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Suresh V. Yadav[a]; Vijaykumar V. Mahajani[a]
[a] Chemical Engineering Department, Institute of Chemical Technology, University of Mumbai, Mumbai, Matunga, India

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Liquid Emulsion Membrane (LEM) Process for Vanadium (IV) Enrichment: Process Intensification

Suresh V. Yadav and Vijaykumar V. Mahajani
Chemical Engineering Department, Institute of Chemical Technology,
University of Mumbai, Mumbai, Matunga, India

Abstract: A liquid emulsion membrane (LEM) system for vanadium (IV) transport has been designed using di-2-ethylhexyl phosphoric acid (D2EHPA), dissolved in *n*-dodecane as carrier. The selection of extractant, D2EHPA, was made on the basis of conventional liquid-liquid extraction studies. The work has been undertaken by first carrying out liquid-liquid extraction studies for vanadium (IV) to get stoichiometric constant (n), and equilibrium constant (K_{ex}), which are important for process design.

Transport experiments were carried out at low vanadium (IV) concentration (ppm level). The studies on liquid emulsion membrane included i) the influence of process parameters i.e. feed phase pH, speed of agitation, treat ratio, residence time and ii) emulsion preparation study i.e., organic solvent, extractant concentration, surfactant concentration, internal strip phase concentration. When the strip phase concentration was 2 mol/dm^3 (H_2SO_4) and feed phase pH 3 better extraction of vanadium was obtained. Higher V_m/V_1 gave higher extraction of vanadium (IV). A simplified, design engineer friendly model was developed.

Keywords: Liquid emulsion membrane (LEM), vanadium (IV) extraction, D2EHPA, Monemul-80 (surfactant)

INTRODUCTION

Process intensification is a powerful tool to make a chemical project more competitive. By process intensification (PI) we mean any chemical engineering

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Address correspondence to Vijaykumar V. Mahajani, Chemical Engineering Department, Institute of Chemical Technology, University of Mumbai, Mumbai, Matunga 400 019, India. Tel.: 91-022-2414 5616; Fax: 91-022-2414 5614; E-mail: vvm@udct.org

development in unit processes or unit operations or equipment or their suitable combination having built-in Safety, Health, Environment, and Quality (SHE-Q) compliances and Energy Conservation (ENCON) philosophy that would result in much higher operating profits from the project. It is expected that PI results in a smaller and safer plant.

The conventional extraction and stripping processes employed to win back metallic elements in concentrated form from lean solution has very large extraction and stripping columns due to very low interfacial area between two phases. The increase turbulence level in both phases might result in emulsion formation, which necessitate de-emulsification/coalescence vessel or result in higher residence time in the separation vessel. The liquid emulsion membrane (LEM) process overcomes above deficiencies and results in process intensification by providing interfacial area say, a thousand times and carrying out extraction and stripping operation simultaneously in the same contactor (1).

At microscopic level in LEM, a stripping phase is encapsulated in the organic phase containing water insoluble extracting agent, emulsifier, additives to improve viscosity if desired, and water transport suppressing agent. The water in oil emulsion is then formed by a high intensity turbulence device in either a mechanically agitated contactor or a static mixer. The emulsion globule contains micro reactors of stripping phase and is generally 1 to 5 microns in size (2–5). The emulsion having high interfacial area is then contacted with aqueous phase having lean metal either in a static mixer or mechanically agitated contactor for extraction. We can use a pipeline static mixer and get away with a large extraction column. Thus process intensification is achieved.

In this research investigation the objective of our study was to demonstrate the application of LEM technique for the recovery of vanadium. We present application of LEM process to concentrate vanadium from lean aqueous solutions. Nowadays, vanadium production is limited to the recovery from industrial wastes (6), low grade (lean) ores, fly ash (7, 8), and spent catalyst (9). The most commonly used method for vanadium recovery involves vanadium solubilization with sulphuric acid. The vanadium solution obtained in the process of winning the metallic content from the source is often dilute in nature. The LEM process presented here as a process intensification tool provides an alternative to the conventional extraction process for enrichment of vanadium.

The commercial spent catalyst streams are likely to contain many other metal elements. For example, from the hydrotreating operation in the petrochemical complex the aqueous stream is likely to be a mixture of nickel, molybdenum with vanadium ions. The extraction of metal ions is pH dependant. Therefore the selectivity will also depend upon pH. While individual extraction studies for nickel (10) and molybdenum (11) have been reported, there is little information available on parametric study of extraction of vanadium by Liquid Emulsion Membrane process. Though, Lozano et al. (12), and Palet et al. (13), presented some studies to recover vanadium (V) by using a supported liquid membrane technique, there is practically no information available in the published literature on the application of the liquid emulsion membrane (LEM) technique as a process intensification tool to recover and concentrate vanadium (IV).

In the present investigation attention has therefore been focused on the enrichment (concentration) of vanadium (IV) from the sulphuric acid media by the LEM technique. The studies pertaining to the complexation stoichiometry of the pickup of the vanadium (IV) by the extracting agent and distribution coefficients as a function of temperature as a prime requirement of the LEM process have been reported here. The various process parameters have been studied to aid technology development of the recovery of vanadium even from the spent catalyst stream containing other metal ions.

EXPERIMENTAL

Chemicals

The main chemical extractant "D2EHPA" was obtained from Spectrochem Pvt. Ltd., Mumbai, India. The surfactant "Monemul-80" (mainly Sorbitan Monooleate) was a gift sample from Mohini Organics (P) Ltd., Mumbai, India. Both were used as supplied without any further purification. All other reagents were obtained from local suppliers of repute and are of analytical reagent grade.

