



Research article

Modeling of gadolinium recovery from nitrate medium with 8-hydroxyquinoline by emulsion liquid membrane

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ABSTRACT

The extraction equilibrium of Gd(III) from nitrate medium by 8-hydroxyquinoline (HOX) in toluene was studied. Liquid–liquid investigations were first carried out. Based on the equilibrium results, the extraction of Gd(III) from aqueous nitrate medium into an emulsion liquid membrane system (ELM) containing 8-hydroxyquinoline in toluene as extractant, HNO₃ as stripping solution, Span-80 as surfactant was studied. The stability of the prepared ELM was studied in terms of the degree of membrane breakage. The different parameters affecting the permeation of gadolinium (III) were also studied.

A general permeation model for the recovery of Gd(III) by the selected membrane is presented. The internal mass transfer in the water in oil (W/O) emulsion drop, the external mass transfer around the drop, the rates of formation and decomposition of the complex at the external aqueous–organic interface were considered.

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1. Introduction

Gadolinium as a lanthanide element has found a variety of applications in nuclear and non-nuclear industries. Gadolinium oxide is widely used in the nuclear power industry as a shielding and fluxing device and it is used in general electric boiling water reactors as a burnable poison [1]. Gadolinium yttrium garnets are used in microwave applications and gadolinium compounds are used in making phosphorus for color TV tubes. About 1% of gadolinium is added to iron, chromium, and related alloys to improve the workability and resistance to high temperature and oxidation. The extreme low noise characteristics of gadolinium ethyl sulphate make it usable in duplicating the performance of amplifiers. Numerous gadolinium (III) complexes are used as active constituents of pharmaceuticals employed as constant agents in clinical MRI diagnostics [2].

The wide applications of gadolinium increased the demand for developing an advanced process to recover such element in high purity and large amount. Liquid membrane technique, as an advanced solvent extraction technique, has attracted great attention for its potential capability in the field of separation, recovery and preconcentration. Emulsion liquid membranes (ELMs) specifically are widely used in different applications [3]. It is reported that various metal ions [4–16] are successfully extracted by emulsion liquid membranes. Few papers

[17–23] were presented on the extraction of lanthanides by ELM.

The current work presents the possible recovery of Gd(III) from nitrate medium using ELM technique. Teramoto et al. [24] proposed a general mass transfer model for the extraction of weak bases and weak acids by ELM in which the diffusion in the W/O emulsion drops. The external mass transfer, chemical and phase equilibria were taken into account. Based on the proposed mass transfer model of Teramoto 1983 [24] and Chan and Lee model 1986 [25], the permeation rate of metal ions through ELM can be quantitatively explained by the proposed models.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical grade. All aqueous solutions were prepared with deionized water. The extractant 8-hydroxyquinoline was obtained from Aldrich and used without further purification. The surfactants used (Span-80, Arlacyle-A, Tween-85 and Span-85) were obtained from Fluka AG. HNO₃ was obtained from Prolabo. The aqueous solutions of gadolinium were prepared by dissolving its nitrate salt in deionized water. Toluene was obtained from Fluka AG.

2.2. Preparations

Unless otherwise stated, the membrane was prepared by mixing 25 ml of toluene containing 0.1 M 8-hydroxyquinoline as a carrier

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Nomenclature

A	concentration of metal ions, M
B	concentration of carrier, M
C	concentration of complex, M
D	molecular diffusivity, cm^2/s
H	concentration of hydrogen ion, M
K_A	overall mass transfer coefficient, cm/s
k_A	mass transfer coefficient of metal ions under investigation through the outer aqueous phase, cm/s
k_B, k_C	mass transfer coefficient of carrier and complex through the oil layer around W/O emulsion drop, respectively, cm/s
k_f	forward reaction rate constant, cm/s
k_m	mass transfer across the interface between the external phase and the membrane phase
k_{me}	mass transfer across the interface between the membrane phase and the internal aqueous phase
k_i	diffusion into the internal aqueous phase
R	radius of W/O emulsion drop
S	total interfacial area between external aqueous phase and W/O emulsion drop, cm^2
t	time, s
V	volume, cm^3
Φ	volume fraction of the internal aqueous phase in W/O emulsion drop
φ	volume fraction of W/O emulsion in W/O/W multi-phase emulsion
D_e	diffusion coefficient of metal ions in the external aqueous phase, cm^2/s
D_C	diffusion coefficient of complex in the membrane phase, cm^2/s
M	molecular weight of solvent
T_k	absolute temperature
V_B	molecular volume cm^3/mol
μ	viscosity of solvent
i	interface

