Jurnal Akademika Kimia 11(1): 46-55, February 2022
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.untad.ac.id/jurnal/index.php/JAK/index

The Effect of Surfactants on Separation of Light Rare Earth Metals using Emulsion Liquid Membrane Method: Review

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Received 23 December 2021, Revised 25 January 2022, Accepted 22 February 2022
doi: 10.22487/j24775185.2022.v11.i1.46-55

Abstract

Rare earth metals (REM) are scarce elements and are only found in the form of complex compounds of phosphate and carbonate. REM consists of 17 elements classified into light REM, medium REM, and heavy REM. This article is focused on lightweight REM, which is widely applied in various industrial fields. Many REM applications are increasing the demand for high-purity and bulk REMs. However, REM has almost the same physical and chemical properties, making it difficult to separate. Therefore, the separation of REM is interesting to study with various methods, one of which is Emulsion Liquid Membrane (ELM). ELM is developing a solvent extraction method involving three phases: the external phase, the internal phase, and the membrane phase. The key to the success of ELM lies in the stability of the emulsion, which is very dependent on the type and concentration of surfactants, so in the ELM process, it is necessary to choose the right concentration and type of surfactant. Therefore, this article was made to know the effect of surfactants such as span-80, span-85, and T154 in separating light REM using the ELM method.

Keywords: Rare earth metals, emulsion liquid membrane, surfactants.

Introduction

Rare earth metals (REM) are a group of metals consisting of 15 lanthanide elements along with scandium and yttrium (Wu et al., 2018). REM has almost the same chemical and physical properties. It is due to its electron configuration, which affects its valence level. An increase in electron shells does not accompany the number of electrons in the REM. Therefore, REM has the same outermost electron, namely 6*s*, with varying numbers of electrons in the 4*f* and 5*d* shells (Cotton et al., 1999). REM is widely applied in conventional industrial fields such as metallurgy, ceramics, magnetism, electronics, and nuclear. In addition, REM and its compounds are also commonly used in advanced industries such as hybrid cars, cell phones, and fluorescent lighting (Torkaman et al., 2015; Xie et al., 2014). The REM is divided into light, medium, and heavy REM. This article focuses on the weak REM group consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), scandium (Sc), and yttrium (Y) (Fontana & Pietrelli, 2009).

In general, REM is not found in free elements but is an alloy in the form of complex compounds. Therefore, in its use in various fields, it is necessary to separate the tough compounds first (Suprapto, 2009). Several methods have been used to separate and purify REM, such as crystallization, chemical precipitation, ion exchange, adsorption, and solvent extraction. On an industrial scale, conventional solvent extraction is usually used to separate rare earth metals (De Morais & Mansur, 2014; Dukov, 1993; El-Hefny & El-Dessouky, 2006; Torkaman et al., 2013). However, the solvent extraction process has several drawbacks, including high chemical consumption, formation of a third phase, and the need for many extraction steps to obtain high purity products (Tasaki et al., 2007; Uezu et al., 1995). In addition, conventional solvent extraction methods are considered less effective at low metal ion concentrations (Suren et al., 2012; Wannachod et al., 2015). Therefore, the solvent extraction method was developed into a liquid membrane-based technology using emulsion liquid membrane (ELM) (Kakoi et al., 1998; Kumbasar & Tutkun, 2006). This development was carried out because ELM resulted in high mass transfer and surface area, simultaneous extraction and stripping in one step, relatively low cost, energy consumption, and the ability to process various compounds relatively quickly (Binnal & Hiremath, 2012).

In principle, emulsion liquid membrane (ELM) involves two liquids that are mixed but cannot dissolve each other. Emulsions can be formed from the aqueous and mixed organic phases

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when an emulsifier is added, known as an emulsifier or surfactant (Mohamed & Ibrahim, 2012). The separation of REM using the ELM method is based on the transport of metal ions through a membrane in the form of a liquid containing a ligand as a carrier (Sulistyani et al., 2016). The ELM system consists of a membrane phase (extractant and surfactant in organic solvents), an internal phase (stripping agent), and an outer phase (metal ion components to be separated). This method is usually started with preparing a surfactant stabilized emulsion. This emulsion contains a carrier in the oil phase and a release agent in the internal phase. The emulsion will be dispersed with relatively low agitation into an external phase containing solutes to be separated (Jusoh & Othman, 2017).

