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Influence of Synergistic Tributyl Phosphate and Di-(2-ethylhexyl)phosphoric Acid for Separation of Gadolinium and Samarium by Emulsion Liquid Membrane

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Gadolinium is one of the rare earth elements, which plays an essential role in modern industry. Its separation from mixtures of other rare earth elements is challenging due to similar physical and chemical properties. The extraction method using an emulsion liquid membrane is an effective and simple method for separating low concentration gadolinium from other rare earth elements mixtures. It is more eco-friendly than the liquid-liquid extraction process and also has various advantages. This study aims to determine the effectiveness, permeability and optimum formulation conditions for the separation of gadolinium and samarium using synergistic ligands tributyl phosphate and di-(2-ethylhexyl)phosphoric acid. The results showed a quantitative extraction (87.40%) of gadolinium ion at the optimum conditions of 0.025 M tributyl phosphate + 0.075 M di-(2-ethylhexyl phosphate), 4% span 80 as surfactant, 9000 rpm emulsification stirring speed and 0.5 M nitric acid as stripping phase, for a feed containing 1.5 mg/L gadolinium ion and 3 mg/L samarium ion at 5 M HNO₃.

Keywords: Emulsion liquid membranes, Synergistic activity, Rare-earth elements.

INTRODUCTION

Rare earth elements (REEs) are gaining popularity due to their distinctive electrical, optical, catalytic and magnetic properties, which have resulted in crucial roles in several industries such as metallurgy, ceramics, magnetism, catalysts, health, automotive, nuclear and semiconductors [1-6]. Among the REEs elements, gadolinium is one of the REEs garnering attention due to its high demand, particularly in the nuclear and non-nuclear, healthcare and digital industries [7,8]. Therefore, considerable effort has been expanded in determining the effective methods of separating gadolinium from its mixture.

Acid digestion and deposition are usually followed by solvent extraction to separate gadolinium from its mixture [1]. Metals can be extracted from a combination using advanced solvent extraction technology also called emulsion liquid membrane (ELM), which is both efficient and safe for the environment [9]. Extraction and stripping occurs simultaneously in ELM technique depedening upon the selectivity of the liquid membrane. The separation is achieved by permitting the solute to diffuse through this liquid phase from the feeding phase to

the collecting phase. The membrane phase is generally immiscible in both the feed and receiving phases, while the other phases are normally miscible [10]. Furthermore, the high mass transfer rate, cheap cost and high energy efficiency, as well as the small amount of organic solvents and extractants required, all contribute to overcome the issue of green chemistry [10,11].

In general, the performance of ELM is affected by two factors, namely mass transfer flux and selectivity [12]. Mass transfer flux is the process from the feed to the stripping phase through the membrane phase [13]. Furthermore, transporting metal ions into the liquid membrane occurs due to the concentration gradient of metal ions in the stripping phase and the feed phase [14]. The membrane selectivity is based on the ratio of the component distribution coefficient between the feed and the membrane phase. However, the difference in concentration causes the solute to diffuse from a high concentration to a low concentration solution. Selecitivity can be improved by using a compound with a higher affinity to remove one of the components [15].

The synergistic molecules for the ELM method offer a competitive alternative. The utilization of two kinds of molecule

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improves the selectivity and efficiency during the separation by ELM [16,17]. Several compounds have been investigated for their ability to selectively separate gadolinium, but among them, organophosphorus based compounds like tributyl phosphate (TBP) and di-(2-ethylhexyl)phosphoric acid di-(2-ethylhexyl)phosphoric acid di-(2-ethylhexyl)phosphate) (D2EPHA) considered the best selection [18]. Although, D2EPHA is a much more selective compound than TBP for recovering rare earth elements [19], on the other hand, TBP has a higher loading capacity than the D2EPHA [20]. The reaction that occurs between the metal compounds follows the cation exchange reaction below:

$$M(H_2O)_{(FP)}^{n+} + H - OX_{(MP)} \iff M(OX)_{n(MP)} + H_{(FP)}^+ + H_2O$$

The success of the ELM method was determined based on the creaming (emulsion leakage is called creaming) number and swelling ratio, which are indicators to measure emulsion stability [21]. When the swelling ratio and creaming number values are close to 0, the emulsion formed is stable. It does not leak either from the stripping phase that comes out of the emulsion or the feed phase that enters the emulsion, which is caused by swelling, coalescence, breaking and flocculation [22,23].

