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Recovery of americium(III) from low acid solutions using an emulsion liquid membrane containing PC-88A as the carrier extractant

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ABSTRACT

A liquid emulsion membrane (LEM) containing PC-88A (2-ethylhexylphosphonic acid-2-ethylhexyl monoester) as the carrier extractant and SPAN-80 as the surfactant was used to pre-concentrate Am^3+ from dilute acid solutions. Out of the various stripping agents evaluated as the internal phase, 0.1 M oxalic acid was found to be the most effective. The effect of various factors such as: external phase pH, equilibration time, PC-88A concentration, SPAN 80 concentration, phase volume ratio, etc. on Am^{3+} mass transfer was investigated. The emulsion was broken by the addition of solvents such as acetone and the actual mass transfer obtained after breaking the emulsion agreed well with that obtained by the difference method.

Keywords: Americium; Liquid emulsion membrane; Separation; PC-88A

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1. Introduction

Recovery of actinides from acidic solutions can be achieved by neutral solvating type extractants such as TOPO (tri-n-octyl phosphine oxide), CMPO (carbamoyl methyl phosphine oxide), etc. or basic extractants such as the tertiary amines [1,2]. On the other hand, their recovery from low acid solutions is carried out using acidic extractants whose extraction properties depend on their pKa values as well as the aqueous phase pH [3]. Many of these extractants are acidic organophosphoric acid extractants which work as liquid cation exchangers. 2-ethylhexylphosphonic acid-2-ethyl hexylmonoester (PC-88A) is one such promising extractant being used for the recovery of actinide ions [4,5]. However, in order to reduce ligand inventory, separation methods based on extraction chromatography and liquid membrane are becoming increasingly popular. Though extraction chromatographic methods based on PC-88A have been used for the recovery of Pu from nitric acid feed solutions [6], such methods suffer from limitations such as leaching out of the extractant and poor solute loading. Therefore, liquid membrane-based separations appear a viable alternative [7].

The specific advantages of liquid membranes include possibility of carrying out simultaneous extraction and stripping, non-equilibrium mass transfer and up-hill transport effect, where metal ions can move from low concentration to high concentration yielding quantitative mass transfer [8]. Out of the various liquid membrane-based separation methods, liquid emulsion membrane (LEM) based separation methods are particularly interesting due to their easy operation, easy scale up, high achievable pre-concentration factor and rapidity [9,10]. Liquid

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emulsion membrane (LEM) was first reported by Li [11] to remove the equilibrium limitations of solvent extraction by combining extraction and stripping in a single operation. The technique subsequently found application even in the process scale recovery of metal ions [12].

The separation by LEM usually involves the preparation of a relatively stable emulsion made from the extractant, strippant (which is also termed as the internal phase (IP)) and a surfactant. The emulsion is prepared in a high speed emulsifier after which it is contacted with the feed phase (also known as the external phase (EP)) by dispersing using a low speed stirrer. The extracted metal ion is directly stripped into the IP and can be recovered by the breaking of the emulsion. The metal ions are transported from the EP to the IP by diffusion facilitated by the carrier. The breaking and maintaining of emulsion has been the key issue in this type of separation methods. Literature cites many reports on the selective separation of metal ions from various types of feed solutions. Emulsion liquid membrane containing PC-88A has been used for the recovery of base metals, Eu, Th and U from acidic waste solutions [13–16]. However, there is no report on the recovery/pre-concentration of Am^{3+} from dilute acidic solutions using LEM containing PC-88A. The present work deals with investigations on the transport behaviour of Am^{3+} from HNO_3 medium. Studies are also carried out under varying experimental conditions such as feed acidity, IP composition, surfactant/extractant concentration, stirring speed, etc.

2. Experimental

2.1. Materials

2-ethylhexylphosphonic acid-2 ethylhexylmono ester (PC-88A) and SPAN 80 were procured from Daihachi, Japan and Fluka, Switzerland, respectively. All the other reagents were of AR grade and were used without further purification. ^{241}Am tracer was purified by a reported method and its radiochemical purity was ascertained by gamma spectrometric analysis [17].

2.2. Distribution studies

Distribution studies were carried out with ^{241}Am as the tracer in different aqueous phase conditions using organic phases containing PC-88A in n-dodecane as the extractant. Equal volumes (2 mL) of the organic phase and the aqueous phase containing the required tracer were taken in stoppered glass tube and agitated in a thermostated water bath at 25±0.1°C for 1 h. The two phases were then centrifuged and assayed by taking suitable aliquots (0.1 mL) from both the phases. The distribution ratio (D_{Am}) was calculated as the ratio of counts per minute per unit volume in the organic phase to that in the aqueous phase. Material balance was with in error limits (±5%).