The key to success in the REM separation process using the ELM method lies in the stability of the emulsion, which is strongly influenced by surfactants. An emulsion is said to be stable if the emulsion is not quickly broken within a certain period. Emulsion stability is highly dependent on surfactant concentration. An increase in surfactant concentration causes an increase in membrane stability through interfacial tension between the phases, which results in finer droplets and smaller agglomerates, leading to a higher contact area, so the emulsion is more stable (Meilinda et al., 2021). However, surfactant concentrations that are too high will make the emulsion too stable because it can increase the viscosity of the membrane, which results in reduced diffusivity of the REM and ligand complex, and swelling of the membrane, thereby decreasing the extraction efficiency. Therefore, in separating REM with ELM, it is necessary to select the right surfactant concentration (Davoodi-Nasab et al., 2018). In addition, the type of surfactant must also be chosen appropriately to minimize water transport during the extraction process (Kumar et al., 2019). Surfactants are amphipathic organic compounds. Contain hydrophobic and hydrophilic sides as stabilizers that will serve as a connecting bridge where the hydrophilic side will bind to the water phase. The lipophilic side will bind to oil to produce a mixture of water and oil (Gaupp & Adam, 2014). Therefore, this review article discusses the effect of surfactants on the separation of light rare earth metals using the method of emulsion liquid membrane (ELM).

Results and Discussion

Surfactant

Surfactants are amphipathic organic compounds that contain a hydrophobic group on the tail and a hydrophilic group on the head to dissolve in organic solvents and water (Bnyan et al., 2018). The tail part of the surfactant will bind to the oil (non-polar), while the head part will bind to the water (polar). Thus, surfactants can be soluble in organic and water solvents (Ahmad et al., 2011).

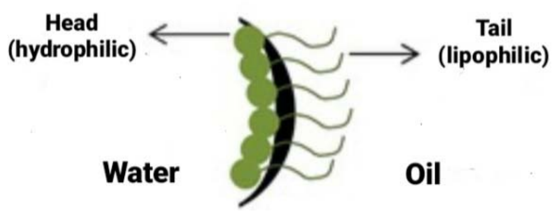

Figure 1. Structure of surfactant (Bjorkegren & Karimi, 2012).

In ELM, the surfactant acts as a stabilizer that will serve as a connecting bridge where the hydrophilic side will bind to the water phase, and the lipophilic side will attach to the oil to produce a mixture of water and oil (Gaupp & Adam, 2014). In this case, the surfactant can lower the surface tension of the two liquid phases. When the membrane and internal phases in the ELM system mix, surfactant molecules will be adsorbed between the two phases, so that the interfacial tension decreases and mixing occur (Bjorkegren & Karimi, 2012). In addition, surfactants can maintain emulsion stability and affect emulsion viscosity and mass transfer processes in the ELM system. Provide specific dynamic properties at the membrane phase interface to prevent membrane damage that can affect the value of separation efficiency and determine the level of emulsion demulsification (Raji et al., 2017).

Type of surfactants In general, surfactants are classified into four main groups, namely (Chakraborty et al., 2010):

1. Anionic surfactants are surfactants whose hydrophilic part is negatively charged. Examples include sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and fatty acid salts.
2. Cationic surfactants are surfactants whose hydrophilic part is positively charged. An example is cetyltrimethylammonium bromide (CTAB).
3. Amphoteric (zwitterionic) surfactants are surfactants whose hydrophilic parts contain positive and negative charges. Examples include dodecyl betaine, dodecyl dimethylamine oxide, and coco amphora glycinate.
4. Non-ionic surfactants, namely surfactants whose hydrophilic part is not charged. Examples include alkyl poly(ethylene oxide), poly(ethylene oxide), and poly(propylene oxide) copolymers.

