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Selective Separation of Gallium from Acidic Leach Solutions by Emulsion Liquid Membranes

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Abstract: The separation and concentration of gallium from acidic leach solutions, containing various other ions such as iron, cobalt, nickel, zinc, cadmium, lead, copper, and aluminium, by an emulsion liquid membrane (ELM) technique using tributyl phosphate (TBP) as carrier has been presented. Liquid membrane consists of a diluent, a surfactant (ECA 4360J), and an extractant (TBP), and 0.1 M HCl or 0.1 M H_2SO_4 were used as the stripping solution. The important variables governing the permeation of gallium and their effect on the separation process have been studied. These variables were membrane type and composition, mixing speed, diluent type, surfactant concentration, extractant concentration, HCl concentration in the feed, acid type of stripping phase, feed concentration, and treatment ratio. The optimum conditions were determined. It was possible to selectively extract 96.0% of gallium from the acidic leach solutions, containing Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al, at the optimum conditions.

Keywords: Acidic leach solution, emulsion liquid membrane, separation and concentration of gallium, solvent extraction, tributyl phosphate (TBP)

INTRODUCTION

Gallium has acquired significant commercial importance due to the potential of much faster computer chips made of gallium arsenides in place of silicon. Gallium arsenides also find increasing applications in optoelectronics,

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semiconductor lasers, solar cells, in analogue microwave devices etc. (1, 2). Due to the increasing demand for gallium in electronics, the recovery of gallium from different primary and secondary sources is of great importance.

Gallium is usually present in small amounts compared to common metals especially (Al, Fe, Zn) since the main sources of gallium are the Bayer solutions of aluminium and the acidic sulphate or chloride solutions from hydrometallurgical production of zinc (3–6).

The ability of solvent extraction to concentrate gallium, and to perform the difficult separations required has been extensively demonstrated in process development work and in commercial applications. Consequently, solvent extraction plays an important role as a separation and concentration technique. The use of high-molecular weight amines, organophosphorus compounds such as tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and di-(2-ethylhexyl phosphoric acid) (D2EHPA) for gallium extraction in chloride media appears to have attracted much attention and has been studied by several workers: extraction of gallium with TOPO (7–9); extraction with TBP (8, 10, 11), extraction with high-molecular weight amines (8, 12, 13); extraction with D2EHPA and phosphinic acid derivatives (8, 14–16).

The organophosphorus compounds such as tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) were used in conventional liquid–liquid extraction system (3). Early work using TBP established that, with increasing hydrochloric acid level, the distribution coefficient of gallium (D_{Ga}) rose to a maximum and then decreased again. Values of the optimum acidity and associated D_{Ga} depend on gallium and TBP concentrations in the aqueous and organic phases, respectively (3). Gallium extraction with TOPO (8, 17) has not been studied as extensively as with TBP. The chemical behavior of these two extractants is similar regarding the dependence on acidity, although at a given level, D_{Ga} for TOPO is greater than for TBP (8). At low acidity the principal extracted species is $GaCl_3 \cdot n\mathrm{TOPO}$ where n = 1 or 2 depending on the extent of loading, while $HGaCl_4 \cdot 3\mathrm{TOPO}$ forms at high acidity (17). Earlier solvent extraction work using TBP (8, 18–20) showed that with increasing HCl concentration, D_{Ga} rises to a maximum and then decreases. At low acidity or in neutral solution, the extracted species is $GaCl_3 \cdot mH_2O \cdot n\mathrm{TBP}$ where $m \leq 2$, while $n = 1$ under the condition of organic saturation and $n = 2$ at low extractant loading (21). The rise in extraction with an increase in acidity is due to the formation of $HGaCl_4 \cdot 3\mathrm{TBP}$ (19, 20, 22).

The following balance exists when TBP extracts gallium from strong hydrochloric acid solutions (3, 7, 13):

$$H^+_{(aq)} + GaCl^-_{4(aq)} + 3\mathrm{TBP}_{(org)} \longrightarrow HGaCl_4 \cdot 3\mathrm{TBP}_{(org)} \qquad (1)$$

When the organic phase containing $HGaCl_4 \cdot 3\mathrm{TBP}$ is contacted with 0.1 M hydrochloric acid or sulfuric acid solution at the membrane-strip phase interface, the overall stripping reaction may be equivalently given by the following reaction:

$$HGaCl_4 \cdot 3TBP_{(org)} \longrightarrow 3TBP_{(org)} + Ga^{3+}_{(aq)} + 4Cl^{-}_{(aq)} + H^{+}_{(aq)} \qquad (2)$$

Emulsion liquid membranes (ELMs) first invented by Li (23) offers a promising technology for separating and concentrating metal ions from aqueous streams. ELMs remove the equilibrium limitations of solvent extraction by combining extraction and stripping in a single stage operation. Furthermore, the large specific interfacial areas associated with ELMs result in higher permeation rates, enable the achievement of higher metal concentrations in the receiving phase and also substantially reduce the inventory of the organic solvent and extractant, thus reducing the investment and operational costs.

