



Research Paper

Studies on Extraction of Hexavalent Uranium by Cyanex-923 with Some Synergistic Ligands

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Abstract - In the present study the systems involving Cyanex-923 as a synergist in the extraction of uranium(VI) using Cyanex-272, TPBD, TNBD, TOPO and their mixtures has been investigated in xylene. Analysis of the extraction data by both graphical and theoretical methods by taking into account complexation of the metal ion in the aqueous phase with inorganic ligands and all plausible complexes extracted into the organic phase. The metal ion is extracted into xylene as $UO_2(NO_3)_2 \cdot 2TRPO$. Infrared spectral data of the extracted complexes have been used to further clarify the nature of the complexes. At given extractant concentration (pH 3), the extraction of U(VI) increases with nitrate concentration. The slope of the plot $\log D$ (where D is the distribution coefficient defined as the ratio of concentration of metal in the organic phase to that present in the aqueous phase) against $\log [NO_3^-]$ is nearly 2 indicating the extraction of neutral species into organic phase. Mixed species of the type $UO_2(NO_3)_2 \cdot 2TRPO \cdot 2S$ and $UO_2(NO_3)_2 \cdot 2TRPO \cdot S$ were obtained with mixtures of Cyanex-923 and S (where $S = \text{Cyanex-272, TOPO}$) may be responsible for the synergism.

Key words: Solvent extraction, Cyanex-923, Uranium, Synergism etc.

Introduction

The Uranium content in the earth crust is about 2 ppm. It is distributed in three natural isotopes with mass 234, 235, and 238 with a natural abundance of 0.005 to 0.720 and 99.275%, respectively ^[1]. ^{235}U is important from the energetic point of view, because of its use in nuclear power reactors (1kg of ^{235}U supplies 2×10^7 kW/h). Moreover, from ^{235}U other important nuclides can be produced. A large number of synthetic isotopes of uranium have been prepared ^[2].

Uranium is the most vital element for nuclear energy programmes. Due to the world demands on uranium the researchers in the field of solvent extraction process developing commercial extraction systems to recover the uranium from its ores. Its natural sources generally contain a sizeable fraction of rare earths which in their own right have diverse technological applications. Thus the methodology adopted for the separation of these metal ions from different ores has always attracted the attention of separation scientists. It may be used to decontaminate rare earth concentrates from uranium radioactivity. These separations are significantly

important also from the point of view of nuclear fuel processing. Solvent extraction offers one of the cleanest technologies for effecting these separations.

Pioneering work on the potential of alternate organo-phosphorous extractants for the separation of uranium (VI) and thorium (IV) has been carried out by Siddal^[3] and Mason and Griffin^[4]. Better separation factors have been reported by Suresh et al.^[5] between uranium (VI) and thorium (IV) using tri-sec-butylphosphate in 1 M HNO_3 solutions (Separation factor = 25.3). A good review on the extraction of uranyl compounds with trioctylphosphine oxide (TOPO) has been published by Kolarik^[6].

Cyanex 923 (TRPO) is a mixture of four Trialkyl phosphine oxides $R_3P(O)$, $R_2R'P(O)$, $RR'_2P(O)$, $R'_3P(O)$ Where $R = [\text{CH}_3(\text{CH}_2)_7]$ - normal octyl $R' = [\text{CH}_3(\text{CH}_2)_7]$ - normal hexyl, which exhibits extraction properties similar to TOPO and has been commercially available from Cytec, Canada. The above solvent mixture has the advantage of being a liquid and is completely miscible with all commonly used hydrocarbons.

Recently, Cyanex 923 has been suggested as a potential extractant by the Authors for the extraction and separation of yttrium from trivalent lanthanides^[7] and for the separation of iron (III) and titanium (IV) from waste chloride liquors of the titanium minerals processing industry^[8]. In the present work, the extraction of uranium (VI) by Cyanex 923, Cyanex 272 Bis(2,4,4-trimethylpentyl)phosphinic acid, TPBD, TNBD and their mixtures has been investigated in xylene

The above solvent mixture has the advantage of being a liquid and is completely miscible with all commonly used hydrocarbons.

