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TRANSPORT OF NEODYMIUM WITH FLAT SHEET CONTAINED LIQUID MEMBRANE USING OCTYL(PHENYL)-*N*,*N*-DIISOBUTYLCARBAMOYL-METHYLPHOSPHINE OXIDE

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ABSTRACT

A study was carried out on the transport of neodymium from nitric acid solution, using a flat sheet contained liquid membrane technique, in order to investigate the feasibility of treating low-level radioactive wastewaters using hollow fiber membrane contactors. The solvent consisted of *n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) as the active carrier in *n*-dodecane. The effect of various modifiers was explored and a mixture of tributyl phosphate (TBP) and isotridecanol was identified as the most effective modifier, minimizing acid co-extraction and preventing third phase formation. The effects of various parameters on Nd transport were examined. These included the effect of acidity, Nd, and sodium nitrate concentrations in the feed and the hydrophilicity of the membranes at the feed and strip interfaces.

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The extraction of Nd from nitric acid to a solvent mixture of CMPO, TBP, and isotridecanol was found to be mainly governed by membrane diffusion. At the feed interface, it was found that a hydrophobic membrane offers higher resistance to mass transfer than a hydrophilic membrane, due to a combination of low distribution coefficient and low diffusivity of the Nd–CMPO complex. Resistance at the strip interface was also lower with a hydrophilic membrane. The rate of acid transport from feed to strip solution was higher with a hydrophilic membrane at the feed interface, and this was found to reduce Nd recovery in the strip solution. These results highlight the importance of the effect of membrane hydrophilicity on the overall mass transfer rates.

Key Words: Liquid membranes; CMPO; Octyl(phenyl)-*N,N*-diisobutylcarboyl-methylphosphine oxide; Nd; Neodymium

INTRODUCTION

New liquid–liquid extraction technologies have the potential to be applied to the treatment of radioactive waste solution containing low concentrations of actinide elements.[1] The supported liquid membrane (SLM) technique is an emerging technology, which has several advantages over the established solvent extraction technology. The process uses a microporous membrane impregnated with a solvent phase to extract a solute from an aqueous feed to an aqueous receiver solution. The SLM process is simple and can be operated with a fraction of the solvent inventory required for solvent extraction. Various researchers have applied this technique to study the transport of actinide elements, especially americium.[2–6] The major drawback of SLM systems is the lack of long term membrane stability caused by the loss of the membrane fluid to the feed or receiver solutions. This problem can be eliminated by placing a bulk solvent phase between two microporous membranes, and controlling the pressures in all three phases to ensure that the two interfaces remain at the membrane pore surface. This contained liquid membrane technique can be studied in a flat sheet configuration, but hollow fibers are favored for practical applications because of their high surface area to equipment volume ratio. When both the feed and receiver solutions are fed through a single hollow fiber module, the technique, developed by Sirkar and co-workers,[7] is known as a hollow fiber contained liquid membrane technique. Two separate membrane contactors can also be used for dispersion-free extraction and stripping, with the solvent circulating between the two modules. This last technique has elements of both solvent extraction and liquid membrane technology.

In all the techniques of solvent extraction, SLM, contained liquid membrane, and membrane contactors, the selectivity of the process is due to the properties of the solvent and, therefore, developments in one technology are often applicable to the other technologies. Thus, the solvent in the tansuranium solvent extraction TRUEX process, developed for the treatment of raffinates generated by the reprocessing of spent nuclear fuel, is useful for the treatment of low-level radioactive wastewater by SLM[8] and hollow fiber membrane contactors.[9]

The TRUEX solvent contains *n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) as the active extractant for actinide extraction. The diluent is generally a normal paraffinic hydrocarbon, such as *n*-dodecane, although chlorinated hydrocarbons such as trichloroethylene have been proposed for use in the treatment of acidic chloride, rather than nitrate wastes.[10] Normal paraffinic hydrocarbon diluents have an advantage that they may be completely incinerated.[11] As aliphatic diluents form a third phase with CMPO, tri-*n*-butyl phosphate (TBP) is added to the organic phase as a modifier.[10,12] Although aromatic diluents do not have a tendency for third phase formation, aliphatic diluents are preferred due to their high distribution ratios.[13]

The presence of TBP enhances nitric acid extraction transfer to the strip solution, which inhibits Am stripping. This issue is dealt within the standard TRUEX flowsheet by the inclusion of a scrub circuit to remove acid from the loaded solvent.[14,15] Scrubbing of the solvent prior to stripping is not possible in a SLM configuration and acid co-transfer has been addressed in a number of ways. Muscatello and Navratil[2] neutralized $7-0.1\,M$ HNO_3 in the feed to prevent acid co-transfer with Am with SLM impregnated with a carbamoylmethylphosphonate. Ramanujam et al.[6] used a strip solution containing formic acid and hydrazine hydrate. This solution provided a buffering effect, preventing acid build up in the strip solution. Chiarizia and Danesi[16] used a series of two SLMs to extract actinides and trivalent lanthanides from nitric acid feed. The first SLM contained CMPO to affect the transfer of actinides from the feed to the first strip solution, from which co-extracted acid was removed by the second SLM containing a primary amine extractant. The strip solution for the second SLM consisted of $4\,M$ NaOH to neutralize extracted acid.

In this work, we have studied the transfer of Nd from nitric acid solution using a flat sheet contained liquid membrane system, and CMPO as the active carrier. Nd was used to simulate the behavior of trivalent actinide elements such as Am. The effect of various modifiers was explored in order to minimize acid co-transfer. An earlier evaluation of membrane contactors for extraction of actinides from radioactive waste streams, using a similar solvent, concluded that the technology would benefit from the use of hydrophilic modules in the stripping process.[9] In the current work, we investigate the effect of changing the hydrophilicity of the membrane supports in both the extraction and stripping processes in order to determine the membrane type combination that will most enhance the overall mass transfer rates.

EXPERIMENTAL

Reagent and Materials

CMPO was supplied by Strem Chemicals, USA. TBP was supplied by BDH Chemicals, Australia and *n*-dodecane by Sigma, Australia. Iso decyl alcohol and iso tridecyl alcohol, known as isodecanol and isotridecanol, were supplied by Exxon Chemicals, Australia. Trioctylphosphine oxide (TOPO), trade name Cyanex 921, was obtained from Cytec, Canada. Neodymium solutions were prepared from neodymium chloride hexahydrate, obtained from Prolab, Australia. Details of the microporous membranes used and their respective suppliers are shown in Table 1.