ELMs for metal extraction are made by forming a water-in-oil (W/O) emulsion, stabilized by a surfactant, the (W/O) emulsion contains the metal extractant (carrier) in the oil phase and the stripping reagent in the internal aqueous phase. This emulsion is then dispersed by a relatively low agitation into a feed phase containing the metal ions to be separated. After extraction, the loaded emulsion is separated from the feed stream, demulsification yields a membrane phase that can be recycled.

The extraction chemistry involved in liquid membrane transport is essentially the same as that in solvent extraction, but the overall transport is governed by kinetic rather than equilibrium parameters (24). The solvent extraction process, however, requires larger volumes of solvent inventory and equipment, and thus higher investment costs and becomes inefficient when the metal ion concentration in the effluent stream is low.

The major parameters influencing the extent of extraction may be the level of agitation in the external phase, acid concentration in the external phase, and the type of organic diluent, surfactant, and extractant concentrations, feed concentration of Ga, and treatment ratio. The nature of extractant which forms a complex with gallium ion is also important. In order to have a better understanding of the dynamics of ELM technique, these parameters need to be studied.

In the present work, the selective separation and extraction of gallium have been investigated from the acidic leach solutions, containing such ions as Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al, by emulsion liquid membranes using tributyl phosphate (TBP) as carrier.

EXPERIMENTAL

Reagents

The liquid membrane phase is composed of a surfactant, a carrier, and a diluent. The surfactant is a nonionic polyamine which is commercially known as ECA 4360J. The mobile carrier is tributyl phosphate (TBP) which is purchased from Daihachi Chemicals, Japan. A commercial kerosene (TUPRAS Oil Company, Turkiye), STA90 NS, toluene, xylene, Escaid 100 and Escaid 200 were used as diluents, whose properties are indicated in Table 1. STA90 NS is an isoparaffinic mixture and contains no aromatics. STA90 NS, ECA 4360J, Escaid 100, and Escaid 200 are the products of ExxonMobil, that were used directly as received from the manufacturer. All other chemicals used were of A.R. grade (Merck, Germany). On the other hand commercial kerosene is a complex mixture of aliphatic origin and also contains aromatics about 15% w/w. HCl solution was used as a strip phase.

Experimental Method

Rotary filter cake of the zinc plant residue (CINKUR Co., Turkiye), together with gallium, consists an average of 12% Zn, 15% Pb, 7% Fe, 0.06% Co, 0.10% Ni, 0.15% Cd, 0.19% Cu, 4% Al, and 380 ppm Ga on mass basis, was leached with hydrochloric acid. The acidic leach liquors were obtained by leaching the rotary filter cake or leach residue. One of the common interfering impurities encountered in the recovery of gallium from ores and waste solutions is iron. As reported by earlier workers (10, 19), the extraction of iron increases with the acidity of feed solution in which iron tends to be in ferric state and has a great tendency to form complexes with chloride ion in the strong HCl media, and thus it reacts with TBP. Therefore, iron (III) in the acidic leach solution had to be reduced to iron (II), with the addition of iron dust, in order to increase the selectivity of Ga towards iron.

The stripping solution (25 mL) was added dropwise to the membrane solution (25 mL), stirred at 1800 min^{-1} for 20 minutes, and passed through a burette in about 10 minutes. The appropriate liquid membrane emulsion was added to a feed solution (250 mL) in a 600 mL-baffled beaker, which contained the acidic leach solution to be extracted. The acidic leach

Table 1. Effect of organic diluent on the extraction of gallium at 20°C

Diluent type	Dielectric Constant[a]	Viscosity (mPa · s)	Density (kg/m^3)	Aromatics (%)	% Ga, extr. in 20 mins
Kerosene	2.2	1.6	830	15	41.7
STA90 NS	—	7.3	850	0	65.1
Toluene	2.24	0.59	860	100	20.0
Xylene	2.26	0.81	860	100	14.8
Escaid 100	?	1.6	815[b]	24	8.1
Escaid 200	?	1.2	750[b]	0	25.0

[a] Reference: (36)

[b] Densities given at 15°C.

solution contained 100 mg/L Ga together with 6045 mg/L Fe, 105 mg/L Co, 210 mg/L Ni, 295 mg/L Cd, 18130 mg/L Zn, 3240 mg/L Pb, 178 mg/L Cu, and 2000 mg/L Al, unless otherwise stated.

The two-phase system was stirred by a variable speed mixer equipped with a turbine-type teflon impeller. The mixing speed of feed solution, HCl concentration in the feed solution, type of diluent, surfactant type, extractant concentration, stripping solution type, treatment ratio, phase ratio, and mixing speed of the emulsion formation were varied to observe their effect on gallium separation. The uptake of metal ions was monitored by removing samples of the feed solution periodically for analysis with an atomic absorption spectrophotometer (Shimadzu AA-6701F model, Tokyo, Japan). At the end of each run, the emulsion was recovered and subsequently broken into its constituent organic and aqueous phases using a high-voltage splitter with niobium electrodes. All the extraction experiments were carried out batchwise and at the ambient temperature of 20 ± 1°C. All aqueous solutions were prepared using deionized water. The details of the experimental technique is reported elsewhere (25).

