Combined Physicochemical and solvent extraction studies of yttrium (III) from chloride medium using bifunctional ionic liquids

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Abstract

The preliminary investigations on solvent extraction of yttrium(III) from chloride solution were carried out using two bifunctional ionic liquids trihexyl(tetradecyl)phosphoniumbis(2,4,4-trimethylpentyl)phosphinate(Cyphos IL 104) and [trioctylmethylammonium][2,4,4-trimethylpentyl phosphinate] [A336/Cy272]in toluene. The effects of influential parameters like aqueous phase acidity, equilibration was investigated. The effect of ionic liquid concentration in the organic phase was also studied. 100% extraction of yttrium was achieved with 0.02M [A336/Cy272] and 0.02M Cyphos IL 104, respectively. Physicochemical studies like density, viscosity and ultrasonic velocity showed that the interaction was increased when more amount of yttrium was loaded to the organic phase.

Key words: Yttrium, [A336/Cy272], Cyphos IL 104, extraction, physicochemical studies

Introduction

Rare earth elements are now highly in demand for advanced technologies due to their unique chemical and physical properties. Yttrium which is one of the rare earth elements has enormousapplicationsin many high-tech industries such as wind turbines, fluorescent lamps, cathode ray tubes, hybrid cars, disc drives,electronic components for missile and others. It is also used to increase the tensile strength of some alloys[1]. The main source of yttrium is xenotime, but it also occurs in other rare earth minerals, monazite and bastnasite. Recent review on yttrium from primary and secondary sources[2] focused on the removal of yttrium from generic wastes, contaminant solutions and electronic wastes through hydrometallurgical process which consists of three steps i.e. leaching, solvent extraction and electro-winning. Solvent extraction is a simple and vital technique used for metal recovery since long back. Literature review reveals that extraction and separation of yttrium from other rare earth elements using different type of classical extractants are studied by many researchers [3-10]. Recently use of green solvents like ionic liquids gained special attention in solvent extraction technique and they are used to extract different metal ions[11-22], rare earth elements[23] from different aqueous solutions. Recovery of rare earth elements from fluorescent lamps using solvent extraction technique was reported by Yang et al[23] where yttrium and europium are readily dissolved in acid solutions but substantial amount of energy is required to dissolve other rare earth metals. N, N-dioctyldiglycolamic acid (DODGAA)dissolved in an ionic liquid [C_4mim][Tf_2N] is used to recover the rare earth elements (Y, Eu, Ce, and La) from the metal impurities (Fe, Al and Zn). The ionic liquid replaced the conventional organic diluents and the system showed high affinity for rare earth extraction compared to an organophosphonic acid extractant, PC 88A.Solvent extraction method was also applied torecover REMs from simulated phosphorus powder [24]. The composition of the simulated powder was 56.62% aluminum oxide, 32.72% rare earth oxides, 4.57% barium oxide, 3.94% magnesium oxide and 2.09% other constituents. Using Aliquat 336 and two organophosphorus acidextractants, P204 and P507, bifunctional ionic liquid extractants were prepared in n-heptane and were used to extract the metals. High concentrations of aluminum nitrate proved to be an efficient salting-out agent and same time maintain the constant ionic strength of the aqueous phase.Isodecanol was added as the phase modifier. 100% stripping was achieved with 0.02M nitric acid. 95.2% rare earth metals were recovered using countercurrent extraction system comprising up to seven stages, phase ratio V_o:V_w=4:1 and pH=0.56.Itis reported that the ionic liquid system shows higher extraction efficiencies as compared to P350 and TBP, but lower than Cyanex 923. The extraction efficiencies decrease in the order: Cyanex 923>[Aliquat 336-P204]=[Aliquat 336-P 507]>P 350>TBP. Larsson and Binnemans[25]recovered rare earths from the raffinates of transition metals using Cyanex 923 as extractant and tricaprymethylammonium nitrate as the diluent. Sun et al[26] studied the separation of scandium from yttrium and lanthanides using alkylated phosphine oxide (Cyanex 925) in tricaprylammonium nitrate[A336][NO_3] from aqueous acidic phase. Distribution ratio of scandium ion was found to be larger when [A336][NO_3] used as diluents in comparison to

$[C_8mim][PF_6]$ and toluene. The literature survey reveals that there are no reports on the extraction of yttrium using the two bifunctional ionic liquids trihexyl(tetradecyl)phosphoniumbis(2,4,4-trimethylpentyl)phosphinate(Cyphos IL 104) and [trioctylmethylammonium][2,4,4-trimethylpentyl phosphinate] [A336/Cy272]. Hence a systematic study on extraction of yttrium from chloride medium was carried out using the above two ionic liquids diluted in toluene, where theeffect of acid concentration, IL concentrations, sodium chloride and yttrium ion concentration were investigated. On the basis of slope analysis the extracted complex and extraction mechanism were proposed. Physicochemical studies on the extraction of yttrium were also investigated.

