Review

Emulsion liquid membrane for heavy metal removal: An overview on emulsion stabilization and destabilization

A.L. Ahmad [a,*], A. Kusumastuti [a,b], C.J.C. Derek [a], B.S. Ooi [a]

[a] School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia
[b] Department of Chemical Engineering, Universitas Negeri Semarang, Kampus Sekaran, Gunungpati, 50229 Semarang, Indonesia

A B S T R A C T

Extraction processes using emulsion liquid membrane (ELM) have received significant attention due to their potential as an effective technique for treatment of industrial liquid wastes. However, the need to obtain desired level of stability is very important in order to overcome the obstacle of the application of ELM at industrial scale. The small droplet diameter of emulsion is a key criterion that will provide a stable emulsion and a larger mass transfer area. Two important factors related to the stability of emulsion such as method of emulsification and mechanism of emulsion breaking is discussed in detail. Various emulsification methods such as mechanical agitation and ultrasound emulsification, as well as the emulsion formulation which includes composition, selection of agent, and operation parameters on emulsion stabilization were presented. Emulsion destabilization in term of emulsion breakdown mechanisms such as coalescence, swelling and leakage was also discussed.

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1. Introduction

Emulsion liquid membrane (ELM) is a promising technique for the separation of contaminants such as metals, weak acids/bases, inorganic species, and hydrocarbons due to the high interfacial area for mass transfer, the ability to remove and to concentrate selectively or collectively, and the requirement of only small quantities of organic solvent. In the ELM process, both extraction and stripping are combined in one stage, which leads to simultaneous purification and concentration of the solute [1]. There is a substantial saving in contacting equipment volume, separate contactors for extraction and stripping processes, which are generally carried out in conventional solvent extraction processes, are not required. The ELM process could be up to 40% cheaper than that of solvent extraction [2]. ELM process generally consists of three steps. The first step is emulsion preparation in which emulsion is prepared by mixing membrane phase and internal phase such as water-in-oil (W/O), water is dispersed into the oil in the form of fine droplets or particles. The second step is permeation of solute through membrane phase from a feed phase to a receiving phase through interfacial contact between emulsion and continuous phase consisting metal waste. The third step is settling of the emulsion and external phases followed by demulsification to recover the membrane phase.

The flow diagram of the batch mixer-settler operation is shown in Fig. 1 [3].

Since ELM invented by Li [4] in 1968, the use of this method for the hydrometallurgical recovery of heavy metals has drawn attention of many investigators. Frankenfeld and Li [5], Martin and Davies [6] and Kitagawa et al. [7] were among the earliest investigators to report the extraction of metal ions. Then, in 1986, the method has been successfully commercialized to remove zinc from wastewater in the viscous fiber industry at Lenzing, AG, Austria [8]. This process can treat up to 75 m³/h of zinc bearing wastewater with the zinc concentration ranging from 0.3 to 200 mg/l. Zinc can be removed with up to 99.5% efficiency [9]. Other three industrial plants for zinc removal are located at Glanzstoff, AG, Austria (700 m³/h capacity), at CFK Schwarza, Germany (200 m³/h capacity), and at AKZO Iede, Netherlands (200 m³/h capacity) [9].

Although this method is very effective and has been successfully applied for zinc removal, but so far its commercial applications on the removal of other heavy metals have been limited by the emulsion instability. The common emulsion instability includes membrane leakage, coalescence, and emulsion swelling. The lack of stability of the emulsion globules will decrease extraction efficiencies [10]. On the other hand, a too stable emulsion causes new problems during its settling and demulsification in the third stage [11]. In order to solve the stability problem of emulsion liquid membrane, its formulation design is foremost important includes selection of carrier, strip agent, surfactant, diluents [8], and preparation method. In this paper, numerous studies to improve the emulsion stability were reviewed. Besides, emulsion breakdown

* Corresponding author. Tel.: +60 4 5995999; fax: +60 4 5941013.
  E-mail address: chlatif@eng.usm.my (A.L. Ahmad).

mechanisms are also presented to clearly highlight the kinetic stability of emulsions.

2. Emulsion stabilization

As mentioned above, both the methods of emulsification and membrane compositions play an important role to produce stable emulsion which is associated to droplet diameter of emulsion. Emulsion droplet is trapped in the emulsion globule as shown in Fig. 1. The droplet diameter can be expressed as Sauter diameter (d_{32}) which is representing the average surface diameter as follow [12]:

$$d_{32} = \frac{\Sigma_i n_i d_i^3}{\Sigma_i n_i d_i^2} = 6\frac{V}{A} \qquad (1)$$

where n_i, d_i are the number and diameter of droplets belonging to the ith class, while V and A are the total volume and area of the dispersed phase, respectively.

Small droplet diameter tends to have better breaking resistant and rapid extraction. If the droplet diameters are too small, however, the emulsion is very difficult to break by any mechanical means [13]. In addition, too many of them are packed into each organic globule and consequently the liquid membrane becomes too thin and ruptures easily [14]. On the other hand, large droplet diameters result in poor stability and extraction efficiency [13] because of a low surface-to-volume ratio [14]. Li et al. [13] suggested that emulsions with droplets in the range 0.3–10 μm (preferably 0.8–3 μm) combine rapid extraction rates, good stability and are readily broken by electrostatic means. Therefore, the precise formation of emulsion will be critical to the success of emulsification processes.

2.1. Emulsification methods

In emulsion preparation, energy must be supplied to produce such meta-stable mixtures. Energy may be provided through various means. The most widely applied method to produce emulsions is mechanical agitation including stirrer, mixer, homogenizer, etc.

Other method is ultrasound generation which is an alternative method to dissipate mechanical energy, required for droplet disruption, in a liquid [15].

2.2. Mechanical agitation

2.2.1. High shear agitation

This method is designed to generate a very strong flow field. In many applications of heavy metals extraction, the membrane phase and internal phase are mixed at higher rotation speed. For this purpose, most investigators used high-speed homogenizers to prepare the emulsions. Due to the high rotation speed of the rotor, the medium to be processed is automatically drawn axially into the dispersion head and then forced radially through the slots in the rotor/stator arrangement. In addition, high turbulence occurs in the shear gap between rotor and stator, which provides optimum mixing of the emulsion. The literatures showed that emulsification speeds up to 24,000 rpm for 1–30 min are needed to form the emulsion with small droplet diameter, depend on the emulsion composition and equipment used.