RESULTS AND DISCUSSION

Mixing Speed of Acidic Leach or Feed Solution

In a mechanically mixed contactor, a high mixing speed promotes mass transfer, however, the shear exerted may break the membrane (26). The effect of mixing speed was studied in the range of 200 to 400 min^{-1} and is shown in Fig. 1. It was observed that for an increase in mixing speed from 200 to 300 min^{-1}, the transfer rate of gallium was increased, but further increase in speed at 400 min^{-1} affected the recovery process. Therefore, at speeds above 300 min^{-1}, leakage of gallium might be started due to shearing of emulsion, which ultimately resulted in a gradual depletion in extraction and stripping. Nevertheless, it was observed that increasing mixing speed from 200 to 300 min^{-1} increased the extraction efficiency. However, further increase in mixing speed from 300 to 400 min^{-1}, except the first two minutes, resulted in reduction in the extent of extraction because of emulsion breakdown.

Effect of HCl Concentration in the Feed Solution

Figure 2 shows the effect of HCl concentration in the feed solution on the extraction of gallium. Clearly, the extraction efficiency of gallium increased significantly as the HCl concentration ranged from 4 to 7 M. However, 7 M HCl showed a poor behavior and the emulsion stability decreased significantly. Similar behavior in gallium systems has been previously reported (8, 9, 12, 19, 27). This may be attributed to the fact that the initial rise in

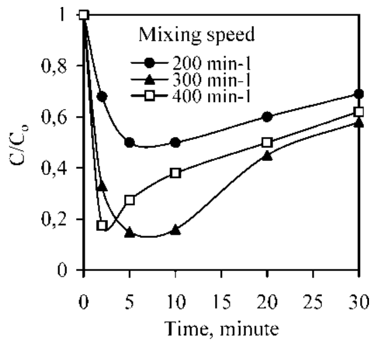

Figure 1. Effect of mixing speed of acidic leach solution or feed phase on the extraction rate of Ga (Initial feed concentration: as stated in experimental; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$; C: Ga concentration in the feed phase at any time, and C_o: initial Ga concentration in the feed phase; C/C_o: dimensionless Ga concentration in the feed phase at any time, (−)).

the rate of extraction with acidity is the formation, in greater amounts, of the extractable species, *$HGaCl_4$*. However, at higher acidities the extraction of HCl also occurs; this consequently reduces the extraction of gallium due to a competitive effect between $GaCl_4^-$ and HCl-TBP complex, as reported by Judin and Bautista (28).

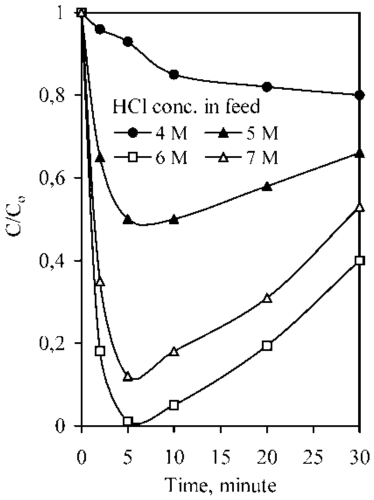

Figure 2. Effect of acid concentration in feed phase on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; mixing speed: 200 min^{-1}; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

Effect of Diluent

It is recognized that the organic diluent influences the performance of many liquid membrane systems (9, 25, 29–33). The permeation behavior of gallium using kerosene, STA90 NS, toluene, xylene, Escaid 100, or Escaid 200 as diluent is presented in Fig. 3, which indicates that STA90 NS provided a better performance, whilst Escaid 100 showed poor behavior. Although aromatics such as toluene and xylene initially provide the highest extent of extraction, after 2 minutes it resulted in a great deal of reduction in the extent of extraction because of emulsion breakdown.

Table 1 lists the physical parameters of the petroleum derived commercial kerosene, STA90 NS, toluene, xylene, Escaid 100, and Escaid 200 along with gallium extraction. Commercial kerosene is a complex mixture of aliphatic origin and also contains about 15% w/w aromatics. STA90 NS is an isopaffinic mixture and contains almost no aromatics. It appears from Table 1 and Fig. 3 that for the six diluents the extent of extraction initially improves, up to 5 minutes, in the following sequence, that is, the lower the viscosity, the higher the extent of extraction. This is in fact expected, but as the time passes the lower viscosity has also a negative effect on the emulsion stability and thus may cause poor transport rates.

It was reported that the rate of extraction increased as the dielectric constant of diluent increased (34), while the opposite view on this effect for six diluents was also reported (35). It was also found that diluents having

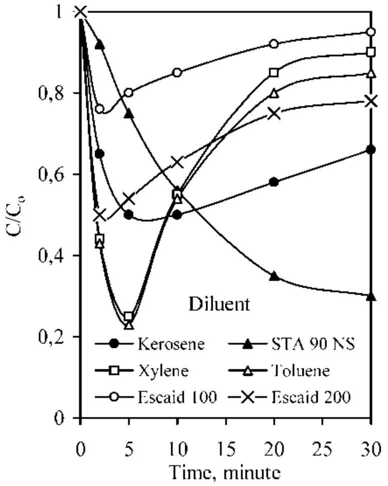

Figure 3. Effect of diluent type on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

higher dielectric constants did not always result in higher rate of transfer (29, 31). Regarding the present work, dielectric constant of STA90 NS is not known, while petroleum fractions have dielectric constants of close range, i.e. 2.5 (36). Therefore, it seems unlikely that the dielectric constant has a significant impact on the transport rates, assuming that the diluents have similar dielectric constants.

