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Liquid-Liquid Extraction of Ir, Ru, and Rh from Chloride Solutions and Their Separation Using Different Commercially Available Solvent Extraction Reagents

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Abstract: The extraction of Ir, Ru, and Rh from their chloride solutions was carried out using different commercially available solvent extraction reagents. The extractants studied were Alamine 300, Alamine 336, Aliquat 336, Cyanex 921, Cyanex 923, Cyanex 471, Cyanex 272, LIX 54, LIX 860N-I and tributyl phosphate (TBP). The distribution coefficients for the metals were determined under different concentrations of Cl^- and H^+ ions in the aqueous phase. The extraction data relating to the consecutive steps of stripping the metal species from the loaded organic phase were also recorded.

The results showed that more than 90% of the Ir can be extracted using Alamine 300, Alamine 336, and Aliquat 336 when less than 0.2 M Cl^- is present in the aqueous phase, and that quantitative stripping of Ir can be performed.

For higher concentrations of Cl^- in the aqueous phase, Cyanex 921 was found to be the best extractant for Ir, although the mixed extractants such as Alamine 336 + LIX 54, Aliquat 336 + LIX 54, and Cyanex 921 + TBP were also found to be useful for the extraction of Ir from high concentration chloride solutions.

For Ru, mixtures of extractants such as Alamine 336 + LIX 54 and Aliquat 336 + LIX 54 were found to be more effective for extraction, as well as better stripping of Ru was obtained from Ru loaded in such organic phases.

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The extraction of Rh proved to be difficult, and a maximum of only 31% extraction was achieved using Alamine 300 in the organic phase and a freshly prepared solution of the rhodium chloro complex in 1 M HCl in the aqueous phase. On the basis of these observations, a complete scheme for the individual separation of Ir, Ru, and Rh was proposed and tested with synthetic solutions of these metal chlorides. This resulted also in the development of a method for the separation and recovery of Ir, Ru, and Rh from hydrochloric acid solutions containing a high concentration of Cl^- ions.

Keywords: Separation, solvent extraction, iridium, rhodium, ruthenium

INTRODUCTION

The recovery of strategic and precious metals (SPMs) such as Ir, Ru, and Rh from different matrices is always a challenging task for a chemist. Due to the scarcity of these metals and their broad industrial applications (1–4), an extensive amount of literature is available on their recovery from different aqueous solutions (5–10). However, the increasing use of these elements in various industries under different complex conditions makes it necessary to develop a tailor-made solution for every separation process.

In the present investigation, different commercially available solvent extraction reagents, such as Alamine 300, Alamine 336, Aliquat 336, Cyanex 921(TOPO), Cyanex 923, Cyanex 471, Cyanex 272, LIX 54, LIX 860N-I, and TBP, were tested for the extraction of Ir, Ru, and Rh. Before starting our work, we took into consideration the solution chemistry of SPMs under different aqueous solution conditions. At different acidities and chloride ion concentrations (as SPMs are normally dissolved in HCl, we selected a chloride system for this work), different species of these elements are present in the aqueous solution (11). If we consider one single valency of any SPM ion, the total breakdown of this ion in the aqueous feed solution can be expressed by the following mathematical expression:

$$[Me^{n+}]_{tot} = \sum_{i=n}^{i=n+2}[H_{i-n}MeCl_i] + \sum_{i=n}^{i=n+1}\sum_{j=0}^{j=i-n}\left[H_jMeCl_i^{(i-j-n+1)-}\right] + \sum_{i=0}^{i=n-1}\left[MeCl_i^{(n-i)+}\right] \tag{1}$$

where $[Me^{n+}]_{tot}$ represents the total metal concentration in the aqueous phase, $\sum_{i=0}^{i=n-1}[MeCl_i^{(n-i)+}]$ is the sum of metal chloro complex cations with n^+ valence, $\sum_{i=n}^{i=n+1}\sum_{j=0}^{j=i-n}[H_j\ MeCl_i^{(i-j-n+1)-}]$ is the sum of ith metal chloro complex anions, and $\sum_{i=n}^{i=n+2}[H_{i-n}\ MeCl_i]$ is the sum of ith metal chloro complex acids.

However, if β_i is considered to be the overall constant of ith complex formation,

$$\left[\mathrm{MeCl}_i^{n-i}\right] = \beta_i[Me^{n+}][Cl^-]^i \tag{2}$$

and

$$[H_{i-n}MeCl_i] = \frac{[H^+]^j[H_{i-n-j}MeCl_i^{j-}]}{K_{aj}} \tag{3}$$

where K_{aj} is the overall jth dissociation constant of the acid. In the case of polyacids, the first dissociation constant is more important, as $\left[H_{i-n-1}MeCl_i^-\right]$ anions predominate in the solution.