In some studies of Sengupta and co-workers [16–18], d_{32} are 3.424, 3.38, and 2.72 μm, respectively, at emulsification speed of 12,000 rpm and time of 30 min. Whereas, Gameiro et al. [19] and Reis and Carvalho [20] found that d_{32} are 2.13 and 1 μm, respectively, prepared at 7,000 rpm and 20 min emulsification. The different size must be caused by the difference of emulsion composition. Nevertheless, most of investigators revealed that the size of internal droplets decreased with the increase of the emulsification speed and time up to a certain level by maintaining other parameters remain constant [16,20–25]. Venkatesan and Begum [21,22] prepared W/O emulsion at 2,000–12,000 rpm for 2–10 min using a high-speed homogenizer. In their conclusion, the optimum conditions could be achieved around emulsification speed 10,000 rpm for 6 min which gave lower breakage. Gasser et al. [25] performed emulsification with an ultra high speed disperser at 3,000–8,000 rpm during 2-10 min for extraction of Co(II) from aqueous solution and found that the lower breakage was obtained for a speed of 7,000 rpm and an emulsification time of 5 min. For
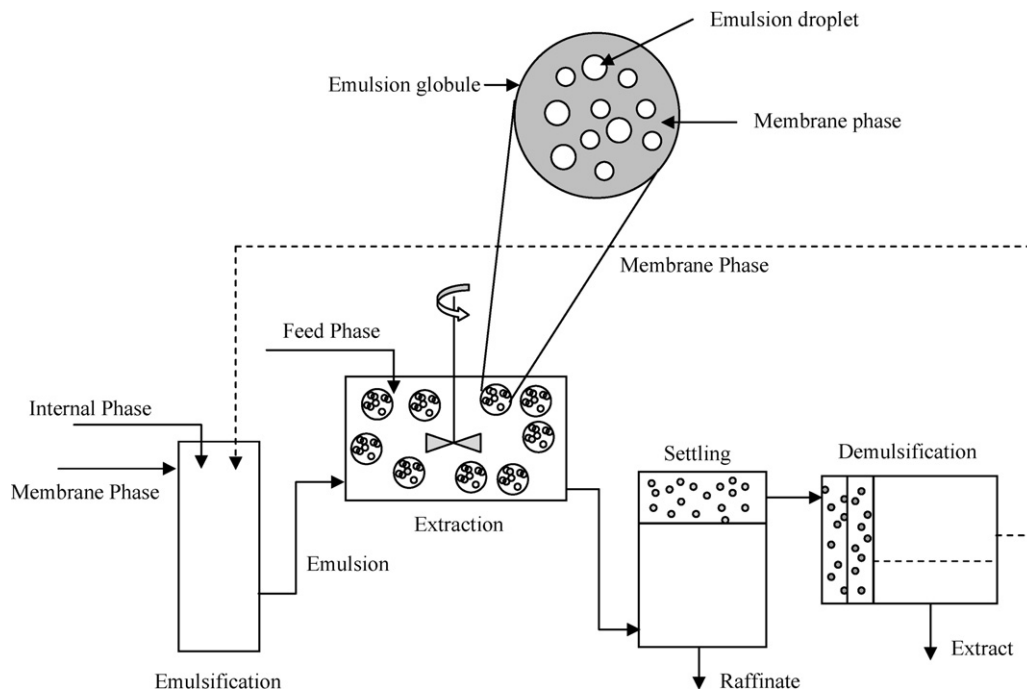

Fig. 1. Flow diagram of batch mixer-settler process of ELM [3].

insufficient emulsification time, the breakage is high because the droplets have a large size, which leads to their coalescence. In contrast, for long emulsification time, the breakage is increased due to high internal shearing leading to a very high number of small droplets by volume unit [22,24,25].

2.3. Low shear agitation

In this system, the flow field is not very intense. Usually, the emulsion is stirred at 1,000–4,000 rpm using overhead stirrers with various stirring tools such as propeller, disk, turbine, toothed disk stirrer, etc. The droplet size is usually relatively large, but will become smaller with longer emulsification time. The literatures showed that emulsification time until 60 min is needed to form the emulsion.

Many researchers have used this system to prepare the emulsion, but very rarely information about emulsion drop size was provided in literatures. Nevertheless, generally the emulsion droplets diameter ranging 1–10 μm [24,26,27]. Kulkarni and Mahajani [28] in their experiment found that the emulsion droplets diameter to be in the right range as mentioned. The emulsion was prepared at 3,000 rpm for 30 min with a six-blade turbine impeller, resulting a stable milky white emulsion with the mean diameter of the droplets varying from 1 to 8 μm [28]. The stable emulsions have much more time to coalesce, better breaking resistant, rapid extraction, and easier settling and demulsification.

Typical photographic of emulsion droplets at various emulsification speeds [29] is given in Fig. 2. As shown, the size and number of emulsion droplets vary according to the agitation rate used in the emulsion preparation. Higher emulsification speed will produce smaller diameter and much more emulsion droplets than that of lower emulsification speed.

2.4. Ultrasound emulsification

Ultrasound processing is a very efficient emulsification technique compared with mechanical agitation [12,15,23]. With ultrasound, the drop size (d_{32} down to 0.3 μm) is much smaller than that given by mechanical agitation under the same conditions, which makes insonated emulsions more stable [23]. A rather stable emulsion can therefore be formed in a relatively shorter processing time [23]. Although ultrasound has been proved to be potential for emulsification, but only few studies focused on using this technique for preparing the W/O emulsions as used in ELM processes of heavy metal ions recovery [30–34]. This may be due to the production of W/O emulsions with high viscosity of continuous phase need higher threshold ultrasonic intensity compared to O/W emulsions. As reported by many researchers, ultrasound emulsification has been widely used to produce O/W emulsions. This process also needs combination of gentle mechanical stirring and insonation, otherwise the two types of emulsions are obtained simultaneously [12]. For ELM separation process, ultrasound emulsification must be managed very well; otherwise it may produce too stable emulsions in relatively short times, causing another problem in the following demulsification process. Besides, for being used in large vessel, some ultrasound probes are needed to provide homogeneity of acoustic field [12]. The ultrasound emulsification studies in production of W/O emulsions resulted globules diameter ranging from 0.01 to 0.1 mm [32,33]. While the emulsion droplets diameter was found to be 50 nm–1.5 μm [15,34].

The literatures indicated that ultrasound power, irradiation time, and probe position are the important parameters on the emulsion stability. Study showed that under the certain experiment condition, the percentage of emulsion breakage decreases with the increase of the ultrasound power until a certain level. Chiha et al. [30] prepared the emulsion at various power (5–35 W) and time

(1–10 min). The author found that the lower emulsion breakage was obtained at an ultrasonic power of 20 W, an emulsification time of 3 min and a distance of 20 mm of the probe from the bottom of emulsification cell which gave fine droplets of the internal aqueous phase. In the experiment of Juang and Lin [35], the d_{32} of internal phase droplet decreased with increasing the ultrasonic power up to 93 W for 1 min. While other study found that the narrow droplet size distribution can be obtained for irradiation time of 60 min and irradiation power of 75 W [36]. The differences of optimum power and time in the studies above can be attributed to the different of the emulsion compositions used, which affect to emulsion viscosity. The cavitation pressure threshold, associated with irradiation power, increases with an increase in the interfacial tension and viscosity of liquid [15,36]. The less viscous liquid in general undergoes cavitation more easily [12]. From these results, it can be described that a sufficient power and time are needed to make a stable emulsion. If the power is too low, the sound field is insufficient to give necessary energy for a good dispersion of aqueous droplets in the membrane phase [30]. On the other hand, if the power is too high, the phenomenon of coalescence is more significant due to the enhanced collision frequency of small droplets with an increase in the number of droplets and increase in the acoustic streaming velocity [30,36].

In summary, Table 1 shows the emulsion droplet and globule size produced by various equipments. As seen, emulsion droplet size is in the order of: mechanical agitation>ultrasound. The smallest droplet size, i.e. nano emulsion, can be produced by using ultrasound. This method also consumes less surfactant and lower energy than others [23]. By optimizing the power or cavitation distribution, this method can be applied in practice and scaled up to industrial use [15].

2.5. Emulsion formulation and its stability

The emulsion composition must be taken very well and suited with the kinds of metal to be extracted which is not only it must has highly extraction rate but also fairly stable against membrane leakage and swelling. Generally, the emulsion composition for heavy metals removal consists of a surfactant, extractant (carrier), internal phase (stripping solution), and membrane phase (diluent).

In metal extraction, mass transfer mechanism occurs due to chemical reaction in membrane phase which is the carrier species may be incorporated into the organic solvent in the membrane phase and gives rise to facilitate transport. The carrier molecule could selectively and reversibly react with the solute. The reversible reaction provides a means of enhancing the solute flux and improving the selectivity at the same time. For example, the extraction reaction of divalent metals (M) with D2EHPA (HX) as carrier would proceed as follows [37]:

$$M^{2+} + n(HX)_{2\,(org)} \rightleftharpoons MX_2(HX)_{2n-2\,(org)} + 2H^+ \tag{2}$$
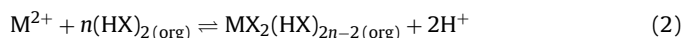
At low metal content for the extraction of metals with D2EHPA, the most probable structure of the extracted complex would be $MX_2(HX)_{2n-2}$ [37].

