

Research Article

Separation of Eu (III), Gd (III) and Permeation by Emulsion Liquid Membrane using Dicyclohexano-18-Crown-6 as Carrier DCTA in stripping phase

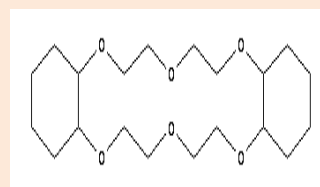
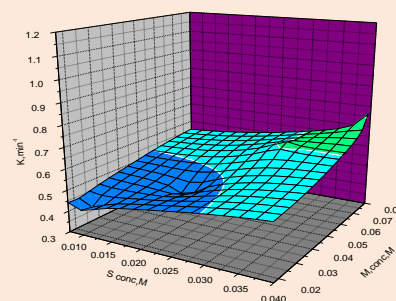
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Abstract

Separation of Eu(III), Gd(III) and permeation by emulsion liquid membrane by water/oil/water (w/o/w). ELM using Dicyclohexano-18-Crown-6 as a carrier, stripping phase DCTA, surfactant as Span 80/85 (ratio 3:1) was carried out experimentally under various operating conditions, study of the various parametric effects were considered under specific conditions. The effect of pH was studied in the range (1-4) and the rate constant was found to be (0.01-0.06), (0.001-0.07) min⁻¹ for gadolinium and europium respectively. The carrier parameter was studied in the range (0.1-0.4)M and the range was found to be (-0.065), (0.01-0.5) min⁻¹ for gadolinium and europium respectively. The effect of DCTA was in range (0.02-0.05)M while the rate constant was (0.06-0.09), (0.062-0.095) min⁻¹. The emulsion liquid membrane as the counter-transport of Eu(III), Gd (III) and H⁺ were facilitated by carrier of Dicyclohexano-18-Crown-6 in Kerosene and use of HNO₃ as feeding phase and DCTA as stripping phase. A simple model was experimentally deduced and in all conditions it is clear that the rate of gadolinium more than europium.

Keywords: Emulsion liquid membrane; Carrier; DCTA; pertraction; Eu(III) and Gd(III)



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Introduction

Liquid membranes have last decades before still one of the advancing and a promised technique in the future. Out of the various techniques available, such as precipitation, adsorption and solvent extraction, for the removal of metals from ammoniacal leach solutions, solvent extraction appears to be the most attractive. This is because it not only offers distinct advantages of ease and flexibility of operations, ability to handle wide range of concentrations and control over the selectivity of the separations, but also because it is a clean technique with the absence of sludge. In spite of these advantages, solvent extraction becomes uneconomical for treating leach solutions having low metal concentrations due to the large inventory of extractant, solvent and strip reagent, solvent losses, solvent carry over etc. These drawbacks can be circumvented using the emulsion liquid membrane technique (ELMs). Since its invention over forty years ago, emulsion liquid membranes and their variant supported liquid membranes have been used to separate a variety of solutes from aqueous as well as organic streams. [1] Studied the permeation of copper from ammoniacal-ammonium carbonate solutions using supported liquid membranes containing LIX 973N as extractant. [2] reported copper extraction from ammoniacal media using ELMs with LIX 54 as extractant and in our earlier studies [3] copper was extracted from ammoniacal solutions using LIX-84I as extractant. These investigations found that the rate of extraction was very fast, reaching quantitative removal in 2 min of contact between feed and emulsion. It was concluded that the loading of copper in the membrane phase governed the rate of extraction, whilst other

physico-chemical factors such as stripping acid concentration, emulsion drop size distribution etc. became important only when as the membrane material. Span 80 (Sorbitan mono-oleate), supplied by S.D. Fine Chemicals, was the emulsifier. The carrier, kerosene and the emulsifier were used directly as received from the manufacturer. Recently, liquid surfactant membranes (LSMs) have been widely applied in the field of biotechnology [1–4]. Most of these products are obtained from dilute aqueous solutions. However, during the extraction process there exist phenomena that the external phase water permeates through the membrane phase into the internal water phase to cause swelling of the emulsion [5]. Emulsion swelling is harmful to the separation efficiency of LSMs because it not only dilutes the extractant concentration in the inner aqueous phase, but also has negative effect on the stability of the emulsion system. Swelling can be classified into two completely different types. The first one is called entrainment swelling, which takes place only in the initial dispersion process. We have proposed the mechanism of entrainment swelling in a LSMs process for the separation of lactic acid and gave a corresponding mathematical model [6]. The second one is called permeation swelling, which occurs when there is a difference of osmotic gradient between the internal and the external aqueous phase. After all, it is very important to solve the swelling problems for the industrial process design as well as the perfection of the LSMs technique. Ohtake et al. [7] and Kinugasa et al. [8] proposed that the permeation swelling was caused by the trans membrane osmosis gradient between the internal and external aqueous phases. Colinart et al. [9] and Bart et al. [10] further pointed out that the characteristic hydrophilic groups of surfactants make this process inevitably occur. Wang and Fu [11] proposed the solubilization–diffusion mechanism for the permeation swelling and gave the corresponding mathematical model for estimating the permeation swelling rate. However, for carrier (extractant) facilitated transport, all above works do not take into account the carrier in the membrane phase, which belong to surface active agents and have special role in the separation process. Thien et al. [12] and Bart et al. [5] experimentally studied the permeation swelling of LSMs where membrane phases contain some carriers. But the different effects on the permeation swelling by surfactants and carriers, respectively, during water transport process were not explained. Only some empirical relations were concluded. In this paper, based on the above works, the permeation swelling mechanism of LSMs during the extraction process has been investigated. We take into account the effects on permeation swelling not only by surfactants but also by carriers. Moreover, a mathematical model for estimating the permeation swelling rate is proposed. Gadolinium is a constituent in many minerals such as monazite and bastnäsite, [13] which are oxides. The metal is too reactive to exist naturally. Ironically, as noted above, the mineral gadolinite actually contains only traces of Gd. The abundance in the earth crust is about 6.2 mg/kg [2]. The main mining areas are China, USA, Brazil, Sri Lanka, India and Australia with reserves expected to exceed one million tonnes. World production of pure gadolinium is about 400 tonnes per year. Gadolinium has no large-scale applications but has a variety of specialized uses. Gadolinium has the highest neutron cross-section among any stable nuclides: 61,000 barns for ^{155}Gd and 259,000 barns for ^{157}Gd . ^{157}Gd has been used to target tumors in neutron therapy. This element is very effective for use with neutron radiography and in shielding of nuclear reactors. It is used as a secondary, emergency shut-down measure in some nuclear reactors, particularly of the CANDU type [14].

