Non-aqueous solvent extraction of rare-earth nitrates from ethylene glycol to *n*-dodecane by Cyanex 923

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ABSTRACT

A solvent extraction process comprising two immiscible organic phases has been developed for the extraction of rare earths. The more polar organic phase was ethylene glycol with dissolved rare-earth nitrate salts and lithium nitrate, while the less polar phase was a solution of the neutral extractant Cyanex® 923 dissolved in n-dodecane. The solvent extraction mechanism was determined by slope analysis and the main species in the organic phase was identified by Extended X-ray Absorption Fine Structure (EXAFS) studies. The extraction from the ethylene glycol solution was compared with extraction from an aqueous feed solution. When compared to aqueous feed solutions, the light rare-earth elements (LREEs) are less efficiently extracted and the heavy rare-earth elements (HREEs) more efficiently extracted from an ethylene glycol feed solutions, resulting into the easy separation of HREEs from LREEs. The separation factors between neighboring elements are higher for this non-aqueous solvent extraction process than for extraction from an aqueous feed solution.

1. Introduction

Solvent extraction (SX) is an important technique in hydrometallurgy for the separation and purification of metals, such as the rare earths (REEs), platinum group metals (PGMs), cobalt, nickel, copper and uranium [1]. In a solvent extraction process, metal ions are distributed between an aqueous phase and a water-immiscible organic phase. At equilibrium, the ratios of the concentrations of a metal ion in the organic phase and the aqueous phase depend on the nature of the metal ions, and differences in these ratios are the basis for the separation of a mixture of metals. Because all hydrometallurgical solvent extraction processes make use of an aqueous phase, one could get the impression that the presence of an aqueous phase is a requirement for solvent extraction. However, two mutually immiscible liquid phases are a sufficient condition. Liquid-liquid extraction from molten salts has been an active research field [2]. Different systems have been considered: (1) molten salt – molten salt; (2) molten salt – molten metal; (3) molten salt – organic solvent [3-10].

Recently, our research group has extended this approach of using molten salts to low-temperature molten salts (ionic liquids) and has shown that two mutually immiscible ionic liquids can be efficient solvent extraction systems for cobalt-nickel separations [11] and for separation of mixtures of rare earths [12]. Foreman described the extraction of rare earths and transition metals from a deep-eutectic solvent (DES) based on choline chloride and lactic acid to an organic phase by Aliquat 336 or bis(2-ethylhexyl)phosphoric acid [13]. Only few examples of separation of metal ions by solvent extraction with two mutually immiscible molecular organic solvents can be found in the literature. Larsen and Trevorrow investigated the distribution of $ZrCl_4$ and $HfCl_4$ between acetonitrile and isoamyl ether [14]. Florence and Farrar studied the solvent extraction of Ni(II) from an anhydrous methanol solution

3

containing a high concentration of lithium halide salts by long-chain amines [15]. Burns and Cattrall described the distribution of Cu(II) between methanolic LiCl solutions and benzene solutions of bis(3,5,5-trimethylhexyl)ammonium chloride [16]. Dean and Eskew used a methylisobutyl ketone/formamide two-phase system for the separation of Tl(III) from Ga(III), In(III), Fe(III), Sn(II) and Sn(IV) [17]. In the latter study the non-aqueous biphasic system was used for selective stripping of Tl(III) with a 1.5 M HBr solution in formamide after extraction to the methylisobutyl ketone (MIBK) phase, rather than for selective extraction. Matsui *et al*. studied the non-aqueous extraction of Zn(II) by trioctylphosphine oxide dissolved in toluene from an ethylene glycol solution containing LiCl [18]. Non-aqueous solvent extraction can offer some advantages compared to conventional solvent extraction with an aqueous feed phase. The mechanism for extraction from a non-aqueous solution might be different from that for extraction from an aqueous solution and this difference could be exploited to develop new, highly selective separation processes. Additionally, non-aqueous solvent extraction can be used for metal ions or metal complexes that have a strong tendency to hydrolyze in water.

The solvent pairs for non-aqueous solvent extraction must fulfil the following conditions: (1) formation of two phases upon mixing and low mutual solubility of the solvents; (2) fast phase separation after mixing (= short phase disengagement time); (3) the extractant must be soluble in the less polar phase; (4) the starting metal compounds or salts must be soluble in the more polar phase and the extracted metal complexes in the less polar phase; (5) the metal compounds must not react with the organic solvents. The first condition is the most difficult to fulfil because many organic solvents are mutually miscible. Several guidelines are available for the initial selection of solvent pairs, such as reported miscibility data [19], the

4

Hildebrand solubility parameter δ for solvents [20] and the mixotropic series [21]. Especially the mixotropic series is a useful tool: the further two solvents are apart in the series, the lesser is the mutual solubility.

In this paper, we show that replacement of water in a solvent extraction process by the polar organic solvent ethylene glycol allows to design a selective process for group separation of heavy rare earths (HREEs) from light rare earths (LREEs). The rare earths are extracted from an ethylene glycol phase with dissolved $LiNO_3$ by the extractant Cyanex® 923 dissolved in n-dodecane. Cyanex® 923 was selected as extractant because it is known that this neutral extractant can efficiently extract rare-earth ions from aqueous nitrate solutions, but not from aqueous chloride solutions [22-27]. Cyanex® 923 is a commercially available extractant that consists of a mixture of four trialkylphosphine oxides: $R_3P=O$, $R_2R'P=O$, $RR'_2P=O$ and $R'_3P=O$, where R = n-octyl and R' = n-hexyl, and its average molecular mass is 348 g mol^{-1} [28,29]. It is completely miscible with most organic diluents and gives a fast phase disengagement.

2. Materials and methods

2.1 Materials and reagents

$Nd(NO_3)_3 \cdot 6H_2O$ (99.9%) and $La(NO_3)_3 \cdot 6H_2O$ (99.9%) were purchased from Alfa Aesar (Ward Hill, USA), $Ce(NO_3)_3 \cdot 6H_2O$ (99.9%) from Sigma-Aldrich (Diegem, Belgium), $Pr(NO_3)_3 \cdot 6H_2O$ (99.9%), $Gd(NO_3)_3 \cdot 6H_2O$ (99.9%), $Dy(NO_3)_3 \cdot 6H_2O$ (99.9%), and $Yb(NO_3)_3 \cdot 6H_2O$ (99.9%) from Strem Chemicals (USA). $LiNO_3$ (99%) was obtained from Sigma-Aldrich (Diegem, Belgium), while n-dodecane (>99%) and ethylene glycol (99.9%)

were purchased from Acros Organics (Geel, Belgium). Cyanex® 923 and bis(2,4,4-dimethylpentyl phosphinic acid (Cyanex® 272) were provided by Cytec Industries (Canada). Tri-*n*-butylphosphate (TBP) was obtained from Alfa Aesar (USA). A silicone solution in isopropanol (SERVA, Electrophoresis GmbH, Heidelberg, Germany) was used to siliconize the TXRF carriers. The gallium standard was purchased from Chem-Lab NV (Zedelgem, Belgium). All other chemicals used were of analytical grade.

2.2 Instrumentation

A benchtop total reflection X-ray fluorescence (TXRF) spectrometer (S2 Picofox model, Bruker) was used to determine the metal concentrations. Batch-mode extraction experiments were carried out by mixing two phases using flat magnetic stirrer (MIX 15 eco model, 2mag magnetic e motion). A Heraeus Megafuge 1.0 was used to centrifuge the samples after equilibrium. The water content was determined by coulometric Karl Fischer titration using a Mettler-Toledo DL39 titrator. The ^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz). ^{31}P NMR spectra were recorded on a Bruker Ascend 400 spectrometer operating at 162 MHz. Acetone-d_6 was used as a solvent for NMR samples. The spectra were analyzed with SpinWorks software. The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^1H and to 85% H_3PO_4 (external reference) for ^{31}P NMR. The Fourier Transform Infrared (FTIR) spectrum was recorded by a Bruker Vertex 70 spectrometer via the attenuated total reflectance (ATR) technique with a Bruker Platinum ATR accessory. The FTIR spectra was analyzed by OPUS software package. An Anton Paar rolling-ball viscometer (Lovis 2000 ME) was used for measuring the viscosity of ethylene glycol. A gas chromatograph, combined with a flame ionization detector

(GC-FID) and Turbomatrix 16 headspace autosampler (HS) (Perkin Elmer, USA) was used

for the determination of ethylene glycol concentration in n-dodecane samples. A Perkin

Elmer CP-SIL 8 CB (5%-phenyl–95%-dimethylpolysiloxane) capillary column, 50 m long,

0.32 mm I.D. and 1.20 m film thickness was used as GC column. The peak area was

determined by the PE TotalChrom Version 6.3.2.0646 software package.

