

Slopes of the lines in the high temperature region (h.t.r) and in the l.t.r are -1567.5 and -3928 , respectively. From the slope and intercept obtained from Fig. 7 and applying the Van't Hoff equations [56, 57], the thermodynamic parameters are calculated as:

$$\log D = -\frac{\Delta H}{2.303RT} + C \quad (14)$$

where R, T, and C are the universal gas constant, absolute temperature, and conditional constant, respectively. Activity coefficients for other components are considered to be constant under the experimental conditions [58].

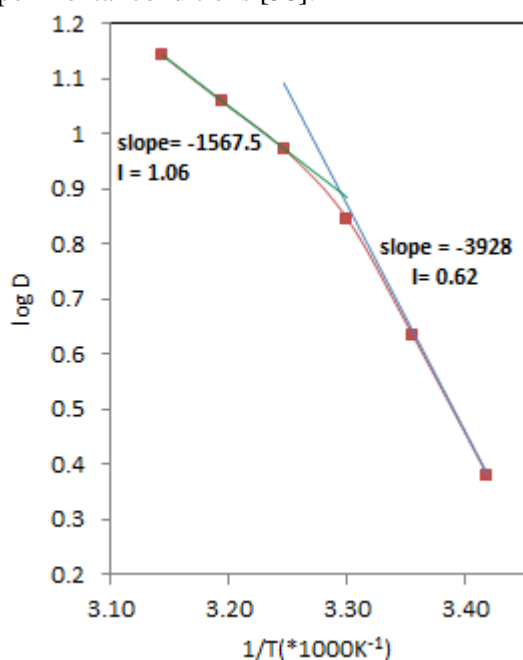


Fig. 7. Relationship between distribution coefficient (D) and reaction temperature under conditions of 0.002 mol L^{-1} Ce(IV), 0.08 mol L^{-1} Cyanex 302, $V_o/V_a = 1$ ($V_a = 10 \text{ mL}$), initial solution pH(eq) 3.54. Eq. time = 20 min.

The slopes equal $-\Delta H/2.303R$. On the basis of Eq. (14) and Fig. 7, the values of ΔH are calculated to be 30.00 at h.t.r and $75.21 \text{ kJ mol}^{-1}$ at l.t.r, indicating that the extraction reaction is endothermic. Therefore, the extraction efficiency increased by temperature raise. Also, the values of the change in the Gibbs free energy (ΔG) and the entropy (ΔS) were calculated from the following equations for extraction reaction at 298 K :

$$\Delta G = -2.303RT \log D \quad (15)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (16)$$

The values of ΔG and ΔS were calculated equal to $23.96 \text{ kJ mol}^{-1}$ and $20.26 \text{ J mol}^{-1} \text{ K}^{-1}$, and $71.76 \text{ kJ mol}^{-1}$ and $11.87 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The positive ΔG specified that the extraction reaction by Cyanex 302 proceeded not spontaneously. The positive values of ΔS indicated that the extraction of Ce(IV) is more efficient at high temperatures.

In a similar research, the thermodynamic study of copper(II) extraction from sulfate, nitrate and chloride media using Cyanex 302 in kerosene has shown that the extraction reaction is endothermic and non-spontaneous [47].

Effect of diluent type

In order to ascertain the impact of diluent type on Ce(IV) distribution, %E-values were evaluated when 0.002 mol L^{-1} Ce(IV) was extracted separately from the same aqueous feed solution by 0.10 mol L^{-1} extractant in various diluents while keeping constant all other conditions ($\text{pH}_{\text{ini}} = 3.6$ and $[\text{SO}_4^{2-}] = 0.0002 \text{ mol L}^{-1}$) (Table 1). It was observed that the percent extraction increases in the following order with the variation of diluent used to prepare the organic solution: CHCl_3 ($D = 1.02$) < CCl_4 ($D = 4.73$) = cyclo- C_6H_{12} ($D = 4.73$) < kerosene ($D = 5.80$) < 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ ($D = 7.36$) = C_6H_4 -(CH_3)₂ (xylene) ($D = 9.85$) < C_6H_6 ($D = 14.44$) = C_6H_5 - CH_3 (toluene) ($D = 14.44$). The study allows concluding on the effect of diluent on the rate of extraction of cerium and on the best ones of the diluents for the cases studied. C_6H_6 and C_6H_5 - CH_3 are very good diluents followed by C_6H_4 -(CH_3)₂ for the extraction of Ce(IV) by Cyanex 302. Kerosene is a better diluent over CHCl_3 , CCl_4 and cyclo- C_6H_{12} .