From these expressions, it can be seen that the availability of a particular type of metal species is highly dependent on the acidity, as well as on the chloride concentration in the aqueous solution. The values of β_i and K_{aj} can provide the quantitative availability of a particular species under given conditions. If β_i is large enough, the probability of the presence of anionic species is higher, but at the same time the value of K_{aj} and the concentration of H^+ will determine the presence of ionic or nonionic species. At low concentrations of H^+, an anion exchange extractant such as Aliquat 336 will be more suitable due to the presence of extractable anionic species in the aqueous phase, whereas at high concentrations of H^+ the presence of an undissociated metal acid complex will require the use of amine or solvating extractants (TBP, TOPO).

These possibilities led us to select all three types of extractants: cationic, anionic, and solvating. In the present investigation, some commercially available extractants (namely Alamine 300, Alamine 336, Aliquat 336, Cyanex 921, Cyanex 923, Cyanex 471, Cyanex 272, LIX 54, LIX 860N-I, and TBP) were tested for extraction and separation of Ir, Ru, and Rh. To target the individual separation of Ir, Ru, and Rh more effectively, and to obtain better extraction behavior, binary mixtures of extractants were also tested. In the solvent extraction experiments, SPMs at higher concentrations show a tendency of third-phase formation. In chemical engineering processes, handling the third phase in the solvent extraction module is a difficult task. The addition of decanol and TBP helped prevent third-phase formation and also improved phase separation.

EXPERIMENTAL

Reagents

The extractants Alamine 300, Alamine 336, Aliquat 336, LIX 54, and LIX 860N-I were donated by Cognis Deutschland GmbH, Germany. Cyanex 921, Cyanex 923, Cyanex 471, and Cyanex 272 were donated by Cytec

Canada Inc., and tributyl phosphate (TBP) was supplied by Merck. Dodecane and kerosene were obtained from Fluka, Germany. These chemicals were used without any purification.

The stock solution of Ir(IV) (1000 ppm Ir in 1 M HCl) was prepared using the following procedure: a weighed quantity (0.9 g) of iridium chloride salt (supplied by dmc^2 DEGUSSA AG) was dissolved in 90 mL of a 1:1 mixture of concentrated HCl (37%) and water. This solution was refluxed and 12 mL of H_2O_2 (30%) was added to it drop-wise over a period of 2 h. After this, air bubbles were passed through the solution to drive off any chlorine that might have developed during the oxidizing reaction. The resulting solution was left to boil for another 4 h to destroy any excess H_2O_2. The solution was then cooled and diluted to 500 mL. The stock solutions of chlorides of Ru(III) and Rh(III) (supplied by dmc^2 DEGUSSA AG) (100 ppm of each) were prepared by dissolving the respective chloride salts in 1 M HCl.

Extraction Procedure

Ten milliliters of aqueous phase containing 50 mg/L of Ir, Ru, or Rh were shaken with an equal volume of organic extractant dissolved in kerosene or dodecane, using a mechanical shaker for 20 min at room temperature ($25 \pm 1°C$). Preliminary experiments showed that this shaking period was sufficient to reach equilibrium. After extraction, the two phases were allowed to separate, and the concentration of metal in the aqueous phase was determined by ICP AES (Spectroflame). The metal concentration in the loaded organic phase was determined by taking the difference between the total initial concentration of metal in the aqueous phase and the metal concentration in the aqueous phase after equilibration.

RESULTS AND DISCUSSION

Extraction and Stripping of Ir(IV)

Table 1 shows the results of the extraction of Ir by different extractants under selected aqueous phase compositions. Over 90% extraction of Ir was obtained by both Alamine 300 and Alamine 336 from low concentrations of HCl in the aqueous phase. When the concentration of HCl was increased from 0.2 to 1 M, a small decrease in the extraction of Ir was noted. Quantitative stripping (cumulative stripping more than 90%) of Ir from both the above extractants was obtained using an NaCl/NaOH mixture. Similarly, 95% extraction of Ir was observed from a 0.2 M HCl solution using Aliquat 336 in the organic phase and a decrease of 8% occurred when the concentration of HCl in the aqueous phase was increased from 0.2 to 1 M. Almost complete stripping of Ir from the loaded organic phase containing Aliquat 336 was achieved using an NH_3/NH_4Cl mixture. No significant effect of H^+ on the extraction

Table 1. Liquid-liquid extraction and stripping of Ir(IV) from its chloride solutions. D_M is the distribution coefficient defined as $D_M = [Ir(IV)]_{org}/[Ir(IV)]_{aq}$ at equilibrium. %E is the percentage of extraction

