Effect of polar molecular organic solvents on non-aqueous solvent extraction of rare-earth elements

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ABSTRACT

The extraction and separation of five different rare-earth elements, La, Nd, Eu, Dy and Yb, from an aqueous chloride solution and from different chloride non-aqueous solutions using the solvating extractant Cyanex 923 was investigated. As previous studies had demonstrated the potential of non-aqueous solvent extraction (NASX) to refine rare earths from ethylene glycol, structural analogues of ethylene glycol (1,2-propanediol and 1,3-propanediol) and to other polar organic solvents (triethylene glycol, dimethylsulfoxide, methanol, *N,N*-dimethylformamide and *N,N*-dimethylacetamide) were studied. The extraction data were interpreted in terms of different solvent properties: dielectric constant, Gutmann donor number, molecular structure and hydrogen-bonding capabilities. Remarkable differences were observed between the extraction behaviour from ethylene glycol, 1,2-propanediol and 1,3-propanediol. Therefore, these solvent systems were further studied to elucidate the speciation of the rare-earth elements by optical absorption and luminescence spectroscopy. Based on these studies, both contact-ion-pair formation and solvation strength are assumed to play an important role in the extraction of rare earths by Cyanex 923 from different polar organic solvents. The differences in extraction behaviour can be exploited to fine-tune the separation of rare earths.

1. Introduction

The separation of rare-earth elements (REEs), i.e. the 15 lanthanides together with yttrium and scandium, is challenging due to close similarities in the chemical properties of adjacent elements. Solvent extraction is currently the technique of choice for REE separation in industry [1,2]. Conventional solvent extraction is based on the selective distribution of the REEs between an aqueous phase and an immiscible organic phase comprising an extractant, a diluent and sometimes a modifier. In *non-aqueous solvent extraction* (NASX), the aqueous phase is partly or completely replaced by a non-aqueous solvent, that is largely immiscible with the other phase containing the extractant [3,4]. In NASX terminology, the terms 'aqueous' phase and 'organic' phase are replaced by the terms *more polar* (MP) phase and *less polar* (LP) phase, respectively. Recently, a remarkably efficient REE separation was reported for NASX from ethylene glycol and from poly(ethylene) glycol 200 (PEG-200) using the solvating extractant Cyanex 923 [5–9]. Cyanex 923 is a commercial extractant, comprising a mixture of trialkyl phosphine oxides (93%), with *n*-octyl and *n*-hexyl chains [10]. To better

understand these observations, the study described here will focus on the effects of different solvents in the MP phase on the extraction and the separation of REE chlorides by Cyanex 923. This implies that the metal ion speciation in these non-aqueous solvents must be studied, as this is essential for understanding of the NASX mechanism. The extraction mechanism of REE ions by Cyanex 923 has been studied in detail in the past, and is generally assumed to follow Equation (1), where the overbar indicates species in the LP phase [11]:

$$\mathrm{REE(S)}_a^{m+} + \mathrm{mX(S)}_b^- + \mathrm{n\overline{L}} \rightleftarrows \overline{\mathrm{REE(X)}_m\mathrm{L}_n} + (a+b)\mathrm{S} \tag{1}$$
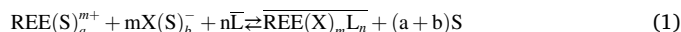
A REE ion (REE^{m+}) is extracted by a solvating extractant (L) to the LP phase as a salt, by associating with anions (X^-), e.g. halides, to maintain the charge neutrality in both phases. In order to transfer the metal salt to the LP phase, the extractant coordinates the REE ion, rendering the metal complex hydrophobic. The extractant molecules have to replace the solvent molecules (S) in the first coordination sphere, and thus have to overcome the stabilisation energy of the MP solvent, i.e. the solvation energy. To stabilise the extracted species, often more than one extractant molecule coordinates to the metal ion. In the case of the trivalent REE

ions, up to four Cyanex 923 molecules can bind to the central metal ion [5,12–14].

The extraction reaction needs to tackle two hurdles: (1) the desolvation of the metal ion and (2) the formation of an inner-sphere complex between the metal ion and anions [15]. Because the 4f orbitals of the REE ions do not participate in covalent bonding, the metal–ligand binding is largely ionic in REE complexes, and thus the number of ligands and their spatial arrangement is largely determined by steric and electrostatic factors [16–20]. REE association to charged ligands thus follows a multistep reaction (Fig. 1), as defined by Eigen: (1) the formation of a solvent-separated ion pair (SSIP) where both the REE ion and anion are surrounded by a solvation shell, (2) the formation of a solvent-shared ion pair (SShIP) in which the REE and anion share the same solvation shell and (3) the formation of a contact ion pair (CIP) where the charged anion is in the first coordination sphere of the REE ion [16,19,21].

As a consequence, the solvation of REE ions strongly influences the thermodynamic stability of the CIPs. While elimination of solvent molecules from the first coordination sphere requires energy for breaking up interactions (positive enthalpy change) and increases disorder (positive entropy change), a cation − anion interaction (negative enthalpy change) is established, with a loss of degrees of freedom (negative entropy change) [16,22]. Whether the Gibbs free energy of CIP formation is net positive or net negative depends on external factors (e.g. ionic strength, temperature, pressure), metal ion properties (e.g. ionic radius, charge density) and solvent properties (e.g. dielectric constant, Gutmann donor/acceptor number) [19]. Furthermore, the activity of ionic species in solution will vary in different solvents, and as a consequence this will influence the extent of extraction [4]. Besides thermodynamics, also the kinetics of complexation play an important role, as the activation energy for water removal from the first coordination sphere of REE ions is high (15 kJ mol^{-1}) [20,23,24].

This paper describes the effect of different *polar molecular organic solvents* (PMOSs) on the extraction and separation of rare-earth ions from an organic chloride feed solution using Cyanex 923, diluted in *n*-dodecane (+10 vol% 1-decanol as modifier). The present paper focusses specifically on ethylene glycol as a solvent in the MP phase, as recent reports revealed significantly enhanced extraction and separation of REEs from this solvent, compared to aqueous solutions. The extraction results from a series of structural analogues, such as 1,2-propanediol and 1,3-propanediol, were compared to those of ethylene glycol. PMOSs having largely different structures and donor properties were investigated as well. Attention is paid to the speciation of rare-earth chloro complexes in non-aqueous solvents, as this topic has been largely neglected so far [25].

