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Studies on the mechanism of transport of lanthanide ions through supported liquid membranes containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier

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Abstract

Praseodymium and holmium have been chosen as representative elements of light and heavy lanthanides, respectively, to characterize the extraction reactions of these elements that are responsible for their separation through supported liquid membranes (SLM) from nitrate media by using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as extractant. In the conditions studied, it has been demonstrated, the formation of two species that can be described as $Ln(NO_3)A_2(HA)_3$ and $LnA_3(HA)_2$, where Ln represents the lanthanide cation and HA the acidic extractant D2EHPA. These results have been obtained by using both graphic and numeric treatments of solvent extraction data. The first one was based on the slope analysis, and the second one, on the use of LETAGROP-DISTR program. The formation constants and relative predominance of each species were calculated. A mechanism for the formation of given species was proposed. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Supported liquid membrane; Solvent extraction; Speciation; Lanthanides; Di-(2-ethylhexyl) phosphoric acid

1. Introduction

There are lots of extractants which are suitable to carry out the separation of lanthanides by both solvent extraction or liquid membranes. Among them, D2EHPA has been widely used and it has provided very good results [1,2]. By studying the variation of the permeability coefficient of lanthanide metals through SLM as a function of the pH of the feed aqueous solution it can be observed that it increases initially with pH, having a maximum in the pH range 3–4 (depending on the element), and then, the coefficient falls down, the permeation being practically nonexistent at pH 4–5 [2,3]. This effect could be due to the formation of several chemical species between the lanthanide ions and D2EHPA, and probably, some of them not being able to permeate through the SLM. In general, the existence of a single species formed between the lanthanide cations and D2EHPA in the organic phase is mainly accepted [1,4]. This species is formed as follows:

$$Ln^{3+} + 3(HA)_2 \rightleftharpoons LnA_3(HA)_3 + 3H^+ \quad (1)$$

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where Ln^{3+} is the lanthanide cation, and HA represents D2EHPA, acid that forms dimers in organic solution [5]. Nevertheless, some authors refer to the existence of other species in organic phase. Thus, Lundqvist et al. [6] reported the formation of a species similar to that shown in reaction (1), but with one of the molecules of extractant in monomeric form:

$$Ln^{3+} + 5/2(HA)_2 \rightleftharpoons LnA_3(HA)_2 + 3H^+ \qquad (2)$$

On the other hand, Sato [7] mentioned the formation of the species $DyCl_3(HA)$, besides $DyA_3(HA)_3$, when the acidity was higher than 2 mol l^{-1}. Recently, Anticó et al. [8] reported the formation of two species, $YA_3{\cdot}2HA$ and YA_3HA, in the solvent extraction of yttrium from chloride media for low and middle metal concentration (1.5×10^{-4}–2.587×10^{-2} mol l^{-1}).

Thus, it follows the importance of speciation studies as an important tool to establish the mechanism of transport of chemical species through SLM. In general, the studies of speciation can be undertaken in two different ways: by identifying all the chemical species present in a system in equilibrium or by determining those that can be subjected to a separation process previous to the identification process without suffering any change. In the first one, the information to evaluate the stability and stoichiometry of the species can be obtained directly, without any previous separation process. In the second case, the study needs two steps. The first step involves the separation of the chemical species, and the second one is the identification of the separated species.

With the exceptions of cerium and europium, the occurrence of the lanthanides is mainly in the trivalent form. Thus, the speciation studies should be addressed to establish the different interactions of these elements with different ligands.

Among the different techniques employed in the studies of the speciation of rare earth elements, solvent extraction is one of the most frequently used [9] and it can be applied both using a batch methodology or a two-phase titration, where the investigated parameters are evaluated in situ [10]. In this work, we report the results obtained on the speciation of rare earth elements in organic solution. To analyse distribution data, both graphical and numerical methodologies were employed. The stoichiometry of the species and corresponding formation constants were obtained.