Stripping of Ce(IV)-loaded organic phase

The maximum Ce(IV) loaded organic phase, after the extraction step, was submitted to a stripping step using various mineral acids such as H_2SO_4 , HNO_3 and HCl solutions at $25 \text{ }^\circ\text{C}$ and $V_o:V_a = 1$. The stripping results are presented in Table 2. It deemed that stripping percentage is roughly acceptable in all three mineral acids used alone. In all cases, the percentage stripping increased by raising concentration of acid. Sulfuric acid (1 M) is sufficient to quantitatively strip off Ce(IV). HNO_3 and HCl can also be utilized in stripping if two-stage stripping is implemented.

Table 1. Effect of diluent type on extraction of Ce(IV). [Ce(IV)]_(ini) = 0.002 mol L⁻¹, pH_(ini) = 3.6, [Cyanex 302] = 0.1 mol L⁻¹, [SO₄²⁻] = 0.0002 mol L⁻¹, T = (25 ± 0.5) °C. Eq. time = 1 h, V_o/V_a = 1, V_a = 10 mL

Diluent	Ce(IV)] _{aq} eq, mol L ⁻¹	Ce(IV)] _o eq, mol L ⁻¹	%E	D
Carbon tetrachloride	0.00035	0.0017	82.54	4.73
Benzene	0.00013	0.0019	93.52	14.44
Toluene	0.00013	0.0019	93.52	14.44
Cyclohexane	0.00035	0.0017	82.54	4.73
1,2-Dichloroethane	0.00024	0.0018	88.03	7.36
Xylene	0.00018	0.0018	90.78	9.85
Chloroform	0.00099	0.0010	50.51	1.02
Kerosene	0.00029	0.0017	85.29	5.80

Table 2. Stripping of Ce(IV)-loaded organic phase using different mineral acid solutions. [Ce(IV)]_o ≈ 0.0018 mol L⁻¹, [Cyanex 301] = 0.10 mol L⁻¹, Eq. time = 1 h, T = (25 ± 0.5) °C, V_o/V_a = 1 (V_a = 10 mL).

Stripping agent	Concentration, mol L	Percentage stripping, %S
	0.1	70.43
H ₂ SO ₄	0.5	94.50
	1.0	98.80
	0.1	85.12
HNO ₃	0.5	94.05
	1.0	98.50
	0.1	44.33
HCl	0.5	84.15
	1.0	92.59

Selectivity studies

The selective extraction of Ce(IV) considering the presence of many associated metal ions and impurities such as Th(IV), and REE(III) (REE = La³⁺, Ce³⁺, Nd³⁺, Gd³⁺ and Yb³⁺) using a solution containing 0.3 g L⁻¹ of the different metal ions in sulfuric acid solution (with pH_(ini) range of approximately 3.0 – 4.5) with 0.1 M Cyanex 302 in kerosene at V_o:V_a = 1 and (25 ± 0.5) °C were investigated. The percent extraction data of the different metal ions shown in Fig. 8 indicate that a selective cerium separation can be done efficiently from H₂SO₄ solution in the pH range of 3-4 as rare earth ions (III) are almost not extracted under these experimental conditions. The

extraction of Th(IV) is low. Therefore, by selecting the appropriate acidity, cerium can be separated from REEs(III) and Th(IV).

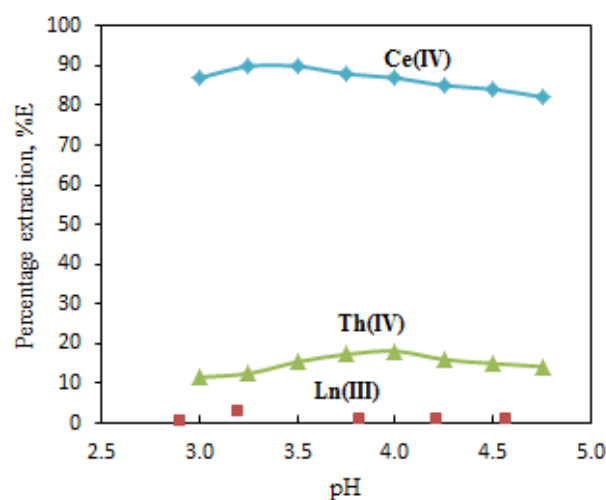


Fig. 8. Selectivity of Cyanex 302 for Ce(IV), Th(IV), and RE(III) under conditions of aqueous feed solution: 0.3 g L⁻¹ of the different metal ions in H₂SO₄ solution (pH_(ini) of approximately 3.0 to 4.5); organic phase: 0.1 M Cyanex 302 in kerosene; V_o/V_a = 1 (V_a = 10 mL); T = (25 ± 0.5) °C.

