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Copper and Cyanide Extraction with Emulsion Liquid Membrane with LIX 7950 as the Mobile Carrier: Part 1, Emulsion Stability

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Abstract: The potential use of emulsion liquid membranes (ELMs) with LIX 7950 as the mobile carrier to remove heavy metals from waste cyanide solutions has been proposed. Relatively stable ELMs with reasonable leakage and swelling can be formed under suitable mixing time and speed during emulsification. The concentration of LIX 7950 and Span 80 in the membrane phase, KOH in the internal phase and the volume ratio of membrane to internal phases are also critical to ELM formation. The efficiency of copper and cyanide removal from dilute cyanide solution by ELMs is related to ELM stability to some extent. More than 90% copper and cyanide can be removed from dilute cyanide solutions by ELMs formed under suitable experimental conditions.

Keywords: emulsion liquid membrane; LIX 7950; stability; copper cyanides

1. Introduction

Waste cyanide solutions are generated industrially on a large scale in gold and silver extraction from ores, electroplating, coal cooking and organic chemical formulation. Heavy metals such as copper zinc and iron may also occur in these solutions, e.g., those waste effluents arising from the gold cyanidation process [1]. Due to the highly toxicity of cyanide and heavy metals to humans and aquatic organisms, strict environmental regulations on the management of waste cyanide solutions have been established. Environmental constraints controlling the discharge of cyanide from gold plants are being tightened by local governments worldwide [2,3]. A considerable number of methods have been developed for recovering valuable metals and cyanide from waste cyanide solutions. Acidification, volatilization, and recovery (AVR) and some modifications have been long practiced in some gold operations, but the high consumption and cost of reagents has significantly limited their application [4–6]. The indirect recovery of metals and cyanide by activated carbon and ion-exchange resin has been proposed. However, the low adsorption capability of carbon and the high cost of resin have severely hampered their wide application in practice [7–10]. The use of solvent extraction process to recover copper from cyanide solution has been suggested. The extraction and stripping of metal cyanide complexes is believed to occur via an ion-exchange mechanism [11–15]. These investigations prove that copper can be effectively extracted from alkaline cyanide solutions by proposed solvent extraction systems.

Extraction processes using emulsion liquid membrane (ELM) have also received significant attention due to their potential application in treating industrial liquid wastes [16–20]. Use of ELMs for hydrometallurgical recovery of heavy metals from waste industrial solutions has been reported by many investigators and some processes have been successfully commercialized to remove various metals from wastewater in industry [21–27]. The potential use of liquid membranes to extract precious metals from alkaline cyanide solutions was also proposed [28–32]. In ELM processes, simultaneous purification/concentration of the target solute can be realized through combining extraction and stripping into one stage, which results in the high interfacial area for mass transfer, the ability to remove/concentrate selectively or collectively, and the requirement of only small quantities of organic solvent. It is believed that the large specific interfacial area associated with ELMs result in higher permeation rates and the transport is governed by kinetic rather than equilibrium parameters which may enable the achievement of higher metal concentrations in fewer separation stages than solvent extraction [33–35]. Consequently, there is a substantial saving in the volume of mixers and settlers for extraction and stripping which are generally carried out in conventional solvent extraction circuits. However, although the technology has been successfully practiced for removing some heavy metals from waste solutions, its operating efficiency is highly dependent on the emulsion instability which commonly includes membrane leakage, coalescence, and emulsion swelling. In order to obtain relatively stable emulsion liquid membranes, its formulation design including selection of carrier, strip agent, surfactant, diluents, and preparation method is critical [36].

The process of recovering copper and cyanide from waste alkaline cyanide solutions through ELMs using the guanidine extractant LIX 7950 as the mobile carrier has been suggested in this research. The factors which may potentially influence the stability of ELMs and the removal of copper and cyanide by ELMs including membrane formula, mixing speed, and phase ratio (volume ratio of membrane to

internal phases) have been examined with the purpose to determine the feasibility of extracting copper and cyanide from waste cyanide solutions by ELMs.

2. Experimental Section

2.1. Materials

LIX 7950, a trialkylguanidine extractant, was used as supplied by the manufacturer (Cognis, Mississauga, ON, Canada). The non-ionic surfactant commercially known as Span 80 (Sinopharm Chemical Reagent, Shanghai, China) was used for stabilizing the emulsion. The diluent was a commercial kerosene which was a complex mixture of aliphatic origin containing about 15%−20% *w/w* aromatics. A small amount of liquid paraffin was used as the additive to facilitate formation of ELMs. Some 1-dodecanol was added as the modifier to facilitate; dissolution of LIX 7950 in the diluent. Synthetic copper cyanide solutions were made up from CuCN and NaCN. All chemicals were of reagent grade and doubly distilled water was used throughout.