2.3 Solubility studies

The mutual solubility experiments were carried out by mixing equal volumes (5 mL) of

ethylene glycol and n-dodecane phases for 30 min. After equilibrium, both phases were

separated by centrifuging at 3000 rpm for 5 min. The experiments were conducted as a

function of nitrate ion concentration and metal ion concentration in ethylene glycol phase and

as a function of extractant concentration in the n-dodecane phase. The objective was to

determine the solubility of Cyanex® 923 in the ethylene glycol phase and to check the

solubility/co-extraction of ethylene glycol to Cyanex® 923/n-dodecane phase. The solubility

of Cyanex® 923 in the ethylene glycol phase was identified using ^{31}P NMR studies and the

solubility of ethylene glycol was estimated by GC-FID.

2.4 EXAFS measurements

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the Nd L3-edge (6213 eV)

were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European

Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam

was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111)

crystal pair. The measurements were done in transmission mode using Ar/He gas-filled ionization chambers at ambient pressure. A brass sample holder with Kapton® windows and a flexible polymeric spacer (VITON®) with a thickness of 1 mm was used as a sample holder.

Standard procedures were used for pre-edge subtraction and data normalization to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the software program Viper [30], were k^4-weighted and Fourier transformed over the k range from 3.14 to 11.04 Å^{-1} and from 2.85 to 8.96 Å^{-1} for Nd present in the ethylene glycol and n-dodecane phase, respectively. The data were fitted using the *ab initio* code FEFF 7.0 [31], which was used to calculate the theoretical phase and amplitude functions that were subsequently used in the non-linear least-squares refinement of the experimental data. Fitting of the model was performed in R space between 0 and 4 Å and 0 and 4.31 Å for Nd present in the ethylene glycol and n-dodecane phase, respectively. Estimated standard deviations are shown between parentheses and calculated by VIPER. S_0 was fixed at 1.1 and calibrated after dissolving NdCl$_3$ in a 1:1 molar ratio in Aliquat® 336 and drying the mixture for 1 day at a Schlenk line at 110 °C.

2.5 Solvent extraction procedure

Solvent extraction experiments were performed by mixing equal volumes of the two phases, i.e. an aqueous solution and Cyanex® 923 in n-dodecane for conventional solvent extraction and ethylene glycol and Cyanex® 923 in n-dodecane for non-aqueous solvent extraction, in glass vials using a magnetic stirrer at 1200 rpm and room temperature (293 ± 2 K) for 15

min, unless otherwise specified. After equilibrium, the phase separation was accelerated by centrifugation for 2 min at 3000 rpm to make sure that no remains of either phases left in the other phase, even though phase disengagement was fast. The concentration of the rare earths in ethylene glycol was determined by TXRF spectrometer after adding a gallium internal standard. Praseodymium was used as internal standard for the experiments with Nd(III). The concentrations of the rare earths in the *n*-dodecane phase were obtained by the difference between the rare-earth concentration in the feed and the raffinate. The quartz glass sample carriers for TXRF measurements were pretreated with 20 μL of a silicone solution in isopropanol and dried in oven for 2 min at 333 K. Then, a sample of 2 μL was added to carrier and dried at 333 K. for 20 min. The samples were measured for 300 s in TXRF spectrometer. All samples were measured in duplicate.

The *distribution ratio D* is defined as the ratio of the total concentration of a compound *M* in the less polar organic phase (c_{solv2}) to the total concentration of the compound in the more polar organic phase (c_{solv1}):

$$D = \frac{c_{solv2}}{c_{solv1}} \tag{1}$$

For two substances M_A and M_B, both distributed between the two organic phases, a *separation factor* β can be defined (where $D_A \geq D_B$):

$$\beta_{A,B} = \frac{D_A}{D_B} \tag{2}$$

The closer this separation factor approaches to unity, the more extraction stages are required to separate the two substances. The *percentage extraction %E* [32,33] is calculated as follows:

$$\%E = \frac{V_{solv2}[M_{solv2}]}{V_{solv2}[M_{solv2}] + V_{solv1}[M_{solv1}]} \times 100 \qquad (3)$$

where V_{solv2} and V_{solv1} are the volumes of the less polar (*n*-dodecane) and the more polar (ethylene glycol) organic phase, respectively. [M_{solv2}] and [M_{solv1}] are the concentrations of *M* in the less and the more polar organic phase, respectively.

3. Results and discussion

3.1 Mutual solubility of the organic phases

The solvent pair ethylene glycol/*n*-dodecane was identified as a promising system for non-aqueous solvent extraction, because test tube experiments indicated that two phases are formed by mixing equal volumes of these two solvents and that no significant volume changes occurred. The nitrate concentration in the ethylene glycol phase could be adjusted by addition of anhydrous $LiNO_3$. This salt was selected because of its good solubility in ethylene glycol. It is possible to prepare a 5 M $LiNO_3$ solution in ethylene glycol. Saturation was observed above 5 M $LiNO_3$.

The mutual solubility of ethylene glycol and *n*-dodecane was measured by recording the ${}^1H$ NMR spectra of both phases after equilibrium. It was found that ethylene glycol and *n*-dodecane were completely immiscible. The ${}^1H$ NMR spectra of both phases after equilibrium revealed that no resonance lines corresponding to ethylene glycol were found in the *n*-

dodecane phase and also no *n*-dodecane was observed in the ethylene glycol phase. In the second step, the mutual solubilities were determined as a function of Cyanex® 923 concentration. ^{31}P NMR spectra of ethylene glycol after equilibrium with Cyanex® 923 indicated no solubility of Cyanex® 923 owing to the absence of resonance lines corresponding to the P=O group in ethylene glycol phase. This means that there is no loss of extractant during the solvent extraction experiments. The solubility of ethylene glycol in Cyanex® 923/*n*-dodecane was estimated by GC-FID. It was found that about 24.5 g L^{-1} of ethylene glycol was co-extracted into 1M Cyanex® 923. In the third step, the solubility of Cyanex® 923 in the ethylene glycol was studied as a function of LiNO$_3$ concentration and La(III) concentration. In none of the experiments, there is loss of Cyanex® 923 to the ethylene glycol phase as indicated by ^{31}P NMR spectra. The co-extracted ethylene glycol content in Cyanex 923 decreased to 20.8 g L^{-1} by addition of 1 M LiNO$_3$ and 10 g L^{-1} of La(III) to the ethylene glycol phase. However, the co-extraction of ethylene glycol could be controlled by pre-saturating the Cyanex® 923 with ethylene glycol. This is common practice for solvating extractants like Cyanex® 923 which can extract acids/water in conventional solvent extraction experiments.

The viscosity of ethylene glycol was measured as a function of the LiNO$_3$ concentration. The viscosity of ethylene glycol increased gradually with increasing the LiNO$_3$ concentration from 22 mPa.s for a 0.5 M solution to 112 mPa.s for a 5 M solution (at room temperature). The measurement of the influence of temperature on the viscosity of ethylene glycol (+1 M LiNO$_3$) indicated that the viscosity gradually decreased with increase in temperature to 11 mPa·s at 323 K.