The initial aqueous solutions and the synthetic feed of known concentration of metal ions were prepared by dissolving an appropriate salt, namely, $VOSO_4 \cdot xH_2O$, in deionized water. The pH was controlled by the addition of sulphuric acid or sodium hydroxide as the case may be to the desired level. Inspection of the colour from preliminary tests showed that vanadium existed in the plus 4 oxidation state in acid solution (14), which was also checked with standard vanadyl (IV) sulphate in sulphuric acid solution procured from Merck.

Apparatus and Procedure

The emulsion was prepared by emulsifying an aqueous acidic solution of strip phase with an organic phase in a mechanically agitated contactor. The organic phase (membrane phase) consisted of a surfactant monemul-80, a carrier reagent D2EHPA, a water suppressing agent, cyclohexanone, and an organic diluent, *n*-dodecane. The internal strip phase (sulphuric acid) was added drop wise into a glass reactor, containing the organic phase. A predetermined volume of 1:1 was maintained for organic phase to the internal strip phase. The reactor content were stirred at 4000 rpm for 30 min with a six-blade turbine impeller of 30 mm diameter in a baffled glass vessel of 70 mm diameter where a stable milky white emulsion was obtained, with a mean diameter of the encapsulated droplets varying from 1 to 8 μm as measured by a Coulter particle size analyzer (Model LS 230). The emulsion was dispersed in the feed phase of vanadyl (IV) sulphate salt from which the vanadium (IV) was extracted. It was possible to separate neatly the emulsion phase from the feed phase quickly in a separator before emulsion starts breaking. The emulsion stability was tested by examining the phase separation over time. The extraction was performed in the same reactor at a speed of 300 rpm. The internal droplet size and emulsion globule size depended upon the concentration of reagents and the hydrodynamics of the system.

Samples of about 5 cm^3 were withdrawn from the extractor at different intervals of time, filtered through an ordinary filter paper, to separate the emulsion from the aqueous feed phase. The emulsion was broken down by heating to about 80°C for the analysis of the strip phase.

The conventional extraction equilibrium experiment were carried by mixing 25 cm^3 of organic phase and 25 cm^3 aqueous phase and then agitated by a magnetic stirrer for 8 h. The samples were analyzed to find out the equilibrium distribution coefficient (K_D). We have found that there is no practical change in concentration of vanadium (IV) after 3 hrs. Also, liquid-liquid extraction studies were carried out for vanadium (IV) at different acidity and different extractant concentration to obtain stoichiometric coefficient of complexation (n), and equilibrium constant (K_{ex}), which are important for process design. All experiments were carried out at 30 ± 1°C and the reproducibility were checked at least twice.

Analytical

Vanadium (IV) concentration in the aqueous phase and the strip phase was determined with the help of High Performance Ion Chromatograph (DIONEX, USA) equipped with GS50 Gradient Pump, ion-pac CS5A column, post column reactor and AD25 Absorbance Detector at a wavelength of 540 nm. The strip phase droplet size and emulsion globule size was measured before and after extraction by Coulter LS 230 laser particle size analyzer, where *n*-paraffin (C_{10}-C_{14}) was used as a background phase for the strip phase droplet size measurement and distilled water as background phase for the emulsion globule size measurement. Moisture pickup by the membrane phase was measured with a microprocessor based digital automatic Karl-Fischer titrator (Model: Veego/Matic-MD India). Error in analysis for the vanadium (IV) analysis was within $\pm 3\%$. Vanadium (IV) retained in the organic phase was calculated using mass balance.

RESULTS AND DISCUSSION

Extraction Equilibria

In order to comprehend the extraction process by LEM, it is necessary that one must have an idea of stoichiometry of complexation, concentration of the stripping agent in the strip phase, and the effect of temperature on extraction and stripping performance. We shall first deal with them before switching over to the LEM studies.

The extraction of vanadium (IV) from the sulphuric acid media by di (2-ethylhexyl) phosphoric acid (D2EHPA) has been studied by Sato et al. (15) and Islam et al. (16). D2EHPA is known to exist as a dimer in non polar solvents. In the extraction of Vanadium (IV) from vanadyl sulphate ($VOSO_4 \cdot xH_2O$) as feed, the oxo-complex VO^{2+} is the dominating cationic species. Then, the extraction reaction for vanadium (IV) by D2EHPA can be expressed as follows:

$$\mathrm{VO^{2+}} + \mathrm{n}\overline{\mathrm{(HR)_2}} \rightleftharpoons \overline{\mathrm{VOR_2(HR)_{2n-2}}} + 2\mathrm{H^+} \qquad (1)$$

The overbar represents material in organic phase. The extraction equilibrium constant, K_{ex}, is expressed as

$$\mathrm{K_{ex}} = \frac{\overline{[\mathrm{VOR_2(HR)_{2n-2}}]}[\mathrm{H^+}]^2}{[\mathrm{VO^{2+}}][\overline{\mathrm{(HR)_2}}]^{\mathrm{n}}} \qquad (2)$$

The distribution coefficient of vanadium (IV), K_D, is defined as follows:

$$\mathrm{K_D} = \frac{\overline{[\mathrm{VOR_2(HR)_{2n-2}}]}}{[\mathrm{VO^{2+}}]} = \frac{\text{(Vanadium in organic phase)}}{\text{(Vanadium in aqueous phase)}} \qquad (3)$$

From above expressions, after appropriate rearrangement and definitions, we have,

$$\log \mathrm{K_D} - 2\,\mathrm{pH} = \log \mathrm{K_{ex}} + \mathrm{n}\log[\overline{\mathrm{(HR)_2}}] \qquad (4)$$

Complexation Stoichiometry

It is seen from equation (4) that it is possible to infer the extraction equilibrium constant, K_{ex} (equation (2)) and the complexation stoichiometry, n (equation (1)) by observing K_D values at known pH of aqueous solution with D2EHPA, (HR) as an independent variable as shown in Fig. 1. The value of n obtained was 2. The extraction equilibrium constant K_{ex} obtained from the intercept of Fig. 1 as 7.43×10^{-2} using D2EHPA as an extractant.

