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Process Intensification via Liquid Emulsion Membrane Technique in Extraction and Enrichment of Rhodium (III) from Chloride Media

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A liquid emulsion membrane (LEM) system as a tool for process intensification has been studied for rhodium recovery using di-2-ethylhexylphosphoric acid (D2EHPA) as a metal carrier and Monemul 80 as a surfactant, dissolved in liquid paraffin. The various process parameters affecting the LEM process, such as extractant, surfactant, and strip phase concentrations, the speed of agitation, the batch contact time, and the treat ratio have been experimentally investigated to get better insight into the process. Perchloric acid was found to be a better stripping agent in the LEM process. It was observed that the extraction of Rh (III) can be significantly more in the absence of a water repelling agent. The maximum enrichment of Rh (III) in the internal phase obtained was 4.3 times with feed phase pH adjusted to 6, perchloric acid (1.5 mol/dm^3), and contact time of 15 min. A mass transfer model to predict the performance of the LEM system was used and found to fit well with the experimental data.

Keywords D2EHPA; enrichment; liquid emulsion membrane (LEM); perchloric acid; rhodium extraction

INTRODUCTION

The process intensification via advanced extraction process, namely, the Liquid Emulsion Membrane (LEM) process has a considerable potential in hydrometallurgy operations where an enrichment of the extracted metal is desired from its low levels of concentration. The recovery of noble metals from aqueous solutions originating from the catalyst preparation, spent catalyst recovery, and recovery of metals from the deposits (fouling) from the reactor downstream equipment is a challenging task. In order for the recovery to become economically viable, the enrichment of noble metals from aqueous stream becomes a very important step in the recovery process.

Rhodium (Rh) being a noble metal, its recovery from the aqueous stream from its low concentration is commercially important. The separation and purification of rhodium are the most difficult aspects in platinum group metal (PGM) refining, mainly because of the complex solution chemistry of Rh in chloride solutions. The complexes formed by rhodium in the chloride solutions exhibit so many different properties that the conventional liquid-liquid extraction process cannot be applied effectively to extract Rh. An excellent critical review with the emphasis on speciation of Rh-chloro complexes has been presented by Benguerel et al. (1). A study of the aqueous chemistry of rhodium (III) chloride complexes, as reported by Benguerel et al., reveals that a variety of rhodium aquo/chloro complex species are present in the solution. These species may range from the completely aquated hexaaquo-rhodate, $Rh(H_2O)_6^{3+}$, to hexachloro-rhodate, $RhCl_6^{3-}$. Mixed aquo/chloro complexes,$[RhCl_{6-n}(H_2O)_n]^{n-3}$, may also be present in the solution (where $0 \leq n \leq 6$). The extent to which each complex exists depends largely on the chloride ion concentration, and also to a lesser degree, on the temperature, age, and the pH of the solution. Several researchers (2–10) have studied the extraction of anionic Rh (by adding salt impurity such as stannous chloride) from the aqueous chloride solution by using the solvent extraction process while Nowottny et al. (11) have studied the recovery of platinum, palladium, and rhodium by reactive extraction. Inoue et al. (12) have studied the separation of rhodium (III) from base metals by using pyridine derivatives and Preston and Du Preez (13) have studied the solvent extraction of platinum group metals (PGM) by using carboxylic acid amides. Swaminathan and Harris (14) and Palmer and Harris (15) have studied the kinetics and mechanism of the reaction of chloride ion with Rh (III) ion in acidic aqueous solution. Ashrafizadeh and Demopoulos (16) have reported that very limited overall extraction of Rh (III) can be achieved by direct liquid-liquid extraction. In their concluding remark, they suggested using the liquid membrane technique to permit continuous transfer of Rh (III) from the aqueous feed phase to a receiving phase.

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They have also studied the extraction of rhodium through supported liquid membrane (SLM) by using Kelex 100 as an extractant (17). Fontas et al. (18) have also reported the use of supported liquid membrane for extraction of Rh (III) using Aliquat 336 as an extractant. Yan and Alstad (19) and Bhandare and Argekar (20) have studied the extraction of rhodium (III) by using di(2-ethylhexyl)phosphoric acid, (D2EHPA), as an extractant. Yan and Alstad (19) obtained 90.70% extraction of Rh (III) from the mixture of Ru (III) and Ir (III) by using solvent extraction while Bhandare and Argekar (20) recovered 100% Rh (III) from the Pt-Rh mixture by using supported liquid membrane (SLM). There exists practically no information in the published literature on the extraction and enrichment of Rh (III) by using the advanced extraction technique, namely, the liquid emulsion membrane (LEM) process.

The LEM is very useful in hydrometallurgical processing to increase the concentration of metallic elements from lean leach solutions and in the treatment of waste streams (21). At a microscopic level in LEM, the aqueous strip phase is encapsulated in the organic phase to form water-in-oil (w/o) type of emulsion. The water insoluble complexing agent is dissolved in organic water immiscible solvent, along with additives such as surfactant, viscosity improver, and water suppressing agent. This constitutes the organic phase in the micro-emulsion of LEM process. The micro-emulsion globules are easily and effectively dispersed in the aqueous phase. An individual emulsion globule acts as a microbatch reactor. Very large numbers of these microglobules provide thousand-folds mass transfer interfacial area resulting in very rapid transport of metal. This in turn reduces the equipment size (volume) for extraction. Further, extraction and stripping is carried out simultaneously in one single contactor thereby eliminating the “stripper” of the conventional recovery system. Thus, the process intensification is realized via the LEM technique. In fact a pipe line contactor with static mixer can then be used commercially. The LEM process is expected to become increasingly important in hydrometallurgical operations to enrich metals from lean ores.

