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1-methylimidazolium di(2-ethylhexyl) phosphate as ionic liquid in Dysprosium extraction from nitrate medium

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Abstract

In this work, a novel room temperature ionic liquid1-methylimidazolium di(2-ethylhexyl) phosphonic acid was synthesized, characterized and tested as extractant in the Dysprosium(III) liquid-liquid extraction. The effects of parameters such as contact time, aqueous to organic phase's volume ratio, metal concentration, ionic liquid concentration, pH levels, ionic strength, and temperature were reported.

The extraction efficiency of Dysprosium(III) ions was increased by increasing the concentration of ionic liquid and wasnegatively influencedby the presence of CH_3COONa salt in the aqueous phase. The results showed also that theextraction process was feasible, spontaneous and most favourable at higher temperature.

Key words: Extraction, Dysprosium, ionic liquid, optimisation, thermodynamic.

1. Introduction

Dysprosium is a rare earth element that has a metallic, bright silver luster, relatively stable in air at room temperature, but dissolving readily in dilute or concentrated mineral acids with the emission of hydrogen[1]. Dy(III) is the most abundant of the heavier lanthanide elements[2]. Due to its thermal neutron adsorption cross-section and high melting point, dysprosium along with special steel is used to make nuclear reactor control rods[3]. Dysprosium is used, in combination with vanadium and other rare earth in making laser materials[1]. Dysprosium–cadmium chalco- genides are sources of infrared radiation for studying chemical reactions; furthermore, it is used for manufacturing compact discs[4,5]. Dy(III) was also used as a fluorescent and dopant to the neodymium magnet alloys and ferrites for microwave, in metallurgy, petroleum industry, electronics and electro optics, biomedicine[6-8]. Dy(III) complexes has also been employed as a magnetic resonance imaging contrast agents[9].

It is important to develop the recycling system of rare earths element such as Dy since especially it is anticipated that over the next 25 years the demand for Dy will rise by 2600%[9]. Several conventional methods, such as chemical precipitation[10], electro-deposition[11], adsorption[12], ion exchange[13], solvent extraction by conventional extractant[14], and supported liquid membrane[15] have been developed for these purposes and researchers encountered various difficulties[16]. More efficient and low-cost removal and recovery methods are needed to overcome these difficulties.

In this context, ionic liquids (ILs), already used in various industrial fields[17], may prove usefuldue to their many unique properties such as negligiblevapor pressure, high thermal stability, non-flammability and good solvating properties together with large spectral transparency, tuneable viscosity and miscibility with water and organic solvents, as well as good extractability for various organic compounds and metal ions[18]. In comparison with conventional molecular solvents, ILs exhibit enhanced distribution coefficients for a number of complexing ligands in the extraction of metal ions from aqueous solutions[19].

This work reports an investigation of 1-methylimidazolium di(2-ethylhexyl) phosphate solubilized in chloroform for solvent extractions of dysprosium ions from nitric aqueous media.

2. Experimental

2.1. Reagents:

All chemicals and reagents used were analytical reagent grade. 1-methylimidazole (98%), sodium chloride, nitric acid (≥ 69%), sodium acetate, ArsenazoIII and buffer solution at pH = 13.0 were purchased from Aldrich. Di (2-ethylhexyl) phosphate, chloroform, hydrochloric acid (37%) were provided from Fluka. Dysprosium oxide (Dy_2O_3, 372.99 $mol.g^{-1}$, 99.9 %) was supplied from Rare Earth Products, Cheshire.

A stock solution of dysprosium(III) (1 $mg.L^{-1}$) was prepared by dissolving 0.1148 g ofDy_2O_3 in hot 10 mL of 1:1 distilled water : HNO_3 and diluted to 100 mL by distilled water. The diluted solutions were prepared by appropriate dilution of the stock solution.

2.2. Apparatus:

All pH measurements were performed with a WTW 3310 Set 2 digital pH meter. The extraction of Dy(III) on the ionic liquid was studied by the batch technique. A multi-post stirrer (Haier model) was used for all extraction experiments. The dysprosium ions concentration, in aqueous phase, was determined spectrophotometrically using a spectrophotometer (Analytik Jena Specord-210 Plus) by means of ArsenazoIII[20]. The absorbance was measured at λ_{max} = 660 nm, in a 1 cm cell. Analysis of IL synthesized was performed using a Bruker nuclear magnetic resonance (DRX500) spectrometer for ^{1}H, ^{13}C and ^{31}P NMR. Analysis by FT-IR spectroscopy was performed using a Cary 630 FTIR from Agilent Technologies, Consort C831 pH meter with combined glass electrode were used for concentration copper ions and pH measurements (Adwa).

