Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Extraction and Separation of Ho, Y, and Er(III) with the Mixtures of Cyanex 302 and Another Organic Extractant

D. B. Wu[ab]; Wei Li[a]; D. Q. Li[a]
[a] Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Science, Chinese Academy of Science, Changchun, P. R. China [b] College of Chemistry, Tongji University, Shanghai, P. R. China

To cite this Article Wu, D. B. , Li, Wei and Li, D. Q.(2007) 'The Extraction and Separation of Ho, Y, and Er(III) with the Mixtures of Cyanex 302 and Another Organic Extractant', Separation Science and Technology, 42: 4, 847 — 864
To link to this Article: DOI: 10.1080/01496390601120698
URL: http://dx.doi.org/10.1080/01496390601120698

Separation Science and Technology, 42: 847–864, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390601120698

The Extraction and Separation of Ho, Y, and Er(III) with the Mixtures of Cyanex 302 and Another Organic Extractant

D. B. Wu
Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Science, Chinese Academy of Science, Changchun, P. R. China and College of Chemistry, Tongji University, Shanghai, P. R. China

Wei Li, D. Q. Li, and Yingxiong
Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Science, Chinese Academy of Science, Changchun, P. R. China

Abstract: The extraction and separation of Ho, Y, and Er(III) with the mixtures of bis(2,4,4-trimetylpentyl)monothiophosphinic acid (Cyanex 302) and another organic extractant, such as acidic organic extractant (di-2-ethylhexyl phosphoric acid P204, 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester P507, di-2-ethylhexyl phosphinic acid P229, and sec-nonylphenoxy acetic acid CA-100), neutral organic extractant (tri-n-butyl phosphate TBP, di-(1-metylheptyl)metyl phosphate P350, and branched trialkylphosphinic oxide Cyanex 925) or primary amine N1923, has been investigated in this paper. The extractability and separation ability for the Ho, Y, and Er with the mixtures of Cyanex 302 and organic extractants has been compared. The synergistic effect of the Ho, Y, and Er extraction with the mixtures of Cyanex 302 and P229, Cyanex 925, CA-100, or N1923 has been explored and the synergistic enhancement coefficients have been calculated. At last, the Y^{3+} synergistic extraction with the mixtures of Cyanex 302 and CA-100 has been determined and the extracted complex has been deduced.

Keywords: Synergistic extraction, separation, Cyanex 302, Ho(III), Er(III), and Y(III)

Received 29 August 2006, Accepted 8 November 2006
Address correspondence to D. Q. Li, Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Science, Chinese Academy of Science, Changchun 130022, P. R. China. Tel.: + 086-431-5262036; Fax: +086-431-5698041; E-mail: ldq@ciac.jl.cn

INTRODUCTION

With increasing demand for rare earth elements and their compounds, the separation and purification of these elements have gained considerable attention in recent years. Various kinds of organic extractants such as di-2-ethylhexyl phosphoric acid (P204), 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (P507), Sec-nonylphenoxy acetic acid (CA-100), tri-n-butyl phosphate (TBP), di-(1-metylheptyl)metyl phosphate (P350) and primary amine N1923 have been widely used in the Rare Earth industry for the separation and purification of these metal ions (1–6). However, even with the above extractants, separation and purification are still known to be difficult due to their similar chemical and physical properties, especially for the neighboring rare earth elements, for example, Ho and Er. Furthermore, the extraction of Y(III) by acidic organic phosphine usually lies between Ho(III) and Er(III), thus, its separation from Ho(III) and Er(III) is known to be more difficult and there is a growing interest in the development of new extractants and extraction systems for their separation of as a group or from one another.

Bis(2,4,4-trimethylpetyl)monothiophosphinic acid (Cyanex 302), a monothio analogues of bis(2,4,4-trimethylpetyl)phosphinic acid (Cyanex 272), has been made commercially available by Cytec Canada Inc (7). It has been reported that this reagent is significantly more resistant toward decomposition by hydrolysis than its phosphoro analogues (8), and its higher pKa value (5.63) than that of P204 (2.79) and P507 (3.24) make the stripping of rare earths, especially for heavy rare earths, take place more easily and at a lower aqueous acidity. More importanly, its separation selectivity to rare earth elements, especially for heavy rare earth ions, is better than other organophosphorous extractants (9). At the same time, it has been found that the unpurified Cyanex 302 has better extraction characters than purified Cyanex 302 and is a promising candidate for industrial application (10). Therefore, unpurified Cyanex 302 is usually used for science research instead of purified Cyanex 302 in order to optimize engineering and technique parameters. In the early work, solvent extraction of rare earths from hydrochloric acid, nitric acid, and sulfuric acid media has been systematically presented and shown favorable performance on the extraction of rare earth ions (11–13). However, there is no information available on the synergistic extraction of Cyanex 302, especially on the extraction using Cyanex 302 with another acidic organic extractant (14).

The synergistic extraction is a phenomenon that sometimes occurs when favorable extraction conditions are produced when using a combination of extractants in such a way that the distribution coefficient obtained is greater than the sum of the distribution coefficients obtained with each extractant alone in the same conditions. There are a few reports on the synergistic extraction and separation of Ho, Y and Er (15). However, most of the work was concerned with synergistic extraction with an acidic organic extractant and a neutral organic extractant, and there was little concern for the two acidic organic extractants (16).

Moreover, the synergistic extraction and separation of Ho, Y, and Er with Cynaex 302 and another extractant has not been reported so far.

In this paper, we systematically investigate the extraction and separation characters of Ho, Y, and Er with the mixtures of Cyanex 302 and another extractant, including acidic organophosphorus extractans P204, P507 and di-2-ethylhexyl phosphinic acid (P229), carboxylic acid extractant CA-100, neutral organophrosphorus extractants Cyanex 925 (a branched trialkylphosphinic oxide), TBP, P350, and prime amine N1923. The synergistic extraction systems mixed with Cyanex 302 and P229, Cyanex 925, CA-100 or N1923 has been explored and the synergistic extraction mechanism of Y^{3+} with the mixtures of Cyanex 302 and CA-100 also has been studied. The aim is to compare the extraction and separation ability for Ho, Er, and Y with the mixtures of Cyanex 302 and various organic extractants, find a excellent separation system, study the synergist effect of Y^{3+} extraction with the mixture of Cyanex 302 and CA-100 and put to use in a well-defined practical application.