2. Experimental

2.1. Products

LaCl$_3$·7H$_2$O (99.99%), EuCl$_3$·6H$_2$O (99.99%), diethylene glycol (DEG, 99%), 1-decanol (98 + %), *n*-dodecane (99%) were purchased from Acros Organics (Geel, Belgium). NdCl$_3$·6H$_2$O (99.9%), DyCl$_3$·6H$_2$O (99.9%) and YbCl$_3$·6H$_2$O (99.9%) were obtained from abcr (Karlsruhe, Germany). Methanol (≥99.8%) and triethylene glycol (TEG, ≥ 99%) were purchased of Sigma − Aldrich (Overijse, Belgium). Propane-1,2-diol (99.8%), formamide (FA, ≥ 99.5 %), nitric acid (65%) and 1000 mg L^{-1} standard solutions of La, Nd, Eu, Dy, Yb and Sc in a 2–5% nitric acid matrix were obtained from Chem-Lab nv (Zedelgem, Belgium). Lithium chloride (≥99%) was obtained from Carl Roth (Karlsruhe, Germany). Dimethylsulfoxide (DMSO, ≥ 99.7%), ethanol (≥99.8%), butan-1-ol (≥99%), and *N,N*-dimethylformamide (DMF, ≥ 99%) were purchased from Fisher Scientific (Loughborough, United Kingdom). *N,N*-dimethylacetamide (DMA, 99%) was obtained from Thermo Fisher (Kandel, Germany). Ethylene glycol (EG, ≥ 99.5%) was purchased from Supelco (Darmstadt, Germany). Propane-1,3-diol (99.8%) and hydrochloric acid (37%) were obtained from VWR BDH chemicals (Fontenay-sous-Bois, France). Cyanex 923 was obtained from Solvay (Vlaardingen, Nederland). Molecular sieves 3 Å, 1–2 mm beads were purchased from Alfa Aesar (Kandel, Germany). Water used during the experiments was of ultrapure quality (18.2 MΩ cm), obtained using a Merck Millipore Milli-Q™ Reference Ultrapure Water Purification System.

2.2. Solvent extraction procedure

The MP feed solutions initially contained between 0 and 3.5 mol L^{-1} LiCl and 0.01 mol L^{-1} of each REE, dissolved in different PMOSs. The LP phase contained 1 mol L^{-1} Cyanex 923 and 10 vol% 1-decanol, diluted in *n*-dodecane. These two phases were contacted for 60 min at a volume phase ratio MP:LP = 1:1 (3 mL : 3 mL), using a Kuhner Lab-Shaker ES-X at 250 rpm, at room temperature. The contact time was considered to be more than long enough, as is was observed that extraction equilibrium is attained within 5 min. Phase separation was accelerated by centrifugation using an Eppendorf centrifuge 5804 at 4000 rpm for 3 min. In case of volume change, the volumes of both phases were determined by a graduated cylinder (±0.1 mL). The MP and LP phase were sampled for elemental analysis by ICP-OES (*vide infra*) and appropriately diluted with a 2 wt% HNO$_3$ solution. Based on these results, the distribution ratio (*D*, Equation (2)) was calculated, which is the ratio of the metal concentration in the LP phase (c_{LP}) over the metal concentration in the MP phase (c_{MP}). The percentage extraction (%*E*, Equation (3)) was calculated from *D*, taking into account the volumes of the MP phase (V_{MP}) and the less polar phase (V_{LP}). The separation factor ($\alpha_{A,B}$, Equation (4)) between two metals, A and B, is defined as the quotient of their distribution ratios, with $\alpha_{A,B} > 1$.

$$D = \frac{c_{LP}}{c_{MP}} \tag{2}$$

$$\%E = \frac{D}{D + V_{MP}/V_{LP}} \bullet 100 \tag{3}$$

$$\alpha_{A,B} = \frac{D_A}{D_B} \tag{4}$$

2.3. Instrumentation

The elemental composition of the MP phases before and after extraction, and of the LP phases after extraction was determined by
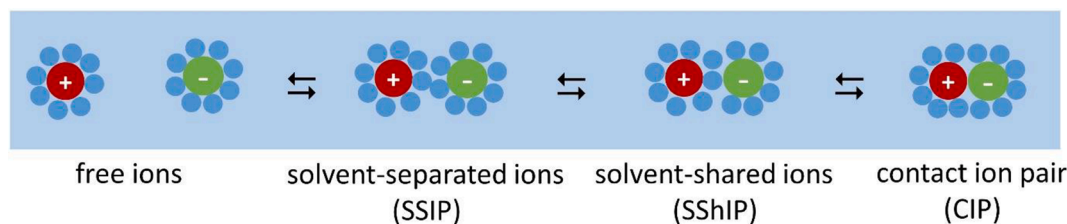

Fig. 1. Graphic overview of the ion-pair multistep reaction, based on Finney et al. [20]. Cations, anions and solvent molecules are represented by red, green and blue circles, respectively.

free ions   solvent-separated ions (SSIP)   solvent-shared ions (SShIP)   contact ion pair (CIP)