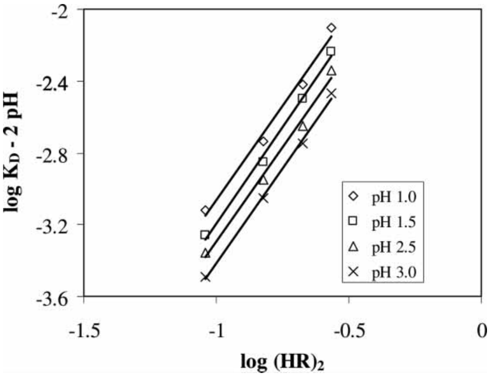

Figure 1. Plot of log K_D-2 pH vs. log $[HR]_2$, diluent = *n*-dodecane, [V (IV)]= 1.96×10^{-3} mol/dm^3, at 30°C. Equilibrium time = 3 h.

Temperature

The distribution coefficient, K_D, for the extraction of vanadyl sulphate in sulphuric acid solution with 0.09 mol/dm^3 D2EHPA in *n*-dodecane was found to increase with temperature, in the range of 303 to 323 K. It is thus possible to infer K_{ex}, extraction equilibrium constant via equation (4). There exists a relationship between K_{ex} and heat and entropy of the equilibrium complexation as follows:

$$\ln K_{ex} = \frac{-\Delta H_R}{RT} + \frac{\Delta S_R}{R} \tag{5}$$

A plot of ln K_{ex} against 1/T, as shown in Fig. 2, gave the enthalpy change of reaction (ΔH_R) 19.92 kJ mol^{-1} and the entropy of reaction (ΔS_R) 0.0569 kJ K^{-1}mol^{-1}. This value is slightly higher than reported earlier by Sato et al. (15), probably because the diluent was *n*-dodecane in our case instead of kerosene used by Sato et al.

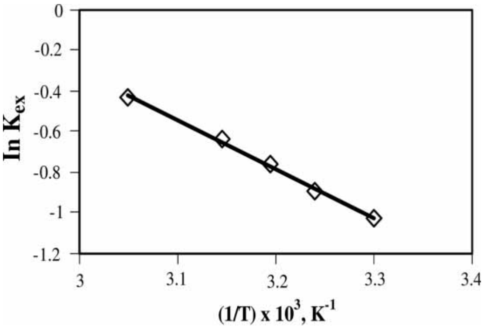

Figure 2. Plot of ln K_{ex} vs. (1/T), diluent = *n*-dodecane, $[C_{HR}]$ = 0.09 mol/dm^3, [V (IV)] =1.96×10^{-3} mol/dm^3, pH = 3.

Stripping Agent Concentration

In order to have an idea about the distribution constant, K_D between D2EHPA and concentrated H_2SO_4 as strip phase, some experiments were performed by varying H_2SO_4 concentration from 0.5 mol/dm^3 to 3 mol/dm^3. The K_D was observed very low after 2 mol/dm^3 acid concentration as shown in Fig. 3 thereby indicating the effectiveness of concentrated H_2SO_4 as a stripping agent. Please note that the final concentration of the stripping agent will depend upon the stability of the membrane (w/o) formed.

LEM Extraction of Vanadium (IV)

The extraction of vanadium (IV) from an aqueous acidic stream by LEM is a series of various transport processes, as shown in Fig. 4, namely:

(i) mass transfer of vanadium (IV) ions from bulk of feed aqueous phase to the external interface of the emulsion globule;
(ii) interfacial complexation reaction between V (IV) ions and D2EHPA at the external interface;
(iii) diffusion of V (IV) complex into emulsion globule; and
(iv) stripping reaction between V (IV) complex and internal acid at the interface of the stripping phase.

The major parameters influencing the extraction were the intensity of turbulence (speed of agitation) in the external phase, pH of the external aqueous phase. The strip phase encapsulated in organic membrane being small in size (<5 microns) behaves as a rigid sphere. There is no-way; one can have independent

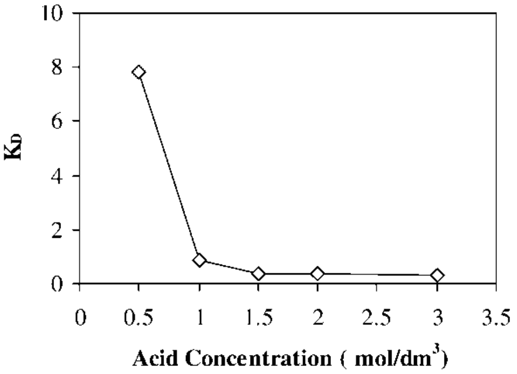

Figure 3. Effect of strip phase acid (H_2SO_4) concentration on distribution coefficient (K_D), diluent = *n*-dodecane, [C_{HR}] = 0.09 mol/dm^3, [V (IV)] =1.96×10^{-3} mol/dm^3, pH = 3.