		Aqueous phase						
Extractant	Organic phase	$[Cl^-]$, M	$[H^+]$, M	D_M	%E	Stripping solution	Stripping[a] step	% Stripping
Alamine 300	15% Alamine 300 + 10% decanol in dodecane	0.2	0.2	13	93	A	I	8.2
						A	II	100
		1.0	1.0	6.8	87	A	I	44
						A	II	92
		4.1	0.1	0.59	37	A	I	8.4
						A	II	76
Alamine 336	15% Alamine 336 + 10% decanol in kerosene	0.2	0.2	16	94	A	I	16
						A	II	97
		1.0	1.0	6.4	86	A	II	15
						A	II	83
		4.1	0.1	0.043	4.1			ND
		4.0	1.0	0.47	32	A	I	7.9
						A	II	91
Alamine 336	15% Alamine 336 + 5% decanol in kerosene	0.1	0.1	14	94	A	I	4.5
						A	II	81
		4.0	1.0	0.52	34	A	I	4.8
						A	II	100

(continued)

Table 1. Continued

Extractant	Organic phase	Aqueous phase [Cl$^-$], M	 [H$^+$], M	D_M	%E	Stripping solution	Stripping^a step	% Stripping
Aliquat 336	15% Aliquat 336 + 10% decanol in kerosene	0.2	0.2	18	95	B	I	100
		1.0	1.0	6.7	87	B	I	100
		4.1	0.1	1.9	65	B	I	100
		4.0	1.0	1.3	56	B	I	100
Cyanex 921	2% Cyanex 921 in dodecane	0.1	0.1	0.4	30	C	I	87
		1.0	1.0	1.4	58	C	I	97
		4.2	0.2	1.2	55	C	I	100
		4.0	1.0		70	C	I	84
Cyanex 923	5% Cyanex 923 in dodecane	0.1	0.1	0.9	47	C	I	88
		4.1	0.1	15	94	C	I	83
TBP	50% TBP in dodecane	1.0	1.0	0.14	12	C	I	72
		4.1	0.1	0.72	42	C	I	80

Alamine 336	15% Alamine 336	4.1	0.1	0.27	21	B	I	100
+	+ 1% LIX 54	1.0	1.0	13	93	B	I	100
LIX 54	in dodecane							
Aliquat 336	15% Aliquat 336	0.1	0.1	32	97	B	I	100
+	+ 15% LIX	4.0	1.0	1.1	53	B	I	100
LIX 54	in dodecane							
Aliquat 336	15% Aliquat 336	4.2	0.2	2.1	68	B	I	53
+	+ 15% LIX 54					B	II	57
LIX 54	in dodecane	4.1	0.1	3.2	76	B	II	77
		1.0	1.0	9.5	90	B	II	21

[a] Stripping step designated by I, II, III, and IV corresponds to the serial number of stripping step with respective stripping solution and the % stripping is the cumulative % stripping after respective step.

A—0.2 M NaOH + 0.35 M NaCl.

B—2 M NH_3 + 3 M NH_4Cl.

C—H_2O.

ND—Not determined.

of Ir suggested that the protonated chloro complex of Ir(IV) is a relatively weak acid and neutral-type extractants could give better results, especially under conditions of a high concentration of chloride ions in the aqueous phase. An increased concentration of Cl^- resulting from using NaCl in the aqueous phase produced a significant decrease in the extraction of Ir by Alamine 300, Alamine 336, and Aliquat 336. This may be due to the masking of the extractant molecule by Cl^- ions. The anion-exchange mechanism for the extraction of Ir(IV) can be given as

$$(i-n-j)\overline{R_3N\cdot HCl} + HMeCl_i^{(i-n-j)-} \rightleftarrows \overline{(R_3NH)_{(i-n-j)}HMeCl_i} + (i-n-j)Cl^- \qquad (4)$$

$$(i-n-j)\overline{R_4N\cdot Cl} + MeCl_i^{(i-n-j)-} \rightleftarrows \overline{(R_4N)_{(i-n-j)}MeCl_i} + (i-n-j)Cl^- \qquad (5)$$

where $MeCl_i^{(i-n-j)-}$ represents the anionic species of the chloro complex of Ir(IV), in the same way as was explained in Eq. (1).

