Selective and Facilitated Transport of Vanadium (VO_2^+) Ion through Supported Liquid Membrane and Effects of Membrane Characteristics

Danial Husseinzadeh

Abstract—A new supported liquid membrane (SLM) system for the selective transport of VO_2^+ ions was prepared in this present work. The SLM was a thin porous polyvinylidene difluoride (PVDF) membrane soaked with Di-(2-ethylhexyl) phosphoric acid (D2EHPA) as mobile carrier in Xylene as organic solvent. D2EHPA acts as a highly selective carrier for the uphill transport of VO_2^+ ions through the SLM. The transport of VO_2^+ ions reached to 64%. In the presence of P_2O7^{-2} ion as suitable masking agent in the feed solution, the interfering effects of other cations were eliminated.

Keywords—Facilitated ion transport, Membrane characteristics, Supported liquid membranes, Vanadium.

I. INTRODUCTION

IN supported liquid membrane (SLM), an organic liquid is immobilized in the pores of a micro porous membrane interposed between two aqueous solutions. At the interface between the feed solution and the membrane, the solute is extracted into the membrane liquid; it then diffuses by itself and/or in a complex form to the other side of the membrane. At the strip solution/ membrane interface, the solute is extracted into the strip solution. In carrier-mediated or facilitated transport, the transfer of a substance is facilitated across SLM by a carrier allocated in the liquid membrane.
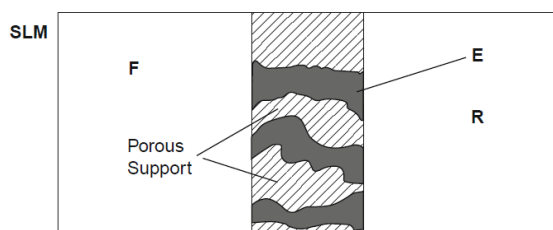

Fig. 1 Configuration of liquid membrane systems, supported (Immobilized) (SLM or ILM). F is the source or feed phase, E is the liquid membrane, and R is the receiving phase [1].

Danial Husseinzadeh is with the Ferdowsi University of Mashhad, Mashhad, Iran (corresponding author to provide phone: +98-915-322-0130; e-mail Danial.husseinzadeh@stu-mail.um.ac.ir).
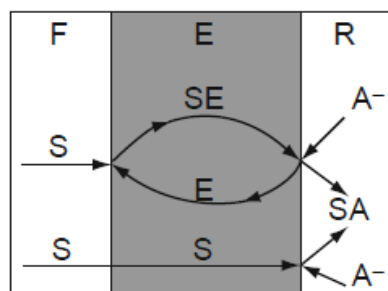
Fig. 2 Schematic mechanisms of facilitated solute transport through the liquid membranes. S is solute to be separated; A are anions co-transported; E is liquid membrane, F is feed solution, and R is stripping solution [1].

A major challenge in SLM is to design carriers and processes that allow the transport of substances by gradients of electrons (redox gradients) [2]-[3], protons (pH gradient) [4]-[5] or other species (concentration gradient) [5].

Some studies [7] indicated the transport of Vanadium through Bulk liquid membrane (BLM) from CRM and real seawater as feed solution and Aliquat 336/dodecane as mobile carrier. Chaudry et all, [8] extracted Vanadium ions through supported liquid membranes and tri-n-octyl amine (TOA) as carrier in cyclohexane diluent. Another study [9] showed Facilitated transport of vanadium by supported liquid membranes to determine the feasibility of this technique for the removal/recovery of this metal from diluted effluents employing mixtures of tertiary amine Alamine 336 and phosphine oxide Cyanex 923 as carrier, dissolved in aromatic diluents.

II. EXPERIMENTAL

Reagent-grade Di-(2-ethylhexyl) phosphoric acid (D2EHPA) from Fluka was used as the mobile carrier. Reagent grade Xylene and other organic compounds from Merck were employed as the membrane organic solvent. Vanadium chloride and chloride salts of other cations of the highest available purity were obtained from Merck without further purification. Doubly distilled deionized water was used

in all experiments.

Atomic absorption (Shimadzo AA-760) spectrophotometer was used for the measurement of metal ion concentrations in the feed and strip or receiving phases. The experiments were carried out in a supported liquid membrane cell fabricated from Perspex and consisting of two horizontal chambers with a volume of 90 ml for each chamber. Each compartment was equipped with a Teflon magnetic stirrer and an inlet for filling and draining the feed and stripping solutions. The supported membrane with an area of 15.9 cm2 was clamped between the two chambers. The microporous Accurel (pore size 0.1 μm), Celgard (pore size 0.1 μm) and PVDF (pore size 0.23 μm) membranes were used as the supporting medium to hold organic solvent containing the mobile carrier.