Table 2 shows some previous studies on heavy metals extraction using different emulsion compositions. As shown, various emulsion compositions were tested. Generally, the most widely used are Span 80 and kerosene for surfactant and diluent, respectively. While the use of extractant and internal phase depend on the kinds of metals to be extracted. For example, in case of copper removal, the use of LIX as an extractant and H_2SO_4 as an internal phase are more favorable than others. While in case of cadmium removal, the use of TOA and TIOA as an extractant and NaOH as an internal phase are the most used by researchers.

It is believed that the properties of the surfactant, extractant, internal phase, and membrane phase, as well as the stirring speed
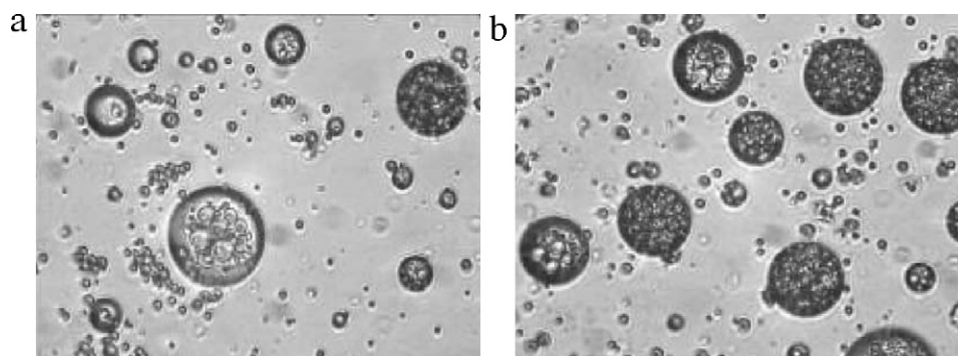
Fig. 2. Photographic of emulsion droplets at: (a) 4,000 rpm and (b) 8,000 rpm [29].

and contact time in the permeation process have significant effect on emulsion swelling and membrane leakage. Adequate disclosure of their effect is described in the section below.

2.6. Effect of surfactant

Surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water [8]. Surfactant plays a very important role in the emulsion formation and in the extraction process. It reduces the interfacial tension between oil and water by adsorbing at the liquid–liquid interface [8], maintains the emulsion stability and influences the transport rate of metal ions [37,39]. Wan and Zhang [40] revealed that the selection of a surfactant is the key measure to reduce emulsion swelling and membrane breakage. Therefore, the choice and development of a suitable surfactant [41–43] and establishment of surfactant concentration correctly will determine the success of ELM process.

There are some considerations of choosing surfactant for ELM separations. The hydrophile–lipophile balance (HLB) of surfactant determines the type of emulsion produced. Surfactants with a low HLB, typically ranging from 1 to 10, are more soluble in oil than water and tend to make a water-in-oil emulsion while those with a high HLB, typically ranging from 10 to 20, are more soluble in water than oil and tend to make an oil-in-water emulsion [8]. While to get stable emulsion, surfactant with least hydration capacity and low diffusivity due to its high molecular weight is preferable [40]. However, for overall ELM process, too stable emulsions are unfavorable for the difficulty in demulsification process.

Many literatures proposed of surfactant concentration to the emulsion stability. Generally, interfacial tension between the phases decreases by increasing the surfactant concentration up to a limiting value which favors the formation of more fine droplets which produces more stable emulsion. However, this effect only stabilizes the emulsion with respect to internal phase leakage; conversely to emulsion swelling [25]. The swelling rate increased with the increase in the surfactant concentration up to a certain value and then fell off with further increase in the surfactant concentration [16,40,44,45]. At the highest concentration, surfactant tends to form aggregates and decrease the emulsion stability. The increase of surfactant concentration also leads to a higher emulsion viscosity. The condition increases the resistance at the interface and does not favor the extraction kinetics which is decreases the diffusion and mass transfer coefficient [26,46–48]. The studies showed that the optimum surfactant concentration ranging from 2 to 5 wt%.

Beside of surfactant concentration, the emulsion stability is also significantly affected by the types of surfactant. Hasan et al. [49] reported that Span 80 with 12% concentration gave the least breakage compared to Span 85 and Arlacel A. Nevertheless, the used of Span 80 as surfactant dramatically increased the emulsion swelling particularly the osmotic swelling as the dispersion operation proceeded [40]. Osmotic swelling as well as emulsion stability increased in the order of surfactants used as: Span 80 > Lan 113A > ENJ-3029 > LMA [40]. Similar results also reported by Nakashio et al. [41] and Kakoi et al. [39] in which the emulsion with Span 80 was relatively easy to swell.

In order to solve the weakness of the commercial surfactants, some authors proposed and tested new type of surfactants for separation of metal ions such as a series of derivatives of glutamic acid dialkyl esters (abbreviated as $2C_{18}\Delta^9 GE$) and

Table 1
Operating condition and emulsion diameter at various emulsification methods.

Equipment	Condition	Diameter	Reference
Blender	Agitation at 12,000 rpm for 30 min	d_{32} (droplet): 3.424 μm	[16]
Blender	Agitation at 12,000 rpm for 30 min	d_{32} (droplet): 3.71 μm	[17]
Blender	Agitation at 12,000 rpm for 30 min	d_{32} (droplet): 2.72 μm	[18,96]
Disperser	Mixed at 7,000 rpm for 20 min	d_{32} (droplet): 2.13 μm	[19]
Dispeser	Mixed for 15 min	Mean globule diameter: 0.169 mm	[97]
Homogenizer	Mixed at 5,000 rpm for 15 min	d_{32} (globule): 0.65 mm	[98]
Disperser	Mixed at 7,000 rpm for 20 min	d_{32} (droplet): 1 μm	[20]
Homogenizer	Mixed at 10,000 rpm for 20 min	d_{32} (droplet): 3 μm	[99]
Colloid mill	Prepared in two steps:		[60]
	mixing of the oil phase at 1,000 rpm for 30 min	Mean droplet diameter: 4.5 μm	
	milling the emulsion in a colloid mill for 3 min	Mean droplet diameter: 1 μm	
Stirrer	Stirred at 4,500–5,000 rpm for 30 min	Mean droplet diameter: 2–6 μm	[100]
Stirrer	Stirred at 3,000 rpm for 30 min	Mean droplet diameter: 1–8 μm	[28]
Ultrasound	Prepared at 15–93 W for 20–30 min	d_{32} (droplet): 50 nm–1.5 μm	[35]
Ultrasound	–	d_{32} (droplet): <1 μm	[15]
Ultrasound	Prepared at 80 W for 15 s	Globule diameter: 0.01–0.1 mm	[32,33]

Table 2
Compositions and conditions of emulsion on heavy metals removal.

