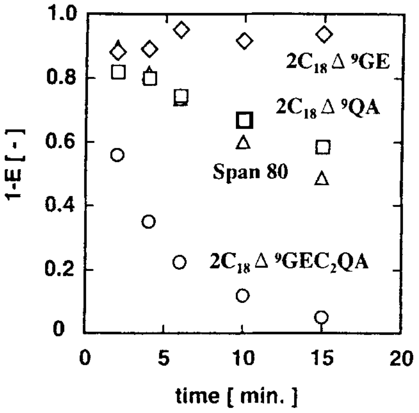

FIG. 7 Effect of surfactants on extraction rate of Yb.

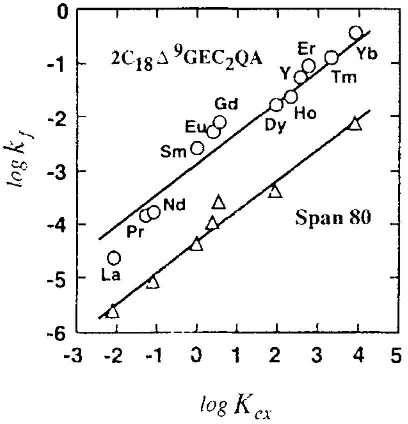

FIG. 8 Relation between the extraction equilibrium constant and the interfacial reaction rate constant with Span 80 and $2C_{18}\Delta^9GEC_2QA$.

often a key factor in the success of a liquid surfactant membrane operation. A more detailed and systematic study about the structure effect in a surfactant on extraction efficiency is now under way.

Figure 8 shows the relation between the extraction equilibrium constant, K_{ex}, and the interfacial reaction rate constant, k_{fM}, with the two surfactants Span 80 and $2C_{18}\Delta^9GEC_2QA$. If the interfacial reaction follows the Eigen mechanism (16), the k_{fM} values should be almost of the same order of magnitude for all the rare earth metals. Clearly, the results in Fig. 8 suggest that the assumption of an interfacial rate at the interface is more reasonable than the assumption of chemical equilibrium (5). The k_{fM} values of $2C_{18}\Delta^9GEC_2QA$ were about 20 times larger than those of Span 80 for all rare earth metals. Since the slope was almost equal in both surfactants, the extraction mechanism cannot be changed in $2C_{18}\Delta^9GEC_2QA$.

CONCLUSION

Extraction and separation of 12 rare earth metals were carried out using LSMs containing PC-88A as a carrier and a synthesized surfactant. It is clear that the structure of the surfactant strongly affects the degree of rare earth extraction by LSMs, and, in particular, the hydrophobic moiety of the surfactant is a key factor in ensuring a high extraction ratio in a short time. The synthesized cationic surfactant $2C_{18}\Delta^9GEC_2QA$ accelerates the extraction rate of rare earth metals in LSM operations remarkably compared with Span 80. The extraction behavior can be explained by a permeation model which takes into account the diffusion of metals in an external aqueous phase, an interfacial reaction, and a break-up of emulsions. Based on the results obtained to date, $2C_{18}\Delta^9GEC_2QA$ appears to be one of the best surfactants currently available for rare earth extraction using LSMs.

ACKNOWLEDGMENTS

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NOMENCLATURE

A	interfacial area defined by $6V_E/d_E$ (m^2)
a_H	activity of hydrogen ion (mol/m^3)
C_i	concentration of species i (mol/m^3)
d_E	diameter of W/O emulsion globule (m)
HR	monomer species of carrier
$(HR)_2$	dimer species of carrier
$K_{(HR)_2}$	interfacial adsorption equilibrium constant of dimer (m^3/mol)
K_S	interfacial adsorption equilibrium constant of surfactant (m^3/mol)
k_b	break-up rate constant defined by Eq. (11) (s)
k_f	interfacial reaction rate constant (m/s)
k_f'	apparent interfacial reaction rate constant [$mol^3/(m^8 \cdot s)$]
k_m	mass transfer coefficient (m/s)
k_o	overall mass transfer coefficient (m/s)
$MR_i jHR$	metal complex species
R	interfacial reaction rate [$mol/(m^2 \cdot s)$]
t	time (s)
V	phase volume (m^3)

Greek Symbols

$\beta_{i/j}$	separation factor between i and j metals (ratio of k_o) (—)
ϵ	break-up ratio of LSM (—)

Subscripts

ad	adsorbed state at the interface
aq	aqueous phase
E	emulsion phase
e	external phase
i	internal phase
M	metal species
org	organic phase
S	surfactant

Superscripts

0	initial state
*	adjacent to interface

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