Equilibrium Distribution Measurements

Equilibrium distribution measurements were carried out by contacting equal volumes of aqueous solutions (0.004–0.037 mol dm^{-3} Nd in 0.01–2 mol dm^{-3} HNO_3) with organic solutions in separating funnels. Organic phases consisted of 0.2 mol dm^{-3} CMPO in *n*-dodecane with various modifiers. After equilibration, the two phases were allowed to separate. Aqueous Nd concentrations were measured using inductive coupled plasma-optical emission spectrometry (ICP-OES) and the acid concentrations were determined by titration using standardized sodium hydroxide solution, after complexing the dissolved Nd with sodium oxalate. Solvent concentrations were determined by stripping three times with 0.01 mol L^{-1} HNO_3 solutions and analyzing the resultant aqueous phases for Nd and acid. Mass balances were 100 ± 5% in all cases. The distribution coefficient for Nd (m_{Nd}) was calculated

Table 1. Microporous Membrane Characteristics

Membrane	Durapore GVHP	Durapore GVWP	GHPolypro
Supplier	Millipore	Millipore	Gelman
Material	Polyvinylidene fluoride	Polyvinylidene fluoride	Polypropylene
Pore size (μm)	0.22	0.2	0.2
Thickness (μm)	125	125	100
Porosity (%)	75	70	
Wetting properties	Hydrophobic	Hydrophilic	Hydrophilic

as $[\mathrm{Nd}]_{\mathrm{solvent}}/[\mathrm{Nd}]_{\mathrm{aqueous}}$ and the distribution coefficient for nitric acid ($m_{\mathrm{HNO_3}}$) was calculated as $[\mathrm{HNO_3}]_{\mathrm{solvent}}/[\mathrm{HNO_3}]_{\mathrm{aqueous}}$.

Permeation Measurements

The transport of Nd from a 2 mol dm^{-3} HNO_3 feed to a 0.01 mol dm^{-3} HNO_3 strip solution, via a bulk solvent phase, was measured in a three compartment membrane permeation cell, shown in Fig. 1. Flat sheet microporous membranes were used to separate aqueous from solvent solutions. No leakages between phases were observed during the course of the experiments which ran up to 95 hr. The feed and strip volumes were 125 mL, and the organic volume was 60 mL. The three phases were stirred using magnetic stirrers. Concentrations of neodymium in the feed and strip compartments were continuously monitored during the experiments, using a Shimadzu Multispec UV–visible spectrophotometer with flow-through cells. Final feed, solvent, and strip concentrations were measured by ICP-OES. Mass balances were between 96 and 106%.

RESULTS AND DISCUSSION

Effect of Modifiers on Nd and Acid Extraction with CMPO

The conventional TRUEX solvent reported in the literature has the composition of 0.2 mol dm^{-3} CMPO and 1.4 mol dm^{-3} TBP in a normal paraffin

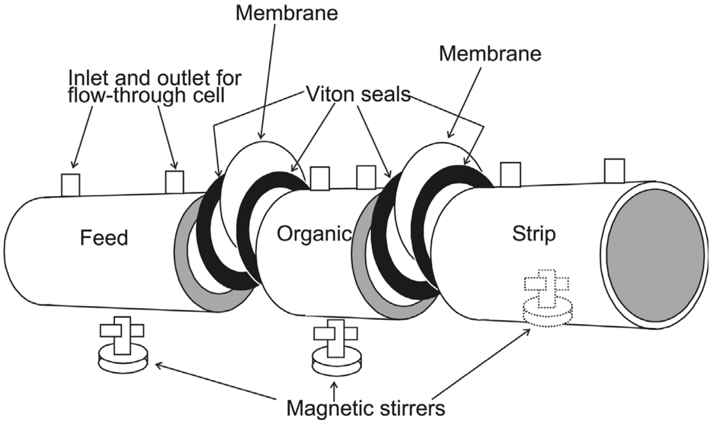

Figure 1. Three-compartment membrane permeation cell.

hydrocarbon diluent. The TBP prevents third phase formation but causes extraction of acid.

Different modifiers were tested in order to identify one that would minimize acid co-extraction, prevent third phase formation, and not adversely affect the distribution coefficient of Nd with CMPO. Results for nitric acid and Nd extraction with CMPO in the presence of modifiers TBP, TOPO, isodecanol, and isotridecanol, are presented in Table 2. The amount of modifier used was the minimum amount required to prevent third phase formation, with Nd solvent loadings of approximately 0.007 mol dm^{-3}.

The results show that the conventional TRUEX solvent co-extracts 27% of the nitric acid present in a 2 mol dm^{-3} feed solution by a single 1:1 contact. Decreasing the TBP concentration reduces acid extraction to 17%. TOPO was found to have a low solubility in the *n*-dodecane/CMPO solution, and was very slow to dissolve. Contacting this solution with an equal volume of 0.007 mol dm^{-3} Nd resulted in third phase formation. Isotridecanol was added to the mixture until the third phase disappeared. The final concentration was 0.13 mol dm^{-3} TOPO, 0.2 mol dm^{-3} CMPO, and 7.5 vol% isotridecanol. This solvent did not significantly decrease acid extraction. The solvent mixtures extracting the least amount of acid were those containing isodecanol or isotridecanol and no TBP or TOPO. However, by using only these modifiers, the extraction of Nd was also adversely affected.

In order to investigate whether acid extraction suppression was due to the addition of isotridecanol or the absence of TBP, further tests were carried out with varying isotridecanol concentrations, keeping the TBP concentration constant. The results, presented in Fig. 2, show that the addition of isotridecanol decreases the distribution coefficient of Nd, but does not affect the distribution coefficient of nitric acid. Thus, the separation factor for Nd over nitric acid

Table 2. The Effect of Modifiers on Neodymium and Acid Extraction with CMPO: *Solvent Composition*: [CMPO] = 0.2 mol dm^{-3} in *n*-dodecane; *Feed*: [HNO$_3$] = 2 mol dm^{-3}, [Nd] = 0.024 mol dm^{-3}, O : A = 1

	Extraction (%)				
Modifier	Nd	HNO$_3$	m_{Nd}	$m_{\mathrm{HNO_3}}$	$\beta^{\mathrm{Nd/HNO_3}}$
1.4 mol dm^{-3} TBP	95	27	21.8	0.41	53
0.7 mol dm^{-3} TBP	94	17	13.0	0.22	59
14 vol% isodecanol	62	6	1.17	0.08	15
14 vol% isotridecanol	82	11	4.0	0.11	36
0.13 mol dm^{-3} TOPO, 7.5 vol% isotridecanol	95	16	17.3	0.18	96
0.28 mol dm^{-3} TBP, 14 vol% isotridecanol	85	10	5.6	0.16	35

