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Selective transport of lanthanides through supported liquid membranes containing non-selective extractant, di-(2-ethylhexyl)phosphoric acid, as a carrier ☆

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Abstract

Permeation of lanthanides (Ln) between aqueous nitrate solutions of different acidity through supported kerosene membrane containing di-(2-ethylhexyl)phosphoric acid (DEHPA) as a carrier has been studied. Mass transfer of Ln cations has been determined in terms of permeability coefficients (*P*) by on-line FIA measurement of metal concentrations in strip solution.

Acidity of feed solution ranged from pH 1.2 to 4.2 (ionic strength 0.1 mol l^{-1} (HNO_3, $NaNO_3$)) while that of strip solution was kept constant at 0.1 mol l^{-1} HNO_3. Carrier concentration has been changed in the range from 10 to 10^3 mmol l^{-1}. Both, the *P* versus feed pH plots measured at low and at high DEHPA concentrations as well as *P* versus DEHPA concentration plots exhibited maxima. Permeability coefficients were decreasing when advancing in the lanthanide series and significant differences in behaviour of individual lanthanides has been observed. The conditions of separation of light and heavy lanthanides and mutual separation of light lanthanides have been suggested. Based on these and previous results, composition of transported species, presence of maxima on measured curves, and formation of gel-like substance in feed solution and on membrane-feed solution interface are discussed.

Keywords: Supported liquid membranes; Di-(2-ethylhexyl)phosphoric acid; Lanthanides; Separation; Speciation

1. Introduction

Separation of individual lanthanides is difficult because of their similarity in chemical properties. Solvent extraction and ion exchange processes are mainly used both in laboratory and in the process industry. However, development of efficient, economical and environment friendly procedures is desirable. Among other extractants as e.g., phosphinic acids [1] and macrocycles [2], dialkylphosphoric acids and, above all, di-(2-ethylhexyl)phosphoric acid (DEHPA) are widely used in extraction chemistry of lanthanides and in their supported liquid membrane (SLM) separations [3–10].

The kinetics of Eu permeation and its mass transfer mechanism in SLM system containing DEHPA as a carrier have been investigated previously [3] and similar SLM has been used for separation of rare earth elements from their binary mixtures [4]. Study

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☆ This paper is dedicated to the memory of Dr. Josef Doležal.

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of lanthanide transport through SLM with DEHPA placed between HCl solutions of different acidity has shown that transport rate exhibits maximum at a certain carrier and HCl concentrations [5]. Decrease of the transport rate at higher carrier concentrations has been explained in terms of decrease of diffusion coefficients while that at lower acidity of the feed solution has been interpreted as a result of membrane effective area reduction due to the deposition of gelled material formed in feed solution. Occurrence of gelled substance has been also mentioned in solvent extraction system. Formation of such a substance on both membrane interfaces was also reported in the study of Eu transport retardation by acetate ions [6]. It was supposed that the solid phase appearing in the system is Eu–DEHPA polymer.

In contrast to usually reported $LnA_3 \cdot 3HA$ (or $Ln(AHA)_3$) species responsible for lanthanide extraction with dialkylphosphoric acids, HA, the extraction of Y(III) from chloride media into kerosene containing DEHPA has been explained by formation of the two species, $YA_3 \cdot 2HA$ and $YA_3 \cdot HA$, [7]. Possibility of occurrence of mixed complexes containing chloride was rejected. At metal concentrations of order 10^{-2} mol l^{-1}, presence of a gel has been observed in aqueous phase. To explain the effects observed in SLM experiments, speciation of lanthanides in solvent extraction system has been studied recently [8]. The lanthanides have been extracted from nitrate media into kerosene phase containing DEHPA. The extraction equilibria is explained by formation of two extractable species of stoichiometry $Ln(NO_3)A_2(HA)_3$ and $LnA_3(HA)_2$. The predominance of the species $Ln(NO_3)A_2(HA)_3$ versus pH follows the pattern of permeation through SLM containing DEHPA, which was already observed for Pr(III) and Nd(III), where a maximum of the permeability coefficients is observed at pH ca. 3 [9]. Relative abundance of this species increases in lanthanide series with atomic number.