2. Experimental

2.1. Reagent and solutions

Di-(2-ethylhexyl) phosphoric acid, D2EHPA (pure reagent, Carlo Erba, Italy), was used as extractant, dissolved in kerosene (low odor, Aldrich, USA) previously washed with NaOH 0.5 mol l^{-1} and HCl 0.5 mol l^{-1}, and then several times with bidistilled water. An organic 1 mol l^{-1} stock solution was prepared by dissolving D2EHPA in kerosene. Final D2EHPA concentration was varied between 0.5 and 10 mmol l^{-1}.

Aqueous stock solutions containing Pr^{3+} or Ho^{3+}, 2.5 mmol l^{-1}, were prepared by dissolving $Pr(NO_3)_3$ or Ho_2O_3 (analytical grade, Fluka, Switzerland) in 0.1 mol l^{-1} HNO_3 and standardized chelatometrically.

Xylenol Orange (Panreac, Spain) and cetylpyridinium bromide (pure, Aldrich, USA) were used as received. All other reagents were of analytical grade purity and purchased from Panreac, Spain.

2.2. Apparatus

Two-phase titration experiments were carried out into a thermostated bath TFB-5 Serie C, SBS (Spain). Aqueous and organic phases were mixed by using a magnetic stirred, Selecta (Spain). The variation of pH was monitored by a pH-meter model 2002, Crison (Spain) equipped with a glass electrode model 52-50, Crison (Spain) and an Ag/AgCl reference electrode model 52-41, Crison (Spain).

Lanthanide concentrations in the aqueous phase were on-line monitored by a FIA spectrophotometric method based on the formation of a coloured complex between the lanthanide ion, xylenol orange and cetylpyridinium bromide [11] which consisted of a model M312 four-path peristaltic pump, Gilson (France), equipped with Tygon tubing, Elkay (USA), a model 1106 injection valve, Omnifit (UK), a model Novaspec II VIS spectrophotometer, Pharmacia (Sweden), an 80 μl flow cell, Hellma (Germany) and a model E586 recorder, Methrom (Switzerland). Transport lines

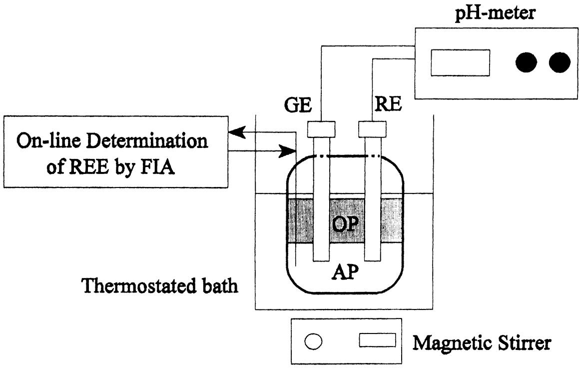

Fig. 1. Schematic representation of experimental manifold. OP: organic phase; AP: aqueous phase; GE: glass electrode; RE: reference electrode.

were made with 0.8 mm i.d. teflon tubing, Tecator (Sweden). Fig. 1 shows a schematic representation of experimental manifold.

2.3. Procedure

The experimental procedure to obtain the solvent extraction data involved two steps. First, the glass electrode used in pH measurements was in situ calibrated into the aqueous phase, in the absence of metal and in the presence of organic solvent, by following the Gran procedure [12]. The aqueous phase consisted of 0.1 mol l^{-1} nitrate solution (HNO_3, $NaNO_3$) and initial pH between 1 and 2. After introducing both the glass and the reference electrodes, the organic solvent (kerosene) was added without extractant. The different volumes of standardized NaOH 0.1 mol l^{-1} were added, and when the equilibrium was reached, the potential was measured, and so, E^0 was calculated. Once the glass electrode was calibrated, the needed volume of the stock solution of Pr^{3+} or Ho^{3+} (initial metal concentration was 4.5 μg ml^{-1}) and D2EHPA were added to aqueous and organic phases, respectively. The volume ratio between phases was kept constant and equal to 1.

After that, the system was mixed up to equilibrium, and then, pH and metal concentration in aqueous phase were measured. Metal concentration in organic phase was calculated by difference. As stability criterion, variations lower than 0.1 mV in 5 min (potential) and 0.001 absorbance units in 15 min (concentration) were chosen. Furthermore, the existence of equilibrium was verified by back titration. This process was repeated for each experimental point.