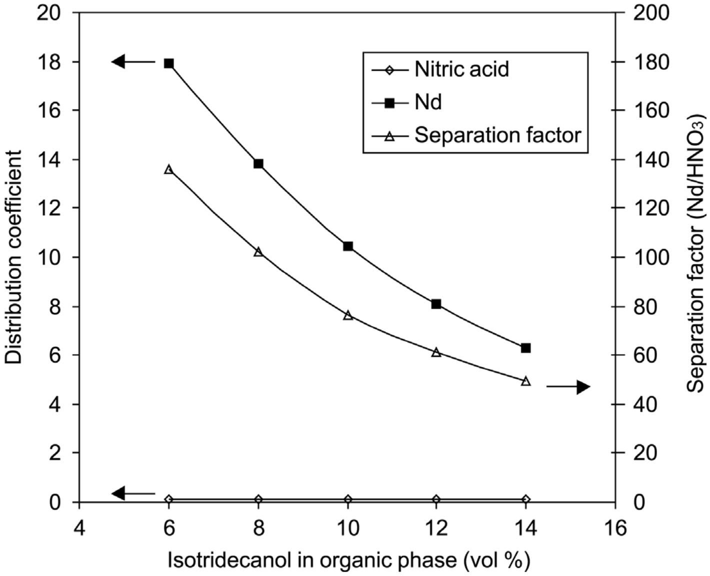

Figure 2. Effect of isotridecanol concentration on neodymium extraction: *Solvent*: [CMPO] $= 0.2\,\mathrm{mol\,dm^{-3}}$, $0.26\,\mathrm{mol\,dm^{-3}}$ TBP in *n*-dodecane; *Aqueous (initial)*: $[\mathrm{HNO_3}] = 2\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{Nd}] = 0.0019\,\mathrm{mol\,dm^{-3}}$.

($\beta^{\mathrm{Nd/HNO_3}}$) decreases from 136 to 49, by increasing the isotridecanol concentration from 6 to 14 vol%. Third phase formation was prevented in these tests by keeping the solvent loading below $0.2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ Nd.

The stripping of Nd and nitric acid was investigated by contacting the loaded solvent three times with dilute nitric acid. Results are shown in Table 3. It is apparent that the percentage of Nd stripped in the first contact is dependent on the amount of acid present in the loaded solvent. Therefore, the solvent mixtures extracting more acid have poorer stripping properties.

The separation factor $\beta^{\mathrm{Nd/HNO_3}}$ is highest with a mixture of TOPO and isotridecanol (Table 2), but this solvent composition has poor stripping properties (Table 3) on account of relatively high acid extraction.

The above results show that substituting TBP with isodecanol or isotridecanol decreases acid extraction. However, Nd extraction is also adversely affected, decreasing the separation factor for Nd over nitric acid. As a compromise, the modifier combination of TBP and isotridecanol was chosen for this testwork, because of its relatively low acid co-extraction and an acceptably high Nd distribution coefficient.

Table 3. The Effect of Modifiers on Neodymium and Acid Stripping with CMPO: *Solvent Composition*: [CMPO] $= 0.2\,\mathrm{mol\,dm^{-3}}$ in *n*-Dodecane, $[\mathrm{Nd}]_{\mathrm{org}} = 0.005{-}0.007\,\mathrm{mol\,dm^{-3}}$; *Strip Solution*: $[\mathrm{HNO_3}] = 0.01\,\mathrm{mol\,dm^{-3}}$ Contacted 3 × at O : A = 1

Modifier	$[\mathrm{HNO_3}]_{\mathrm{org}}$ $(\mathrm{mol\,dm^{-3}})$	Nd Stripped (%)[a]			$\mathrm{HNO_3}$ Stripped (%)[a]		
		1	2	3	1	2	3
$1.4\,\mathrm{mol\,dm^{-3}}$ TBP	0.58	9.6	35	47	72	22	6
$0.7\,\mathrm{mol\,dm^{-3}}$ TBP	0.34	19	62	—	73	15	—
14 vol% isodecanol	0.15	98.7	1.2	0.07	98.9	1.1	0
14 vol% isotridecanol	0.20	82	—	—	61	—	—
$0.13\,\mathrm{mol\,dm^{-3}}$ TOPO, 7.5 vol% isotridecanol	0.30	20	59	—	66	11	—
$0.28\,\mathrm{mol\,dm^{-3}}$ TBP, 14 vol% isotridecanol	0.27	78	22	—	94	5.6	—

[a] 1, 2, 3 denotes consecutive strips of the organic phase. Percentage strip at each contact calculated as a function of Nd loaded in the solvent.

Equilibrium Measurements for CMBO, TBP, and Isotridecanol Solvent

Effect of Nitric Acid Concentration on Nd Extraction

The complex formed between CMPO and Nd has the stoichiometry $Nd(NO_3)_3 \cdot 3CMPO$[14] and therefore Nd extraction is expected to be favored by high nitrate concentrations. Figure 3 shows the effect of increasing nitric acid on Nd extraction. It is apparent that as the nitric acid concentration increases, so does the distribution coefficient of Nd. The trend measured for the CMPO/TBP/isotridecanol solvent is similar to that measured for the TRUEX solvent, but lower extractions were observed with the former solvent mixture. Careful measurements of the nitric acid extracted (Table 4) indicate that the nitric acid distribution coefficient is not significantly affected by equilibrium nitric acid concentration, and therefore the separation factor β^{Nd/HNO_3} is highest at higher nitric acid concentrations.

Effect of Nd Concentration in the Feed

With the TRUEX solvent, the maximum theoretical stoichiometric loading for Nd is 0.066 mol dm^{-3}, although it is reported that, in practice, loadings greater

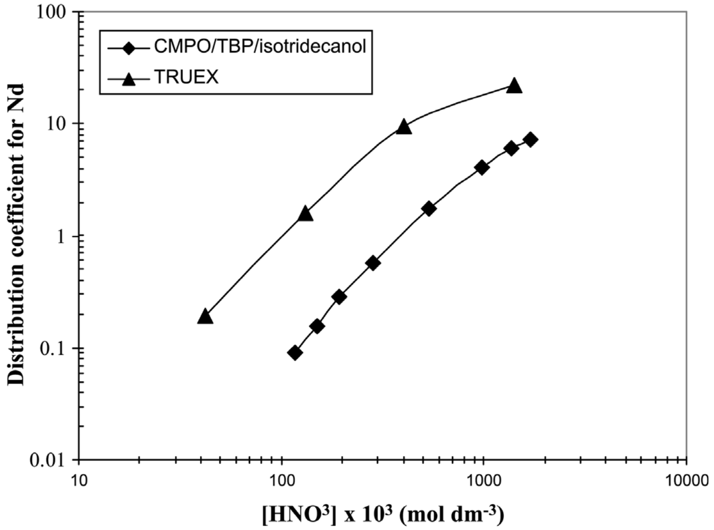

Figure 3. Distribution of neodymium as a function of nitric acid concentration: *TRUEX*: [CMPO] = 0.2 mol dm^{-3}, 1.4 mol dm^{-3} TBP in *n*-dodecane; *CMPO/TBP/isotridecanol*: [CMPO] = 0.2 mol dm^{-3}, 0.3 mol dm^{-3} TBP, 14 vol% isotridecanol in *n*-dodecane.