Detailed study [10] on SLM transport of lanthanides by using similar conditions as described above, except of the carrier that was replaced by di(*n*-octyl) phosphoric acid (DOPA), has shown, by analyzing metal transport versus pH, that at least two species take part in membrane transport. In the system with DOPA, formation of a gel-like substance was not observed. However, at lower feed solution acidity and higher carrier and metal concentrations, decrease of the transport was observed and explained by the presence of species unable to permeate through the membrane. Good separation of La, Ce, Pr, and Nd from heavier lanthanides (membrane separation factor, calculated as the ratio of permeability coefficients, $\alpha = P_i/P_{i+1} = 3.0$ for Nd/Sm couple) as well as La from other lanthanides ($\alpha = 3.4$ for La/Ce) was achieved.

In this work, the effect of feed solution acidity and that of the carrier concentration on permeation of seven lanthanide cations have been compared. Conditions for lanthanide mutual separation and composition of the species blocking the liquid membrane for transport are discussed.

2. Experimental

2.1. Reagents and solutions

Europium nitrate and oxides of Tb, Ho, Tm, and Lu of analytical grade purity as well as pure nitrates of Pr and Sm were purchased from Fluka, Switzerland. Stock solutions of 2.5 mmol l^{-1} Ln in 0.1 mol l^{-1} HNO_3 were standardized chelatometrically.

Di-(2-ethylhexyl)phosphoric acid (DEHPA), general purp. reag. (BDH Chemicals, England), xylenol orange (Panreac, Spain) and cetylpyridinium bromide monohydrate, pure (Aldrich, USA) were used as received. Stock solutions of DEHPA were prepared in kerosene (Petronor, Spain) that was purified by washing it with 0.5 mol l^{-1} sodium hydroxide, water, 0.5 mol l^{-1} hydrochloric acid and water until no Cl^- was observed in this water by reaction with $AgNO_3$. Ammonia was distilled isothermally and water was redistilled in a quartz still. All other reagents were of analytical grade purity and purchased from Panreac, Spain.

Feed solutions of pH 1.2–4.2 (acidity adjusted with diluted nitric acid or sodium hydroxide) contained lanthanide at initial concentration of 4.2 μg ml^{-1}. Their ionic strength was kept constant at 0.1 mol l^{-1} (HNO_3, $NaNO_3$). As a strip solution, 0.1 mol l^{-1} nitric acid was used.

2.2. Procedure and apparatus

Microporous poly(vinylidenedifluoride) film, Durapore GVHP 047 00 (Millipore, USA), of 125 μm thickness was used as solid support. Nominal porosity of the support was 75% and effective pore size was 0.22 μm. In membrane experiments, effective surface area of liquid membrane being in contact with solutions was 9.43 cm^2.

SLMs were prepared by soaking the polymeric support in kerosene solution of DEHPA and agitating during 1 min in an ultrasonic bath. Afterwards, support was softly blotted with filter paper and placed between the two compartments for feed and strip solutions (220 ml each) in the transport cell (described elsewhere [11]). In membrane experiments both aqueous solutions were stirred at 1300 rpm. For a new experiment, the polymeric support was rinsed with water, dried with filter paper and shortly by air, washed in kerosene by using ultrasonic bath, dried and reimpregnated with DEHPA–kerosene solution. A given support was reused in up to 50 experiments with a good reproducibility of results. When not used, the washed support was stored in kerosene.

Metal concentrations in feed and stripping solutions were monitored on-line by a flow injection analysis (FIA) spectrophotometric method based on the reaction of Ln with xylenol orange in the presence of cetylpyridinium bromide [12]. If a sample of strip solution (pH ca. 1) was injected, a negative signal was obtained because buffer capacity of the FIA system was not sufficient to keep the acidity at the optimum value of pH 4.5. Therefore, lanthanide concentrations in strip solution, $c(\mathrm{Ln}) < \mathrm{ca.}\ 1\,\mu\mathrm{g\,ml}^{-1}$, were determined from this negative signal which decreased linearly with increasing metal concentration.

The data used to determine the permeability coefficient values were collected during 30 min from the beginning of the experiment. Feed solution acidity was monitored during the run. Experiments were performed at controlled temperature of 23 ± 1°C.

Model 506 pH-meter (Crison, Spain) equipped with U455-S7 glass-Ag/AgCl combined electrode (Ingold, Switzerland) and standard buffers of pH 4.0 and 7.0 (Crison, Spain) were used for pH measurements.