3.2 Selection of extractant

Solvent extraction of Nd(III) from ethylene glycol (+1 M LiNO$_3$) was carried out using Cyanex[®] 923, Cyanex[®] 272 and TBP in *n*-dodecane in order to find the suitable extractant (Figure 1). The structures of the three extractants are given in Scheme 1. It was observed that Cyanex[®] 923 showed good extraction capacity towards Nd(III). The extraction capacity of Cyanex[®] 923 was far greater than Cyanex[®] 272 and TBP. The extraction order can be given as follows: Cyanex[®] 923 >> Cyanex[®] 272 > TBP. This can be explained on the basis of *Gutmann donor number* (DN) which is defined as the negative ΔH value of adduct formation between SbCl$_5$ and an electron-pair donor solvent in dilute solutions in the non-coordinating solvent 1,2-dichloroethane [34]. The extraction power depends on the *Gutmann donor number*. The higher the donor number, the stronger is the interaction between a Lewis acidic metal complex and the donor solvent (a solvent with a dissolved donor molecule acting as the extractant). The metal extraction takes place from a solvent with a lower donor number to a solvent with a higher donor number. Phosphine oxides, which are present in Cyanex[®] 923, are among the molecules with the highest donor number. *n*-Dodecane acts merely as a diluent and the extraction power is due to the phosphine oxide molecules. The donor number and the corresponding extractive power for phosphine oxides can be given as: $R_3P=O > R_2(OR)P=O > R(OR)_2P=O > (RO)_3P=O$.
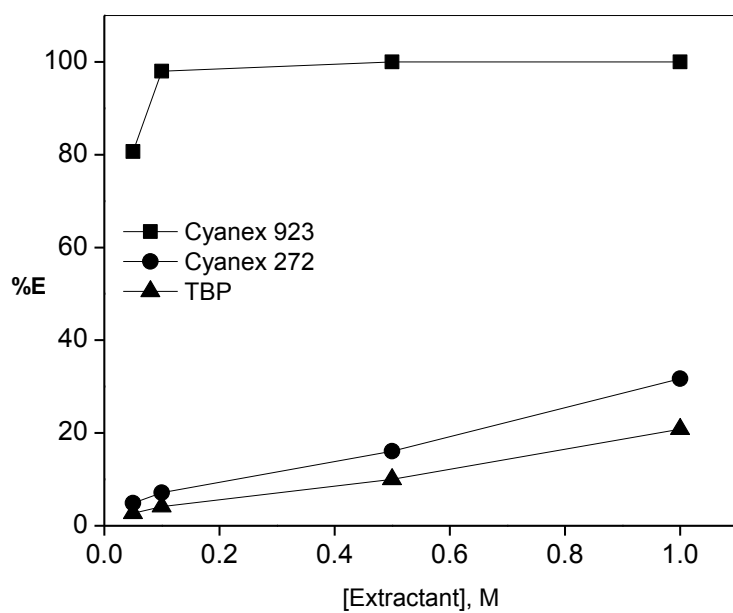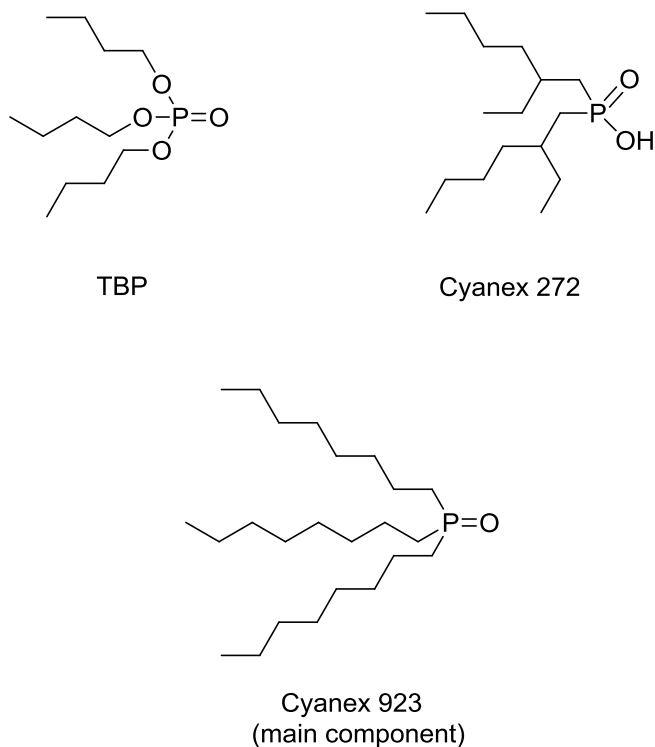
Figure 1. Influence of extractant concentration on the extraction of Nd(III). [Nd(III)] = 7.53 $\times$ 10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M, RT, equilibration time = 30 min.

Scheme 1. Structures of tri-*n*-butylphosphate (TBP), Cyanex® 272 and Cyanex® 923. For Cyanex® 923, the main component $R_3P=O$ (R = octyl) is shown. Other components include $R_2R'P=O$, $RR'_2P=O$ and $R'_3P=O$ (R = octyl, R' = hexyl).

3.3 Extraction of Nd(III)

The extraction of Nd(III) from ethylene glycol solution was studied as a first model system. It is important to determine the equilibration time while studying systems that are more viscous than conventional aqueous systems. Figure 2 shows the variation of %*E* as a function of the equilibration time. It was found that equilibrium was reached very fast, within 2 min. Prolonged equilibration times did not affect the %*E* value. However, to ensure that

equilibrium was reached, all the subsequent experiments were carried out at an equilibration time of 15 min.
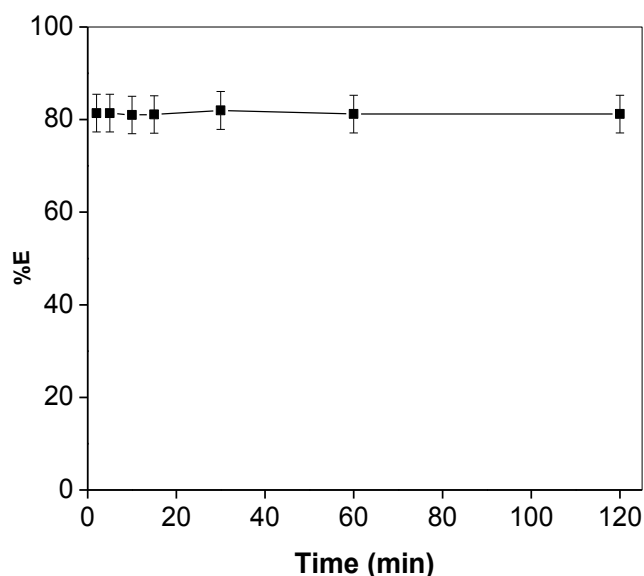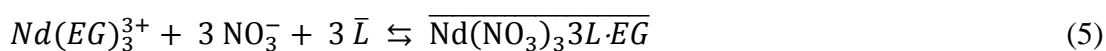

Figure 2. Effect of equilibration time on the extraction of Nd(III) from ethylene glycol. [Nd(III)] = 6.07×10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M, [Cyanex$^{®}$ 923] = 0.05 M in *n*-dodecane, RT.

The extraction of Nd(III) from ethylene glycol containing 1 M LiNO$_3$ was studied by varying the concentration of Cyanex$^{®}$ 923. The percentage extraction of Nd(III) increased from 13.3 to 98.0% with increasing Cyanex$^{®}$ 923 concentration (0.01−0.1 M) as expected. Furthermore, a plot of log D versus log[Cyanex923] is a straight line with a slope of 2.85 ± 0.16. This shows that three molecules of Cyanex$^{®}$ 923 are involved in the extraction reaction (Figure 3). The extraction of Nd(III) by Cyanex$^{®}$ 923 was studied as a function of the nitrate ion concentration in the ethylene glycol solution to investigate the effect of the salting-out

agent (Figure 4). The %*E* of Nd(III) increased from 25.8 to 79.8 with an increase in the nitrate ion concentration from 0.1 to 1 M. This increase in %E values is an indication for the participation of the nitrate ion in the extracted complex.

