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Vanadium(V) ions transport through tri-*n*-octyl amine cyclohexane supported liquid membranes

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Abstract

The transport study of V(V) ions through supported liquid membranes (SLM), based on tri-*n*-octyl amine (TOA) as carrier in cyclohexane diluent, supported in polypropylene hydrophobic micro-porous film has been carried out. The effect of concentration of HCl, V(V) ions (in feed) and TOA (in membrane) has been investigated. Three different stripping reagents, H_2O, HNO_3 (0.1–1 M) and Na_2CO_3 (0.188–0.94 M), have been used to determine their effect on V(V) ions transport. Increase in the HCl concentration leads to an increase of the amount of V(V) ions extracted in the organic phase. However, beyond a concentration of 2 M HCl it decreases. Similarly, increase in the TOA concentration leads to an increase of the amount of V(V) ion extracted in the organic phase but beyond 30% it decreases. Increase in the V(V) ions concentration in the feed, leads to an increase in the flux across the membrane. In addition, out of the three strippents used it was found that HNO_3 was the best of these. The species involved for transport across the membrane is $R_3NH\,VO_2Cl_2$. The mechanism of transport is coupled co-ions transport with H^+ and Cl^- coupled ions.

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Keywords: Vanadium(V) ions; Tri-*n*-octylamine; Cyclohexane; Supported liquid membranes; Extraction

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1. Introduction

Various high molecular weight amines have been used in the extraction of vanadium [1]. Some workers have also focused their study to the extraction of U(IV) ions from HCl solution [2,3]. Chaudry et al. have carried out a study using tri-*n*-butyl phosphate as a carrier in SLM [4]. Some work has also been done on V(V) ions for the removal of these ions from uranium leach liquors by classical solvent extraction but from acid sulphate solutions [5]. No work on V(V) by using tri-*n*-octyl amine-cyclohexane based membrane, from HCl solutions, has been carried out earlier. Liquid anion exchange separation at microgram level of V(V), Nb(V) and Ta(V) has been done from succinate solution [6]. But their work is limited to very low-level concentrations of these elements. They used benzene as diluent and extracted from pH 4 to 5 aqueous solutions. They did not work with coupled transport membranes. Schroetternva et al. [9] also limited their work to solvent extraction of V to amines under different conditions. This work has been done to study the effect of HCl and tri-*n*-octyl amine (TOA) concentration on the flux of V(V) ions across TOA-cyclohexane membrane. The effect of various stripping agents like that of Na_2CO_3 solution, HNO_3 solution and water has also been studied.

2. Theoretical

2.1. Reaction at the feed side membrane face

It is reported in the literature that vanadium exists in acid solution as VO_2^+ [7,8,10]. Tri-*n*-octyl molecules may be represented as R_3N, where R stands for octyl group. In acidic solution, the R_3N molecules get protonated to form R_3N^+H which may associate with the metal ions. NH_4VO_3 salt has been used in this

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Abbreviations: SLM, supported liquid membrane; TOA, tri-*n*-octylamine; R_3N, tri-*n*-octylamine; K_v, equilibrium constant; D_{mv}, distribution coefficient; *G*, factor for activity coefficient; *J*, flux; C_{1m}, concentration of ion at feed side membrane phase; C_{2m}, concentration of ion at strip side membrane phase; *D*, diffusion coefficient; D_f, diffusion coefficient towards feed side; D_s, diffusion coefficient towards stripping side; *P*, permeability coefficient; η, viscosity (centipoise); *T*, absolute temperature; *n*, number of moles of H^+ or R_3N associated in the complex; *k*, Boltzman constant

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work. It ionizes as reported below:

$$NH_4VO_3 \rightleftharpoons VO_3{}^+ + NH_4{}^+ \tag{1}$$

If the feed solution is acidic then:

$$H^+ + NH_4VO_3 \rightleftharpoons VO_2{}^+ + H_2O + NH_3\uparrow \tag{2}$$

It has been reported that the species of vanadium as ions are as under [8]:

$$\underset{\mathrm{II}}{[VO_4]^{3-}} \xrightarrow{\mathrm{pH}\,12} \underset{\mathrm{III}}{[VO_3OH]^{2-}} \xrightarrow{\mathrm{pH}\,10} \underset{\mathrm{IV}}{[V_2O_6OH]^{3-}} \xrightarrow{\mathrm{pH}\,9} \underset{\mathrm{V}}{[V_3O_9]^{3-}}$$

$$\xrightarrow{\mathrm{pH}\,6.5} \underset{\mathrm{VI}}{V_2O_5(H_2O)_n} \xrightarrow{\mathrm{pH}\,2.2} \underset{\mathrm{VII}}{[V_{10}O_{28}]^{6-}} \xrightarrow{\mathrm{pH}<1} \underset{\mathrm{I}}{VO_2{}^+} \tag{3}$$

So, in the strongly acidic solution:

$$VO_2{}^+ + (n+1)HCl \rightleftharpoons [VO_2(Cl)_{n+1}]^{n-} + (n+1)H^+ \tag{4}$$

and

$$n\underset{\mathrm{org}}{R_3N^+H} + \underset{\mathrm{aq}}{[VO_2(Cl)_{n+1}]^{n-}} \rightleftharpoons \underset{\mathrm{org}}{(R_3NH)nVO_2Cl_{1+n}} \tag{5}$$

where n indicates the number of R_3N molecules associating with vanadium ions to make a neutral complex, which is extractable into the organic membrane liquid phase.