The challenge of separating out individual rare earth metals from a slurry of multiple elements in the same group and near together in the periodic table is the reason for this study. The approach developed in this study is a purification process from the combination of two rare earth metals, in particular for gadolinium . However, gadolinium is always found together with samarium, although in small concentrations. The present work investigated the synergistic effects of tributyl phosphate (TBP) and di-(2-ethylhexyl)phosphoric acid (D2EHPA) molecules for the separation of gadolinium and samarium by the ELM method. The effect of optimized parameters, such as surfactant concentration, homogenizer speed, synergistic ligand (TBP:D2EPHA), stripping phase and feed phase concentration, was also investigated.

EXPERIMENTAL

The chemicals *viz*. samarium nitrate, gadolinium nitrate, nitric acid (65%), Span-80 (60%), *n*-hexane (95%), tributyl phosphate (97%), di-(2-ethylhexyl phosphate) (97%) were of the highest purity and procured from Sigma Aldrich, USA.

General procedure

Optimization of emulsion liquid membrane conditions:

The organic phase was prepared by mixing tributyl phosphate (TBP) and di-(2-ethylhexyl)phosphoric acid (D2EHPA), as well as Span-80 with various concentration in the range of 2-4.5%, then dissolved in 25 mL of *n*-hexane. Subsequently, 25

mL of nitric acid was added with a specific concentration variation and stirred with a homogenizer until an emulsion was formed at a particular speed. The emulsion formed was then used to extract gadolinium and samarium in the feed phase with a volume ratio of emulsion and a feed phase 1:1 at an extraction time of 30 min. In present work, the concentration of both metals was prepared from monazite mineral, which contains 1.5 ppm Gd and 3 ppm Sm. The concentrations of Gd and Sm obtained from the ELM separation method were then analyzed by ICP-OES. Final, the optimal conditions were determined by extracting the parameters using the ELM approach as described in Table-1.

Membrane diffusion process: Diffusion of metal ions across a liquid membrane can be calculated using eqn. 1 [14]:

$$\frac{dN}{d\theta} = DA \frac{\Delta C}{\Delta X} \tag{1}$$

where $dN/d\theta$ is the amount of material that diffuses into the membrane in a unit of time; D is the diffusion coefficient; A is the interface area; ΔC is the different concentrations of the material in the internal phase and phase feed; and ΔX is the thickness of the membrane.

The value of $\Delta A/\Delta X$ in eqn. 1 is replaced by D'[V_m/V_E], from which we get [14]:

$$\frac{dN}{d\theta} = D' \left(\frac{V_m}{V_E} \right)$$

$$D' = \ln \frac{C_{in}}{C_{out}} \times \frac{1}{\theta} \times \frac{V_M}{V_E}$$
(2)

where D' is the effective diffusion coefficient (penetration rate); $V_{\text{M}}/V_{\text{E}}$ is the volume ratio of membrane phase (emulsion) to the feed phase (external); C_{in} is the concentration of material in internal phase after separation; C_{out} is the concentration of material in feed phase after separation; and θ is the contact time of emulsion in the feed phase.

Swelling ratio was calculated by analyzing the volume increase or decrease of the membrane following extraction. In contrast, the creaming number was determined by measuring the change in volume after stripping, while the swelling ratio was calcuated by measuring the change in membrane phase (eqns. 3 and 4) [22]:

Creaming number =
$$\frac{V_{\text{Final}} - V_{\text{Initial}}}{V_{\text{Initial}}}$$
(3)

Swelling ratio =
$$\frac{V_{Initial}}{V_{Initial}}$$
 (4)

where V_{Final} and $V_{Initial}$ = the stripping phase volume after and before emulsion, respectively.

TABLE-1 VARIATION OF EMULSION LIQUID MEMBRANE PARAMETER CONDITIONS WITH SYNERGISTIC LIGANDS												
Variable	1	2	3	4	5	6	7					
Surfactant concentration (%)	2	2.5	3	3.5	4	4.5	-					
Homogenizer speed (rpm)	6000	7000	8000	9000	10000	_	-					
Concentration of (TBP: D2EPHA) (M)	0.0:0.10	0.01:0.09	0.025:0.075	0.05:0.05	0.075:0.025	0.09:0.01	0.10:0.0					
Stripping phase concentration (M)	0.25	0.50	1.00	1.50	2.00	2.5	_					
Feed phase concentration (M)	3	3.5	4	4.5	5	5.5	6					