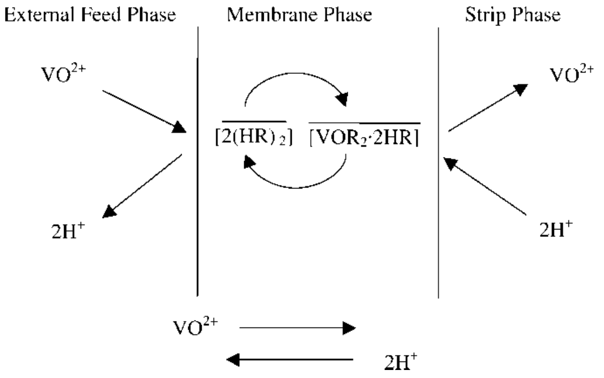

Figure 4. Mechanism of facilitated transport of vanadium (IV).

control on turbulence in strip-phase microreactors. The strength of the acid in the strip phase played an important role during extraction. An increase in the level of agitation in the external (phase 3) phase resulted in decrease in the mass transfer resistance in the feed phase. However, it also resulted in the breakage of the emulsion globules (phase 2) phase thereby reducing the overall efficiency of the extraction. Thus there exists optimum speed of agitation to balance two opposing effects. The other parameters affecting the rate and extent of extraction are the concentration of surfactant used in the organic phase and volume ratio of the emulsion phase to aqueous phase (V_m/V_1). In order to have a better understanding of the dynamics of LEM technique, these parameters were studied.

The performance of the LEM extraction technique was measured with the help of following terms: extent of extraction (Ex). Enrichment (En), treat ratio (TR) and swelling (Sw) defined as follows:

$$\%\text{Ex} = \frac{C_{l(0)} - C_{l(\text{t})}}{C_{l(0)}} \times 100 \tag{6}$$

$$\text{En} = \frac{C_{in(\text{t})}}{C_{l(0)}} \tag{7}$$

$$\text{TR} = \frac{\text{Volume of emulsion phase } (V_m)}{\text{Volume of feed phase } (V_l)} \tag{8}$$

$$\%\text{Sw} = \frac{V_{\text{in,t}} - V_{\text{in,o}}}{V_{\text{in,o}}} \tag{9}$$

The success of the LEM process depends upon the stability of the emulsion. If the emulsion is highly stable, the recovery of the strip phase (for winning back vanadium) and the organic phase for recycle becomes difficult to achieve by the demulsification process. Therefore the process parameters in the emulsion formulation and extraction need to be carefully selected.

Model Development

The LEM extraction is a process of mass transfer accompanied by chemical reaction. Doraiswamy and Sharma (17) have presented a comprehensive account of the theoretical aspects of mass transfer with chemical reaction. The reactions involved at the interfaces in this process are expected to be instantaneous and the overall rate of the reaction components to be controlled by the diffusion of reaction components to the reaction plane in the aqueous phase as depicted in Fig. 5.

In order to account the observation that the rate of extraction depends upon the intensity of turbulence in the aqueous phase, a simple model is developed to aid process design engineer and the following assumptions are made:

(a) An ideal batch reactor is under complete mixing and constant temperature operations.
(b) Carrier and solvent are insoluble in water.
(c) Since the carrier is consumed on the outer interface of the membrane and is regenerated on the inner interface, by instantaneous reaction, it is therefore assumed that the carrier concentration in the membrane phase is constant.
(d) The emulsion globules are uniform and have no internal circulation. The internal droplets are evenly distributed in the globules.
(e) No coalescence and redispersion occur between all emulsion globules.
(f) The external phase is well mixed. Mass transfer resistance in this phase is restricted to the external boundary layer surrounding the globules.
(g) The distribution coefficient and diffusivity are constant. Emulsion breakage and swelling are neglected.

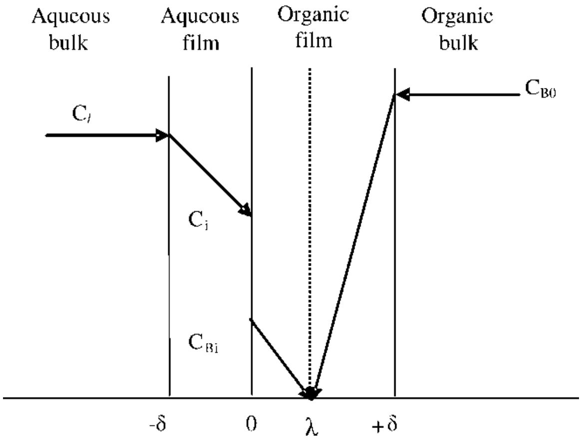

Figure 5. Mass transfer with instantaneous chemical reaction with aqueous side resistance (film theory).

The complexation reaction of lean VO^{2+} solution is deemed to be an instantaneous reaction, with a part of the resistance to mass transfer on the aqueous side. The following equations will then hold:
Mass transfer in bulk of aqueous stream-

$$R_A a = k_{LA} a (C_l - C_i) \tag{10}$$

An instantaneous complexation reaction in the diffusion film in the membrane phase

$$R_A a = k_{LB} a C_{Bi} \left(1 + \frac{C_{B0}}{ZC_{Bi}} \times \frac{D_B}{D_A}\right) \tag{11}$$

Solving Equation (10) along with Equation (11) gives the value of C_i explicitly,

$$C_i = \left(\frac{k_{LA} a C_l - k_{LB} a \times [C_{B0}/Z] \times D_B/D_A}{k_{LA} a + k_{LB} a \times K_D}\right) \tag{12}$$

Substituting for interfacial concentration C_i, in equation (10),

$$R_A a = \left(\frac{C_l K_D + [C_{B0}/Z] \times D_B/D_A}{K_D/k_{LA} a + 1/k_{LB} a}\right) \tag{13}$$

Integrating equation (13),

$$\ln\left(\frac{Y_1}{Y_2}\right) = \alpha(t_2 - t_1) \tag{14}$$

Where,

$$\alpha = K_L a \tag{15}$$

$$\frac{1}{K_L a} = \frac{1}{k_{LA} a} + \frac{1}{K_D k_{LB} a} \tag{16}$$

and

$$Y_1 = \left(C_{l,1} K_D + \left[\frac{C_{B0}}{Z}\right] \times \frac{D_B}{D_A}\right) \tag{17}$$

$$Y_2 = \left(C_{l,2} K_D + \left[\frac{C_{B0}}{Z}\right] \times \frac{D_B}{D_A}\right) \tag{18}$$

We do not have knowledge of k_{LB}a. However, k_{LA} might be computed by the correlations presented by Skelland and Lee (18). In the absence of reliable, and experimentally validated, correlations, for mass transfer coefficient in liquid emulsion membrane system for individual phases, we have decided to use the concept of overall mass transfer coefficient. In our opinion this is more sound approach. We feel majority of the resistance would be in aqueous system.