2.3. Ionic Liquid Synthesis:

Di(2-ethylhexyl) phosphoric acid (D2EHPA) (6.448 g, 20 mmol) was mixed with 1-bu- tylimidazole (2.483 g, 20 mmol) and the mixture was shakenfor 24 h at room temperature (25°C)) till the formation of a yellow viscous liquid. The viscous liquid was rinsed with large amount of ethyl acetate in a separation funnel. After that, solvent was evaporated in rotary evaporator and remained liquid was dried on anhydrous magnesium sulfate. The yield was about 98%. The purity of final product was characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and FTIR (figure 1).

- ^{1}H NMR, δ/TMS (ppm): 0.96 (m, 15H, CH_3), 1.33 (m, 18H, CH_2), 1.56(m, 4H, CH), 3.93 (m, 4H, CH_2O P), 5.0 (t, 1H, NH), 5.72 (q; 1H, CH_{ar}), 5.89 (q; 1H, CH_{ar}), 6.36 (q; 1H, CH_{ar}), 7.11 (s, 1 H, P(OH)).
- ^{13}C NMR, δ/TMS (ppm): 11.6; 14.1; 68.8; 117.8; 119.1; 142.5, 21.7; 23.0; 23.3; 29.3; 30.4; 30.6; 32.6; 34.2; 22.4; 40.3; 108.1; 108.5; 118.0; 141.5.
- ^{31}P NMR, δ/H3PO4 (ppm): 0.02.
- IR, ν (cm^{-1}): 895 (w), 1045 (P-OC, vS, L), 1240 (P = O, S, L), 1380 (w), 1470 (m), 1685 (w, L), 2855 (S), 2955 (vS).

δ, chemical shift; ν, wave number; s, singulet; d, dou-blet; t, triplet; q, quadruplet; quint, quintuplet; sext, sex-tuplet; m, multiplet; J, coupling constante;ar, aromatic; S, strong; L, large; w, weak.

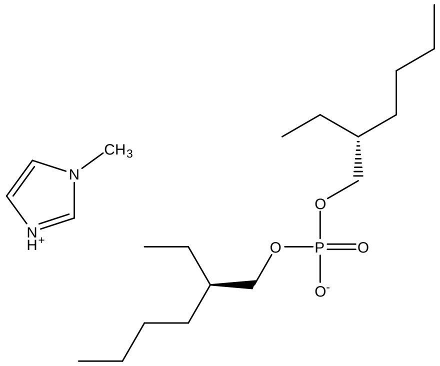

Fig. 1. Structure of 1-methylimidazolium di(2-ethylhexyl) phosphate ionic liquid (IL).

2.4. Extraction studies:

Solvent extraction experiments were carried out in in a 60 mL separating funnel by shaken, at room temperature (25°C), equal volumes (5 mL) of aqueous and pre-equilibrated organic phases (ionic liquid and solvent) for necessary time to reach the extraction equilibrium. Independent extraction experiment as a function of time suggested that 10 min duration was sufficient for achieving equilibrium condition and thereafter the organic and aqueous phases were allowed to settle for phase separation. The concentrations of dysprosium in different aqueous phase samples were determined by Arsenazo (III) based spectrophotometric methodsand those in the organic phases were calculated by the difference of the dysprosium concentration in the aqueous phase before and after extraction[20]. All measurements were performed at least twice under the same conditions, and the relative standard deviations were less than 5%.

The distribution ratio (D) of dysprosium was calculated as:

$$D = [Dy(III)]_{org(eq)}/[Dy(III)]_{aq(eq)} \qquad (1)$$

where $[Dy(III)]_{org(eq)}$ and $[Dy(III)]_{aq(eq)}$ refer to dysprosium concentrations in organic and aqueous phases, respectively, under equilibrium condition.

Percentage extraction (%E) is defined as:

$$\% E = \frac{[Dy(III)]_{aq(i)} - [Dy(III)]_{aq(eq)}}{[Dy(III)]_{aq(i)}} \qquad (2)$$

where $[Dy(III)]_{aq(i)}$ and $[Dy(III)]_{aq(eq)}$ are initial and equilibrium dysprosium concentration in the aqueous phase respectively.