and 2 ml of Span-80 as a surfactant. To this mixture, 25 ml of the stripping aqueous solution, HNO_3 (2 M), was added. The solution was then emulsified with an ultra-high speed homogenizer IKA, Ultra-Turrax T25 (USA). A stirring speed of 9000 rpm was used for 5 min to form the emulsion. The W/O emulsion was then poured into the external aqueous phase containing ions to be extracted. The system was stirred with a magnetic stirrer of the type Cole palmer (USA) of variable speeds. Samples were taken at interval times from the external aqueous phase for analysis using UV-vis spectrophotometer.

2.3. Determination and calculation

The concentration of gadolinium (III) was determined spectrophotometrically using Arsenazo-III [26]. In all experiments the results were taken in terms of concentration of metal ions permeated to the membrane at different time intervals. The permeation percentage (%P) was calculated by the relation:

$$\%P = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_t are the initial concentration of metal ions in the feed solution and its concentration after time interval t , respectively.

The stability of the prepared ELM was studied in terms of the degree of leakage of a yellow dye (as a tracer) from the internal

phase (stripping solution) to the external phase (feed solution) by the following expression [27]

$$\%B = \left(\frac{[\text{dye}]_{\text{ex},t}}{[\text{dye}]_{\text{in},o}} \right) \times 100 \quad (2)$$

where B is the emulsion breakage and the subscripts, ex,t and in,o , are the dye concentration in the external aqueous phase at time t , and its original concentration in the internal aqueous phase, respectively. The optimum operating conditions, if not specified, were as follows: initial concentration of metal ion = 100 ppm, treating ratio of the membrane to the external phase = 1:10, carrier concentration = 0.1 M 8-hydroxyquinoline (HOX), the concentration of HNO_3 in the external phase was 0.001 M and its concentration in the stripping phase was 2 M.

3. Results and discussion

3.1. Liquid-liquid extraction

Liquid-liquid extraction was first carried out to select the suitable conditions for the extraction and stripping processes to be applied in the ELM system for the recovery of Gd(III) ions from nitrate media using 8-hydroxyquinoline in toluene as a carrier. The influence of hydrogen ion concentration on the extraction of Gd(III) ions by 0.1 M 8-hydroxyquinoline in toluene was studied. The results obtained presented as a relation between hydrogen ion concentrations, $[\text{H}^+]$, and the values of the distribution ratio, D , on a log-log scale (Fig. 1). The relation obtained showed a general decrease in D as the $[\text{H}^+]$ increases. The slope value of the straight line was around -2 for the Gd(III) ions. The obtained data indicate the release of two hydrogen ions from 8-hydroxyquinoline into the aqueous medium.

The effect of 8-hydroxyquinoline concentration diluted with toluene on the extraction of Gd(III) from 0.001 M HNO_3 was investigated in the range of 0.01–0.1 M. The values of distribution ratio (D) were plotted versus the corresponding extractant concentrations on a log-log scale (Fig. 2). The data obtained shows that the D values of Gd increase linearly by increasing the carrier concentration and a slope equals three was obtained. Based on the slope analysis of the data obtained from the effect of hydrogen ion concentration and that of HOX concentration, the extraction equilibrium can be