Table 1. Overall mass transfer coefficient ($K_{LA}a$) as a function of speed of agitation (rpm)

$K_{LA}a \times 10^6$ (s^{-1})	Speed of agitation (rpm)
0.46	100
0.99	200
2.14	250
6.15	300

We thus see that an overall mass transfer coefficient is a function of the intensity of the turbulence (speed of agitation) in the aqueous phase. In our experiments we observed K_{LA} a dependency on the speed of agitation as shown in Table 1.

Figure 6 shows a Plot of experimental data directly compared with the predicted concentration from equation (14). Thus after knowing the value of the slope (mass transfer coefficient) for a particular batch of reaction one can easily predict the performance of LEM system for vanadium extraction.

Emulsion Preparation Parametric Study

We shall discuss various parameters affecting emulsion preparation specific to our system.

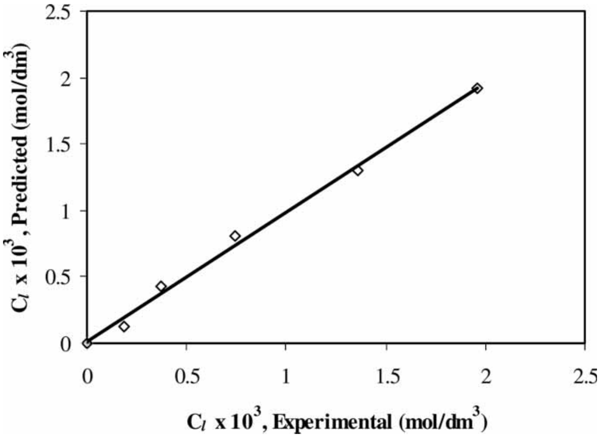

Figure 6. Plot of experimental data directly compared to eq. 14 [speed of agitation: 300 rpm; TR: 1:10; C_{HR}: 0.09 mol/dm^3; feed phase: 1.96×10^{-3} mol/dm^3 of V (IV); strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

Organic Membrane Phase (Diluent)

The organic solvent used to make a membrane should have reasonably good viscosity otherwise viscosity improvers are required. The solvent must satisfy the SHE (safety, health, and environment) compliance. The chemical oxygen demand (COD) imparted to the aqueous phase by the solvent must be as low as possible and must be amenable to simple biotreatment. Otherwise, the vanadium depleted aqueous phase might necessitate elaborate effluent treatment to meet discharge standards.

We have found *n*-dodecane meets these requirements adequately. Kulkarni and Mahajani (10) have used this solvent in molybdenum recovery. Instead of *n*-dodecane, a paraffin stream from linear alkyl benzene (LAB) manufacturing can also be used advantageously. In this investigation we have used *n*-dodecane as a solvent for the membrane phase.

Surfactant Concentration

The surfactant (Monemul 80) was used to stabilize the w/o emulsion based on its HLB (Hydrophilic-Lypophilic Balance) Value. A higher surfactant concentration resulted in higher emulsion stability but also increased swelling. The mechanism of water transport in LEM is via diffusion of the hydrated surfactant. The hydrophilic portion of the surfactant molecule pickup water at aqueous feed phase-membrane phase interface and shuttles through the membrane phase and gets dehydrated by releasing water at the strip phase interface (19). Thus water gets transported from the feed phase to the strip phase. With increase in surfactant concentration, the process of hydration and dehydration enhances, leading to higher emulsion swelling. A higher concentration of the surfactant increased emulsion swelling and it adversely affected the strip phase enrichment. To optimize the surfactant concentration, which provides minimum swelling and optimum membrane stability experiments were carried out. The effect of surfactant (Monemul 80) concentration on enrichment is shown in Fig. 7. It was observed that 0.07 mol/dm^3 of surfactant was a good tradeoff between two opposing effects.

Apart from the above, water is likely to get transported due to osmotic pressure difference between the feed and the strip phase. Please note H_2SO_4 has a very good affinity for water.

Water Transport Suppressing Agent

Swelling phenomenon observed in LEM due to surfactant explained above can be minimized if not, eliminated by adding cyclohexanone as a water repelling agent. The addition of cyclohexanone to the membrane phase alters the micellization mechanism such that the surfactant molecules cover cyclohexanone over strip phase droplets during micellization. When cyclohexanone concentration is increased micelle formation proceeds till it reaches a fixed value, and any further

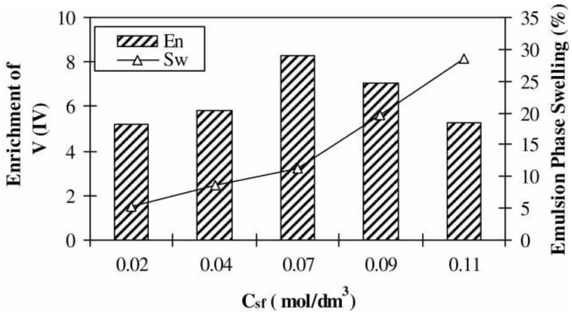

Figure 7. Effect of surfactant concentration on the enrichment of vanadium (IV) and swelling of emulsion [speed of agitation: 300 rpm; TR: 1:10; C_{HR}: 0.09 mol/dm^3; feed phase: 1.96×10^{-3} mol/dm^3 of V (IV); strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

increase in concentration tends to reverse the encapsulation. Moisture pickup of the membrane phase as analyzed by Karl-Fischer titration method as a function of cyclohexanone concentration is shown in Fig. 8. It was observed that moisture pickup remained more or less constant at a lower level in 0.3 mol/dm^3 to 0.4 mol/dm^3 range. Therefore, further studies were conducted with 0.3 mol/dm^3 of cyclohexanone (minimum required) in the membrane phase.