Surfactants for light REM separation by ELM method The ELM system has two types of emulsions: type emulsion water-oil-water (W/O/W), where the oil phase separates the internal and external water phases.

The second type is type emulsion oil-water-oil (O/W/O), where the water phase separates the oil phase internal and external (Hussein et al., 2019). The nature of the surfactant determines the type of emulsion used. These properties depend on the hydrophilic-lipophilic balance (HLB) of the surfactant. HLB is a parameter of the balance of the size and strength of the hydrophilic and lipophilic sites of the surfactant molecule (Gupta et al., 2019). An HLB value ranging from 0 to 20 is required (Nollet et al., 2019). Surfactants with low HLB (0-10) prefer lipids and tend to form W/O/W emulsions, while surfactants with high HLB (11-20) are more hydrophilic and tend to form O/W/O emulsions. In separating light REMs using the ELM method, suitable surfactants to make W/O/W emulsions are surfactants with HLB values between 4-8 (Chakraborty et al., 2010).

There are several surfactants used in the separation of light rare earth metals using the ELM method, including the following:

(1) Span-80

Span (sorbitan fatty acid esters) is a surfactant with a low HLB value that acts as a lipophilic non-ionic emulsifier to make W/O emulsions (Bnyan et al., 2018). Sorbitan monooleate (span-80) is a derivative of sorbitan which is generally used to maintain the stability of emulsions with a pleasing shape (Sajjadi, 2006). Span-80 is a sorbitan ester with the chemical name sorbitol monooleate ($C_{24}H_{44}O_6$), a mixture of ester particles from sorbitol with oleic acid. Span-80 comprises a non-polar alkyl tail and a polar oleic ion head. The non-polar tail of span-80 will stick to the oil, and the polar head will stick to the water (Kopanichuk et al., 2018). Span-80 has a molecular weight of 428 g/mol and has a hydrophilic-lipophilic balance (HLB) value of 4.3 so it tends to be more soluble in the organic water phase (Hong et al., 2018). Span-80 is the most frequently used surfactant in the separation of light rare earth metals using the ELM method, such as the separation of Th and Ce, separation of U and Ce, separation of Nd, separation of Y and Dy, separation of Sc, and separation of La and Nd. The following is the chemical structure of the span-80 molecule (Park, 2006).

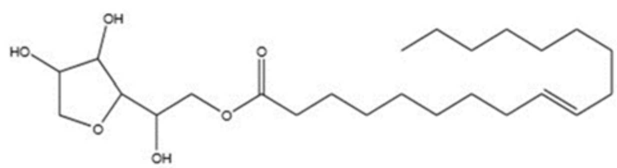

Figure 2. Molecular structure of span-80 (Park, 2006)

(2) Span-85

Sorbitan trioleate (span-85) is a sorbitan ester; its chemical name is sorbitol trioleate ($C_{60}H_{108}O_8$), a mixture of ester particles of sorbitol with three oleic acids. Span-85 has a molecular weight of 958 g/mol and has a hydrophilic-lipophilic balance (HLB) value of 1.8 so it tends to be more soluble in the organic phase (Hong et al., 2018). Span-85 has been used to separate light rare earth metals by the ELM method, such as separating Nd (Davoodi-Nasab et al., 2017). The following is the chemical structure of the span-85 molecule (Martins et al., 2017).

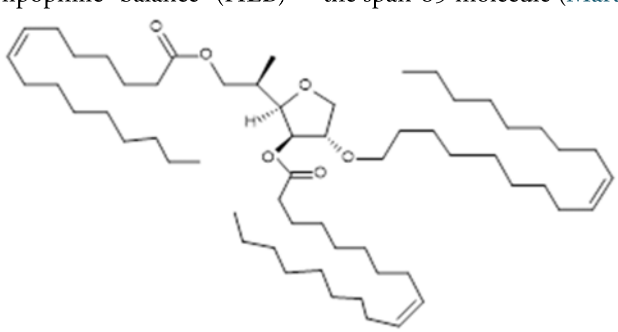

Figure 3. Molecular structure of span-85 (Martins et al., 2017).