The reason that provides better performance may be due to the solvation effect in the membrane solution. It is argued that a diluent which strongly solvates the extractant will probably tend to remove this reagent from the interface which would have an adverse effect on the rate of attainment of equilibrium. However, a diluent which does not solvate the extractant will probably be unable to dissolve sufficient of the reagent for a commercial extraction process (37). The requirement is for a solvent which allows a reasonable concentration of the extractant at the interface whilst dissolving sufficient of the extracted complex. Interactions between diluent-extractant, diluent-surfactant, or any combinations may be significant and therefore it may be very difficult to draw a firm conclusion on this effect, as reported elsewhere (9).

Effect of Surfactant Type

Figures 4 and 5 indicate the effects of surfactant type on the gallium extraction with the diluents kerosene and STA90 NS, respectively. It is observed from Figs. 4 and 5 that though Span 80 initially gives the higher rate of extraction than ECA 4360J, but it gradually deteriorates. This is in agreement with the results reported in various studies, that is, the membranes incorporated with Span 80 shows less resistance to mass transfer than those with other surfactants, but it suffers from some drawbacks: osmotic swelling, poor chemical stability due to hydrolysis, and macroemulsion formation (30, 38–43). It is also reported that ECA 4360J can form very stable emulsions compared to Span 80 (44, 45), but it has also some shortcomings, such as higher interfacial mass transfer resistance (46, 47) and interactions with organic and inorganic acids (40). Therefore ECA 4360J gives better performance.

Effect of Surfactant Concentration

Figures 6 and 7 indicate the effects of surfactant (ECA 4360J) concentration on the gallium extraction with the diluents kerosene and STA90 NS, respectively. From Fig. 6, in the membrane system formed with the diluent kerosene, it is observed that an increase in surfactant concentration from 2% to 12% initially causes a decrease in the extraction efficiency, up to 5 minutes. Thereafter the emulsion stability gradually deteriorates and an increase in the surfactant concentration increases the efficiency. On the other hand, from Fig.7, in the membrane system formed with the diluent STA90 NS, an

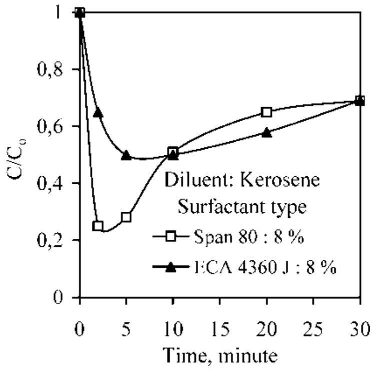

Figure 4. Effect of surfactant type on the extraction rate of Ga (Initial feed concentration: as stated before; kerosen: 82%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1{:}1{:}10$).

increase in the surfactant concentration from 2 to 12%, decreases the gallium extraction efficiency due to the mass transfer resistance caused by the surfactant film, as reported previously (29, 47, 48). From Fig. 7, it was observed that a decrease in the surfactant concentration increased the efficiency, and not causing any deterioration in the emulsion stability. Therefore one may

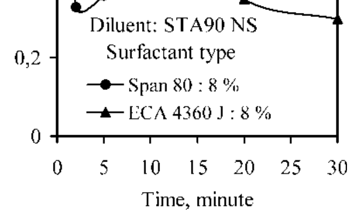

Figure 5. Effect of surfactant type on the extraction rate of Ga (Initial feed concentration: as stated before; surfactant (Span 80 or ECA 4360J): 8%; STA90 NS: 82%; TBP: 10%; mixing speed of feed solution: 200 min^{-1}; feed solution acid concentration: 5 M HCl; stripping solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1{:}1{:}10$).

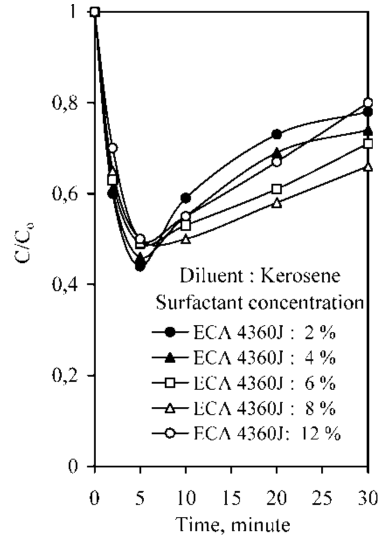

Figure 6. Effect of surfactant concentration on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 2–12%; kerosen: 78–88%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