3. Results and Discussion

3.1. Variation of equilibration time:

Dysprosium (III) was extracted from a nitric acid solution by 1-methylimidazolium di(2-ethylhexyl) phosphate ionic liquid dissolved in chloroform, with variation of different extraction parameters. For these experiments, a Dy(III) concentration of 1.4 mmol.L^{-1} and a 1-methylimidazolium di(2-ethylhexyl) phosphate concentration of 5.0 mmol.L^{-1} was used. The volume ratio of the organic to the aqueous phase was 1:1. The initial pH and temperature was 5.8 and 20 °C respectively. The first parameter that was varied was the equilibration time, in order to determine the time required to reach the equilibrium condition (Fig. 2). Extraction was fastest; maximum extraction was obtained after only 10 min. In the present work, the equilibration time of 10min was used for all further extraction studies.

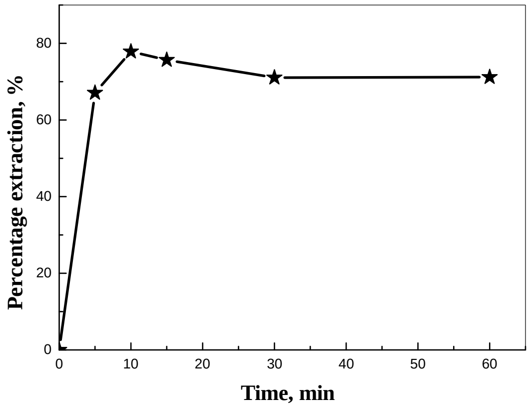

Fig.2.Variation of percentage extraction of Dy(III) as a function of the equilibration time. [Dy(III)] = 1.4 mmol.L^{-1}, [IL] = 5 mmol.L^{-1}, pHi = 5.8, T = 20 °C, A/O = 1.

3.2. Effect of dysprosium concentration:

The effect of dysprosium(III) concentration in the aqueous phase on the extraction was carried out by varying the concentration in the range of 1.40 to 15.4 mmol.L^{-1} at pH = 5.8. The percent extraction were determined in each case at phase ratio =1 and temperature 25 °C. The results of this study are illustrated in figure 3. From the plot it is evident that the percent extraction value decrease with increase in Dy(III) ion concentration in aqueous solution, which is likely due to decrease in effective concentration of IL concentration in the organic phase as a result of its complex formation with the metal ion.

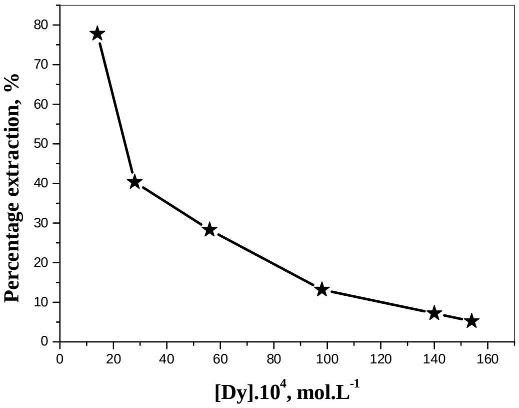

Fig. 3. Variation of percentage extraction of Dy(III) as a function of the initial concentration of Dy(III) in aqueous phase. [IL]=5 mmol.L^{-1}, pH$_i$ = 5.8, t = 10 min, A/O = 1.

3.3. pH effect:

The initial pH of the aqueous phase plays a very significant role in the overall performance of the extraction system, affecting the complex formation and the extraction efficiency. To obtain the optimum conditions, the extraction of Dy(III) was studied from aqueous nitrate solutions containing 0.14 mmol.L^{-1} dysprosium metal ion by 5.0 mmol.L^{-1} 1-methylimidazolium di(2-ethylhexyl) phosphate (MIm$^+$.DEHP$^-$) ionic liquid at a 1:1 phase ratio at different initial pH values ranged from 3.1 to 6.0. The initial pH was adjusted by HNO_3 acid or NaOH solution. As can be seen from figure 4, extraction of dysprosium increases when the initial pH of the solution was increased from 3.1 to 4.3. This reveals that the extraction of Dy(III) is pH dependent, and the pH could affect the stability of the complex. At initial pH > 4.3, extraction of Dy(III) increased. Therefore, pH of sample solutions was adjusted at 4.3 on the subsequent experiments.