3. Results and discussion

The experimental data were expressed in terms of permeability coefficients P, determined from linear relationship derived by Danesi [13]. To avoid discrepancies arising from the formation of a gel-like substance in feed solution, variations of lanthanide concentration have been monitored as the differences between the initial metal concentration in feed solution, c_0, and its concentration in strip solution at time t, c_s and, thus, Danesi equation was used in the following form:

$$\ln\frac{c_0}{c_0 - c_\mathrm{s}} = \frac{Q}{V_\mathrm{f}}Pt \qquad (1)$$

Here Q is the effective area of liquid membrane (area of membrane support corrected to porosity value) and V_f the feed solution volume.

Differences in the transport of lanthanide cations at carrier concentrations ranging from 0.010 to $1\,\mathrm{mol\,l}^{-1}$ are demonstrated in Fig. 1. The runs were performed at pH values near to the position of maxima on P versus pH curves. Lanthanide permeability is increasing rapidly with carrier concentration reaching maxima at around $50\,\mathrm{mmol\,l}^{-1}$ DEHPA for all lanthanides studied. For the elements from Pr to Lu, the P values of these maxima decrease when increasing the atomic number and both, their shape and decrease of permeability at higher carrier concentrations are sharper. For

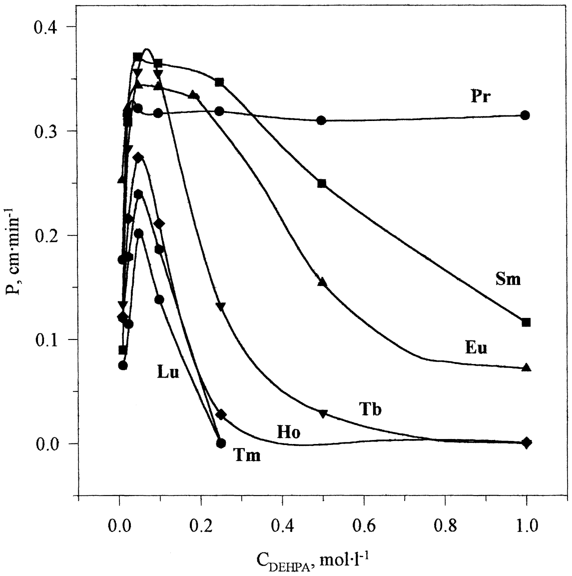

Fig. 1. Effect of carrier concentration. Feed: lanthanide 4.2 $\mu\mathrm{g\,ml}^{-1}$, $0.1\,\mathrm{mol\,l}^{-1}$ $\mathrm{NaNO_3}$, Pr: pH 2.85; Sm: 2.78; Eu: 2.85; Tb: 2.45; Ho: 2.12; Tm: 2.54; Lu: 2.50. Strip: $0.1\,\mathrm{mol\,l}^{-1}$ $\mathrm{HNO_3}$. SLM: DEHPA in kerosene.

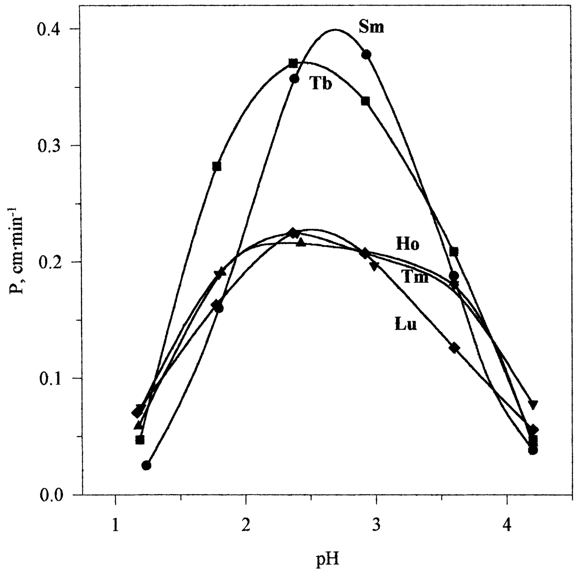

Fig. 2. Effect of feed solution pH at low carrier concentration. Feed and strip solutions as in Fig. 1. SLM: 50 mmol l^{-1} DEHPA in kerosene.