Material and Methods

Cyanex 923, Cyanex-272, supplied by Cytec, Canada were used after purification^[9]. Trioctylphosphine oxide (TOPO) was obtained from E.Merck (India) Limited. Xylene of analytical reagent quality was used as a diluent in the present work. All the other chemicals used were of analytical reagent grade.

Stock solutions of uranium(VI) were prepared by dissolving appropriate amounts of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. One milliliter of concentrated nitric acid was added to 100 ml of solution to suppress hydrolysis. The initial metal ion concentration was maintained at 1×10^{-4} M for uranium(VI) for all extraction studies.

Preparation of metal complexes

The metal complexes were prepared by the following solvent extraction procedure: Uranyl nitrate dissolved in water was gradually added to a well stirred solution of Cyanex 923 and the synergistic ligands in xylene and then refluxed for 1 hour. The aqueous phase was changed with fresh metal ion solution after every 1 hour till the organic phase was completely loaded with metal ion. The organic phase was then separated. The Nicolet Nexus 670 FTIR spectrometer using KBr (Neat) was used to obtain the FTIR spectra of the loaded organic phase. The KBr (Neat) containing a film of metal ion solution was put under an FTIR lamp to evaporate xylene completely. For comparison, the IR spectrum of pure Cyanex 923 was also taken.

Solvent extraction procedure

Distribution ratios were determined by shaking equal volumes of aqueous and organic phase for 30 min in a glass Stoppard vial with the help of a mechanical shaker at $303 \pm 1^\circ$ K. The solutions were allowed to settle, centrifuged, separated and assayed spectrophotometrically using a Hitachi 220 double beam microprocessor based spectrophotometer. Uranium (VI) was determined spectrophotometrically as its Arsenazo III complexes in 1 M HCl solution at 660nm respectively. The absorbance of the complexes was measured within 5 min of mixing. The metal concentrations in the aqueous phase were computed from the respective calibration graphs. The concentration of the metal ion in the organic phase was then obtained by a material balance. These concentrations were used to obtain the distribution ratio, D .

Solvent extraction conditions

Solvent extraction studies were made on solutions of 0.1-1.0 mol/dm³ sodium nitrate at 30°C. The initial pH of the aqueous

phase was generally maintained at 3 by adding either nitric acid. The initial RE metal concentration was never exceeded 1×10^{-6} mol/dm³. Solutions of TPBD (0-0.5 mol/dm³), TNBD (0-0.4 mol/dm³), TRPO (0-0.6 mol/dm³), Cyanex 272 (0-0.005 mol/dm³) were used. The temperature was maintained at 30°C.

Results

Effect of nitrate ion concentration

The influence of nitrate concentration over the range (0.5 to 2.0N) on the extraction of uranium (VI) has been studied by maintaining constant acidity (0.03N HNO_3) in the aqueous phase and Cyanex 923 (0.001M) in xylene for uranium (VI) in the organic phase and the results are shown in Figure 1.

The extraction of metal ion increases rapidly with increase in nitrate concentration. The plot of log D vs Log $[\text{NO}_3^-]$ is linear with a slope of ~ 2 . It is clear that two molecules of nitrate ions are involved in the extractable complexes of uranium (VI)

Effect of extractant concentration

The effect of Cyanex 923 concentration (5×10^{-4} M to 4×10^{-3} M) on the extraction of uranium (VI) has been investigated at 1M NaNO_3 containing 0.03M HNO_3 Figure 2. It can be seen that the extraction of uranium (VI) increases with increase in Cyanex 923 concentration in the organic phase. From the slope of the plot it is inferred that two molecules of Cyanex 923 are involved in the extracted complexes of uranium (VI).