The addition of reagents was done in a different way depending on the experiment. Two different kinds of experiments were performed:

1. *Metal distribution in function of acidity of the aqueous phase*. Three different series of experiments were performed for each metal. In the case of Pr^{3+}, the pH was varied between 1.7 and 3.0 while D2EHPA concentration was kept constant and equal to 2, 5 and 8 mM for each series. In the case of Ho^{3+}, the pH values were between 1.0 and 2.3, being 1, 2 and 3 mM the concentration of D2EHPA in each series of experiments.
2. *Metal distribution in function of D2EHPA concentration in the organic phase*. Two series of experiments were performed for each metal. D2EHPA concentration in the organic phase was varied between 1 and 9 mM for Pr^{3+}, being the pH 2.02 and 2.37 for each series. In the experiments with Ho^{3+}, D2EHPA concentration was varied between 0.5 and 10 mM, and pH were 1.22 and 1.40, respectively.

3. Results

The extraction data were treated by using two different procedures. First, a preliminary graphic analysis was done, and afterwards a more exhaustive numerical treatment was applied.

Graphic analysis. In general, the extraction of lanthanide ions, Ln^{3+}, with D2EHPA, HA, can be expressed as follows:

$$\mathrm{Ln}^{3+} + \frac{(m+n)}{2}(\mathrm{HA})_{2\mathrm{org}} \rightleftharpoons \mathrm{LnA}_m(\mathrm{HA})^{3-m}_{n\,\mathrm{org}} + m\mathrm{H}^+ \tag{3}$$

where, for the sake of simplicity, we have supposed the no influence of ionic medium and the formation of mononuclear species, which is reasonable for the concentration of metal used.

From Eq. (3) we can obtain the expression:

$$\log D = \log K_{\mathrm{ex}} + \frac{(m+n)}{2}\log[(\mathrm{HA})_2] + m\mathrm{pH} \tag{4}$$

where D is the distribution ratio of lanthanides between the organic and aqueous solutions and K_{ex} is the extraction constant. Thus, by representing log D vs. pH and log D vs. log[$(HA)_2$] we will obtain the values of coefficients m and n, and then we will establish the stoichiometry of the species formed in the organic phase and will calculate their extraction constants.

Numerical analysis. After the graphic analysis had been performed, the distribution data were analysed with the LETAGROP-DISTR program [13]. This program allows to select the model that better explains the behaviour of the studied system. So, by using the experimental data, the computer calculates the formation constants of the species included in each model by minimizing the error-square sum

$$U = \sum_{1}^{N_p} (\log D_{\text{calculated}} - \log D_{\text{experimental}})$$

for the N_p experimental points available.

3.1. Speciation of Pr^{3+}

3.1.1. Graphic analysis

The results obtained for the variation of log D on pH are shown in Fig. 2. As can be observed, straight lines with a slope value 3 were obtained in the extraction experiments with 5 and 8 mM D2EHPA. This indicates the formation of at least one species, formed by exchanging three protons. When D2EHPA concentration was lower (2 mM), the slope obtained was 2.5, indicating the formation of at least two species, one formed by exchanging three protons (probably the same than before) and another one with only two protons. In this case, a nitrate ion must be present in the complex to preserve the neutrality. The presence of nitrate in these kind of complexes has been previously reported [14,15]. From above it follows that the coefficient m can assume the values 3 and 2.