It was, therefore, thought desirable to conduct bench–scale investigation of the application of the LEM process to aid the recovery of Rh (III) from aqueous solution. The readily available di-2-ethylhexylphosphoric acid (D2EHPA) was used as a complexing agent (shuttle). It was thought desirable first to generate data on rhodium (III) chloride dissolved in acidic water to understand thoroughly the process before working on the actual stream from the plant.

Various process parameters such as strip-phase concentration, concentration of extractant, concentration of surfactant, speed of agitation, contact time, and emulsion to aqueous phase treat ratio etc. were studied to aid technology development.

EXPERIMENTAL

Chemicals

The rhodium salt ($RhCl_3$) containing ~40% Rh was obtained from Thomas Baker, India. The calibrating standard was purchased from Ranbaxy Fine Chemicals Ltd. (RANKEM), India. The surfactant, Monemul 80 (sorbitan monooleate), was a gift sample by Mohini Organics Pvt. Ltd., Mumbai, India. An extractant, di-2-ethylhexylphosphoric acid (D2EHPA), procured from Spectrochem Pvt. Ltd., Mumbai, India. Liquid paraffin (light) was procured from a local supplier of repute. Liquid paraffin (C_{14}–C_{16}, a mixture of tetradecane, pentadecane, and hexadecane) was used as an organic diluent for the membrane preparation. Perchloric acid (70%) procured from Merck was used as a stripping agent. All reagents were used as received without any further purification.

Apparatus and Procedure

The conventional liquid-liquid extraction experiments were carried out in order to determine the effectiveness of the extracting solution and the stoichiometric coefficient of complexation between Rh and D2EHPA. These experiments were carried out by mixing the organic phase and the aqueous phase in the ratio 1:1 (v/v) in a magnetically stirred glass flask. The entire assembly was maintained at constant temperature at $303 \pm 0.1\,K$ using a constant temperature water bath. The extraction was carried out for 2 hrs to ensure that the equilibrium was attained. It was observed that the equilibrium was practically attained by the solutions after 30 min. The samples from the aqueous phase were analyzed for Rh (III) to compute overall distribution coefficient (K_D).

The emulsion was prepared by emulsifying an aqueous solution of perchloric acid (inner strip phase) with an organic phase (membrane phase). The membrane phase consisted of predetermined proportions of nonionic surfactant (Monemul 80), water repelling reagent (cyclohexanone), carrier (D2EHPA) and an organic diluent (liquid paraffin). The internal strip phase of aqueous perchloric acid was added drop-wise into the glass reactor (ID = 46 mm) with continuous stirring at high speed of 3500 rpm within 10 min. Stirring was carried out in a glass reactor with a six-blade turbine glass impeller (22 mm in diameter). A milky white stable emulsion was obtained. The emulsion stability was 30 min which is good enough for the LEM process. During the LEM experiments, the emulsion was added at once, in the desired treat ratio, to the feed phase from which rhodium is to be extracted. The mixture was stirred gently at a speed of 400 rpm with a six-blade paddle impeller for a short period of time. At the end of the experiment, the emulsion and the aqueous feed phases were separated by gravity separation using a separating funnel. A clear phase separation was observed within 8–10 min. The emulsion was then broken down by heating it to about 353 K to analyze the inner strip phase. All experiments were carried out at 303 K. The constant temperature was maintained by using a digital temperature indicator and controller with an accuracy of ± 0.1 K.

Analytical Techniques

The analysis of Rh (III) in an aqueous chloride solution at ppm level was performed by cyclic voltammetry technique using Trace Metal Analyzer (797 VA Computrace, Metrohm Micro-Devices, Switzerland). A voltage ramp is applied across the electrodes through an electrolyte. There is a flow of current when an element is reduced or oxidized at the electrode. This electrochemical reaction produces the current and the corresponding current is measured by the conductivity meter. The current produced during the reaction is proportional to the concentration of metal ion in the measuring flask. The content of Rh (III) at ppm level in the aqueous phase was measured by a differential pulse (DP) voltammetry technique using the hanging mercury drop electrode (HMDE) mode. The instrument was calibrated by diluting a standard (1000 mg/dm^3) solution (atomic absorption spectroscopy, AAS, grade rhodium solution). Supporting electrolyte for determination of rhodium (III) was prepared by using 35% hydrochloric acid and 37% formaldehyde solution (22).

All the experiments were repeated at least twice to check the reproducibility and the results obtained were within 5% experimental error.

RESULTS AND DISCUSSION

Extraction Equilibria

The extracting agent used for the present study was di-2-ethylhexylphosphoric acid, (D2EHPA). The water insoluble organic phase was of liquid paraffin as organic solvent or diluent. This diluent forms the main component of the organic membrane. D2EHPA has a tendency to exhibit a dimer form in non-polar solvents, such as liquid paraffin used in this study. For all computational purposes we have taken the concentration in the monomer form. It is always desirable to have an idea of stoichiometry of complexation and the effect of temperature on the extraction efficiency. Initially, Rh solution of known concentration was made alkaline (pH > 8) by caustic to covert chloro-compound to hydrated form and then the pH was adjusted towards acidic range by HCl. The constant of extraction, K$_{ex}$, and the stoichiometric coefficient, (3-x), for the overall extraction equilibrium, shown in Eq. (4), can be estimated from the distribution ratio (K$_D$) obtained through conventional solvent extraction experiments keeping the pH (adjusted to 6) and the chloride ion concentration (0.02 M) of the aqueous phase constant. Each time a fresh Rh solution was prepared (as mentioned above) and was used immediately, to avoid any effect of speciation and aquation on extraction efficiency of Rh.