Carrier Concentration

The carrier or extractant, D2EHPA, facilitates metal transport through the membrane phase by shuttling the complex formed with the metal ion from

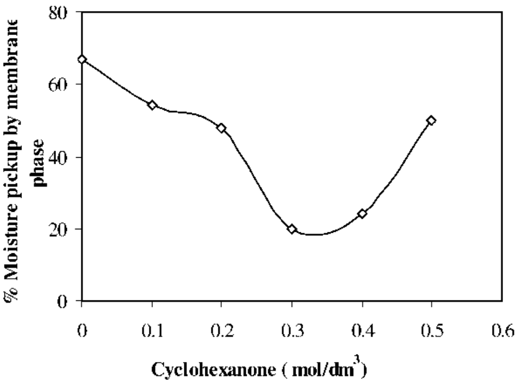

Figure 8. Effect of cyclohexanone concentration on the moisture pickup by membrane phase for extraction of vanadium (IV) [speed of agitation: 300 rpm; TR: 1:10; C_{HR}: 0.09 mol/dm^3; feed phase: 1.96×10^{-3} mol/dm^3 of V(IV); strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{sf}: 0.07 mol/dm^3; feed phase pH = 3].

the aqueous phase-membrane interface to the membrane- strip phase interface. The effect of carrier concentration on vanadium (IV) transport was studied in the range 0.03 mol/dm^3 to 0.15 mol/dm^3 of D2EHPA. Figure 9 exhibits the effect of carrier concentration on swelling (%) and vanadium (IV) transport. It was observed that vanadium (IV) extraction as well as the final stripping increased with increase in carrier concentration from 0.03 mol/dm^3 to 0.09 mol/dm^3. Further, when the concentration was increased from 0.09 mol/dm^3 to 0.15 mol/dm^3, the extraction of vanadium (IV) increased while the final stripping got affected. This is because of two reasons; by increasing the D2EHPA concentration maximum percentage of vanadium (IV) remained in the complex form (in membrane phase) without getting stripped, which in turn affects the final recovery by the LEM process. Further, by increase in extractant concentration, swelling was also increased, thereby diluting the strip phase. Please note that D2EHPA in liquid membrane is not to be saturated with vanadium (IV), but it should merely act as a shuttle to carry vanadium (IV) ions from one side (water-membrane interface) of the membrane to the other side (membrane-sulfuric acid interface). In all the experiments the concentration of D2EHPA was maintained at 0.09 mol/dm^3, unless otherwise stated.

Concentration of Stripping Agent

To investigate the influence of the strip phase concentration on vanadium (IV) transfer, the concentration of the strip phase was varied from 1 mol/dm^3 to 4 mol/dm^3. Figure 10 shows the effect of concentration on the extraction, enrichment of vanadium (IV), and swelling of emulsion. Swelling increased with the acidity of internal droplets, because of the increased difference in the osmotic

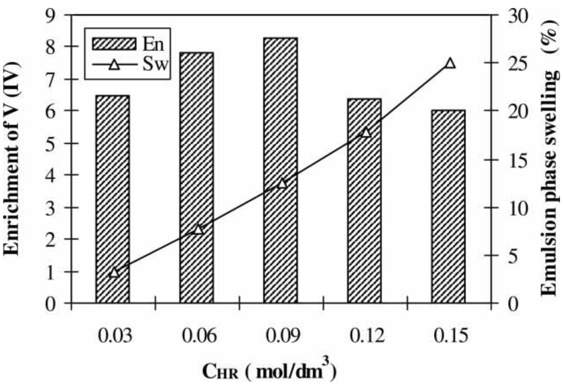

Figure 9. Effect of extractant concentration on the enrichment of vanadium (IV) and swelling of emulsion [speed of agitation: 300 rpm; TR: 1:10; C_{sf}: 0.07 mol/dm^3; feed phase: 1.96 × 10^{-3} mol/dm^3 of V (IV); strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{cyclo}: 0. 3 mol/dm^3; feed phase pH = 3].

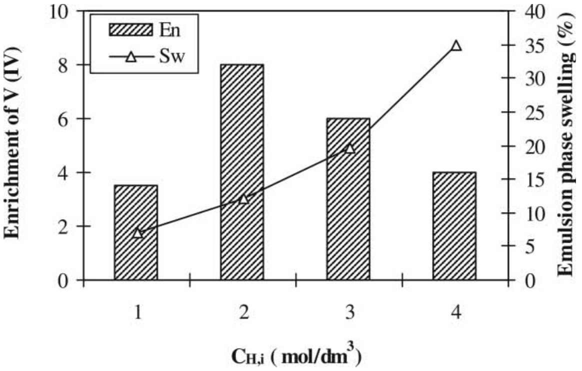

Figure 10. Effect of strip phase H_2SO_4 concentration on the enrichment of vanadium (IV) and swelling of emulsion [speed of agitation: 300 rpm; TR: 1:10; C_{sf}: 0.07 mol/dm^3; feed phase: 1.96×10^{-3} mol/dm^3 of V (IV); C_{HR}: 0.09 mol/dm^3; Diluent: n-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

pressure between the feed and strip phase. It was found that the extraction and final enrichment increased when the acid concentration was varied from 1 mol/dm^3 to 2 mol/dm^3. However, further increase in the concentration of acid in the strip phase from 2 mol/dm^3 to 4 mol/dm^3 reduced the extent of extraction and enrichment. It was as a result of increase of swelling which caused more amount of water to permeate through the membrane causing the internal droplet to swell and coalesce. Thus, a concentration of 2 mol/dm^3 was found appropriate.