Solute	Surfactant	Extractant	Internal phase	Diluent	Reference
Copper	ENJ 3029 Paranox 100	LIX 64N Acorga P5100	H_2SO_4	S100N Isopar M LOPS	[13]
Copper	Span 80 ECA 4360J $2C_{18}\Delta^9GE$ $2C_{18}QA$	LIX 65N	H_2SO_4	n-Heptane	[41]
Copper	Span 80	LIX 984N-C	H_2SO_4	Kerosene	[16]
Copper	Span 80	LIX 84	H_2SO_4	Kerosene	[17]
Copper	Span 80	LIX 84 I	H_2SO_4	Kerosene	[18]
Copper	Span 80	LIX 622 LIX 84	H_2SO_4	Kerosene	[47]
Copper	Span 80	D2EHPA	$CuSO_4$ and disodium salt	Kerosene	[35]
Copper	Span 80	LIX-860 N-IC	H_2SO_4	Kerosene	[57,76,119]
Copper	ECA 4360J	LIX 54 LIX 84-I	H_2SO_4	Shellsol T	[19]
Copper	Span 80	D2EHPA	H_2SO_4	Hexane Heptanes Dodecane	[30]
Copper, nickel and cobalt	PEG	PEG	Potassium hydroxide	1,2-Dichloroethane	[38]
Chromium	ECA 4360J	TOA	$(NH_4)_2CO_3$	Kerosene	[58]
Chromium	ECA 4360J	Alamine 336	$(NH_4)_2CO_3$	Kerosene	[102]
Chromium	Span-80 Arlacel-A Span-85	TOPO	NaOH	Cyclohexane	[49]
Chromium	Span 80	TBP	NaOH	Hexane Heptanes Dodecane	[24]
Chromium	Span 80	DEPA	H_2SO_4	Kerosene	[103]
Chromium	Span 80	Alamine 336	NaOH	Kerosene	[104]
Nickel	Span 80	D2EHPA	H_2SO_4 NaOH HCl	Kerosene n-Heptane	[101]
Nickel	Span 80	DBHQ	H_2SO_4	Kerosene	[69]
Nickel	ECA 4360J	HQ	EDTA	Kerosene	[106]
Cobalt	ECA 4360J	TOA	H_2SO_4	Kerosene	[70]
Cobalt	ECA 4360J	TIOA	H_2SO_4	Kerosene	[107]
Cobalt	Span 80	CYANEX 923	H_2SO_4	Cyclohexane	[25]
Cobalt	ECA 4360J	PC 88A	HCl	Kerosene	[108]
Cobalt	Span 80	DBHQ	H_2SO_4	Kerosene	[71]
Cobalt	Span 80	TOPO	NH_4OH	Kerosene	[72]
Cobalt	Span 80	TBP	NH_4OH	Kerosene	[73]
Cobalt	PX 100	PC 88A	H_2SO_4	n-Heptane	[117]
Cobalt and nickel	ECA 4360J	Alamine 300	NH_4OH	Kerosene	[109]
Cobalt and nickel	Span 80	TOPO	NH_3	Kerosene	[46]
Zinc	ECA 4360J	D2EHTPA	H_2SO_4 and LiCl	Paraffinic solvent	[20]
Zinc and copper	Span 80	D2EHPA	H_2SO_4	Iso-dodecane	[63]
Zinc	Span 80	D2EHPA	H_2SO_4	Kerosene	[110]
Zinc	Span 80	PC 88A	HCl	Kerosene	[111]
Zinc	Span 80 $2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA$	PC 88A	H_2SO_4	n-Heptane	[42]
Silver	Span 80	D2EHPA	Hypophosphorous acid	Kerosene	[74]
Silver	Span 80	Cyanex 302	H_2SO_4	Kerosene	[65]
Silver	Span 80	D2EHPA	HCl HNO_3 H_2SO_4	Kerosene	[116]
Lead	Span 80	D2EHPA	H_2SO_4	Kerosene	[62]
Lead and cadmium	ECA 5025	D2EHPA	HCl, H_2SO_4	Tetradecane	[112]
Mercury	Span 80	TOA	NaOH	Toluene	[64]
Cadmium	Span 80	TOA	NaOH	Oxylene	[48]
Cadmium	Span 80	D2EHPA	HNO_3	Bayol 92	[60]
Cadmium	Span 80	TOA	NH_4OH	Kerosene	[105]
Cadmium	Span 80	D2EHPA	HCl	Kerosene	[37]
Cadmium	R-$C_6H_9O_2N_2$–$(C_2H_5N)_n$	TIOA	NaOH	Toluene Cyclohexane Kerosene	[75]
Cadmium	Span 80	Aliquat 336	NH_4OH	Kerosene	[66]
Gallium	ECA 4360J	TBP	HCl	Kerosene	[113]
Gold	LK 80	MIBK	NaOH, Na_2SO_3	Liquid paraffin	[26,27]

Table 2 (*Continued*)

Solute	Surfactant	Extractant	Internal phase	Diluent	Reference
Molybdenum	Polyamine Monesan	Aliquat 336	NaOH	Mixed of xylene, dodecane, heptane and kerosene	[28]
Ruthenium	Monemul Span 80	TOA	Perchloric acid	Liquid paraffin	[53]
Platinum and palladium	Span 80 PX 100	TLA TOMAC TBP TOPO TIBPS	HCl	n-Heptane	[39]
Platinum and Palladium	Span 80 PX100 $C_{18}/C_{18}\Delta^9QA$ $2C_{18}\Delta^9QA$	TLA TOMAC TBP TOPO TIBPS	Perchloric acid	n-Heptane	[39]
Palladium	Span 80 $2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA$ $2C_{18}\Delta^9GEC_2QAC_2PA$	DDTPA	Thiourea	n-Heptane	[51]
Palladium	Span 80 PX100	MSP-8	Thiourea	n-Heptane	[114]
Uranium	Span 80	TOPO	Na_2CO_3	Paraffin	[61]
Uranium	Span 80	Aliquat 336	Na_2CO_3	Kerosene	[115]
Heavy metals: Co, Ni, Cu, Cd	Span 80	8-Quinolinol	HCl	Toluene	[32]
Heavy metals: Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Pb(II)	Span 80	8-Quinolinol	HCl	Toluene	[34]
Trace elements: Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn	Span 80	D2EHPA, PC 88A	$HCl + H_2SO_4$	Kerosene	[118]
Rare earth metals	$2C_{18}\Delta^9GE$	$^tOct[4]CH_2COOH$	H_2SO_4	Toluene	[56]
Rare earth metals	$2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA$	PC 88A	H_2SO_4	n-Heptane	[43]
Rare earth metals	Span 80 $2C_{18}\Delta^9GEC_2QA$	PC 88A	H_2SO_4	n-Heptane	[50]
Rare earth metals	$2C_{18}\Delta^9GE$	$^tOct[1]CH_2COOH$ $^tOct[4]CH_2COOH$ $^tOct[6]CH_2COOH$	H_2SO_4	Toluene	[55]
Heteropolyanion	Span 80	TIBA	H_2SO_4	n-Heptane	[67]
Cephalexin	Span 80	Aliquat 336	Citrae buffer	n-Heptane Kerosene	[99]

dialkyl-type quaternary ammonium salts (abbreviated as $2C_{18}QA$) [41], L-glutamic acid dioleyl ester quaternary ammonium chloride (abbreviated as $2C_{18}\Delta^9GEC_2QA$) [42,43,50], L-glutamic acid dioleyl ester quaternary ammonium phosphoric acid (abbreviated as $2C_{18}\Delta^9GEC_2QAC_2PA$) [50], and polyamine-type polymeric surfactant (LMA) [40,52]. The new type surfactants in general form a stable emulsion and enhance the extraction rate in an even lower concentration range than do the commercial surfactants. The internal droplet diameter of $2C_{18}\Delta^9GE$ and $2C_{18}\Delta^9GEC_2QA$ were found about 4.7 and 4.9 μm, respectively [42]. The polymeric surfactant LMA showed much better performances and at concentration of 2.0% much more stable liquid membrane could be formed and the total emulsion swelling ratio was only 3.77% in 60 min which was much lower than Span 80, Lan 113A and ENJ-3029 [39]. However, the production of synthesized surfactants is limited in laboratory scale only due to the synthesis of surfactants takes a long time to complete [15].