The overall extraction equation for rhodium, as reported by Yan and Alstad (19), can be represented as

$$\begin{aligned} &Rh(H_2O)_6^{3+} + xCl^- + (3-x)(\overline{HA})_2 \\ &\Leftrightarrow \overline{Rh(H_2O)_{6-x}Cl_x((HA)_2)_{3-x}} + (3-x)H^+ + xH_2O \end{aligned} \tag{1}$$

The over bar represents the organic phase and (HA) refers to D2EHPA. From the above equation, the extraction constant can be written as-

$$K_{ex} = \frac{\left[\overline{Rh(H_2O)_{6-x}Cl_x((HA)_2)_{3-x}}\right][H^+]^{3-x}}{\left[Rh(H_2O)_6^{3+}\right][Cl^-]^x\left[\overline{(HA)_2}\right]^{3-x}} \tag{2}$$

and the distribution ratio (K$_D$) is expressed as-

$$K_D = \frac{\left[\overline{Rh(H_2O)_{6-x}Cl_x((HA)_2)_{3-x}}\right]}{\left[Rh(H_2O)_6^{3-}\right]} \tag{3}$$

Combining Equations (2) and (3) and rearranging, we can have

$$\log K_D = (3-x)\log\left[\overline{(HA)}_2\right] + \log K_{ex} + x\log[Cl^-] + (3-x)pH \tag{4}$$

By plotting a straight line of log K$_D$ versus log [(HA)$_2$], as shown in Fig. 1, the stoichiometric complexation coefficient, (3-x), between Rh (III) and D2EHPA was found to be unity and hence the value of x to be 2. The observed extraction constant (K$_{ex}$) was calculated as 33.3×10^{-2}, at 303 K.

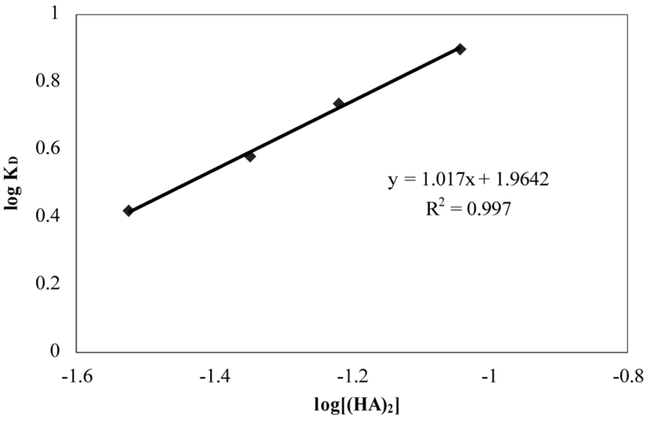

FIG. 1. Plot of log K$_D$ Vs log [(HA)$_2$] as in Equation 4. (diluent: liquid paraffin, $C_{i\,f} = 9.72 \times 10^{-5}$ mol/dm^3, [Cl$^-$] = 0.02 M, feed phase pH = 6, contact time: 2 hr).

TABLE 1
K_{ex} as a function of temperature

T (K)	K_{ex}
293	0.495
303	0.333
313	0.259
323	0.189

Temperature

From the process engineering point of view the temperature is a very important parameter in any extraction process. The extraction constant, K_{ex}, (for the extraction of Rh (III) from aqueous chloride media with D2EHPA in liquid paraffin) was found to decrease with temperature, in the temperature range of 298 to 313 K. The values of K_{ex} were inferred by measuring K_D values at different temperature and then using Eq. (4). Table 1 exhibits the inferred values of K_{ex} as a function of temperature. In all subsequent experiments, we have used temperature 303 K unless otherwise mentioned.

Effect of pH

Some liquid-liquid extraction equilibrium experiments were carried out at constant carrier concentration (0.045 mol/dm^3) to observe the effect of aqueous phase pH on the extraction of Rh (III). Benguerel et al. (1) reported that aquated species of rhodium are present in the solution at $pH > 3$. The pH was varied in the range of 3–9 as shown in Fig. 2. Increase in the pH of the aqueous phase (up to $pH = 6$) increases the extraction efficiency of Rh (III) and similar observation was reported by Yan and Alstad (19). This was probably due to an increase in the rate of aquation reactions of rhodium at higher pH. The change in the initial pH of the aqueous feed phase was measured once the equilibrium was attained. The carrier, di-2-ethylhexylphosphoric acid, dissociates at the aqueous-organic interface, liberating hydrogen ions in the aqueous phase which in turn reduces the equilibrium pH. Talekar and Mahajani (23) have also reported the similar observation while studying the extraction of cadmium (II) using di-2-ethylhexylphosphoric acid as carrier.

Effect of Chloride Ion Concentration

To check the effect of chloride ion concentration on extraction of Rh (III), a few liquid-liquid extraction experiments were carried out by introducing a salt, sodium chloride, as a source of chloride ions. As reported by Yan and Alstad (19), the hydrated rhodium may exist stably for some time (possibly for some days) depending on the concentration of the chloride ion and the acidity of the solution. The salt was added to the aqueous solution containing Rh (III) and then the pH was adjusted to the desired value. The chloride ion concentration in the aqueous feed phase was increased from 0.1 to 0.7 mol/dm^3, as shown in Fig. 3. It was observed that the extraction of Rh (III) decreased with increased concentration of chloride ion in the aqueous feed phase. The degree and the rate of formation of rhodium-chloro complexes depend mainly on the chloride ion concentration, pH and the age of the solution. As the chloride ion concentration increases the rate of aquation reactions decreases enhancing the formation of rhodium into nonextractable anionic or neutral Rh-chloro complexes.