2.2. Procedure

To prepare ELMs, designated volume of LIX 7950, 1-dodecanol, Span 80, liquid paraffin, and kerosene were emulsified in a 250 mL beaker through a mechanical mixer with an overhead disk-propeller. A portion of KOH solution used as the internal stripping solution was added dropwise to the stirred membrane solution till obtaining the desired volume ratio of internal to membrane phases. The mixed solution was stirred continuously to obtain stable ELMs.

For stability and extraction tests, designated volume of ELMs prepared through the described procedure was added to a 500 mL beaker filled with the feed solution (100 mL). Mixing was provided with a mechanical stirrer with four Teflon-coated turbine-type impellers. All tests were conducted at the indoor temperature of 20 ± 1 ℃ (except defined otherwise). After the desired extraction time, the emulsions were separated from the mixture through a 125 mL separator and the obtained aqueous solution was filtrated with Whatman No. 3 filter paper to remove any entrained organic before analysis. The emulsions were recovered and subsequently broken into its constituent organic and aqueous phases through a high speed centrifuge. Samples of organic phase were filtered with 1 PS Phase Separation paper and samples of aqueous phase were filtered with Whatman No. 3 filter paper to remove any entrained organic phase before analysis.

2.3. Analysis and Calculation

The solution pH was measured with a pH meter using a combined glass electrode. Metals in aqueous samples were analyzed by atomic absorption spectrophotometry (AAS) and Ion coupled Plasma (ICP-MS, PerkinElmer, Shanghai, China) and their content in the organic phase was calculated by mass balance. Total cyanide content in the aqueous solution was determined by the standard distillation method [37]. The morphology of ELMs is determined by a metallographic microscope. To determine the leakage of ELMs, a portion of the feed solution (without K^+) was mixed with equal volume of ELMs with K^+ in the internal stripping solution; after mixing for the designated time, ELMs were separated from the external aqueous phase (the raffinate) and was further de-emulsified

thoroughly through heating and centrifuge. The volume of the raffinate, the membrane phase and the internal phase and the concentration of tracer K^+ in each aqueous phase were measured. The apparent leakage (breakage) of ELMs is calculated by the following equation:

$$\delta = \frac{C_{KR} \times V_R}{C_{Ki} \times V_i} \times 100\%$$
(1)

where

δ: the apparent leakage (breakage) of ELMs, %;

C_{KR}: the molar concentration of K^+ in the raffinate, mol/L;

C_{Ki}: the molar concentration of K^+ in the initial internal phase, mol/L;

V_R: the volume of the raffinate, L;

V_i: the volume of the initial internal phase, L;

The apparent swelling of ELMs is simply defined as following:

$$\eta = \frac{V_E' / V_R - V_E / V_f}{V_E / V_f} \times 100\%$$
(2)

where

V_E: the apparent volume of emulsions before contacting the feed, L;

V_E': the apparent volume of emulsions after extraction, L;

V_f: the initial volume of feed, L;

The removal (or extraction) of the target species from feed by ELMs is calculated through the following equation:

$$E = \frac{C_f \times V_f - C_R \times V_R}{C_f \times V_f} \times 100\%$$
(3)

where

E: the removal (or extraction) of the target species from the feed solution by ELMs, %;

C_f: the molar concentration of the target species in the feed, mol/L;

C_R: the molar concentration of the target species in the raffinate, mol/L;

3. Results and Discussion

3.1. Influence of Mixing for ELM Formation

In order to ensure a potential transport of copper cyanides through ELMs, a relatively stable ELM with reasonable leakage and swelling has to be constructed. Preliminary investigations indicated the input energy for the preparation emulsions played an important role in forming such meta-stable ELMs. When the stirring speed of the mixer is fixed at 4500 RPM, images of ELMs formed under different emulsification time are shown in Figure 1. At the emulsification time of 5 min, the formed ELMs have a relatively large size. They tend to decrease with increasing stirring time, resulting in more uniform droplets of ELMs, e.g., more uniform ELMs are produced after 15 min of stirring than 5 min of stirring. However, when the emulsification time exceeds 25 min, more ELMs start to distort to connect with others to form a semi-continuous phase. It is believed that small droplet tends to have