For experimental trails, the feed chamber was filled with ion solution. Strip solution was poured in the other chamber. Both solutions were stirred at 1200 rpm to avoid concentration polarization at the membrane surface. Samples were taken at regular time intervals from the feed and strip compartments and analyzed by Atomic Absorption Spectrometer. All experiments were carried out at ambient temperature.

III. Results and Discussions

A. Preparation of supported liquid membrane

In this study, D2EHPA with the traditional name of Di-(2-ethylhexyl) phosphoric acid was employed as the mobile carrier. The carrier was dissolved in Xylene as organic solvent and impregnated in the pores of the support. The prepared SLM was contacted with the feed or source phase containing Vanadium ions (initial concentration 5x10-5 mol/lit) in acidic conditions on one side and the strip or receiving phase containing the stripping agent on the other side. Vanadium ions were extracted from the source phase into the receiving phase. In the feed-SLM interface, vanadium forms a neutral complex VOL (L: Ligand). At the SLM-receiving phase interface, vanadium is extracted from the organic phase.

For optimization of VO^{2+} ion transport, the effects of experimental variables were elucidated. The tested parameters were: concentration of the ligand (Di-(2-ethylhexyl) phosphoric acid) in the membrane phase, types of organic solvents (CHCl3, CCl4, Toluene, o-Xylen, Isooctane) and types of support membrane (PVDF, Accurel, Celgard).

B. Effects of carrier concentration

The influence of the concentration of Di-(2-ethylhexyl) phosphoric acid in the organic phase (Xylene) on the transport of vanadium ions is presented in Figure 3. The transport of vanadium through supported liquid membrane increased with increasing the ligand concentration up to a certain concentration and decreased afterwards.

Maximum transport (64%) of VO^{2+} ion occurred at the concentration of about 0.09 M of ligand (Di-(2-ethylhexyl)
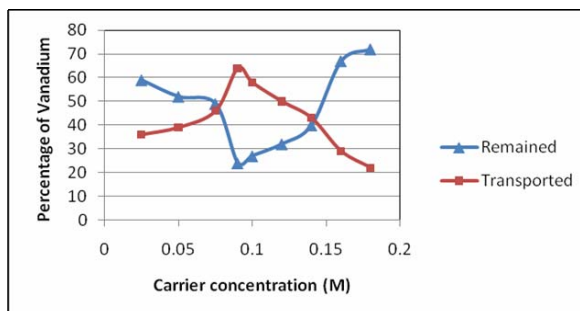

Fig. 3 Effect of carrier concentrations on transport of VO_2^+ ions through SLM
Feed: $5x10^{-5}$ M Vanadium, 0.2 HCl
Strip: 3.5 M HNO_3
Membrane: PVDF
Transport time: 4 hours

phosphoric acid in Xylene). Higher concentration of carrier has a decreasing effect in the transport of VO^{2+} ions. This is probably due to the more difficult releasing of the cation into the strip solution as a result of its firm bounding to the carrier and the increasing viscosity of the liquid membrane. The ligand concentration of 0.09 M was selected for further studies.

C. Effects of organic solvent

The type of organic solvent influences the transport efficiency. The results for transport of VO^{2+} ions through supported liquid membrane employing various solvents are presented in Table 1. Maximum transport (64%) of VO^{2+} ions occurred in the presence of Xylene as organic solvent in SLM.

The VO^{2+} transport, in different solvents depends on two factors: penetration coefficient and boiling point of the solvent. The penetration coefficient is an intrinsic property of the solvent and mainly depends on the viscosity of the solvent.

The boiling points of the solvents alongside with the efficiency of VO^{2+} transport (percentage of VO^{2+} in strip) are presented in Table 1. The Table indicates that the solvents with higher boiling points result in higher efficiency. SLM consists of a very thin layer of liquid membrane i.e. carrier and solvent. If the solvent with a low boiling point is employed in SLM, the possibility of solvent evaporation is higher. This results in lower liquid membrane, lower carrier and therefore lower ion transport through SLM. Solvents with higher boiling point are more stable in SLM.

D. Effects of support type

We investigated the transport of VO^{2+} ions through different membrane supports in optimum conditions. The results are presented in Table 2.

The maximum transport of VO^{2+} ions occurred while PVDF membrane was employed as the support for SLM. This may be attributed to the effect of the pore size of PVDF (0.23 μm) compare to the pore size of Celgard or Accurel (0.1 μm). The support with the larger pore size (PVDF) accommodates

TABLE I
EFFECT OF ORGANIC SOLVENTS ON TRANSPORT OF VO_2^+ IONS THROUGH SLM

Solvents	BOILING POINT ($^{\circ}$C)	Percentage of VO_2^+ in feed	Percentage of VO_2^+ in strip
$CHCl_3$	61	73	21
CCl_4	77	69	34
Isooctane	99	55	40
Toluene	110	36	49
o-Xylen	144	24	64

TABLE II
EFFECT OF SUPPORT TYPE ON TRANSPORT OF VO_2^+ IONS THROUGH SLM

Membrane support	Polymer	Pore size	Percentage of VO_2^+ in feed	Percentage of VO_2^+ in strip
PVDF	Polyvinyleden defluoride	0.23 μm	24	64
Celgard	Polypropylene	0.1 μm	70	20
Accurel	Polypropylene	0.1 μm	65	26

more liquid (carrier plus solvent) providing greater passage media for transport of VO^{2+} ions through SLM.