Table 4. Separation Factors for Nd over Nitric Acid in the CMPO, TBP, and Isotridecanol System: *Solvent Composition*: [CMPO] = 0.2 mol dm^{-3}, 0.3 mol dm^{-3} TBP, 14 vol% Isotridecanol in *n*-Dodecane, $[\mathrm{Nd}]_{\mathrm{initial}} = 0.005$ mol dm^{-3}

$[\mathrm{HNO_3}]_{\mathrm{aq}}$ (mol dm^{-3})	m_{Nd}	$m_{\mathrm{HNO_3}}$	$\beta^{\mathrm{Nd/HNO_3}}$
0.116	0.09	0.034	2.7
0.150	0.16	0.040	3.9
0.193	0.28	0.052	5.4
0.284	0.57	0.063	9.1
0.539	1.76	0.082	22
0.976	4.04	0.11	38
1.376	5.95	0.12	50
1.712	7.28	0.12	59

than 0.06 mol dm^{-3} results in third phase formation.[17] The loading curve with the CMPO/TBP/isotridecanol solvent mixture is shown in Fig. 4 and the highest solvent loading measured was 0.03 mol dm^{-3} Nd. The m_{Nd} decreases from 7.2 to 3.3 as the equilibrium aqueous Nd concentration increases from 0.0006 to

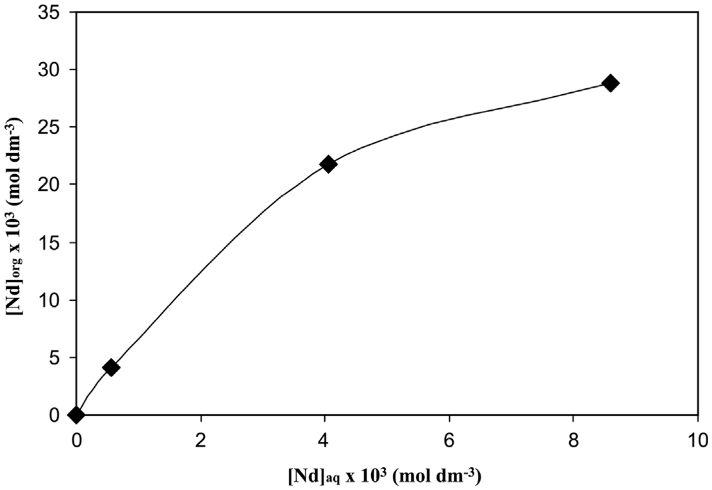

Figure 4. Loading curve for neodymium with CMPO/TBP/isotridecanol: *Solvent*: [CMPO] = 0.2 mol dm^{-3}, 0.3 mol dm^{-3} TBP, 14 vol% isotridecanol in *n*-dodecane; *Aqueous*: $[\mathrm{HNO_3}] = 1.7$ mol dm^{-3}.

0.009 mol dm^{-3}. No third phase formation was observed in any of the loading tests with CMPO/TBP/isotridecanol. The Nd loading capacity of the solvent is not a crucial parameter in a bulk liquid membrane process as in a solvent extraction process, because extraction and stripping occur simultaneously and, therefore, the Nd concentration in the solvent is not expected to approach its maximum limit.

Extraction of Nitric Acid

The actual acid concentration measured in the solvent is shown in Fig. 5. Data for both the TRUEX solvent and the CMPO/TBP/isotridecanol solvent presented show that with the latter solvent mixture, acid concentration in the solvent is much reduced. However, considering that Nd solvent loadings will at the most be of the order of 0.03 mol dm^{-3}, in molar terms, nitric acid loading will always be higher than that of Nd.

Effect of Nitrate Concentration on Nd Extraction

The extraction of Nd from high nitrate and low acid concentration was measured and results are shown in Table 5. With the TRUEX solvent, it was

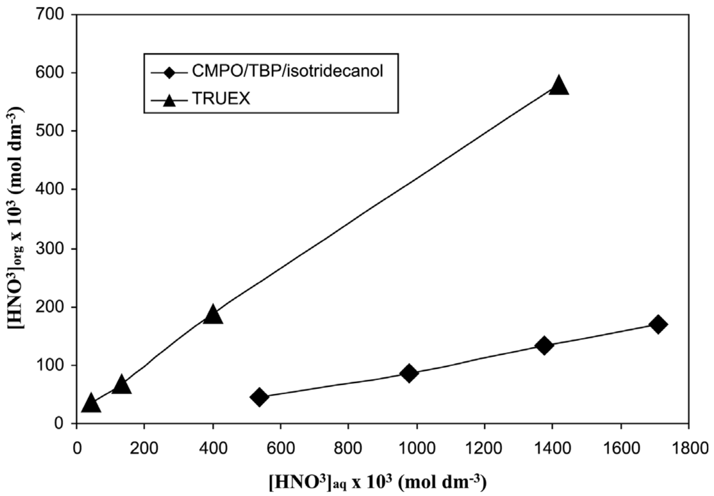

Figure 5. Acid extraction by TRUEX and CMPO/TBP/isotridecanol solvent: *TRUEX*: [CMPO] = 0.2 mol dm^{-3}, 1.4 mol dm^{-3} TBP in *n*-dodecane; *CMPO/TBP/TID*: [CMPO] = 0.2 mol dm^{-3}, 0.3 mol dm^{-3} TBP, 14 vol% isotridecanol in *n*-dodecane.

Table 5. Effect of Sodium Nitrate on Nd Extraction: *TRUEX*: [CMPO] $= 0.2\,\text{mol dm}^{-3}$, $1.4\,\text{mol dm}^{-3}$ TBP in *n*-Dodecane; *CMPO/TBP/Isotridecanol*: [CMPO] $= 0.2\,\text{mol dm}^{-3}$, $0.3\,\text{mol dm}^{-3}$ TBP, 14 vol% Isotridecanol in *n*-Dodecane; *Feed*: $[NO_3] = 2\,\text{mol dm}^{-3}$, $[Nd] = 0.024\,\text{mol dm}^{-3}$

Solvent	Feed	m_{Nd}
CMPO-TBP-isotridecanol	$2\,\text{mol dm}^{-3}$ HNO_3	7.3
CMPO-TBP-isotridecanol	$2\,\text{mol dm}^{-3}$ $NaNO_3$	11
TRUEX	$2\,\text{mol dm}^{-3}$ HNO_3	22
TRUEX	$2\,\text{mol dm}^{-3}$ $NaNO_3$	218

found that m_{Nd} increases by an order of magnitude with a $2\,\text{mol dm}^{-3}$ sodium nitrate feed, compared to a $2\,\text{mol dm}^{-3}$ nitric acid feed. A similar comparison for the CMPO/TBP/isotridecanol system shows that the m_{Nd} is not significantly affected. A similarly significant increase in the distribution coefficient with a change from nitric acid to sodium nitrate using the TRUEX solvent was reported for Am.[18] The higher m_{Nd} measured for the TRUEX solvent is due to the absence of nitric acid in the feed and therefore, in the solvent. With the CMPO/TBP/isotridecanol solvent system, nitric acid extraction is limited and therefore, the absence of nitric acid in the feed does not markedly affect m_{Nd}.