The optimization was carried out by adjusting the concentration of the ligand while keeping the stirring speed and selected surfactant constant and the next-to-last stage involves a change in the concentration of the phase. The variation in the concentration of Gd and Sm in the stripping and feed phases was determined at each stage using ICP-OES. The performance of this ELM separation method was determined based on the measurements of extraction efficiency, stripping efficiency and

separation factor using the following eqns. 5-7 [24]:

$$E(\%) = \frac{[M^{3+}]_0 - [M^{3+}]_t}{[M^{3+}]_0} \times 100$$
 (5)

$$S(\%) = \frac{[M^{3+}]_{\text{strip}}}{[M^{3+}]_{t}} \times 100$$
 (6)

$$SF = \frac{K_{d_a}}{K_{d_b}} \tag{7}$$

$$K_{d} = \frac{[M^{3+}]_{stat}}{[M^{3+}]_{mobile}}$$
 (8)

where %E = extraction efficiency; %S = stripping efficiency; $[M^{3+}]_0$ = initial metal concentration in the feed phase; $[M^{3+}]_t$ = metal concentration after extraction in feed phase; $[M^{3+}]_{strip}$ = metal concentration in stripping phase; $[M^{3+}]_{stat}$ = metal compound concentration of stationary phase; $[M^{3+}]_{mobile}$ = metal compound concentration of mobile phase phase; SF = separation factor; K_{d_A} and K_{d_B} = distribution coefficient of metal A and metal B, respectively.

RESULTS AND DISCUSSION

The emulsion liquid membrane (ELM) extraction method has advantages over ordinary solvent extraction, namely simultaneous, high diffusion and mass transfer rates and the use of less organic solvents. Although the ELM method is quite effective, this method still has interfer-ences. Factors that lead to membrane leakage, swelling and creaming formation on the membrane and membrane breaks can all affect the stability of an emulsion. The effectiveness of ELM process depends on a number of parameters, including emulsification method, agitation mechanism, surfactant effect, extractant effect, phase internal/stripping and feed phase [25,26].

Surfactant concentration effect: A surfactant with low hydration capacity, low diffusivity and a high molecular weight is required to get the stable emulsions [16]. While the demulsification process is not likely to be affected by the emulsion's

stability [16,27], however, an ideal surfactant concentration is necessary; since the stability of emulsion is greatly depend on the surfactant concentration. When liquid membrane emulsion develops either of cracking, creaming or flocculation, it becomes ineffective for use in the separation process [18].

In this study, the HLB value of the surfactant Span-80 is 4.3, therefore it was chosen since it fulfills the HLB criteria [28]. The detail of the emulsion formulations with various concentrations of surfactants is given in Table-2, where the result swelling ratio and creaming number are shown in Fig. 1.

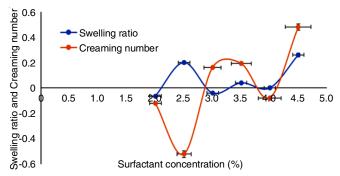


Fig. 1. The relationship between creaming number and swelling ratio with surfactant concentration

As shown in Table-2, the best creaming number and swelling ratio can be achieved with the 4% surfactant concentration, which is close to 0. However, when the surfactant concentration exceeds 4%, the membranes become thick, viscous and difficult for the analytes to pass through. An increase in the surfactant concentration leads to the formation of aggregates, which reduces the emulsion stability, diffusion rate and mass transfer coefficient. Meanwhile, a surfactant concentration of less than 4% leads to the formation of an unstable emulsion [20,21].

Under the emulsion conditions, gadolinium and samarium were successfully separated, with an extraction efficiency of 72.53% and an extraction efficiency of 27.13% for samarium, respectively while the stripping efficiency of Gd and Sm was 84.92% and 69.65%, respectively.

Effect of stirring speed: The stirring system is essential to obtain the right size of the emulsion membrane droplets, resulting in a sufficiently good stripping phase [29,30]. A rapid stirring system in the agitation process causes the formation of small droplet diameter. The surface area of the permeation becomes more significant and the mixing process between the droplets becomes slower [31]. In contrast, the slow stirring agitation process produces a larger diameter of droplets joining

	TABLE-2 SURFACTANT CONCENTRATION VARIATIONS IN THE ELM METHOD											
No	Surfactant	irtactant	Feed phase initial volume	Feed phase volume after extraction (mL)	Stripping phase volume after extraction (mL)	Membrane volume (mL)		Creaming number	Swelling ratio			
	conc. (70)		(mL)			Initial	Final	пишьст	Tatio			
1	2.0	4	50	53.2	22	50	46.8	-0.12	-0.064			
2	2.5	4	50	40	12	50	60	-0.52	0.2			
3	3.0	4	50	52	29	50	48	0.16	-0.04			
4	3.5	4	50	48	29.8	50	52	0.192	0.04			
5	4.0	4	50	50	23	50	50	-0.08	0			
6	4.5	5	50	37	37	50	63	0.48	0.26			

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the membrane, causing the emulsion membrane to break easily [32]. However, a sufficient stirring speed is required for the collision to occur and form an optimal emulsion. In this study, the effect of stirring speeds were examined at 6000, 7000, 8000, 9000, and 10000 rpm on the emulsion membranes.