(3) T154

Polyisocrotyl succinimide (T154) is a polyamine surfactant with a long hydrocarbon chain structure. Surfactant T154 is a non-ionic surfactant and has high stability in acidic conditions, so that it can be used in the ELM method. Surfactant T154 has been used to separate light rare earth metals by the ELM method to separate lanthanides (Chen et al., 2018).

Effect of surfactant concentration plays a significant role in forming a stable emulsion (Anitha et al., 2015). Emulsion stability will increase with increasing surfactant concentration. The increased surfactant concentration can reduce the interfacial tension between the membrane and internal phases, making the emulsion more stable. However, an increase in surfactant concentration that is too large can affect the separation process, including causing emulsion instability, difficulty breaking the emulsion at the end of the operation, and increasing the membrane viscosity, which can inhibit the transfer of rare earth metal ions in the membrane (Zhang et al., 2016).

(1) Span-80

Span-80 is the most frequently used surfactant in the separation of light rare earth metals by the ELM method, such as in the separation of U and Ce (Washito et al., 1996), separation of Sc (Wang et al., 2011), separation of Th and Ce (Purwani & Biyantoro, 2013), separation of Ce (Hachemaoui et al., 2015), separation of Nd (Anitha et al., 2015), and separation of Y and Dy (Basuki & Pamungkas, 2019).

Washito et al. (1996) performed the separation of U and Ce using a span-80 surfactant with concentrations from 1-8%. The data obtained are listed in **Figure 4**. The figure shows that the creaming rate continues to decline or approaches nil with the addition of span-80 at a 1-4 % concentration. Furthermore, at a concentration of 5-6%, the number is obtained creaming with a value of zero. And at a concentration of 7-8%, the rate creaming increased or further away from zero. It shows that the best emulsion liquid membrane is span-80 with a concentration between 5-6% of the organic phase volume because an emulsion can be said to be stable if it has a number equal to 0 (Washito et al., 1996).

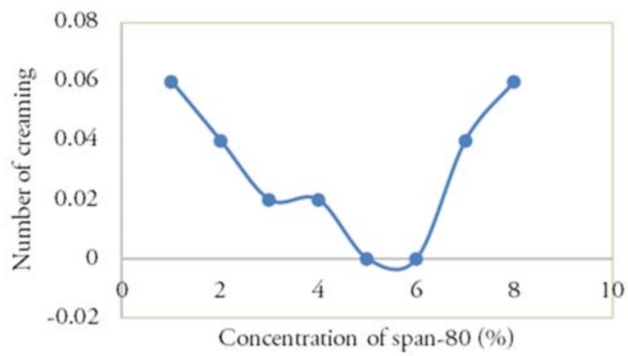

Figure 4. The effect of span-80 on the number creaming (Washito et al., 1996).

The surface will decrease with surfactant concentration to a certain level in the membrane phase, which can favor the formation of finer emulsion granules. Still, increasing surfactant concentration can reduce the interface. A surfactant that is too high in the membrane will increase the viscosity of the emulsion so that it can slow down the diffusion of the complex in the membrane phase and cause swelling of the emulsion (Meilinda et al., 2021).

Purwani et al., (2002) performed the separation of La and Nd using a span-80 surfactant with varying concentrations from 3-7%. The data obtained are listed in **Figure 5**, which shows extraction efficiency La and Nd increased when the addition of 3-5% span-80. The maximum values at a concentration of 5% were 55.55 and 41.63%.