2. Experimental

2.1 Materials

The stock solution of yttrium (III) chloride (0.1 M) was prepared by accurately weighing calculated amount of yttrium chloride in double distilled water and poured in a volumetric flask of desired volume. From this the working solutions were prepared as required for the experiment. The organic phase extractants used for the investigations were trihexyl(tetradecyl) phosphoniumbis(2, 4,4-trimethylpentyl)phosphinate(Cyphos IL 104) and [trioctylmethylammonium][2,4,4-trimethylpentyl phosphinate] [A336/Cy272]. Cyphos IL 104 was kindly supplied by Cytec Canada. It was used as received. Aliquat 336 was purchased from sigma-aldrich and Cyanex 272 was the gift sample of Cytec Canada. Both these extractants were mixed in equal proportions to prepare the ionic liquid [A336/Cy272] following the procedure of Fortunyetal[27].Toluene was used as the diluent as Cyphos IL 104 is highly viscous and soluble in toluene.

All other reagents used were of analytical grade.

2.2 Experimental Methods

2.2.1. Liquid-liquid extraction procedure

All the experiments were carried out by taking equal volumes of the aliquots of the organic and aqueous solutions in a separating funnel and shaken for 5 minutes except for time variation study. After phase separation, the aqueous phase was collected and the equilibrium pH of the solution was measured. Then the amount of yttrium present after and before extraction was measured using an UV-Visible spectrophotometer (Elico make) at 654 nm following the procedure of Arsenazo III spectrophotometric determination of rare earth elements. The concentration of yttrium in the organic phase was calculated using mass balance. The distribution ratio 'D' which is the ratio of concentration of yttrium in the organic phase to that of aqueous phase was found out. From that the % extraction was calculated using the formula

$$\%E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \qquad (1)$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively. All the experiments were carried out at $25 \pm 1^{o}C$.

2.2.2 Physicochemical studies

The density was determined at 298.15 K by using a specific gravity bottle (25 ml capacity) by relative measurement method as described elsewhere[28]. A minimum of five observations were taken and differences in any two readings did not exceed ±0.02%.The ultrasonic velocity was measured at 298.15 K by using an ultrasonic interferometer having a frequency of 2MHz (Model No.F-81, Mittal Enterprises, New Delhi) with an overall accuracy of ±0.5 m/s. For the measurement of viscosity Ostwald viscometer (25 ml capacity) was used in a water thermostat whose temperature was controlled to ±0.05 K. The time of flow of water and the solutions were determined with a digital stop clock with an accuracy of 0.01s.The accuracy of the viscosity measurement was $\pm 0.3 \times 10^{-3}$ c P.

3. Results and discussion

3.1 Effect of shaking time

The time required to attain the equilibrium could be a crucial point in solvent extraction process.To find out the equilibration time, experiments were carried out at equal phase ratios from the aqueous solutions containing 0.001 M YCl_3, 0.01 M NaCl, 0.0025 M HCl which were extracted with 0.005 M [A336/Cy272] and 0.01 M Cyphos IL 104, respectively in the time intervals 1 minute to 20 minutes. The results plotted in Fig.1 showed that 5 minute equilibration time is sufficient for yttrium to reach equilibrium in case of both the ILs diluted in toluene.