2.3. Transport studies

The emulsification was performed with an ultra high speed motor as well as a specially designed turbine Plexiglas impeller, manufactured indigenously. The two phases (organic phase containing a required concentration of PC-88A in n-dodecane and internal phase, which was usually oxalic acid) were placed into a beaker, and preparation of the emulsion was carried out at 10,000 rpm (as a maximal speed) during 5 min. Typically, 100 mL of the w/o emulsion had the following composition: 10 mL of internal phase (0.1 M oxalic acid), 1% SPAN 80 and 5–10% PC-88A in n-dodecane. Usually, 5 mL of the w/o emulsion was poured into the external aqueous phase in a beaker containing the required radiotracer, and was stirred at a speed of 200 rpm. Stirring was usually carried out using a Remi (India) variable speed magnetic stirrer using Teflon coated stirring bars. A schematic representation of LEM set up is given in Fig. 1. Samples were taken out at regular intervals and assayed using NaI(Tl) gamma-scintillation detector. Demulsification was carried out using various methods which included addition of organic solvents such as acetone to the emulsion. The material balance in these studies was found to be within ±5%.

3. Results and discussion

3.1. Solvent extraction studies

As the liquid emulsion membrane studies are based on the efficiency of extraction and stripping, preliminary studies were carried out using Am(III) from pH solutions. Extractants such as PC-88A exist as a dimer in the organic phase when relatively non-polar organic diluent is used [18]. Assuming similar behaviour in the present system, the extraction equilibrium is represented as:

$$Am^{3+} + 3(HR)_2 \rightleftharpoons Am\,(HR_2)_3 + 3H^+ \quad (1)$$

Similar extracted species were reported for Eu^{3+} extraction using PC-88A by Lee et al. [15]. In the present

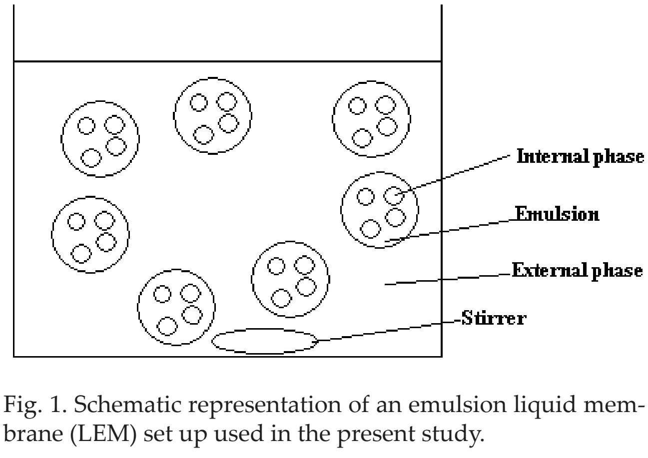

Fig. 1. Schematic representation of an emulsion liquid membrane (LEM) set up used in the present study.

Table 1
Solvent extraction and subsequent stripping of Am^{3+} from pH solutions using 10% PC-88A in n-dodecane

Extraction data		Stripping data (D_{Am})*	
pH	D_{Am}	1.0 M HNO_3	0.1 M oxalic acid
1.0	0.55	0.88	0.53
2.0	15.4	0.046	0.045
3.0	19.8	0.056	0.038
4.0	34.2	0.043	0.040
5.0	13.9	0.042	0.035

*The organic phases from the extraction studies were used for the stripping studies

studies, the extraction studies were carried out from aqueous phase pH values in the range 1.0–5.0 and the distribution ratio values (D_{Am}) for 10% PC-88A in n-dodecane are listed in Table 1. An increase in the D_{Am} values was observed up to pH 4 after which a decrease was observed. The stripping studies were carried out using two strippants viz. 1.0 M HNO_3 and 0.1 M oxalic acid (Table 1). As the D_{Am} values were marginally lower with 0.1 M oxalic acid, it was used as the IP in all subsequent studies.