The IR spectra of loaded Cyanex® 923 shows absorption bands at 1465, 1289, and 1028 cm^{-1} corresponding to vibrations of the coordinated nitrate ion in the Cyanex® 923/*n*-dodecane phase (Figure 5) [35,36]. The band at 1124 cm^{-1} can be assigned to the P=O group in loaded Cyanex® 923, which is shifted due to the coordination to the rare-earth ions from 1147 cm^{-1} in pure Cyanex® 923. The bands at 2956, 2922 and 2853 cm^{-1} are due to C-H vibrations of *n*-dodecane. Note that ethylene glycol bands cannot be observed in the IR spectra of loaded Cyanex® 923/*n*-dodecane phase because of the low concentration of ethylene glycol. EXAFS measurements confirmed the presence of three nitrate ions in the primary coordination shell of Nd(III) in the organic phase, suggesting the species in the organic phase as Nd(NO$_3$)$_3$·3L (*vide infra*).

Based on these findings, it is suggested that Nd(III) is extracted as a neutral complex (*neutral mechanism*) with three coordinated Cyanex® 923 molecules:

$$\text{Nd}^{3+} + 3EG \leftrightarrows Nd(EG)_3^{3+} \tag{4}$$

$$Nd(EG)_3^{3+} + 3\,\text{NO}_3^- + 3\,\overline{L} \leftrightarrows \overline{\text{Nd(NO}_3)_3 3L \cdot EG} \tag{5}$$

Here the bar represents a molecule in the *n*-dodecane phase and *L* stands for a Cyanex923 molecule. It must be mentioned that the stoichiometry of the extracted complex is the same as what is observed for extraction of rare-earth ions by Cyanex® 923 and tri-*n*-butylphosphate (TBP) [37].
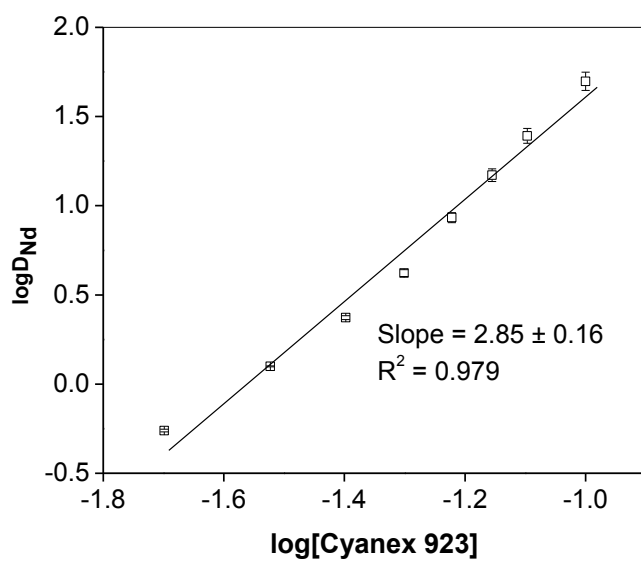
Figure 3. Variation of the distribution ratio of Nd(III) as a function of the Cyanex® 923 concentration. [Nd(III)] = 7.53×10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M, [Cyanex® 923] = 0.01−0.1 M in *n*-dodecane, RT, time = 30 min.
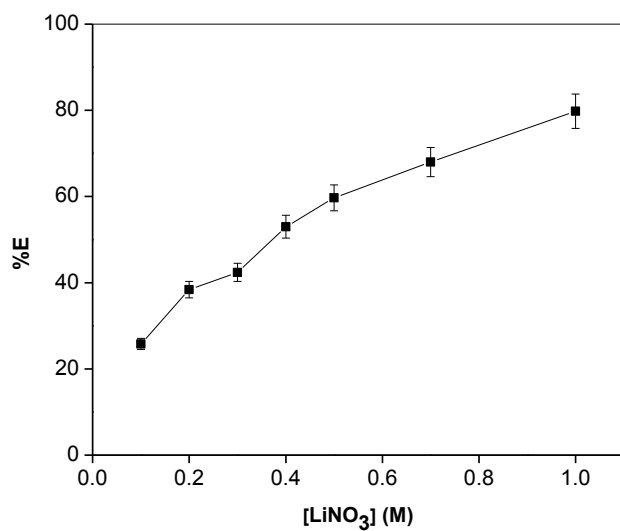
Figure 4. Variation of the *%E* of Nd(III) as a function of nitrate ion concentration. Experimental conditions: [Nd(III)] = 7.01 × 10^{-3} M in ethylene glycol, [LiNO₃] = 0.1–1 M, [Cyanex® 923] = 0.05 M in *n*-dodecane.
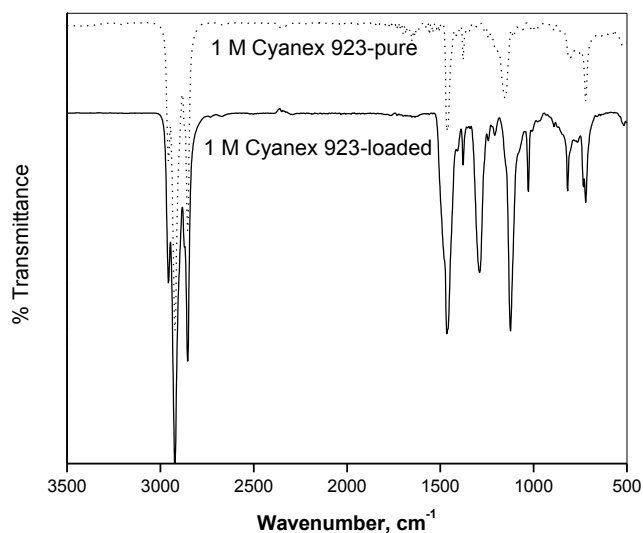

Figure 5. FTIR spectra of Cyanex® 923 before and after loading with Nd(III).

3.4 Speciation studies by EXAFS

EXAFS analysis of the Nd(III) complex in the ethylene glycol phase showed close to nine coordinating oxygen atoms in the first shell positioned at two different positions (Fig. 6). This suggests a tricapped trigonal prism configuration, similar to the hydration of Nd(III) in water [38]. Therefore, the number of oxygen atoms was constrained to 6+3 (Table 1). The fit resulted in two distances, three oxygen atoms are positioned at 2.616 Å (σ^2 = 0.008 Å^2) and 6 oxygens at 2.485 Å (σ^2 = 0.009 Å^2). The number of hydrogen atoms (N = 12) was constrained to be twice the number of oxygen atoms at the shortest distance. Any fit including the three

extra hydrogen atoms attached to the oxygen atoms of ethylene glycol at the capping position lead to impossible parameters for this path, which is due to the low contribution of these scattering atoms to the EXAFS function. A third shell of carbon atoms, was found at 3.469 Å ($\sigma^2 = 0.008$ Å^2). If N was allowed to vary, a degeneracy of 1.4 and a Debye Waller factor of 0.002 Å^2 was found, which is too low to be physically possible at room temperature. As both parameters are strongly correlated, the number of carbon atoms was constrained to three, giving a reasonable σ^2 of 0.008 Å^2. The carbon atoms were found at 3.469 Å, which results into a calculated Nd-O-C bond angle of 114°. A model with six carbon atoms resulted in a bad fit of the Nd-C scattering path suggesting as well monodentate ligating ethylene glycol molecules. This is remarkable as a bidentate coordination mode of ethylene glycol is more probable than a monodentate one [39,40]. A model that assumes monodentate coordinating nitrate ligands in the capping positions, results in a goodness of the fit which was higher (8.9%) than in case of capping ethylene glycol molecules (8%) and a higher σ^2 of 0.012 Å^2. Moreover, monodentate coordination of nitrate ions to trivalent rare-earth ions is very unlikely. Also a bidentate ligating nitrate ions could be excluded because the data are lacking the single and multiple scattering paths involving the furthest oxygen atom of nitrate. Therefore, it can be concluded that Nd(III) is coordinating to six water molecules on the corners of the prism and three monodentate ethylene glycol molecules at the capping positions. The stoichiometry of the Nd(III) complex can therefore be written as $Nd(H_2O)_6(EG)_3$, where EG = ethylene glycol.