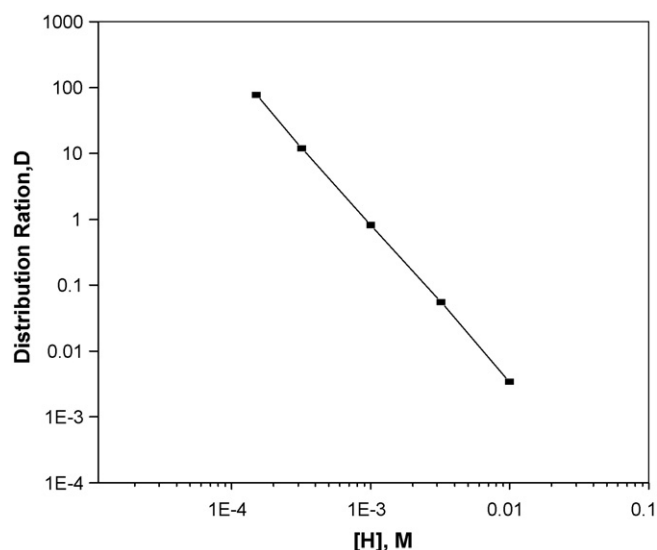


Fig. 1. Effect of hydrogen ion concentration on the distribution ratio of Gd(III) by 0.1 M HOX.

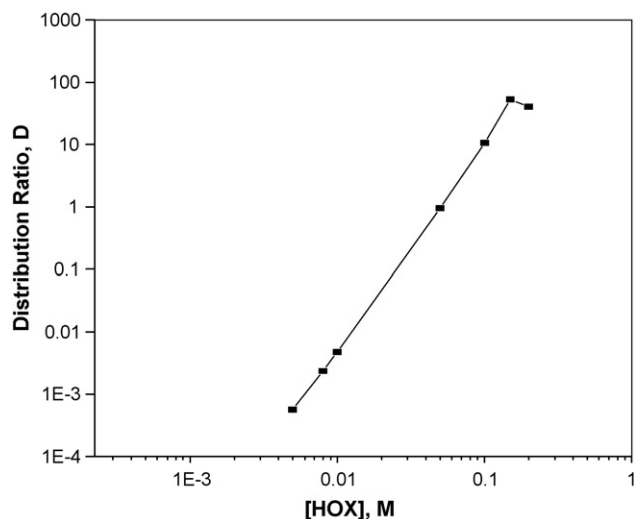


Fig. 2. Effect of HOX concentration on the extraction of Gd(III) from 0.001 M nitric acid.

represented by the following equilibrium:



The extraction constants (k_{ex}) of the formed metal complex species is given by

$$k_{ex} = \frac{[A(HB)(B)_2]_{org}}{[A^{3+}][HB]^3} = \frac{D[H^+]^2}{[(HB)^3]} \quad (4)$$

Aqueous solutions of HNO₃, H₂SO₄, HCl, Na acetate, Na oxalate and Na citrate were experimented as stripping agents. The data obtained are given in Table 1. It is clear that HNO₃ is the best stripping agent for Gd(III) ions from their organic phase.

3.2. Emulsion liquid membrane system

Based on the results from liquid–liquid investigations, a membrane system was prepared consists of 8-hydroxyquinoline in toluene as a carrier, HNO₃ as a stripper, span-80 as a surfactant. First, the stability of emulsion liquid membrane was studied. Membrane break-up causes a decrease in the separation efficiency due to the leakage of the separated ions from the internal aqueous phase to the external aqueous phase [28]. The different parameters affecting the permeation of Gd(III) through the selected membrane were also studied.

3.2.1. Effect of surfactant types

The effect of surfactant types on the amount of the tracer leaked from the internal aqueous phase to the external aqueous phase was studied using different surfactants with constant concentration 2% (v/v). The different surfactants experimented were Span-80, Arlacyl-A, Span-85, and Tween-85. The leakage percentage for the investigated surfactants was studied as a function of time (Fig. 3). It

Table 1
Stripping of Gd(III) from HOX in toluene with different stripping agents.