inductively coupled plasma–optical emission spectroscopy (ICP-OES) using a PerkinElmer Avio 500 device. For the measurement of the MP phases, the ICP-OES was equipped with a GemCone High Solids nebuliser, baffled cyclonic spray chamber, 2.0 mm inner diameter alumina injector and PerkinElmer Hybrid XLT torch. To a 10 mL mixture, 10 μL of MP phase sample solution and 50 μL of Sc internal standard (1000 mg L^{-1}) were added and diluted with 2 wt% HNO$_3$. A calibration curve was constructed for each measurement, using 6 solutions having the following concentrations of each REE: 0, 0.01, 0.1, 1, 5 and 10 mg L^{-1}. A scandium solution (5 mg L^{-1}) was added as internal standard to all of these calibration solutions. For the measurement of the LP phase, the ICP-OES was equipped with a Meinhard Low-Flow nebuliser, baffled cyclonic spray chamber, 1.2 mm inner diameter alumina injector and a PerkinElmer Hybrid XLT torch. Measurements were performed in both the axial and radial position of the optical emission system. For calculations, only the axial results were used. The wavelengths selected for data analysis were the following: Sc 361.383 nm, La 408.672 nm, Nd 401.225 nm, Eu 381.987 nm, Dy 353.170 nm and Yb 328.937 nm. The luminescence excitation and emission spectra for Eu(III) were measured in Hellma Analytics high precision quartz cuvettes (10 × 10 mm) on an Edinburgh Instruments FLS 980 spectrofluorometer equipped with a continuous xenon arc source and a red-sensitive PMT detector. A filter removing all wavelengths below 430 nm was placed between the sample and exit slit for the removal of stray excitation light. The solvents making up the samples [ethylene glycol (EG); 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD)] were dried on molecular sieves (3 Å, 1–2 mm), activated at 300 °C for at least 24 h. The final water content was 0.12 wt%, 0.01 wt% and 0.04 wt% for EG, 1,2-PD and 1,3-PD, respectively. 1.832 g of EuCl$_3$·6H$_2$O was dissolved in 10 mL of non-aqueous solvent to obtain 0.1 mol L^{-1} europium solutions. The crystal water of europium(III) chloride was not removed prior to dissolution in the solvent mixture. However, the crystal water content was taken into account for the preparation of all samples, except for the pure non-aqueous solvent sample. Excitation spectra were measurement from 250 to 425 nm, with the emission monochromator set at λ_{em} = 592 nm. Emission spectra were recorded from 500 to 800 nm with the excitation wavelength of λ_{exc} = 394 nm. The spectral widths in the excitation and emission spectra were 3.0 and 0.5 nm, respectively. The wavelength step for pure solvents was 0.2 nm and that for the solvent–water mixtures was 1.0 nm. Luminescence lifetimes of the abovementioned solutions were measured using the same spectrofluorometer, while using a μF920 xenon flashlamp operating at a frequency of 100 Hz. The used wavelengths were λ_{exc} = 394 nm and λ_{em} = 592 nm or 614 nm, while the time interval was 2 ms. UV–Vis spectra were recorded on an Agilent Cary 5000 UV–VIS-NIR spectrometer. The settings of the spectrophotometer were: a step size of 0.020 nm, a spectral bandwidth of 0.040 nm and an average time per data point of 0.300 s. Each sample was scanned from 550 to 600 nm. The water content of the MP phases was determined by coulometric Karl Fischer titration on a Mettler − Toledo C30S compact titrator and HYDRANAL®-Coulomat AG anolyte.

2.4. Preferential solvation experiments

Mixtures of water with dry EG, 1,2-PD or 1,3-PD were prepared at concentrations from 0 to 100 mol% water at intervals of 10 mol%. These mixtures all had a concentration of 0.1 mol L^{-1} EuCl$_3$•6 H$_2$O. The water of crystallisation was taken into account during preparation of the PMOS − water mixtures. The decay of luminescence intensity (λ_{em} = 592 nm or 614 nm) was measured through the *Time Correlated Single Photon Counting* (TCSPC) method, and the subsequently obtained decay curves were tail-fitted in Origin 2018b using a mono-exponential decay function (ExpDec1). The luminescence lifetimes (τ) could be calculated from these fits using the expression in Equation (5), with I(t) the intensity measured at time t and I_0 the intensity at t = 0 ms [26].

$$I(t) = I_0 \exp\left(\frac{t}{\tau}\right) \tag{5}$$

3. Results and discussion

3.1. Extraction studies

The extraction behaviour of five representative REE ions, i.e. La(III), Nd(III), Eu(III), Dy(III) and Yb(III), from different PMOSs, was investigated (Fig. 2). Various concentrations of LiCl were added to these solvents as salting-out agent. As Li$^+$ is strongly solvated due to its high charge density, the addition of LiCl reduces the water or solvent activity and thus enhances extraction. Moreover, an increase of chloride concentration in the MP phase further increases extraction due to increased CIP formation [27]. The concentration of each respective REE was 0.01 mol L^{-1} in all extraction experiments. As the experiments were not performed with ultradry solvents and anhydrous salts, and were not carried out in a dry or inert atmosphere, a small amount of water was present in each MP feed solution, typically about 1 wt%. A detailed overview of the water content in the different PMOSs can be found in Table S1 in Supporting Information (SI). The LP phase consisted of 1 mol L^{-1} Cyanex 923 (C923) diluted in *n*-dodecane, with 10 vol% 1-decanol added as a modifier, since some of the studied solvent extraction systems were found to form a third phase. Although the extractant concentration has a distinct impact on the extraction efficiency, it was chosen to keep this concentration constant for all the experiments. Typically, lowering the concentration of extractant, which was present in large excess in all experiments, would lead at some point to saturation effects, which we wanted to avoid in this study.

Solvent extraction tests from aqueous solutions were performed to compare these results with those of the NASX experiments. To avoid hydrolysis of the REE ions, the MP phase contained about 0.01 mol L^{-1} HCl. The percentage extraction as a function of the LiCl concentration is shown in Fig. 3 and Table S2. Up to a concentration of 1.5 mol L^{-1} LiCl, hardly any REEs were extracted. A further increase in salt concentration eventually led to an increase in extraction efficiency and distribution ratios, with a more pronounced increase for the heavy REEs (HREEs). A positive extraction sequence is thus obtained, i.e. stronger extraction of HREEs than of light REEs (LREEs)[27,28]. These observations are in agreement with literature data [2,5,29]. It is well known that REE cations are strongly hydrated by water molecules, leading to lower extraction efficiencies, particularly when using solvating or basic extractants, because water hampers CIP formation with the weakly coordinating chloride ions. Besides coordinating to the REE ions, water also strongly solvates the chloride anions, a contribution that should not be overlooked [30,31]. Upon increasing the LiCl concentration, the water activity decreases, favouring CIP formation and thus leading to a higher distribution ratios. In terms of separation efficiency, the separation factors were too low to be of practical use, also at the highest LiCl concentrations, as shown in Table S3.