The mechanism for extraction of a Dy(III) ion from the aqueous phase to the organic phase is the ion exchange mechanism. The Dy^{3+} ion or a positively charged Dy(III) complex are extracted from water to the organic phase by cation exchange, while simultaneously ionic liquid cations (1-methylimidazolium) are transferred to the water phase for the reasons of charge balance[21]. According CHEAQS and MEDUSA software, the predominate species of Dy(III), in this pH interval, are Dy^{3+}, Dy$(NO_3)^{2+}$ and Dy$(OH)^{2+}$[22]. Depending on the type of positively charged Dy(III) complex that is formed, the ion exchange mechanism can be represented by the following equations (eq. 3-5):

$$Dy^{3+} + 3\,NO_3^- + 3\,\overline{(MIm^+.DEHP^-)} \leftrightarrow \overline{Dy(DEHP)_3} + 3\,MIm^+.NO_3^- \tag{3}$$

$$Dy(NO_3)^{2+} + 2\,NO_3^- + 2\,\overline{(MIm^+.DEHP^-)} \leftrightarrow \overline{Dy(NO_3)(DEHP)_2} + 2\,MIm^+.NO_3^- \tag{4}$$

$$Dy(OH)^{2+} + 2\,NO_3^- + 2\,\overline{(MIm^+.DEHP^-)} \leftrightarrow \overline{Dy(OH)(DEHP)_2} + 2\,MIm^+.NO_3^- \tag{5}$$

Here the bar represents again molecules and ions in the organic phase. The pH dependence can be explained by the competition between the extraction of protons (or acid molecules) and the extraction of metal ions (or metal salts): IL are able to extract acids at low pH values[21,23].

3.4. Volume ratio effect:

The effect of aqueous/organic phase ratio (A/O) has been studied using aqueous solution containing 1.4mmol.L^{-1} of dysprosium with 5.0mmol.L^{-1} of ionic liquid at initial pH of 4.3. The results presented in figure5 indicate that the extracted metal percentage decreased with increasing the A/O phase ratio. The variation of the phase ratio from 1.0 to 3.5 lead to a decrease in the yield of extracted metal from 90.2 to 10.2 %.Therefore, phase volume ratio was adjusted at 1 on the subsequent experiments.

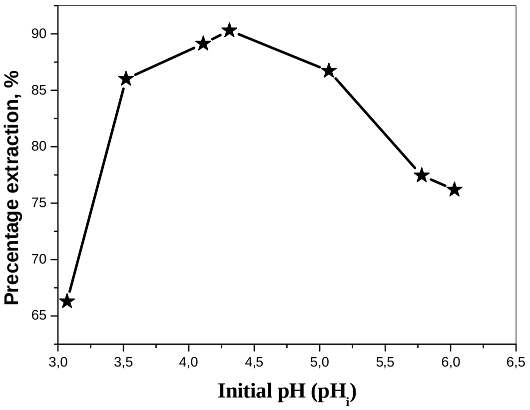

Fig. 4. Variation of the percentage extraction of Dy(III) as a function of the initial pH of the aqueous phase. [Dy(III)] =1.4x10^{-3} mol.L^{-1}, [IL] = 5.0x10^{-3} mol.L^{-1}, T = 20 °C, t = 10 min, A/O = 1.

3.5. Effect of ionic liquid concentration:

The effect of ionic liquid (IL) concentration on the extraction yield of dysprosium was studied in the range 1.0 – 7.0 mmol.L^{-1}. The operating conditions used were initial pH = 4.3, A/O phase ratio = 1 and T = 25 °C.

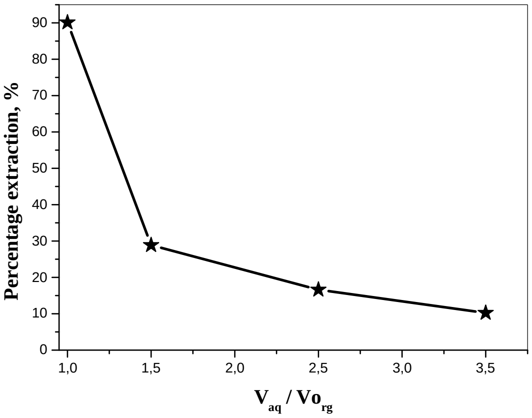

Fig. 5.Variation of percentage extraction of Dy(III) as a function of the aqueous/organic phase ratio (A/O). [Dy] =1.4 mmol.L^{-1}, [IL] =5 mmol.L^{-1}, pHi = 4.3, t = 10 min.

It was observed that the extraction yield increased strongly with increase of extractant concentration (figure 6). In the extractant concentration range [1.0 – 7.0 mmol.L^{-1}], the increase was from 18.3 to 91.1 %.