We have taken a lump parameter approach in a sense we are not considering which species of Rh (III) is extracted. In LEM, we have all the time Rh (III) transported from an aqueous phase to inner membrane phase by the shuttle D2EHPA that is continuously regenerated.

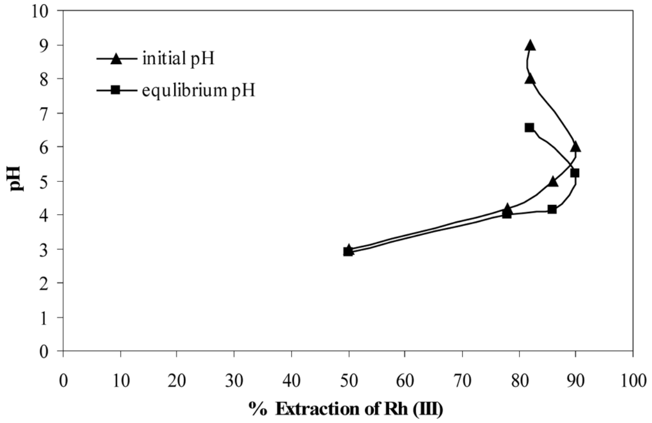

FIG. 2. Effect of pH on extraction of Rh (III). (diluent: liquid paraffin, $C_{i\,f} = 9.72 \times 10^{-5}$ mol/dm^3, $[HA] = 0.045$ mol/dm^3, contact time: 2 hr).

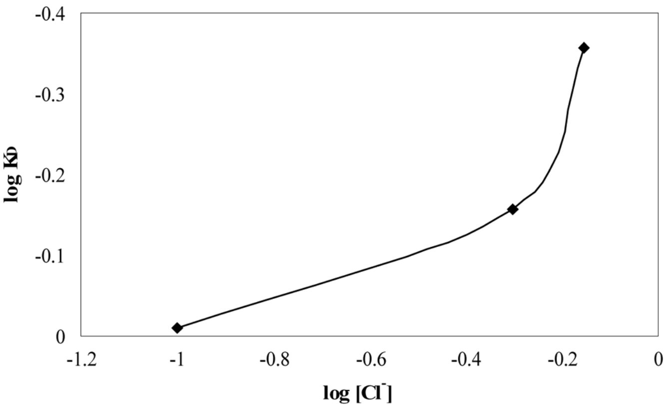

FIG. 3. Effect of chloride ion concentration. (diluent: liquid paraffin, $C_{i\,f} = 9.72 \times 10^{-5}$ mol/dm^3, feed phase $pH = 6$, contact time: 2 hr).

Transport Mechanism in LEM

The extraction rate of Rh (III) from an aqueous stream by LEM is a series of various transport processes, namely:

(i) mass transfer of Rh (III) ions from the bulk of feed liquid phase to the external interface of the emulsion globule,
(ii) interfacial complexation reaction between Rh (III) ions and D2EHPA at the external interface with the release of H^+ ions in bulk of aqueous stream resulting in decrease of pH
(iii) diffusion of the Rh (III) complex into the emulsion globule,
(iv) stripping reaction between Rh (III) complex and internal acid at the interface of the stripping phase, and
(v) back diffusion of regenerated D2EHPA to the external interface of the emulsion globule for extraction of Rh (III). The extractant is, thus, just a shuttle in the membrane phase.

The selection of the organic membrane phase, the strip phase (stripping agent), the surfactant, and the extractant are the key parameters of the membrane formulation. The process parameters such as treat ratio, extraction time, and speed of agitation reflect in utility of the LEM technique.

Membrane Phase

It is obvious that the organic membrane phase has to be "water insoluble." In spite of this there is always some finite solubility in water at the ppm level of this "water insoluble" membrane phase. This solubility at the ppm level imparts Chemical Oxygen Demand (COD) or Biochemical Oxygen Demand (BOD) to the aqueous feed phase from which metal is extracted. Therefore, the "water insoluble" membrane phase should be bio-degradable when the feed aqueous stream goes to the effluent treatment plant. From the safety point of view, non-flammable organic membrane phase is always desirable. In addition, it should not be toxic to work force operating the plant. In other words, it should satisfy safety, health, and environment (SHE) compliance easily. Further, the diluent should not only dissolve extracting/carrying agent but also the complex formed. The liquid paraffin mixture satisfies all these criteria and is readily available from a hydro-cracker product stream of any refinery and therefore, was the obvious choice.