Gadolinium is also used in nuclear marine propulsion systems as a burnable poison. Gadolinium also possesses unusual metallurgic properties, with as little as 1% of gadolinium improving the workability and resistance of iron, chromium, and related alloy alloys to high temperatures and oxidation. Gadolinium-153 is produced in a nuclear reactor from elemental europium or enriched gadolinium targets. It has a half-life of 240 ± 10 days and emits gamma radiation with strong peaks at 41 keV and 102 keV. It is used in many quality assurance applications, such as line sources and calibration phantoms, to ensure that nuclear medicine imaging systems operate correctly and produce useful images of radioisotope distribution inside the patient [17]. It is also used as a gamma ray source in X-ray absorption measurements or in bone density gauges for osteoporosis screening, as well as in the Lix is cope portable X-ray imaging system [15]. Relative to most other elements, commercial applications for europium are few and rather specialized. Almost invariably, they exploit its phosphorescence, either in the +2 or +3 oxidation state. It is a doping in some types of glass in lasers and other optoelectronic devices. Europium oxide (Eu_2O_3) is widely used as a red phosphor in television sets and fluorescent lamps, and as an activator for yttrium-based phosphors. Color TV screens contain between 0.5 and 1 g of europium oxide [16]. Whereas trivalent A recent (2015) application of europium is in quantum memory chips which can reliably store information for days at a time; these could allow sensitive quantum data to be stored to a hard disk-like device and shipped around the country [17]. So the separation of Eu^{+3} and Gd^{+3} is very important because it can be used as for many applications in nuclear, industrial, and environmental fields

Experimental

Apparatus and procedure

The formation of a stable emulsion membrane needs a high speed motor as well as special type impeller. A high speed stirring, (Eng.) Ltd, UK, of 7000 rpm was used; the stainless steel stirring rod was coupled to a specially designed turbine type plexi-glass impeller. Mixing of the external phase with the membrane was achieved by a magnetic stirrer obtained from Witey Electric (West Germany) of variable speed ranging from 100 – 14000 rpm. All experiments were carried out at stirring state between 200-1000 rpm. All samples used in this work were weighted using an analytical balance produced by Precisa (Switzerland), having maximum sensitivity of 10^{-4} g. Hydrogen ion concentrations in solutions were measured using a digital pH-meter of type CG-820 Schott Gerate from Germany a connected to a combined electrode which was standardized by suitable standard buffer solutions. The deviations in the readings were in the range of ± 0.02 at the laboratory temperature $25 \pm 2^\circ\text{C}$.

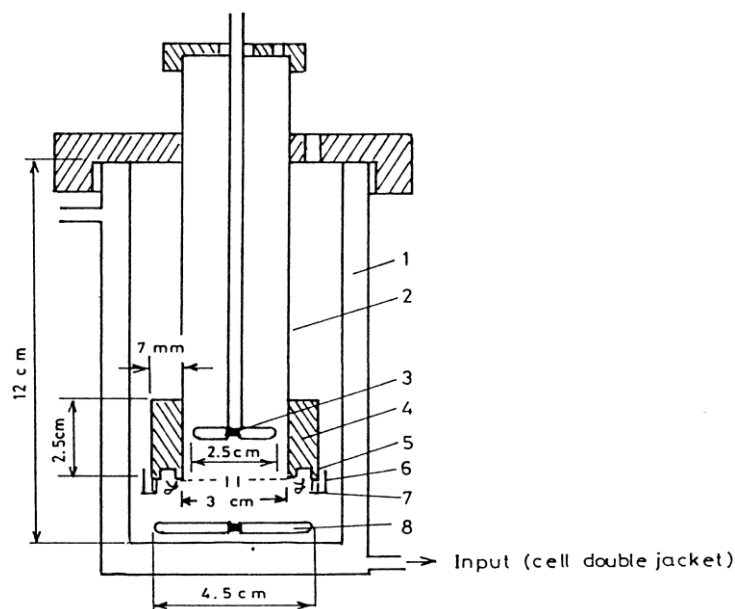


Figure 1 Scheme of Pertraction apparatus: (1) double shield glass outer vessel, (2) Plexiglas inner tube, (3) Teflon cross stirring blade, (4) Teflon holder, (5) silicon rubber ring, (6) niobium holder, (7) titanium holder, (8) magnet

Preparation of Reagent

The external aqueous solution [feed] was prepared by dissolving Eu(III) or Gd(III) for HNO_3 (2.5M) to produced $\text{Eu}(\text{NO}_3)_3$ or $\text{Gd}(\text{NO}_3)_3$ purchased from (Merk Ltd Co). The organic solution was prepared by dissolving Di-Cyclohexano-18-Crown-6 (Fluka) as carrier, using surfactant SPAN 80/85(monoleat span and trioleat) at different ratio (Fluka) as a surfactant in commercial GR grade of kerosene. The internal aqueous solution was prepared by dissolving a strong acid in distilled water. All chemical reagent grade or better, and were used as received. A water-in-oil addition (w/o/w) type emulsion was prepared by slow addition of the internal aqueous solutions to organic solution in a homogenizer) high speed generator 1300-1500rpm. Operating at a round 7000 rpm Gold steam (Eng.) Ltd, UK.

Preparation of Emulsion liquid membrane

Surfactant SPAN 80 and 85 were the products of Atlas Chemical Industries. Other chemicals were analytical grade. A turbin type impeller was used for preparation of the liquid membrane with membrane/stripping solution DCTA Diamino1,2(Cyclohexane /tetra acetic acid) and volume ratio $r_{II}=1$ at a mixing rate 4000-6000 rpm for 5-10 min. the extraction of multiple w/o/w emulsion was performed in a double. Jacketed cell thermostated at 15°C by stirring 5 ml of emulsion with a magnetic bar (50x10 mm) stirrer at 300-700 rpm with 50ml of outer [feed] solution, i.e. volume ratio $r_I=1$. some types of emulsions had a great stability for more than two months.⁽¹⁸⁾

Extraction procedure

The emulsion phase was added to the feed solution initially containing 500ppm of Eu(III) nitrate where the ratio of feed solution to membrane, and the solution was mixed at 300rpm for an extraction time of 20min. The emulsion liquid membrane was used in the study of the permeation of the metal ion. The formed complex between Eu(III) ions and Di-Cyclohexano-18-Crown-6. A diffuses through the liquid membrane to interface of the stripping inner droplets. Thus, there action of back-extraction occurred, where the Eu(III) is pre-concentrated in the stripping phase and the extractant is regenerated. All extraction experiments were carried out in batch system at the room temperature of 25°C. The experiment was repeated three times and Calculation. The average value of 20mL of aqueous solutions of Eu(III) were taken for analysis and their concentration were determined spectrophotometrically

Analytical subdual

The analytical subdual of the experiments was given in term of yield of extraction of metal ions, which is defined by Eq. (1). Yield of extraction