E. Selectivity of SLM for VO^{2+} transport

The selectivity of SLM for transport of vanadium ions in the presence of other cations in the source phase was investigated. The results are presented in Table 3. For different cations tested, only Al^{3+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} ions were transported with VO^{2+} ions.

In agreement with the Pearson's Hard and Soft Acids and Bases principles, Di-(2-ethylhexyl) phosphoric acid (Ligand) as a soft base has affinity for most soft cations. As indicated in Table 3, transports of these cations are negligible and have no serious effect on transport of vanadium ions. However, the interfering effects of these cations were successfully eliminated by addition of 0.005 M P_2O7^{-2} as masking agent in the feed or source phase. Masking agent provides a special complex with interfering cations (Al^{3+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}) and prevents the formation of complexes for these cations with Di-(2-ethylhexyl) phosphoric acid (carrier). This results in low transport of interfering cations through SLM. In this case the transport efficiency of VO^{2+} ions is reduced to 60%.

IV. CONCLUSIONS

A supported liquid membrane (SLM) was successfully prepared for efficient and selective separation of VO^{2+} ions from a mixture of cations. The SLM contained 0.09 M Di-(2-ethylhexyl) phosphoric acid as the mobile carrier in Xylene as organic solvent. It was found that, the Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is a good carrier for selective transport of vanadium ions through SLM via formation of VO-carrier neutral complex. Polymeric PVDF membrane with 0.23 μm pore size was the support media of choice. The effects of the presence of interfering cations (Al^{3+}, Fe^{3+}, Pb^{2+},

TABLE III
EFFECT OF THE PRESENCE OF SOME CATIONS IN THE FEED ON TRANSPORT OF V IONS THROUGH SLM

Cation mixtures	Cation	Transported	Remained
Mg^{2+}, Ba^{2+}, Ca^{2+}, VO_2^+	VO_2^+	61	24
	Mg^{2+}	0	97
	Ba^{2+}	0	100
	Ca^{2+}	0	95
Na^+, K^+, Li^+, Cs^+, VO_2^+	VO_2^+	62	24
	Li^+	0	95
	Cs^+	0	97
	K^+	0	96
	Na^+	0	97
Al^{3+}, VO_2^+	VO_2^+	62	24
	Al^{3+}	7	74
Pb^{2+}, Fe^{3+}, VO_2^+	VO_2^+	63	23
	Fe^{3+}	8	66
	Pb^{2+}	18	68
Zn^{2+}, Cd^{2+}, VO_2^+	VO_2^+	63	22
	Cd^{2+}	12	58
	Zn^{2+}	10	68

Feed: 5x10-5 M of different cations, 0.2 M HCl
Strip: 3.5 M HNO3
Ligand: 0.09 M Di-(2-ethylhexyl) phosphoric acid in Xylene
Membrane type: PVDF

Cd^{2+}, Zn^{2+}) were successfully eliminated by using $P2O7^{-2}$ as masking agent in the source phase.

REFERENCES

[1] Liquid membranes, Principles and applications in chemical separation and wastewater treatment. Editor: Valadimir S. Kislik.W.-K. Chen, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth, 1993, pp. 123–135.
[2] Matsuo, T. (1982), Pure Appl. Chem, 54, 1693.
[3] Robinson, J. N; Hamilton, D. J. (1991), Chem. Soc, 20, 49.
[4] Ohakara, M; Nakatsuji, X. (1985), Topics Curr. Chem, 128, 37.
[5] Hiriciga, A; Lehn, J. M. (1983), Proc. Natl. Acad. Sci. USA, 80, 6426.
[6] Malmstrom, B. G. (1993), Acc. Chem. Res, 26, 332.
[7] Jose, A; Lo´pez-Lo´pez, Carolina Mendiguchı´a, Juan J. Pinto, Carlos Moreno. (2010), Trends in Analytical Chemistry, (article in press).
[8] M. Ashraf Chaudry; Naheed Bukhari, M. Mazhar, Fatima Tazeen. (2007), Separation and Purification Technology, 54, 227–233.
[9] Luis J. Lozano; Carlos Godı´nez, Francisco J. Alguacil. (2005), Hydrometallurgy, 80, 196– 202.