Nd Transport with Flat Sheet Contained Liquid Membrane

Permeation experiments measured the transport of Nd from a high nitric acid feed to a strip solution, low in nitrate, using the CMPO/TBP/isotridecanol solvent system. A three-compartment batch cell (Fig. 1) was used to identify the most significant resistance to the transport. The flat sheet contained liquid membrane system consists of two membranes and three stirred bulk phases. There are two liquid–liquid interfaces. The position of the interface depends on the type of membrane support used. If the support is hydrophobic, the membrane pores are filled with the solvent phase and the interface is on the feed or strip side of the membrane. If the support is hydrophilic, the membrane pores are filled with the aqueous phase and the interface is on the solvent side of the membrane. A schematic diagram of the facilitated co-current coupled transport is shown in Fig. 6. The driving force for the reaction is the nitrate concentration gradient between the feed solution and the strip solution. The total mass transfer resistance is due to the contributions made by:

(i) diffusion of Nd across the feed aqueous diffusion layer;
(ii) extraction reaction of Nd with CMPO at the feed–solvent interface;

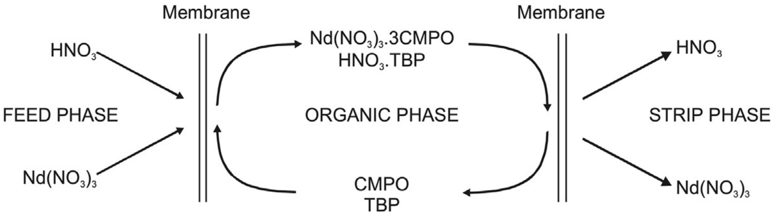

Figure 6. Transport of neodymium and acid with contained liquid membrane.

(iii) diffusion of Nd across a hydrophilic membrane at the feed–solvent interface or diffusion of Nd–CMPO complex across a hydrophobic membrane at the feed–solvent interface;
(iv) diffusion of Nd–CMPO complex across the solvent diffusion layer at the feed side;
(v) diffusion of Nd–CMPO complex across the solvent diffusion layer at the strip side;
(vi) diffusion of Nd across a hydrophilic membrane at the solvent–strip interface or diffusion of Nd–CMPO across a hydrophobic membrane at the solvent–strip interface;
(vii) stripping reaction of Nd–CMPO at the solvent–strip interface; and
(viii) diffusion of Nd across the strip aqueous diffusion layer.

An example of the Nd concentration profiles obtained during a Nd permeation experiment with the three-compartment batch cell is shown in Fig. 7. The profiles seem to be continuous curves because on line measurements were taken every 10 min. The Nd concentration in the feed decreases with time, but the decrease in the feed solution is not matched by an equivalent increase in the strip solution due to the accumulation of Nd in the bulk solvent phase.

The initial fluxes of Nd from feed to solvent (J^{F}) and the overall flux (J^{S}) were determined from Eqs. (1) and (2) by measuring the initial maximum slope of the concentration vs. time curves for the feed and strip solutions, respectively.

$$J^{\mathrm{F}} = \frac{V_{\mathrm{F}}}{A_{\mathrm{F}}}\frac{\mathrm{d}[\mathrm{Nd}]_{\mathrm{F}}}{\mathrm{d}t} \tag{1}$$

$$J^{\mathrm{S}} = \frac{V_{\mathrm{S}}}{A_{\mathrm{S}}}\frac{\mathrm{d}[\mathrm{Nd}]_{\mathrm{S}}}{\mathrm{d}t} \tag{2}$$

The mass transfer coefficient from feed to solvent ($K_{\mathrm{a}}^{\mathrm{F}}$) was calculated from the plot of $\mathrm{Ln}([\mathrm{Nd}]_{\mathrm{t,F}}/[\mathrm{Nd}]_{\mathrm{initial,F}})$ vs. time, taking the slope to be equal to $K_{\mathrm{a}}^{\mathrm{F}}A_{\mathrm{F}}/V_{\mathrm{F}}$.

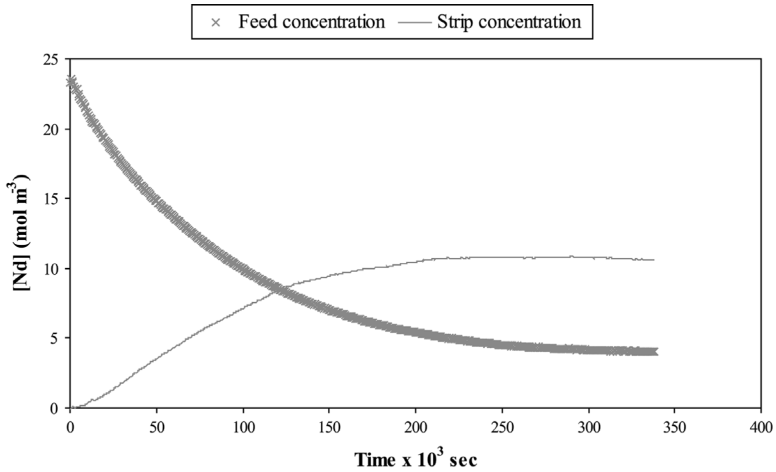

Figure 7. Neodymium concentration profiles in three compartment cell: *Solvent*: [CMPO] $= 0.2\,\text{mol dm}^{-3}$, $0.3\,\text{mol dm}^{-3}$ TBP, 14 vol% isotridecanol in *n*-dodecane; *Feed*: [HNO_3] $= 2\,\text{mol dm}^{-3}$, [Nd] $= 0.024\,\text{mol dm}^{-3}$; *Strip solution*: [$HNO_3$] $= 0.01\,\text{mol dm}^{-3}$.