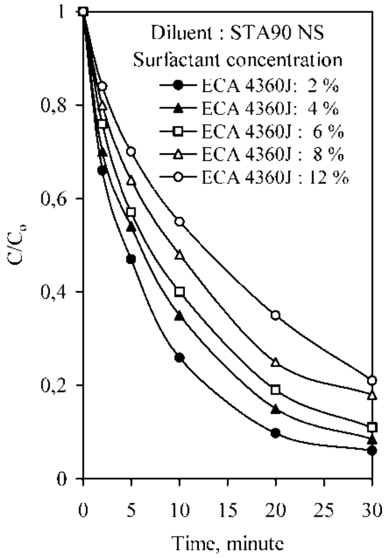

Figure 7. Effect of surfactant concentration on the extraction rate of Ga (Initial feed concentration: as stated before; STA90 NS: 78–88%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

argue that the diluent-surfactant interaction in the membrane phase is so important and thus it may affect the extraction rates (26). This was indeed already given in Fig. 3. From Fig. 6, in the system formed with the diluent STA90 NS, it was observed that an increase in surfactant concentration did not affect the stability of the emulsion, but did enhance the emulsion resistance to mass transfer. This is also in agreement with the similar experimental study carried out with TOPO (9). However, a decrease in surfactant concentration increased the recovery of gallium and did not reduce the stability of emulsion. Nevertheless, Fig. 7 showed that surfactant concentration of 2% w/w was the best for gallium extraction.

Effect of Extractant Concentration

Figure 8 shows the effect of extractant (TBP) concentration on the ELM extraction of gallium. It is observed that when the TBP concentration ranges from 4% to 10% the gallium extraction initially increases up to 5 minutes except for 10%, thereafter the emulsion stability gradually decreases and thus the efficiency decreases. The extractant concentration of 6% gives the best performance for the gallium recovery.

Effect of Stripping Solution

Since both the extraction and stripping processes in the liquid membrane system occur simultaneously for continuous transport of metal ion, it is

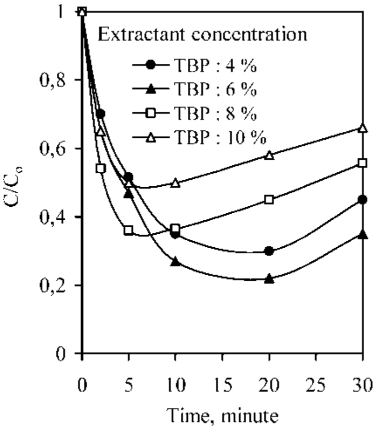

Figure 8. Effect of extractant concentration on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82–88%; TBP: 4–10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

significant to explore the effect of acid type in stripping phase in order to enhance effective ion transport by conducting an efficient reaction at the membrane-stripping phase interface. 0.1 M HCl and 0.1 M H_2SO_4 as stripping solutions are compared in Fig. 9. Among the two acids, 0.1 M H_2SO_4 stripping solution initially showed much better performance than 0.1 M HCl. This was also confirmed by some workers (8, 12, 27, 49).

Effect of Treatment Ratio

The treatment ratio, defined as the volume ratio of aqueous feed solution (V_F) to the emulsion phase (V_E), plays an important role in determining effectiveness of emulsion liquid membranes. Experiments were conducted to study the effect of treatment ratio on the extraction efficiency. The treatment ratio (V_F/V_E) was varied from 5:1 to 10:1, as indicated in Fig. 10. The lower the value of the treatment ratio (V_F/V_E), the more emulsion per unit feed volume is used, and the more emulsion globules are formed; therefore, the mass transfer area for extraction enlarges and the extraction rate increases. This can be realized from Fig. 10 where the extraction rate grows with the decrease in the treatment ratio. This was made by increasing the feed phase volume, while keeping the emulsion phase volume constant.

Effect of Phase Ratio

The effect of the phase ratio of aqueous phase to membrane phase (V_s/V_m) on the extraction rate, by maintaining membrane volume constant, is depicted in

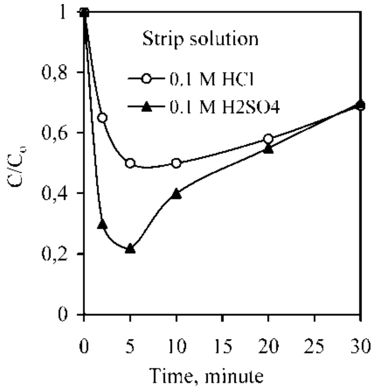

Figure 9. Effect of stripping solution acid type on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; mixing speed of emulsion: 2000 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

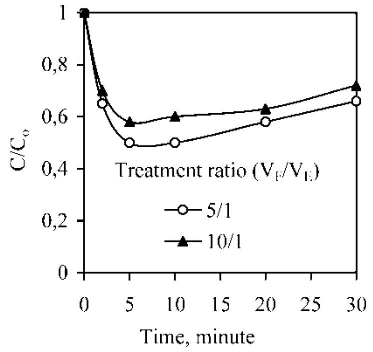

Figure 10. Effect of treatment ratio on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}; V$_s$/V$_m$: 1).