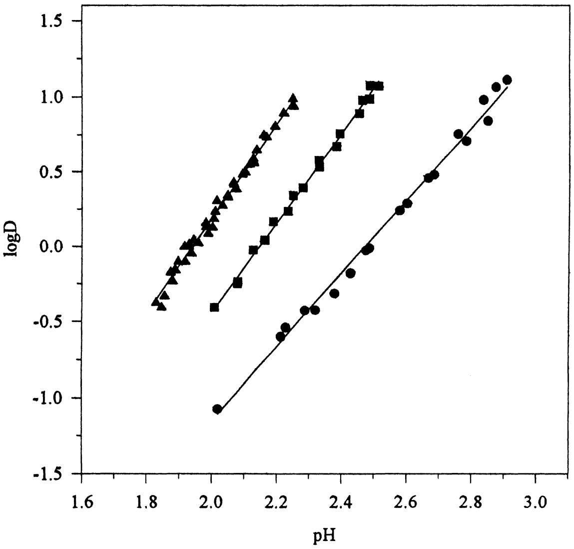

Fig. 2. Variation of log D of praseodymium vs. pH at different D2EHPA concentrations: (●) 2; (■) 5; (▲) 8 mM.

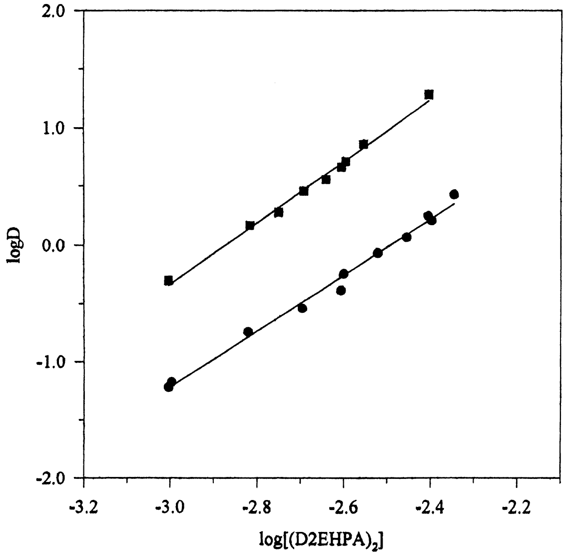

Fig. 3. Variation of log D of praseodymium vs. D2EHPA concentration at different pH values: (●) 2.02; (■) 2.37.

Fig. 3 shows the variation of log D on D2EHPA concentration, considering this extractant as a dimer. For both pH values the slope of the line obtained was 2.5. With these results, and by using expression (4), we can conclude that the sum of the coefficients m and n must be 5, and then the stoichiometry of the species formed in the organic phase can be calculated. These species, together with their extraction constants (calculated from Eq. (4)), are shown in Table 1.

3.1.2. Numerical analysis

Among the different models tested, the results obtained for the most significant ones are given in Table 2. As can be observed, best results were obtained with model 1, which is in agreement with

Table 1
Species of Pr^{3+} and Ho^{3+} in organic phase and their formation constants, obtained with graphic analysis

m	n	Species	log β
3	2	$PrA_3(HA)_2$	12.14
2	3	$Pr(NO_3)A_2(HA)_3$	14.57
3	2	$HoA_3(HA)_2$	14.96
2	3	$Ho(NO_3)A_2(HA)_3$	16.83

graphic analysis. All the models containing the species mainly mentioned in the bibliography, $PrA_3(HA)_3$ were either rejected or gave worse results. Model 3 was rejected because of the higher errors obtained for the formation constants.

Thus, the reactions regarded as responsible for the extraction seem to be:

$$Pr^{3+}+5/2(HA)_{2org} \rightleftharpoons PrA_3(HA)_{2org}+3H^+ \quad (\beta_{Pr(032)})$$

$$Pr^{3+}+NO_3^-+5/2(HA)_{2org} \rightleftharpoons Pr(NO_3)A_2(HA)_{3org} +2H^+ \quad (\beta_{Pr(123)})$$

the formation constant being: log $\beta_{Pr(032)}$=12.12±0.04; log $\beta_{Pr(123)}$=14.7±0.1, where subscripts denote NO_3^-, A^- and HA, respectively.