3.2. Transport studies

The mechanism of Am^{3+} transport through the liquid emulsion membrane includes the following basic steps: (1) Am^{3+} diffuses from the EP to the boundary of the LEM phase; (2) Am^{3+} forms a complex with PC-88A at the EP–LEM interface; (3) the complex diffuses inside the LEM; (4) Am^{3+} is stripped at the internal phase (IP); (5) PC-88A diffuses from the IP through the LEM to the LEM–EP interface to form a complex again with Am^{3+}. The transport mechanism is illustrated in Fig. 2. The permeability coefficients were calculated as per the following equation:

$$\ln\left(C_t / C_0\right) = -\left(V_1 / V_2\right) P t \tag{2}$$

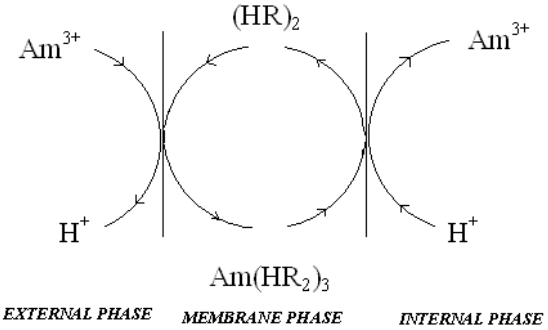

Fig. 2. Transport mechanism of Am(III) using PC-88A (HR) in the LEM system.

where C_t and C_0 are the concentrations of metal ion in the feed side at times t and 0 respectively. V_1 and V_2 are the volumes of the emulsion and external phases, respectively. The cumulative percent transport of Am (%T) at a given time is determined by the following equation,

$$\%T = 100 \cdot \left(C_0 - C_t\right) / C_0 \tag{3}$$

3.2.1. Effect of nature of the internal phase

Several stripping agents viz. 0.1 M oxalic acid, 0.1 M EDTA, 0.1 M alpha-hydroxy iso-butyric acid (AHIBA) and buffer mixture (0.4 M formic acid, 0.4 M hydrazine hydrate and 0.1 M citric acid) were used as the internal phase. However, some of them such as EDTA led to instability of the emulsion. As shown in Fig. 3, the extraction of Am was most efficient with 0.1 M oxalic acid. Increasing the oxalic acid concentration to 0.5 M led to higher extraction rate but lower emulsion stability. Hence, in all subsequent studies, 0.1 M oxalic acid was used as the strippant in the internal phase.

3.2.2. Effect of external phase pH

Effect of the external phase (EP) pH on the extraction of Am-241 using 10% PC-88A in the emulsion was studied by adjusting the pH using a buffer (0.1 M acetate buffer was used for pH 4.0 and 5.0) and without a buffer. It may be noted that pH values > 5 were not used in the present study in view of possible hydrolysis of Am(III). The results indicate most efficient mass transfer at pH 2 and lower %T data were obtained at lower (where increase in transport rate was observed up to 60 min) as well as higher pH values (where a plateau was observed beyond 15 min, Fig. 4). Use of buffer solutions for maintaining the aqueous phase pH did not have any significant effect on

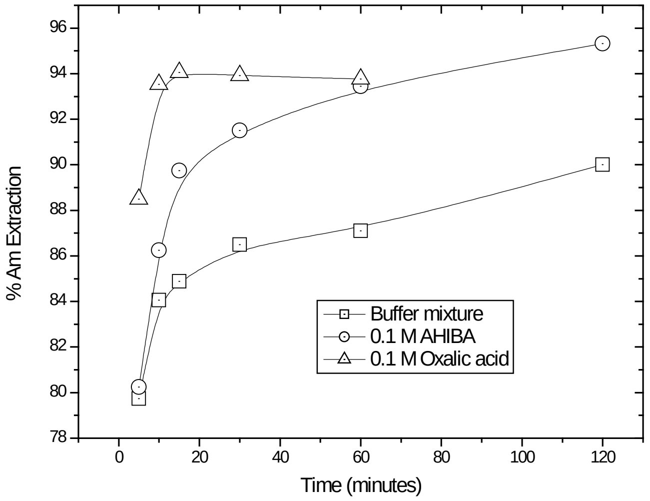

Fig. 3. Effect of strippant nature on Am extraction. External phase: pH 2; [PC-88A] = 10% (v/v).

