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# Solvent Extraction Study of Rare Earths from Nitrate Medium by the Mixtures of TBP and D2EHPA in Kerosene

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## Abstract

The application of isomolar mixtures of tributylphosphate(TBP) and di-(2-ethylhexyl)phosphoric acid(D2EHPA) in kerosene at room temperature of 35±1°C for extractive separation of individual rare earths from mixed rare earth nitrate feed solution compared with 50%TBP in kerosene has been studied. The distribution coefficients ($K_d$) and the synergistic coefficients $[S=(K_{d,a})_{TBP,D2EHPA}/\{(K_{d,a})_{TBP}+(K_{d,a})_{D2EHPA}\}]$ were investigated. It was found that the $K_d$ of heavy rare earths are higher when the solvents were 1.5 M and 1.0 M isomolar mixtures of TBP and D2EHPA in kerosene compared with 50%TBP in kerosene. Ce gave significant synergism phenomenon ($S>1$) when the organic phase was 1.0 M isomolar (TBP-D2EHPA)/kerosene but La showed antagonistic effect ($S<1$) when 1.5 M isomolar (TBP-D2EHPA)/kerosene was the solvent. The rest including Y performed synergism.

**Keywords:** synergism, rare earths, TBP, D2EHPA

## Introduction

The terms 'Rare Earths' is the group of 17 chemically similar metallic elements which includes scandium, yttrium, and the lanthanides. The lanthanides are the series of elements with atomic number 57 to 71. The first seven lanthanides, La to Eu, are the cerium subgroup or 'light' rare earths. The remaining eight elements, Gd to Lu, together with Y are belong to the yttrium subgroup or 'heavy' rare earth elements(1). Yttrium behaves as though its atomic number is 67.5(2).

For the extractive separation of rare earth elements, phosphororganic extracting agents are usually applied which are either neutral [especially tributylphosphate (TBP) or acidic [mainly di-(2-ethylhexyl) phosphoric acid (D2EHPA)]. Commercially, TBP is the extractant used in Rhone-Poulence and Thorium (UK) rare earth solvent extraction. D2EHPA is used for rare earth separation by solvent extraction at the Indian Rare Earths plant at Alwaye (1).

The application of synergistic mixtures of TBP and D2EHPA for rare earth solvent extraction is one of the possibilities to separate rare earths. Synergism is the extraction behavior when the distribution coefficient ratio, $(K_d)_{1,2}$ , in extraction by the mixtures of these extractants is larger than the sum of individual ratios, $(K_d)_1+(K_d)_2$ , which are found during extractions by individual extractants under the same conditions (3).

A synergistic phenomenon can be characterized by the synergistic coefficient expressed as:

$$S = (K_d)_{1,2} / [(K_d)_1+(K_d)_2]$$

Where, subscript "1" means system "1", subscript "2" means system "2" and subscript "1,2" means synergistic system between "1" and "2".

If $S > 1$, synergism is present.
For $S = 1$, there is no synergism.
If $S < 1$, antagonistic effect happens.

In 1963, Bray, L.A. and F.P.Roberts (4). of Hanford Laboratories coextracted cerium, promethium and other trivalent rare earths into 0.4 M D2EHPA diluted with 0.2 M TBP and kerosene. In 1989, Slavetskii, A. J. et al.(5). extracted nitric acid and cerium by 1.0 M isomolar mixtures of D2EHPA and TBP in decane from solutions of different concentrations of nitric acid and lithium nitrate. The synergistic effect diminished with the

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increase of the concentrations of nitric acid and lithium nitrate.

In 1992, Jedináková, et al.(3). investigated the synergistic extraction of Eu(III) and some other rare earth elements from nitrate solutions ($HNO_3$ and $LiNO_3$) by the mixtures of TBP and D2EHPA in n-hexane and cyclohexane. The synergistic effect was found in all investigated metals in extraction from 0.1 M $HNO_3$ plus 3 M $LiNO_3$. In 1993, A.M.EL-KOT (6). found antagonistic effects when the extraction of $Nd^{3+}$, $Eu^{3+}$ and $Tm^{3+}$ was studied by the mixtures of D2EHPA and TBP.