better breaking resistant and rapid extraction, but will be very difficult to de-emulsify by mechanical methods. In addition, too many of them are packed into each organic globule and, consequently, the liquid membrane becomes too thin and ruptures easily. However, large droplets may cause poor stability and extraction efficiency due to the low surface-to-volume ratio. Thus, emulsions with the droplet diameter in the range 0.3–10 μm (preferably 0.8–3 μm) have been suggested considering reasonable ELM stability [16,18].
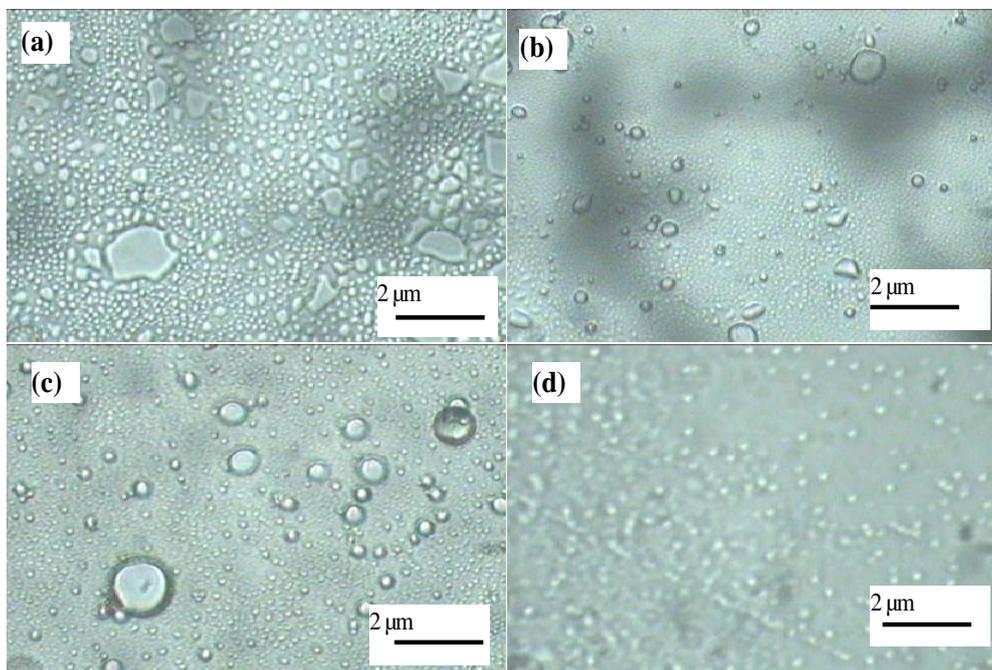
Figure 1. Photographic of ELM droplets formed under different stirring times. (Membrane phase: 6% *v/v* LIX 7950, 2% *v/v* 1-dodecanol, 5% *v/v* Span 80, 1% *v/v* paraffin, balanced with kerosene; Internal stripping solution: 0.1 mol/L KOH; Volume ratio of the membrane phase to the internal phase: 1:1; Mixing speed: 4500 RPM; Mixing time: (**a**) 5 min; (**b**) 15 min; (**c**) 25 min; (**d**) 35 min).

The effect of emulsification time on ELM stability and removal of copper and cyanide from the external solution by ELMs is shown in Figure 2. Under the experimental conditions, a high leakage (>40%) was observed when the emulsification time is 5 min. This is probably because the short stirring time for emulsification results in relatively large but unstable ELM droplets which tend to break up easily when contacting with the external solution. Accordingly, a negative value for ELM swelling (data not shown in Figure 2) was obtained at emulsification time of 5 min due to high breakage of ELMs (partial internal solution has released to the external phase). The ELM leakage decreases to 8% when the emulsification time is 10 min and maintains at 5% when the emulsification is further increased. Relatively small ELM swelling (η < 2%) was observed when the stirring time for emulsification varied from 10–35 min. Copper removal from the external phase by ELMs is only about 50% at the emulsification time of 5 min. This is probably due to high leakage of the resulted ELMs. It increases up to 90% at the emulsification time of 10 min and remains stable when the emulsification time increases from 10–35 min, indicating effective ELMs have formed under these conditions. Under experimental conditions, cyanide extraction with ELMs shows virtually the same values as copper

extraction. Thermodynamic calculation indicates that copper mainly occurs as $Cu(CN)_3^{2-}$ in the feed. The analysis of the internal phase after extraction showed the extracted species also mainly occur as $Cu(CN)_3^{2-}$. Since LIX 7950 is a strong organic basic extractant, the extraction of $Cu(CN)_3^{2-}$ through ELMs formed with LIX 7950 as the mobile carrier is thus an anion exchange process. The extraction chemistry of copper cyanides by resulted ELMs can be expressed as following:

At the interface of external and membrane phases:

$$2RG_{org} + 2H_2O + Cu(CN)_3^{2-} = (RGH^+)_2\,Cu(CN)_3^{2-}{}_{org} + 2OH^- \tag{4}$$
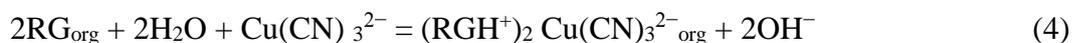
At the interface of membrane and internal phases:

$$(RGH^+)_2\,Cu(CN)_3^{2-}{}_{org} + 2OH^- = 2RG_{org} + 2H_2O + Cu(CN)_3^{2-} \tag{5}$$
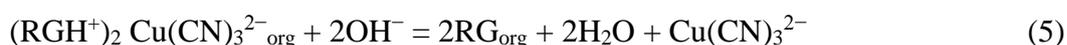
where RG denotes the guanidine extractant LIX 7950 and RGH^+ is its protonized form. The effect of mixing speed for ELM formation on leakage and swelling of ELMs is shown in Figure 3. The mixing speed exhibits an insignificant effect on the ELM swelling ($\eta < 2\%$) when it varies from 2500–7500 RPM. However, a leakage of 12% was observed when the mixer speed for ELM formation was maintained at 2500 RPM, which probably was due to high breakage of unstable ELM droplets formed under low input energy for emulsification. Correspondingly, the removal of copper and cyanide from the external phase by ELMs is only about 45% in this case. Copper and cyanide removal increases to 90% when the mixing speed for ELM formation increases to 3500 RPM. Further increase of the mixing speed (up to 7500 RPM) shows insignificant effect on copper and cyanide removal by ELMs.
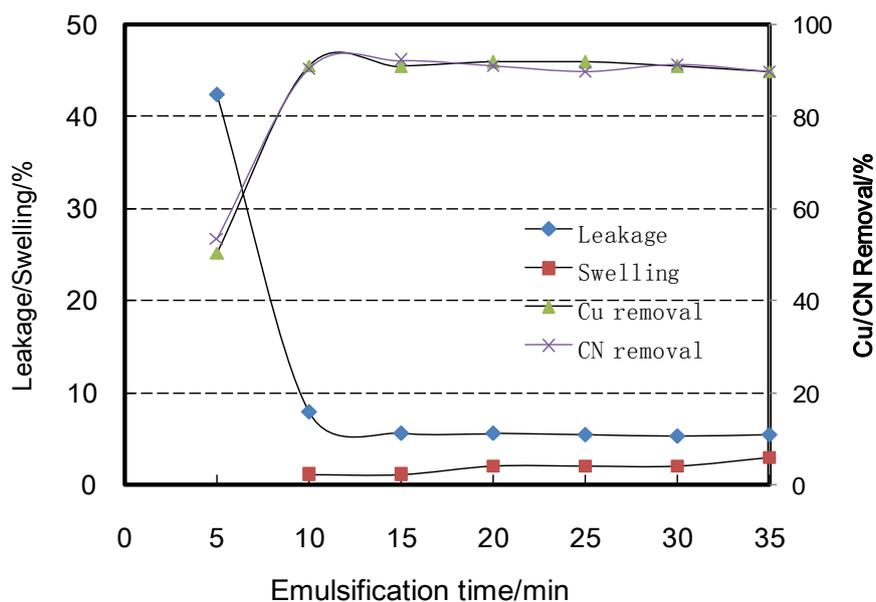
Figure 2. Effect of emulsification time on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 6% *v/v* LIX 7950, 2% *v/v* 1-dodecanol, 5% *v/v* Span 80, 1% *v/v* liquid paraffin, balanced with kerosene; Internal solution: 0.05 mol/L KOH; Volume ratio of membrane to internal phases: 1:1; Mixing speed: 4500 RPM. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T = 19.3$ mg/L, $[CN]_T = 23.6$ mg/L, pH 9.5. Mixing of ELMs and the external solution: 15 min at 300 RPM).
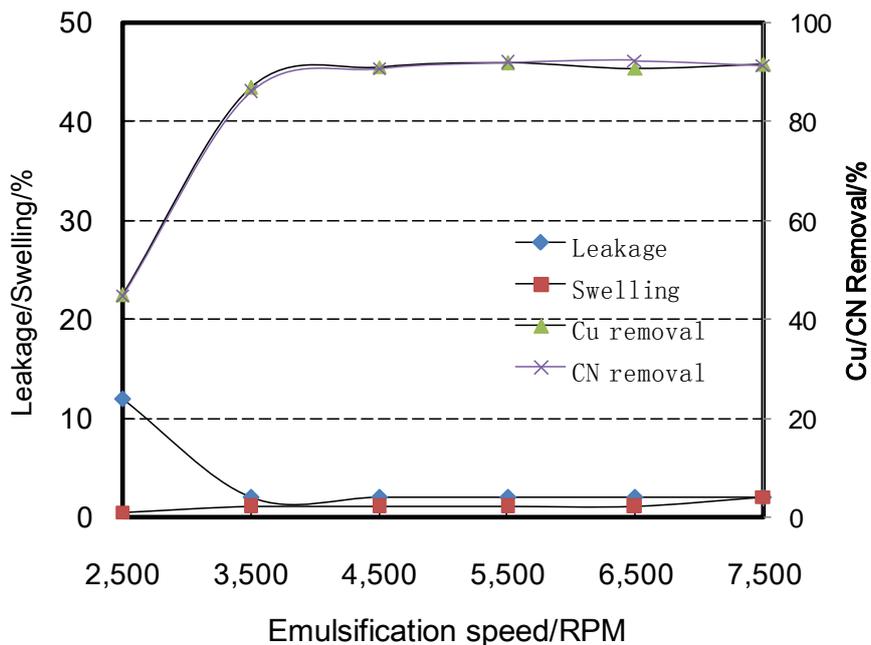
Figure 3. Effect of emulsification speed on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 6% *v/v* LIX 7950, 2% *v/v* 1-dodecanol, 5% *v/v* Span 80, 1% *v/v* liquid paraffin, balanced with kerosene; Internal phase: 0.05 mol/L KOH; Volume ratio of membrane to internal phases: 1:1; Mixing time: 15 min. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T$ = 19.3 mg/L, $[CN]_T$ = 23.6 mg/L, pH 9.5. Mixing of ELMs and the external phase: 15 min at 300 RPM).