The solvent extraction system comprising ethylene glycol (EG) as MP phase has already been studied thoroughly for the separation of REEs [5–7,9]. In order to increase our understanding on the effect EG has on REE extraction and separation using C923, closely resembling solvents were investigated as well: 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD). No volume changes were observed after the extraction experiments. Compared to the extraction from aqueous solution, the extraction of the HREEs from ethylene glycol was greatly enhanced (Fig. 4, Table S4). Extraction of the LREEs did not increase significantly, so that the separation factors were significantly higher (Table S3). At LiCl concentrations above 1 mol L^{-1}, the separation factors decreased again, as quantitative HREE extraction was reached. On the one hand, the overall enhanced extraction was most likely caused by the lower dielectric constant of EG (Table 1), as solvents with lower dielectric constants cannot separate charged species through solvation as
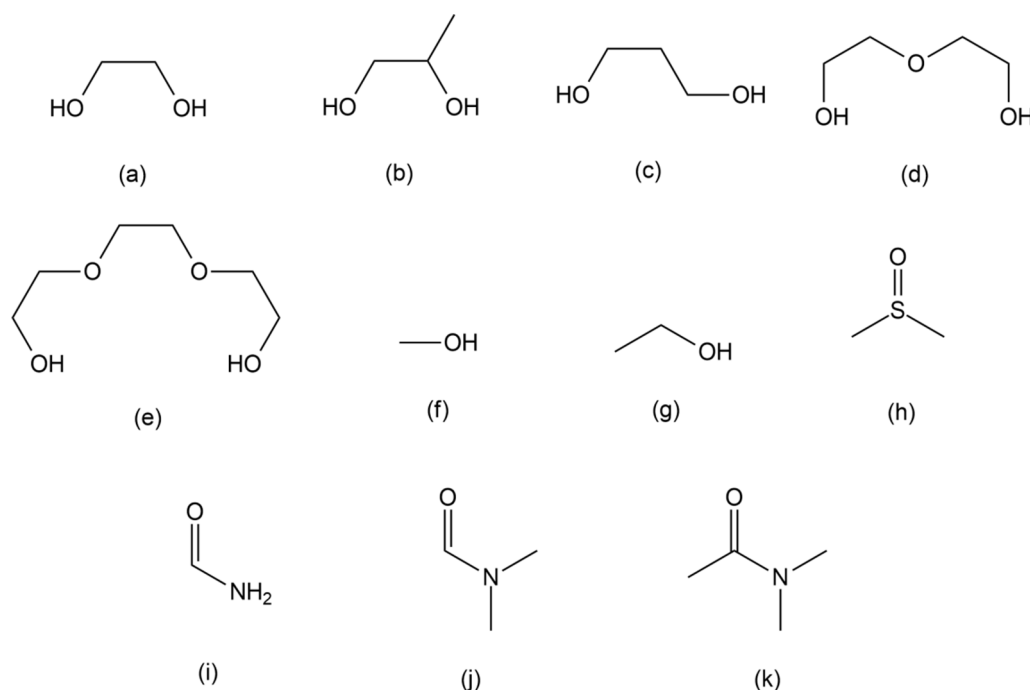
Fig. 2. Structures of the polar molecular organic solvents (PMOSs) considered in this paper: (a) ethylene glycol, (b) 1,2-propanediol, (c) 1,3-propanediol, (d) diethylene glycol (DEG), (e) triethylene glycol (TEG), (f) methanol, (g) ethanol, (h) dimethyl sulfoxide (DMSO), (i) formamide (FA), (j) *N,N*-dimethylformamide (DMF), (k) *N,N*–dimethylacetamide (DMA).
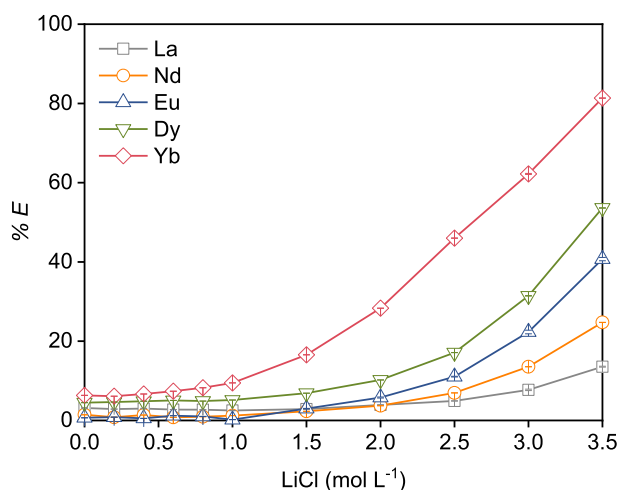

Fig. 3. Influence of the LiCl concentration on the separation of La(III), Nd(III), Eu(III), Dy(III) and Yb(III) from aqueous solution. Conditions: MP: [REE] = 0.01 mol L^{-1} (each), [LiCl] = 0–3.5 mol L^{-1}, [HCl] = 0.01 mol L^{-1}; LP: [C923] = 1 mol L^{-1} dissolved in *n*-dodecane + 10 vol% 1-decanol; phase ratio MP:LP = 1:1; t = 1 h, room temperature.

efficiently, resulting in increased CIP formation between the REEs and chloride ions. On the other hand, the Gutmann donor number (D$_N$) of EG is slightly higher than that of water, which implies a stronger solvation of REEs by EG and a lower extraction efficiency and distribution ratios. However, even though the Gutmann donor number for EG is higher than that of water, alcohols generally show a weaker coordination towards metal cations [32,33]. It is conceivable that the enhanced separation is partially the consequence of the balance between the solvation of the REE ions and the coordinating ability of the extractant to the REE. While ion solvation increases slightly across the lanthanide series, the results in Fig. 4 and Table S4 show a noticeably larger increase in extraction efficiency and distribution ratios for the HREEs compared to the LREEs,