Table 1. Selected degeneracies (N), bond distances (r) and Debye-Waller factors (σ^2) for Nd(H$_2$O)$_6$(EG)$_3$.

|	N	r (Å)	σ^2 (Å^2)
Nd - O	6	2.485(2)	0.009(1)
Nd - O	3	2.616(1)	0.008(1)
Nd - H	12	2.919(31)	0.012(4)
Nd - C	3	3.469(12)	0.008(2)
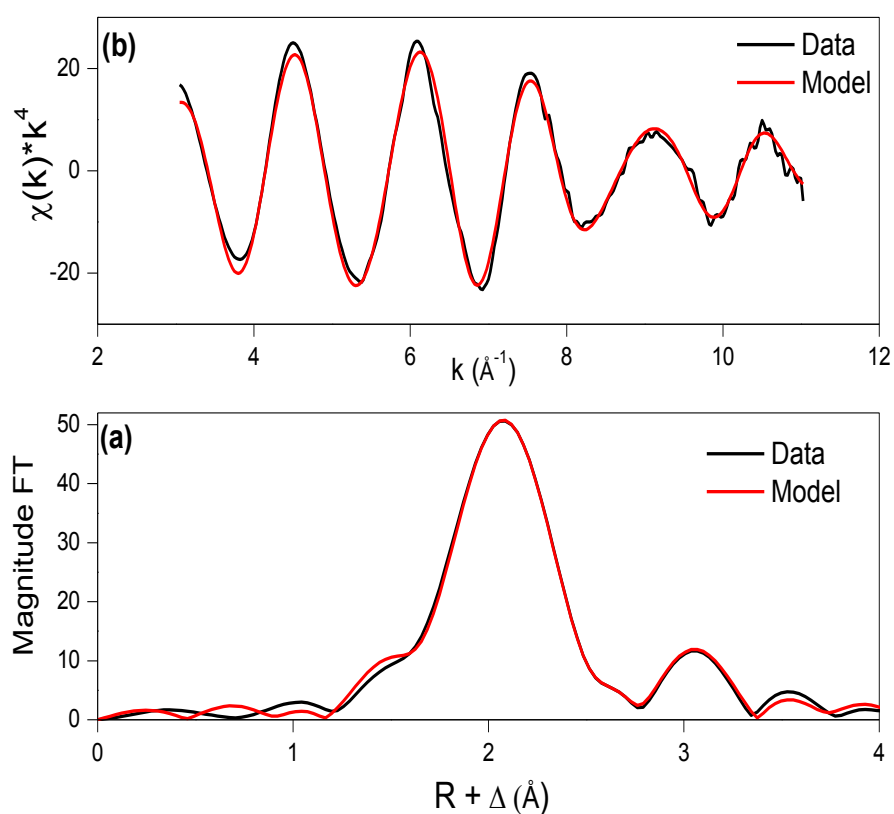
Figure 6. Fourier transform and fitted model of the EXAFS spectrum of Nd(H$_2$O)$_6$(EG)$_3$ (a) and EXAFS function $\chi(k)*k^4$ and fitted model of Nd(H$_2$O)$_6$(EG)$_3$(b).

The EXAFS function of Nd present in the Cyanex® 923/*n*-dodecane phase was modelled based on the crystal structure of Nd(NO$_3$)$_3$(t*ert*-butylphosphine oxide)$_2$ found by Bowden *et al.* [41]. The sum of the single scattering paths to the closest oxygen atoms of the phosphine oxide and the nitrate anions was constrained to nine (Fig. 7). This coordination number was selected based on the assumption that three nitrates are coordinating and the fact that three coordinating phosphine oxides were found by slope analysis. This complex is than similar to the one found for the extraction of Ln from an aqueous solution [37]. The Debye-Waller factor were constrained to be above 0.008, which is a reasonable value for this kind of back-scatterers in the first shell (Table 2). From the crystal structure of Nd(NO$_3$)$_3$(t*ert*-butylphosphine oxide)$_2$, it can be concluded that the multiple scattering paths involving the phosphorus and the oxygen atoms of the phosphine oxide have almost of the same distances because of an Ln-O-P angle close to 180°. To reduce the number of free parameters and the strength of the fit, the Debye-Waller factors and the distances of the two, three and four leg scattering paths involving the phosphorus atoms (and bonded oxygen atom) were set to be equal. This results in a large Debye-Waller factor. The same constrains were made for the scattering paths involving the nitrogen and oxygen atoms of the nitrate anion. In this way, the number of free parameters was equal to 11 and there were 7 degrees of freedom. A fit of the data resulted in three bidentate coordinating nitrate anions and three phosphine oxide ligands.

Table 2. Selected degeneracies (N), bond distances (r) and Debye-Waller factors (σ^2) for the Nd(III) complex extracted by Cyanex® 923 into the *n*-dodecane phase.

	N	r (Å)	σ^2 (Å^2)	Bond distance in Ref. 39 for Nd
Nd - O	5.9(1)	2.521(2)	0.008(1)	2.56
Nd - O	3.1(1)	2.363(4)	0.008(1)	2.35
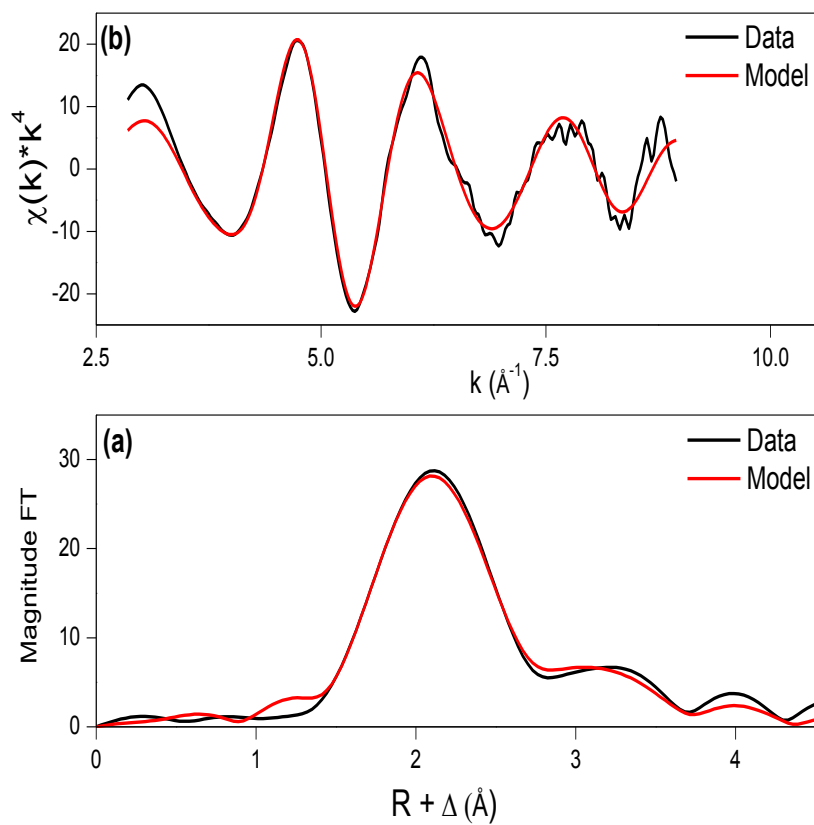
Figure 7. Fourier transform and fitted model of the EXAFS spectrum of $Nd(NO_3)_3(Cyanex^{\circledR}$ 923$)_3$ (a) and EXAFS function $\chi(k)*k^4$ and fitted model of the EXAFS spectrum of $Nd(NO_3)_3(Cyanex^{\circledR}$ 923$)_3$(b).