Effect of Membrane Support Pre-wetting

Preliminary permeation experiments were performed with dry membranes placed in the batch permeation cell. The experiments were repeated using membranes that had been pre-wetted with solvent in the case of a hydrophobic membrane and aqueous in the case of a hydrophilic membrane. It was found that, with the hydrophobic membrane in the feed side, there was no significant change in the J^{F} measured (Experiments 1–3, Table 6). With the hydrophilic membrane, fluxes improved by 37% with the membrane in the strip side and 100% with the membrane in the feed side (Experiments 7–9, Table 6). Hydrophobic membranes should be preferentially wetted by the solvent phase and hydrophilic membranes should be preferentially wetted by the aqueous phase.[19] These tests have shown that pre-wetting is important to ensure that the membrane pores are filled with the desired solvent phase.

Effect of Membrane Type At the Feed–Solvent Interface

The effect of changing the membrane hydrophilicity at the feed–solvent interface is shown in Fig. 8. The two membranes have very similar characteristics (Table 1) in terms of membrane thickness (δ_{m}), pore size, and porosity (ε), but differ in that GVHP is hydrophobic and GVWP is hydrophilic. The membrane at the

Table 6. Fluxes Measured for Nd Permeation Tests: *Solvent*: [CMPO] = 0.2 mol dm^{-3}, 0.3 mol dm^{-3} TBP, 14 vol% Isotridecanol in *n*-Dodecane; *Feed*: [HNO$_3$] = 2 mol dm^{-3}, [Nd] = 0.024 mol dm^{-3}; *Strip Solution*: [HNO$_3$] = 0.01 mol dm^{-3}

Experiment Number	Membrane Feed–Strip Interfaces	J^F (mol m^{-2} sec^{-1})	K_a^F (m sec^{-1})	J^S (mol m^{-2} sec^{-1})
	Hydrophobic–hydrophilic			
1	GVHP–GVWP[a]	4.3×10^{-6}	2.0×10^{-7}	2.7×10^{-6}
2	GVHP–GVWP[b]	4.2×10^{-6}	1.9×10^{-7}	3.7×10^{-6}
3	GVHP–GVWP[b]	4.7×10^{-6}	2.3×10^{-7}	3.7×10^{-6}
4	GVHP–GVWP[c]	2.9×10^{-6}	1.5×10^{-7}	2.4×10^{-6}
5	GVHP–GVWP[d]	1.1×10^{-5}	6.9×10^{-7}	7.6×10^{-6}
	Hydrophobic–hydrophobic			
6	GVHP–GVHP	4.0×10^{-6}	1.9×10^{-7}	2.1×10^{-6}
	Hydrophilic–hydrophilic			
7	GVWP–GVWP[a]	1.2×10^{-5}	5.3×10^{-7}	4.9×10^{-6}
8	GVWP–GVWP[b]	2.5×10^{-5}	1.1×10^{-6}	8.8×10^{-6}
9	GVWP–GVWP[b]	2.4×10^{-5}	1.1×10^{-6}	8.8×10^{-6}
10	GVWP–GVWP[c]	9.2×10^{-6}	6.2×10^{-7}	6.5×10^{-6}
11	GHPolypro–GHPolypro	1.9×10^{-5}	9.0×10^{-7}	7.2×10^{-6}
12	GVWP double–GVWP	1.1×10^{-5}	4.9×10^{-7}	4.6×10^{-6}

[a] Membranes not pre-wetted, all other experiments with pre-wetted membranes.
[b] Experiments 2 & 3 and 8 & 9 are repeat experiments.
[c] Feed 1.9 mol dm^{-3} NaNO$_3$ + 0.1 mol dm^{-3} HNO$_3$.
[d] TRUEX Solvent, Feed 1.9 mol dm^{-3} NaNO$_3$ + 0.1 mol dm^{-3} HNO$_3$.

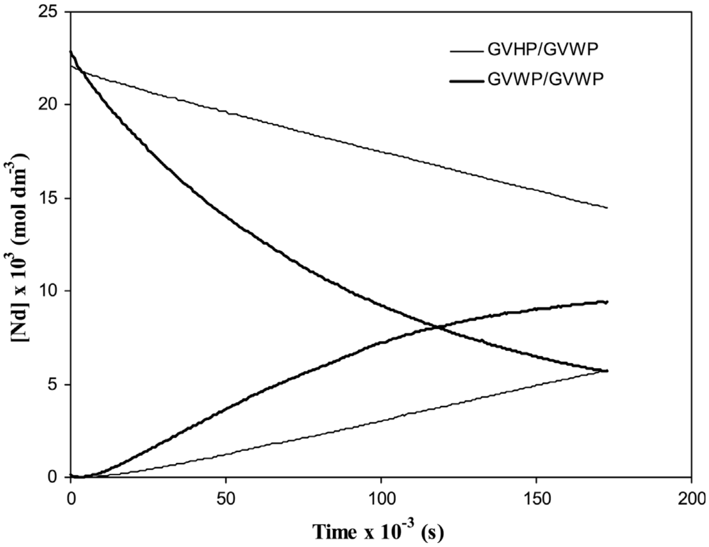

Figure 8. Effect of changing membrane at feed–solvent interface: *GVHP/GVWP*: Hydrophobic/hydrophilic membrane at the feed and strip interface; *GVWP/GVWP*: Hydrophilic membrane at both the feed and strip interface; *Solvent*: [CMPO] = $0.2\,\mathrm{mol\,dm^{-3}}$, $0.3\,\mathrm{mol\,dm^{-3}}$ TBP, 14 vol% isotridecanol in *n*-dodecane; *Feed*: $[\mathrm{HNO_3}] = 2\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{Nd}] = 0.023\,\mathrm{mol\,dm^{-3}}$; *Strip solution*: $[\mathrm{HNO_3}] = 0.01\,\mathrm{mol\,dm^{-3}}$.

solvent–strip interface, GVWP, was not changed. Details of initial fluxes measured are shown in experiments 3 and 9 of Table 6. It can be seen that the permeation rate is higher for the hydrophilic membrane. This result is surprising, as it has been stated that for liquid–liquid extraction, where the distribution coefficient $m^{\mathrm{F}} > 1$, hydrophobic membranes offer lower resistance to mass transfer.[20,21] This general statement is based on the analysis of mass transfer, where the chemical reactions occurring at the interface are assumed to be instantaneous. In a flat sheet configuration, the overall mass transfer coefficient for extraction from feed to solvent, K_{a}, is dependent on the individual mass transfer coefficients for the aqueous diffusion layer ($k_{\mathrm{a}}^{\mathrm{F}}$), membrane diffusion ($k_{\mathrm{m}}^{\mathrm{F}}$), and solvent diffusion layer ($k_{\mathrm{o}}^{\mathrm{F}}$). K_{a} can be described by Eq. (3) for extraction with a hydrophobic membrane and Eq. (4) for extraction with a hydrophilic membrane.[22]