EXPERIMENTAL

Materials

CA-100(purity >98%), P204, and P507 were kindly donated by the Tianjin Xiandai factory of China. CA-100 was purified by washing with carbonate, hydrochloric acid and distilled water in turn and finally saponified with ammonia water and the rate of ammonia saponification was 86.8%. In order to restrain the formation of the third phase, the 1% (v/v) methylheptanol has been adulterated into the mixtures of Cyanex 302 and CA-100. P204 and P507 were used without further purification. Primary amine N1923 (purity > 99%), TBP, P350, and P229 were supplied by the Shanghai Organic Institute of China and used as received. Cyanex 302 (bis(2,4,4-trimetylphety) mono thio phosphinic acid: 80%) and Cyanex 925 (supplied by Cytec Canada, Inc.) were used without further purification. The extractants were dissolved in heptane to the required concentration.

Stock solutions of rare earths were prepared from their oxides by dissolution in concentrated hydrochloric acid and standardized by EDTA titration with xylenol orange as the indicator. All the other reagents were of analytical grade.

Apparatus

A Shimadzu Model UV-365 spectrophotometer was used for measuring absorbance. A Model pHs-3C pH meter calibrated daily with 4.01 and 6.86 standard buffer solution was employed for measuring pH value in aqueous phase.

Extraction and Analytical Procedure

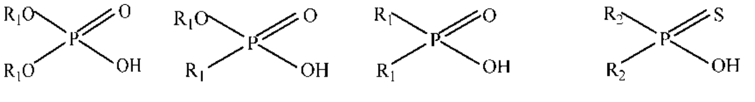
Liquid-liquid extraction was carried out by shaking equal volumes (5.0 ml) of aqueous and organic phases in equilibrium tubes using a mechanical shaker at 298 ± 1K. After phase separation, the concentration of rare earth ions(III) in the aqueous phase was determined spectrophotometrically at 655 nm, using Arsenazo(III) as an indicator at pH 2.8 in chloroactic acid – sodium hydroxide buffer solution. The concentration of the rare earth ions(III) in the organic phase was obtained by mass balance. The distribution ratio, D, was taken as the ratio of the concentration of rare earths(III) in the organic phase to that in the aqueous phase. Sodium chloride was used to maintain ion strength of the aqueous phase at $1.0\ \mathrm{mol l^{-1}}$. The aqueous pH, in the range from 1.0 to 2.0, has been kept by hydrochloric buffer and that from 2.0 to 3.0 has been maintained by potassium biphthalate buffer.

RESULTS AND DISCUSSION

The Effect of Aqueous pH on the Extraction and Separation of Ho, Y, and Er with the Mixtures of Cyanex 302 and another Organic Extractant

The effect of aqueous pH on the extraction percent has been illustrated in Figs. 1–3. It can be seen that with increasing pH values, the extraction percent increases correspondingly. The extraction efficiency of rare earth by mixtures of Cyanex 302 and other organic extractants has the following order: Cyanex 302 + P204 > Cyanex 302 + P507 > Cyanex 302 + P229 ~ Cyanex 302 + Cyanex 925 ~ Cyanex 302 > Cyanex 302 + P350 > Cyanex 302 + TBP > Cyanex 302 + CA-100 > Cyanex 302 + N1923.

Among the acidic organophsosphrous extractants, the structures of them are as follows:



P204 P507 P229 Cyanex 302

where $R_1 = CH_2CH(C_2H_5)C_4H_9$; $R_2 = CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$.

In the earlier work, the work on the rare earth ion extractions using these acidic organophsosphrous extractant alone was performed. The result demonstrates that the extractability order is P204 > P507 > Cyanex 302 (P229), which is due to the increase of C-P numbers resulting in decreasing K_a values and activities of the functional group P(O)OH (17). From Figs. 1–3, it can be seen that the extractability order for the mixtures of Cyanex 302 and acidic extractant is the same as that for the

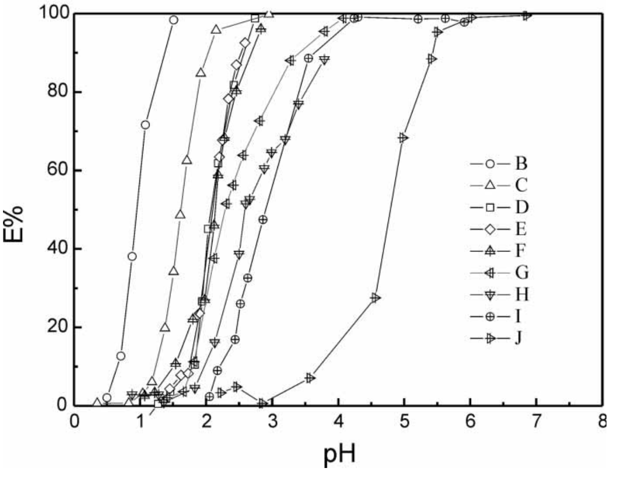


Figure 1. The effect of pH values on the extraction percent of $HoCl_3$ with the different mixtures of Cyanex 302 and organic extractants. $[Ho^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035 M. [Cyanex 302]:[organic extractants] = 1:1. B. Cyanex 302+ P204 C. Cyanex 302 + P507 D. Cyanex 302 E. Cyanex 302 + P229 F. Cyanex 302 + Cyanex 925 G. Cyanex 302 + P350 H. Cyanex 302 + TBP I. Cyanex 302 + CA-100 J. Cyanex 302 + N1923.