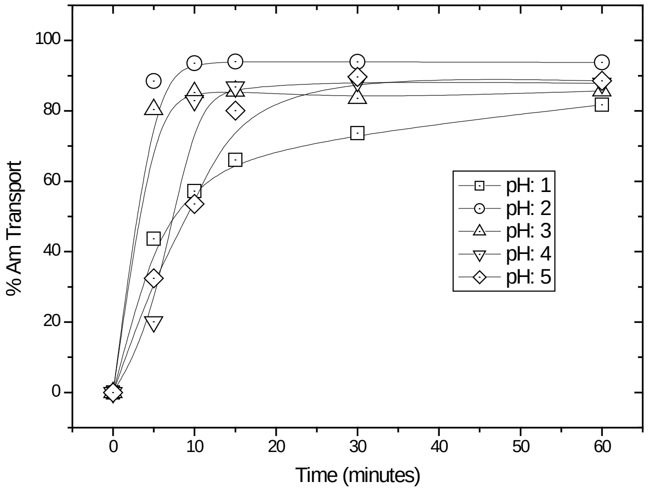

Fig. 4. Transport of ^{241}Am as a function of external phase pH.

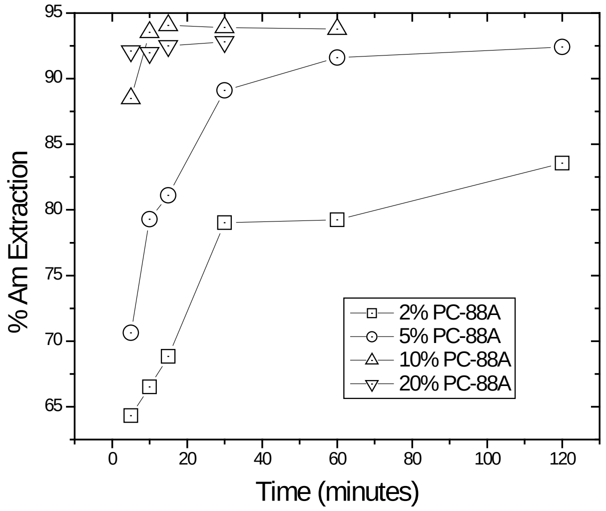

Fig. 5. Effect of carrier extractant concentration on Am extraction. EP = pH 2.0, IP = 0.1 M oxalix acid.

the transport profiles. The permeability coefficient was calculated for pH 1 external phase as $(1.86\pm0.35)\times10^{-3}$ s^{-1} while the extractions from external phases maintained at higher pH values were much faster and the errors associated with these data were also higher. Though no literature report is available in identical systems, the permeability coefficient value calculated from the transport data for a flat sheet supported liquid membrane study (though no comparison can be made as the transport systems are different) for Am(III) transport using PC-88A is $(2.62\pm0.78)\times10^{-3}$ cm/s [19]. On the other hand, the permeability coefficient of Pu(IV) in a similar LEM system containing PC-88A as the carrier was reported to be 8.33×10^{-3} s^{-1} [20]. As Pu(IV) extraction is usually to a much higher extent as compared to the extraction of Am(III), the present data appear to be in line with the literature report.

3.2.3. The effect of extractant concentration

The effect of PC-88A concentration on Am transport was studied using 2%, 5%, 10% and 20% PC-88A in n-dodecane used as the extractant while making the emulsions. As shown in Fig. 5, the transport rates increased with increasing PC-88A concentration. However, the PC-88A concentration can not be increased indefinitely as the emulsion stability decreased with increasing PC-88A concentration. When 20% PC-88A was used, the emulsion breaking was observed automatically even before 60 min.

3.2.4. The effect of surfactant concentration

In an ELM system, a surfactant added as an emulsifier in the liquid membrane phase affects not only the stability of the liquid membrane but also the swelling of the emulsion and the rate of metal extraction. The effect of SPAN-80 fraction in the emulsion was also varied in the range 1–5% and the extraction of Am(III) from the EP at pH 2.0 was studied using 0.1 M oxalic acid as the IP and 10% PC-88A as the extractant. As shown in Fig. 6, increasing the fraction of surfactant concentration decreased the Am extraction efficiency. It appeared that with increasing surfactant concentration the kinetics of extraction may be affected [21]. Though maximum transport efficiency was observed for 1% SPAN-80, the emulsion was not stable and disintegrated after 20 min. Therefore, all experiments