Stripping agents	% of Gd stripping
2 M HCl	85
2 M HNO ₃	90
2 M H ₂ SO ₄	83
2 M Na acetate	53
2 M Na oxalate	62
2 M Na citrate	46

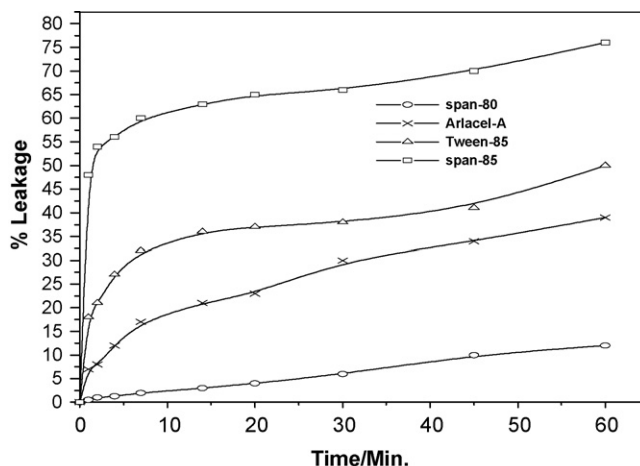


Fig. 3. Effect of different surfactant types on the stability of ELM.

was found that Span-80 shows the highest stability for the prepared emulsion membrane.

3.2.2. Effect of surfactant concentration

Since Span 80 showed the highest stability of the prepared membrane therefore the effect of its concentration on the amount of yellow dye leaked from the internal aqueous phase to the external aqueous phase was studied (Fig. 4). It was found that with increasing the surfactant concentration in the range 0.4–2.0%, the stability of emulsion globules increases. This is due to the fact that as the concentration of surfactant increases the surfactant will be adsorbed to a greater extent, hence a more compact and more strongly adsorbed interfacial film of surfactant molecules would be formed.

3.2.3. Effect of nitric acid concentration in the external aqueous phase

The effect of nitric acid concentration in the external aqueous phase on the permeation percent of gadolinium through the prepared ELM is given in Fig. 5. Different nitric acid concentrations were used ranging from 0.001 to 0.5 M. It was found that the permeation % of gadolinium decreases with increasing nitric acid concentration in the external aqueous phase. This may be due to at low nitric acid concentration, more metal–carrier complexes had formed at the feed membrane interface causing an increase in the concentration gradient which increases permeation of gadolinium

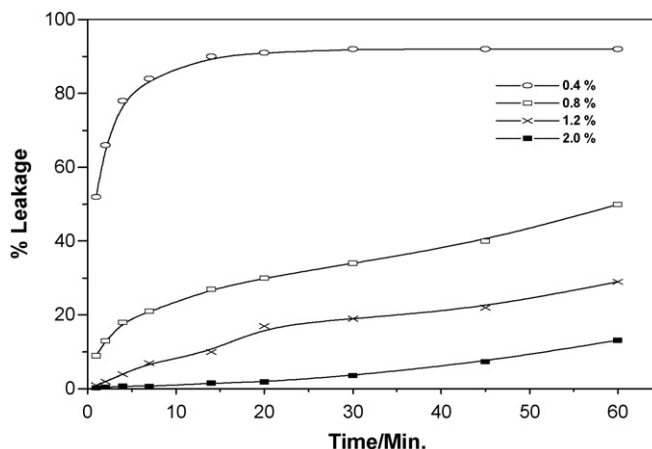


Fig. 4. Effect of span-80 concentration on the stability of ELM.

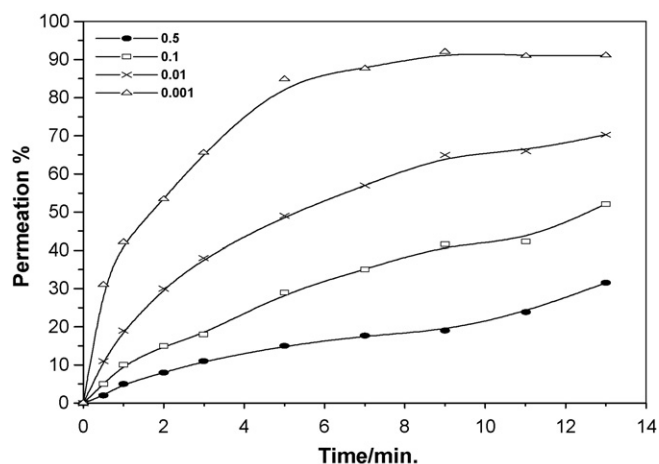


Fig. 5. Effect of nitric acid concentration in the external aqueous phase on the permeation % of Gd(III).