CONCLUSIONS

Cyanex 302 extracts Ce(IV) from sulfuric acid medium at pH above 3.0. The equilibration time is 20 min. The recovery of Ce(IV) can be regulated by controlling the extractant and pH of aqueous feed solutions. Cyanex 302 is a forward-looking extractant for the Ce(IV) extraction. At various concentration levels of the experimental parameters, extraction equilibrium reactions were proposed. It is seen that at all conditions, [Ce(OH)₂(HA₂)₂] is the extractable species though reacting Ce(IV) species in the aqueous phase may vary with its concentration and pH levels. Aromatic diluents appear as better diluents over other categories; kerosene is a better

diluent than CHCl_3 , CCl_4 and cyclo- C_6H_{12} . The temperature-sensitive extraction process of this metal in the studied system is endothermic ($\Delta H < 0$). The positive value of ΔG reveals that the extraction reaction proceeds not spontaneously, and the positive value of ΔS indicates that extraction of Ce (IV) is more desirable at high temperatures.

REFERENCES

1. S. Kuang, Z. Zhang, Y. Li, G. Wu, H. Wei, W. Liao, *Hydrometallurgy*, **167**, 107 (2017).
2. Y. Chen, X. Wang, X. He, Q. An, Z. Zuo, *J. Amer. Chem. Soc.*, **143**, 4896 (2021).
3. M. Xu, V. Smolenski, Q. Liu, A. Novoselova, K. Jiang, J. Yu, J. Liu, R. Chen, H. Zhang, M. Zhang, *J. Chem. Therm.*, **152**, 106260 (2021).
4. Y. Shan, Y. Liu, Y. Li, W. Yang, *Sep. Pur. Tech.*, **250**, 117181 (2020).
5. J.-Y. Kim, U.-S. Kim, M.-S. Byeon, W.-K. Kang, K.-T. Hwang, W.-S. Cho, *J. Rare Earths*, **29**, 1075 (2011).
6. J. Zhao, S. Meng, D. Li, *Sol. Extr. Ion Exch.*, **22**, 813 (2004).
7. E. Allahkarami, B. Rezai, *J. Env. Chem. Eng.*, **9**, 104956 (2021).
8. S. Milani and F. Zahakifar, *Braz. J. Chem. Eng.*, **39**, 553 (2022).
9. E. M. Abu Elgoud, Z. Ismail, Y. El-Nadi, H. Aly, *Chem. Pap.*, **74**, 2461 (2020).
10. M. M. Khataei, S. B. H. Epi, R. Lood, P. Spégel, Y. Yamini, C. Turner, *J. Pharm. Bio. Anal.*, **209**, 114487 (2022).
11. C. Li, H. He, M. He, Y. Gao, M. Zhang, C. Jiao, *J. Rad. Nuc. Chem.*, **1** (2021).
12. K. Li, J. Chen, D. Zou, Y. Deng, D. Li, *Hydrometallurgy*, **190**, 105155 (2019).
13. S. Ilyas, H. Kim, R. R. Srivastava, *Rare Met. Tech.*, Springer, 2021, p. 303.
14. S. Alamdar Milani, M. Ashtianifar, F. Zahakifar, *J. Appl. Res. Chem. Pol. Eng.*, **5**, 87 (2021).
15. R. D. Abreu, C. A. Morais, *Min. Eng.*, **23**, 536 (2010).
16. W. Liao, G. Yu, D. Li, *Sol. Extr. Ion Exch.*, **19**, 243 (2001).
17. L. Wang, Y. Yu, X. Huang, Z. Long, D. Cui, *Chem. Eng. J.*, **215**, 162 (2013).
18. D. Xu, Z. Shah, Y. Cui, L. Jin, X. Peng, H. Zhang, G. Sun, *Hydrometallurgy*, **180**, 132 (2018).
19. R. Mu, J. Chen, D. Zou, K. Li, D. Li, *Sep. Pur. Tech.*, **209**, 351 (2019).
20. D. Li, Z. Wang, G. Zeng, Z. Xue, *J. Chin. Rare Earths Soc.*, **2**, 9 (1984).