The bi-functional surfactant which can serve two functions as a carrier and an emulsifier was also developed and tested. It may eliminate the addition of an extractant to ELM system [38]. Kakoi et al. [39] reported that the bi-functional surfactant not only stabilized a W/O emulsion in a relatively low concentration but also showed a high extraction ability. From the view points of the stability and the swelling of emulsions, two kinds of bi-functional surfactants, $C_{18}/C_{18}\Delta^9QA$ and $2C_{18}\Delta^9QA$, were found to be more

effective than conventional commercial surfactants (PX 100 and Span 80) [39].

2.7. Effect of extractant

Extractant acts as a 'shuttle' to carry the metal element through the liquid membrane [53]. However, its presence in membrane phase can decrease the emulsion stability. This is caused by the competitive adsorption with the surfactant as they have opposite behaviour. Interfacial tensions increased with an increase in carrier concentration in the membrane phase leading to formation of larger sized emulsion globules in the dispersed emulsion [18], conversely, interfacial tensions decreased by increasing the surfactant concentration up to a specific value. Gu et al. [10] revealed that the key criterion in selecting a carrier is that it and the complex formed must be soluble in the membrane phase, but not soluble in both the internal and feed phase. Further precipitation within the membrane or at the interfaces must also be prevented [54]. To obtain an efficient and selective mobile carrier for a specific metal ion, Kakoi et al. [55,56] developed a novel cyclic carrier such as $^tOct[1]CH_2COOH$, $^tOct[4]CH_2COOH$ and $^tOct[6]CH_2COOH$ for rare earth metals extraction. Among them, $^tOct[4]CH_2COOH$ was found to be interfacially active because it decreased the interfacial tension at lower concentrations, therefore the molecules adsorb at the oil–water interface together with the surfactant molecules. Fur-

thermore, ^{t}Oct[4]CH$_2$COOH molecules adsorbed might inhibit the orientation of surfactant molecules at the interface owing to the bulky molecules, hence increasing the emulsion stability [55].

A great number of studies gave evidence that not only the type but also the concentration of extractant affects the emulsion stability. Emulsion breakdown can occur at high concentration of carrier, since the carrier and its complex with the metal present interfacial characteristics that provoke loss of internal aqueous solution [57]. Besides, a very high content of carrier in the membrane does not result in a benefit due to the increase in viscosity, which leads to larger globules [24,25]. It was observed that emulsions containing 10% (v/v) LIX 84 I in the membrane resulted in globule sizes $d_{32} = 0.436$ mm while emulsions having 5% (v/v) LIX 84 I gave globules having $d_{32} = 0.406$ mm [18]. The literature showed that the different of d_{32} values affected the extraction rates in which the lower d_{32} gave higher extraction rate. This effect on extraction rate became significant in short contact times of about 15 min [18]. On the other hand, increase in emulsion viscosity affects the dispersion behaviour of the emulsion that causes a decline in the interfacial areas [17]. It was reported that increasing the concentration of extractant promoted the permeation swelling, which diluted the stripping solution. Chiha et al. [24] investigated the effect of the concentration of TBP as the carrier in the membrane phase for extraction of chromium (VI). It is seen that increasing the amount of carrier led to a decrease of the stability of the emulsion. This behaviour was due to the interfacial properties of the TBP that generated the formation of a reversed emulsion O/W, which involved the rupture of the emulsion. The best value of the carrier concentration was found to be about 20% (w/w). Other studies reported that 4% of extractant concentration gave a better emulsion stability and overall mass transfer using TOA and TOPO, respectively [37,58,59]. In case of cadmium removal, Sznejer and Marmur [60] recommended that 5% concentration of D2EHPA as the carrier in emulsion was the optimum condition. Swelling effect is more serious when D2EHPA concentrations is increased [35]. Further, from an economic point of view, a lower concentration of carrier is always preferred since carrier is the most expensive agent among the other components of membrane [28,61].

2.8. Effect of internal phase and diluent

The presence of both type and concentration of an internal phase and/or diluent in the emulsion have a significant effect on emulsion stability and so does the volume ratio of the internal phase to diluent. Generally, the increase of internal phase concentration until certain level will increase emulsion stability [62]. Beyond a critical internal phase concentration, the emulsion becomes unstable.

Many studies were conducted to examine the effect of internal phase concentration to the emulsion stability. Fouad [63] found that 1.5 M sulfuric acid in the internal phase was recommended as the optimum condition. Further increased in the concentration did not affect the zinc extraction. This was a result of the increases in the ionic strength difference between internal and external phases that resulted in an increase in swelling, which resulted in greater amounts of water to permeate through the membrane causing the internal droplets to swell and coalesce. The osmotic pressure difference between the internal and external phases is most probably responsible for the swelling [34]. Other researcher found that concentration of sulfuric acid for cobalt extraction which gives the lowest breakage is 0.5 M [25]. While Sabry et al. [62] reported that when the sulfuric acid concentration increases from 0.25 to 1 M, the stability of the emulsion increases, but decreases when the acid concentration is gradually increased from 1 to 3 M. For HCl as an internal phase, Matsumiya et al. [32] found that the optimum HCl concentration was 1.5 M which gave 95% metals recovery. Below 1.5 M HCl solution, there was leakage of internal phase caused by

the osmotic pressure difference between the internal and external solutions. A higher HCl concentration also led to emulsion swelling, thus lowering the recoveries abruptly [32].

The differences of hydrogen ions chemical potential between internal and external phase are the main driving force for extraction. The increase of internal phase acidity certain level will increase extraction efficiency due to its differences in chemical potential. However, at higher acidity level, the extraction will decrease due to the membrane swelling problem. Swelling is caused by the increase of ionic strength difference between internal and external phases.

In case of NaOH as an internal phase in emulsion, Li et al. [64] found that the optimum concentration of NaOH on mercury extraction was 0.05 M. The stability of the emulsion decreased when the NaOH concentration increased due to the reaction between NaOH and Span 80 that involved a reduction in the properties of the surfactant that consequently led to an emulsion destabilization [24]. Emulsion swelling increased with the basicity of internal droplets, because of the increased difference in the osmotic pressure between feed and strip phase [61].

The emulsion resistance was also affected by types of internal phase. Othman et al. [65] revealed that sulfuric acid was more preferable in making the acidic thiourea solution than HCl because it made the emulsion almost stable during the extraction operation of silver. This is due to sulfate ion which is a much softer ion compared to chloride ion, thus do not easily form metal salts that can interrupt the interfacial activity between membrane and receiving phase. The breakup of emulsion occurred continuously when using HCl as a thiourea solution. This indicates that the presence of salt in the receiving phase results in interfacial film breakdown that leads to membrane leakage. Therefore, once the formation of salts in the receiving phase take place, the membrane structure becomes unstable and breakdown. Thus, the water transferred from the internal to external phases and the volume of emulsion phase decreased. On the other hand, Kankekar et al. [53] reported that the use of concentrated H$_2$SO$_4$ enhanced the water transportation thereby resulting in swelling. To solve the problem, the author used perchloric acid as a strippant at 2 M. The effect of internal phase type has also been investigated by Kumbasar [66]. It was found that NH$_3$ solution as internal phase gave higher extraction efficiency and more stable emulsion than Na$_2$CO$_3$, (NH$_4$)$_2$CO$_3$ and NaOH on extraction of cadmium.

In case of diluent, there are some requirements on the selection of the diluent i.e. low solubility in the internal and external aqueous phase, compatibility with the extractant and surfactant and inability to form new phases, moderate viscosity (not too low as to compromise membrane stability), having a density that is sufficiently different to the aqueous phase, low toxicity, and high flash point [54]. Aliphatics are generally preferred than aromatics diluent because of its low solubility in water and produce better emulsion stability [65]. Besides, the high density diluent is more favorable for O/W emulsion. In contrast, W/O emulsion is preferred to use the low density diluent. In addition, the viscosity of diluent is also an important parameter to choose the diluent [30]. Nevertheless, the most widely used is kerosene since it is the cheapest diluent. The properties of some type of commercial diluent particularly density and viscosity is given in Table 3.