through the peripheral oil layer. At high nitric acid concentration, the univalent hydrogen ions are more concentrated at the membrane interface than the trivalent metal ions. This may result in a competition with the metal ions at the feed membrane interface and increasing the reverse reaction. Therefore, the permeation rate of the metal at interface decreases [24].

3.2.4. Effect of nitric acid concentration in the internal aqueous phase

The influence of nitric acid concentration in the internal aqueous phase on the permeation percent of gadolinium through ELM is given in Fig. 6. Different nitric acid concentrations ranging from 0.5 to 3.0 M were used. The results showed that the permeation of gadolinium increases with increasing nitric acid concentration from 0.5 to 2 M. This may be due to the increase in the capacity of the internal aqueous phase by increasing its concentration, which delay the accumulation of gadolinium carrier complex in the peripheral oil layer. Hence the concentration gradient of the complex in the membrane phase increases leading to increase in the permeation percent of gadolinium [14]. Further increase of nitric acid concentration up to 3 M causes a decrease in its permeation rate. This may be due to the decrease in the ELM stability on using higher concentration of nitric acid [29].

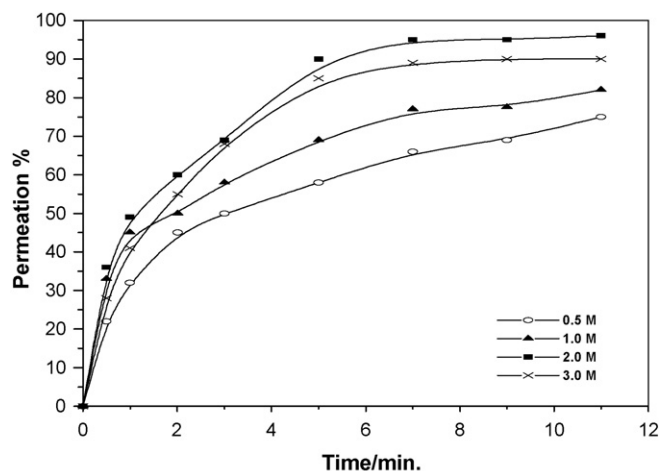


Fig. 6. Effect of nitric acid concentration in the internal aqueous phase on the permeation % of Gd(III).

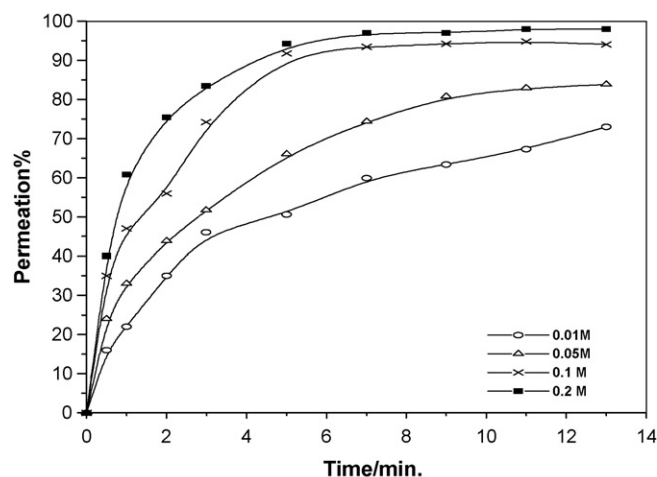


Fig. 7. Effect of HOX concentration on the permeation % of Gd(III).