21. L. Xinghua, X. HUANG, Z. Zhaowu, L. Zhiqi, L. Ying, *J. Rare Earths*, **27**, 119 (2009).
22. D. Li, Z. Wang, G. Zeng, Z. Xue, *J. Chin. Rare Earth Soc.*, **2**, 9 (1984).
23. L. Jun, W. Zhenggui, L. Deqian, M. Gengxiang, J. Zucheng, *Hydrometallurgy*, **50**, 77 (1998).
24. W. Liao, G. Yu, D. Li, *Acta Met. Sin.*, **14**, 21 (2001).
25. M. Ugajin, S. Ajuria, *IAEA-TEC DOC-337* (1985).
26. K. Soldenhoff, *Proc. Int. Sol. Ext. Conf.*, **1** (1996).
27. Z. Dan, C. Ji, L. Deqian, *J. Rare Earths*, **32**, 681, 2014.
28. D. Li, Y. Bai, X. Sun, S. Liu, 52nd Conf. of Met., (2013).
29. A. A. Abdeltawab, S. Nii, F. Kawaizumi, K. Takahashi, *Sep. Pur. Tech.*, **26**, 265 (2002).
30. C. Basualto, F. Valenzuela, L. Molina, J. Munoz, E. Fuentes, J. Sapag, *J. Chil. Chem. Soc.*, **58**, 1785 (2013).
31. N. Krishnamurthy, C. K. Gupta, *Extr. Met. Rare Earths*, CRC press, 2015.
32. J. Saji, M. Reddy, *Sep. Sci. Tech.*, **38**, 427 (2003).
33. J. Saji, K. S. John, M. Reddy, *Sol. Extr. Ion Exch.*, **18**, 877 (2000).
34. M. Ulewicz, W. Walkowiak, *Env. Pro. Eng.*, **31**, 73 (2005).
35. W. Rickelton, *JoM*, **44**, 52 (1992).
36. A. Saily, S. Tandon, *Fresenius' J. Anal. Chem.*, **360**, 266 (1998).
37. B. Gupta, Z. Begum, *Sep. Pur. Tech.*, **63**, 77 (2008).
38. T. Miaomiao, J. Qiong, L. Wuping, *J. Rare Earths*, **31**, 604 (2013).
39. S. Tong, X. Zhao, N. Song, Q. Jia, W. Zhou, W. Liao, *Hydrometallurgy*, **100**, 15 (2009).
40. B. K. Tait, *Hydrometallurgy*, **32**, 365 (1993).
41. N. El-Hefny, J. Daoud, *J. Rad. Nucl. Chem.*, **261**, 357 (2004).
42. R. K. Biswas, A. K. Karmakar, *Sep. Sci. Tech.*, **49**, 278 (2014).
43. Y. Zhu, J. Chen, R. Jiao, *Sol. Extr. Ion Exch.*, **14**, 61 (1996).
44. H. Khalifa, B. Barsoum, *Mic. J.*, **18**, 428 (1973).
45. T. H. Handley, *Talanta*, **12**, 893 (1965).
46. K. C. Sole, J. B. Hiskey, *Hydrometallurgy*, **30**, 345 (1992).
47. N. El-Hefny, J. Daoud, *Sol. Extr. Ion Exch.*, **25**, 831 (2007).
48. K. C. Sole, T. L. Ferguson, J. B. Hiskey, *Sol. Extr. Ion Exch.*, **12**, 1033 (1994).
49. A. Almela, M. Elizalde, *Hydrometallurgy*, **37**, 47 (1995).
50. E. Paatero, T. Lantto, P. Ernola, *Sol. Extr. Ion Exch.*, **8**, 371 (1990).
51. B. Bouchaud, J. Balmain, G. Bonnet, F. Pedraza, *J. Rare Earths*, **30**, 559 (2012).
52. R. Marsac, F. Réal, N. L. Banik, M. Pédrot, O. Pourret, V. Vallet, *Dalton Transactions*, **46**, 13553 (2017).
53. L. O. Tuazon, Iowa State University, 1959.
54. R. L. Moore, R. C. Anderson, *J. Amer. Chem. Soc.*, **67**, 167 (1945).
55. E.L. King, M.L. Pandow., *J. Am. Chem. Soc.*, **74**, 1966 (1952).
56. F. Islam, H. Rahman, M. Ali, *J. Inorg. Nucl. Chem.*, **41**, 217 (1979).
57. T. Wongsawa, W. Ampronpong, N. Traiwongsa, U. Pancharoen, W. Punyain, S. Phatanasri, *J. Tai, Inst. Chem. Eng.*, **122**, 40 (2021).
58. D. Mohapatra, K. Hong-In, C.-W. Nam, K.-H. Park, *Sep. Pur. Tech.*, **56**, 311 (2007).