Some improvement in the extraction of Ir (specifically from high concentrations of Cl^- in the aqueous solutions) was observed when using mixed extractants such as Alamine 336 with LIX 54 and Aliquat 336 with LIX 54. Practically negligible extraction ($< 2\%$) of Ir(IV) from 0.1 to 4 M HCl was obtained when 15% LIX 54 or LIX 860N-I or Cyanex 272 were used in the organic phase. This suggests that Ir(IV) forms a very strong complex with chloride anions. Among the neutral extractants studied, 42% extraction of Ir was recorded with 50% TBP from 4 M chloride solution. Extraction of Ir was poor with Cyanex 272, while Cyanex 921 and Cyanex 923 showed very good extraction of Ir. Cyanex 923 exhibited a greater tendency toward third-phase formation when metal extraction was carried out from solutions containing higher concentrations of HCl. By using 2% Cyanex 921 in the organic phase, 58% of the Ir was extracted from a 1 M HCl solution. The stripping of Ir (>95%) from the Ir charged organic phase containing 2% Cyanex 921 was performed using distilled water. As far as the simplicity of the Ir stripping from the organic phase is concerned, Cyanex 921 stands out from all the other extractants studied. The possible chemical equilibrium in the extraction of Ir using Cyanex 921 can be given as

$$H_{i-n}MeCl_i + qL \rightleftarrows \overline{H_{i-n}MeCl_i\cdot qL} \qquad (6)$$

where $H_{i-n}MeCl_i$ represents the extractable neutral chloro complex of Ir(IV).

The selective extraction of Ir(IV) from the mixture of Ir-Ru-Rh, as well as favorable stripping conditions, encouraged us to study the extraction of Ir by Cyanex 921 in more detail and under different experimental conditions. Figure 1 shows the influence of acidity on the extraction of Ir(IV) by 2% Cyanex 921 dissolved in kerosene at a 2 M concentration of Cl^- in the

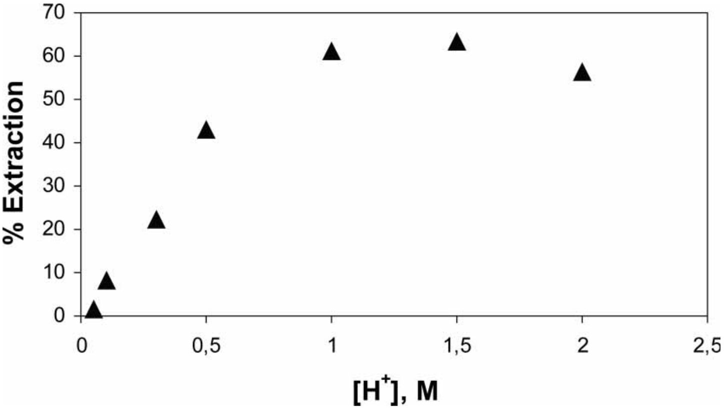

Figure 1. Extraction of Ir(IV) by 2% Cyanex 921 dissolved in kerosene as a function of [H^+] at a constant (2 M) concentration of chloride ions in the aqueous phase.

aqueous phase. The extraction of Ir with respect to the concentration of H^+ decreased after reaching a maximum. This is due to the more competitive extraction of HCl at its higher concentrations in the aqueous phase by Cyanex 921. At concentrations of over 50 ppm of Ir in the aqueous phase feed, a third phase appeared between the organic and aqueous interface. We found that TBP could be used as a solvent modifier to eliminate the problem of third-phase formation.

Extraction and Stripping of Ru(III)

Table 2 shows the results obtained for the extraction and stripping of Ru(III) by various extractants under the given experimental conditions. More than 80% of Ru(III) was extracted by both Alamine 300 and Alamine 336 from aqueous solutions with concentrations of Cl^- above 4 M. A decrease of approximately 50% in the extraction of Ru was recorded when the concentration of Cl^- was reduced from 4 to 1 M. Alamine 300 and Alamine 336 were found to behave very similarly with regards to metal extraction. In the case of Aliquat 336 in the organic phase, 88% extraction of Ru was achieved from a 4.2 M Cl^- solution containing 0.2 M H^+. Although Ru was efficiently extracted by all three of the extractants above, problems in stripping the metal ions from the loaded organic phase were observed. A maximum of 37% stripping of Ru was obtained from the organic phase containing 15% Alamine 300 with 10% decanol dissolved in kerosene. These results indicate an anion exchange mechanism in the extraction of Ru from chloride solutions, and the probable equations for the extraction are similar to those given for Ir(IV) (Eqs. 4 and 5) for Alamine 336 and Aliquat 336 respectively.