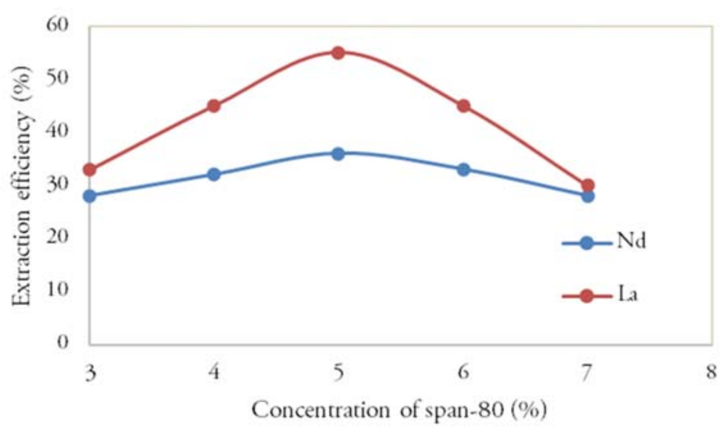

Figure 5. The effect of span-80 on the extraction efficiency of La and Nd (Purwani et al., 2002).

However, at a concentration of 6-7%, the extraction efficiency of La and Nd decreased. It shows that the best extraction efficiency for separating La and Nd is span-80 with a concentration of 5% (Purwani et al., 2002). The increase in surfactant concentration causes a decrease in the surface tension between the air phase and the oil phase so that a more stable emulsion is obtained. However, an excessive increase in surfactant concentration will cause a decrease in the extraction percent. The cause is that too much surfactant in the membrane phase will increase the viscosity of the emulsion so that it can slow down the diffusion of the complex in the membrane phase (Hidayah et al., 2017).

Wang et al. (2011) performed the separation of Sc using a span-80 surfactant with concentrations varying from 1-7%. **Figure 6** shows the addition of 1-3% span-80 increased the extraction efficiency up to 98.5% at a concentration of 3% span-80. However, there was a decrease in extraction efficiency at a 5-7% concentration. This case shows that the best extraction efficiency for Sc^{3+} separation is span-80 with a concentration of 3% (Wang et al., 2011).

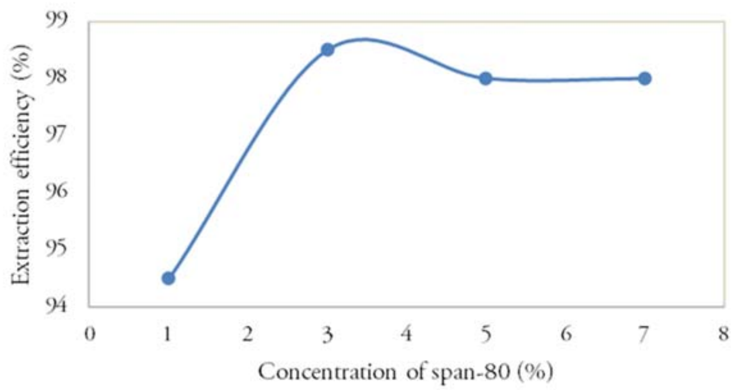

Figure 6. The effect of span-80 on the extraction efficiency of Sc^{3+} (Wang et al., 2011).

Purwani & Biyantoro (2013) separated Th and Ce using a span-80 surfactant with 2.5-4.5% concentrations. The data obtained are listed in **Figure 7**. The figure shows that the use of span-80 less than 3.5% causes the emulsion to be less stable. It can be seen from the creaming and ratios swelling very high and low, namely 50 and -30, because an emulsion is said to be tough if it has a number creaming and a ratio projecting close to 0. At the use of span-80 above 3.5%, the water phase trapped in the organic phase increases because the external aqueous phase enters the emulsion system and joins the aqueous phase. Internally, some of the aqueous phases are trapped in the organic phase. However, as much as 4.5% span-80 causes an increase in creaming and swelling ratio (Purwani & Biyantoro, 2013). A large surfactant concentration can reduce the interfacial surface to produce a stable emulsion. In contrast, a low surfactant concentration causes emulsion damage so that the creaming number and swelling ratio are high (Kumar et al., 2019).