3.5 Thermodynamic parameters

The extraction of Nd(III) by Cyanex® 923 in *n*-dodecane from ethylene glycol was performed at temperatures ranging from 300 K to 333 K, to determine the influence of the temperature on the extraction process. It was observed that the distribution ratio decreased with increasing temperature. The enthalpy of the extraction was derived from the slope of the plot of log*D* versus 1000/T (K^{-1}) using the Van 't Hoff equation [42]:

$$\Delta H_{tot} = \frac{-2.303\,R\,\Delta\log D}{\Delta(1/T)} \qquad (6)$$

The enthalpy change during the extraction was found to be -9.9 kJ mol^{-1}, showing that the extraction process is exothermic (Figure 8). The change in Gibb's free energy (ΔG) can be calculated from equation (7):

$$\Delta G = -2.303\,RT\,\log K_{ex} \qquad (7)$$

The average value of logK_{ex} was obtained from variation of extractant and nitrate ion concentrations. The value of ΔG was found to be -29.8 kJmol^{-1}. This indicates that the process is energetically favored and spontaneous. The change in entropy (ΔS) at a fixed temperature can be evaluated using equation (8):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad\qquad (8)$$
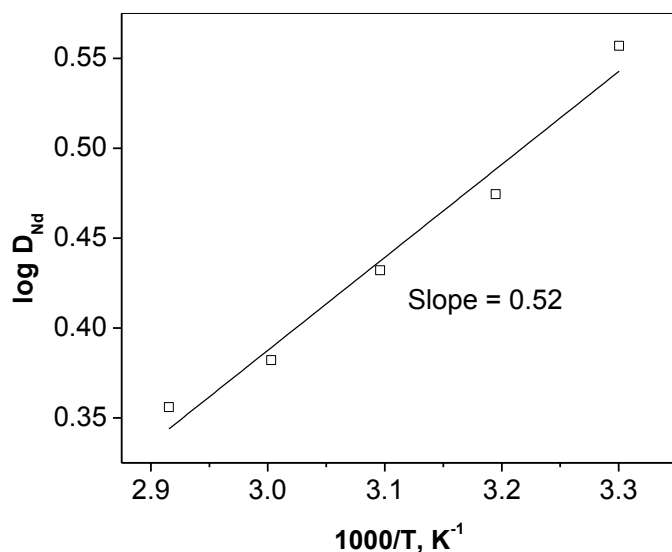
The value of ΔS was determined to be 67.7 $JK^{-1}mol^{-1}$.

Figure 8. Influence of the temperature on the distribution ratio of Nd(III). [Nd(III)] = 6.7 × 10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M, [Cyanex® 923] = 0.05 M, temperature = 303–343 K, R^2 = 0.967.

3.6 Effect of metal ion concentration

The effect of metal concentration was investigated using a 0.05 M Cyanex® 923 solution in *n*-dodecane by varying the metal concentration in the ethylene glycol phase. The %*E* decreased gradually with an increase in the metal concentration in the feed (Figure 9). The loading of Cyanex® 923 increased with increasing in metal concentration in the feed up to 1430 mg L^{-1}

and a plateau region corresponding to maximum loading was observed for higher metal

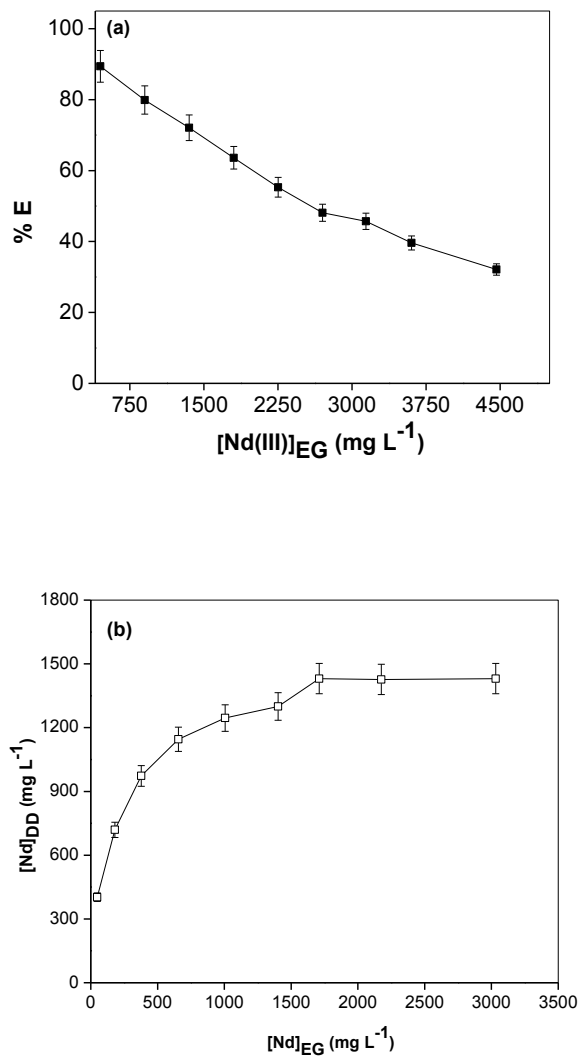concentration in the feed solution.

Figure 9. (a) Variation of the %*E* of Nd(III) as a function of the initial Nd(III)

concentration in the ethylene glycol phase and (b) extraction isotherm of Nd(III). $[Nd(III)]_{Feed}$

$= 450–4500$ mg L^{-1}, $[LiNO_3] = 1$ M, $[Cyanex^® 923] = 0.05$ M in *n*-dodecane, RT.

3.7 Influence of water

The water content of ethylene glycol feed solution (containing the rare-earth salt) was 0.05 wt%. Most of the water was introduced via the water of hydration of the hydrated rare-earth nitrate salts. To investigate the influence of larger quantities of water, water was gradually added to the Nd(III) feed solution. It was observed that the %E gradually increased as a function of the water concentration until 30% (v/v) (Figure 10). For higher concentrations of water, the %E remained constant as a function of the water concentration. Nd(III) is less efficiently extracted from an ethylene glycol feed solution than from an aqueous feed solution. This can be explained on the basis of solvation of metal ions in non-aqueous solvents. The activity of cation is suppressed in the non-aqueous solvent environment and this leads to poor extraction of the metal ion to the less polar organic phase. These observation are similar to the results observed by Shibata *et al.* from the extraction of Cu(II) from mixed aqueous-organic solutions of DMSO by bis(2-ethylhexyl)phosphoric acid (D2EPHA) diluted in hexane [43].
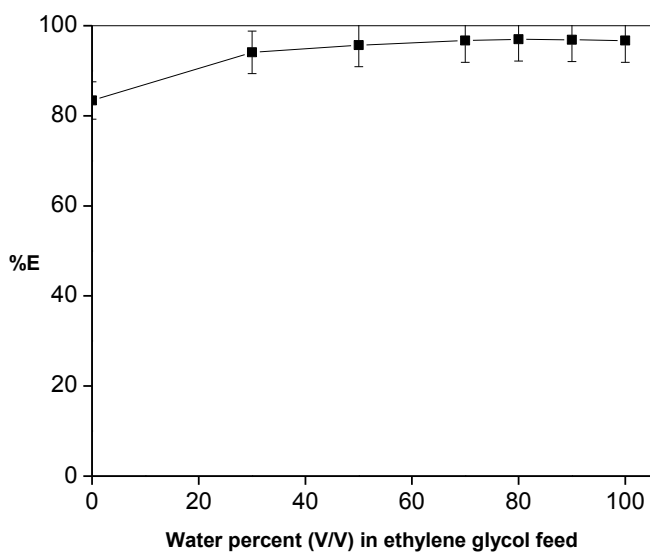
Figure 10. Influence of the water percent in ethylene glycol (EG) phase on the extraction of Nd(III) by Cyanex® 923 in *n*-dodecane. [Nd(III)] = 6.47×10^{-3} M, EG = 0–100% (v/v), [LiNO$_3$] = 1 M, [Cyanex® 923] = 0.05 M, RT.