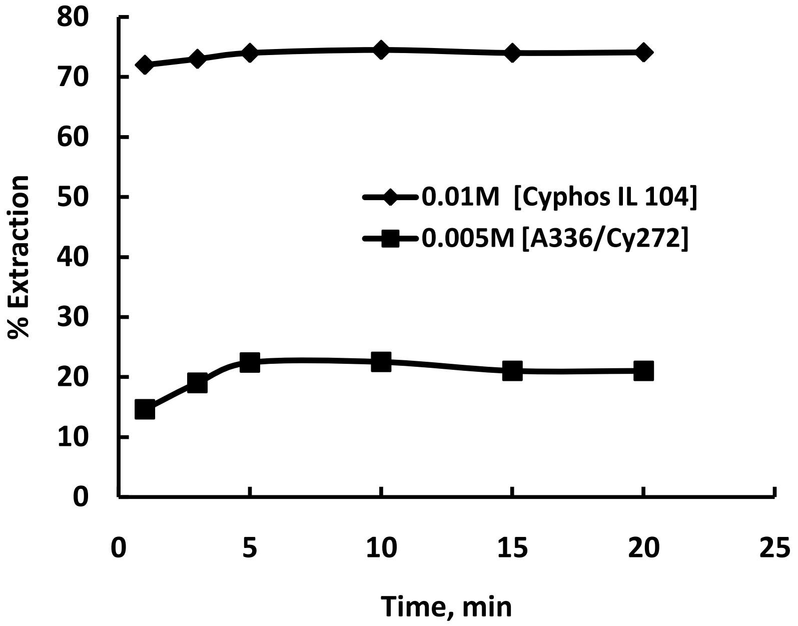

Fig.1: Effect of shaking time on extraction of yttrium.Aq. phase: 0.001M YCl_3, 0.01M NaCl, 0.0025M HCl

3.2Effect of extractant concentration

The aqueous solutioncontaining 0.001M YCl_3, 0.01M NaCl, 0.0025M HCl was equilibrated with different concentrations of [A336/Cy 272] and Cyphos IL 104 over the range 0.0025-0.02 M at equal phase ratios.It was observed that extraction of Y (III) increased with increase in concentration of both the ionic liquids.100% extraction of yttrium (III) was observed for both of ionic liquids [A336/Cy272]and CyphosIL 104 having concentration of 0.02M[Fig.2].However the extraction of yttrium (III) was more pronounced with [A336/Cy 272] than Cyphos IL 104.Log-log plots of distribution ratio and IL concentration yield slopes of ~ 4.0 for both Cyphos IL 104 and [A336/Cy272] indicating involvement of four extractant molecules per mole of yttrium(III) extraction[Fig.2].

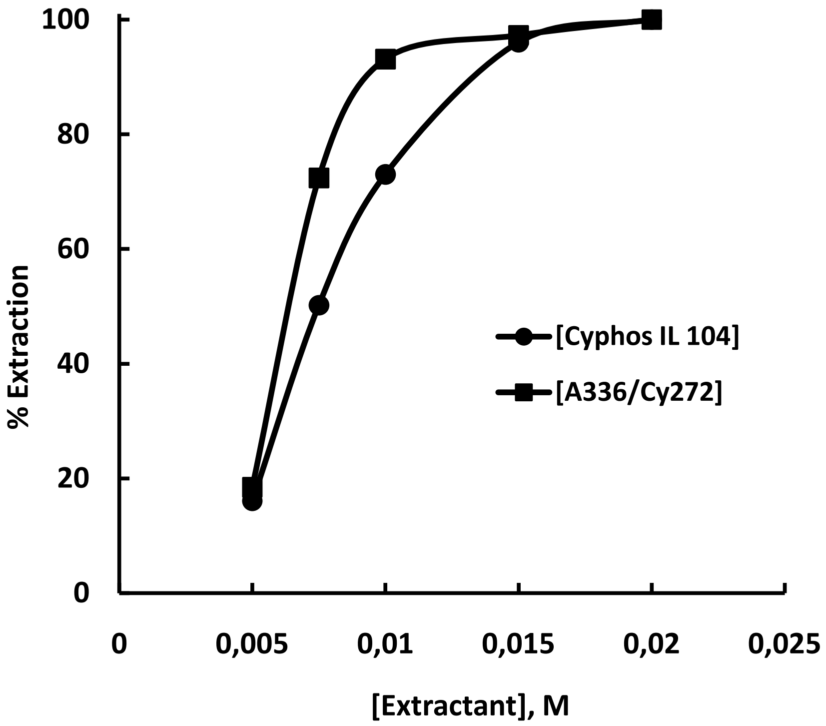

Fig.2: Effect of extractant concentration on yttrium extraction.

3.3. Effect of HCl concentration

To evaluate the effect of acid concentration on extraction efficiency of yttrium experiments were carried out varying the HCl concentration in the range 6.0 x $10^{-5}$to 0.027 M. The yttrium concentration was 0.001M and the [A336/Cy272]and Cyphos IL 104 concentrations were 0.005 and 0.01 M, respectively. The data in Fig. 3 showed that the percentage extraction of yttrium decreased with increase in HCl concentration for both the ionic liquids which may be due to extraction of acids by the ionic liquids at higher acid molarities.