Selection of Strip Phase

The stripping agent encapsulated in the organic membrane phase plays an important role in the LEM process. Extraction and stripping take place simultaneously in the LEM process. Instability of the membrane due to swelling and breakage of emulsion globule is one of the major drawbacks of the LEM process which can be minimized, although it cannot be eliminated, with an appropriate stripping agent. Thus, the selection of the stripping agent is the key to the success of LEM process. A series of experiments were carried out with different acids such as, methane sulphonic acid (MSA), hydrochloric acid (HCl), and perchloric acid in water to study their stripping ability. As shown in Fig. 4, the stripping ability of these acids was found to be decreased in the following order: perchloric acid > hydrochloric acid > MSA. In the present work, therefore, perchloric acid was used as a stripping agent for the enrichment of Rh (III). The extraction and enrichment of Rh (III), and percent swelling of the emulsion phase were calculated as follows-

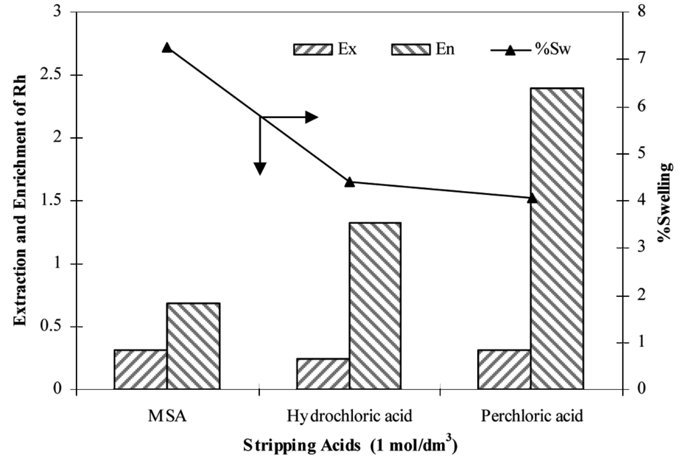

FIG. 4. Selection of stripping agent. (diluent: liquid paraffin, [M80] = 0.03 mol/dm^3, [HA] = 0.05 mol/dm^3, $C_{i,f} = 9.72 \times 10^{-5}$ mol/dm^3, feed pH = 6, TR = 1:10, contact time = 7 min, speed of agitation = 400 rpm, T = 303 K).

$$Extraction,\ Ex = \frac{(C_{i,f} - C_f)}{C_{i,f}} \tag{5}$$

$$Enrichment,\ En = \frac{C_s}{C_{i,f}} \tag{6}$$

$$\%\,Swelling = \frac{(V_{i,e} - V_{f,e})}{V_{i,e}} \times 100 \tag{7}$$

The concentration of perchloric acid was varied in the concentration range of 1 to 3 mol/dm^3, as shown in Fig. 5. An enrichment of almost 3 times was achieved when 1.5 mol/dm^3 concentration of perchloric acid was used. For higher concentration of the strip phase, swelling of the emulsion increases significantly. This increase in the swelling makes the emulsion unstable and thus, ultimately reduced the enrichment of Rh (III).

Surfactant

Monemul 80 (sorbitan monooleate) is a non-ionic surfactant having hydrophilic-lipophilic balance (HLB = 4.3). The surfactant, Monemul 80, is biodegradable and has a

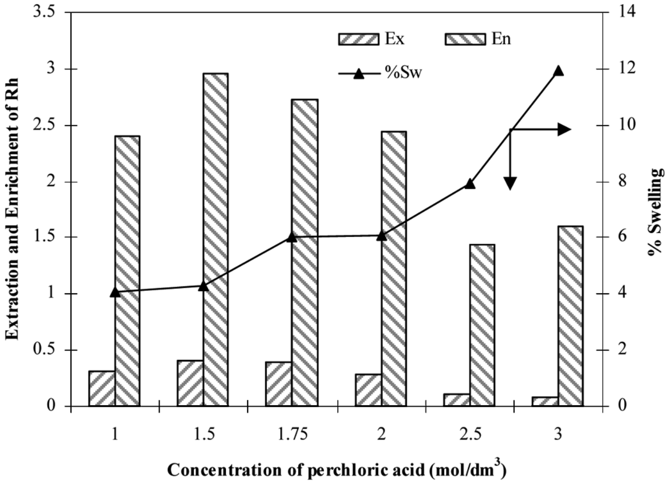

FIG. 5. Effect of concentration of strip phase on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [HA] = 0.05 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, contact time = 7 min, speed of agitation = 400 rpm, T = 303 K).

good tendency to form water-in-oil (w/o) type of emulsion. A higher surfactant concentration usually results in higher emulsion stability. At the same time a higher concentration of the surfactant often causes a decrease in the transport rate of metal ions because the reaction between the metal ions and the carrier is inhibited by the adsorption of surfactant molecules at the reaction interface. Yan and Pal (24) have described the role of surfactant in osmotic swelling of the emulsion. The concentration of the surfactant, Monemul 80, was varied in the range of 0.01 to 0.07 mol/dm^3 (0.5 to 3% v/v) to study the effect of the concentration of Monemul 80 on the performance of LEM. As shown in Fig. 6, it was observed that the maximum enrichment (3 times) was obtained when 0.03 mol/dm^3 (1.5% v/v) of Monemul 80 was incorporated in the membrane phase.

Carrier

The carrier, di-2-ethylhexylphosphoric acid, has been widely used to extract and separate the number of metal cations in a wide range of operating conditions due to its chemical stability, and high selectivity for the particular metal species. Further, D2EHPA has very low solubility in the aqueous phase (25). The carrier concentration was varied in the range of 0.03 to 0.11 mol/dm^3 of D2EHPA, as shown in Fig. 7. It was observed that the enrichment increased with the increase in carrier concentration from 0.03 to 0.06 mol/dm^3 (1 to 3.5% v/v) of D2EHPA. Further increase in the concentration of the carrier from 0.06 to 0.11 mol/dm^3 reduced the enrichment. This may be justified as with increasing concentration of D2EHPA, the maximum percentage of Rh (III) remains in the organic membrane form (as a Rh-D2EHPA complex) without getting stripped off and, thus, affecting the enrichment adversely. Similar observations were reported by Yadav and Mahajani (26). Therefore, further experiments were carried out with 0.06 mol/dm^3 (2% v/v) of D2EHPA in the membrane phase, unless otherwise mentioned.

