Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Poisoning of Liquid Membrane Carriers in Extraction of Metal Ions

Yuchun Wang[a]; Dexian Wang[a]
[a] DEPARTMENT OF CHEMISTRY, JIANGXI NORMAL UNIVERSITY, NANCHANG, PEOPLE'S REPUBLIC OF CHINA

To cite this Article Wang, Yuchun and Wang, Dexian(1992) 'Poisoning of Liquid Membrane Carriers in Extraction of Metal Ions', Separation Science and Technology, 27: 3, 341 — 347
To link to this Article: DOI: 10.1080/01496399208018884
URL: http://dx.doi.org/10.1080/01496399208018884

SEPARATION SCIENCE AND TECHNOLOGY, 27(3), pp. 341–347, 1992

Poisoning of Liquid Membrane Carriers in Extraction of Metal Ions

YUCHUN WANG and DEXIAN WANG
DEPARTMENT OF CHEMISTRY
JIANGXI NORMAL UNIVERSITY 330027
NANCHANG, PEOPLE'S REPUBLIC OF CHINA

Abstract

In the extraction of desired metal (scandium, mixed rare earths) ions using chelating extractants (TTA, HDEHP) as liquid membrane carriers, the carriers will become poisoned owing to the presence of even minute quantity of certain high ionic potential ions in the feed solution. The reason for the poisoning of carriers is that those ions have so much greater affinity than the desired ions for the membrane carrier that the ion–carrier coordination compound cannot be stripped at the interior interface of the membrane and gradually no more free carrier transports any metal ions across the membrane. The calculated results are in agreement with the experiments, and methods to avoid the poisoning are given in the paper.

INTRODUCTION

As means of effective separation and preconcentration, emulsion liquid membranes (ELMs) have found application in many fields including biochemical separation (*1*), wastewater treatment (*2*), hydrometallurgy (*3, 4*), and preconcentration in analytical chemistry (*5*). Much work on extracting various metal ions by ELM has been reported. When a specific metal ion is to be separated by ELM from a mixture of many different ions, the coexisting ions may act as competitors against the specific ion for the carrier in the membrane, which complicates the problem. We intended to extract scandium from the leachate of wolframite residue and succeeded in extracting scandium by TTA-mediated ELM from a mixture of Fe, Mn, Ca, RE (mixed rare earths), Ti, and Sc. However, further studies showed that a minute quantity of zirconium in the feed solution makes the membrane carrier unable to transport metal ions. We propose the phenomenon to be poisoning of liquid membrane carriers.

EXPERIMENTAL

2-Thenoyltrifluoroacetone (TTA) was AR grade, and di(2-ethylhexyl) phosphoric acid (HDEHP) was CP grade. Sc_2O_3 and $Zr(SO_4)_2 \cdot 4H_2O$ were 99.9% pure, and the mixed rare earths (RE) were mainly heavy rare earths. 1-Phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP) was obtained from Eastchina Normal University.

The water-in-oil emulsion was prepared by high speed agitation of 40 mL hydrochloric acid of 2–3 *M* with 60 mL kerosene solution of 0.0135 *M* TTA and 4% N2O5 (as surfactant). The emulsion was dispersed into the exterior feed solution at a stirring speed of 300 rpm, and the extraction of metal ions was conducted. The pH of the feed solution was adjusted by adding saturated NaAC solution and measuring with a pH meter. After extraction, the loaded interior solution was obtained from the emulsion by high voltage electrostatic coalescence.

The concentrations of Fe^{2+}, Mn^{2+}, and Ca^{2+} were determined by flame atomic absorption spectrometry. RE^{3+}, Sc^{3+}, and Zr^{4+} were determined colorimetrically with Arsenazo-III. The mixture of RE^{3+}, Sc^{3+}, and Zr^{4+} was first extracted with PMBP-benzene and then stripped with formic acid of pH 2.4, 5% HCl, and 2% $H_2C_2O_4$–4 *M* HNO_3, respectively. After proper treatment of each stripped solution, RE^{3+}, Sc^{3+}, and Zr^{4+} were separately determined colorimetrically with Arsenazo-III.

RESULTS AND DISCUSSION

TTA is a selectively good extractant which extracts most metal cations at various pH conditions. Sc^{3+} can thus be separated from other cations by selective control of the pH of the feed solution. Figures 1 and 2 exhibit the extraction yields of Sc^{3+} and RE^{3+}, respectively, by TTA-mediated ELM at different pHs of the feed solution.

It is seen that high pH values benefit the extraction of metal ions, which follows the extraction reaction

$$M^{n+} + n\mathrm{HTTA}_{(0} \rightleftharpoons \mathrm{M(TTA)}_{n(0)} + n\mathrm{H}^{+}$$

Comparison of the two figures indicates that Sc^{3+} can be separated from RE^{3+} at pH 2.2–2.5 with ELMs.

Titanium cation gradually hydrolyzes at pHs higher than 1.7, but experiments show that it is not extracted by a TTA-mediated ELM during its hydrolysis at pH 1.7–2.5. Fe^{2+}, Mn^{2+}, and Ca^{2+} were found not to be extracted at pH 1–3. Sc^{3+} can therefore be separated from a mixture containing the above-mentioned ions by controlling the feed pH to 2.2–2.5. The separation results for the mixture are listed in Table 1.