In order to increase the stability and ideal behaviour of the emulsion droplets, Chakravarti et al. [32,47] used kerosene and different mixtures of liquid paraffin in kerosene. They found that with increasing quantities of liquid paraffin in the membrane phase, an emulsion hindered extraction of copper(II), this may be due to a gradual increase in the viscosity of both the membrane phase and the emulsion with increasing quantities of liquid paraffin [32]. In their experiment, 8.6 wt% of liquid paraffin in membrane phase made the emulsion stable [47]. Some studies have been done to compare the performance of diluent on the W/O emulsion stability.

Table 3
Density and viscosity of some types of diluent.

Material	Density (kg/m^3)	Viscosity (cP)
Kerosene	810	1.3
Toluene	866.90	0.59
n-Heptane	684	0.386
Shellsol T	761	1.4459
Hexane	654.8	0.3
Dodecane	749.3	1.34
1,2-Dichloroethane	1253	0.84
Cyclohexane	778.5	0.98
Iso-dodecane	747	1.2699
Tetradecane	762	3.19
Oxylene	879	8.102
Dimethylbenzene	865	1.3

Fig. 3. Effect of stirring speed on extraction of silver and emulsion breakage [65].

Study showed that the membrane was slightly more stable in heptane than in hexane because of the improvement of certain physical properties of the membrane and in particular its viscosity [67]. The opposite result was reported by Chiha et al. [24,30]. They found that the suitable diluent for a good stability of the W/O emulsions was hexane with viscosity of 0.294 cP, because hexane is less viscous than heptanes and dodecane (0.386 and 1.34 cP, respectively) [30]. The break-up of the emulsion for a contact time of 7 min was 0.009%, 0.79% and 0.93% for hexane, heptane and dodecane, respectively [24]. Skelland and Meng [68] proposed the use of non-Newtonian fluid to solve the membrane instability. Their investigation have proved the effectiveness of non-Newtonian fluid in ELM separation processes, with regard to simultaneously enhanced stability, retained or improved permeability, and reduced swelling. Further, stabilization of the membrane will obtained from the smaller droplets of internal phase because of the low apparent viscosity of the non-Newtonian membrane during the emulsification stage.

Another factor affecting the membrane stability is volume ratio of internal phase to diluent (V_{int}/V_m). Generally, increasing V_{int}/V_m decreases the emulsion stability. Kumbasar and co-worker [69–73] reported that increasing the stripping solution volume made the emulsion unstable and there was leakage of stripping solution into the feed solution, due to an increase of the emulsion viscosity and also an increase of the internal droplets diameter. Increase in droplet diameter decreases the interfacial contact area between the emulsion and the continuous phase and thereby decreases the percentage extraction of metal [24,49]. Other author reported that the thickness of film in droplets thin off when the volume of the stripping phase increases [30]. For higher V_{int}/V_m, the volume of membrane solution is not enough for enclosing all the stripping solution [58]. Conversely, lower V_{int}/V_m leads to a thicker and more stable membrane phase, which impedes the diffusing process and increases the consumption of membrane phase [74]. Mortaheb et al. [75] also revealed that the strength of emulsion wall and its resistance against breakage increase with decreasing V_{int}/V_m. In the experiment of Wan and Zhang [40], V_{int}/V_m can affect the surfactant concentration at the interface of membrane/aqueous phases and in the bulk membrane phase, thus affecting emulsion swelling. They found that entrainment and osmotic swelling increase with the decreasing of V_{int}/V_m.

2.9. Effect of extraction stirring speed and contact time

Stirring speed plays an important role in the membrane stability and the rate of metal transfer through emulsion liquid membrane. Higher stirring speeds can lead to more swelling and globule rupture [63,71]. Emulsion becomes swell rapidly due to an increase in the rate of water transport into the emulsion [17,40]. Valenzuela et al. [57,76] also mentioned that an excessive stirring speed produced coalescence and finally breakdown emulsion globules, making the primary emulsion unstable and favoring the undesired
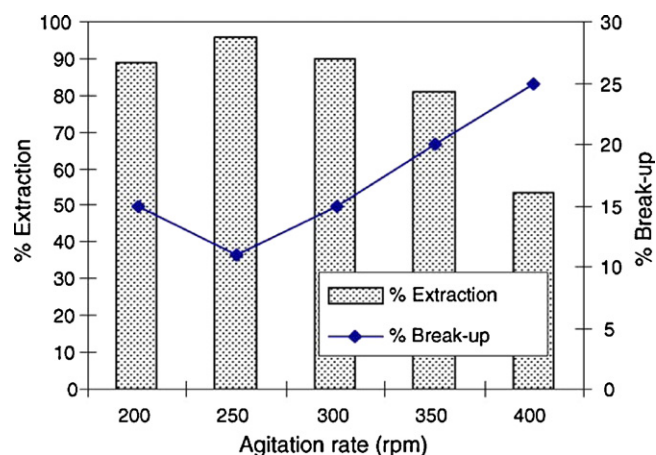
transport of strip liquor towards the external continuous aqueous phase. The shear induced breakage of fragile emulsion droplet near tip of the impeller or impact on the wall of a contactor imposes upper limit on the stirring speed [28]. Eventhough, the rates of mass transfer increases with the increase of stirring speed. For lower stirring speed, the size of the emulsion globules increases and the interfacial area available for mass transfer decreases [58]. Therefore, appropriate stirring speed needs to be selected for optimal performance of emulsion liquid membrane.

Study showed that a good stability of the W/O emulsions for chromium extraction was obtained for stirring speeds ranging from 200 to 275 rpm. Increasing the stirring speed above a critical value (300 rpm) affected the stability of the emulsion [58]. Similar result was obtained by Gasser et al. [25] in case of cobalt removal. In the experiment of Othman et al. [65], the optimum stirring speed for separation of silver was found at 250 rpm which gave 95% extraction and about 12% emulsion breakage as shown in Fig. 3. While, other study showed that the best stirring speed to ensure a good stability of the W/O emulsion and to enhance the interfacial area available for mass transfer on the copper removal was 200 rpm [30] and for cadmium extraction was 280 rpm [75]. Based on these studies, it can be said that the optimum stirring speed which gave better emulsion stability and rate of metal extraction is very closely depend to the conditions of parameters used, such as the emulsion compositions and the equipment, and types of metal to be extracted.