Table 2. Liquid-liquid extraction and stripping of Ru(III) from its chloride solutions. D_M is the distribution coefficient defined as $D_M = [Ru(III)]_{org}/[Ru(III)]_{aq}$ at equilibrium. %E is the percentage of extraction

		Aqueous phase						
Extractant	Organic phase	$[Cl^-]$, M	$[H^+]$, M	D_M	%E	Stripping solution	Stripping[a] step	% Stripping
Alamine 300	15% Alamine 300 + 10% decanol in kerosene	4.2	0.2	5.5	85	D	I	35
						D	II	37
		1.0	1.0	0.75	43	D	I	16
						A	II	28
						A	III	40
		0.05	0.05	0.09	8.2	—	—	ND
Alamine 336	15% Alamine 336 + 10% decanol in kerosene	4.2	0.2	4.8	83	A	I	17
						A	II	24
		1.0	1.0	0.78	44	A	I	51
						A	II	55
		0.05	0.05	0.075	7			ND
		0.1	0.1	0.11	10	A	I	15
						A	II	22
		4.0	1.0	3.5	78	A	I	12
						A	II	10
Alamine 336	15% Alamine 336 + 5% decanol in kerosene	0.1	0.1	0.85	46	A	I	5.2
						A	II	20
		4.0	1.0	13	93	A	I	15
						A	II	10

Aliquat 336	10% Aliquat 336	4.2	0.2	7.6	88	E	I	13
	+ 10% decanol	0.1	0.1	0.28	22	B	I	75
	in kerosene					B	II	83
		1.0	1.0	1.7	63	F	I	11
		4.0	1.0	11	92	B	I	54
						B	II	23
Cyanex 921	2% Cyanex 921	4.2	0.2	0.17	15	C	I	6.3
	in kerosene	4.1	0.1	0.065	6.1	C	I	6.5
		1.0	1.0	0.19	16			ND
		0.1	0.1	0.19	16	C	I	13
		4.0	1.0	0.075	7	C	IC	54
						C	IIC	1.0
Cyanex 921	2% Cyanex 921	4.2	0.2	0.22	18	C	I	100
+	+ TBP	4.1	0.1	<0.01	0.4	C	I	100
TBP	in kerosene	1.0	1.0	<0.01	1.0	C	I	100
Alamine 336	15% Alamine 336	4.1	0.1	42	98	D	I	8
+	+ 1% LIX 54					A	II	14
LIX 54	in dodecane					B	III	16
						E	IV	75
Alamine 336	15% Alamine 336	4.1	0.1	3.6	86	D	I	4
+	+ 15% LIX 54					A	II	15
LIX 54	in dodecane					B	III	16
						E	IV	70
						E	V	81

(continued)

Table 2. Continued

		Aqueous phase						
Extractant	Organic phase	$[Cl^-]$, M	$[H^+]$, M	D_M	%E	Stripping solution	Stripping[a] step	% Stripping
Aliquat 336	15% Aliquat 336	4.2	0.2	13	93	D	I	19
+	+ 15% LIX 54					B	II	62
LIX 54	in dodecane					E	III	74
		0.1	0.1	0.5	34.0	B	I	34.0
		4.0	1.0	32.3	97.0	B	I	97.0

[a] Stripping step designated by I, II, III, and IV corresponds to the serial number of stripping step with respective stripping solution and the % stripping is the cumulative % stripping after respective step.

A—0.2 M NaOH + 0.35 M NaCl

B—2 M NH_3 + 3 M NH_4Cl.

C—H_2O.

D—0.35 M NaCl.

E—4 M HCl.

F—M $NaHCO_3$.

ND—Not determined.

A far lesser degree of extraction of Ru (< 2%) was achieved from its acidic chloride solutions when cationic-type extractants (such as LIX 54 and LIX 860N-I) were used. A maximum of 16% Ru was extracted by Cyanex 921 (2% in kerosene) from the 1 M HCl solution. In the experiments with mixed extractants, the use of Cyanex 921 with TBP showed no improvement in the extraction of Ru. However, when LIX 54 was used with Alamine 336 and Aliquat 336, a great improvement in the extraction and stripping of Ru was observed. In the case of Aliquat 336 + LIX 54, the extraction of Ru from 4.2 M Cl^- solution was 93%, and 73% stripping was achieved in the three-step stripping process. These results suggested the possibility of an additional cation-exchange mechanism in the overall extraction of Ru by these mixed extractants. Additional stripping was obtained in the third step of reextraction with 4 M HCl, which may be due to the reprotonation of LIX 54.