$$(Y) \% = \frac{C_0 - C}{C_0} \times 100 \dots\dots\dots (1)$$

Where C_0 and C are the initial and final concentration of Eu (III) in the feed phase, respectively. Mass transfer of these cations has been determined in terms of permeability coefficients (P) by measurement of metal concentrations in strip solution. The permeability coefficient increases with increase in pH acidity of feed solution¹⁻. The synthesis and spectroscopic study of the complexes of Eu(III) and Gd(III) with DC18C8 are described. The number of water molecules (n) in the first coordination sphere of the Eu(III) ion has been determined through comparison between the experimental and theoretical Stark levels, giving $n=3$, where the geometry of Eu(III) complex has been previously optimized using the Sparkle model. Based on this number of water molecules it has been predicted that the excited states for the complex Eu DC18C6·3H₂O and the results have been used to carry out an experimental and theoretical analysis of the intensities of the 4f–4f transitions and intramolecular energy transfer processe [1]. Solvent extraction is widely used in the recovery and separation of metals from aqueous solutions [2]. A limitation in traditional solvent extraction is that a large inventory of solvent is required, especially when processing dilute solutions. Liquid membrane systems have now become an alternative separation technique for metals from dilute solutions as they offer advantages over conventional solvent extraction such as the use of minimal amounts of solvent and low capital cost [2-5] The significant interesting aspects of SLM (supported liquid membranes) system are the continuous and simultaneous extraction and stripping of chemical species. The SLM system is interesting, attractive and effective because it can remove metal ions from dilute solutions with uphill ion transport mechanism [6-13]. The extractant was DC18C6, for the liquid-liquid extraction separation of metal ions. Although some investigations have been done on ion transport through liquid membrane by using extractant as carriers [14-19], the exploration of ion transport aspects of rare earth elements with solvating extractants are lacking. In order to consider its practical applications, ELM system consisting of two aqueous phases separated by a ELM carrier was explored for the preconcentration of rare earth metal ions from low concentration aqueous solutions [20-22]. It is essential to have a suitable choice of carriers with high stability. Although rare earth metals have attracted attention as magnetic, optical and superconducting materials, they have the inherent disadvantage that their mutual separation is very difficult because they have similar physical and chemical properties. Transport of Eu (III) and Gd (III) between aqueous oxide solutions through ELM containing (DC18C6 as a carrier in kerosen has been studied. Mass transfer of these cations has been determined in terms of Rate constants measurement of metal concentrations in strip solution.

Results and discussion

In emulsion liquid membrane experiments carried out in this work the following conditions are considered;

- The feed to the emulsion used is constant, i.e. a constant interface area for ion transport in the ELM, and

- The concentration of the separated elements in feed solution is much lower than the concentration of the carrier in membrane and their chemical interaction does not change the concentration of the carrier at the interface.

Therefore, a pseudo-first order kinetic law can approximate most of the results on membrane extraction (pertraction) according to the following:

$$C/Co = -Kt \quad (1)$$

$$\log \left(1 - \frac{R}{R_{\infty}} \right) = -kt \quad (2)$$

or

$$R = R_{\infty}(1 - e^{-kt}) \quad (3)$$

Where R is the yield of recovery (dimensionless fraction) at time t and R_{∞} is the yield at pseudo-equilibrium and k is the effective rate constant of membrane extraction (min^{-1}), which consists from a hydro dynamically influenced part and distribution dependent part. Therefore, all results were statistically treated by standard least-square method on a PC computer (program) to obtain the parameters R_{∞} and k. C is the metal concentration in feed against time, min^{-1} , Co is the initial metal concentration. The proposed mechanism of pertraction of Gd^{3+} and Eu^{3+} is shown in **Figure 2**.

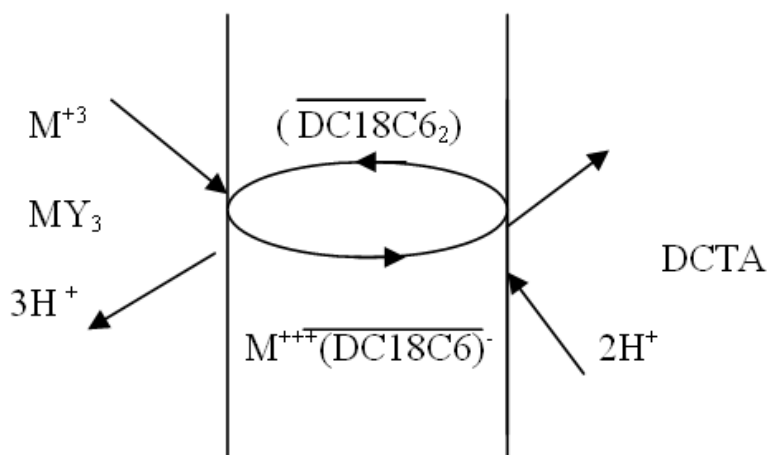
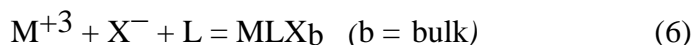
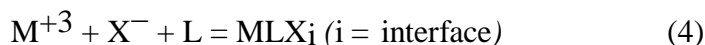


Figure 2 Mechanism of transport of M(Gd^{3+} or Eu^{3+}) by ELM.



The Effect of Feed Solution pH on Eu^{+3} and Gd^{+3}

Influence of the feed solution $\text{HNO}_3/\text{NaNO}_3$ acidity, pH(1-4), while NaNO_3 is kept constant .1M other wise stated. The **Figures 3** and **4** Dipect the transport of Gd^{+3} and Eu^{+3} against tim,min as a function pH .The rate of transport Gd^{+3} and Eu^{+3} as afunction of pH was studied the pH of the feed phase varied from 1 to 4 and the results was shown in respectively. The adjustment of pH was fixed by adding 0.1 mol/L NaOH drop wise to highly acidic feed solution. As seen in Figure 3 and 4. The Gd^{+3} and Eu^{+3} extraction percentage increased with increasing pH value from 1 up to 4. With further increase in feed phase pH from 4 to, Gd^{+3} and Eu^{+3} extractions percentage decreased studying. Effect of

feed acidic from pH(1-4). From this study, it was observed that with lowering the feed acidity the rate of metal ion transport also decreases. According to Eq. (2), the distribution ratio K_d will be decreasing as we lower the acidity of feed which in turn decrease the extraction of metal ion from feed side and hence decrease the rate of transport of metal ion. As observed, the experimental results very well with acceptable level of deviation. Figures 3 and 4 for Eu^{+3} and Gd^{+3} of extraction increases as the pH increases While $\text{Gd}^{+3} \gg \text{Eu}^{+3}$ due gadolinium break (4f-4f) transitions and intermolecular energy transfer process. From **Figures 5 and 6**, it is obvious that the optimum condition for rate constants of maximum extraction for Eu^{+3} and Gd^{+3} at pH(1-4), the rate of pertraction is 0.91 min^{-1} and 0.72 min^{-1} respectively for 0.04 M DC18C6 /kerosene, 0.08M DCTA stripping phase at pH=4 to give a pertraction yield 98% for Eu^{+3} and 60% for Gd^{+3} with maximum rate 0.3 min^{-1} respectively. Plotting log K against logarithm of the variables under study gives its power dependency. From the plot, it was found that at 25°C and the ratio of membrane weight to the outer phase 1:30. The rate of permeation of Eu^{+3} and Gd^{+3} can be represented by the following relations.