Fig. 11. From Fig. 11, the initial rate of extraction increases as the phase ratio increases, and phase ratio of 1:1 was found to be the best for the extraction of gallium.

Effect of Mixing Speed of Emulsion

Figure 12 shows the effect of the mixing speed emulsion on the extraction of gallium. An increase in the speed also leads to a reduction in the size of droplets (strip phase), thereby increasing the membrane-strip phase interfacial

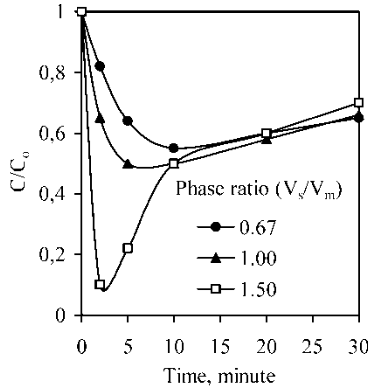

Figure 11. Effect of phase ratio on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; mixing speed: 200 min^{-1}; feed solution acid concentration: 5 M HCl; strip solution: 0.1 M HCl; mixing speed of emulsion: 2000 min^{-1}).

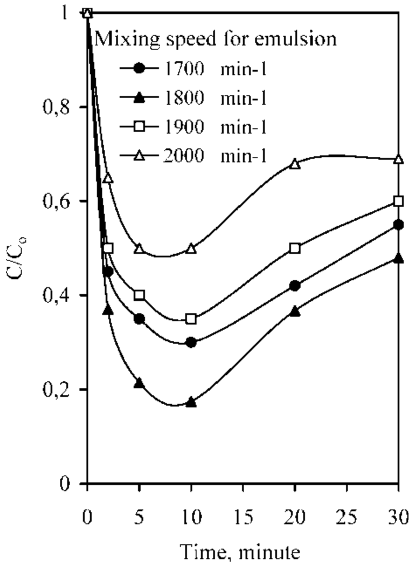

Figure 12. Effect of mixing speed in emulsion preparation on the extraction rate of Ga (Initial feed concentration: as stated before; ECA 4360J: 8%; kerosene: 82%; TBP: 10%; mixing speed of feed soln.: 200 min^{-1}; fed soln. acid concentration: 5 M HCl; strip solution: 0.1 M HCl; $V_s/V_m/V_F = 1{:}1{:}10$).

area and hence the mass transfer rates. The finer droplets are also relatively unstable and therefore it leads to a reduction in the extraction efficiency due to emulsion breakage and the spillage of the internal reagent along with the extracted species. Therefore, the extent of extraction increases as the speed increases from 1700 to 1800 min^{-1}, but decreasing at the higher speeds, as shown in Fig. 12.

Extraction of Gallium using the Optimum Conditions

The optimum conditions were obtained from the earlier experiments. The membrane phase consisted of the surfactant ECA 4360J (2% w/w), the carrier reagent TBP (6% w/w), and the diluent STA90 NS (92% w/w). HCl concentration in the feed solution, concentration and type of acid in the stripping solution, mixing speeds of the emulsion and of the feed solution, and the volume ratio of stripping phase/organic phase/feed phase ($V_s/V_m/V_F$) were kept at the values of 6 M, 0.1 M H_2SO_4, 1800 min^{-1}, 300 min^{-1}, and 1:1:10, respectively.

From Fig. 13, it was observed that 99% extraction of gallium was achieved within 5 min, and the emulsion stability was also maintained during the experimental process.

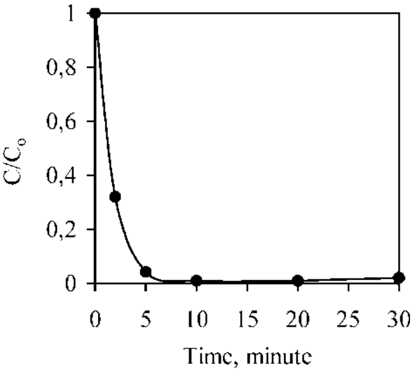

Figure 13. The extraction of Ga at the optimum conditions (Initial feed concentration: as stated before; ECA 4360J: 2%; STA90 NS: 92%; TBP: 6%; mixing speed: 300 min^{-1}; feed solution acid concentration: 6 M HCl; strip solution: 0.1 M H_2SO_4; mixing speed of emulsion: 1800 min^{-1}; $V_s/V_m/V_F = 1{:}1{:}10$).

The variations in concentration of Ga, Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al against time, at the optimum conditions, are indicated in Table 2. As the gallium concentration in the feed solution decreases with time, the concentrations of Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al almost remain fairly steady. Within 30 min, the percentages of extraction of Ga, Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al were found to be of 96.0, 3.4, 6.2, 2.2, 2.1, 14.1, 4.2, 15.2, and 0.2%, respectively, as shown in Table 2. The metal ion concentrations in the feed phase against time and that in the stripping phase in 30 min are given in Table 2. Copper and cadmium were extracted into the stripping solution at the highest ratio, as compared to the other metal ions.