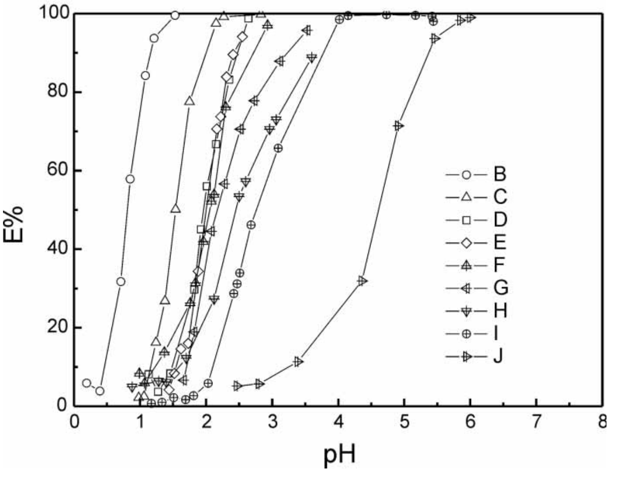


Figure 2. The effect of pH values on the extraction percent of YCl_3 with the different mixtures of Cyanex 302 and organic extractants. $[Y^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035M. [Cyanex 302]:[organic extractants] = 1:1 B. Cyanex 302+ P204 C. Cyanex 302 + P507 D. Cyanex 302 E. Cyanex 302 + P229 F. Cyanex 302 + Cyanex 925 G. Cyanex 302 + P350 H. Cyanex 302 + TBP I. Cyanex 302+ CA-100 J. Cyanex 302 + N1923.

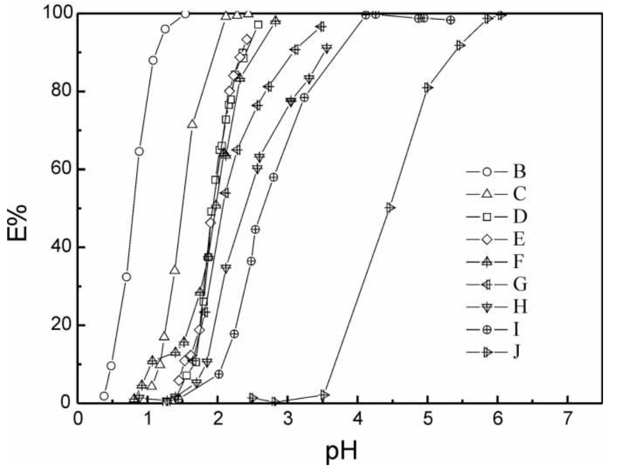


Figure 3. The effect of pH values on the extraction percent of $ErCl_3$ with the different mixtures of Cyanex 302 and organic extractants. $[Er^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035 M. [Cyanex 302]:[organic extractants] = 1:1. B. Cyanex302+ P204 C. Cyanex 302 + P507 D. Cyanex 302 E. Cyanex 302 + P229 F. Cyanex 302 + Cyanex 925 G. Cyanex 302 + P350 H. Cyanex 302 + TBP I. Cyanex 302+ CA-100 J. Cyanex 302 + N1923.

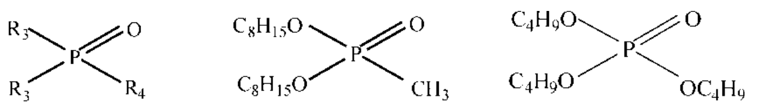
extractant alone. The reason can be explained as follows. For the mixtures of Cyanex 302 and P204 or P507, the extractability of P204 and P507 alone is so strong that the contribution of Cyanex 302 might be null in the case of P204 and P507, especially at lower aqueous pH, for example, at pH 1.31, the extraction by P204 + Cyanex 302 is 99.5% and with P507+ Cyanex 302 is 59.4%, while the extraction with Cyanex 302 alone is only 5.3%. Therefore, the extractability order for the mixtures of Cyanex 302 and P204 or P507 is still to be Cyanex 302 + P204 > Cyanex 302 + 507 > Cyanex 302. Cyanex 302 and P229 have the same C-P numbers, somewhat higher extractability for the mixture of Cyanex 302 and P229 than Cyanex 302 alone may be due to the substitution of the oxygen in P═O bond by a sulphur atom in the phosphinic derivative displaces the $pH_{0.5}$ extraction value to appreciably more acid levels, thus allowing rare earth extraction from more acidic solutions (18). The phenomena that the adulteration of methylheptanol into the CA-100 can decrease the extractability has been reported in the earlier work (19) and data presented in Table 1 clearly demonstrates that $\Delta pH \approx 0.63$. In fact, if there is no methylheptanol, the extractability for the mixtures of Cyanex 302 and CA-100 is stronger than Cyanex 302 alone. Because the extractability of CA-100 ($pH1/2 = 3.01$ without methylheptanol) alone is weaker than that of Cyanex 302 alone (3), it can be deduced that there may be a synergistic effect in the mixtures of Cyanex 302 and CA-100.

Table 1. The effect of methylheptanol on the rare earth ion extractions

Rare earth ions	$pH_{1/2}$ value before adulterating the methylheptanol	$pH_{1/2}$ value after adulterating the methylheptanol	$pH_{1/2(after)} - pH_{1/2(before)}$
Sc	2.14	2.72	0.58
Eu	2.71	3.39	0.68
Yb	2.94	3.57	0.63
Ho	2.94	3.58	0.63
Y	3.01	3.64	0.63
Er	2.98	3.65	0.67

$[RE^{3+}] = 3.0$ mM, $[NaCl] = 1.0$ M, $t = 25^0C$, [Cyanex 302] + [CA-100] = 0.035 M, [Cyanex 302]: [CA-100] = 1:1, [methylheptanol] = 1%(v/v).

For these neutral organophsosphrous extractants, their structures are as follows:



Cyanex 925 P350 TBP

where R_3 and R_4 are alkyls having the different structures.

As is well known, the extraction of metal ion using the neutral organophsosphrous extractant usually takes place at higher aqueous acidity and increasing C-P bond numbers in neutral organophosphrous extractants makes oxygen more negative, which benefits the solvation extraction mechanism (20). Therefore, the extractability order for the mixture of Cyanex 302 and Cyanex 925, P350 or TBP should be Cyanex 302 + Cyanex 925 > Cyanex + P350 > Cyanex 302 + TBP. Moreover, it seems that even an antagonistic effect in the mixtures of Cyanex 302 and TBP or P350 could be read from Figs. 1–3.