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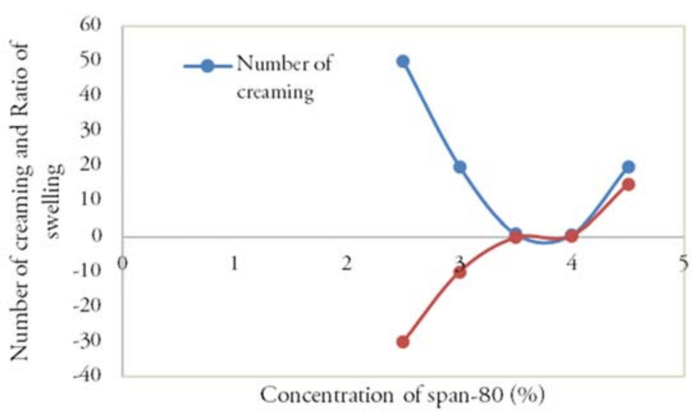

Figure 7. The effect of span-80 on number creaming and ratio swelling (Purwani & Biyantoro, 2013).

Anitha et al. (2015) have separated Nd using span-80 surfactants with concentrations of 0.5-5%. The data obtained are listed in **Figure 8**. The figure shows that the neodymium extraction increased with increasing surfactant concentration from 0.5 – 2% (v/v). However, the total extraction of Nd(III) decreased with a further increase in the Span-80 concentration. It is was due to mass transfer (viscosity increase) and osmotic swelling caused by a large amount of surfactant present in the system. A surfactant concentration of 1% (v/v) was optimal to compensate for mass transfer and osmotic swelling (Anitha et al., 2015).

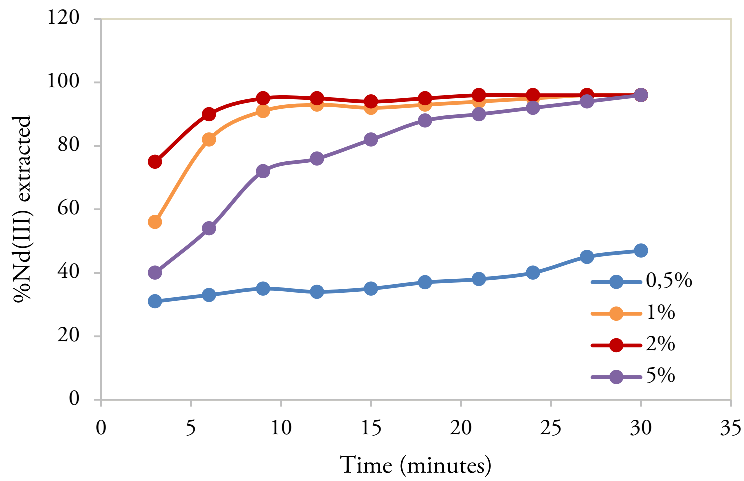

Figure 8. Effect of the surfactant concentration on the extraction of Nd (Anitha et al., 2015).

(2) Span-85

Span-85 has been used to separate light rare earth metals by the ELM method, such as in the Nd separation conducted. The data in **Figure 9** shows was found that there was a significant interaction of MWCNT concentration with a concentration of span-85. These factors can increase the extraction efficiency at an increase from a lower level, but after specific values, the efficiency tends to decrease. Based on the optimization results, the optimum condition for the span-85 concentration range is 2.1 (%v/v) with a predicted maximum efficiency of 99.03% (Davoodi-Nasab et al., 2017).

(3) T154

T154 has been used to separate light rare earth metals using the ELM method, as in the separation of RE^{3+} conducted by Chen et al., (2018). In this study, surfactants T154 and span-80 were used to compare concentrations varying from 4 % to 16%. **Figure 9** shows that T154 and span-80 have different effects on the extraction efficiency of RE^{3+}. In this study, the emulsion containing 8% T154 was suitable and stable throughout the processing time, and the highest extraction rate reached 82.68%. Increasing or decreasing the surfactant concentration from 8 to 16 % or 8 to 4 % resulted in a slight decrease in the amount of RE^{3+}, as shown in **Figure 9**.