Extraction and Stripping of Rh(III)

In the case of Rh, all three types of extractants were found to be inefficient in extracting more than 30% of Rh from aqueous chloride solutions (Table 3). In the case of Alamine 300, a maximum of 31% extraction of Rh was obtained when a freshly prepared solution of rhodium chloro complex in 1 M HCl was used. Under similar conditions, 27% and 20% extraction of Rh was obtained using Alamine 336 and Aliquat 336 respectively in the organic phase. The stripping of Rh from all three of the anion exchange extractants studied was poor. Practically negligible extraction of Rh was noted when the organic phase contained Cyanex 921, Cyanex 923, Cyanex 272, and TBP. The very poor extraction of Rh into the organic phase is due to the complex chemistry of Rh(III) in chloride aqueous solutions (12–14), as a variety of rhodium aqua/chloro complexes usually exists in aqueous solutions. According to the literature (15, 16), Rh(I) can be extracted efficiently and can be obtained by reducing Rh(III) to Rh(I) using Sn(II). This process of reduction, however, requires the introduction of an additional salt impurity ($SnCl_2$) into the aqueous phase.

Scheme for the Separation of Ir(IV), Ru(III), and Rh(III)

The varying degrees of extraction of different metal ions using different extractants under varying aqueous conditions provide scope for the separation of Ir, Ru, and Rh from a mixture of all three. Figure 2 is a flow diagram for our proposed separation scheme. In the usual industrial separation processes, one has to deal with highly salted solutions; hence, the separation process was studied using a feed solution containing high concentrations of Cl^-. We decided to begin the separation process with 2% Cyanex 921 dissolved in

Table 3. Liquid-liquid extraction and stripping of Rh(III) from its chloride solution. D_M is the distribution coefficient defined as $D_M = [Rh(III)]_{org}/[Rh(III)]_{aq}$ at equilibrium. %E is the percentage of extraction

		Aqueous phase						
Extractant	Organic phase	$[Cl^-]$, M	$[H^+]$, M	D_M	% Extraction	Stripping solution	Stripping[a] step	% Stripping
Alamine 300	Alamine 300	1.0	1.0	0.45	31	D	I	23
	15% + decanol					A	II	45
	10% in kerosene					A	III	52
Alamine 336	Alamine 336	1.0	1.0	0.37	27	A	I	53
	15% + decanol					A	II	57
	10% in kerosene	0.1	0.1	0.43	30	A	I	8.7
							II	5.6
		4.0	1.0	0.075	6.7	A	I	58.1
							II	50
Cyanex 921	Cyanex 921	4.0	1.0	<0.02	0.57			ND
	2% in kerosene							
Aliquat 336	Aliquat 336	1.0	1.0	0.25	20	F	I	3
	15% + decanol	4	1	0.022	2.2			
	10% in dodecane							
Aliquat	Aliquat 336	4.0	1.0	0.031	3	B	I	0
+	15% + LIX 54							
LIX	15% in dodecane							

[a] Stripping step designated by I, II, III, and IV corresponds to the serial number of stripping step with respective stripping solution and the % stripping is the cumulative % stripping after respective step.

A—0.2 M NaOH + 0.35 M NaCl; B—2 M NH_3 + 3 M NH_4Cl; C—H_2O; D - 0.35 M NaCl; F—0.02 M $NaHCO_3$; ND—Not determined.

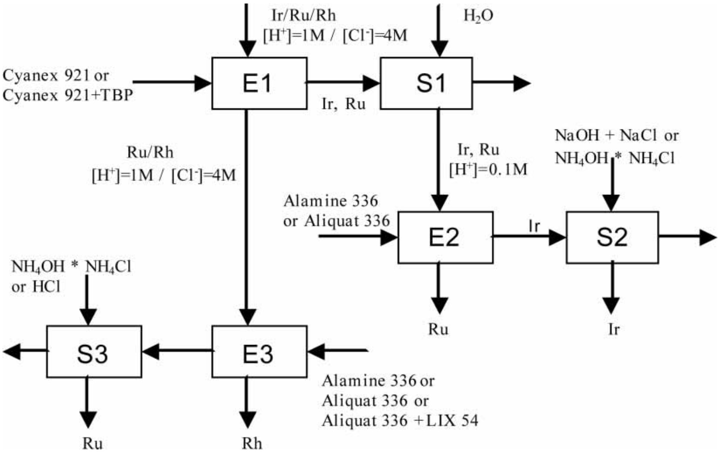

Figure 2. Scheme for the separation of Ir, Ru, and Rh from their chloride solutions.

kerosene. The reasons for this choice were the following: the extraction of Ir was good enough to yield quantitative transfer of Ir into the organic phase, extraction of Ru was poor, extraction of Rh was practically negligible, and it was feasible to completely strip the Ir from the loaded organic phase using distilled water. The aqueous stripped product obtained from this extraction step contained only chloride anions of stripped metal salt and very low quantities of hydrochloric acid. These conditions mean that it is possible to separate Ir and Ru by properly blending the concentrations of acid and chloride in the aqueous phase. At low concentrations of HCl, Ir can be extracted using Alamine 336 or Aliquat 336. By increasing the concentration of Cl^-, Ru can be extracted using a mixture of LIX 54 and Alamine 336 or Aliquat 336. Similarly, the raffinate from the first solvent extraction process with a high concentration of Cl^- ions can be equilibrated with a mixture of LIX 54 and Alamine 336 or Aliquat 336 to selectively extract Ru and hence to separate the nonextracted Rh in the raffinate. The above separation processes can be repeated to obtain better refined products of the individual metal ions.