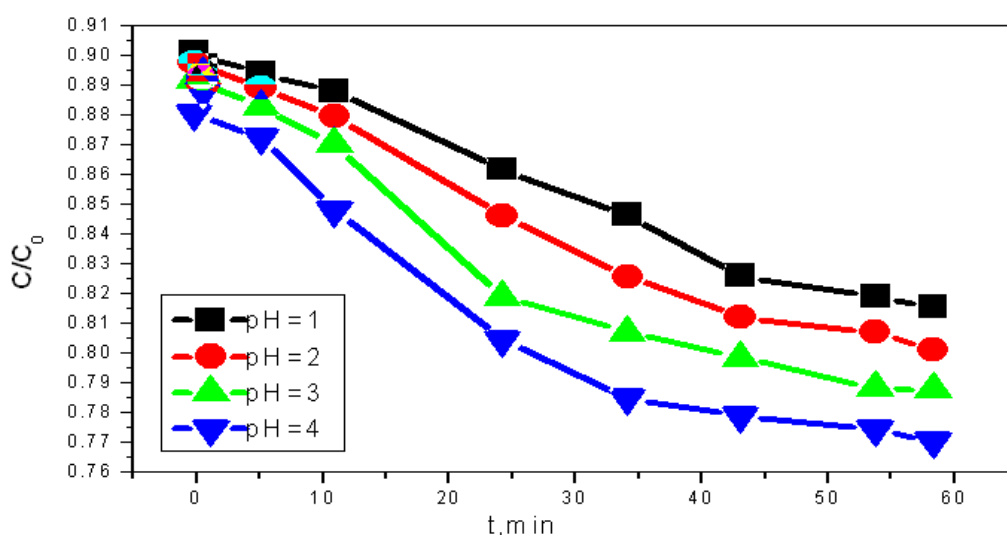


fig.3.plot of C/C_0 dimensions against time at t,min

for extraction of Gd^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA ,from feed= 0.1M NaNO_3 ,xpH,ELM.

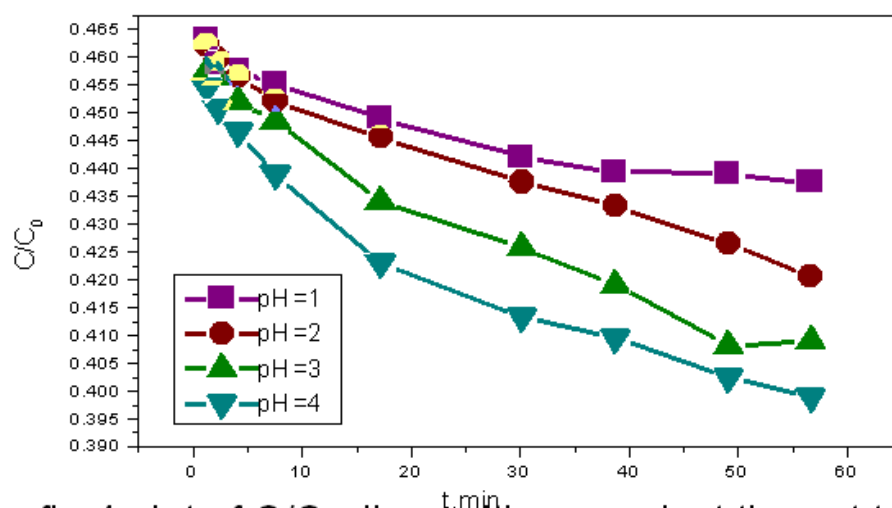


fig.4.plot of C/C_0 dimensions against time at t,min

for extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA ,from feed= 0.1M NaNO_3 ,xpH,ELM.

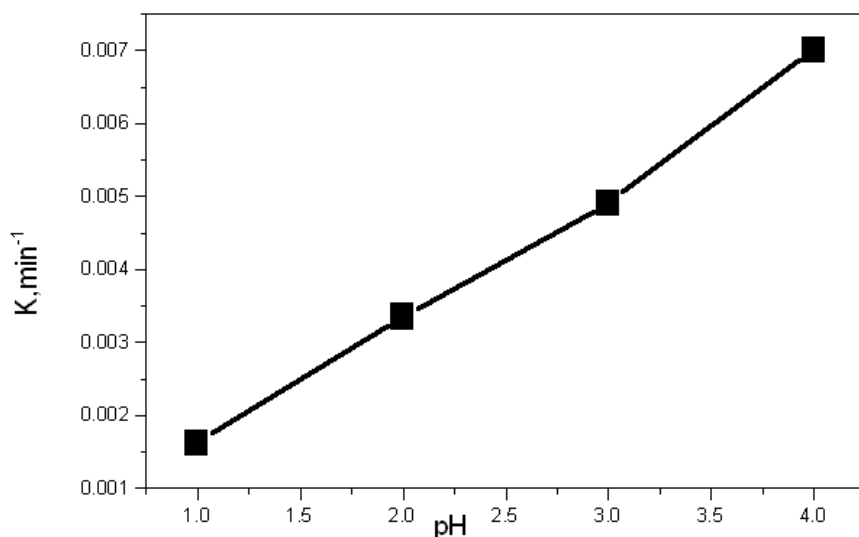


fig.5. Influence of pH on the rate constant K, min^{-1} of extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene, $S=0.02$ DCTA, from feed= 0.1M NaNO_3 , x pH, ELM.

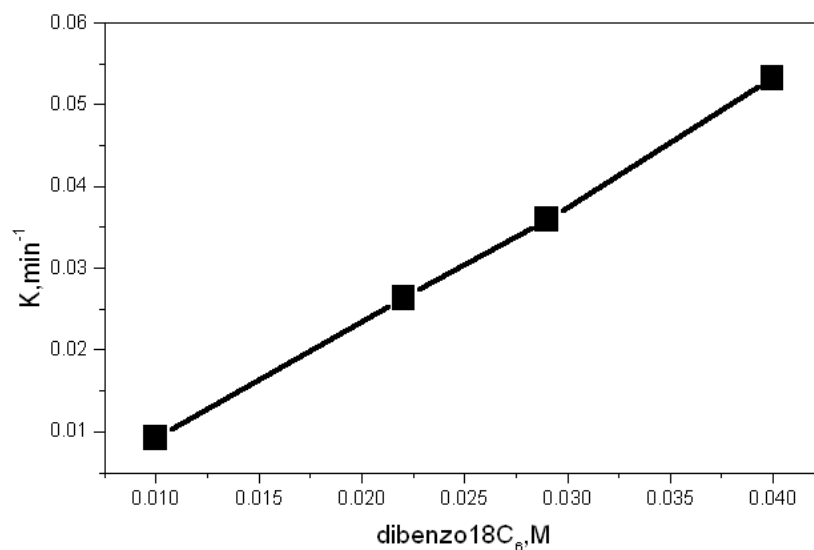
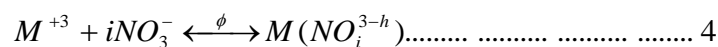
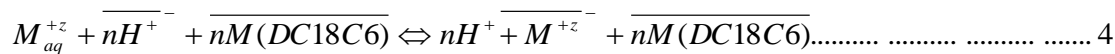


fig.6. Influence of pH concentration on the rate constant K, min^{-1} of extraction of Gd^{+3} by $M=0.04\text{M}$ DB18C6/kerosene, $S=0.02$ DCTA, from feed= 0.1M NaNO_3 , x pH, ELM.



$$\alpha_I = \left[\frac{m(NO_3^{3-I})}{m_{tot}} \right] - \frac{(\gamma_{M^{+3}})^{+3} (\gamma_{no_3^-}) / \gamma_{n(no_3)} \beta_I [NO_3]^i}{1 + \sum_1^4 (\gamma_M^{3+}) (\gamma(NO^-) / \gamma_{M(NO_3)^{3-i}})^2 \beta_i (NO^-)^i} \dots (5)$$

Where H_{aq}^{+} is the hydrogen ion concentration, β is the stability constant NO_3 is anion and M is the cations Eu^{+3} and Gd^{+3} , the bar indicates organic phase. The ELM is considered stable when its ability to mediate active mass transport in the system investigated conserved for a sufficiently pertraction time. ELM containing DC18C6/in kerosene was investigated as a function of the feed acidity and membrane composition. It is appeared, however, that HNO_3 acid acts as complexing agents in extraction of Eu^{+3} and Gd^{+3} ; in the case of the solvents with lower dielectric permeativity, it proceeds obviously in a form of ionic associated of the type $\text{Me}[\text{BC18C6}] [\text{NO}_3]_2$.