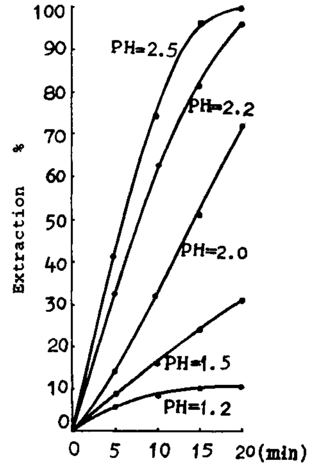

FIG. 1. Effect of feed pH on the extraction of Sc^{3+} by TTA-mediated ELM. Emulsion (30 mL) was added to 300 mL feed of 100 mg Sc^{3+}/mL, 22°C.

As zirconium often occurs with scandium in nature, it is necessary to separate scandium further from the mixture of scandium and zirconium by ELM. But the ELM in this formulation failed to extract scandium from the mixture (see Table 2).

When the feed solution containing Zr^{4+} alone was treated with TTA-mediated ELM, as shown in Table 3, the concentration of Zr^{4+} always

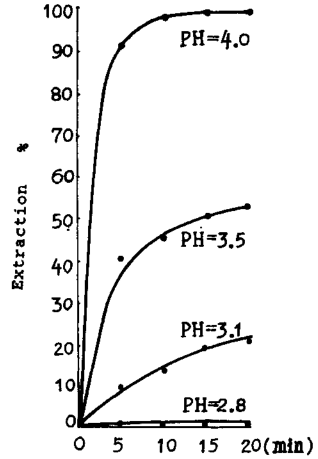

FIG. 2. Effect of feed pH on the extraction of RE^{3+} by TTA-mediated ELM. Emulsion (20 mL) was added to 300 mL feed of 500 mg RE/L, 22°C.

TABLE 1
ELM Separation of Sc^{3+} from a Mixture of Fe^{2+}, Mn^{2+}, Ca^{2+}, RE^{3+}, Sc^{3+}, and Ti^{4+} at pH 2.2–2.5 and 22°C[a]

Component	Fe	Mn	Ca	RE	Ti	Sc	(mg/L)
Feed	8000	2200	1630	330	100	60	
Raffinate	8000	2200	1630	330	Turbid	4	
Interior solution	370	130	125	77		1400	

[a] Volume ratio of emulsion to feed (Ref) = 1:15.

dropped a little or remained unchanged. The concentration of Zr^{4+} in the interior solution was found to be close to zero.

Solvent extraction experiments indicate that Zr^{4+} has a great affinity for TTA, that TTA can extract Zr^{4+} from strongly acidic solution, and that it is extremely difficult to strip Zr^{4+} from TTA. Only concentrated hydrochloric acid, 5–6 *M* $HClO_4$ (*6*), or 0.5 *M* HF–0.5 *M* HNO_3 will do this stripping. In our formulated ELM using 2 *M* HCl as the stripping solution, Zr^{4+} was extracted into the membrane but not stripped into the interior solution. When an ELM extracts a mixture of Sc^{3+} and Zr^{4}, both kinds of the ions compete in complexing the carrier TTA at the external interface of the membrane, and Zr^{4+} quickly combines with TTA until all the TTA in the membrane forms the coordination compound of Zr^{4+} because Zr^{4+} predominates over Sc^{3+} in their competition owing to their extraction constants. [The extraction constants of TTA-bezene to Zr^{4+} and Sc^{3+} are 9.2 and −0.3, respectively (7).] In this case TTA no longer transports metal ions across the membrane, hence the poisoning of liquid membrane carriers.

Calculated results of the ELM system support this explanation. As shown in the above experiments, the concentration of TTA in the membrane is 0.0135 *M*, the volume ratio of membrane to interior solution is

TABLE 2
Extraction of Zr^{4+} and Sc^{3+} from Their Mixture by ELM at pH 2.5 and 27°C[a]

T (min)	0	5	10	30
Zr (mg/L)	100	89	86	86
Sc (mg/L)	100	94	95	93

[a] Ref = 1:15, where the concentration of metal refers to that in the exterior solution except where noted.

TABLE 3
Extraction of Zr^{4+} by ELM at 27°C, Ref = 1:20

	Zr (mg/L)		
T (min)	pH 1.8	pH 2.0	pH 2.5
0	88	92	86
5	75	88	78
10	76	75	76
20	73	76	73

5:4, so the membrane volume is 5/9 that of the emulsion. When 15 mL emulsion is employed to treat 300 mL of feed solution of Zr^{4+} at 90 mg/L, the amount of TTA is $0.0135 \times (5/9) \times 15 \times 10^{-3}$, or 1.1×10^{-4} mol. The amount of possibly extracted Zr^{4+} in the form of $Zr(TTA)_4$ (*6*) is $(1.1 \times 10^{-4})/4$, or 2.8×10^{-5} mol, while the total amount of Zr^{4+} in the feed solution is $(90 \times 300 \times 10^{-6})/92$, or 2.9×10^{-4} mol.