Water Repelling Agent

LEM technique is constrained by the transport of water from the aqueous phase into the membrane phase which causes swelling of the emulsion phase. The major disadvantages of swelling are the dilution of the inner stripping phase and instability of the membrane phase. Mukkolath et al. (27) have proposed the addition of water repelling reagent, cyclohexanone, in the organic membrane phase to restrict the transport of water into the membrane phase. We are extracting the cationic form of Rh (III) which is surrounded by six water molecules as represented in

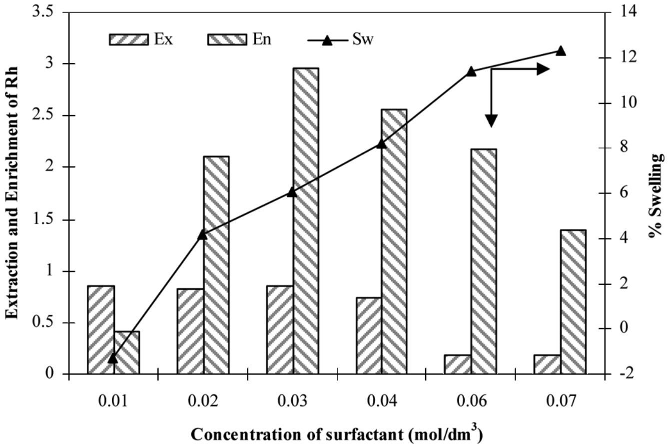

FIG. 6. Effect of concentration of surfactant on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [HA] = 0.05 mol/dm^3, [HClO$_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, contact time = 7 min, speed of agitation = 400 rpm, T = 303 K).

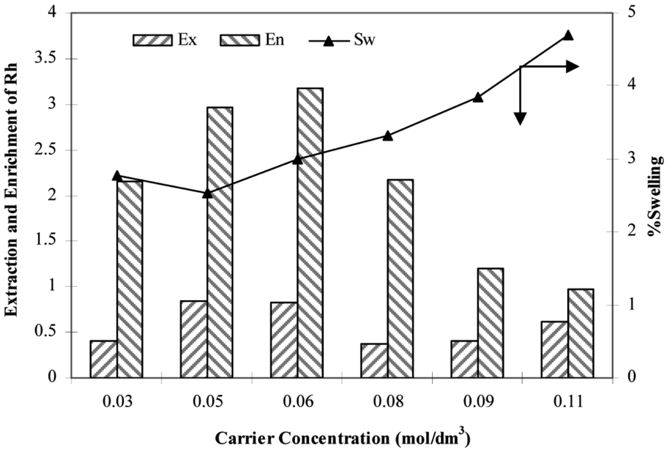

FIG. 7. Effect of carrier concentration on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [HClO$_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, contact time = 7 min, speed of agitation = 400 rpm, T = 303 K).

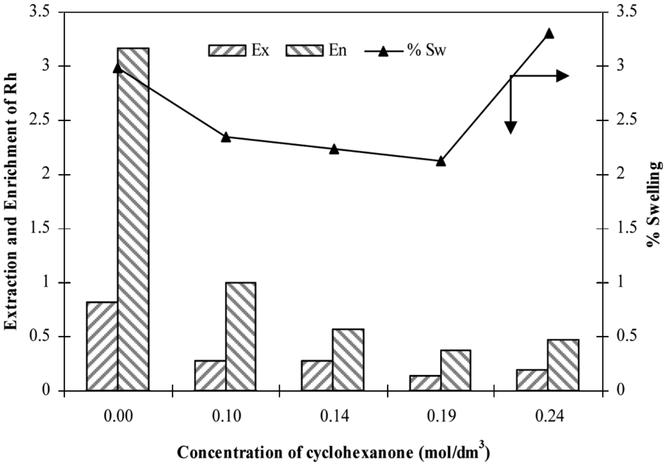

FIG. 8. Effect of concentration of cyclohexanone on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [$HClO_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, contact time = 7 min, speed of agitation = 400 rpm, T = 303 K).

Eq. (1). It was, therefore, thought desirable to study the effect of concentration of cyclohexanone, in the membrane phase, on the extraction efficiency of LEM. The concentration of cyclohexanone was varied from 0–0.24 mol/dm^3 (0–2.5% v/v) in the membrane phase. As shown in Fig. 8, it was observed that the extraction efficiency of the LEM decreased with the addition of the cyclohexanone in the membrane phase. The maximum extraction and enrichment of Rh (III) was obtained when no cyclohexanone was incorporated in the membrane phase. Hence, it was decided to carry out the experiments without the addition of cyclohexanone.

Contact Time

The contact time (residence time) is one of the key parameters in LEM extraction. It is the time for which the emulsion phase is in contact with the aqueous feed phase for effective extraction. The longer contact time causes more water transport into the internal phase, resulting in the swelling of the membrane and subsequently may initiate the breakage of the emulsion phase. The contact time was studied in the range of 4–25 min, as shown in Fig. 9. It was observed that as the contact time increased from 4 min to 25 min, the swelling increased linearly while the enrichment of Rh (III) attained the maximum value (4.3 times) at 15 min and then decreased. This fall down in enrichment was mainly due to increased swelling of the emulsion phase. A similar observation was reported by Thien et al. (28). The selection of contact time was solely made on the basis of maximum enrichment of Rh (III) in the internal phase and hence all the further experiments were carried out with the contact time of 15 min, unless otherwise specified.