Effect of Feed Concentration

The effect of initial gallium concentration in the solution on the extent of extraction is shown in Fig. 14, using the optimum parameters. The gallium concentration in the feed or external phase was varied from 100 to 300 mg/L by spiking the leach solution. At the optimum conditions, as can be seen from Fig. 14, the gallium concentration in the acidic leach solution was reduced from 100 to 1.1 mg/L, from 200 to 2.6 mg/L within 10 minutes, from 300 to 3.6 mg/L within 20 min. On the other hand the gallium concentrations in the stripping solutions increased from zero to 989, 1974, and 2964 mg/L, within the periods given above, respectively. The higher the gallium concentration in the acidic feed solution is the higher the driving force for the gallium transfer, and thus the higher the extent of extraction is, as shown in Fig. 14.

Table 2. Experimental Results in the optimum conditions (Initial feed concentration: as stated before; ECA 4360J: 2%; diluent (STA90 NS): 92%; extractant (TBP): 6%; mixing speed: 300 $\min^{-1}$; feed solution acid concentration: 6 M HCl; stripping soln: 0.1 M H_2SO_4; mixing speed of emulsion: 1800 $\min^{-1}$; $V_s/V_m/V_F = 1:1:10$; V_s/V_m: 1)

	Experimental results								
	Initial concentration in the feed phase, C_o	Dimensionless concentration in the feed, C/C_o						Strip phase in 30 min, C, mg/L	% extracted into strip phase
Metal ion	(mg/L)	t = 0	2 min	5 min	10 min	20 min	30 min	(exp)	in 30 min
Ga	100	1	0.320	0.041	0.011	0.010	0.022	960	96.0
Fe	6045	1	0.972	0.974	0.963	0.950	0.963	2060	3.41
Co	105	1	0.952	0.931	0.902	0.901	0.933	65	6.19
Ni	210	1	0.983	0.972	0.964	0.953	0.971	46	2.19
Zn	18130	1	0.981	0.969	0.961	0.960	0.972	3887	2.14
Cd	295	1	0.922	0.871	0.843	0.831	0.852	415	14.1
Pb	3240	1	0.969	0.960	0.942	0.931	0.953	1373	4.24
Cu	178	1	0.901	0.863	0.831	0.810	0.842	270	15.2
Al	2000	1	0.999	0.998	0.998	0.998	0.998	30	0.15

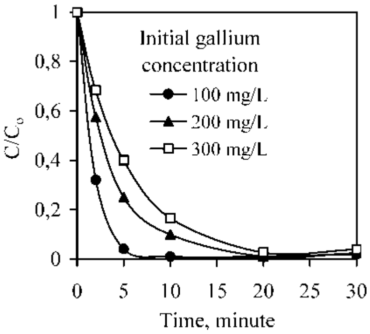

Figure 14. Effect of gallium concentration in the feed solution on the extent of extraction at the optimum conditions (Initial feed concentration: 100–300 mg/L Ga plus the others as stated before; ECA 4360J: 2%; STA90 NS: 92%; TBP: 6%; mixing speed: 300 min^{-1}; feed solution acid concentration: 6 M HCl; strip solution: 0.1 M H_2SO_4; mixing speed of emulsion: 1800 min^{-1}; $V_s/V_m/V_F = 1:1:10$).

Membrane Selectivity

The separation factors (α_{ij}) of gallium with respect to the other ions that exist in the solutions are given in Table 3. The separation factor (α_{ij}) is given as follows:

$$\alpha_{ij} = \frac{(C_i/C_j)_{strip}}{(C_i/C_j)_{feed,o}} \tag{3}$$

where C_i and C_j are the concentrations of i and j components in the stripping and initial feed phases.

At the end of one experiment, in 30 min, liquid membrane selectivity of gallium with respect to other ions are reasonably high. The separation factors for gallium are shown in Table 3. Within 30 min, the calculated and measured separation factors, α_{calc} and α_{exp} respectively, compared reasonably well, except for nickel, zinc, and aluminium (Table 3). After 30 min, the strip solution concentrations of Ga, Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al, in one-stage process, were obtained as 960, 2060, 65, 46, 3887, 415, 1373, 270, and 30 mg/L, respectively. This could be further improved by introducing more stages into the process. When a second stage liquid membrane process was applied to this strip solution, containing 0.1 M HCl, the feed solution would have about 480 mg/L Ga, 1030 mg/L Fe, 32.5 mg/L Co, 23 mg/L Ni, 1944 mg/L Zn, 207.5 mg/L Cd, 687 mg/L Pb, 135 mg/L Cu, and 15 mg/L Al since the feed phase would have to have 6 M HCl at the optimum conditions. In order to achieve this feed solution, an equal volume of concentrated HCl solution (37% or about 12 M HCl) must be added into the strip solution so that final feed concentration would contain about 6 M HCl. Assuming similar operating conditions, a new strip solution would consist of about 4608 mg/L Ga, 351.2 mg/L Fe, 20.1 mg/L Co,