Emulsion stability is also closely related to the contact time on the extraction process. Experiments by various researchers [24,32,53,61] indicated that the emulsion breakage increases with increase in contact time. This is due to the fact that a longer contact time generally results in higher water transport into the inner strip phase causing the membrane to swell and the emulsion may break eventually. Therefore, an adequate contact time must be selected for better functioning of the process. It was reported that the optimum contact time on the rhutenium extraction was about 8 min [53]. Similar result was obtained by Bechiri et al. [67] on the heteropolyanion complex extraction in aqueous solution. Kulkarni and Mahajani [28] reported the effect of contact time on the extraction of molybdenum and found that the mean diameter of emulsion droplets was 2.15 μm initially while the diameter become 3.40 μm after 8 min of contact with the external feed phase. The optimum contact time was found at about 3 min which gave approximately 10% emulsion swelling with nearly 90% extraction efficiency as shown in Fig. 4 [28]. In case of uranium removal, study showed that the optimum contact time was 15 min since a further increase in contact time, excessive swelling of internal phase started and resulted in more breakage of emulsion and caused leak-
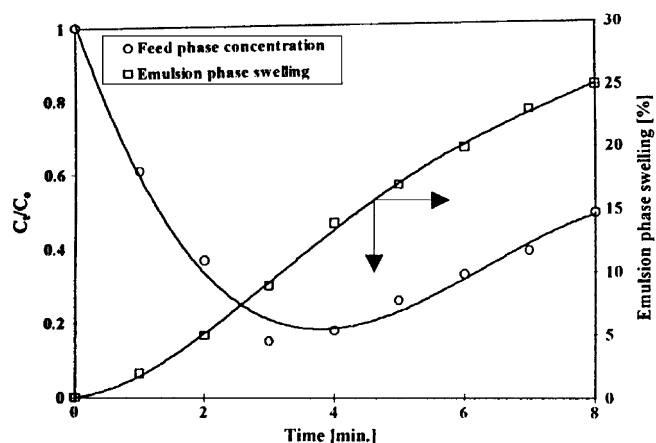
Fig. 4. Effect of residence time on concentration of molybdenum and emulsion swelling [28].

age of uranium from the internal phase to the external phase [61]. The different optimum contact time in metal extraction as revealed before shows that each metal has different optimum contact time in compliance with the conditions of parameters used.

3. Mechanism of emulsion destabilization

The various instability mechanisms resulting in the breakdown of emulsion. Hou and Papadopoulos [77] described the possible mechanisms of breakdown of W/O/W type dispersions as follows: (i) coalescence of the internal aqueous droplets into larger internal droplets (ii) coalescence of the emulsion globules suspended in the external continuous phase (iii) expulsion of the internal droplets following rupture of the thin membrane film during interaction of the internal and external continuous phases, and (iv) swelling or contraction due to water permeation through the oil membrane by diffusion.

Adequate disclosure of emulsion instability mechanisms including coalescence, swelling, and leakage as well as the parameters affecting the breakdown of emulsion is described in the section below.

3.1. Coalescence

Stability of double emulsions is generally understood as the resistance of the individual globules against coalescence [8]. Coalescence means the aggregation of emulsion due to the fusion of two or more individual droplets to form a bigger one. Coalescence is not a single stage process but comprises at least four elementary steps, including contact at a distance that allows attractive interaction; the drainage of the continuous phase film between the drops; the rupture of the film; and the collapse of the droplets. The lifetimes of thin films between drops determine the coalescence rate [78]. In the emulsion droplet, coalescence happens in a wide time scale.

Coalescence is started by the approach of two or more droplets. Depending on the volume ratio of the two phases as well as the viscosity ratio, shear could lead to coalescence and destruction of the emulsion. In the emulsification process, there is a competition between breakup and coalescence, in which the hydrodynamic consequences are unclearly explained [79]. Droplet coalescence depends on precise molecular details of droplet interfaces, causing the difficulty of prediction. Droplet coalescence are caused by some factors, i.e. relative magnitude of forces between droplets; resistance of interface to disruption; duration of contact between droplets; and shearing and tearing of interfaces.

Droplet coalescence between sample withdrawals can be prevented by the use of surfactant, which is expected to rapidly adsorb at incompletely covered droplet surfaces. The reduction of attraction can also minimize coalescence. It can be done by avoid contact of two droplets in along time, to reduce depletion. The droplets contact can be prevented by adding thickening or gelling agent. Increasing repulsion, by increasing film thickness, can reduce coalescence. Another way to reduce coalescence is using polymeric emulsifier. The use of polymeric emulsifier can increase resistance to membrane rupture.

3.2. Swelling

Emulsion swelling is the phenomenon of the increase in emulsion volume during operation, due to the incorporation of the external phase solvent or external phase itself into the emulsion globules [10]. It is detrimental extraction process not only because it dilutes the internal stripping phase and the solute that has been concentrated in the internal droplets within the globules, but also because it changes the rheological behaviour of the emulsion [17]. Swelling can trigger the breakdown of the globules which finally decrease the separation efficiency. Swelling can also cause a significant increase in the viscosity of the primary W/O emulsion, leading to serious problems in the final demulsification step [45]. It has been reported that the economic advantage of ELM for copper permeation over solvent extraction is lost when osmotic swelling involves more than 30–40% [80]. Meanwhile, in terms of processing, an emulsion swelling of 10% is considered manageable [81].

Basically, there are two types of swelling, i.e. osmotic and entrainment swelling [10]. Osmotic swelling causes an increase in volume of the internal phase due to the large difference of the osmotic pressure between the internal and external phase, leading to the water transport from the external phase into the internal phase [40]. While entrainment swelling is caused by the entrainment of the external phase into the internal phase due to the repeated coalescence and re-dispersion emulsion globules during the dispersion operation thus causing an increase of internal phase volume [40]. Studies showed that osmotic swelling is caused by many parameters including surfactant, carrier, difference in ionic strength, residence time, viscosity of solvent, pH, temperature, and globules size [40,44,82–90], whereas for entrainment swelling, beside influenced by the mentioned parameters in osmotic swelling, other parameters are water volume fraction in W/O emulsion, inner water drop size, acidity and salinity of aqueous phase, and agitation speed [40,45,91–93].

Several different mechanisms to explain the swelling of ELM globules have been proposed [68,82–84,90,92]. Yan and Pal [44] summarized the proposed mechanisms as follows: (1) molecular diffusion of water from external aqueous phase to internal aqueous droplets; (2) micelle assisted transport of water from external aqueous phase to internal water droplets, accordingly, water transport is facilitated through the membrane (oil) phase by inverse micelles of surfactant present in the membrane phase; (3) transfer of water from external aqueous phase to internal water droplets via hydration of surfactant molecules; and (4) entrainment and emulsification of the external aqueous phase in the emulsion globules due to excess surfactant present in the primary emulsification step.

Mechanisms (1)–(3) absolutely describe the mechanism of the osmotic swelling. In most situations of ELM processes, mechanisms (1) and (3) are the probable reasons for swelling [54]. Mechanism (4) is related to the mechanism of the entrainment/isotonic swelling. Yan and Pal [93] expounded the mechanisms of isotonic swelling as follows: (1) multiple-body collision mechanism, in which the entrapment of the continuous phase fluid occurs when at least four dispersed globules high concentrations collide with each other; (2) two-body collision mechanism, in which during collision

of two droplets, a film of the continuous phase fluid gets entrapped between the colliding globules, leading to the formation of internal droplets; and (3) drop deformation mechanism, in which the interface of the dispersed globules tends to develop a concave surface due to the presence of surfactant at the interface.

The measurement of emulsion swelling can be done by different methods [40] including the volume variation, internal phase droplet size variation, viscosity variation, density variation, tracer method and Carl-Fisher method. However, these methods suffer a number disadvantages i.e. they are incapable of determining both the emulsion swelling and membrane breakage in the same experiment and cannot specify the osmotic swelling and entrainment swelling either [40]. In order to overcome the limitations of these methods, Wan and Zhang [40] proposed a new method, called bi-tracer method, to determine simultaneously the osmotic swelling ratio (S_{os}), the entrainment swelling ratio (S_{en}) and the membrane breakage ratio (ε) as shown in the following equations:

$$S_{ac} = S_{os} + S_{en} = \left[\left(1 - \frac{C_{e,I}}{C_{i,I}^0} \right) \left(\frac{C_{i,I}^0 - C_{i,I}}{C_{i,I} - C_{e,I}} - \frac{C_{e,I}(1 + R_{oi}^0)}{R_{ew}^0(C_{i,I} - C_{e,I})} \right) \right.$$
$$\left. + \frac{C_{e,I}(1 + R_{oi}^0)}{R_{ew}^0 C_{i,I}^0} \right] \times 100\% \tag{3}$$