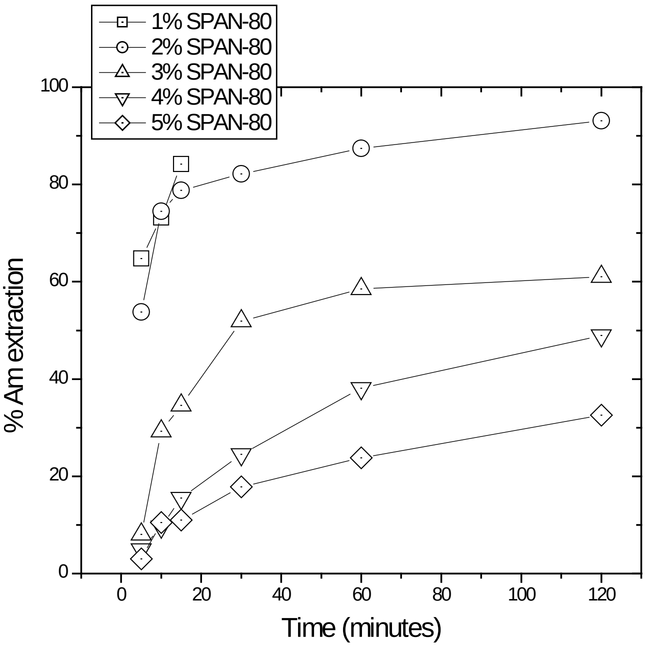

Fig. 6. Effect of surfactant concentration in the emulsion on Am extraction. Internal phase: 0.1 M oxalic acid; external phase: pH 2.0, extractant: 10% PC-88A.

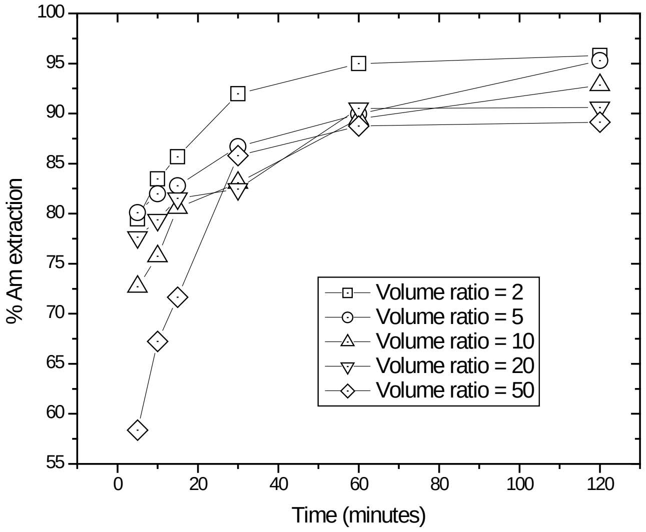

Fig. 7. Effect of phase volume ratio (EP:LEM) on the extraction of Am(III). External phase: pH 2.0, internal phase: 0.1 M oxalic acid, extractant: 10% PC-88A.

were carried out using 2% SPAN-80 as the emulsifying agent.

3.2.5. *Effect of external phase: emulsion volume ratio*

The main advantage of the LEM is its easy scale up options available. This can be achieved by increasing the EP volume for a given volume of the liquid emulsion. In the present studies, the EP to emulsion volume ratio was varied in the range 2–50 and the data are presented in Fig. 7. As shown in the figure, the mass transfer rate was faster in case of low volume ratios. This is clearly seen in the initial stages of the % Am extraction vs. time plots. With increasing the volume ratio, the mass transfer becomes slower as a higher contact time must be needed due the increase in the external phase volume.

3.2.6. *Stability of the emulsion and the emulsion breaking*

The stability of the emulsion was found to be good up to at least 2 h in most of the cases investigated in the present work. Increasing the internal phase volume and concentration of oxalic acid (0.5 M or above) in the IP had a detrimental effect on the emulsion stability. Similarly, the emulsion was also not stable when the surfactant concentration was low. Attempts to make emulsion with 0.5% SPAN-80 were not successful and that made with 1% SPAN-80 yielded limited stability.

The breaking of the emulsion was subsequently required to recover the extracted Am from the internal phase. This was done by different techniques such as applying potential and heating. In the present study, it was achieved by adding few drops of acetone. Quantitative recovery of Am (as indicated by the % extraction data shown above) was observed by this method.

4. Conclusions

In conclusion, the present study has shown that Am can be effectively pre-concentrated from pH solutions using PC-88A based LEM with a volume reduction factor of >10. Though dilute nitric acid can be used as the internal phase, 0.1 M oxalic acid yielded better stripping results. This method can be used for Am recovery from waste solutions and also can be used for separation from other elements which are not extracted under the given conditions.

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