3.2. Influence of KOH in the Internal Phase

The mobile carrier LIX 7950, a tri-alkylguanidine, is a strong organic base having an intermediate basicity between that of primary amines and quaternary ammonium salts (pKa is approximately 12). It is capable of being protonated to form a guanidinium cation at the operating pH of cyanidation (usually 10–11). This guanidinium cation can form an ion-pair with metal cyanides such as $Cu(CN)_3^{2-}$, resulting in metal extraction from the cyanide solution. By increasing the basicity of the aqueous phase, the guanidinium cation is converted to the neutral guanidine functionality. The neutral guanidine functionality no longer forms an ion-pair with metal cyanides, causing metal cyanides to be stripped from the organic phase [13]. Therefore, in order to extract metal cyanide species from alkaline cyanide solutions, the ideal internal phase of ELMs would be a solution with pH higher than 12. ELM leakage and swelling with different KOH concentration in the internal solution are shown in Figure 4. Insignificant emulsion swelling (η < 1%) was observed when KOH concentration in the internal phase varied from 0.05–1 mol/L, indicating the increase of ionic strength in the internal phase exhibits an insignificant effect on the change of volume ratio of ELMs to the external aqueous solution under experimental conditions. However, the ELM leakage increases significantly when the KOH concentration in the internal phase is higher than 0.25 mol/L. It was believed that high concentration of KOH might significantly increase the osmotic pressure difference between internal and external phases and thus result in emulsion leaking. It was also reported that the potential reaction between KOH and the surfactant Span 80 might result in reduced properties of the surfactant and consequently lead to an