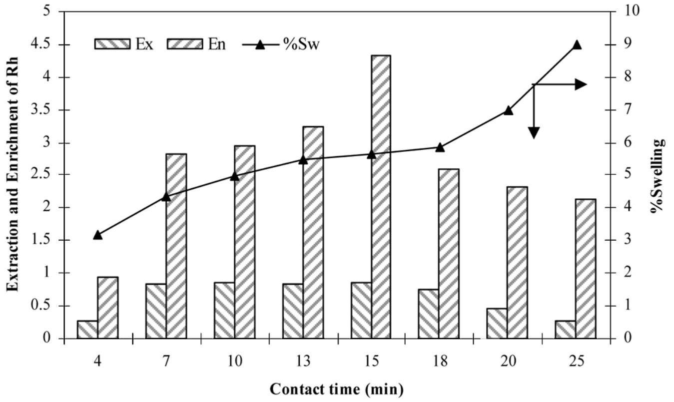

FIG. 9. Effect of contact time on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [$HClO_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, speed of agitation = 400 rpm, T = 303 K).

Speed of Agitation

The speed of agitation is a very important process parameter. By increasing the speed of agitation (intensity of turbulence) we can increase the rate of transport of Rh (III) present at ppm level in the feed solution. However, due to increased shear there is a danger of breakage of the membrane formed. In order to balance these effects one has to be careful not only in selecting a contactor but in having a proper level of contact between the feed phase and the emulsion by controlling the speed of agitation. The effect of the speed of agitation on enrichment of Rh (III) was studied in the range of 100–600 rpm, as shown in Fig. 10. While an increase in speed of agitation would increase the interfacial area and the mass transfer coefficient, up to certain speed of agitation beyond which increase in the speed of agitation is likely to break the emulsion phase because of increased shear on the emulsion globules. It was observed that increasing the speed of

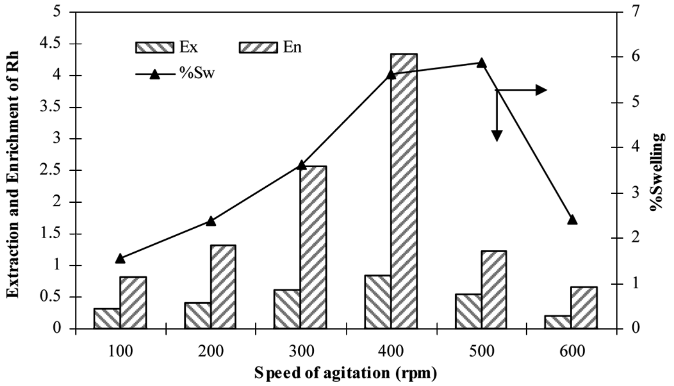

FIG. 10. Effect of speed of agitation on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [$HClO_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, contact time = 15 min, T = 303 K).

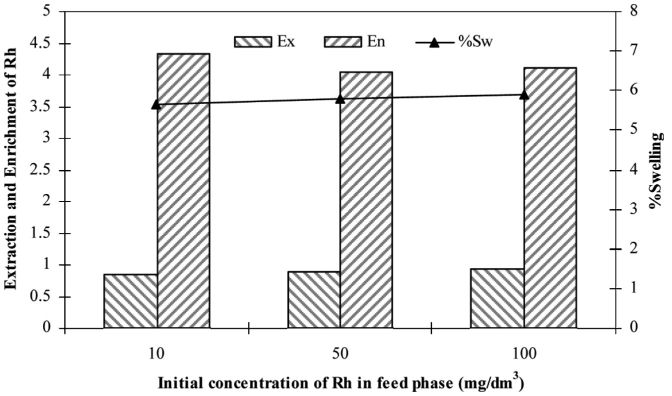

FIG. 11. Effect of initial concentration of Rh (III) in the feed phase on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [HClO$_4$] = 1.5 mol/dm^3, feed pH = 6, TR = 1:10, speed of agitation = 400 rpm, contact time = 15 min, T = 303 K).

agitation from 100 to 400 rpm increased the extraction and enrichment efficiency of the system, but further increase in the speed of agitation from 400 to 600 rpm resulted in decreasing the extraction and enrichment efficiency. The maximum extraction and enrichment of Rh (III) was obtained at 400 rpm.

Initial Concentration of Rh (III) in Feed Phase

A series of experiments were carried out to study the effect of initial concentration of Rh (III) in the feed phase on extraction and enrichment efficiency of the LEM system. The concentration was varied from 10 to 100 mg/dm^3 of Rh (III) in the feed phase as shown in Fig. 11. It was observed that as the initial concentration of Rh (III) in feed increased the fraction extraction of Rh (III) also increased from 0.84 to 0.925, but no significant change was observed in enrichment of Rh (III).