Thus for the LEM system under consideration following parameters was optimized:

- Solvent: n-dodecane
- Surfactant concentration: 0.07 mol/dm^3
- Water transport suppressing agent concentration: 0.3 mol/dm^3
- Carrier concentration: 0.09 mol/dm^3
- Strip phase sulfuric acid concentration: 2 mol/dm^3

LEM Process Parametric Study

The parameters affecting the performance of the LEM extraction process could be residence time, pH of aqueous feed phase, level of agitation during extraction, and treat ratio.

Residence Time

The residence time plays an important role for the LEM extraction of vanadium (IV). The longer residence time resulted in more transfer of water inside the internal phase, which caused the membrane to swell, and subsequently might have initiated breakage of the emulsion phase (10). Figure 11 exhibits the fraction of original metal remained in aqueous feed phase and swelling as a function of residence time. The increase in swelling of the internal phase was also analyzed by coulter particle analyzer, which is exhibited in Fig. 12. The mean diameter of emulsion droplets was 2.60 μm initially while after 10 min of contact with external feed phase; the diameter went up to 4.86 μm. More than 90% extraction of vanadium (IV) occurred at the end of 4 min. The higher residence resulted in the higher concentration of vanadium (IV) in the feed phase. This is due to leakage of vanadium (IV) to the external phase owing to breakage of internal strip phase. Therefore, it was decided to carry out all the remaining LEM experiments, using a contact time of 4 min.

Feed Phase pH

Figure 13 exhibits the effect of pH of external aqueous phase on the enrichment of vanadium (IV). Generally, more than 90% of the vanadium (IV) ion could be extracted at a pH of about 3. Beyond pH 3 some part of vanadium (IV) ion gets transformed into V (V) ions as can be confirmed by the observation of change in color of the aqueous solution from blue to green. The osmotic pressure difference resulting out of increase in pH of the feed phase drives water to the internal phase thereby swelling of the same. Thus feed phase pH 3 was thought appropriate.

Speed of Agitation

The effect of agitation speed was studied in the range of 100 to 500 rpm and is shown in Fig. 14. While an increase in the level of agitation would increase

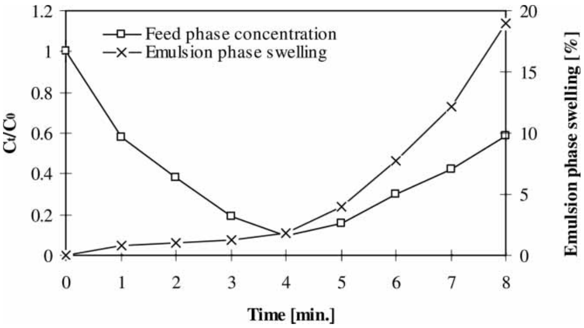

Figure 11. Residence time selection for extraction of vanadium (IV) with respect to swelling of emulsion.

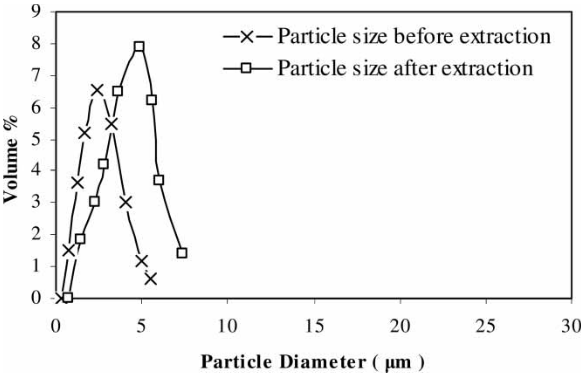

Figure 12. Particle sizes of internal phase before and after LEM extraction.

interfacial area and the mass transfer coefficient, upto some level of agitation beyond which increase in agitation level is likely to break the emulsion droplets thereby reducing the overall enrichment and extraction.

It was observed that increasing speed of agitation from 100 to 300 rpm increased the rate of extraction. This was due to an increase in volumetric mass transfer coefficient, $k_{LA}a$, in the aqueous feed phase, but further increase in speed of agitation from 300 to 500 rpm resulted in the reduction in the extent of extraction similar behavior was reported by Kulkarni and Mahajani (11); Thien et al. (20). At the same time the swelling also increased. There thus exists a trade-off between these two opposing effects. Therefore, the speed of agitation plays an important role in a mechanically agitated contactor. In our experiments we have used speed of agitation 300 rpm.