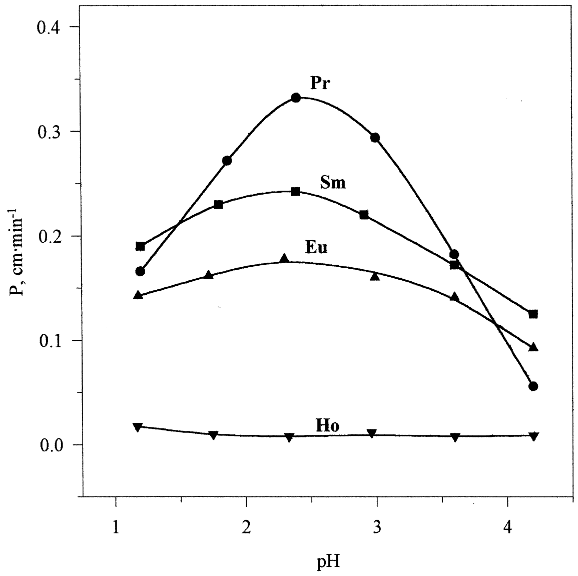

Fig. 3. Effect of feed solution acidity at high carrier concentration. Feed and strip solutions as in Fig. 1. SLM: 0.5 mol l^{-1} DEHPA in kerosene.

Pr, the decrease of permeability was also observed but at carrier concentrations higher than 1 mol l^{-1}.

The effect of feed solution pH on permeability was studied at 50 mmol l^{-1} (Fig. 2) and at 500 mmol l^{-1} DEHPA (Fig. 3) in the membrane. At lower carrier concentration, the P versus pH curves possess maxima situated at pH 2.8 for Sm to pH 2.5–2.6 for lanthanides from Ho to Lu. According to their maximum P values, the lanthanides follow the same order as in Fig. 1. A great difference is observed between light lanthanides together with Tb and heavy lanthanides. The shape of curves for heavy lanthanides is nearly identical and their flat maxima reach approximately half of the P values found for light lanthanides. By increasing carrier concentration, all the pH curves become broader and greater differences can be observed among values of permeability coefficients of individual lanthanides in Fig. 3. Maxima are shifted to lower pH values, i.e. to pH 2.5 for Pr and 1.8–2.7 for Sm and Eu. As shown on the example of Ho, permeation of heavy lanthanides is suppressed at high DEHPA concentrations.

Spatial plots in Fig. 4 were computed for Pr, Eu and Ho from their P versus pH and P versus DEHPA concentration data. With increasing atomic number the area with high P values becomes smaller and thus, varying both, the acidity of feed solution and the carrier concentration, the permeation of individual lanthanides through the membrane can be controlled and conditions for mutual separation of lanthanides can be established.

The decrease of permeation with increasing atomic number of lanthanide can be explained by the increase of the stability of complexes formed with DEHPA. As the diameter of Ln(III) cations decreases in lanthanide series due to lanthanide contraction, stability of the complexes is rising and Ln re-extraction on membrane-strip solution interface proceeds only partly or is even fully suppressed at given strip solution acidity. Fig. 5 shows the effect of aqueous phase acidity on re-extraction of Pr and Ho in liquid–liquid extraction system. Thus it is obvious that at the acidity of strip solutions used in SLMs experiments, i.e. 0.1 mol l^{-1} HNO_3, Pr is re-extracted while Ho remains in the organic phase. Nevertheless, when the aqueous phase acidity is increasing, Ho(III) becomes also to be re-extractable. On the other hand, the decrease of permeability with increasing carrier concentration could be partially explained in terms of the decrease of diffusion coefficients of transported species with increasing viscosity of DEHPA solution.