Figure 3 shows the experimental results for the separation of Ir, Ru, and Rh from aqueous solutions containing 50 ppm of Ir, 50 ppm of Ru, 50 ppm of Rh, 4 M of Cl^-, and 1 M HCl. In the first step of extraction [Fig. 3(A)], 32.2 ppm of Ir along with 8.7 ppm of Ru were extracted into the 2% Cyanex 921/kerosene medium, which was stripped using distilled water. In the first stripping step, 19.3 ppm of Ir and 3 ppm of Ru were recovered into the aqueous phase which was then subjected to three different extraction steps: with 15% Alamine 336 containing 10% decanol in kerosene, [Fig. 3(B1)], 15% Alamine 336 containing 5% decanol in kerosene [Fig. 3(B2)], and 15% Aliquat 336 containing 15% decanol in kerosene [Fig. 3(B3)]. The

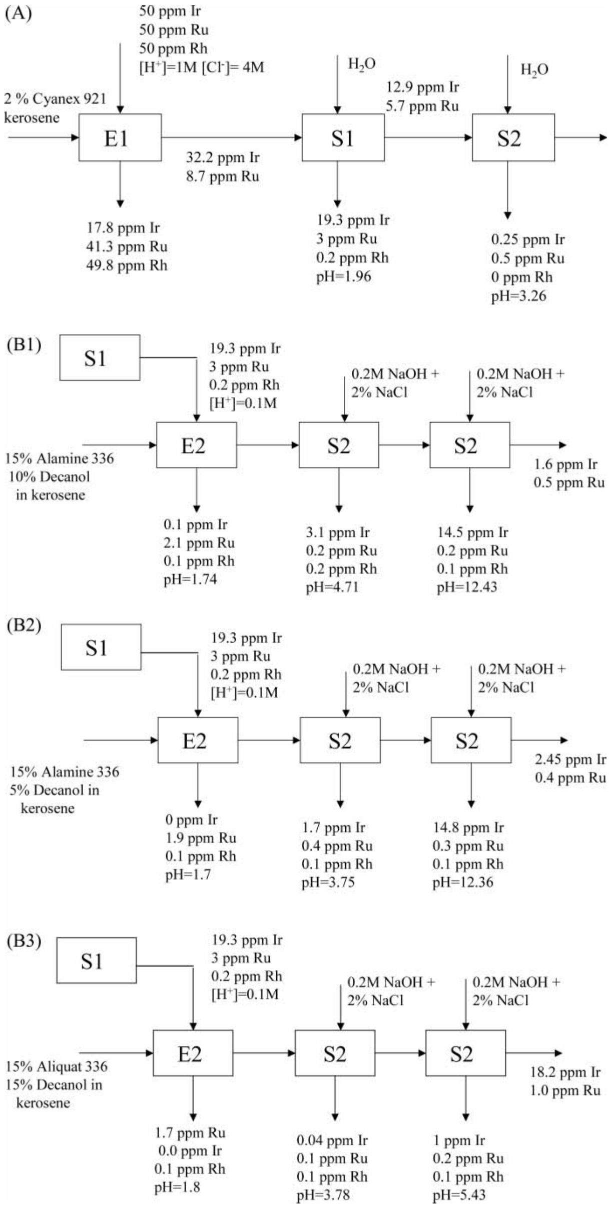

Figure 3. Experimental results of the proposed separation scheme: (A) first step, (B1) second step with 15% Alamine 336 + 10% decanol in kerosene, (B2) second step with 15% Alamine 336 + 5% decanol in kerosene, (B3) second step with 15% Aliquat 336 + 10% decanol in kerosene, (C1) third step with 15% Alamine 336 + 10% decanol in kerosene, (C2) third step with 15% Aliquat 336 + 10% decanol in kerosene, (C3) third step with 15% Aliquat 336 + 15% LIX 54 in dodecane.