Fig. 2 showed that the results of the optimized stirring speed variation at 9000 rpm produce a creaming number and swelling ratio close to 0. The results of gadolinium and samarium separation showed that the extraction efficiency of gadolinium and samarium from the Gd-Sm mixture is 74.11% and 23.83%, while their stripping efficiency is 85.02% and 70.11%.

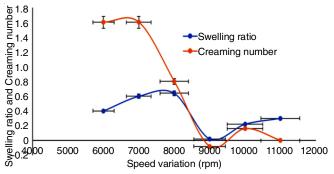


Fig. 2. The relationship between creaming number and swelling ratio with the emulsion stirring speed

Effect of concentration: The presence of ligands in the emulsion membranes plays the role of binding analyte in feed and preventing the surfactant from interfering with the emulsion stability [29,32]. Therefore, the ligand needs to form complexes with the analyte and dissolve in the membrane phase [33]. The TBP and D2EHPA ligands form an uncharged complex that allowed the metal ions (Gd or Sm) to pass through a non-polar liquid membrane phase to the stripping phase. In addition, ligand spreads back within the membrane phase surface to form the complex with analyte in the feed phase, after releasing metal ions in the stripping phase [34]. In this work, the extractant D2EHPA forms complex compounds with REEs in the aqueous phase, acting as a complexing ion to reduce the positive charge of metal ions following dissociation and the release of H⁺ions. Meanwhile, TBP functions as a neutral extractant by solvating the complex compound formed between D2EHPA and metal ions, increasing the solubility of the complex compound and allowing it to be dispersed to the organic phase [34].

Fig. 3 show that the mixture composition of TBP: D2EPHA ligands produces the most stable emulsion with the lowest swelling ratio and creaming values at a concentration of 0.025 M TBP and 0.075 M D2EPHA. Furthermore, this composition shows the extraction efficiency against Gd and Sm ions to be 82.80% and 38.00%, respectively (Fig. 4). In addition, the stripping efficiency of gadolinium ions obtained in this composition is 82.85%, with a Gd-Sm separation factor of 7.85.

Stripping phase concentration effect: The extraction efficiency is related to the concentration of stripping phase due to the difference in chemical potential and ionic strength of the aqueous phase [16,35]. In addition, the difference in the osmotic pressure between the stripping phase, such as nitric acid and the feed phase significantly affects the emulsion swelling [32,36].

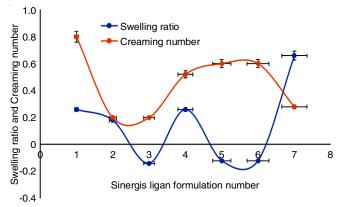


Fig. 3. The relationship between the response (swelling ratio and creaming number) with synergistic ligands concentration variations

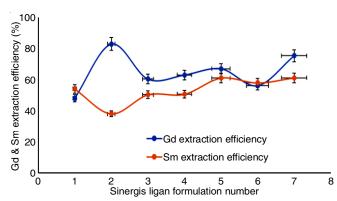


Fig. 4. The relationship between the response (Gd and Sm extraction efficiency) with synergistic ligands concentration variations

Fig. 5 showed that 0.5 M nitric acid is the optimal concentration of the stripping phase. This is reflected by the high gadolinium extraction efficiency of 86.90% and the resulting high separation factor value of 6.62 (Gd to Sm) compared to most other concentrations of the stripping phase. In addition, the emulsion formed in 0.5 M nitric acid is the most stable, which is shown by a creaming number of 0.40 and a swelling ratio of 0.30 (Fig. 6).