The extraction of lanthanides by D2EHPA and TBP can be expressed by the following equations (3).

$$M^{3+} + \overline{n(HA)_2} \rightleftharpoons \overline{MA_{2n}H_{2n-3}} + 3H^+$$

$$M^{3+} + 3NO_3^- + \overline{3L} \rightleftharpoons \overline{M(NO_3)_3L_3}$$

A is the anion of D2EHPA. The bar denotes species presented in the organic phase.

For the mixture of TBP and D2EHPA, the solvent extraction equation can be written as:

$$M^{3+} + pNO_3^- + \overline{mL} + \overline{n(HA)_2} \rightleftharpoons \overline{MA_{2n}H_{2n-3+p}(NO_3)_pL_m} + (3-p)H^+$$

In this research, rare earth nitrate solution was obtained from monazite processing of Rare Earth Research and Development Center (RRDC), Office of Atoms for Peace. TBP is the extractant used for rare earths solvent extraction process of this center. In this work, isomolar mixtures of TBP and D2EHPA in kerosene were applied as the new extractants compared with TBP. The synergism phenomenon was studied together with the distribution coefficients.

## Experimental

### Chemicals

Di-(2-ethylhexyl)phosphoric acid, D2 EHPA, 95%(Sigma) and tributylphosphate, TBP, 98%(BDH) were used as the extractants. Kerosene (Jet A-1, Shell) was employed as the organic diluent. Aqueous feed solution was rare earth nitrate in diluted nitric acid with compositions: 152,279 ppm La, 5,083 ppm Ce, 19,296 ppm Pr, 70,500 ppm Nd, 11,395 ppm Sm, 150.97 ppm Eu, 5,960 ppm Gd, 1,119 ppm Dy and 6, 674 ppm Y.

### Apparatus

A Gerhardt laboratory shaking machine, Type LS5, was used to mix aqueous and organic solutions. An inductively coupled plasma atomic emission spectrometry, ICP-AES (Spectro Analytical Instruments, Spectroflame M Type FM V05), was applied for individual rare earths analysis. Free acidity of rare earth nitrate feed solution was analyzed using pH meter, Hanna instruments 8521.

### Analysis

Each experimental condition was repeated twice and two samples were obtained. Each sample was analyzed in duplicate for concentrations of individual rare earths by ICP-AES. The concentrations of the samples were calculated automatically compared with the calibration curves of the standards. The results of each condition were determined from the average values of two samples or four ICP-AES analyses.

The standard deviation of each result was also calculated. The percentage relative errors, (standard deviation/average value)x100, were determined. The average values of percentage relative error of individual rare earths are as the following : La 1.48%, Ce 1.49%, Pr 1.59%, Nd 1.57%, Sm 1.68%, Eu 1.86%, Gd 1.56%, Dy 2.24% and Y 3.40%

The pH measurement was applied to determined free acidity of rare earth nitrate feed solution(7-8). The pH of $(NH_4)_2SO_4$ solution containing nitric acid with known pH, volume and normality was measured. The rare earth nitrate solution sample was added to this $(NH_4)_2SO_4$ solution and then its pH was checked. The free acidity of the sample was calculated from the difference of pH measurement and the value obtained was 0.2001 N.

### Procedure

(1) Equal volumes (25mL) of both phases were equilibrated in a separatory funnel by

laboratory shaking machine at 200 rpm, 10 minutes. The room temperature was 35±1°C. Aqueous phase feed was rare earth in diluted nitric acid. Organic phase were 50%(1.8 M) TBP in kerosene, 1.5 M and 1.0 M isomolar mixtures of TBP and D2EHPA in kerosene.

Both phases were equilibrated in duplicate and were allowed to stand for 10 minutes after mixing. After phase separation, two aliquots of raffinate and feed were collected for ICP-AES analysis. Each sample was analyzed in duplicate.

(2) By the same procedure, equal volumes (25mL) of both phases were equilibrated in a separatory funnel. Aqueous phase feed was the same but organic phases were 0.2, 0.3, 0.4, 0.6, 0.8, 0.9 and 1.2 M TBP in kerosene and 0.2, 0.3, 0.4, 0.6, 0.8, 0.9 and 1.2 M D2EHPA in kerosene. Raffinate and feed were analyzed in duplicate for individual rare earths by ICP-AES.