Consequently approximately 10% of the Zr^{4+} will be extracted into the membrane, which is in agreement with the results in Table 3.

In general, many metal ions with a high ionic potential might cause poisoning of carriers when chelating extractants are used as the liquid membrane carriers.

Another example of poisoning of liquid membrane carriers is illustrated in Fig. 3 where HDEHP is used as the membrane carrier in extracting rare earths. The HDEHP-mediated ELM with HCl as the interior solution can efficiently concentrate rare earths (*3*), but the presence of a minute amount of Sc^{3+} would cause poisoning of the carrier because even concentrated hydrochloric acid fails to strip Sc^{3+} from HDEHP. Th^{4+}, Zr^{4+}, and Hf^{4+} act similarly under the same conditions.

In apolar solvent, HDEHP extracts Sc^{3+} as follows:

$$Sc^{3+} + 3(HA)_{2(0)} \rightleftharpoons Sc(HA_2)_{3(0)} + 3H^+$$

According to the above formulation, 20 mL emulsion contains 7.4×10^{-4} mol HDEHP or 3.7×10^{-4} mol of the dimer $(HDEHP)_2$, either of which can extract Sc^{3+} to the amount of 1.2×10^{-4} mol.

In Fig. 3 the feed in Curve b contained 1.7×10^{-4} mol Sc^{3+}, which was enough to complex all of $(HDEHP)_2$, but about 95% RE^{3+} was extracted before the carrier in the membrane was completely poisoned because RE^{3+} was much in excess of Sc^{3+}.

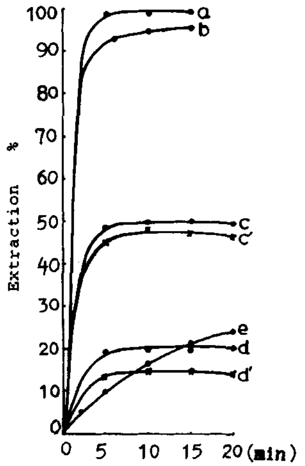

FIG. 3. Poisoning of the carrier by Sc^{3+} in the extraction of RE^{3+} with HDEHP-mediated ELM, 22°C. Conditions: 60 mL kerosene containing 0.062 *M* HDEHP and 4% N205 was emulsified with 40 mL of 6 *M* HCl. The emulsion (20 mL) was added to 300 mL of the feed solution which contained 2.5 g NaAc and (a) 200 mg RE^{3+}/L; (b) 200 mg RE^{3+}/L in the presence of 8.6 mg Sc^{3+}/L; (c and c') mixture of 200 mg RE^{3+}/L (c) and 38 mg Sc^{3+}/L (c'); (d and d') mixture of 200 mg RE^{3+}/L (d) and 110 mg Sc^{3+}/L (d'); and (e) 200 mg RE^{3+}/L, treated with the emulsion which had been employed in treating 200 mL of 60 mg Sc^{3+}/L for 5 min.

In Curves c' and d', 1.1×10^{-4} mol Sc^{3+} was extracted into the membrane, which is identical with the calculated results. When the carrier was poisoned completely, leveling of the extraction curve occurred.

In Curve e, most of the carrier was poisoned by Sc^{3+}, but the remainder still played an effective role in transporting RE^{3+} across the membrane.

CONCLUSIONS

From the above mechanism of poisoning, we infer that the poisoning of liquid membrane carriers is a common phenomenon. In particular, the carriers in supported liquid membranes might become poisoned when they are employed for a long time in treating feed solution with complex components.

There are ways to avoid poisoning:

(1) Replace the interior stripping solution to ensure that the desired metal ion and the probable impurities in the membrane are stripped, and then separate the desired metal ion from the impurities by other means.

(2) Remove the component that causes the poisoning of the carrier from the feed solution before extracting the desired metal ions by ELM.

(3) If the component causing the poisoning is determined to be present in a very minute quantity so that only part of the carrier is poisoned, the component's effect is negligible. The efficiency of reusing the membrane, however, would be affected. On the other hand, for an analytical preconcentration process, a better selectivity of the interior solution is obtained by allowing the minute impurity to remain within the membrane while the ion to be determined is stripped and concentrated in the interior solution.

REFERENCES

1. M. P. Thien and T. A. Hatton, *Sep. Sci. Technol.*, *23*, 819 (1988).
2. M. Ruppert, J. Draxler, and R. Marr, *Ibid.*, *23*, 1659 (1988).
3. M. Teramoto, T. Sakuramoto, T. Koyama, H. Matsuyama, and Y. Miyake, *Ibid.*, *21*, 229 (1986).
4. N. N. Li, R. P. Cahn, D. Naden, and R. W. M. Lai, *Hydrometallurgy*, *9*, 277 (1983).
5. Xu Shushen, Li Yongtao, and Tian Jian, *Fen Xi Hua Xue*, *17*, 1028 (1989) (in Chinese).
6. J. Hala, *J. Inorg. Nucl. Chem.*, *29*, 187 (1967).
7. E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.*, *67*, 48 (1948).

Received by editor December 12, 1990