For prime amine N1923, the synergistic extraction of rare earth with the mixtures of purified Cyanex 302 and acidified N1923 has been reported in the earlier work (14). The weaker extractability for the mixtures of Cyanex 302 and N1923 than Cyanex 302 in the used pH range is due to the competition extraction of hydrochloric acid and rare earth ion.

If the values of $\Delta pH_{1/2}$ are used to compare the separation selectivity, defining the separation factors, $\log \beta = 3\Delta pH_{1/2}$ (21), Table 2 clearly projects the results that the mixtures of Cyanex 302 with acidic organic extractants can weaken their separation ability to Ho, Y, and Er; and the case of the mixtures of neutral organophosphrous extractants or N1923 with Cyanex 302 is on the contrary, and this is of significance to practical application, especially for the mixtures of N1923 and Cyanex 302, so large separation factors, 3.24

Table 2. The $pH_{1/2}$ values and separation factors of rare earth ion extractions with the mixtures of Cyanex 302 and different extractants

B	P204+	P507+	P229+	Cya302	Cy925+	TBP+	P350+	CA100+	N1923+
$pH_{1/2(Ho)}$	0.92	1.62	2.09	2.10	2.18	2.31	2.62	2.92	4.80
$pH_{1/2(Y)}$	0.85	1.54	2.02	2.01	2.04	2.16	2.46	2.75	4.61
$pH_{1/2(Er)}$	0.82	1.50	1.96	1.95	1.97	2.07	2.36	2.64	4.44
$\Delta pH_{1/2(Ho\text{-}Y)}$	0.07	0.08	0.07	0.09	0.14	0.15	0.16	0.17	0.19
$\Delta pH_{1/2(Y\text{-}Er)}$	0.03	0.04	0.04	0.06	0.07	0.09	0.10	0.11	0.17
$\beta_{Ho/Y}$	1.62	1.74	1.62	1.86	2.63	2.81	3.01	3.24	3.72
$\beta_{Y/Er}$	1.23	1.32	1.32	1.51	1.62	1.86	2.00	2.14	3.24
$\beta_{Ho/Er}$	1.99	2.29	2.13	2.80	4.26	5.22	6.02	6.93	12.0

B denotes the organic extractant; $[RE^{3+}] = 3$ mM, [NaCl] = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035 M. [Cyanex 302]:[organic extractants] = 1 : 1.

for $\beta_{Y/Er,}$ 3.72 for $\beta_{Ho/Y}$ and 12.0 for $\beta_{Ho/Er}$ that Ho, Y, and Er can be realized effectively by mutual separation.

The Effect of Mole Fraction of Cyanex 302 on the Extraction and Separation of Ho, Y, and Er

At constant total concentration of the mixture, the effect of mole fraction of Cyanex 302 on the extraction has been given in Figs. 4–6. It can be seen that with increasing mole fraction of Cyanex 302 in the mixtures, the distribution ratio D, increases in the mixture of Cyanex 302 and P350 or TBP, decreases in the system of the mixed Cyanex 302 with P204 or P507, first increases and then decreases in the system of the mixed Cyanex 302 P229 and Cyanex 925, CA-100 or N1923. Therefore, we can say that the mixtures of P229, Cyanex 925, CA-100 or N1923 with Cyanex 302 have a synergistic effect on rare earth extractions.

According to Xu et al. (22), the synergistic enhancement coefficients R, $R = D_{mixtures}/D_{Cyanex\ 302} + D_B$,(B denotes another extractant in the mixtures) can be calculated and the values are listed in Table 3. It gives us a clear impression that there is an obvious synergistic effect in the mixtures of Cyanex 302 and P229, Cyanex 923, CA-100, and N1923. The largest

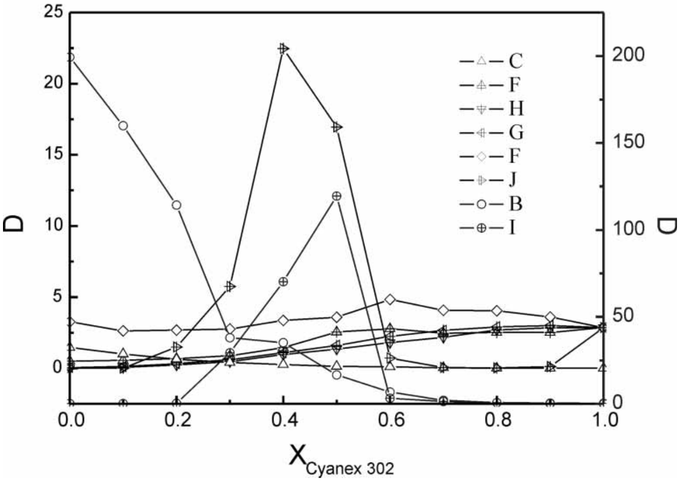


Figure 4. The synergistic effect on $HoCl_3$ extractions with the different mixtures of Cyanex 302 and organic extractants $[Ho^{3+}] = 3$ mM, (H, Na) = 1.0M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035M. [Cyanex 302]:[organic extractants] = 1:1. B. Cyanex 302 + P204, pH = 1.31 C. Cyanex 302 + P507, pH = 1.31 E. Cyanex 302 + P229, pH = 2.41 F. Cyanex 302 + Cyanex 925, pH = 2.41 G. Cyanex 302 + P350, pH = 2.41 H. Cyanex 302 + TBP, pH = 2.41 I. Cyanex 302 + CA-100, pH = 2.41 J. Cyanex 302 + N1923, pH = 2.41.