Effect of Carrier (DC18C6/kerosene)

Depending on the previous results, a composition of Gd^{+3} and Eu^{+3} is 0.1M MHNO_3 , for the membrane solution was chosen. Unless otherwise stated, the composition of feeding solution remained at 0.1M HNO_3 . The effect of membrane concentration (0.01-0.04 DM C18C6/kerosene M), **Figures 7 and 8** on the pertraction of Gd^{+3} and Eu^{+3} . It shows the five min, cm^{-1} e transport kinetics in terms of C/C_0 Vs time curves. It was noticed that there is a deviation from linearity after five min, cm^{-1} - five min, cm^{-1} of pertraction. It is obvious that the DC18C6 concentration moderately increases the initial flux of the metal through the membrane and exhibits a maximum at 0.04M DC18C6/kerosene. The rate of extraction was calculated for (0.01-0.04 M), **Figures 9 and 10** of carrier to give the rate K, min^{-1} in range (0.1-0.3) min^{-1} Figure 7-10 for gadolinium Gd^{+3} and Eu^{+3} , respectively. Where by comparing to Gd^{+3} and Eu^{+3} it shows a very high of for Gd^{+3} than Eu^{+3} for instance, the rate of membrane extraction can be influenced by viscosity of the membrane phase. The calculated values of the effective permeability coefficients of the extracted complex of Gd^{+3} is very high than Eu^{+3} in the membrane lie in a high, as shown in Figures 7 and 8. The permeability coefficients of the metal investigated through ELM calculated from the slopes of the linear parts of the C/C_0 Vs time` plot. It is clear that, there is an effective increase of rate constant for Gd^{+3} than Eu^{+3} upon the prescence of 0.04M DC18C6/kerosene. Alone, also increases upon the prescence of Gd^{+3} in the feed. This higher rate constant is probably due to an effect of gadolinium break. Very marked. Could be due to the evaluated the rate constant of Gd^{+3} and $\text{Eu}^{+3} \text{min}^{-1}$, from nitric acid concentration with 0.04M DC18C6/kerosene. The effect of viscosity on the diffusivity was also considered in the process of diffusion. An increase in viscosity, it is expected with the increase in the ligand concentration and thereby the diffusivity (D) of species of /complex will be affected by the following relation $\text{Do}_c (1/\eta)$ where η = viscosity of the medium. Viscosity was measured for different concentration of ligand and the diffusivity was experimentally measured for the case of 1 mm/L of DC18C6/kerosene ligand concentration of solution. By the above mentioned relation, diffusivity was calculated for other cases of ligand concentration.

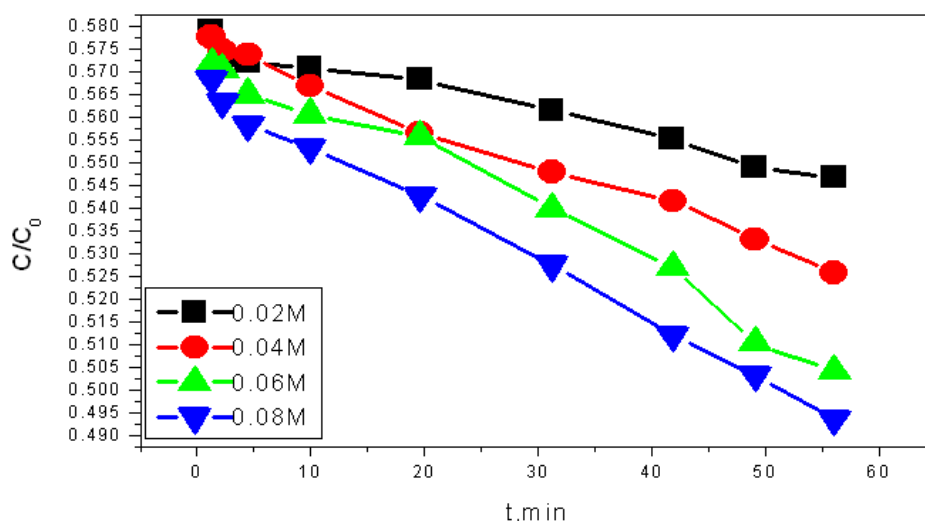


fig.7. plot of C/C_0 dimensions against time at t,min
for extraction of Gd^{+3} by M=0.04M DB18C6/kerosene
,S=xM DTPA ,from feed=0.1M NaNO_3 ,xpH,ELM.

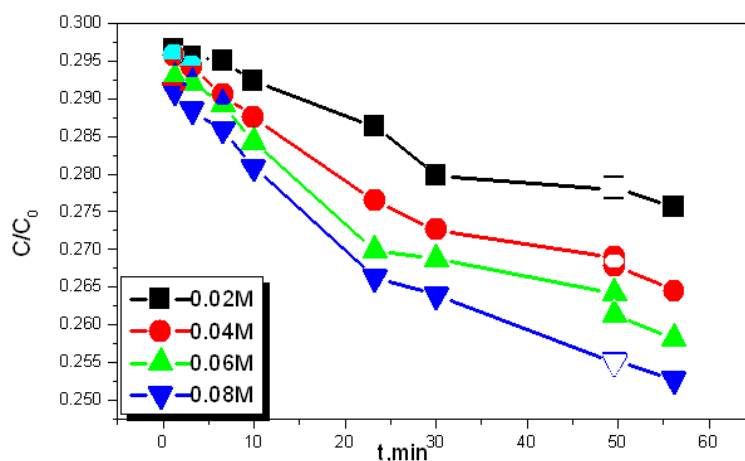


fig.8.plot of C/C_0 dimensions against time at t, min
for extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=x\text{M}$ DTPA ,from feed= 0.1M NaNO_3 , $x\text{pH}$, ELM.

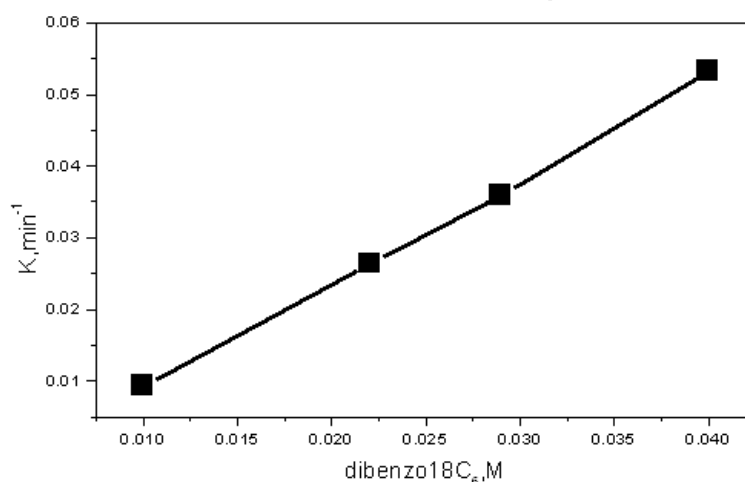


fig.9.Influence of membrane concentration on the rate constant
 K, min^{-1} of extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA ,from feed= 0.1M NaNO_3 , $x\text{pH}$, ELM.