suggesting that differences in REE–extractant interaction predominate. This might for instance be explained by increased ion-pair formation in PMOSs (*vide infra*), lowering the total charge of the REE–complex, and thus decreasing the effect of solvation. In 1,2-PD (Table S5), an even more pronounced increase in distribution ratios was observed, with LREE extracting more efficiently at lower LiCl concentrations compared to the extraction from EG, leading to smaller separation factors (Table S3). Concerning 1,3-PD, all REEs are extracted almost quantitatively at the lowest salt concentrations. The decrease in extraction efficiency at higher LiCl concentration could be caused by a decreased mass transfer due to the high viscosity of the MP phase. As for the explanation for differences in extraction behaviour in the different glycols, one could first have a look at the solvent properties (Table 1). While a lower dielectric constant for 1,2-PD and 1,3-PD compared to EG can explain the observed increase in extraction efficiencies, it is difficult to explain the differences between 1,2-PD and 1,3-PD. A possible cause might be found in the molecular structure (Fig. 2). EG is known to exhibit different coordination modes: not only bidentate coordination, but also monodentate binding, as well as creation of bridged, polymeric structures [34–37]. The bidentate coordination results in a stronger binding of EG to the cation. The same would apply to 1,2-PD, given the position of the hydroxyl groups is the same. However, in 1,3-PD, bidentate coordination would be less evident, causing the solvation strength to be lower in this solvent (*vide infra*) and increasing the extraction efficiency.

Besides the abovementioned glycols, also diethylene glycol (DEG) and triethylene glycol (TEG) were investigated. No extraction results could be obtained for DEG due to formation of a white precipitate. While both LiCl and rare-earth chlorides were perfectly soluble in DEG when dissolved separately, addition of a REE-containing DEG solution to a LiCl-containing solution caused the formation of a precipitate. This precipitate was not further investigated. Such issues were not observed in TEG-based MP feed phases, and the extraction results showed quantitative extraction for all REEs, except for La(III) at lower LiCl concentration (Figure S1, Table S7). TEG could thus be a suitable solvent for the separation of La(III) from the other REEs. It is plausible that the interaction of TEG with the larger La(III) ion is much stronger compared to
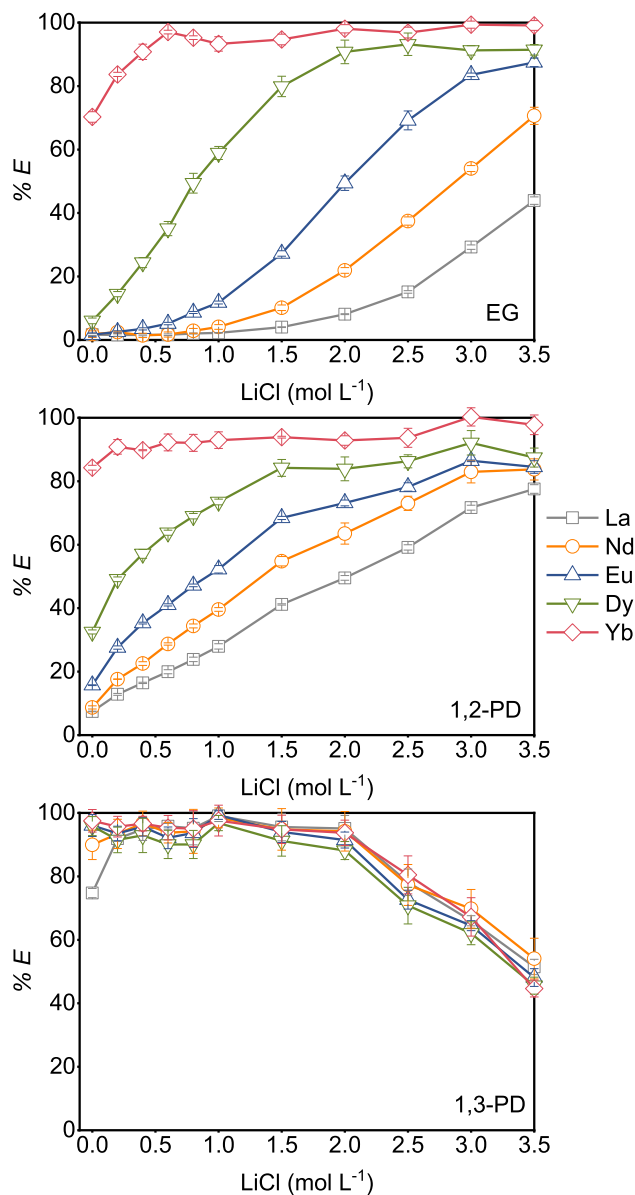
Fig. 4. Influence of the LiCl concentration on the separation of La(III), Nd(III), Eu(III), Dy(III) and Yb(III) from EG, 1,2-PD and 1,3-PD. Conditions: MP: [REE] = 0.01 mol L^{-1} (each), [LiCl] = 0–3.5 mol L^{-1}; LP: [C923] = 1 mol L^{-1} dissolved in *n*-dodecane + 10 vol% 1-decanol; phase ratio MP:LP = 1:1; t = 1 h, room temperature.

Table 1
Overview of the static dielectric constants and the Gutmann donor numbers (D$_N$) of the solvents considered in this study.

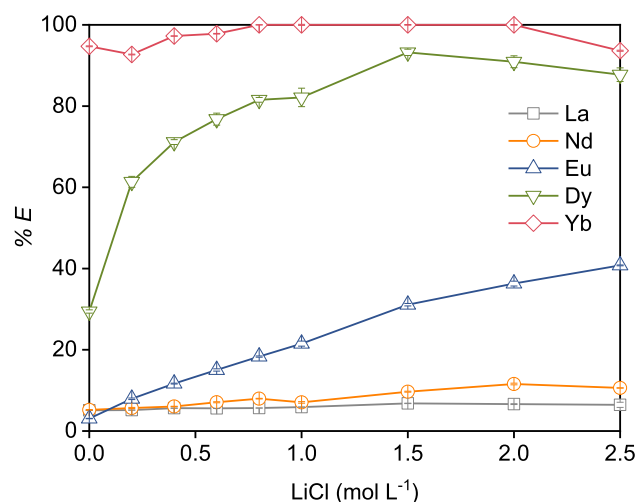| Solvent	Static dielectric constant (293 K) [38,39]	Gutmann donor number (D$_N$) [40–43]
water	78.3	18.0
methanol	33.0	19.0
ethanol	25.3	18.5
ethylene glycol	41.4	20.0
1,2-propylene glycol	32.0	
1,3-propylene glycol	35.1	
diethylene glycol	31.5	
triethylene glycol	23.7	
dimethyl sulfoxide	47.2	29.8
formamide	111.0	36.0
N,N-dimethylformamide	38.3	26.6
N,N-dimethylacetamide	38.9	27.8