With the obtained results, the distribution diagram for the system $Pr^{3+}-NO_3^--$D2EHPA was constructed and is shown in Fig. 4. As can be observed, $Pr(NO_3)A_2(HA)_3$ is the first species formed in the organic phase and is predominant in the pH range 1.8–2.7. This can be correlated with the experiments performed for the separation of lanthanides with supported liquid membranes (SLM) [2,4]. The perme-

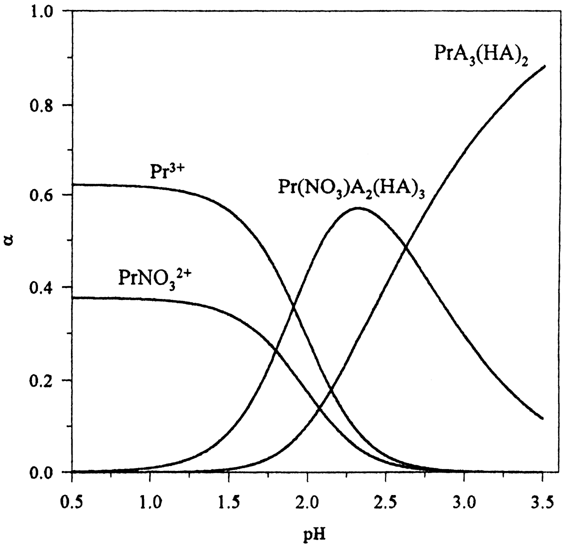

Fig. 4. Distribution diagram of $Pr^{3+}-NO_3^--$D2EHPA system for a volume ratio 1:1 (org:aq). Experimental conditions: Pr^{3+}: 3×10^{-5} M; D2EHPA: 5×10^{-3} M; NO_3^-: 0.1 M.

Table 2
Results of numerical analysis for the different extraction models, using the LETAGROP-DISTR program, for Pr^{3+} (N_p=76) and Ho^{3+} (N_p=54)

	Model	Species	log β	U	σ(log D)
Pr^{3+}	1	$PrA_3(HA_2)$	12.12±0.04	0.151	0.045
		$Pr(NO_3)A_2(HA)_3$	14.7±0.1		
	2	$PrA_3(HA)_3$	15.94±0.03	0.552	0.086
		$Pr(NO_3)A_2(HA)_3$	Rejected		
	3	$PrA_3(HA)_2$	12.1±0.1	0.139	0.044
		$Pr(NO_3)A_2(HA)_3$	14.55 MAX 14.81		
		$PrA_3(HA)_3$	15.21 MAX 15.55		
Ho^{3+}	1	$HoA_3(HA)_2$	13.78 MAX 14.44	0.440	0.100
		$Ho(NO_3)A_2(HA)_3$	17.77±0.08		
	2	$HoA_3(HA)_3$	17.60 MAX 18.54	0.446	0.101
		$Ho(NO_3)A_2(HA_3)$	17.8±0.1		
	3	$HoA_3(HA)_2$	13.78 MAX 14.56	0.441	0.146
		$Ho(NO_3)A_2(HA)_3$	17.8±0.1		
		$HoA_3(HA)_3$	Rejected		

The error in the constant is given as ±3σ(log β). For $\sigma(\beta)\geq0.2\beta$ the 'best' value of log β and the maximum value MAX(log[β+3$\sigma\beta$]) are given. $\sigma(\log D)=(U/(N_p-N_k)^{1/2})$ indicates the standard deviation in log D (N_p and N_k are the number of experimental points and adjusted constants, respectively).

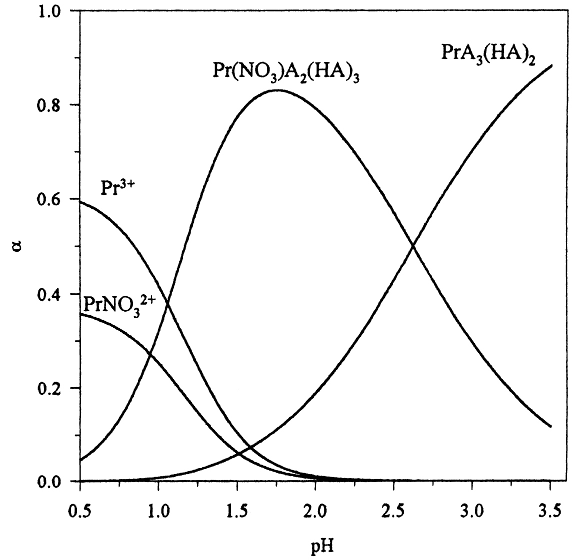

Fig. 5. Distribution diagram of $Pr^{3+}-NO_3^--$D2EHPA system for a volume ratio 1:1250 (org:aq). Experimental conditions: Pr^{3+}: 3×10^{-5} M; D2EHPA: 5×10^{-3} M; NO_3^-: 0.1 M.