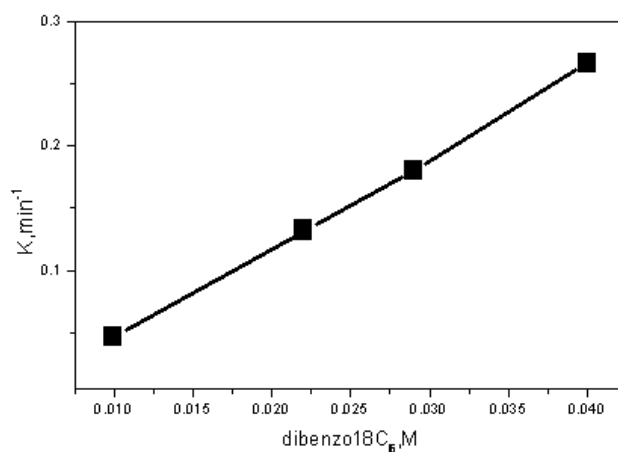


fig.10.Influence of membrane concentration on the rate constant
 K, min^{-1} of extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA ,from feed= 0.1M NaNO_3 , $x\text{pH}$, ELM.

Effect of stripping phase acid concentration DCTA

Figures 11 and 12, an increase in the internal phase stripping acid concentration increases the rate and extent of extraction as shown in **Figures 13 and 14**. In range (0.02-0.04), When DCTA was 0.02 M, the rate of extraction was minimum while at DCTA = 0.08 M the rate of extraction was maximum. At DCTA = 0.05M the rate was intermediate to the other two conditions, but rates are relatively closer to the case where DCTA was 0.08 M. (DC18C6)_{TOT} should give a straight line with slope of q . Since the Gd^{+3} and Eu^{+3} concentrations is low, the rate reaction in min^{-1} concentration of DC18C6 bound in the complexes can be neglected compared with the total initial extractant concentration. The effect of DCTA concentration on the pertraction rate was evaluated in range 0.01-0.08) min^{-1} . As in Figures 13, 14. To determine the slopes of the linear parts of the C/C_0 Vs time plot. It is clear that, there is an effective increase of rate constant for Gd^{+3} than Eu^{+3} upon the presence of 0.04M DC18C6/kerosene. Alone, also increases upon the presence of Gd^{+3} in the feed is higher for gadolinium than europium. His higher rate constant is probably due to an effect of gadolinium break. Very marked. Could be due to the evaluated the rate constant of Gd^{+3} and Eu^{+3} min^{-1} , from nitric acid concentration with 0.04M DC18C6/kerosene. While the rate constant (0.09, 0.06) for Gd^{+3} and Eu^{+3} . The minimization of the error-square sum defined by:

$$U = \sum (\log D_{cal} - \log D_{exp})^2 \quad (7)$$

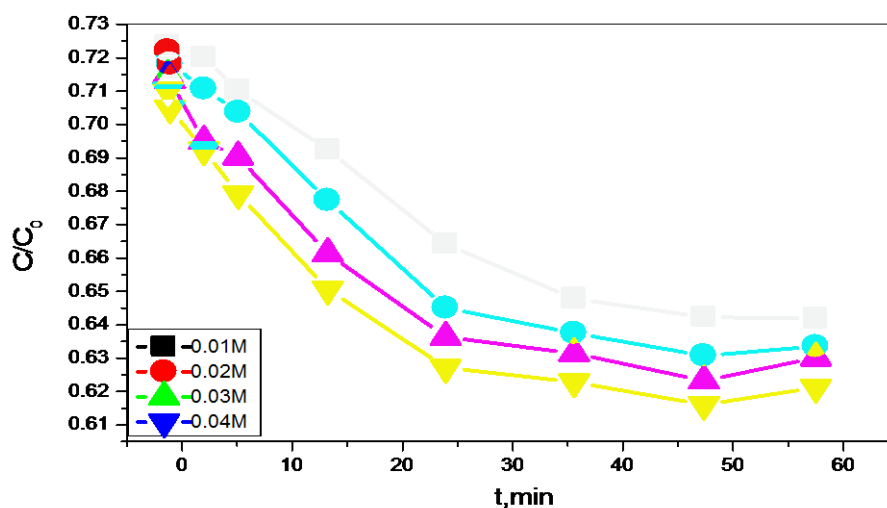


fig.11. plot of C/C_0 dimensions against time at t, min
for extraction of Gd^{+3} by $M=xM$ DB18C6/kerosene
, $S=0.02$ DCTA , from feed = 0.1M $NaNO_3$, pH=4, ELM.

Where D_{exp} is the experimental value of the distribution ratio and D_{cal} is the corresponding value calculated from the relevant mass balance equations for the proposed model. According to the results of the graphical analysis and taking into consideration other possible reactions, ie the extraction of HNO_3 by DC18C6 several metal- DC18C6 species are introduced. The corresponding values of the formation constants and the values of statistical parameters that quantify the goodness of the proposed system to fit the experimental data.

A mathematical stripping model was developed to analyze and predict the transport of Eu^{+3} and Gd^{+3} by ELM from aqueous solution containing nitrate medium, DC 18C6 in kerosene in xylene as membrane and DCTA as stripping phase. The analysis of pertraction rates based on the ionization constants of DCTA and different pH's is proposed and tested on a mathematical model. Under various experimental conditions, the transport of Eu^{+3} and Gd^{+3} can be governed by either of, the mass transfer of the external boundary layer, by diffusion in the membrane phase, or by combination of these effects. The proposed model satisfactorily predicts the experimental results. A mathematical model we plotted as 3-D dimension **Figures 15 and 17**, and contour lines **Figures 16 and 18** for gadolinium and europium respectively. Under various experimental conditions, the transport of Gd^{+3} and Eu^{+3} can be governed by either of, the mass transfer of the external boundary layer, by diffusion in the membrane phase, or by combination of these effects. The proposed model satisfactorily predicts the experimental results.