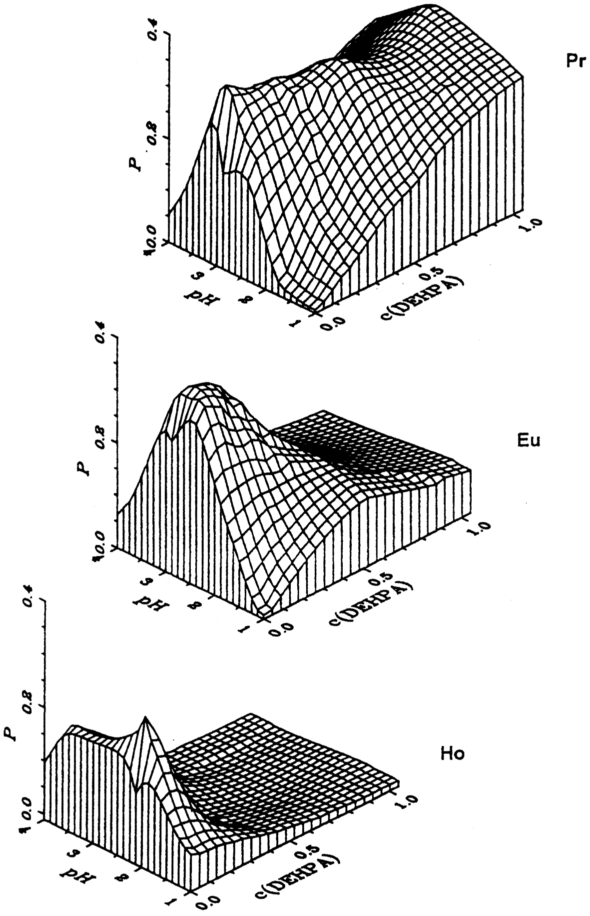

Fig. 4. Effect of feed solution acidity and carrier concentration (mol l^{-1}) on permeability coefficients (cm min^{-1}) of Pr, Eu, and Ho cations. Calculated by means of data presented in Figs. 1–3 and P versus pH data measured for Pr and Eu at 25 mmol l^{-1} DEHPA.

It follows from the results presented above that the group of light lanthanides can be fully separated from heavy ones whose transport practically does not proceed at high DEHPA concentrations. Also, at these experimental conditions, the differences in permeability among light lanthanides are greater and this phenomena could be used for their mutual separation.

To obtain further information on the gel-like substance, conditions leading to its formation and its composition have been investigated. In the 30th min of measurement of primary data, c(Ln) versus time, concentration of metal was estimated in both, the strip and feed solutions. Consequently, percentage of metal 'in membrane' %M, was calculated as the difference between the total amount of metal (100%) and the corresponding value found in feed (%F) and stripping (%S) solutions:

$$\%M = 100 - \%F - \%S \tag{2}$$

The %M value included also the portion of metal that was bound in gel-like substance present at the side of feed-membrane interface and/or in feed solution.

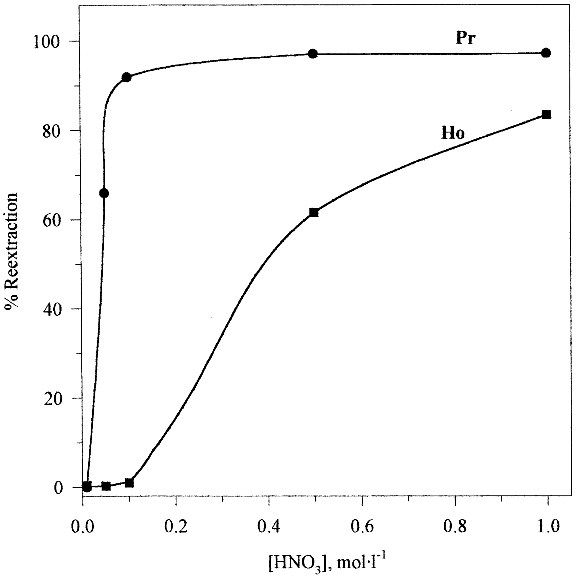

Fig. 5. Re-extraction of lanthanide from kerosene in dependence on aqueous phase acidity. Total lanthanide concentration 4.5 μg ml^{-1}, 25 mmol l^{-1} DEHPA in kerosene, volume ratio of phases equal to one. Re-extraction time 30 min.

At pH 2.1–2.9, sharp increase of %M value was observed up to 250 mmol l^{-1} DEHPA while at carrier concentration of 0.5 to 1 mol l^{-1} the curves P versus c(DEHPA) become flat. Higher values of %M were found at pH > 3 and e.g., at pH 4.2 and 50 mmol l^{-1} DEHPA, %M attained 24% for Sm and 32% for Lu. At high carrier concentration of 0.5 mol l^{-1}, more than 90% of the total amount of heavy lanthanides was present 'in membrane' as demonstrated in Fig. 6. Formation of a solid substance in feed solution was favoured by increasing the pH and carrier concentrations as well as by the increase of the atomic number of the lanthanide.