2.2. Reaction at the strip side membrane face

If the complex formed is $(R_3NH)nVO_2Cl_{1+n}$ and the water is the strippent, the solution being nearly neutral the complex will decompose as under:

$$(R_3NH)_nVO_2Cl_{1+n} + H_2O$$
$$\rightleftharpoons nR_3N + H_3O^+ + VO_2{}^+ + (n+1)Cl^- \tag{6}$$

$$H_3O^+ + VO_2{}^+ \rightleftharpoons HVO_3 + H_2O \tag{7}$$

The vanadyl ions are stripped by water just like zirconyl or hafonyl ions [9]. When HNO_3 is used as strippent there is less tendency of $[VO_2(NO_3)_{n+1}]^{n-}$ type of complex formation. So when $[VO_2Cl_{n+1}]^{n-}$ ions reach the stripping phase it reacts with nitrate ions being more in concentration and decomposition of the complex takes place. $VO_2{}^+$ after dissociation from Cl^- ions gets converted into $VO_3{}^-$ through reaction (7).

If Na_2CO_3 is used as strippent and $[VO_2Cl_{n+1}]^{n-}$ species comes in contact with Na_2CO_3 solution the Cl^- ions tend to associate with Na^+ ions. Thereby, $VO_2{}^+$ ions are liberated from $[VO_2Cl_{n+1}]^{n-}$ and are thus converted to $VO_3{}^-$. In the alkaline conditions produced in the stripping phase the species III–V may also be formed, which after dissociation will stay in the stripping phase. As such, the overall mechanism of transport of vanadium ions is represented, as shown in Fig. 1.

2.3. Vanadium ions transport mechanism

The vanadyl complex then diffuses through membrane phase under concentration gradient as shown in Fig. 2.

Here C_1 and C_2 are bulk solution concentrations of vanadium ions and C_{1m} and C_{2m} the membrane phase concentrations of vanadium ions, 1 stands for feed side and 2 for strip side in Fig. 2.

Keeping in view the reaction (5) which is rewritten here:

$$n\underset{\mathrm{org}}{R_3N} + n\underset{\mathrm{aq}}{H^+} + \underset{\mathrm{aq}}{(VO_2Cl_{n+1})^{n-}} \rightleftharpoons \underset{\mathrm{org}}{(R_3NH)_nVO_2Cl_{n+1}}$$

The equilibrium constant K_v can be written as under:

$$K_v = \frac{[(R_3NH)_nVO_2Cl_{n+1}]_{\mathrm{org}}G}{[R_3N]^n_{\mathrm{org}}[H^+]^n_{\mathrm{aq}}[(VO_2Cl_{n+1})^{n-}]_{\mathrm{aq}}} \tag{8}$$

The subscripts (aq) and (org) represent aqueous and organic liquid phases.

In this case, G is added as a factor for the activity coefficients of all the species involved in above reaction. If D_{mv} stands for the distribution coefficient of the vanadium ions for distribution between the membrane and aqueous phases then:

$$D_{\mathrm{mv}} = \frac{[(R_3NH)_nVO_2Cl_{n+1}]_{\mathrm{org}}}{[(VO_2Cl_{n+1})^{n-}]_{\mathrm{aq}}} \tag{9}$$

and Eq. (8) can be written as:

$$K_v = \frac{D_{\mathrm{mv}}\,G}{[R_3N]^n_{\mathrm{org}}[H^+]^n_{\mathrm{aq}}} \tag{10}$$

$$D_{\mathrm{mv}} = \frac{K_v}{G}[R_3N]^n_{\mathrm{org}}\,[H^+]^n_{\mathrm{aq}} \tag{11}$$

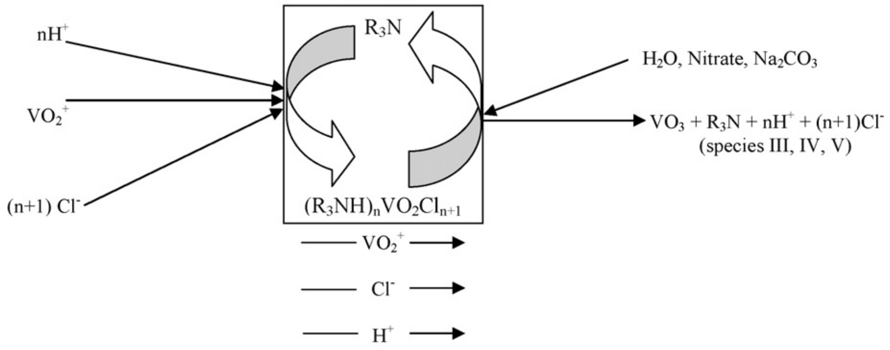

Fig. 1. Mechanism of vanadium(V) ion transport.

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