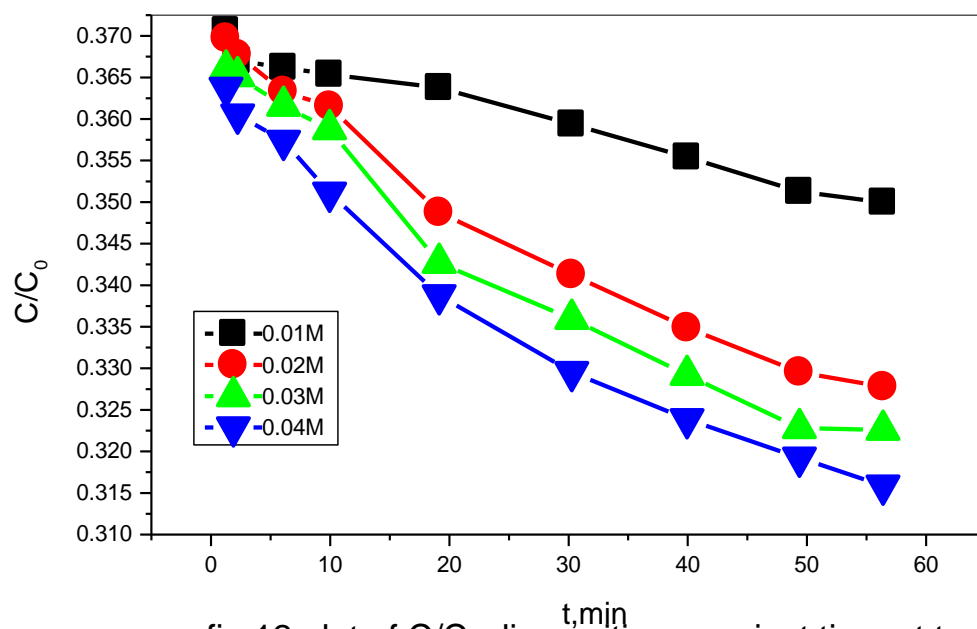


fig.12. plot of C/C_0 dimensions against time at t, min
for extraction of Eu^{+3} by $M=x\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA, from feed= 0.1M NaNO_3 , $\text{pH}=4$, ELM.

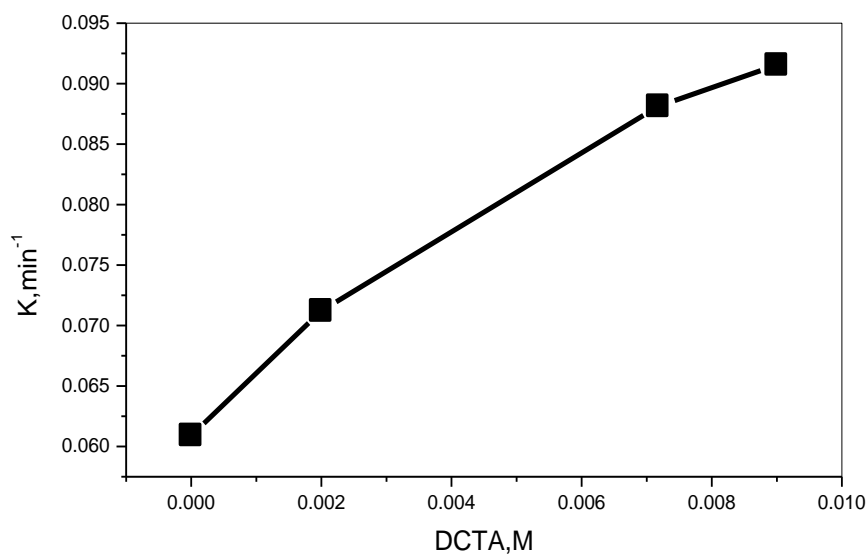


fig.13. Influence of strip concentration on the rate constant
 K, min^{-1} of extraction of Eu^{+3} by $M=0.04\text{M}$ DB18C6/kerosene
, $S=0.02$ DCTA, from feed= 0.1M NaNO_3 , pH , ELM.

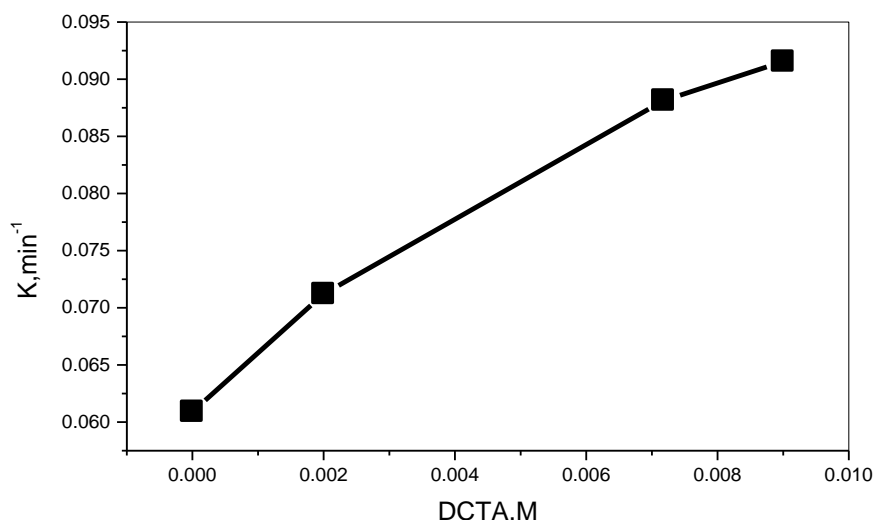


fig.14. Influence of strip concentration on the rate constant

K, min^{-1} of extraction of Gd^{+3} by $M=0.04\text{M}$ DB18C6/kerosene, $S=0.02$ DCTA, from feed= 0.1M NaNO_3 , xPH, ELM.

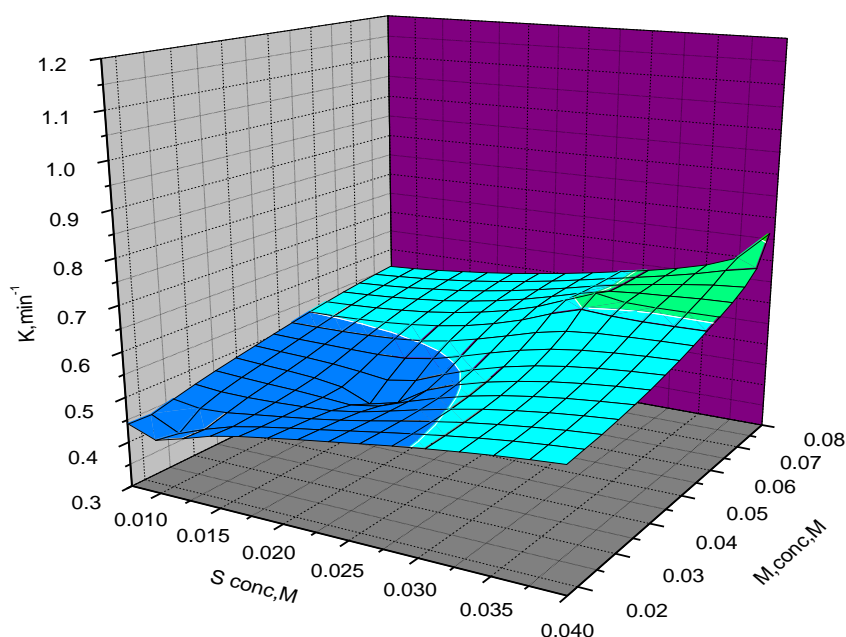


fig.15.3-D optimization between 0.08M DC18C6/kerosene, 0.04M S and k^{-1} for pertraction of Gd^{+3} by ELM

Optimization

Figures 15-18. The transport of Gd^{+3} and Eu^{+3} in all is obvious that the optimum condition for maximum extraction for Eu^{+3} and Gd^{+3} as 0.04M DC18C6 /kerosene, 0.08M DCTA stripping phase at $\text{pH}=4$ to give a pertraction yield 98% for Eu^{+3} and 60% for Gd^{+3} with maximum rate 0.3 min^{-1} respectively. Plotting $\log K$ against logarithm of the variables under study gives its power dependency. From the plot, it was found that at 25°C and the ratio of membrane weight to the outer phase 1:30. The rate of permeation of Eu^{+3} and Gd^{+3} can be represented by the following relations.

$$\frac{d_c}{d_t} = K[pH]^{0.6}[DC18C6]^{0.3}[DCTA]^{0.44} \dots\dots\dots \text{for Gd}^{+3} \quad (8)$$

$$\frac{d_c}{d_t} = K[pH]^{0.2}[DC18C6]^{0.16}[DCTA]^{0.3} \therefore \dots\dots\dots \text{for Eu}^{+3} \quad (9)$$

For the above relation it is obvious that pertraction rate depend strongly on the DCTA concentration at pH= 4 which is completely satisfied with the experimental results.