$$\text{Hydrophobic membrane: } \frac{1}{K_{\mathrm{a}}^{\mathrm{F}}} = \frac{1}{m^{\mathrm{F}}k_{\mathrm{o}}^{\mathrm{F}}} + \frac{1}{m^{\mathrm{F}}k_{\mathrm{m}}^{\mathrm{F}}} + \frac{1}{k_{\mathrm{a}}^{\mathrm{F}}} \tag{3}$$

$$\text{Hydrophilic membrane: } \frac{1}{K_{\mathrm{a}}^{\mathrm{F}}} = \frac{1}{m^{\mathrm{F}}k_{\mathrm{o}}^{\mathrm{F}}} + \frac{1}{k_{\mathrm{m}}^{\mathrm{F}}} + \frac{1}{k_{\mathrm{a}}^{\mathrm{F}}} \tag{4}$$

$$k_{\mathrm{m}} = \frac{D\varepsilon}{\delta_{\mathrm{m}}\tau} \tag{5}$$

The difference between Eqs. (3) and (4) lies in the middle term. The mass transfer coefficient for diffusion across the membrane can be calculated using Eq. (5). The values for δ_{m} and ε are known. Values for tortuosity (τ) of 2.2 for the Millipore GVHP membrane[23] and τ values ranging between 1.5 and 2.7 for hydrophilic membranes have been reported.[20] For the purpose of the current calculations, a value of 2.2 was used for both membranes. For the diffusivity (D) of Nd in the solvent, a value of $0.49 \times 10^{-10}\,\mathrm{m^2\,sec^{-1}}$ reported by Danesi for $\mathrm{Am(NO_3)_3 3CMPO}$ in 0.2 M CMPO with diethyl benzene as a diluent, was assumed. The value of $6.0 \times 10^{-10}\,\mathrm{m^2\,sec^{-1}}$, reported for the diffusivity of Eu in $2\,\mathrm{mol\,dm^{-3}}$ nitrate was used for the diffusivity of Nd in $2\,\mathrm{mol\,dm^{-3}}$ $\mathrm{HNO_3}$. Under the experimental conditions shown in Fig. 8, the measured $m_{\mathrm{Nd}} = 4.3$. Calculated $k_{\mathrm{m}}(\mathrm{GVHP}) = 1.3 \times 10^{-7}$ for the hydrophobic membrane and $k_{\mathrm{m}}(\mathrm{GVWP}) = 1.5 \times 10^{-6}$ for the hydrophilic membrane. It can therefore be shown that the term $1/mk_{\mathrm{m}}(\mathrm{GVHP}) > 1/k_{\mathrm{m}}(\mathrm{GVWP})$. This means that the hydrophobic membrane at the feed interface offers higher resistance to mass transfer, due to a combination of low distribution coefficient and low diffusivity of the CMPO complex.

A different hydrophilic membrane, GHPolypro, was also tested. The pore size and thickness were comparable to the GVWP membrane, and similar permeation rates were obtained in both instances (Experiment 11, Table 6).

The effect of doubling the membrane thickness, on the permeation rate of Nd from feed to solvent, was tested, by placing two hydrophilic membranes at the feed–solvent interface. A single hydrophilic membrane was used at the solvent–strip interface in both instances. The initial flux from feed to solvent (Experiments 9 and 12, Table 6) is approximately half of that measured for a single membrane, which indicates that under the experimental conditions investigated, the transport from feed to solvent is mainly controlled by membrane diffusion at the feed–solvent interface.

Effect of Membrane Type at the Solvent–Strip Interface

The effect of changing the membrane hydrophilicity at the solvent–strip interface was investigated by measuring the overall permeation rate with a membrane combination of hydrophobic–hydrophobic and hydrophobic–hydrophilic at the feed–solvent and solvent–strip interfaces, respectively. Results of the tests (Experiments 2, 3, and 6, Table 6) show that the permeation rate from feed to solvent is the same, but the overall permeation, J^{S}, is slower with the hydrophobic membrane at the solvent–strip interface. These results can be explained in terms of the relationship between $k_{\mathrm{m}}^{\mathrm{S}}$ and the mass transfer coefficient from solvent to strip, $K_{\mathrm{o}}^{\mathrm{S}}$, which can be described by Eqs. (6) and (7) as given in Ref.[22].

$$\text{Hydrophobic membrane}: \ \frac{1}{K_{\mathrm{o}}^{\mathrm{S}}} = \frac{1}{k_{\mathrm{o}}^{\mathrm{S}}} + \frac{1}{k_{\mathrm{m}}^{\mathrm{S}}} + \frac{m^{\mathrm{S}}}{k_{\mathrm{a}}^{\mathrm{S}}} \tag{6}$$

$$\text{Hydrophilic membrane}: \ \frac{1}{K_{\mathrm{o}}^{\mathrm{S}}} = \frac{1}{k_{\mathrm{o}}^{\mathrm{S}}} + \frac{m^{\mathrm{S}}}{k_{\mathrm{m}}^{\mathrm{S}}} + \frac{m^{\mathrm{S}}}{k_{\mathrm{a}}^{\mathrm{S}}} \tag{7}$$

The major difference between Eqs. (6) and (7) again lies in the middle term. Since m^{S}, for strip acid concentrations between 0.01 and 0.5 mol dm^{-3} is <0.1, it follows that, $m_{\mathrm{d}}^{\mathrm{S}}/k_{\mathrm{m}}^{\mathrm{S}}(\mathrm{GVWP}) < 1/k_{\mathrm{m}}^{\mathrm{S}}(\mathrm{GVHP})$ and therefore, resistance with a hydrophobic membrane on the strip–solvent interface is higher than that of hydrophilic membrane. However, from these calculations, it would be expected that if the transport from solvent to strip was mainly controlled by membrane diffusion, J^{S} for Nd with a hydrophilic membrane would be at least an order of magnitude faster than the flux measured with a hydrophobic membrane at the strip interface. Since the differences in fluxes measured were less than double, it would appear that resistances due to chemical reaction rate or diffusion layers are significant contributors to the overall resistance.

The Effect of Membrane Type on Acid Co-extraction

As discussed previously, acid is extracted by TBP and reports to the strip solution. Figure 9 shows the acid concentration profiles in both the feed and strip compartments for selected batch permeation experiments. It is apparent that acid extraction rate is higher when hydrophilic membranes GVWP or GHPolypro are used at the feed interface than when the hydrophobic membrane GVHP is used. There is an approximate five-fold difference in the acid flux rates measured. This can be explained by a similar analysis to that carried out for Nd permeation. For nitric acid extraction, and equilibrium acidities ranging from 0.5 to 1.7 mol dm^{-3} (Table 4), $m_{\mathrm{HNO_3}} = 0.08–0.12$. On comparing Eqs. (3) and (4), it can be shown that the very low distribution coefficient favors the permeation of acid from feed to solvent with a hydrophilic membrane.