Fig. 5. Influence of the LiCl concentration on the separation of La(III), Nd(III), Eu(III), Dy(III) and Yb(III) from DMSO. Conditions: MP: [REE] = 0.01 mol L^{-1} (each), [LiCl] = 0–3.5 mol L^{-1}; LP: [C923] = 1 mol L^{-1} dissolved in *n*-dodecane + 10 vol% 1-decanol; phase ratio MP:LP = 1:1; t = 1 h, room temperature.

smaller REE ions, for the same reason as the selectivity of crown ethers towards certain metal ions. While TEG can wrap itself around the La(III) ion efficiently as a tridentate ligand, it cannot do this with the smaller REE ions [44].

High separation factors for REEs are found not only for extraction from EG, but also from DMSO (Fig. 5, Table S8). No volume changes were observed during solvent extraction. Compared to EG, the separation of the middle rare-earth elements (MREEs) Eu(III) and Dy(III) is much more pronounced, i.e. the maximum separation factors are 36 and 11 for DMSO (1.5 mol L^{-1} LiCl) and EG (1 mol L^{-1} LiCl), respectively. DMSO has a slightly higher dielectric constant and larger Gutmann donor number than EG (Table 1), which would suggest that the distribution ratios in DMSO would be lower. This is the case for the LREEs, but not for the HREEs, which are extracted more efficiently from DMSO than from EG. However, one has to be cautious when comparing the bulk properties of such a different solvent. DMSO is an aprotic solvent, while

the protic EG forms a network of hydrogen bonds, affecting the bulk solvent structure and ultimately also affecting the speciation of the rare-earth cations, as well as the solvation of the chloride anions. Chloride anions are more strongly solvated in protic solvents such as EG. This partially explains why the observed extraction behaviour from DMSO is not too different from that observed for EG [31].

The other solvents investigated were the alcohols methanol (MeOH) and ethanol (EtOH), and the amides formamide (FA), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA). Only the results for MeOH, DMF and DMA will be briefly discussed, as EtOH and FA could not be used for solvent extraction experiments due to their significant miscibility with the LP phase. Extraction results from MeOH (Figure S3, Table S9) are in line with the expectations, given the low dielectric constant and the low Guttmann donor number. Small separation factors (α ≈ 1) for the MeOH system were observed. The lower distribution ratios from MeOH at lower LiCl concentrations can be explained by the loss of extracted metal species to the MP phase at lower LiCl concentrations, as reported by Hala [45]. When the LiCl concentration is increased, the mutual solubility, and hence loss of the extracted species decreases, resulting in the quantitative extraction observed at [LiCl] = 2 mol L^{-1}. Extraction from DMF and DMA showed similar results, with an overall higher distribution ratio for all REEs compared to water, and poor separation between the REEs (Fig. S3–4,

Table S10–11). These comparable results are the consequence of their analogous structure and similar dielectric constants. Results for LiCl concentrations above 1 mol L^{-1} in DMA were not obtained, due to the poor solubility of LiCl in this solvent. Still, by comparing the results for both analogous solvents, two observations can be made: (1) extraction at low LiCl concentration from DMA is less efficient than from DMF; (2) for LiCl concentrations above 0.8 mol L^{-1} LiCl, extraction of HREEs from DMA is more efficient, and slightly larger separation factors were found. The first observation can be explained by the slightly better donor properties of DMA compared to DMF, resulting in stronger solvation in DMA solutions. However, it has been shown that DMA exhibits a solvent steric effect, originating from the slightly bulkier acetyl group (-C(O)CH$_3$) compared to the formyl group (-C(O)H) in DMF [46,47]. This causes the rare-earth ions to form CIPs more readily in DMA, which is more pronounced at higher chloride concentrations, while in DMF, SSIPs are more prevalent. Hence, extraction efficiency is higher from DMA at these conditions, explaining the second observation.

3.2. Spectroscopic characterisation

The remarkable differences between the analogous glycol structures of EG, 1,2-PD and 1,3-PD are assumed to be due to changes in solvation strength and speciation. The increase in extraction efficiency observed in the glycols, compared to that in water, is assumed to be caused by an increase in CIP formation, resulting from a lower dielectric constant. To validate this hypothesis, UV–Vis absorption spectroscopy was used to detect the presence of CIPs of rare-earth chloride complexes in different non-aqueous solutions. The spectroscopic measurements were performed on glycol solutions containing 0.1 mol L^{-1} NdCl$_3$ and 0, 0.5, 1, 1.5, 2, 2.5 and 3 mol L^{-1} LiCl, except for 1,3-PD, having a maximum solubility of 2 mol L^{-1} for LiCl. Fig. 6 shows the $^4G_{5/2} \leftarrow {}^4I_{9/2}$ hypersensitive transition (565–600 nm) of the Nd(III) ion in each solvent, for the LiCl concentration extremes [48,49]. Compared to aqueous solutions, a solvatochromic shift towards longer wavelengths, i.e. a bathochromic shift, was observed for the glycols, with the size of the shift following the order: EG ≈ 1,2-PD < 1,3-PD. This shift is a result of the nephelauxetic effect, which originates from a decrease in interelectron repulsion through electron cloud expansion, caused by increased interaction of the REE ion with its surrounding ligands [26]. Besides the effect the glycol molecules can have when solvating Nd(III), Frey and Horrocks state that inner-sphere chloride anions cause the largest nephelauxetic effect [50]. The differences in formation of chloride CIPs

in the different glycols are thus strongly influencing the magnitude of the bathochromic shifts. Furthermore, upon increasing the LiCl concentration in the Nd(III) solutions, the position of the absorption bands gradually shifted towards longer wavelengths for each glycol solution, while no such shift was observed in water. This is in agreement with earlier observations for rare-earth ions in aqueous chloride solution, when compared with methanolic chloride solution [25,51]. Besides small bathochromic shifts, also significant hyperchromic shifts were observed in all solvents, but these results are not consistent as some of the peaks in the spectrum of EG (577.5 and 573.0 nm), 1,2-PD (<578 nm) and 1,3-PD (<580 nm) actually showed hypochromic shifts. These changes in intensity of the hypersensitive transition seem to be related to the environment of the REE ions, e.g. the electron-donating ability of a solvent [49,52–54].