Aiming at estimation of composition of metal complex species formed 'in membrane', a correlation

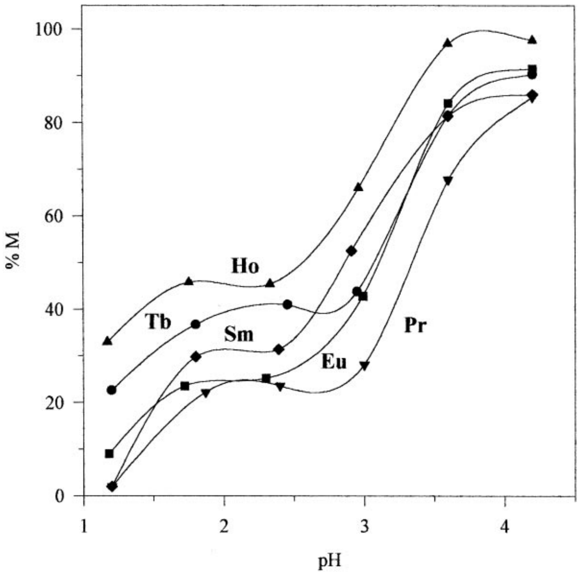

Fig. 6. Difference between total amount of lanthanide and amount determined in feed and strip solutions in percentage as a function of feed solution acidity. Conditions given in Fig. 3 except of Tb where c(DEHPA) = 0.25 mol l^{-1}.

between various amounts of DEHPA in liquid membrane and amount of Eu(III) found 'in membrane' has been investigated. The measurement of permeability coefficient was done at pH 5.1–5.7 in the 30th min of run when membrane was saturated of metal and still the metal transport into stripping solution did not proceed already and thus, a steady state was reached. The amount of DEHPA was calculated from its concentration ranging between 25 and 100 mmol l^{-1} and the membrane volume of 108 μl that was estimated from weight of impregnated support and kerosene density and corrected for the surface area being in contact with solutions. By plotting the amount of DEHPA against the amount of lanthanide 'in membrane', a straight line was obtained, with the slope value of 3.18. Supposing that only one kind of species would be formed at given experimental conditions, the ratio of Ln/DEHPA would be equal to 1 : 3 in this species. However, as shown in previous study [8] of this extraction system, $Ln(NO_3)A_2(HA)_3$ and $LnA_3(HA)_2$, i.e. species with the ratio of Ln/DEHPA = 1 : 5, can be extracted into kerosene phase. Thus, the obtained value of the slope equal to 3.18 can be explained only by simultaneous presence of further species with Ln/DEHPA < 3 which could be e.g., solid polymeric species similar to those reported earlier [6,14].

4. Conclusions

Based on our previous works [8–10] and the presented results, several conclusions on transport of lanthanides through kerosene membrane containing dialkylphosphoric acid as a carrier can be described. The main species transported from nitrate media are $Ln(NO_3)A_2(HA)_3$ whose distribution curves [8] fits well with the shape of experimental curves *P* versus pH and *P* versus c(DEHPA). However, at low acidity gradient over the membrane, transport of other species can proceed at low feed solution pH [10]. Decrease of permeability observed in the lanthanide series can be explained in terms of stability of complexes and re-extraction of lanthanide cations.

The similarities between the pattern of permeability coefficient versus pH and the distribution of the species $Ln(NO_3)A_2(HA)_3$ versus pH may indicate that the thermodynamic parameters are responsible of the transport behaviour of the related metal transport. Thus, one can conclude that the suggested separation of Ln by these type of liquid membranes can be predicted from the corresponding thermodynamic behaviour. The $LnA_3(HA)_2$ species [8] probably do not take part in lanthanide membrane transport but, as shown in this work, they are not identical with gel-like solid substance appearing in feed solution and on the membrane-feed solution interface at higher pH and higher DEHPA concentrations. It seems reasonable to suppose in agreement with previously published results [14] that polymeric species can be formed at given experimental conditions.

The differences among properties of various dialkylphosphoric acids used as carriers [9,10, this work] becomes evident in different behaviour of lanthanides at membrane transport and therefore, can be employed in separation of different groups of lanthanides and/or in the mutual separation of adjacent elements.

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