(3) Concentrations of individual rare earths in organic phase were calculated from the following equations.

$$[C_i]_{org} = [C_i]_F - [C_i]_{aq}$$

where, C = concentration
subscript "i" : individual rare earths ( i = a, b, c,. )
"org" : organic phase
"aq" : aqueous phase
"F" : feed

The distribution coefficient(9). $K_d$, was determined as the ratio,

$$K_d = [C_i]_{org} / [C_i]_{aq}$$

The synergistic coefficient(3). S, was calculated as

$$S = (K_d)_{1,2} / [(K_d)_1 + (K_d)_2]$$

where, subscript "1" means system of TBP/ kerosene – $RE(NO_3)_3$/dil.$HNO_3$
subscript "2" means system of D2EHPA/ kerosene – $RE(NO_3)_3$/dil.$HNO_3$
and subscript "1,2" means system of (TBP-D2EHPA)/kerosene – $RE(NO_3)_3$/dil.$HNO_3$

## RESULTS AND DISCUSSION

### Distribution coefficient

The distribution coefficients of synergistic mixtures compared with 50%TBP/kerosene are presented in Table 1. Plots of distribution coefficients vs. atomic numbers are illustrated in Figure 1 and 2. The effective atomic number of Y is equivalent to 67.5. It is found that the distribution coefficient increases with atomic number. The distribution coefficients of heavy rare earths, when the solvents are 1.5 M and 1.0 M (TBP-D2EHPA)/kerosene, are higher compared with 50%TBP/kerosene. Y gives remarkable distribution coefficients when the solvents are higher with D2EHPA. The distribution coefficients of rare earths when the solvents are 1.0 M TBP-0.0 M D2EHPA in kerosene and 50% (1.8 M) TBP/kerosene are similar, almost constant and not more than 2.

**Table 1**. Distribution coefficients of rare earths at various solvents

| Sovents | Distribution coefficient ($K_d$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | La | Ce | Pr | Nd | Sm | Eu | Gd | Dy | Y |
| T1.8 | 0.1588 | 0.2823 | 0.5119 | 0.6806 | 1.1635 | 0.9164 | 1.5562 | 1.8924 | 1.4643 |
| T0D1.5 | 0.1241 | 0.1404 | 0.1595 | 0.1618 | 0.2806 | 0.2410 | 0.6618 | 3.3426 | 22.3888 |
| T0.3D1.2 | 0.0432 | 0.1152 | 0.1607 | 0.1619 | 0.3438 | 0.3068 | 0.8942 | 3.4666 | 15.2345 |
| T0.6D0.9 | 0.0573 | 0.1275 | 0.2027 | 0.2086 | 0.4544 | 0.4129 | 1.1442 | 3.6012 | 11.2346 |
| T0.9D0.6 | 0.0588 | 0.1409 | 0.2508 | 0.2722 | 0.5694 | 0.5265 | 1.2605 | 3.3364 | 7.6507 |
| T1.2D0.3 | 0.0647 | 0.1425 | 0.3015 | 0.3306 | 0.6505 | 0.6056 | 1.1819 | 2.4917 | 4.1418 |
| T1.5D0 | 0.0788 | 0.1854 | 0.3718 | 0.4725 | 0.8382 | 0.7808 | 1.1968 | 1.4823 | 1.1513 |
| T0D1.0 | 0.0972 | 0.0840 | 0.1166 | 0.1136 | 0.1572 | 0.2402 | 0.3096 | 1.6168 | 9.0778 |
| T0.2D0.8 | 0.1113 | 0.0959 | 0.1437 | 0.1395 | 0.2530 | 0.3407 | 0.5904 | 2.4449 | 9.9275 |
| T0.4D0.6 | 0.1194 | 0.0882 | 0.1622 | 0.1616 | 0.3042 | 0.3956 | 0.6827 | 2.2327 | 6.0142 |
| T0.6D0.4 | 0.1140 | 0.1453 | 0.2175 | 0.2264 | 0.4070 | 0.5080 | 0.8020 | 2.1474 | 4.4334 |
| T0.8D0.2 | 0.1098 | 0.1208 | 0.2075 | 0.2306 | 0.4214 | 0.5067 | 0.7371 | 1.6364 | 2.6505 |
| T1.0D0 | 0.1090 | 0.1507 | 0.2808 | 0.3328 | 0.5627 | 0.6401 | 0.7963 | 1.1142 | 0.9988 |

Note: For solvents: T is TBP; D is D2EHPA; Unit of the numbers is Molar.