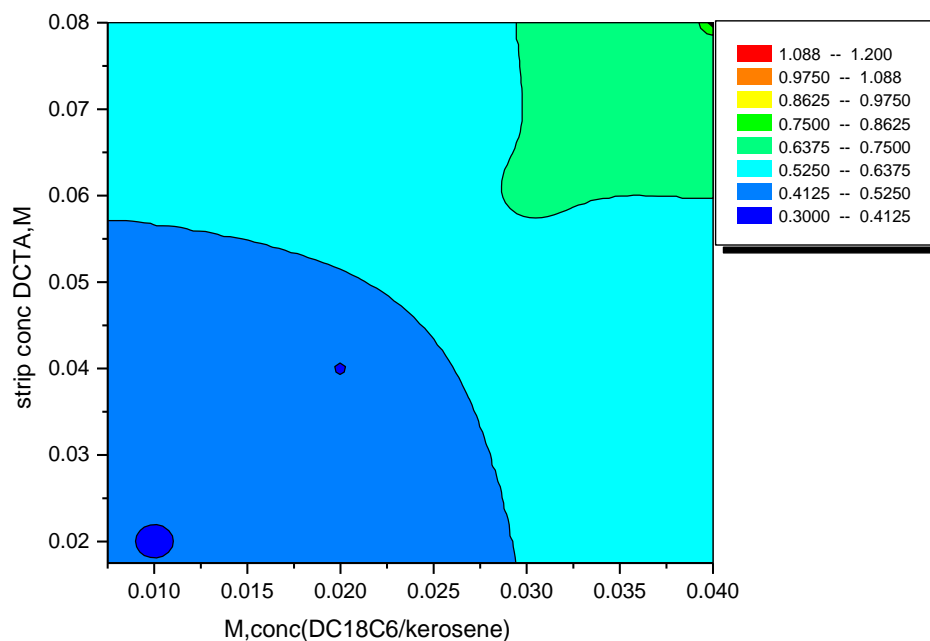


Figure 16 Contour plot for Gd^{+3} pertraction by DC18C6/kerosene as strip, Stripping DCTA, M by ELM

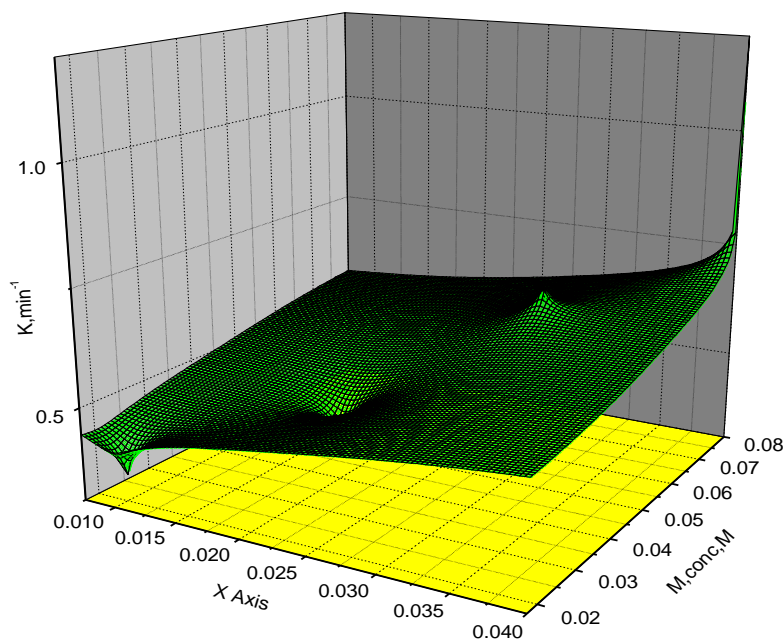


fig.17.3-D optimization between 0.08M DC18C6/kerosene ,0.04 M S and k^{-1} for pertraction of Eu^{+3} by ELM

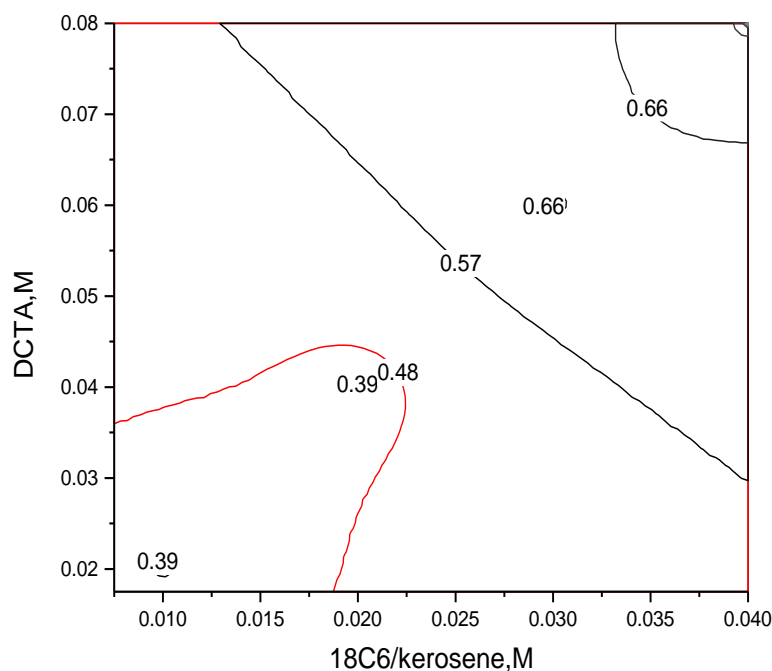


fig.18. Contour plot for Gd^{+3} pertraction by DC18C6/kerosene as strip, Stripping DCTA, M by ELM

Conclusion

A mathematical stripping model was developed to analyze and predict the transport of Eu^{+3} and Gd^{+3} by ELM from aqueous solution containing nitrate medium, DC 18C6 in kerosene in xylene as membrane and DCTA as stripping phase. The analysis of pertraction rates based on the ionization constants of DCTA and different pH's is proposed and tested on a mathematical model. Under various experimental conditions, the transport of Eu^{+3} and Gd^{+3} can be governed by either of, the mass transfer of the external boundary layer, by diffusion in the membrane phase, or by combination of these effects. The proposed model satisfactorily predicts the experimental results.

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