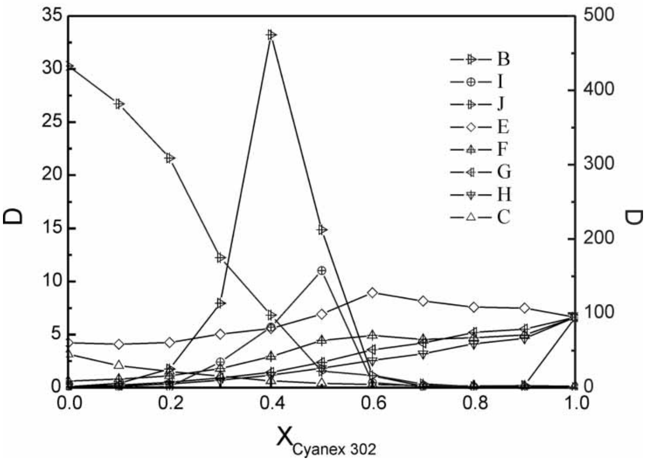


Figure 5. The synergistic effect on YCl_3 extractions with the different mixtures of Cyanex 302 and organic extractants $[Y^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035 M. [Cyanex 302]:[organic extractants] = 1:1. B. Cyanex 302+ P204, pH = 1.31 C. Cyanex 302 + P507, pH = 1.31 E. Cyanex 302 + P229, pH = 2.41 F. Cyanex 302 + Cyanex 925, pH = 2.41 G. Cyanex 302 + P350, pH = 2.41 H. Cyanex 302 + TBP, pH = 2.41 I. Cyanex 302 + CA-100, pH = 2.41 J. Cyanex 302 + N1923, pH = 2.41.

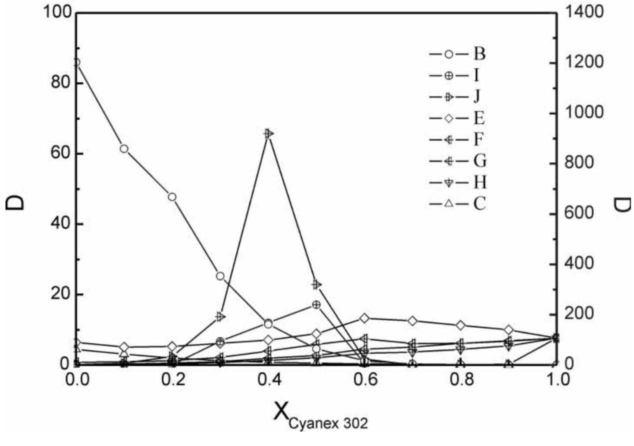


Figure 6. The synergistic effect on $ErCl_3$ extractions with the different mixtures of Cyanex 302 and organic extractants [Er3 +] = 3 mM, (H, Na) = 1.0 M, t = 25°C, [Cyanex 302] + [organic extractants] = 0.035M. [Cyanex 302]:[organic extractants] = 1:1. B. Cyanex 302 + P204, pH = 1.31 C. Cyanex 302 + P507, pH = 1.31 E. Cyanex 302 + P229, pH = 2.41 F. Cyanex 302 + Cya925, pH = 2.41 G. Cyanex 302 + P350, pH = 2.41 H. Cyanex 302 + TBP, pH = 2.41 I. Cyanex 302+ CA-100, pH = 2.41 J. Cyanex 302 + N1923, pH = 2.41.

Table 3. The synergistic enhancement coefficients of Ho, Y and Er extractions with the mixtures of Cyanex 302 and other organic extractants

	P229			Cy925			CA100			N1923		
B ($X_{(Cy302)}$)	R(Ho)	R(Y)	R(Er)	R(Ho)	R(Y)	R(Er)	R(Ho)	R(Y)	R(Er)	R(Ho)	R(Y)	R(Er)
0.1	0.81	0.92	0.78	0.74	0.66	0.59	1.32	1.18	1.71	0.001	0.55	0.56
0.2	0.84	0.90	0.79	0.70	0.61	0.59	1.67	1.34	2.19	2.12	1.27	1.55
0.3	0.88	1.02	0.90	0.72	0.74	0.76	2.12	1.89	3.67	5.48	3.90	5.89
0.4	1.08	1.08	1.02	1.00	0.97	1.13	5.88	5.18	7.60	16.1	12.3	21.3
0.5	1.17	1.27	1.26	1.51	1.22	1.52	12.0	11.9	12.9	4.58	4.43	5.60
0.6	1.60	1.58	1.86	1.44	1.16	1.38	0.39	0.63	0.39	0.34	0.28	0.35
0.7	1.36	1.38	1.72	1.14	0.94	1.09	0.21	0.23	0.16	0.02	0.027	0.013
0.8	1.37	1.23	1.53	1.05	0.87	0.98	0.16	0.23	0.16	0.007	0.019	0.008
0.9	1.24	1.17	1.32	0.96	0.82	0.97	0.18	0.24	0.21	0.034	0.035	0.024

synergistic effect obtained is at X_{Cya302} equal to 0.6, 0.5, 0.5, and 0.4 for the systems of P229 + Cyanex 302, Cyanex 925 + Cyanex 302, CA-100 + Cyanex 302, and N1923 + Cyanex 302, respectively.

Table 4 gives the separation factors of Ho, Y, and Er in the mixtures of the Cyanex 302 and another organic extractant. It can be seen that the separation selectivity of Ho, Y and Er varies with different mole fractions of Cyanex 302 in the mixtures. The separation factors β which the maximum is at $X_{Cya302} = 0.6-0.9$ means that the synergistic extraction and extraction by Cyanex 302 alone play the primary role in the mixed system, and the maximum is at $X_{Cya302} = 0.1-0.4$ means that the synergistic extraction and extraction by another organic extractant alone play the primary role in the mixed system. Comparing the values of β at $X_{Cya302} = 0.5$ and $X_{Cya302} = 1$, we can know that the separation selectivity of Ho, Y, and Er by Cyanex 302 alone is higher than that by the mixtures of Cyanex 302 with P229 and lower than that by the mixtures of Cyanex 302 with Cyanex 925 or N1923, which is in consistence with the results obtained in Table 2. It worth noticing whatever large the β at $X_{Cya302} = 1$ is, there are always several values of β at X_{Cya302} unequal to 1 more than it, therefore, we can say that proportional adulteration of P229, Cyanex 925, CA-100 or N1923 into Cyanex 302 can improve the separation selectivity to Ho, Y, and Er.