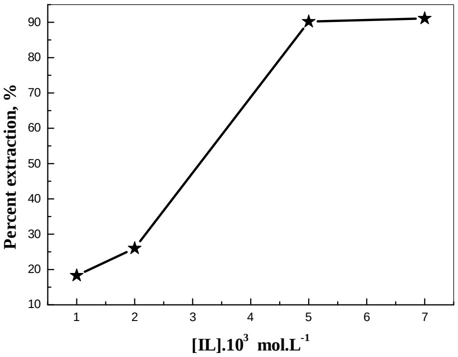

Fig. 6. Variation of percentage extraction of Dy(III) as a function of the initial concentration of IL in organic phase. [Dy]=1.4 mmol.L^{-1}, A/O =1, t = 10 min, pH =4.3, A/O = 1.

3.6. Determination of the metal–organic complex species:

The complex stoichiometry for the extraction reaction can be determined using slope method[24]. As illustrated in figure 7, the linear relationship between logD and log[IL] at initial pH 4.3 is obtained with a slope of 2.23 (~2). The slope show the stoichiometry between $(MIm^+.DEHP^-)$:Dy^{3+}reagents and is equal to 2:1. The extraction equation of dysprosium in nitrate medium with $(MIm^+.DEHP^-)$ diluted in chloroform can be represented by the general equilibrium equation(eq. 7)[23]:

$$Dy^{3+} + 3NO_3^- + 2\overline{(MIm^+.DEHP^-)} \leftrightarrow \overline{Dy(MIm^+.DEHP^-)_2(NO_3)_3} \qquad (6)$$

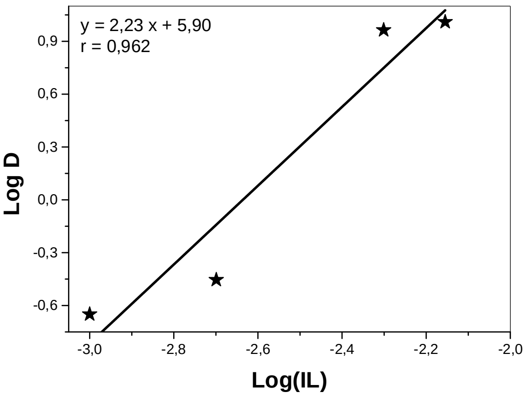

Fig. 7. Effect of ionic liquid concentration on the distribution coefficient of dysprosium. [Dy]=1.4 mmol.L^{-1}, A/O = 1, t = 10 min, pH=4.3, A/O = 1.

3.7. Effect of the presence of sodium acetate in aqueous phase:

In aqueous solutions, ionic strength is an important factor in chemical reactions, because it affects the rates at which ions react with each other and thus, the equilibrium and the extent to which the reaction occurs. The addition of salts can decrease[24] or promote[25] the extraction efficiency of analytes.

In order to verify this effect, the extraction experiments was conducted by equilibrating 5 mmol.L^{-1} ionic liquid with 1.4mmol.L^{-1} of Dy(III) cation in the presence of different amount of CH_3COONa salt (figure 8). The corresponding decrease in percent extraction of Dy(III) with increasing CH_3COONa amount can be attributed to increasing Na^+ concentration who enters in competition with Dy(III) during the extraction with $MIm^+.DEHP^-$[24].

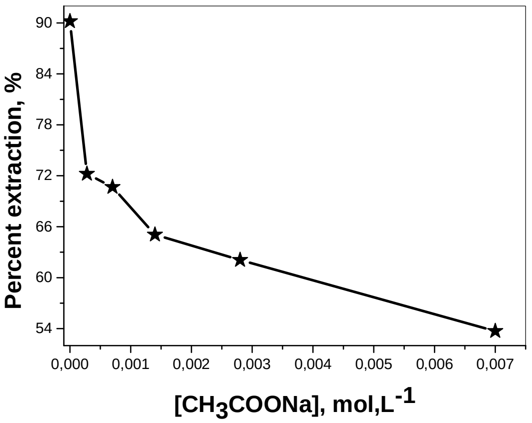

Fig. 8. Effect of the presence of CH_3COONa on the dysprosium extraction. [Dy] =1.4 mmol.L^{-1}, [IL] = 5 mmol.L^{-1}, pHi= 4.3, t = 10 min, A/O = 1.