(continued)

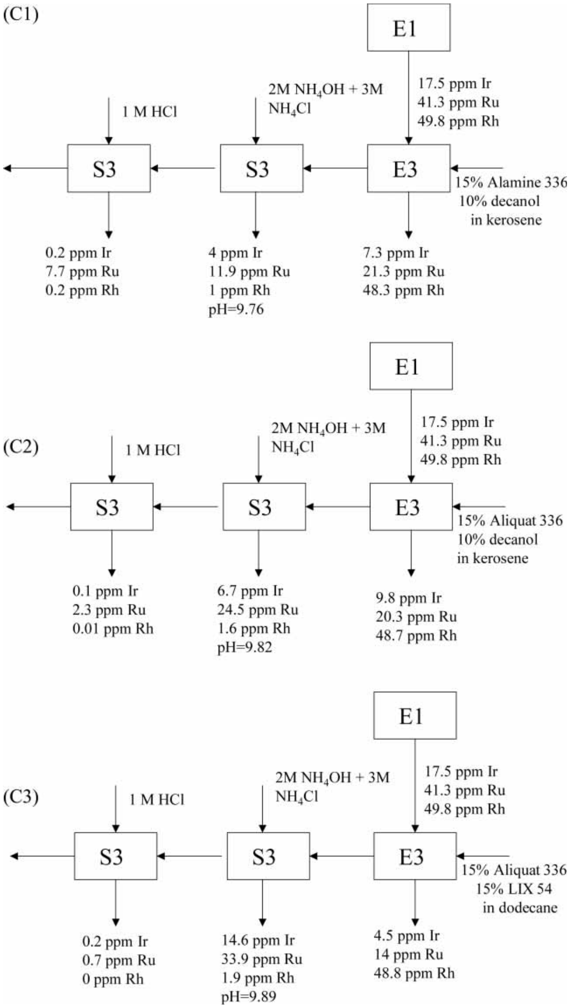

Figure 3. Continued.

best extraction and stripping of Ir were obtained when 5% decanol was mixed with Alamine 336. In this case, about 40% of the Ru was coextracted along with the Ir. In the case of Aliquat 336, more than 97% of the Ir was extracted into the organic phase. During the stripping stage, we observed that a greater number of equilibrations were necessary to neutralize the extracted HCl in the organic phase and then to obtain quantitative recuperation of Ir into the aqueous phase. Similar to Step 2, the third step was carried out in three different ways; see Figs. 3(A-C). In this third step, the raffinate from the first extraction was processed mainly for the separation of Ru and Rh. To this end, only the following single extractants were used initially: Alamine 336 and Aliquat 336 with 10% of decanol. In both of these cases, around 45–50% of the Ru and the Ir was coextracted into the organic phase. In subsequent stripping processes, only about 40% of the Ir and 50% of the Ru could be extracted back into the aqueous phase from the organic phase containing 15% Alamine 336 with 10% decanol in kerosene. The stripping of Ru was better from Ru-loaded organic phase containing 15% Aliquat 336 and 10% decanol in kerosene. As expected, good results were obtained with 15% Aliquat 336 and 15% LIX 54 in dodecane. In this case, 66% of the Ru and 74% of the Ir was extracted into the organic phase and complete stripping of both of these metal ions was accomplished using 2 M $NH_4OH + 3$ M NH_4Cl in the aqueous phase. Except for very low concentration values (< 0.2 ppm), the material balance obtained in all these experiments was in the range of ± 5%.

CONCLUSIONS

Having evaluated the extraction performance of different extractants with respect to the recovery of Ir, Ru, and Rh, the following conclusions have been drawn.

1. Efficient ($>$90%) extraction of Ir(IV) can be achieved using anion-exchange extractants when the concentration of Cl^- in the aqueous phase is low ($<$0.2 M). Complete stripping of loaded Ir(IV) from such extractants is feasible.
2. For the extraction of Ir(IV) from solutions containing higher concentration of Cl^-, Cyanex 921 is the best choice of extractant. Greater selectivity for Ir with respect to Ru and Rh and also the quantitative stripping ($>$95%) of Ir(IV) from a loaded organic phase containing 2% Cyanex 921 or 2% Cyanex 921 + TBP by water are the most suitable conditions with respect to further hydrometallurgical separation and purification operations.
3. Ru(III) is best extracted with anion-exchange extractants, but poor stripping feasibility from the loaded organic phase limits their application. Use of mixed extractants, such as Alamine 336 + LIX 54 or Aliquat 336 + LIX 54, gave better results for the extraction and the stripping of Ru(III).
4. Poor extraction of Rh(III) was noted for all the types of extractants studied. This property of Rh(III) causes it to remain in the aqueous phase throughout the extraction steps.
5. The experiments for separating Ir, Ru, and Rh from a solution containing a mixture of them by manipulating organic and aqueous phase compositions gave promising results. A multistage application of this separation scheme could produce good partitioning of these three elements.

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