Synergistic Extraction of YCl_3 with the Mixtures of Cyanex 302 and CA-100

Taking into account there are only two kinds of anions in the aqueous phase, it can be deduced that Y^{3+} exists in the form of $YCl_x^{(3-x)+}$ or $Y(OH)_x^{(3-x)+}$ and the extraction of Y^{3+} can be expressed as:

$$Y^{3+}_{(a)} + (3-x)L^-_{(a)} + mH_2A_{2(O)} + nH_2B_{2(O)} \overset{K_{12}}{\longleftrightarrow} YH_{2m+2n-x}A_{2m}B_{2n}L_{3-x(O)} + xH^+_{(a)} \quad (1)$$

Then, the distribution ratio D_{12} and the equilibrium constant K_{12} of the synergistic extraction should be:

$$D_{12} = D_T - D_1 - D_2 = \frac{[YH_{2m+2n-x}A_{2m}B_{2n}L_{3-x}]_{(O)}}{[Y^{3+}]_{(a)}} \quad (2)$$

$$K_{12} = \frac{[YH_{2m+2n-x}A_{2m}B_{2n}L_{3-x}]_{(O)}[H^+]^x_{(a)}}{[Y^{3+}]_{(a)}[L^-]^{3-x}_{(a)}[H_2A_2]^m_{(o)}[H_2B_2]^n_{(o)}} \quad (3)$$

where D_T denotes the total distribution ratio of the mixture system, and D_1, D_2 are the distribution ratios of the Cyanex 302 and CA-100. H_2A_2 and H_2B_2 refer to the dimeric form of Cyanex 302 and CA-100, respectively (3, 23), L denotes the OH^- or Cl^-. The subscript (a) and (o) denote the aqueous phase and the

Table 4. The separation factors values of Ho/Y, Y/Er and Ho/Er in the mixtures of Cyanex 302 and different extractants

	P229			Cyanex 925			CA-100			N1923		
B (X_{Cya302})	$\beta_{Ho/Y}$	$\beta_{Y/Er}$	$\beta_{Ho/Er}$	$\beta_{Ho/Y}$	$\beta_{Y/Er}$	$\beta_{Ho/Er}$	$\beta_{Ho/Y}$	$\beta_{Y/Er}$	$\beta_{Ho/Er}$	$\beta_{Ho/Y}$	$\beta_{Y/Er}$	$\beta_{Ho/Er}$
0.0	1.29	1.51	1.94	1.25	1.21	1.51	1.30	1.41	1.83	1.09	0.68	0.74
0.1	1.56	1.24	1.93	1.48	1.06	1.56	1.16	2.05	2.37	1.15	1.11	1.27
0.2	1.59	1.23	1.95	1.62	1.13	1.83	1.05	2.29	2.40	1.18	1.38	1.62
0.3	1.83	1.21	2.21	2.04	1.19	2.42	1.17	2.72	3.18	1.38	1.72	2.37
0.4	1.66	1.26	2.09	2.03	1.35	2.74	1.15	2.06	2.36	1.47	1.97	2.89
0.5	1.53	1.28	1.95	1.74	1.31	2.27	1.31	1.51	1.97	1.86	1.53	2.84
0.6	1.85	1.48	2.73	1.77	1.50	2.65	2.13	0.86	1.83	1.59	1.41	2.24
0.7	2.00	1.53	3.06	1.84	1.33	2.44	1.45	0.99	1.43	2.46	0.57	1.40
0.8	1.87	1.49	2.78	1.87	1.30	2.43	1.93	0.92	1.77	3.29	0.50	1.64
0.9	2.07	1.32	2.73	1.97	1.35	2.65	1.93	1.18	2.27	1.97	0.80	1.57
1.0	1.60	1.35	2.14	1.60	1.15	1.84	2.00	1.08	2.16	1.60	1.15	1.84

organic phase, respectively. When the temperature and ionic strength in the aqueous phase have been kept constant, taking logarithms, the log D_{12} of the mixed system should be:

$$\log D_{12} = \log K_{12} + xpH + m\log[(H_2A_2)] + n\log[(H_2B_2)] + (3 - x)\log[L^-]_{(a)} \quad (4)$$

In order to determine the extracted complexes in the CA-100 + Cyanex 302 system, a series of experimental were carried out. As shown in Fig. 7, the plots of log D_{12} versus pHeq at fixed concentration of Cyanex 302 and CA-100 give straight lines with slopes of about 2.0, and this apparently indicates that two hydrogen ions are librated in forming the complex for the extraction system and the value of "x" is equal to 2. In fact, in such pH range, the contribution of CA-100 is so weak that the value of D_2 can be neglected, that is, D_{12} = DT-D1. Similarly, at fixed aqueous acidity and concentration of one extractant, the effect of another extractant concentration on the extraction was illustrated in Fig. 8. The approximate slope of 2.0 indicate that 2 H_2A_2 and 2 H_2B_2 molecule are attached to the synergistic species extracted into the organic phase, and the maximal synergistic enhancement can be obtained at the mole fraction $X_{HA} = 0.5$. According to the stability constant of Y^{3+} with OH^- or Cl^-, it can be deduced that OH^- is prone to take part in the extraction and Cl^- is barely extracted into organic phase,