ability coefficient of Pr^{3+} through the SLM was observed to increase from pH 1 to 2.5 and then, it decreased up to pH 3.5–4. So, the species mentioned before can be assumed to be responsible for the transport of Pr^{3+} through the SLM. To confirm this fact, the distribution diagram was recalculated for the volume ratio occurring in the liquid membrane system (1:1250/organic:aqueous). As shown in Fig. 5, the predominance of the species $Pr(NO_3)A_2(HA)_3$ increased notably, reaffirming our hypothesis.

3.2. Speciation of Ho^{3+}

3.2.1. Graphic analysis

The procedure performed was similar to that followed for Pr^{3+}. The results obtained for the variation of log D vs. pH and D2EHPA concentration are shown in Figs. 6 and 7, respectively. The species formed in the organic phase in the $Ho^{3+}-NO_3^--$D2EHPA system were identical to those formed for Pr^{3+}, and are included, together with their formation constants, in Table 1.

3.2.2. Numerical analysis

The results of the computer analysis of the models studied for Ho^{3+} are also included in Table 2, the results being again very similar to those obtained for Pr^{3+}. In this case, the reactions proposed as responsible for the extraction of Ho^{3+} are:

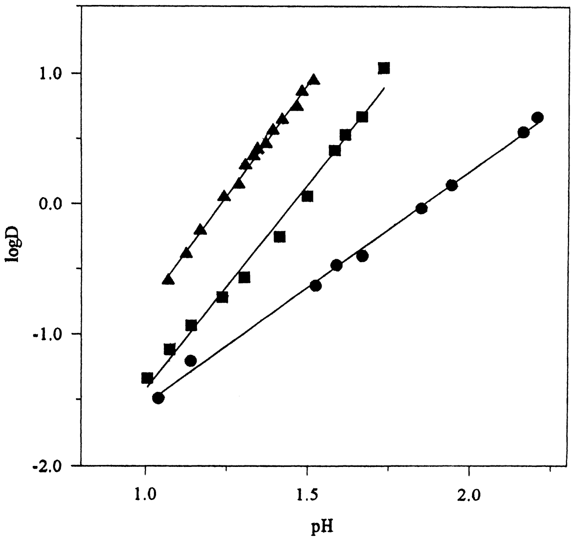

Fig. 6. Variation of log D of holmium vs. pH at different D2EHPA concentrations: (●) 1; (■) 2; (▲) 3 mM.

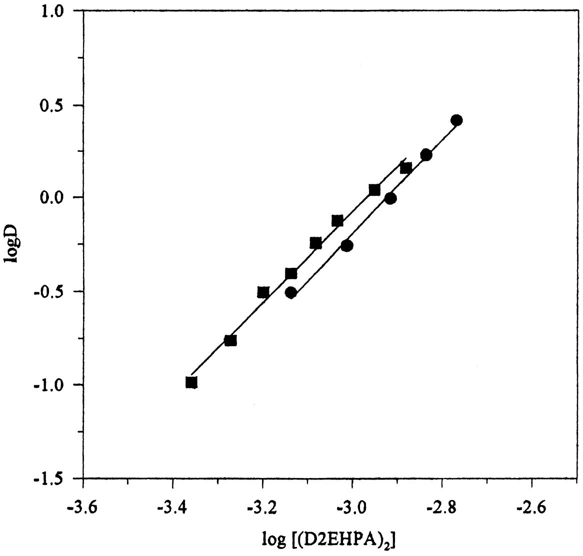

Fig. 7. Variation of log D of holmium vs. D2EHPA concentration at different pH values: (●) 1.22; (■) 1.40.