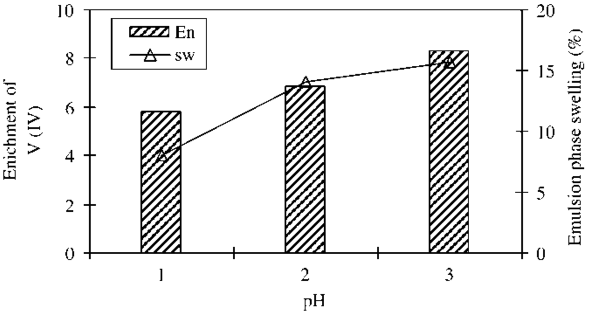

Figure 13. Effect of feed phase pH on the enrichment of vanadium (IV) and swelling of emulsion [speed of agitation: 300 rpm; TR: 1:10; C_{sf}: 0.07 mol/dm^3; feed phase: 1.96×10^{-3} mol/dm^3 of V (IV); C_{HR}: 0.09 mol/dm^3; strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

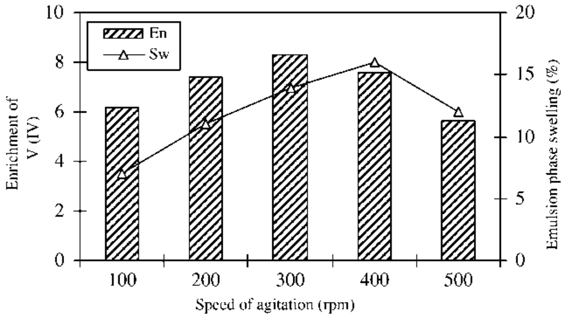

Figure 14. Effect of speed of agitation on the enrichment of vanadium (IV) and swelling of emulsion [TR: 1:10; C_{sf}: 0.07 mol/dm^3; feed phase: 1.96 × 10^{-3} mol/dm^3 of V (IV); C_{HR}: 0.09 mol/dm^3; strip phase: 2 mol/dm^3; diluent: n-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

Effect of Treat Ratio (TR)

The treat ratio defined as the ratio of emulsion phase volume (V_m) to aqueous phase volume (V_l), plays important role in determining effectiveness of LEM. The treat ratio was varied by changing the amount of feed phase (V_l) added to the emulsion phase (V_m) keeping the volume of latter constant. Figure 15 exhibits the effect of treat ratio on enrichment of vanadium (IV) and swelling of emulsion. The treat ratio was varied from 1:20 (0.05) to 1:5 (0.2). There a steady increase in the extraction of metal with increasing

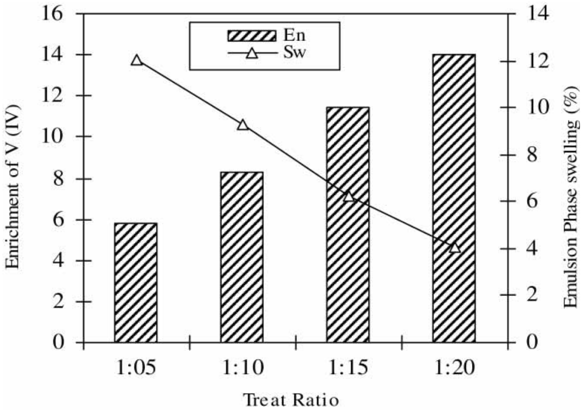

Figure 15. Effect of treat ratio on the enrichment of vanadium (IV) and swelling of emulsion [speed of agitation: 300 rpm; C_{sf}: 0.07 mol/dm^3; feed phase: 1.96 × 10^{-3} mol/dm^3 of V (IV); C_{HR}: 0.09 mol/dm^3; strip phase: 2 mol/dm^3; diluent: *n*-dodecane; C_{cyclo}: 0.3 mol/dm^3; feed phase pH = 3].

values of V_m/V_1, while swelling of the emulsion had no profound effect. With increase in treat ratio, the volume of both the carrier and the stripping agent, i.e. the volume of emulsion as a whole increased. Therefore, the surface area for mass transfer owing to the formation of a larger number of emulsion globules increased. As a result, a higher degree of extraction was obtained but the enrichment was less. The lower treat ratio means less amount of emulsion is used to extract vanadium (IV), which is desired from process point of view to have maximum enrichment with respect to feed phase vanadium (IV).

CONCLUSIONS

The removal of vanadium (IV) from its dilute acidic media through liquid surfactant membranes was studied with respect to various process parameters. D2EHPA, Monemul 80 and sulphuric acid were used as a carrier, surfactant and stripping agent, respectively. It was found that vanadium (IV) extraction was maximum when the internal phase concentration of acid was kept 2 M and the pH of the feed phase nearly 3. It was found that the concentration of the surfactant, the quantity of extractant, and the internal phase acid concentration are important factors for getting maximum recovery. These quantities are optimized in the present investigation. Based on these results a simplistic predictive model has been developed which fits well with experimental findings and aids to process design.

NOMENCLATURE

A	Vanadium metal specie
B	extractant (D2EHPA)/organic phase
C	initial metal ion concentration (mol/dm^3)
C_{cyclo}	cyclohexanone concentration (mol/dm^3)
C_l	concentration of metal in external feed phase (mol/dm^3)
C_H	concentration of acid (mol/dm^3)
C_{HR}, C_{B0}	carrier concentration (mol/dm^3)
C_{sf}	surfactant concentration (mol/dm^3)
D_A, D_B	diffusivity (m^2/s)
En	enrichment (recovery %)
Ex	extraction (fraction)
ΔH_R	heat of reaction (kJ $mole^{-1}$)
H_2R_2	dimeric species of D2EHPA
$k_{LA}a$, $k_{LB}a$	mass transfer coefficient (s^{-1})
$K_{LA}a$	overall mass transfer coefficient (s^{-1})
K_{ex}	equilibrium constant
K_D	distribution coefficient

Over bar	organic phase
R_Aa	the transfer rate of A (mol/m^3 s)
R	universal gas constant (8.314 kJ mole^{-1} K^{-1})
ΔS_R	entropy of reaction (kJ mole^{-1} K^{-1})
T	temperature (K)
TR	treat ratio
V_{in}	volume of internal phase (m^3)
V_l	volume of feed phase (m^3)
V_m	volume of emulsion phase (m^3)
Z	stoichiometric constant
δ	film thickness (m)
λ	reaction plane

Subscripts

0	initial
m	emulsion phase
ex	external phase
f	final
in	internal
i	interface
t	time

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