Table 3. Separation factors of gallium with respect to other ions (Initial feed concentration: as stated before; ECA 4360J: 2%; diluent (STA90 NS): 92%; extractant (TBP): 6%; mixing speed: 300 min^{-1}; feed solution acid concen: 6 M HCl; strip solution: 0.1 M H_2SO_4; mixing speed of emulsion: 1800 min^{-1}; $V_s/V_m/V_F = 1{:}1{:}10$; V_s/V_m: 1)

	Separation factors, $\alpha_{\text{Ga/Me}}$							
Metal	t = 0 min	2 min	5 min	10 min	20 min	30 min (calculated)	30 min (exp)	% Err.[a]
Fe	0.00	24.3	36.9	26.7	19.8	26.4	28.2	6.4
Co	0.00	14.2	13.9	10.1	10.0	14.6	15.5	5.8
Ni	0.00	40.0	34.3	27.5	21.1	33.7	43.8	23.1
Zn	0.00	35.8	30.9	25.4	24.7	34.9	44.8	22.1
Cd	0.00	8.72	7.43	6.30	5.86	6.61	6.82	3.1
Pb	0.00	21.9	24.0	17.0	14.3	20.8	22.7	8.4
Cu	0.00	6.87	7.00	5.85	5.21	6.19	6.33	2.2
Al	0.00	680	480	495	495	489	640	23.6

% Error[a] $= \alpha_{\exp} - \alpha_{calc} / \ \alpha_{\exp}\, x100$.

50.4 mg/L Ni, 416.0 mg/L Zn, 292.6 mg/L Cd, 291.3 mg/L Pb, 205.2 mg/L Cu, and 22.5 mg/L Al at the end of 30 min operation during second stage.

The two major contaminants were iron and zinc. Iron tends to be in a ferric state and has a great tendency to form complexes with chloride ion, in the form of $FeCl_4^-$, in concentrated acidic chloride media, and thus forming complexes with TBP similar to that of gallium as given by Eq. (1). Therefore the oxidized iron (in ferric state) in solution competes with gallium for extraction, and thus it results in a reduction in gallium extraction yield (50). The oxidation state of iron in the feed solution has not been determined, but its importance has been taken into consideration in this study. Since Fe^{2+} is not extracted by TBP, the relatively high iron extraction can be reduced by reduction of Fe^{3+} by addition of iron powder, given in Eq. (4), as reported elsewhere (4, 10).

$$2\ Fe^{3+} + Fe \longrightarrow 3Fe^{2+} \tag{4}$$

Complete reduction to Fe^{2+} is difficult but a reduction yield of 96.6% was easily obtained. Therefore this increased the gallium extraction significantly, and only 3.4% of the existing iron in the feed was extracted into strip solution. However, an addition of iron powder, slightly in excess, into the feed solution hardly caused any cementation of copper in the feed in a highly concentrated chloride media. In fact both the lead and copper could be removed from the relatively less acidic strip solution (0.1 M HCl) with the addition of H_2SO_4 and iron powder in an equivalent amount, as a result of precipitation and cementation of $PbSO_4$ and Cu, respectively. The remaining zinc in the solution could be readily removed using a suitable extractant such as di-(2-ethylhexyl) dithiophosphoric acid (DTPA) by a liquid membrane process, or solvent extraction (51). The iron in the feed mixture could be further removed either by liquid membrane or solvent extraction in the third stage. Finally, depending on the process used to concentrate the gallium in solution a purification step for the gallium production using electrolysis was reported (52).

From the experiments in Table 3, and from the above discussions, the gallium in the acidic leach solutions could be separated from the complex mixture, containing various other ions such as Fe, Co, Ni, Zn, Cd, Pb, Cu, and Al, selectively, using emulsion type liquid membranes under the given conditions.

CONCLUSIONS

An emulsion liquid membrane process using TBP as a carrier to extract the gallium from a complex acidic leach solution has been investigated. From this study, the following conclusions can be drawn:

1. Increasing the surfactant (ECA 4360J) concentration caused a decrease in the gallium extraction due to mass transfer resistance of the surfactant

film. When using STA90 NS as diluent, a low concentration was found to be the best for separation of gallium.

2. The highest gallium extraction rate was obtained with 6% w/w TBP concentration.
3. Though among diluents (kerosene, STA90 NS, xylene, toluene, Escaid 100 and Escaid 200), STA90 NS appeared to show a better performance than others.
4. A 6 M HCl concentration in the feed solution was found to be the best, below this the extraction rate decreased and above this the membrane was unstable.
5. Phase ratio and mixing speed of emulsion were determined to be 1:1 and 1800 min^{-1}, respectively.
6. The conditions are possible that 99% of the gallium could be selectively extracted within 10 min from strong acidic leach solutions containing gallium, iron, cobalt, nickel, zinc, cadmium, lead, copper and aluminium, using TBP as a carrier.
7. The liquid membrane selectivity of gallium with respect to the other ions, that existed in the leach solutions, was reasonably high. The gallium concentration could be increased about ten times in one stage, and using more stages the selectivity and concentration of gallium could be further improved.
8. At the optimum conditions, the higher the gallium concentration in the feed solution the lower the extent of gallium extraction was obtained, as the gallium concentration ranged from 100 to 300 mg/L.

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