3.8 Screening of solvents as polar phase

The extraction of Nd(III) from ethylene glycol was compared with different solvents that are immiscible with *n*-dodecane. Figure 11 indicates that extraction of Nd(III) is more efficient from ethylene glycol than from *N,N*-dimethylformamide (DMF) and methanol (CH$_3$OH). In addition, ethylene glycol (EG) can be considered as best solvent from an environmental point of view, considering the non-volatile nature and high boiling point [44]. It is interesting to note that the extraction order in the solvents follows their acceptor number and dielectric constant [20]. The *acceptor number* (AN) is a measure of the electrophilic behavior of a solvent relative to SbCl$_5$ [45]. The solvents considered in this study and their dielectric

constant of solvents are listed in Table 3. The solvent with highest acceptor number showed
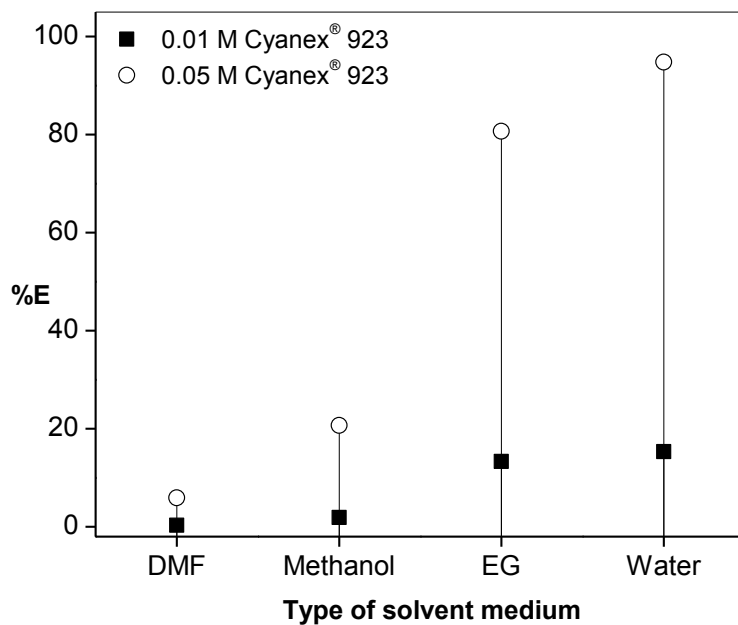
the highest percentage extraction.

Figure 11. The extraction of Nd(III) from different solvent feed solutions by Cyanex® 923.

[Nd(III)] = 6.7×10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M.

Table 3. Acceptor number and dielectric constants of solvents

Solvent	Acceptor Number[43]	Dielectric constant[20]
Water	54.8	80.4
EG	42.8	37.0
Methanol	41.3	32.6
DMF	16	26.6

3.9 Influence of diluents

The influence of the nature of different diluents on the extraction of Nd(III) from ethylene glycol by Cyanex® 923 was studied (Figure 12). The physical properties of the diluent play an important role in the solvent extraction of metals. The extraction is higher using aliphatic diluents than aromatic diluents. Based on the experimental results, *n*-dodecane can be considered as the best diluent.
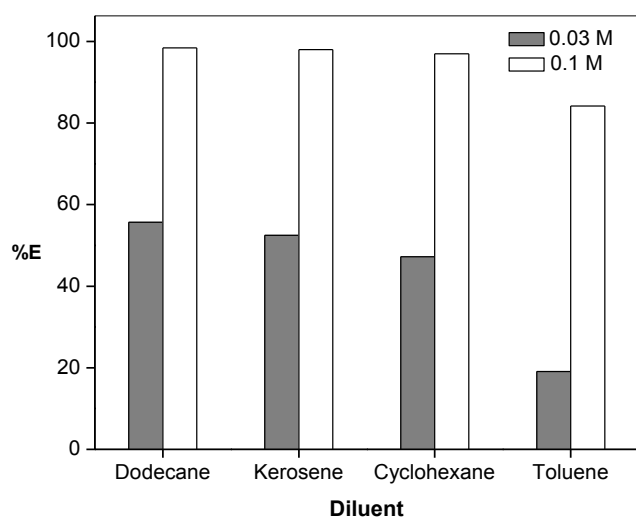

Figure 12. The influence of diluent on the extraction of Nd(III) by Cyanex® 923. [Nd(III)] = 6.7×10^{-3} M in ethylene glycol, [LiNO$_3$] = 1 M, [Cyanex® 923] = 0.03 M and 0.1 M, RT.

The performance of the ethylene glycol / (*n*-dodecane + Cyanex® 923) system was compared with that of the corresponding aqueous system, for several rare-earth ions. The extraction parameters for the two extraction systems were the same, except that water was the polar solvent in the aqueous system and ethylene glycol in the non-aqueous system. The

concentration of each rare-earth ion was $(1.07 \pm 0.2) \times 10^{-3}$ M. The extractions were performed from mixture of different rare earths. The extraction of the rare-earth ions increases with increasing in their atomic number in both systems, but differences are observed for the two extraction systems (Figure 13). The extraction of the light rare earths is less efficient from ethylene glycol than from aqueous solutions. On the other hand, the extraction of heavy rare earths increases in ethylene glycol medium as a function of the atomic number, so that the separation of heavy rare earths from light rare earths is facilitated. For extraction of rare-earth nitrates from aqueous solution by Cyanex® 923, the separation factor β for neighboring heavy rare earths is virtually equal to 1.00, so that no separation of mixtures of rare earths is possible. The separation factor of the Dy+Yb pair over La+Ce+Pr+Nd was found to be 54.5 at 0.03 M Cyanex® 923 in n-dodecane from ethylene glycol medium, whereas it was only 2.3 from aqueous solutions. This indicates that the ethylene glycol / (n-dodecane + Cyanex® 923) system can be used for group separations of the heavy rare earths from the light rare earths.
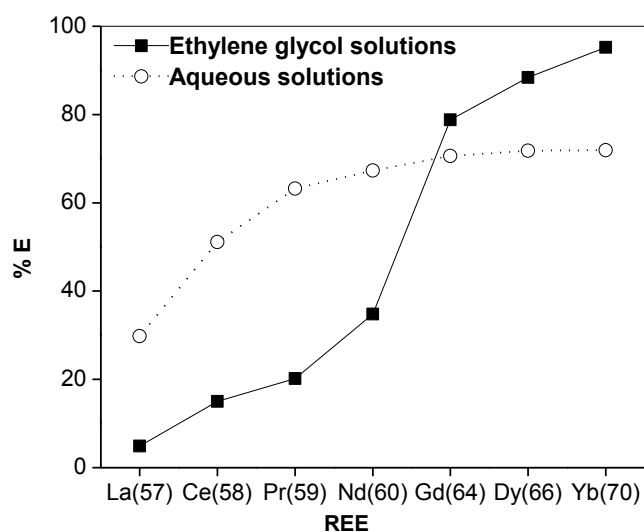
Figure 13. Comparison of extraction behavior of a mixture of trivalent rare-earth ions from aqueous solutions and from non-aqueous ethylene glycol solutions using 0.03 M Cyanex[®] 923 in *n*-dodecane. [RE(III)] = $1.07 \pm 0.2 \times 10^{-3}$ M (each), [LiNO$_3$] = 1 M, RT.