emulsion destabilization [36]. The removal of copper and cyanide from the external solution by ELMs exhibits insignificant change when KOH concentration varies from 0.05–0.5 mol/L (Figure 4), indicating 0.05 mol/L KOH in the internal phase is good enough for stripping copper cyanides from the membrane phase under experimental conditions. High KOH concentration (>0.5 mol/L) in the internal phase results in a slight decrease of copper and cyanide removal probably due to increasing breakage of ELMs.
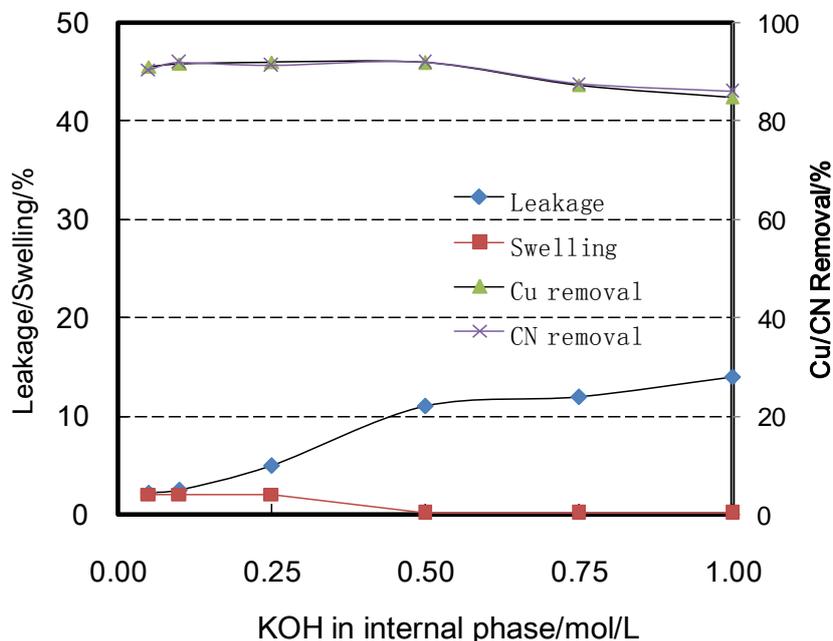
Figure 4. Effect of KOH on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 6% *v/v* LIX 7950, 2% *v/v* 1-dodecanol, 5% *v/v* Span 80, 1% *v/v* liquid paraffin, balanced with kerosene; Volume ratio of membrane to internal phases: 1:1; Mixing for emulsification: 15 min at 4500 RPM. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T = 19.3$ mg/L, $[CN]_T = 23.6$ mg/L, pH 9.5. Mixing of ELMs and the external phase: 15 min at 300 RPM).

3.3. Influence of Extractant and Surfactant

A great number of studies indicated that both extractant and surfactant played important roles in the ELM formation [16,36]. The mobile carrier, LIX 7950, acts as a "shuttle" to carry the target species through ELMs in this case. Effects of concentration of LIX 7950 and Span 80 in the membrane phase on ELM stability and copper and cyanide removal are shown in Figures 5 and 6, respectively. Under the experimental conditions, both ELM leakage and swelling slightly decrease when the concentration of LIX 7950 in the membrane phase increases from 1% *v/v*–6% *v/v*. Both ELM leakage and swelling are lower than 2% when LIX 7950 concentration varies from 6% *v/v*–10% *v/v*. Correspondingly, the removal of copper and cyanide from the external phase with ELMs increases with an increase of LIX 7950 concentration when it varies from 1% *v/v*–6% *v/v*. Further increase of LIX 7950 concentration exhibits an insignificant effect on copper and cyanide removal from the external phase by ELMs. A number of studies has given evidence that both extractant and surfactant concentration would potentially affect the emulsion stability. On one hand, increasing extractant concentration in the

membrane phase may potentially facilitate the transport of target species from the external phase to the membrane phase. On the other hand, a high content of extractant in the membrane phase may result in increased viscosity which may affect the dispersion behavior of ELMs and cause a decline in interfacial area, and, consequently, lead to a slow extraction rate of target species. Besides, using less extractant is always preferred in practice from an economic point view since, in most cases, extractant is usually the most expensive agent among membrane components [36].
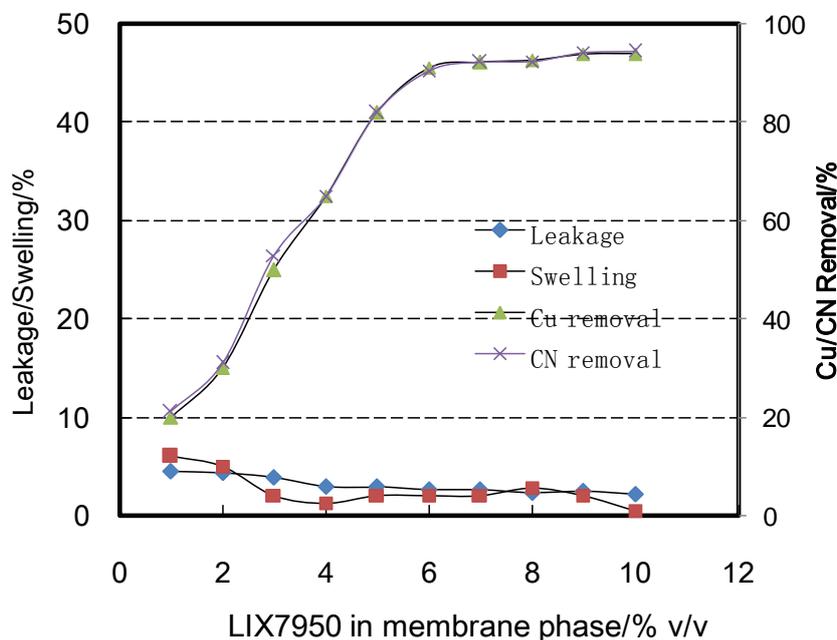
Figure 5. Effect of LIX 7950 concentration on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 2% *v/v* 1-dodecanol, 5% *v/v* Span 80, 1% *v/v* liquid paraffin, balanced with kerosene; Internal phase: 0.05 mol/L KOH solution. Volume ratio of the membrane phase to the internal phase: 1:1; Mixing for emulsification: 15 min at 4500 RPM. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T = 19.3$ mg/L , $[CN]_T = 23.6$ mg/L, pH 9.5. Mixing of ELMs and the external phase: 15 min at 300 RPM).