$$Ho^{3+}+5/2(HA)_{2org} \rightleftharpoons HoA_3(HA)_{2org}+3H^+ \quad (\beta_{Ho(032)})$$

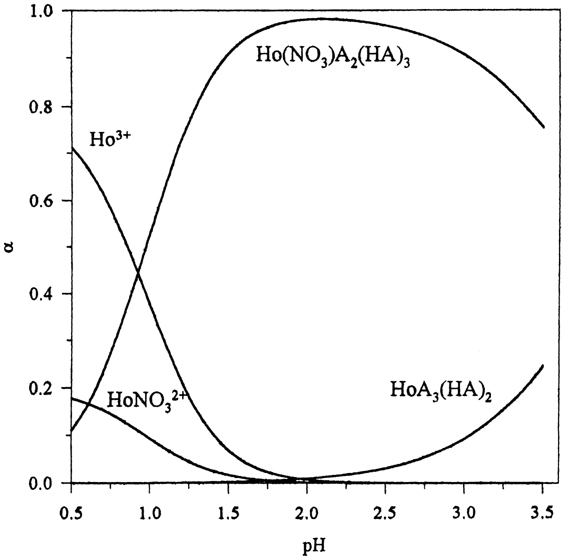

Fig. 8. Distribution diagram of Ho^{3+}–NO_3^-–D2EHPA system for a volume ratio 1:1 (org:aq). Experimental conditions: Ho^{3+}: 3×10^{-5} M; D2EHPA: 2×10^{-3} M; NO_3^-: 0.1 M.

$$Ho^{3+} + NO_3^- + 5/2(HA)_{2org} \rightleftharpoons Ho(NO_3)A_2(HA)_{3org} + 2H^+ \quad (\beta_{Ho(123)})$$

the formation constant being: $\log \beta_{Ho(032)}=13.78$ MAX 14.44; $\log \beta_{Ho(123)}=17.77\pm0.08$.

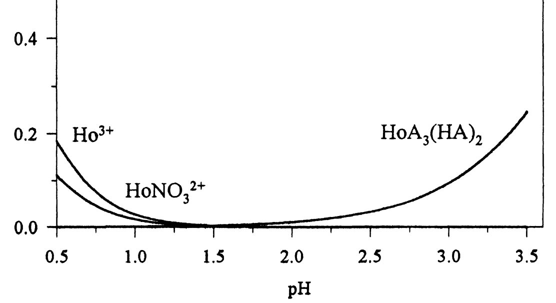

Fig. 9. Distribution diagram of Ho^{3+}–NO_3^-–D2EHPA system for a volume ratio 1:1250 (org:aq). Experimental conditions: Ho^{3+}: 3×10^{-5} M; D2EHPA: 2×10^{-3} M; NO_3^-: 0.1 M.

With these results, the distribution diagrams for volume ratios of 1:1 and 1:1250 were calculated and plotted in Figs. 8 and 9, respectively.

As observed, the behaviour of the system was very similar to that shown for Pr^{3+}, but the predominance of the species $Ho(NO_3)A_2(HA)_3$, responsible for the transport though SLM, was even higher for Ho^{3+} than for Pr^{3+}.

4. Conclusions

It can be concluded that, in the studied conditions, two species are formed in the organic phase when the extraction of lanthanides from nitrate media is performed with D2EHPA dissolved in kerosene. In general, these two species can be described as $Ln(NO_3)A_2(HA)_3$ and $LnA_3(HA)_2$ and they strongly depend on the pH of the feed aqueous solution. The first species increases its predominance when advancing in the lanthanide series and it is responsible for the transport of lanthanide cations through supported liquid membranes. In this case, the mechanism of transport is a coupled transport mediated by a carrier, and more exactly, of coupled counter-transport type. Due to the presence of nitrate ions in the transported complex, this anion is co-transported from feed to stripping solution. Thus, this complex is transported across the membrane and on its downstream side the reverse reaction proceeds. Energy for lanthanide transport is gained from the transport of protons from the stripping acid solution to the feed aqueous solution, with higher pH value.

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