The influence of variation in the concentration of the extractant Cyanex[®] 923 in the *n*-dodecane phase on the extraction efficiency was investigated. The concentration of Cyanex[®] 923 was varied between 0.01 M and 0.1 M. Extraction from ethylene glycol medium was compared with extraction from aqueous solution (Figure 14). A first trend that can be observed is that the %*E* increases with increasing Cyanex923 concentration, as expected. For extractions from aqueous solutions, the %*E* values for the different rare-earth ions are very similar (except for La(III) and Ce(III)) so that separation of mixtures of rare-earth ions is impossible under these experimental conditions. For extraction from ethylene glycol, the different rare-earth ions show different %*E* and *D* values at each of the Cyanex[®] 923 concentrations investigated.
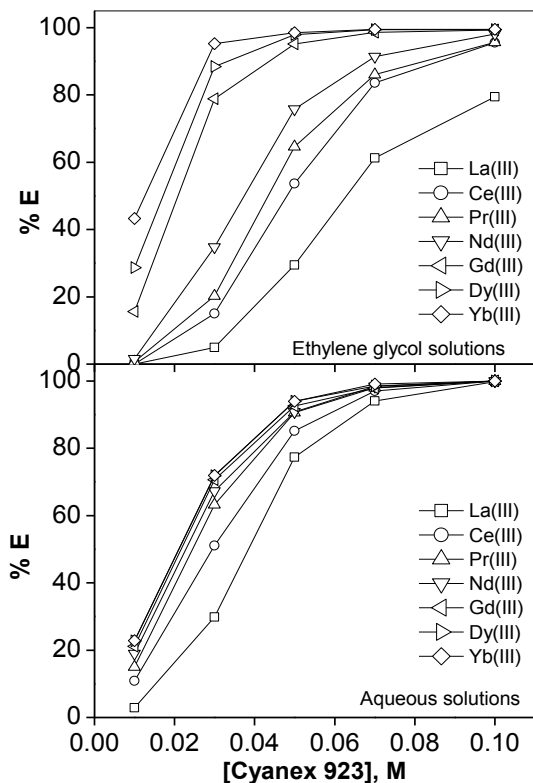
Figure 14. Influence of the Cyanex® 923 concentration on the extraction of a mixture of trivalent rare-earth ions from aqueous solutions and non-aqueous ethylene glycol solutions. [RE(III)] = $1.07 \pm 0.2 \times 10^{-3}$ M (each) in EG, [LiNO$_3$] = 1 M, [Cyanex® 923] = 0.01–0.1 M in n-dodecane, RT.

3.10 Separation of Dy(III) and Nd(III)

The separation of binary mixtures of Nd(III) and Dy(III) in ethylene glycol was studied, with Nd(III) being a representative light rare earth and Dy(III) a representative heavy rare earth. In Figure 15, the separation factors β $_{Nd,Dy}$ are compared for aqueous and non-aqueous solutions

(ethylene glycol) for different concentrations of Cyanex® 923 and from solutions containing 1.07×10^{-3} M of Nd(III) and . 1.07×10^{-3} M of Dy(III). This figure clearly shows that the separation factors are much larger for extraction from ethylene glycol than from aqueous solutions. In fact, no separation of Nd(III) and Dy(III) can be achieved by extraction from aqueous solution with Cyanex® 923 under these conditions. Extractions from ethylene glycol solutions with three different concentrations (1 gL^{-1}, 5 g L^{-1} and 10 g L^{-1} of each element) of binary mixtures of Nd(III) and Dy(III) were studied as a function of the Cyanex® 923 concentration (Figure 16). The separation factor of Dy(III) over Nd(III) is 24.6 from ethylene glycol for a Cyanex® 923 concentration of 0.01 M, whereas the separation is only 1.2 for extraction under similar experimental conditions from aqueous solutions. It was not possible to calculate separation factor values for Cyanex® 923 concentration of 0.1 M since there is close to 100% extraction of both Dy(III) and Nd(III) under these condition. The separation efficiency depends both on the concentrations of the extractant and the metal ion. The maximum separation factors for solutions containing 1, 5 and 10 g L^{-1} of metal ions were 25.1, 13.0 and 12.9, respectively. These separation factors suggest that separation of binary Nd(III)/Dy(III) mixtures is possible by extraction from an ethylene glycol solution by Cyanex® 923, even at industrially relevant concentrations of rare-earth salts of 10 g L^{-1}. For the highest Cyanex® 923 concentrations, it is not possible to calculate D values and thereby separation factor $\beta_{Nd,Dy}$ since there is 100% of extraction. This is due to the fact that in the presence of a large excess of extractant compared to the concentration of the rare-earth ions in the feed solution, there is little competition between the two ions for extraction by the extractant molecules so that even the least extractable ion is extracted in an appreciable amount.
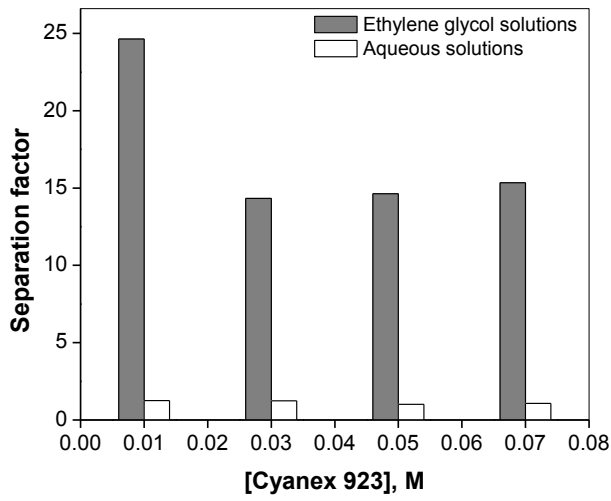
Figure 15. Comparison of the separation factors of Dy(III) over Nd(III) from aqueous solutions and non-aqueous ethylene glycol solutions for extraction by Cyanex® 923 in *n*-dodecane.
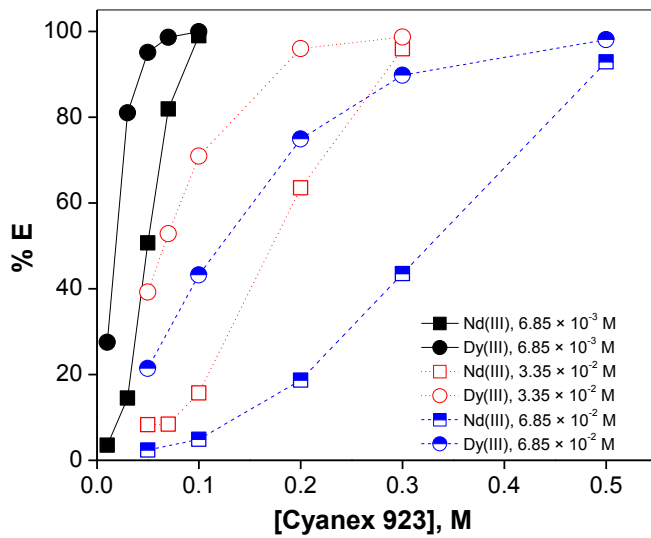

Figure 16. Influence of the Cyanex® 923 concentration on the extraction of a binary mixture of Nd(III) and Dy(III) from ethylene glycol solutions at room temperature.

3.11 Stripping studies

After extraction, the rare-earth could be stripped from the *n*-dodecane phase by addition of oxalic acid so that the rare-earth oxalates precipitated (precipitation stripping) [46]. Stripping of the loaded Cyanex® 923/*n*-dodecane phase was carried out using oxalic acid and water (Table 4). 100% stripping was found with 0.01 M oxalic acid and also with water.

Table 4. Stripping of Nd(III) from Nd(III) loaded 0.1 M Cyanex® 923

Oxalic acid, M	0.01	0.05	0.1	0.5	Water
% Stripping	100	100	100	100	100

[Nd(III)] in loaded phase = 6.6×10^{-3} M

3.12 Recycling studies

The reuse of 0.05 M Cyanex® 923/*n*-dodecane was studied for five extraction and stripping cycles. First, Cyanex® 923/*n*-dodecane was loaded with Nd(III) and then the loaded Cyanex® 923 was stripped with water. The extraction and stripping percentages corresponding to a single extraction and stripping cycle are 80% and 100%, respectively. The spent Cyanex® 923/*n*-dodecane was used for a second extraction/stripping cycle. The procedure was repeated for five cycles. The extraction percent of Nd(III) was remain unchanged (80 ± 2 %) after five extraction cycles and stripping percent of 99± 2% after 5 stripping cycles. This indicates the very good recycling capacity and stability of the extraction system.

4. Conclusions

Solvent extraction with two mutually immiscible organic phases can offer advantages over conventional extraction from an aqueous phase to an immiscible organic phase as shown for the extraction of trivalent rare-earth ions from ethylene glycol solutions by the neutral extractant Cyanex® 923 dissolved in n-dodecane. This extractant system performs better for the group separation of heavy rare earths from light rare earths than the corresponding conventional extraction system with an aqueous phase. Also the separation of binary mixtures of Nd(III) and Dy(III) are possible by this new solvent extraction system.

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