For the surfactant (Span 80) aspect, under the experimental conditions, high ELM leakage was observed when the content of Span 80 in the membrane phase was low, e.g., more than 20% of leakage with 3% *v/v* Span 80. Accordingly, ELM swelling exhibits little change when the Span 80 concentration varies from 1% *v/v*–9% *v/v*. Test results indicate that stable ELMs can be only formed when the concentration of Span 80 is higher than 5% under the experimental conditions. The removal of copper and cyanide from the external phase with ELMs is relatively low (only 55%) when the concentration of Span 80 in the membrane phase is 3% *v/v*. Copper and cyanide removal increases to about 91% when the content of Span 80 in the membrane phase is 4% *v/v* and remains stable when it varies from 4% *v/v*–6% *v/v*. Further increase of Span 80 in the membrane phase leads to a decrease of copper and cyanide extraction. Many studies propose that surfactant can reduce the interfacial tension between oil and water by adsorbing at the liquid–liquid interface; thus, maintaining the emulsion stability and the transport of target species through the membrane [16,34–36]. However, it should be

noted that, at a high concentration, surfactant may form emulsions that are stable with a higher emulsion viscosity. Consequently, decreasing copper and cyanide extraction with ELMs was observed at a high content of Span 80 in the membrane phase.
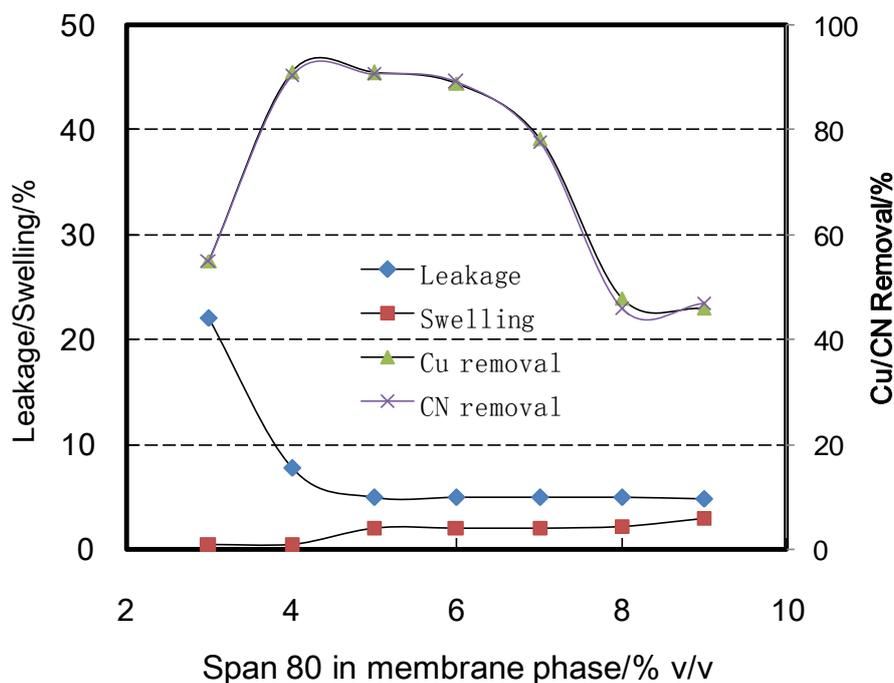
Figure 6. Effect of Span 80 concentration on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 2% *v/v* 1-dodecanol, 1% *v/v* liquid paraffin, balanced with kerosene; Internal phase: 0.05 mol/L KOH solution. Volume ratio of the membrane phase to the internal phase: 1:1; Mixing for emulsification: 15 min at 4500 RPM. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T = 19.3$ mg/L, $[CN]_T = 23.6$ mg/L, pH 9.5. Mixing of ELMs and the external phase: 15 min at 300 RPM).