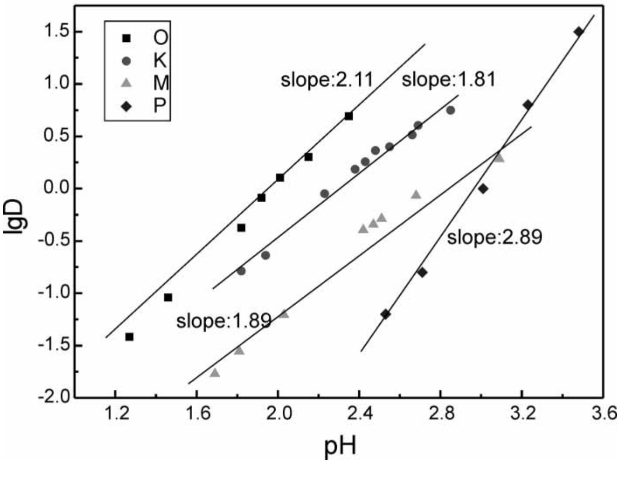


Figure 7. The effect of aqueous pH on synergistic extraction of YCl_3 with the mixture of Cyanex 302 and CA-100. $[Y^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C. O. The relationship: $\log D_1$vs. pH, Cyanex 302 = 0.0175 M. K. The relationship: $\log D_{12}$ vs. pH, [Cyanex 302] = [CA-100] = 0.0175 M. M. The relationship: $\log D_{12}$ vs. pH, [Cyanex 302] = 0.021 M; [CA-100] = 0.014 M. N. The relationship: $\log D_1$vs. pH, CA-100 = 0.0175 M.

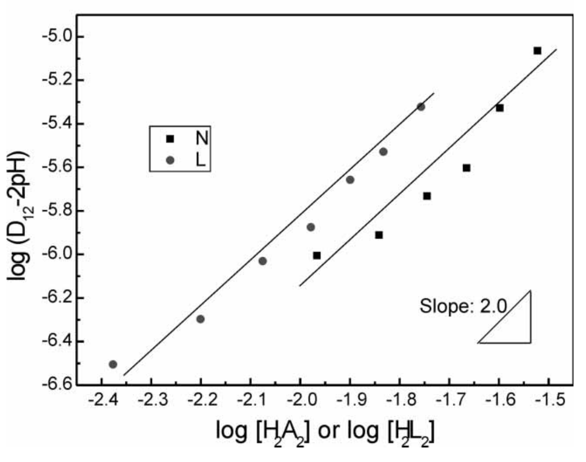


Figure 8. The effect of extractant concentration on synergistic of YCl_3 with the mixture of Cyanex 302 and CA-100. $[Y^{3+}] = 3$ mM, (H, Na) = 1.0 M, t = 25°C. N. The relationship: $logD_{12}$-2pH vs. log $[CA\text{-}100]_{(O)}$, $C_{Cyanex\ 302} = 0.0175$ M, pH = 1.70 HCl buffer solution L. The relationship: $logD_{12}$-2pH vs. log $[Cyanex\ 302]_{(O)}$, $C_{CA\text{-}100} = 0.0175$ M, pH = 2.80 KH_2PO_4 buffer solution.

and this assumption can be confirmed by detecting the effect of Cl^- on the extraction, and the Fig. 9 clearly project the result that Cl^- has not been extracted into the organic phase. Thus, the extraction mechanism can be

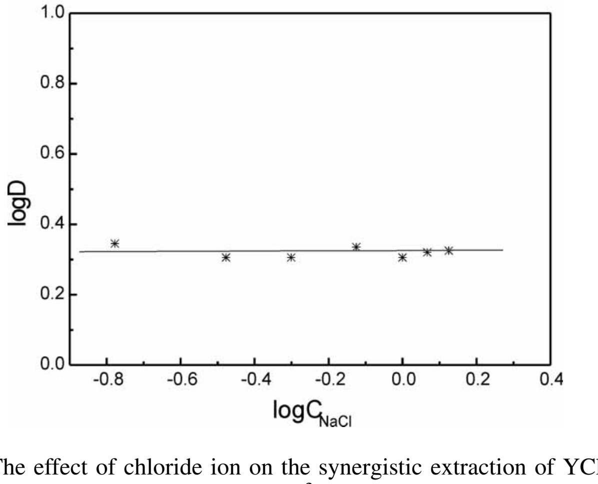


Figure 9. The effect of chloride ion on the synergistic extraction of YCl_3 with the mixture of Cyanex 302 and CA-100. $[Y^{3+}] = 3$ mM, pH = 2.8 $ClCH_2COOH$–NaOH, [Cyanex 302] = [CA-100] = 0.0175 M.

rewritten as:

$$Y(OH)^{2+} + 2H_2A_2 + 2H_2B_2 \overset{K_{12}}{\longleftrightarrow} Y(OH)A_4B_4H_6 + 2H^+ \quad (5)$$

The equilibrium constant (log K_{12}) is calculated to be -3.55 ± 0.03.

CONCLUSIONS

The extraction and separation of Ho, Y, and Er by the mixtures of Cyanex 302 and another organic extractant, such as P204, P507, P229, CA-100, Cyanex 925, TBP, P350, or N1923 has been studied in the present paper. Their mixtures show same effect and the extractability order for Ho, Y, and Er with the mixtures of Cyanex 302 and organic extractants is: Cyanex 302 + acidic organic extractants > Cyanex 302 + neutral organic extractants > Cyanex 302 + primary amine N1923. The mixtures of Cyanex 302 and P204, P507, TBP, or P350 has no synergistic effect, the mixtures of Cyanex 302 and P229 or Cyanex 925 has a weak synergistic effect and the mixtures of Cyanex 302 and CA-100 or N1923 has an obviously synergistic effect on the Ho, Y, and Er extraction. In addition, it has been known that the synergistic enhancement coefficients vary with different mole fraction of Cyanex 302 in the mixtures and the largest synergistic effect can be obtained at X_{Cya302} is 0.6, 0.5, 0.5, and 0.4 for the mixtures of P229 + Cyanex 302, Cyanex 925 + Cyanex 302, CA-100 + Cyanex 302, and N1923 + Cyanex 302, respectively. At the same time, it can be concluded that the separation selectivity of Ho, Y, and Er vary with different mole fractions of Cyanex 302 in the mixtures and therefore large separation factor values, for example, 3.24 for $\beta_{Y/Er}$, 3.72 for $\beta_{Ho/Y}$, 12.0 for $\beta_{Ho/Er}$ in the mixtures of N1923 and Cyanex 302 that Ho, Y, and Er can be realized effectively with mutual separation. In addition, the synergistic extraction mechanism of Cyanex 302 with CA-100 has been determined and the extracted complex has been deduced to be $Y(OH)A_4B_4H_6$.