3.2.5. Effect of 8-hydroxyquinoline concentrations

The effect of HOX concentrations as a carrier in the range from 0.01 to 0.2 M in toluene, on the permeation of gadolinium was studied. As shown in Fig. 7, the permeation percent increases with increasing HOX concentration. This is due to the fact that, with increasing HOX concentration, the formation of HOX/gadolinium ion complex is greater at the feed/membrane interface. Hence the concentration gradient increases in the peripheral oil layer, therefore increasing the percent of gadolinium permeation through ELM [30].

3.3. Modeling of the permeation process

A general permeation model for the permeation of gadolinium by emulsion liquid membrane using HOX as mobile carriers is presented. This model is based on that previously developed by Teramoto et al. [24]. The external mass transfer k_A around the drop, the rate of formation and decomposition of complex k_f at the aqueous/organic interface and the internal mass transfer of carrier and complex in the W/O emulsion drop k_B and k_C , respectively were calculated.

As shown in Fig. 8, the basic steps of metal permeation through the liquid emulsion membrane include the following: (i) the metal ion diffuses from the external aqueous phase to the boundary of the membrane phase, (ii) metal ion forms a complex with carrier on the external interface, (iii) the complex diffuses to the center of the emulsion globule, (iv) a stripping reaction occurs when the

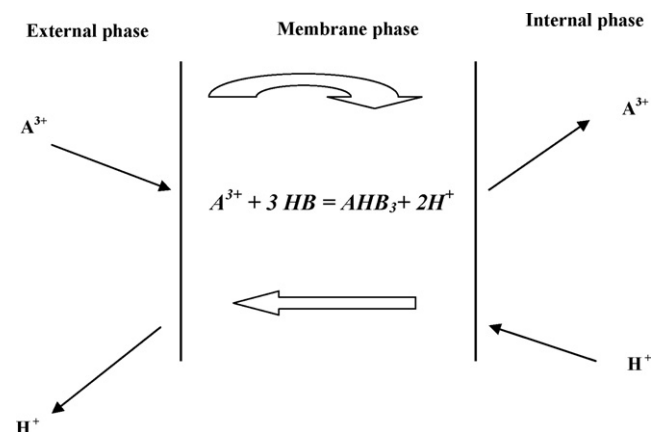


Fig. 8. Mechanism of facilitated transport of metal ion.

complex diffuses toward the internal aqueous phase and the metal ion is released to the internal aqueous phase, (v) carrier diffuses from the internal interface to the external interface and forms a complex again with the metal ion.

In order to simplify the mathematics of model development the following assumptions are made: (i) an ideal batch system is under complete mixing and constant temperature operation, (ii) carrier and solvent are insoluble in water, (iii) physical and transport properties are constant during the permeation process and (iv) the droplets dispersed in the emulsion globules are immobile and are uniformly distributed.

The values of k_A (the mass transfer around the drop) and k_f (the rate of formation of complex at the aqueous/organic interface) were obtained as follows; the rate determining step of gadolinium extraction changes depending on the experimental conditions that, $A_{I,0}$ (initial metal ion concentration in the external phase) is low compared with B_0 (initial concentration of carrier), the rate is limited by diffusion of gadolinium through the external aqueous stagnant film if H_I (hydrogen ion concentration in the external phase) is sufficiently low, and by the reaction at the interface of the emulsion drop if H_I is high. When the reverse reaction is ignored, the extraction rate is expressed as follows [20,31]:

$$\frac{V_I dA_I}{dt} = k_A S(A_I - A_{I,i}) = \frac{k_f S A_{I,i} B_i}{H_I} = \frac{A_I S}{1/k_A} + \frac{H_I}{k_f B_0} = K_A S A_I \quad (5)$$

Integration of Eq. (5) gives

$$\ln \frac{A_I}{A_{I,0}} = \ln y = - \left\{ \frac{K_A a_0}{1 - \Phi} \right\} t = \left\{ \frac{3K_A \Phi}{(1 - \Phi)R} \right\} t \quad (6)$$

where

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{H_I}{k_f B_0} \quad (7)$$

Experiments were carried out at various hydrogen ion concentrations with other conditions kept constant. As shown in Fig. 9, the plot of $\ln y$ against t gives straight lines. K_A values are calculated from their slopes. Fig. 10 indicates that the plot of $1/K_A$ against H_I also gives straight lines in accordance with Eq. (7). The values of k_A and k_f were calculated from their intercept and slope, respectively.