3.4. Influence of Volume Ratio of Membrane to Internal Phases

The influence of volume ratio of membrane phase to internal phase (V_m/V_{int}) on ELM stability was also examined (Table 1). It was found that at low V_m/V_{int}, ELMs exhibited higher leakage, for example, a leakage of 12.5% when V_m/V_{int} was maintained at 1:3. Relatively lower leakage was observed when V_m/V_{int} varied from 2:1 to 1:2. The swelling of ELMs was also insignificant in this range of V_m/V_{int}. These results are generally in accordance with the literature. It was believed that increasing the volume of internal solution made ELMs unstable due to an increase of the size of internal droplets, resulting in decreasing interfacial contact area between the emulsion and the external phase. Other authors reported that the thickness of film in droplets thinned off when the volume of the stripping phase increased [34,36]. For higher V_{int}/V_m, the volume of membrane phase is not enough for enclosing all the stripping solution, thus resulting in higher leakage [36]. ELM leakage and swelling significantly increased with increasing V_m/V_{int} when it was higher than 3:1. Though, usually lower V_{int}/V_m leads to a thicker and more stable membrane phase, it was found that too high V_m/V_{int} also resulted in unstable ELMs (high leakage and swelling). Wang and Zhang [38] reported that V_{int}/V_m might affect the

surfactant concentration at the interface of membrane/aqueous phases and in the bulk membrane phase, and the entrainment and osmotic swelling might increase decreasing V_{int}/V_m, which resulted in unstable ELMs. Correspondingly, when V_{int}/V_m varies from 1:2 to 1:1, more than 90% of copper and cyanide removal with ELMs was achieved and lower copper and cyanide removal was observed at both higher and lower V_{int}/V_m.

Table 1. Effect of volume ratio of membrane to internal phases on ELM stability and copper and cyanide removal. (For ELMs formation, membrane phase: 2% *v/v* 1-dodecanol, 1% *v/v* liquid paraffin, balanced with kerosene; Internal phase: 0.05 mol/L KOH solution. Mixing for emulsification: 15 min at 4500 RPM. The external aqueous phase: dilute copper cyanide solution, $[Cu]_T = 19.3$ mg/L, $[CN]_T = 23.6$ mg/L, pH 9.5. Mixing of ELMs and the external phase: 15 min at 300 RPM).

V_m/V_{int}	Leakage, %	Swelling, %	Cu_{ext}, mg/L	CN_{ext}, mg/L	Cu Removal, %	CN Removal, %
1:3	12.5	1	4.3	5.1	78.0	78.2
1:2	2.5	2	0.9	1.2	95.5	94.9
1:1	3	2	1.7	2.2	91.0	90.8
2:1	4	8	10.8	13.0	44.3	45.0
3:1	15	10	11.7	13.9	39.3	41.2
4:1	18	12	11.3	13.3	41.3	43.8
5:1	28	18	10.8	13.2	44.0	44.0

4. Conclusions

The use of emulsion liquid membranes with LIX 7950 as the mobile carrier to recover metals and cyanide from waste cyanide solutions has been proposed. The concentration of LIX 7950 and Span 80 in the membrane phase, KOH in the internal phase, volume ratio of internal to membrane phases, and mixing during emulsification are critical factors for forming stable ELMs. Relatively stable ELMs with reasonable leakage and swelling can be formed under suitable formulas of membrane components. The extraction of copper and cyanide can be usually obtained when ELMs with relatively low leakage and swelling are formed. However, excessive Span 80 in the membrane phase may result in low copper and cyanide removal from dilute cyanide solutions with ELMs.

Author Contributions

Dianku Lu wrote and edited the manuscript. Yongfeng Chang and Wei Wang helped with emulsion liquid membrane preparation and data collection. Feng Xie supervised experimental work and data analysis. Edouard Asselin and David Dreisinger helped with data analysis and interpretation.

Conflicts of Interest

The authors declare no conflict of interest.

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