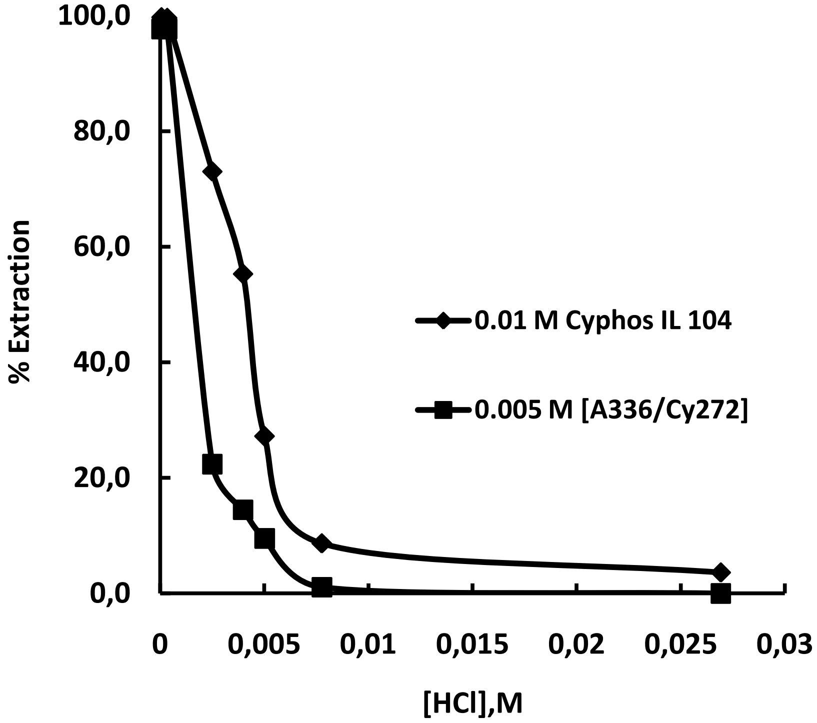

Fig.3. Effect of HCl concentration on extraction of yttrium.Aq. phase: 0.001M YCl_3, 0.01M NaCl.

3.4 Physicochemical studies

Solvent extraction is mainly occurs with an aqueous phase containing the metal ions and an organic phase comprising of an extractant and a diluent. Some properties of liquids such as viscosity, surface tension, density, polarity are important in solvent extraction process. Extractability of metal ions using different extractants depends on solute-solvent interaction. Viscosity is one of the main factors which determine the diffusion of metal species across the liquid membrane[30]. These interactions can be studied by using the techniques such as measurement of density, viscosity, conductance and ultrasonic speed etc., which throws light on the molecular environment[31-33]. Physicochemical property studies have been undertaken in the present investigation to measure the density, viscosity and ultrasonic velocity of different systems, like pure extractant, mixture of extractant and diluent and that of the loaded metal organic phase to study the type and strength of interactions present. The results were reported in Table 3.The perusal of Table 3reveals that the measured parameters, i.e. density, viscosity and ultrasonic velocity are more in the loaded organic phase followed by the extractant-diluent mixture (Cyphos IL 104 +toluene and [A336/Cy272] + toluene) and then the pure diluent, toluene. As the number of molecules increases, the medium becomes denser, sound velocity increases and it leads to lesser compressibility.Further, the increase in the number of particles simply increases the frictional resistance between the layers of the medium and that tends to increase the coefficient of viscosity. In loaded organic phase, the density, viscosity as well as ultrasonic velocity is more in 0.1 M CyphosIL 104in toluene and 0.1 M [A336/Cy272] in toluene as compared to 0.01 M CyphosIL 104 in toluene and 0.005 M [A336/Cy272] in toluene, respectively.In 0.1 M CyphosIL 104, the density, viscosity and ultrasonic velocity are more in the loaded organic phase with 0.1M NaCl as compared to that with 0.025 M NaCl. But in 0.1 M [A336/Cy272],the density, viscosity and ultrasonic velocity is more in the loaded organic phase with 0.025 M NaCl than with 0.1 M NaCl.It may be due to the accumulation of more mass in the components in these systems.

From the ultrasonic velocity (U), density(d) and viscosity co-efficient (η) data, the following derived parameters such as K_s, Z, R,W and L_f were calculated using the standard equations[34-40].

$$K_s=1/U^2d \tag{4}$$

$$Z = Ud \tag{5}$$

$$R = \overline{M}\, d^{-1}\, U^{1/3} \tag{6}$$

$$W = \overline{M} d^{-1} K_s^{-1/7} \tag{7}$$

$$L_f = K' K_s^{1/2} \tag{8}$$

where$\overline{M}$ is the effective molecular weight ($\overline{M} = \Sigma\, m_i x_i$),in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents, respectively. K′ is the Jacobson's constant which is temperature dependent and is obtained from the literature[35,36].