ACKNOWLEDGEMENTS

The authors wish to thank Cytec Canada Inc. for supplying Cyanex 302. The project was supported by the State Key Project of the Foundation Research (2004CB719506) and National Natural Science Foundation of China (20371046).

REFERENCES

1. Lena, T.G. and Smutz, M. (1968) The extraction of neodymium and samarium by di(2-ethylhexyl) phosphinic acid from aqueous chloride, perchlorate and nitrate systems. *J. Inorg. Nucl. Chem.*, 30: 621–637.

2. Ahmed, A.A., Susumu, N., Fumio, K., and Katsuroku, T. (2002) Extraction of lanthanides and yttrium with PC-88 from aqueous phosphate media, Proceeding of the International Solvent Extraction Conference, (ISEC'2002) 1070–1075.
3. Wang, Y.G., Yue, S.T., Li, D.Q., Jin, M.J., and Li, C.Z. (2002) Solvent extraction of scandium(III), yttrium(III), lanthanides(III) and divalent Metal ions with sec-nonylphenoxy acetic acid. *Solvent Extraction and Ion Exchange*, 20 (6): 701–716.
4. Xu, G.Q. (1995) *The Rare Earths, 2nd ed*; Metallurgy Industrial Publishing Company: Beijing, P.R. China., 469–499, 612–727.
5. Zhao, Y.L. and Li, D.Q. (1990) Liquid-liquid extraction of Sc(III) with di-(1-metylheptyl)metyl phosphate. *Yingyong Huaxue* (in Chinese) 7 (2): 1–4.
6. Li, D.Q., Ji, E.R., and Xu, W. (1985) Extraction mechanism of rare earth elements(III) ions(III) and yhorium(IV) from sulfuric acid solutions by primary amine N1923. *New Frontiers in Rare Earth Science and Applications Science*, 1: 36–38.
7. American Cyanamid Company, Cyanex 272, Cyanex 302, Cyanex 301, Technical Brochures, 1990.
8. Rickelton, W.A. and Boyle, R.J. (1990) The selective recovery of zinc with new thiophosphinic acids. *Solvent Extraction and Ion Exchange*, 8: 783–797.
9. Zhang, X.F. and Li, D.Q. (1993) The solvent extraction of rare earth ion(III) with bis(2,4,4-trimetylphety) phosphinic acid. *Yingyong Huaxue* (in Chinese) 10 (4): 72–76.
10. Wang, C. and Li, D.Q. (1995) Solvent extraction of Sc(III), Zr(III), Th(III), Fe(III) and Lu(III) with thiosubstituted organophosphinic acid extractants. *Solvent Extr. Ion Exch.*, 13 (3): 503–523.
11. Li, D.Q. and Luo, A.Q. et al. (1996) Solvent extraction of trivalent lanthanides with Cyanex 302 from acidic aqueous chloride solution. *Value Adding through Solvent Extraction*, 1: 165–170.
12. Yuan, M., Luo, A.Q., and Li, D.Q. (1995) Solvent extraction of lanthanides in aqueous nitrate media by Cyanex 302. *Acta Metallurgica Sinica*, 8: 10–14.
13. Xue, L.Z. and Li, D.Q. et al. 1995) Liquid-Liquid extraction of rare earths (III) from acidic sulfate solutions with Cyanex 302. *Journal of Rare Earth* (Special Issue). 2: 657–660.
14. Kong, W., Wang, C., and Li, D.Q. (1997) Synergistic extraction of rare earth elements by the mixtures of HBTMPTP and prime amine. *Chemical Journal of Chinese Universities*, 18: 177–181.
15. Zahir, Md.H. and Masuda, Y. (1997) Extractive separation of trivalent lanthanide metals with a combination of di(2-ethylhexyl)phosphoric acid and 1,10-phenanthr. *Talanta*, 44: 365–371.
16. Sun, X.B., Zhao, J.M., Meng, S.L., and Li, D.Q. (2006) Synergistic extraction and separation of yttrium from heavy rare earths using mixture of sec-octyl phenoxy acetic and bis(2,4,4-trimetylpentyl)phosphinic acid. *Analytical Chimica Acta*, 553: 83–88.
17. Jia, Q., Zhan, C.H., Li, D.Q., and Niu, C.J. (2004) Extraction of zinc(II) and cadmium(II) by using mixtures of primary amine N1923 and organophosphorus acids. *Separation Science and Technology*, 39 (5): 1111–1123.
18. Alguacil, F.J., Cobo, A., and Caravaca, C. (1992) Study of the extraction of zinc(II) in aqueous chloride media by Cyanex 302. *Hydrometallurgy*, 31: 163–174.
19. Wang, Y.G., Meng, S.L., Li, D.Q., Jin, M.L., and Li, C.Z. (2002) Extraction of rare earth ions by sec-nonylphenoxy acetic acid (ISEC, 2002), 436–440.
20. Ritcey, G.M. and Ashbrook, A.W. (1984) *Theory and Practice in the Solvent Extraction Principles and Applications to Process Metallurgy*; Elsevier Science Publishing Company Inc, 37.

21. Li, D.Q. (1998) *The Progress of Extraction and Separation Techniques for Rare Earth*; Ni, J.Z. and Hong, G.Y. (eds.), Science Publishing Company: Beijing. (in Chinese), 27–28.
22. Xu, G.X., Wang, W.Q., and Wu, J.G. (1963) Extraction chemistry of the unclear fuel (I): synergistic extraction with chelating and complexing extractants. *Atomic Energy Science and Technology* (in Chinese). 7: 487–508.
23. Tait, B.K. (1993) Cobalt-nickel separation: the extraction of cobalt(II) and nickel(II) by Cyanex 301, Cyanex 302 and Cyanex 272. *Hydrometallurgy*, 32: 365–372.