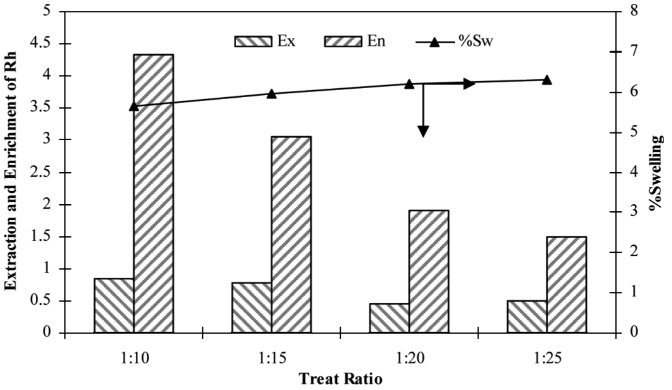

FIG. 12. Effect of treat ratio on extraction and enrichment of Rh (III). (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [HClO$_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, speed of agitation = 400 rpm, contact time = 15 min, T = 303 K).

TABLE 2
Overall mass transfer coefficient (K_La) as a function of speed of agitation (rpm)

Speed of agitation (rpm)	$K_La \times 10^5$ (s^{-1})
100	0.91
200	1.03
300	1.12
400	1.20

Treat Ratio (TR)

The ratio of the emulsion phase to the aqueous feed phase on volume basis is termed as treat ratio (TR) and is one of the important parameters in an LEM process. A series of experiments were conducted to study the effect of treat ratio on the effectiveness of the LEM system. The treat ratio was varied from 1:10 to 1:25 (emulsion phase: aqueous phase), as shown in Fig. 12. It was observed that there was continuous decrease in the extraction and enrichment of Rh (III) as the TR changed from 1:10 to 1:25 while there was no profound effect on the swelling of the emulsion phase.

The Mass Transfer Model

A realistic and simple mass transfer model has been developed by Yadav and Mahajani (26). Following that model, the overall mass transfer coefficient, K_La was calculated as a function of speed of agitation for transport of Rh (III) in the LEM extraction process. It is given in Table 2. The comparison of experimentally obtained extraction and that from the model is shown in Fig. 13. The simple model proposed by Yadav and Mahajani (26) to predict the

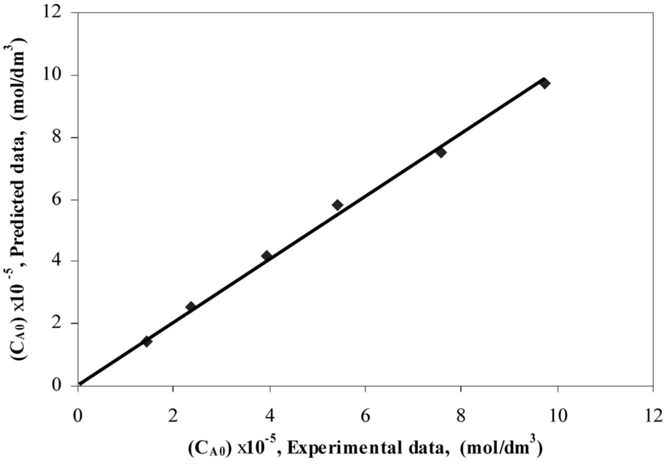

FIG. 13. Plot of experimental data directly compared with model-predicted data. (diluent:liquid paraffin, [M80] = 0.03 mol/dm^3, [HClO$_4$] = 1.5 mol/dm^3, $C_{i,f}$ = 9.72 × 10^{-5} mol/dm^3, feed pH = 6, TR = 1:10, speed of agitation = 400 rpm, contact time = 15 min, T = 303 K).

performance of the LEM system was found to be adequate to fit well the experimental data.

CONCLUSION

In order to support liquid emulsion membrane (LEM) studies conventional liquid-liquid batch extraction experiments were conducted to study the effect of temperature on the extraction behavior of rhodium. The stoichiometric complexation coefficient, between Rh (III) and D2EHPA, was found to be unity and the extraction constant (K_{ex}) was calculated as 33.3×10^{-2}, at 303 K.

It was observed that the extraction of Rh (III) was pH sensitive and exhibits good extractability when the pH of the feed phase was adjusted to 6.

It is possible to realize process intensification via the LEM process in enriching Rh (III) from a very dilute aqueous stream to aid the recovery of the same. The membrane phase consisted of the carrier D2EHPA (0.06 mol/dm^3), the surfactant Monemul 80 (0.03 mol/dm^3) in paraffin encapsulated the aqueous stripping phase containing perchloric acid (1.5 mol/dm^3).The maximum enrichment of Rh (III) in the internal phase obtained was 4.3 times with contact time of 15 min, agitation speed of 400 rpm, and treat ratio of 1:10.

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NOMENCLATURE

C_{A0}	concentration of Rh (III) ions in feed phase at time t (mol/dm^3)
C_{Ai}, $(\overline{C_{Ai}})$	concentration of Rh (III) ions in the external feed phase and membrane phase interface (mol/dm^3)
$(\overline{C_{B0}})$	D2EHPA concentration in organic phase (mol/dm^3)
$C_{i,f}$	initial concentration of Rh (III) in the feed phase (mol/dm^3)
C_f	concentration of Rh (III) in the feed phase after extraction (mol/dm^3)
C_s	concentration of Rh (III) in the strip phase (mol/dm^3)
En	enrichment of Rh (III) in Eq. (7)
Ex	fraction extraction of Rh (III) in Eq. (6)
K_D	distribution coefficient
K_{ex}	extraction equilibrium constant
K_La	overall mass transfer coefficient (s^{-1})
M80	Monemul 80
R	universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1})
Sw	percent swelling of the emulsion phase in Eq. (8)
T	temperature (K)
TR	treat ratio of emulsion to aqueous phase (v/v)
$V_{i,e}$	initial volume of the emulsion phase (dm^3)
$V_{f,e}$	final volume of the emulsion phase (dm^3)

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