$$S_{en} = \frac{C_{i,II}}{C_{e,II}^0(C_{i,II} - C_{e,II})} \left[\frac{1 + R_{oi}^0}{R_{ew}^0}(C_{e,II}^0 - C_{e,II}) - C_{e,II} \right] \times 100\% \tag{4}$$

$$\varepsilon = \frac{C_{e,I}}{C_{i,II}^0(C_{i,I} - C_{e,I})} \left[\frac{1 + R_{oi}^0 + R_{ew}^0}{R_{ew}^0}(C_{i,I} - C_{i,I}^0) \right] \times 100\% \tag{5}$$

where S_{ac} is the actual swelling ratio; $C_{i,I}^0$, $C_{i,I}$, $C_{e,I}$ are the initial concentration of tracer I in the internal phase, the concentration of tracer I in the internal and external phase at time t, respectively; $C_{e,II}^0$, $C_{i,II}$, $C_{e,II}$ are the initial concentration of tracer II in the external phase, the concentration of tracer II in the internal and external phase at time t, respectively; while R_{oi}^0 and R_{ew}^0 are the initial volume ratio of the oil phase to the internal phase and the initial volume ratio of the external phase to the emulsion, respectively, and expressed as:

$$R_{oi}^0 = \frac{V_o^0}{V_i^0} \tag{6}$$

$$R_{ew}^0 = \frac{V_{em}^0}{V_e^0} \tag{7}$$

$$V_{em}^0 = \frac{V_o^0}{V_i^0} \tag{8}$$

where V_i^0, V_o^0, V_{em}^0 are the initial volume of the internal phase, the oil phase and the emulsion, respectively.

From the equations above, measuring the concentrations of tracers I and II in the internal and external phases and knowing the initial operation conditions (R_{oi}^0, R_{ew}^0) and the initial concentrations of tracers in the external or internal phase, the actual swelling, entrainment swelling, osmotic swelling and the membrane breakage ratio could be simultaneously obtained.

3.3. Leakage

The membrane leakage/breakage occurs when portions of the internal phase spill into the external phase. During leakage, the stripping agent and previously extracted solute is leaked into the external phase [94]. As a result, the driving force for mass transfer decreased and the raffinate concentration increased, thereby

lowering the extraction efficiency [10]. Martin and Davies [6] mentioned that the breakdown of the emulsion affects the mass transfer process in two ways. The first is a direct lowering of the transfer efficiency by short circuiting back into the raffinate phase. The second is by a reduction in the interfacial area of the membrane. Membrane leakage at the rate of ∼0.1% is allowable for a practical process [95].

It is generally agreed that the properties of the surfactant, diluent, internal phase, and its volume fraction have significant effects on membrane leakage [10]. Pfeiffer et al. [94] also reported that leakage is not only affected by surfactant type and concentration, but also by emulsion preparation procedure, electrolyte concentration, membrane material, and extraction-vessel stir rate. It is possible to reduce the membrane leakage by raising the amount of surfactant, but as a result of this osmosis/swelling is also increased [85]. In the experiment of Bart et al. [86] the surfactant was found to solubilize sulfuric acid by inverse micelles at the interface receiving phase/membrane phase and transport it to the feed phase.

Many methods for determining the membrane leakage can also be used in swelling determination as discussed before. However, most of the researchers used tracer method. The researchers assumed tracer solubility in the membrane phase is negligible. The tracer is dissolved in internal phase of emulsion. After extraction process, the tracer concentration in the external phase is measured to determine the membrane leakage by the following equation [40]:

$$\varepsilon(\%) = \frac{V_e C_{e,I}}{V_i^0 C_{i,I}^0} \times 100 \tag{9}$$

where V_e and $C_{e,I}$ are volumes of external phase and tracer concentration in the external phase after extraction. While, V_i^0, $C_{i,I}^0$ are initial volume of internal phase and initial concentration of tracer in the internal phase. Further, they adopted the bi-tracer method for measuring the membrane breakage ratio as shown in Eq. (5).

Some literatures also defined the emulsion leakage in terms of breakage rate constant (K_b) as suggested by Goto et al. [42] as follows:

$$\ln(1 - \varepsilon) = -K_b t \tag{10}$$

where t is time and ε is calculated from Eq. (9).

Another simple method to investigate membrane leakage is by measuring pH of the external phase. The emulsion breakage represents the ratio in percentage of the volume of internal phase leaked into the external phase by splitting (V_S) to the initial volume of the internal phase (V_{int}) as given in Eq. (11), while the volume V_S is calculated by the mass balance from the external phase measure before and after contact as shown in Eq. (12) [24,30,62].

$$\varepsilon = \frac{V_s}{V_{int}} \times 100 \tag{11}$$

$$V_s = V_{ext} \frac{10^{pH_0} - 10^{pH}}{10^{pH} - C_{H^+}^{int}} \tag{12}$$

where V_{ext} is the initial volume of external phase, $C_{H^+}^{int}$ is the initial concentration of H^+ in the internal phase, pH_0 is the initial pH of the external phase and pH is the external phase pH being in contact with the emulsion after a certain time of stirring.

4. Conclusion

Emulsion liquid membrane is a promising method for industrial waste water recovery including heavy metals. The successful application is not only depend on the selection of suitable emulsification method but also the emulsion formulation in accordance with the solute which is to be recovered. This is related to the emulsion stability that it still remains a great challenge in the application of the ELM at industrial scale. Emulsion instability occurs

through various physical mechanisms such as coalescence, swelling and leakage. The last two mechanisms were found to be the main problem in practical use of ELM which can decrease the extraction efficiency and cause the emulsion breakdown. Swelling is caused by surfactant, carrier, difference in ionic strength, residence time, viscosity of diluent, pH, temperature, globules size, water volume fraction in W/O emulsion, droplet size, acidity and salinity of aqueous phase, and agitation speed. While membrane leakage is significantly affected by the properties of the surfactant, diluent, internal phase and its volume fraction, emulsion preparation procedure, electrolyte concentration, membrane material, and stirring speed of extraction. It is believed that the small droplet diameter of emulsion is a key criterion that will provide a stable emulsion and a larger mass transfer area. Mechanical agitation using homogenizer, mixer, stirrer, etc. is the most widely used method in emulsion preparation. However, the method usually produces bigger emulsion droplet and consumes relatively higher amount of energy. The current upcoming technology is applying ultrasound to produce nano-emulsion. This method does not only consume the least energy and surfactant but also can be scaled up which make the process feasible. Beside emulsion preparation method, the composition and properties of each component in the emulsion can significantly affect the emulsion performance, in term of emulsion breakdown resistance and extraction process. Carrier acts as a 'shuttle' to carry the metal element through the liquid membrane. The complex formed with the carrier must be soluble in the membrane phase, but not soluble in both the internal and continuous phase. The concentration of carrier should be minimized to prevent emulsion breakage and to minimize the cost of the process since it is the most expensive component. The existence of surfactant, particularly synthesized surfactants can overcome the interfacial tension problem between oil and water thus enhances the emulsion stability. The use of bi-functional surfactant not only overcomes the limitations of commercial surfactants but also eliminates the addition of carrier. Several factors must be considered in the selection of internal and membrane phase. Ionic strength, pH, and the presence of organic species in internal phase will influence the emulsion stability. For membrane phase, the selection is not only based on the density and viscosity but also on the chosen equipment. Besides, the use of non-Newtonian fluid is conducive to solve the membrane instability. Other than the emulsion composition, the operation parameters such as stirring speed and contact time also have significant effect on the emulsion stability. An adequate stirring speed and contact time must be selected to obtain the optimum condition of emulsion. However, many studies showed that too stable emulsion tends to give lower extraction efficiency and rate. Hence, the need of optimization study is important to be done continuously to make the overall emulsification process commercially viable.

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