It was impossible to determine k_B or k_C in the W/O/W multiphase system, however, a rough estimate was made by the extraction experiment using an agitation vessel 7 cm and 14 cm height equipped with magnetic stirrer. 200 ml of the aqueous gadolinium solution was first introduced into the vessel. Then, 50 ml of the W/O emulsion phase was carefully poured over the aqueous phase so as not to disturb the interface.

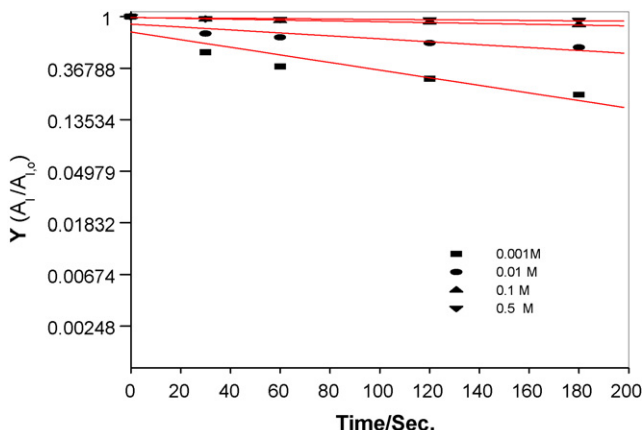


Fig. 9. Determination of $k_{k,s}$ of Gd(III).

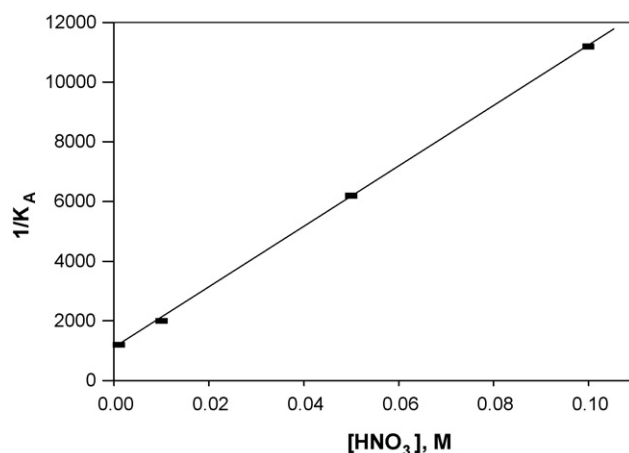


Fig. 10. Determination of mass transfer coefficient k_A and rate of formation of complex k_f of Gd(III).

Stirring in the emulsion phase was started at 100 rpm and samples were taken from the external aqueous phase for analysis. Under the condition that $A_{I,0}$ was sufficiently high and $H_{I,0}$ was considerably low, the resistance of the aqueous stagnant film diffusion and the interfacial reaction could be neglected. It was anticipated that the diffusion rate of the complex in the emulsion phase would be fast due to the convection caused by agitation. The experimental results are shown in Fig. 11.

Gadolinium concentration in the external aqueous phase decreased linearly with time, suggesting that, the rate of the extraction was independent of gadolinium concentration. This means that, on the aqueous side of the oil layer almost the entire carrier was consumed by complexation with gadolinium. Thus the extraction rate is expressed by

$$\frac{-V_I dA_I}{dt} = \frac{k_B S(B_0 - B_i)}{2} = \frac{k_B S(B_0 - 0)}{2} \quad (8)$$

from Eq. (8) and the data shown in Fig. 12 the value of k_B was calculated. The value of k_C was estimated using the relation

$$k_C = k_B \left(\frac{D_C}{D_B} \right) \quad (9)$$

The diffusion coefficient of carrier (B) and complex (C) estimated by Wilk-Chang is given in the following equations and given in