Permeation Rate vs. Nd Recovery

The above discussion has shown that a combination of hydrophilic membrane at the feed interface and a hydrophilic membrane at the strip

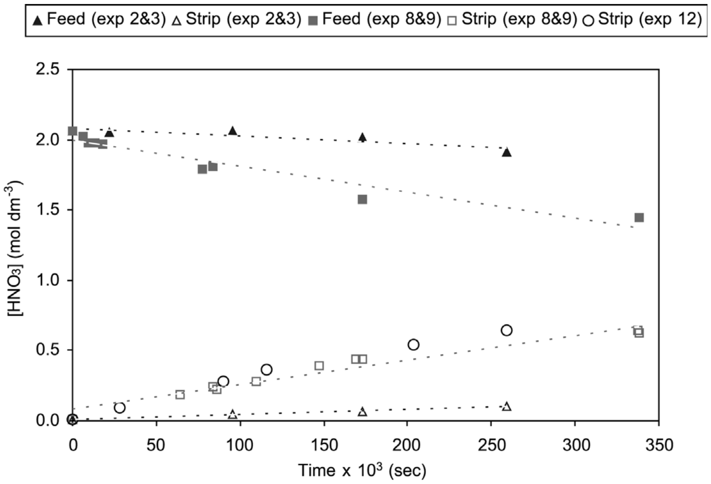

Figure 9. Acid concentration profiles in feed and strip compartments: *Experiments 2 and 3*: GVHP/GVWP membrane at feed and strip interface; *Experiments 8 and 9*: GVWP membrane at feed and strip interface; *Experiment 11*: GHPolypro membrane at feed and strip interface.

interface, favors the rate of permeation of both Nd and nitric acid, with 0.2 *M* CMPO, 0.3 *M* TBP, and 14 vol% isotridecanol in *n*-dodecane. However, nitric acid extraction is detrimental to Nd stripping from the solvent. In experiment 8, which was run for 94 hr, 83% of the Nd was extracted from the feed solution, but only 45% of the Nd reported to the strip solution. Thus there was a significant amount of Nd, which was transferred to the solvent that was not stripped. This is because the acid concentration in the strip compartment increased over the same period from 0.01 to 0.65 mol dm^{-3} HNO_3, increasing the m^S_{Nd} for Nd, from <0.01 to >1 (see Fig. 3). High m^S_{Nd} values prevent effective Nd stripping from the solvent and restrict Nd recovery.

From the point of view of Nd recovery, a combination of hydrophobic membrane in the feed interface and hydrophilic membrane in the strip interface, can achieve higher recoveries, albeit at lower rates. This is exemplified by comparing the Nd recoveries in experiments 2 and 8. After 48 hr, 26 and 41% of the Nd reported to the strip with a hydrophobic/hydrophilic and hydrophilic/hydrophilic membrane combination, respectively. After 72 hr, Nd recovery with a hydrophobic/hydrophilic membrane combination was still increasing in a linear fashion and was measured at 42% whilst recovery with a hydrophilic/hydrophilic membrane combination remained nearly static at 45%.

Permeation Rate of Nd from Low Acid, High Nitrate Feed Solutions

Batch permeation experiments were carried out with feed solutions containing low acid (0.1 mol dm^{-3} HNO_3) and high nitrate (1.9 mol dm^{-3} $NaNO_3$). Two solvent mixtures were tested, namely, CMPO/TBP/isotridecanol and TRUEX. Results of initial permeation fluxes are shown in experiments 4, 5, and 10 of Table 6. With the CMPO/TBP/isotridecanol system, there was a slight decrease in the overall flux caused by the change in feed from nitric acid to sodium nitrate, but the trend of faster rates for hydrophilic membranes at both interfaces was similar to that measured in nitric acid. This was expected since the measured distribution coefficient for Nd extraction was similar for both nitric and sodium nitrate media (Table 5). Extraction of Nd with the TRUEX solvent, however, is favored by sodium nitrate media, and this is reflected by the higher fluxes measured in experiment 5, where a hydrophobic membrane was used at the feed interface. The absence of nitric acid in the feed also allowed for higher Nd extraction and higher Nd recovery in strip (99% Nd extraction and 77% Nd recovery after 83 hr).

CONCLUSIONS

This work identified a solvent system consisting of CMPO, TBP, and isotridecanol for transporting Nd from nitric acid solution in a contained liquid membrane system. This solvent mixture differs from the conventional TRUEX solvent in that, the TBP concentration is reduced by 80% and therefore acid co-extraction is minimized. Isotridecanol acts as a modifier, preventing third phase formation. Nd extraction from 2 mol dm^{-3} nitric acid was acceptable, although lower than that was measured for the TRUEX solvent.

A flat sheet, three compartment batch permeation cell was used to identify the major resistances to mass transfer. The extraction of Nd from nitric acid to CMPO/TBP/isotridecanol solvent was found to be mainly governed by membrane diffusion. At the feed interface, it was found that a hydrophobic membrane offers higher resistance to mass transfer than a hydrophilic membrane, due to a combination of low distribution coefficient and low diffusivity of the Nd–CMPO complex. Resistance at the strip interface was also lower with a hydrophilic membrane. The rate of acid transport from feed to strip solution was higher with a hydrophilic membrane at the feed interface, and this was found to reduce Nd recovery in the strip solution.

NOMENCLATURE

A	membrane area (m^2)
D	diffusivity (m^2 sec^{-1})

J^F	flux measured from feed to solvent ($\mathrm{mol\,m^{-2}\,sec^{-1}}$)
J^S	flux measured from feed to receiver ($\mathrm{mol\,m^{-2}\,sec^{-1}}$)
K_a^F	overall mass transfer coefficient from feed to solvent ($\mathrm{m\,sec^{-1}}$)
K_a^S	overall mass transfer coefficient from solvent to strip ($\mathrm{m\,sec^{-1}}$)
k	individual mass transfer coefficient ($\mathrm{m\,sec^{-1}}$)
$m_{\mathrm{Nd\ or\ HNO_3}}$	distribution coefficient for Nd or nitric acid
t	time (sec)
V	volume ($\mathrm{m^{-3}}$)

Greek letters

δ_m	membrane thickness (m)
ε	porosity
τ	tortuosity

Subscripts

a	aqueous
F	feed
m	membrane
o	solvent
S	strip

Superscripts

F	feed to solvent
S	solvent to strip

Acronyms and abbreviations

CMPO	*n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide
TBP	tri-butyl phosphate
TOPO	trioctylphosphine oxide
TRUEX	tansuranium solvent extraction process using CMPO and TBP solvent

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