## Synergism

Figure 3-6 show 1.5 M and 1.0 M isomolar (TBP-D2EHPA)/kerosene vs. synergism. Heavy rare earths (Gd, Dy and Y) give synergism phenomenon. For light rare earths, Ce has significant synergism phenomenon when the organic is 1.0 M isomolar (TBP-D2EHPA) /kerosene. The maximum of $S_{Ce}$ is approximately 5 for (0.4 M TBP-0.6 M D2EHPA)/kerosene. When the solvent is 1.5 M isomolar(TBP-D2EHPA)/kerosene, La performs antagonistic effect but it has synergism when the solvent is 1.0 M isomolar (TBP-D2EHPA) /kerosene. The remaining of light rare earths (Pr, Nd, Sm and Eu) gives synergistic effect.

It is possible to leave La in raffinate while the most are extracted to organic phase because of the antagonistic effect of La. Because of its significant synergism phenomenon, Ce prefers to be in the organic phase. By using these synergistic mixtures, La can be separated from Ce.

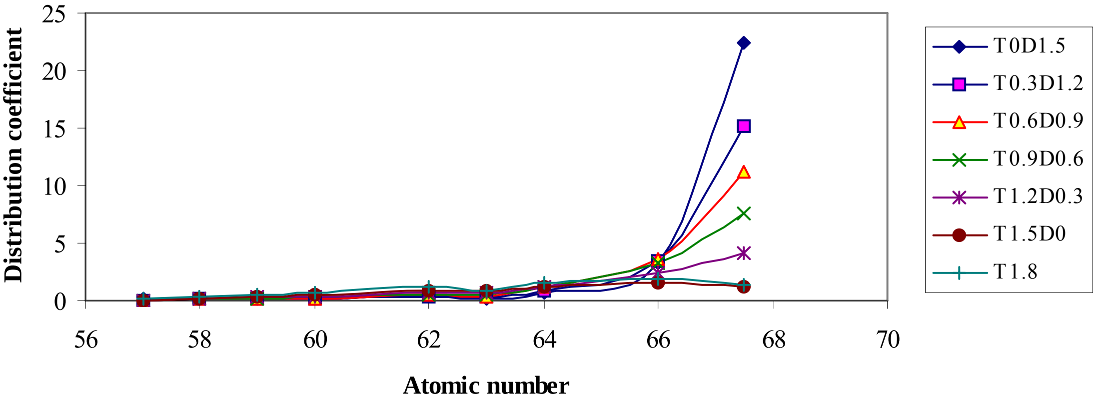

**Figure 1.** Distribution coefficients of rare earths in 1.5 M(TBP-D2EHPA)/kerosene compared with 50%TBP/kerosene(1.8 M) as a function of atomic numbers.

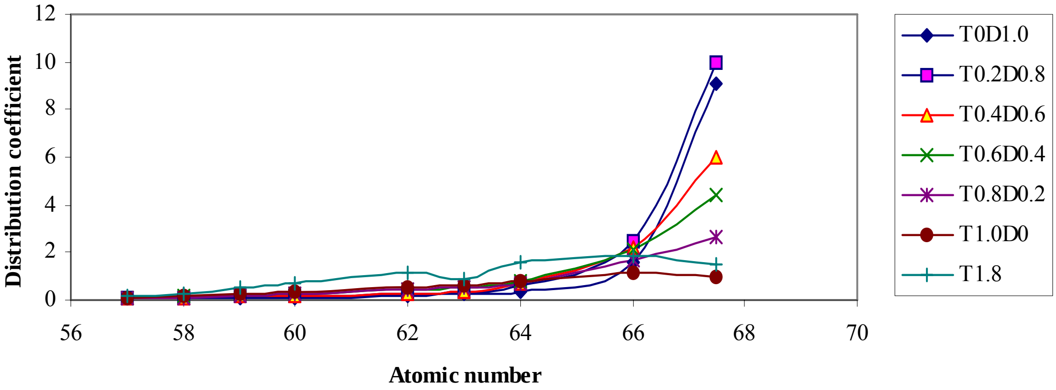

**Figure 2**. Distribution coefficients of rare earths in 1.0 M(TBP-D2EHPA)/kerosene compared with 50%TBP/kerosene(1.8 M) as a function of atomic numbers.