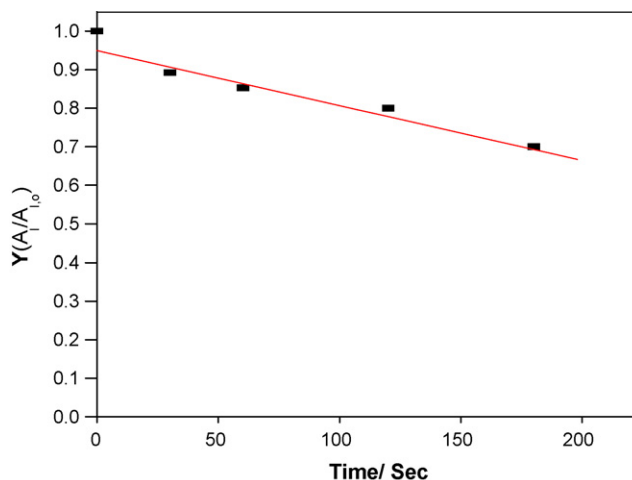


Fig. 11. Determination of mass transfer coefficient of carrier molecule in Gd(III) permeation.

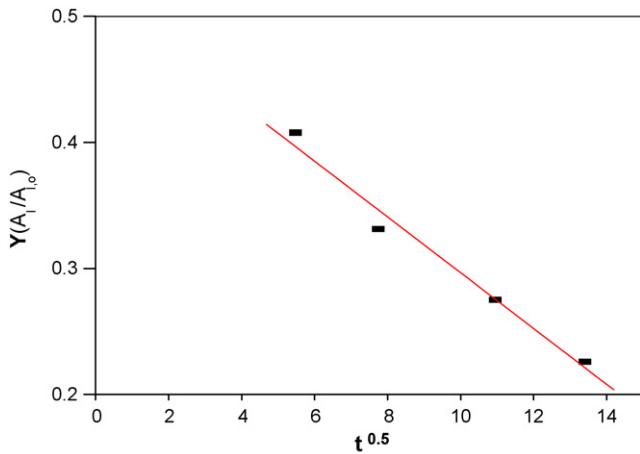


Fig. 12. Determination of diffusion coefficient of Gd(III) complex.

Table 2

The values of various physical parameters.

Parameters	Gadolinium
k_A	3.06×10^{-3} cm/s
k_B	7.15×10^{-4} cm/s
k_C	1.5×10^{-7} cm/s
D_B	2.08×10^{-5} cm ² /s
D_C	4.39×10^{-9} cm ² /s
k_f	1.6×10^{-3} cm/s
δ	290.9 μ m

Figs. 11 and 12

$$\frac{A_I}{A_{I,0}} = \frac{S(2\Phi D_C)^{0.5}(B_0 H_{III,0t})^{0.5}}{3A_{I,0}V_I} \quad (10)$$

$$D_B = \frac{7.4 \times 10^{-8}(\varphi M)^{0.5}T_k}{\mu V_B^{0.6}} \quad (11)$$

The oil layer thickness δ can be calculated as $\delta = D_B/k_B$. The values of k_A , k_B , k_C , D_B , D_C , k_f and δ for different investigated parameters are calculated and the results obtained are given in Table 2.

4. Conclusion

The results obtained from permeation of Gd(III) through the prepared ELM showed that, after 5 min of stirring, ~95% of Gd(III) can be permeated and separated using the prepared ELM from an external aqueous solution containing 100 ppm of Gd(III) dissolved in 0.001 M nitric acid medium.

Experimental data on the extraction of Gd(III) by emulsion liquid membrane using 8-hydroxyquinolin as a carrier were analyzed on the basis of general permeation model. In the general permeation model, the diffusion in the W/O emulsion drop, the external mass transfer around the drop, the rate of the formation, were addressed. The decomposition of the complex at the aqueous–organic interface, membrane thickness and the leakage of the internal phase to the external phase due to the membrane breakup were taken into account. The present model used in this study gives a better understanding and conforming to the experimental results.

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