The solvation of REEs in EG, 1,2-PD and 1,3-PD was studied by luminescence spectroscopy. The Eu(III) ion is well known for its strong luminescence due to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 6$) transitions in the red spectral region, and it is particularly suited as a spectroscopic probe to investigate the coordination environment of REE ions [26]. Luminescence spectra of Eu(III) in chloride environment were recorded for different concentrations of EG, 1,2-PD and 1,3-PD in mixtures with water ($\lambda_{exc} = 394$ nm) (Figure S5). All spectra show a clear increase in the intensity of $^7F_2 \rightarrow {}^5D_0$ transition with increasing glycol content, suggesting the formation of more asymmetric complexes. For all glycols, and especially for 1,3-PD, an increase in PMOS concentration was accompanied by an increase in the intensity of the $^7F_0 \rightarrow {}^5D_0$ transition, indicating the presence of species of C$_{nv}$, C$_n$ or C$_s$ symmetry [26]. The luminescence lifetime (τ) is an expression of the total rate of decay to the ground levels, both radiative and non-radiative, and is defined as the time over which the population in excited states has decreased by $1/e$ [26]. The rate of decay is strongly influenced by the chemical environment of the excited species. In electrolyte solutions of different solvents, a metal cation can exhibit preferential coordination towards one or the other solvent in its first coordination sphere, and as such, the ratio of mole fraction of PMOS and water in the first coordination sphere might differ significantly from the one observed in the bulk solution. This phenomenon, called *preferential solvation*, can be investigated by measuring luminescence lifetimes, as water molecules and other –OH and –NH containing ligands are known to lower luminescence lifetime through energy transfer via –OH or –NH oscillation [33,55]. Preferential solvation can be represented by the mole fraction of PMOS in the first solvation sphere (L_s) as a function of its mole fraction in the bulk (x_s), as shown in Fig. 7 for EG, 1,2-PD and 1,3-PD. L_s was calculated using the
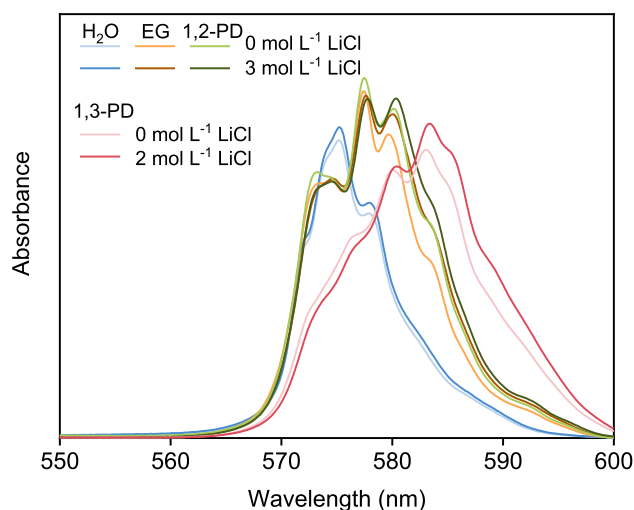

Fig. 6. Effect of the LiCl concentration on the electronic spectra of Nd(III) in H$_2$O, EG, 1,2-PD and 1,3-PD. Conditions: [Nd(III)] = 0.1 mol L^{-1}; [LiCl] = 0 or 3 mol L^{-1} for H$_2$O, EG, 1,2-PD; [LiCl] = 0 or 2 mol L^{-1} for 1,3-PD; room temperature.
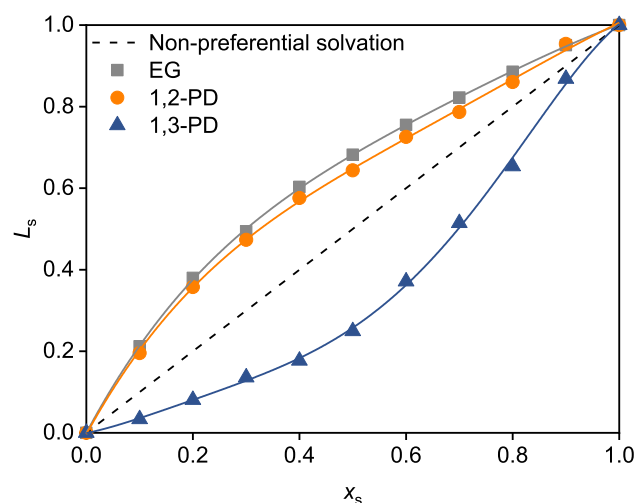

Fig. 7. Influence of PMOS content (x_s) on the composition of the first coordination sphere of Eu(III) (L_s) in binary mixtures of EG, 1,2-PD and 1,3-PD with water.

luminescence decay constants, i.e. the inverse value of the luminescence lifetimes, in pure water (k_w), pure PMOS (k_s) and in the different PMOS/water mixtures (k_{mix}). The k_{mix} can be defined as the sum of the individual contributions of both water and PMOS in the first coordination sphere (Equation (6)). Furthermore, the sum of the mole fractions of PMOS and water in the first coordination sphere is by definition equal to 1 (Equation (7)). Rearrangement of both equations gives the expression shown in Equation (8), which was used to calculate the L_s values at different x_s. This formula implies two assumptions: (1) each water and PMOS molecule contributes separately to the non-radiative decay; (2) the total number of solvent molecules coordinating to Eu(III), i.e. the solvation number, remains constant over the entire compositional range [56]. The lifetime and k-values for each mixture composition can be found in Table 2. The results shown in Fig. 7 show that Eu(III) prefers coordination to EG and 1,2-PD over coordination to water, whereas this is not the case for 1,3-PD. This agrees with the observations made during the solvent extraction experiments, i.e. increased efficiency for extraction from 1,3-PD due to a lower solvation strength compared to EG and 1,2-PD.