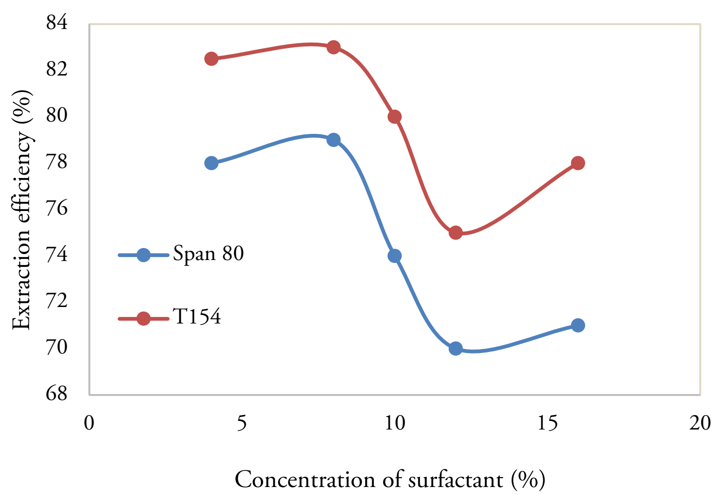

Figure 9. Effect of surfactant concentration on the extraction efficiency of REM (Chen et al., 2018).

The extraction efficiency of T154 was superior to that of span-80. When span-80 was used as a surfactant, Emulsions break easily under the influence of acids and alkalis, which are easily damaged. As a result, the stability of the liquid membrane is reduced. This effect is because Span-80 is an ester surfactant with short hydrocarbon chains and is hydrophilic because its oxygen moiety is readily hydrolyzed in an acidic or basic environment. In contrast, T154 is a polyamine surfactant with high carbon content and has a long hydrocarbon chain structure and a nitrogencontaining hydrophilic component. ELM with span-80 tends to break easily and is not strong enough to withstand high acidity, while ELM with T154 is more stable against swelling. That is, decreasing swelling can increase the extraction efficiency of RE^{3+}. Low molecular weight and low concentration surfactants have the potential to produce emulsions with smaller droplet sizes when used in conjunction with colloidal particles. Therefore, further studies for RE^{3+} were carried out using T154 as a surfactant in ELM (Chen et al., 2018).

A summary of various concentrations and types of surfactants in the separation of light rare earth metals using the membrane emulsion liquid method is shown in **Table 1**.

Table 1. Types and concentrations of surfactants in the separation of light REMs using the ELM method.

Method	REM	Types of Surfactants	Concentrations of Surfactants	Results	References
ELM	U and Ce	Span-80	1-8 % (Opt. 5%)	%E U = 23.65% Ce = 7.09%	(Washito et al., 1996)
	La and Nd	Span-80 and Tween 80	3-7% (Opt. 5%)	%E La = 55.55% Nd = 41.63%	(Purwani et al., 2002)
	Nd	Span-80	0.5-5% (Opt. 1%)	%E Nd = 97%	(Anitha et al., 2015)
	Sc	Span-80	I-7% (Opt. 3%)	%E Sc = 98%	(Wang et al., 2011)
	Th and Ce	Span-80	2.5-4% (Opt. 3.5%)	%E Th = 46.41% Ce = 84.54%	(Purwani & Biyantoro, 2013)
	Ce	Span-80	1-7% (Opt. 3%)	%E Ce = 98%	(Hachemaoui et al., 2015)
	Nd	Span-85	2,1 %	%E Nd = 99.03%	(Davoodi-Nasab et al., 2017)
	RE	T154 and Span-80	4-16% (Opt. 8%)	%E RE = 82.68%	(Chen et al., 2018)
	Y dan Dy	Span-80	5%	Separation Factor Y-Dy = 7.57	(Basuki & Pamungkas, 2019)

Acknowledgments

The author gratefully acknowledges the support from Research and Technology Grants or the National Research and Innovation Agency through the Higher Education Excellence Basic Research scheme (1207/UN.6.3.1/PT.00/2021).

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