Effect of feed phase concentration: One of the working mechanisms of the ELM method is the existence of an osmotic pressure system, namely the transfer of ions from high concen-

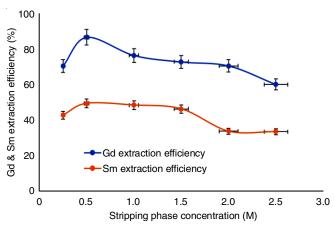


Fig. 5. The relationship between Gd and Sm extraction efficiency with stripping phase concentration variations

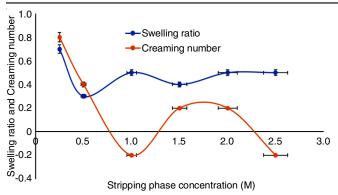


Fig. 6. The relationship between the response (swelling ratio and creaming number) with stripping phase concentration variations

tration to low concentration until an equilibrium state is reached. The difference in pH between the feed phase and the stripping phase is the main force as the driving force for the transfer of analytes for various ELM-based separation processes, this is due to the difference in hydrogen ion concentration in the two phases which results in differences in osmotic pressure. If the pH difference between the feed phase and the stripping phase increases, it can increase the chances of the membrane swelling and if pH difference is too low, the driving force of the analyte will be lower from the feed phase to the stripping phase. Therefore, it is necessary to optimize to obtain the optimal pH difference between the feed phase and the stripping phase [32,36]. Therefore, it is necessary to optimize the concentration of feed phase, such as nitric acid.

Fig. 7 shows that 5 M nitric acid feed phase is the optimum concentration. The Gd and Sm extraction efficiency at this condition is 87.40% and 50.40%, respectively. Moreover, the Gd-Sm separation factor is 6.83, higher than most other feed phase results. Fig. 8 showed that the emulsion formed is relatively stable as indicated by the value of creaming number and swelling ratio, which are 0.4 and 0.26, respectively. Therefore, it was concluded that the formulation with a stripping and feed phase of 0.5 M and 5 M nitric acid, respectively, forms an emulsion with a high gadolinium extraction efficiency.

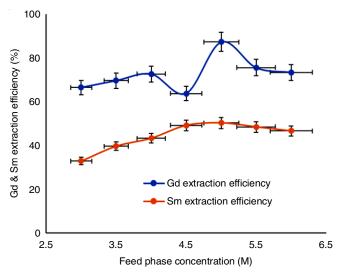


Fig. 7. The relationship between Gd and Sm extraction efficiency with feed phase concentration variations

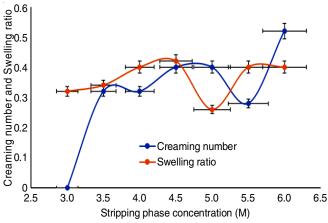


Fig. 8. The relationship between the response (swelling ratio and creaming number) with feed phase concentration variations

Mass diffusion coefficient: The performance of the ELM method is evaluated by mass transfer flux from the feed to the stripping phase through the membrane phase [13,14]. The mass transfer during the separation of Gd and Sm is determined by the diffusion coefficient (D'). The higher diffusion coefficient for Gd is related to a higher rate of Gd diffusion from the feed to the stripping phase. The diffusion coefficient is calculated according to eqns. 10 and 11 and found to be 0.063 and 0.0033, respectively for Gd and Sm.

$$D'_{(Gd)} = \ln \frac{C_{in}}{C_{out}} \times \frac{1}{\theta} \times \frac{V_{M}}{V_{E}}$$
(10)

$$D'_{(Sm)} = \ln \frac{C_{in}}{C_{out}} \times \frac{1}{\theta} \times \frac{V_{M}}{V_{E}}$$
(11)

where $D'_{(Gd) \text{ or } (Sm)}$ = effective diffusion coefficient (Gd or Sm); V_M/V_E = volume ratio of membrane phase (emulsion) to the feed phase; C_{in} = concentration of the material in internal phase after separation (Gd or Sm); C_{out} = concentration of the material in feed phase after separation (Gd or Sm); θ = contact time of the emulsion in the feed phase.

Conclusion

In this work, the optimal conditions of the separation efficiency and permeability of gadolinium and samarium using synergistic two ligands viz. tributyl phosphate and di-(2-ethylhexyl)phosphoric acid (D2EPHA) were achieved by through emulsion liquid membrane (ELM) technique. The optimum conditions were achieved at surfactant concentration Span-80 = 4%, emulsion stirring speed = 9000 rpm, concentration of synergistic ligand (TBP:D2EPHA) = 0.025 M:0.075 M, stripping phase concentration = 0.5 M nitric acid, feed phase concentration = 5 M nitric acid, extraction time = 30 min, membrane volume ratio and feed phase volume = 1:1. The extraction efficiency of Gd and Sm ions = 87.40% and 50.40%, respectively, while the stripping efficiency of Gd and Sm = 97.48% and 89.55%, respectively. Meanwhile, the emulsion formed by this formulation is relatively stable, resulting in a quite small chance of leakage. This is indicated by the swelling ratio and creaming number values close to 0 (creaming number = 0.40 and swelling ratio = 0.26).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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