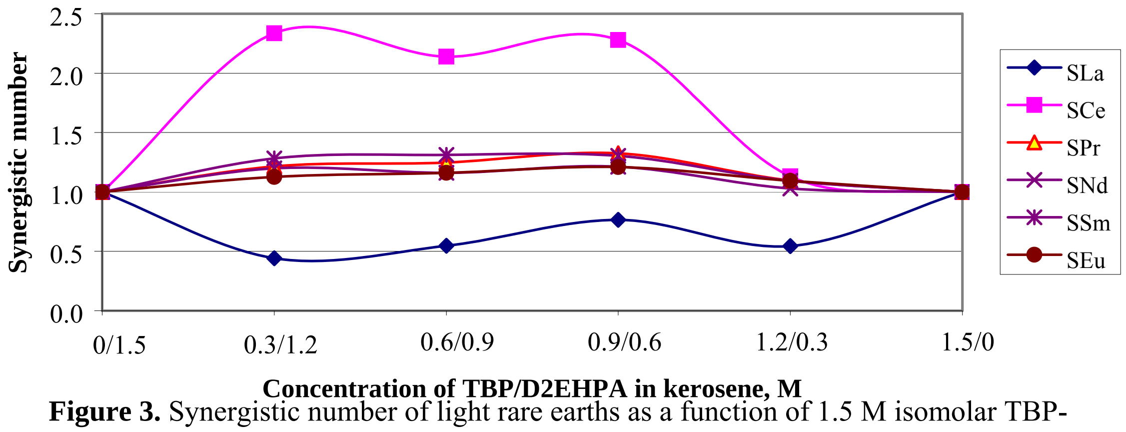

**Figure 3.** Synergistic number of light rare earths as a function of 1.5 M isomolar TBP-D2EHPA in kerosene.

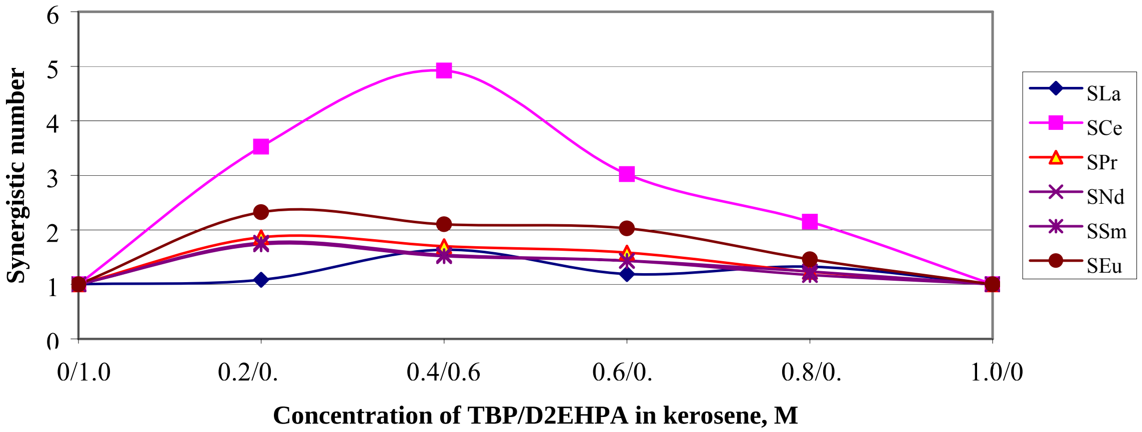

**Figure 4.** Synergistic number of light rare earths as a function of 1.0 M isomolar TBP-D2EHPA in kerosene.

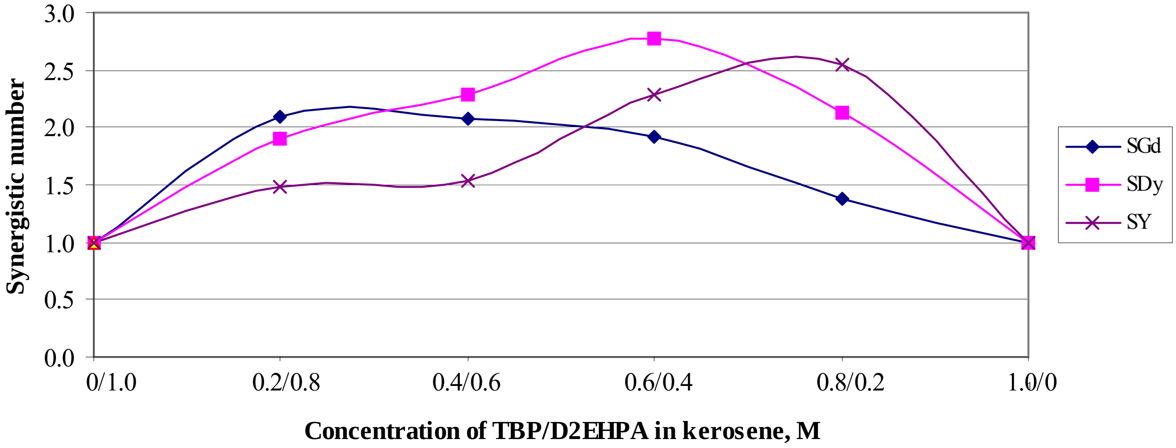

**Figure 5.** Synergistic number of heavy rare earths as a function of 1.5 M isomolar TBP-D2EHPA in kerosene.

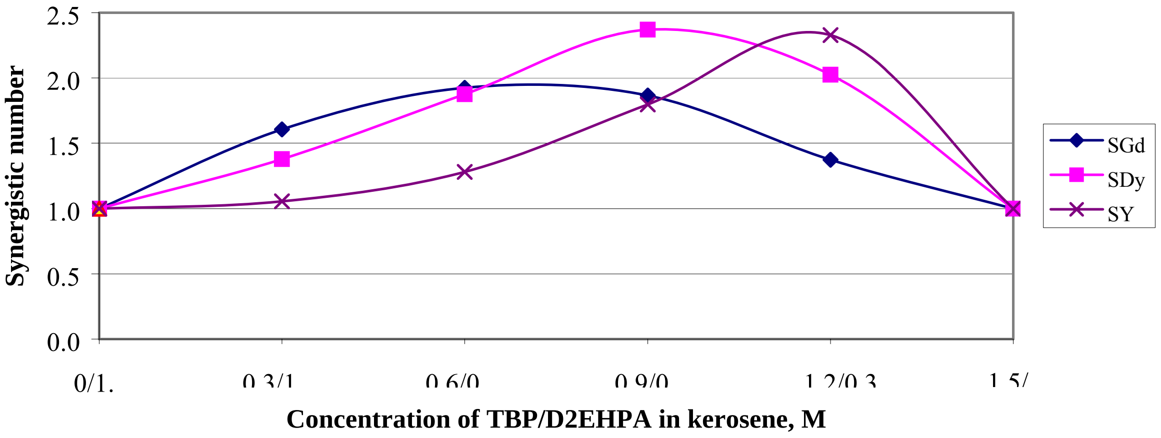

**Figure 6.** Synergistic number of heavy rare earths as a function of 1.0 M isomolar TBP-D2EHPA in kerosene.

## CONCLUSIONS

(1) The distribution coefficients increase with increasing of atomic number. The distribution coefficients of heavy rare earths are higher when the solvents are 1.5 M and 1.0 M isomolar mixtures of TBP and D2EHPA in kerosene compared with 50%TBP in kerosene.

(2) Ce has significant synergism phenomenon when the organic phase is 1.0 M isomolar (TBP-D2EHPA)/kerosene. La shows antagonistic effect when the solvents applied are 1.5 M isomolar mixtures of TBP and D2EHPA in kerosene. The rest gives synergism phenomenon.

(3) As a result, it is possible to separate La to raffinate using 1.5 M isomolar (TBP-D2EHPA) /kerosene. Separation of Ce can be performed by 1.0 M isomolar (TBP-D2EHPA)/kerosene, especially (0.4 M TBP-0.6 M D2EHPA)/kerosene. Y can be extracted either by1.0 M, 1.5 M isomolar (TBP-D2EHPA)/kerosene or 1.0 M D2EHPA /kerosene because of its remarkable distribution coefficients.

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