The isentropic compressibility (K_s) and also free length (L_f),the distance between the surfaces of the molecules is less in loaded organic phase as compared to the corresponding extractant-diluent mixture.It shows that there is more interaction in the loaded organic phase.Since the acoustic impedance is a measure of the resistance offered by the liquid medium to the sound wave and is a function of the elastic property of the medium, it depends on the structural changes of the solution. Acoustic impedance (Z), Molar sound velocity(R) and molar compressibility (W) are more in loaded organic phase.The increasing trend of acoustic impedance (Z), molar compressibility (W) or molar sound velocity(R) indicates the availability of more number of components in a given region, thus leading to a tight packing of the medium and increase in the interactions.

If there occurs metal-metal interaction, then there are larger variations in the values of density, viscosity and ultrasonic velocity and the related parameters. But since there are not large variations, it is suggested that there is extractant-diluent interaction and/or metal-extractant interaction. In the studied systems, density, viscosity and ultrasonic velocity are less in extractant-diluent system, so it is suggested that the interaction between metal and extractant is predominant. Further,if the interaction between extractant and diluents is more, then the extractant is less available for extraction of metal. So it is concluded that the interaction between metal and extractant is significant leading to complex formation.

4 Conclusions

Fundamental studies on extraction of yttrium(III) using the two ionic liquids [A336/Cy272] and Cyphos IL 104 diluted in toluene were investigated. Five minutes of shaking time was enough to reach the equilibrium. The percentage extraction of yttrium(III) decreased with increase in HCl concentration for both [A336/Cy272] and Cyphos IL 104. Though quantitative extractions (100%) of yttrium(III) were achieved with both [A336/Cy272] and Cyphos IL 104 having concentrations of 0.02M, but the ytrrium(III) extraction was more pronounced with [A336/Cy272] compare to Cyphos IL 104. The measurement of density, viscosity, and ultrasonic speed predicts that the metal-extractant interaction was predominant. The future study aims at to get 100% recovery of the metal ions and separation of yttrium from other rare earth elements.

Table 3: Values of density, d (kg m^{-3}),viscosity (Pa.s), ultrasonic velocity, U (ms^{-1}), K_s(m^2N^{-1}), Z($Kgm^{-2}s^{-1}$), R($m^{-8/3}$ $s^{-1/3}$), W($N^{-1}m^{-1}$) and L_f (m) for the systems:

Yttrium+Cyphos IL 104 +Toluene, Cyphos IL 104 + Toluene, Yttrium+ [A336/Cy272] +Toluene and [A336/Cy272] +Toluene at 298.15 K.

	d	H	U	$K_s \times 10^{10}$	$Z \times 10^{-4}$	R	W	$L_f \times 10^{10}$
Toluene	861.28	0.596	1304.0	6.83	112.31	1.169	2.181	5.37
0.01 M Cyphos IL 104 in toluene	861.96	0.599	1306.8	6.79	112.64	1.177	2.198	5.36
Yttrium loaded 0.01 M Cyphos IL 104 in toluene	862.12	0.604	1307.6	6.78	112.73	1.178	2.199	5.35
0.1 M Cyphos IL 104 in toluene	863.35	0.715	1308.0	6.77	112.92	1.267	2.365	5.34
Yttrium loaded 0.1 M Cyphos IL 104 in toluene	866.37	0.724	1309.6	6.73	113.46	1.268	2.368	5.33
Yttrium loaded 0.01 M Cyphos IL 104 in toluene from 0.025 M NaCl,0.001 M YCl_3 solution	862.54	0.609	1307.0	6.79	112.73	1.177	2.197	5.35
Yttrium loaded 0.01 M Cyphos IL 104 in toluene from 0.1 M NaCl,0.001 M YCl_3 solution	863.35	0.610	1327.2	6.58	114.58	1.182	2.205	5.27
0.005 M [A336/Cy272] in toluene	862.73	0.603	1288.0	6.99	111.12	1.166	2.178	5.44
Yttrium loaded 0.005M[A336/ Cy272] in toluene	862.98	0.604	1296.0	6.90	111.84	1.168	2.181	5.40
0.1 M [A336/Cy272] in toluene	865.60	0.723	1288.4	6.96	111.52	1.243	2.323	5.42
Yttrium loaded 0.1 M	866.82	0.738	1288.8	6.95	111.72	1.245	2.326	5.41

[A336/Cy272] in toluene								
Yttrium loaded 0.005M[A336/ Cy272] in toluene from 0.025 M NaCl,0.001 M YCl_3 solution	862.41	0.609	1290.4	6.96	111.29	1.167	2.179	5.43
Yttrium loaded 0.005M[A336/ Cy272] in toluene from 0.1 M NaCl,0.001 M YCl_3 solution	862.29	0.604	1284.4	7.03	110.75	1.165	2.177	5.45

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