$$k_{mix} = L_w k_w + L_s k_s \tag{6}$$

$$L_w + L_s = 1 \tag{7}$$

$$L_s = \frac{k_w - k_{mix}}{k_w - k_s} \tag{8}$$

The *degree of preferential solvation* (K_{PS}, Equation (9)) offers a more quantitative tool for comparison [56], and it is defined as the ratio of the composition of the first coordination sphere, i.e. the mole fraction of solvent over the mole fraction of water in the first coordination sphere (L_s/L_w), over the bulk composition, i.e. the mole fraction of solvent over the mole fraction of water in the bulk (x_s/x_w).

$$K_{PS} = \frac{(L_s/L_w)}{(x_s/x_w)} \tag{9}$$

As preferential solvation depends on the relative Gibbs free energies of solvation of the different solvents towards Eu(III), it therefore can be considered to be a measure for the solute–solvent interaction strength [23]. According to the K_{PS} results shown in Fig. 8, the interaction strength follows the order: 1,3-PD < water < 1,2-PD ≈ EG. The K_{PS} values agree well with the observations made during solvent extraction, as it supports the assumption of a lower solvation strength for 1,3-PD, which could promote extraction. While EG and 1,2-PD might solvate the rare-earth ions more strongly according to these results, which is contradictory to the extraction results, it does not take into account the solvation of chloride ions, which is lower in non-aqueous media compared to aqueous ones, nor does it take it into account other solvent properties, such differences in relative electric permittivity.

4. Conclusion

The influence of several polar molecular organic solvents on the extraction behaviour of REE chlorides by the solvating extractant Cyanex 923 has been examined. In all cases, the extraction of the REEs increased compared to that from aqueous solutions. The separation of the REEs was significantly enhanced when ethylene glycol or dimethyl sulfoxide was selected as the more polar phase. The extraction behaviour of the ethylene glycol analogues 1,2-propanediol and 1,3-propanediol was found to correlate with the dielectric constant and solvent donor parameters. This suggests that both an increase in contact-ion-pair formation with chloride anions and a decrease in solvation strength might explain the observed differences in extraction behaviour. UV–Vis absorption spectra of Nd(III) in the abovementioned glycol solutions showed distinct bathochromic shifts, with supports the hypothesis of the enhanced contact-ion-pair formation in these solvents. The preferential solvation was further studied by luminescence lifetime

Table 2
Overview of the lifetime values (τ) and luminescence decay constants (k) of Eu (III) in EG, 1,2-PD and 1,3-PD mixtures with water. The concentrations of the organic solvent have been expressed in the mole fraction scale.

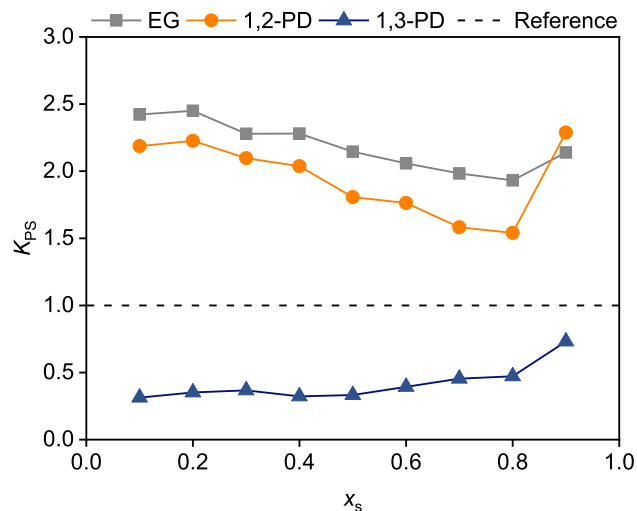| x_s	τ (ms)			k (ms^{-1})		
	EG	1,2-PD	1,3-PD	EG	1,2-PD	1,3-PD
0	0.117			8.53 ($=k_w$)		
0.1	0.132	0.131	0.119	7.59	7.66	8.38
0.2	0.146	0.144	0.122	6.85	6.94	8.18
0.3	0.158	0.156	0.126	6.35	6.42	7.94
0.4	0.171	0.168	0.129	5.86	5.96	7.76
0.5	0.181	0.177	0.134	5.51	5.66	7.45
0.6	0.193	0.189	0.145	5.19	5.30	6.92
0.7	0.204	0.199	0.159	4.89	5.02	6.30
0.8	0.217	0.213	0.176	4.62	4.70	5.70
0.9	0.231	0.234	0.210	4.33	4.28	4.77
1	0.243	0.245	0.238	4.11	4.07	4.19
				($=k_{EG}$)	($=k_{1,2\text{-PD}}$)	($=k_{1,3\text{-PD}}$)

Fig. 8. Influence of PMOS content (x_s) on the degree of preferential solvation (K_{PS}) of Eu(III) in binary mixtures of EG, 1,2-PD and 1,3-PD with water. The concentrations are expressed in mole fraction.

measurements on glycol solutions of 0.1 mol L^{-1} Eu(III). As the degree of preferential solvation of Eu(III) by 1,3-propanediol was significantly lower than for the other glycols, the increased extraction of the REEs from 1,3-propanediol can be explained by a lower solvation strength. The approach in present study of ion-pair formation and solvation strength for REEs in non-aqueous solvents can be used as a predictive tool for further extraction studies. However, it is not always possible to explain the extraction behaviour on the basis of these solvent parameters alone, as, for instance, the solvation of anions and bulk solvent–solvent interactions might also play an important role. Further research on the speciation of REE complexes in non-aqueous media by different spectroscopic techniques such as Raman, NMR and EXAFS might further contribute to a better understanding of the mechanism of non-aqueous solvent extraction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

The following contents are presented in the Supporting Information file, free of charge: an overview of the water content in different MP phases (Table S1), an overview of the distribution ratios for all solvents (Table S2, Table S4–11) an overview of separation factors for extraction experiments from water, EG, 1,2-PD and 1,3-PD (Table S3), extraction plots for TEG, MeOH, DMF and DMA (Figures S1–4), Eu(III) emission spectra recorded in EG, 1,2-PD and 1,3-PD mixtures with water (Figure S5). Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.121197.

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