3.8. Temperature effect:

The effect of temperature on the Dy(III) extraction from nitrate solution by 1-methylimidazolium di(2-ethylhexyl) phosphate(IL) at pHi = 4.3, A/O = 1, [IL] = 5 mmol.L^{-1} and concentration of Dy (III) =1.4 mmol.L^{-1} is studied. This study is efficient for the determination of thermodynamic data such as, the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). ΔG is calculated using the following equations:

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

$$\Delta G = -RTLnD \qquad (8)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), and T the temperature (K). The relation between ΔG, ΔH and ΔS can be described by Van't Hoff correlation in Eq. 9.

$$\mathrm{LnK} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (9)$$

Figure 9 shows the percent extraction (%) of Dy(III) ions as a function of the temperature. It can be seen that the percent extractionslightly increases with increasing temperature,the percent extraction increases from 90.8 to 94.9 % when the temperature increases from 298 to 318 K. This increase in extraction with increase in temperature may be due to increase in stability of the extracted complex with increase in temperature.

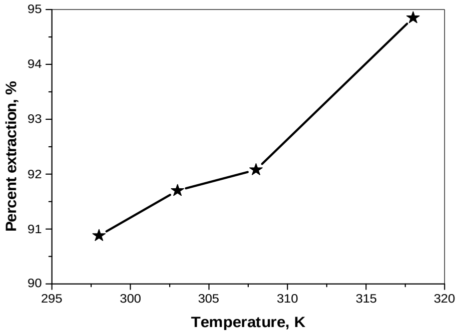

Fig.9. Effect of temperature on the percentage extraction of Dy(III).[Dy] =1.4 mmol.L^{-1}, [IL] = 5 mmol.L^{-1}, pHi = 4.3, t = 10 min, A/O = 1.

The values of ΔH and ΔS can be calculated from the slope and intercept of the plot of lnD versus 1/T, respectively. The lnD versus (1/T) plot is shown in Fig. 10, giving a slope of –2900.81, intercept of 11.98 and r = 0.959. The results mentioned in table 1 indicate positive values of ΔH, confirm that Dy(III)extraction by this ionic liquid is an endothermic process and suggest that a large amount of heat is consumed to transfer the Dy(III) ions from aqueous into the organic phase. Positive values of ΔS indicate an increase in the randomness of the extraction process in the investigated system. The negative values for Gibbs free energy change showed that the extraction process was feasible and spontaneous thermodynamically. In addition, decrease in ΔG values (from -5.56 kJ mol^{-1} at 298 K to -7.55 kJ mol^{-1} at 318 K) with increase in temperature showed that the extraction was most favorable at higher temperature.

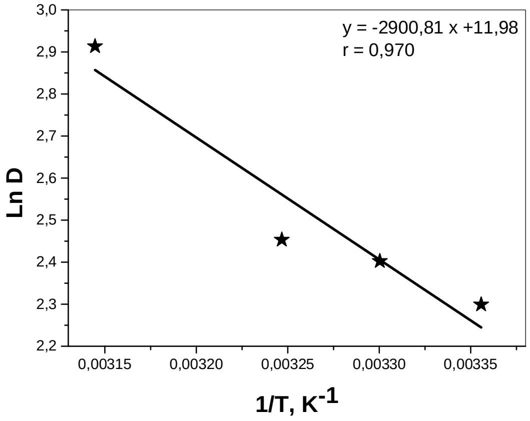

Fig. 10. Plot of Eq. 8 for the Dy(III) extraction by 1-methylimidazolium di(2-ethylhexyl) phosphate. [Dy] =1.4 mmol.L^{-1}, [IL] = 5 mmol.L^{-1}, pHi = 4.3, t = 10 min, A/O = 1.

Table 1. Thermodynamics parameters for extraction process of Dy(III) by 1-methy- limidazolium di(2-ethylhexyl) phosphate

T, K	D	ΔG, $kJ.mol^{-1}$	ΔH, $kJ.mol^{-1}$	ΔS, $J.mol^{-1}.K^{-1}$	r
298	9.96	- 5.56	+24.12	+99.60	0.995
303	11.05	- 6.06			
308	11.63	- 6.56			
318	18.42	- 7.55			

4. Conclusions

The following conclusions are drawn from the present liquid–liquid extraction of dysprosium(III) by 1-methylimidazolium di(2-ethylhexyl) phosphate process:

Effect of time concluded that 10 minutesis enough to obtain maximum extraction. The phase volume ratio equal to 1.0 is the better to carry a good extraction.

Good extraction is obtained in initial pH interval varied between 3.5 and 4.5. Sodium acetate salt addition decreases percent extraction of Dysprosium(III) ions.

Positive enthalpy indicates that extraction phenomena follow the endothermic type process.

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