Extraction by mixtures

The effect of extraction by mixtures is studied by taking Cyanex 923, NaNO_3 concentrations as constant and varying the other extractant at once and keeping the concentration of other extractant and NaNO_3 as constant and Cyanex 923 as varying one. The log - log plots for extraction of U(VI) from 1 mol/dm³ nitrate solutions by mixtures of Cyanex-923-Cyanex-272 [0.25-2.5 mol/dm³ Cyanex 923 0.25-1.5 mol/dm³ Cyanex-272 in xylene], Cyanex-923-TPBD [0.5-1.75 mol/dm³ Cyanex-923 0.5-1.75 mol/dm³ TPBD in xylene], Cyanex-923-TNBD [0.75-1.75 mol/dm³ Cyanex-923 0.5-1.75 mol/dm³ TNBD in xylene], Cyanex-923-TOPO [0.5-1.75 mol/dm³ Cyanex-923 0.5-1.75 mol/dm³ TOPO in xylene], are given in figs. 3 to 10. Mixed species of the type $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TRPO} \cdot \text{S}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot \text{TRPO} \cdot \text{S}$ were obtained with mixtures of Cyanex-923 and S (where S= Cyanex-272, TOPO, TPBD, TNBD) may be responsible for the synergism.

The slope of the plot, log D -log Cyanex-923 concentration at constant S concentration [Figure 3-6] is ~ 2 indicating that the number of TRPO molecules participating in the complex formation are unaltered by the presence of the second extractant (TRPO/Cyanex-272/TNBD) concentration. On the other hand the log D - log (TRPO/Cyanex-272/TNBD) concentration plot at fixed second extractant (Cyanex-923) concentration [S] has a slope value ~ 1 showing that it involves both substitution and addition reactions [Figure 7-8]. The log-

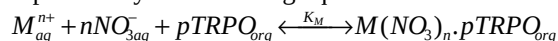
log plots for the second extractant [s] at fixed TRPO have slopes varying from 1 to 2 [Figure 9-10].

FTIR Spectrum of the extracted complex of Uranium (VI)

The IR spectrum of the extracted complexes are shown in table (1). The stretching frequency of the P=O in Cyanex-923 has shifted from 1153 cm⁻¹ to 1108 cm⁻¹ in UO₂(NO₃)₂. 2TRPO complex and 1102, 1100, 1143 cm⁻¹ in the synergistic extraction with Cyanex 272, TNBD, TPBD as synergistic ligands respectively. This indicates a stronger interaction between the phosphine oxide and uranium (VI) with Cyanex 923 and even this is not affected in the presence of other synergistic ligands. The strong and sharp bands at 926-924 cm⁻¹ confirms the stretching of uranyl ion.

Theory

The extraction mechanism of RREs from nitrate medium by a solvating solvent such as Cyanex-923 can be expressed by the following equation.



(1) Where Mⁿ⁺ represents UO₂²⁺. The equilibrium constant (K_M) for reaction (1) can be written as:

$$K_M = \frac{[M(NO_3)_n \cdot pTRPO]}{[M^{n+}][NO_3^-]^n[TRPO]^p} \quad (2)$$

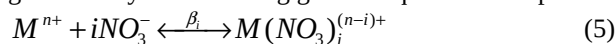
The Eq. (2) may also be represented in terms of concentrations and activity coefficients as:

$$K_M = \frac{[M(NO_3)_n \cdot pTRPO]}{[M^{n+}][NO_3^-]^n[TRPO]^p} \cdot \frac{\gamma_{M(NO_3)_n \cdot pTRPO}}{\gamma_{M^{n+}} \gamma_{NO_3^-}^n \gamma_{TRPO}^p} \quad (3)$$

Where, γ represent the activity coefficient and the parentheses represent the concentration of each species. However, in the present experiments the concentration of TRPO in the organic phase (5X10⁻⁴ to 4X10⁻⁴ M), and hence the metal complex in the organic phase, is very low as compared to the concentration of nitrate ion (0.5 to 2.0 M) in the aqueous phase. Thus the activities of the metal complex and TRPO in the organic phase have been consider as equal to their equilibrium concentration in the organic phase. The activity coefficient of the nitrate ion and the metal ion in the aqueous phase were calculated by using Bromley's formulation^[10]. Hence Eq. (3) can be rewritten as:

$$K_M = \frac{[M(NO_3)_n \cdot pTRPO]}{[M^{n+}] \gamma_{M^{n+}} [NO_3^-]^n \gamma_{NO_3^-}^n [TRPO]^p} \quad (4)$$

The aqueous phase complexation of UO₂²⁺ with nitrate ion is governed by the following generic equilibrium expression:



Where i = 1 or 2. The values of the stability constant (log β₁ = -0.3) of UO₂²⁺ [11] were taken from the literature. Then the distribution ratio, D, of the metal ion can be written from Eqs. (4) and (5) as:

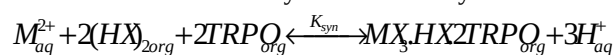
$$D = \frac{K_M [NO_3^-]^n \gamma_{NO_3^-}^n [TRPO]^p}{\left(1 + \sum_{i=1}^2 \beta_i [NO_3^-]^i \gamma_{NO_3^-}^i \gamma_{M^{n+}} \right)} \quad (6)$$

The mixtures of two extractants say S^I and S^{II} extracts U(VI) more than the sum of the extractions [ΣD] due to individual

components at the corresponding concentrations and may be mathematically denoted as

$$D_{syn} = D_s^I + D_s^{II} + \Delta D$$

Where ΔD gives the magnitude of the synergistic enhancement of extraction. The synergistic enhancement is more pronounced at higher concentrations of the extractant. The slope of the log D-log [extractant] concentration plot decreases progressively with increase in the concentration of the second extractant. This study assuming that the formation of metal ligand complexes is responsible for the enhancement, extraction mechanism may be described by



Where M²⁺ = UO₂²⁺, HX=TPBD, TNBD, Cyanex-272, TOPO

Conclusion

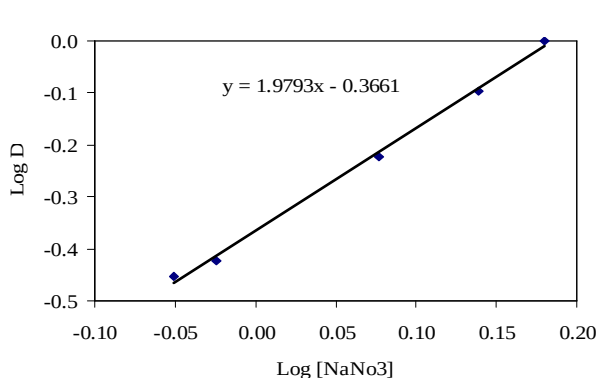
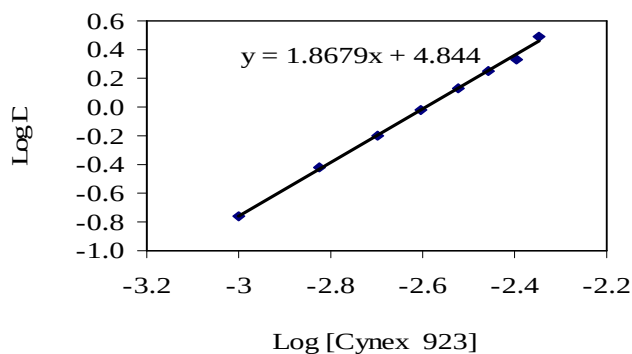
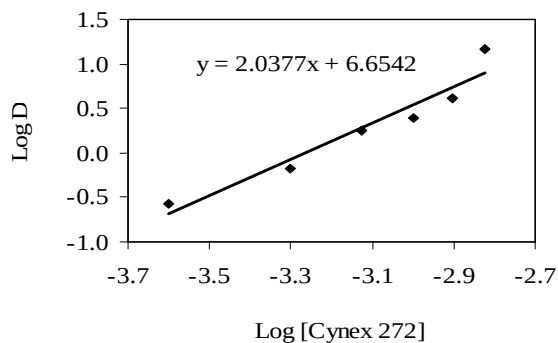
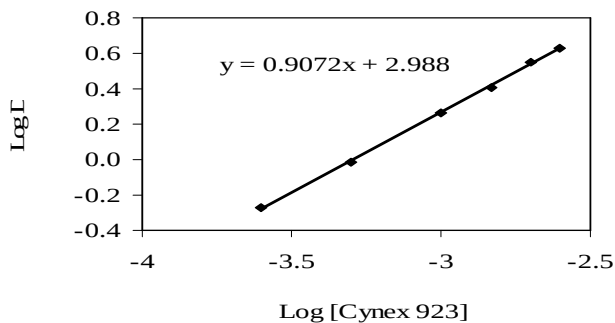
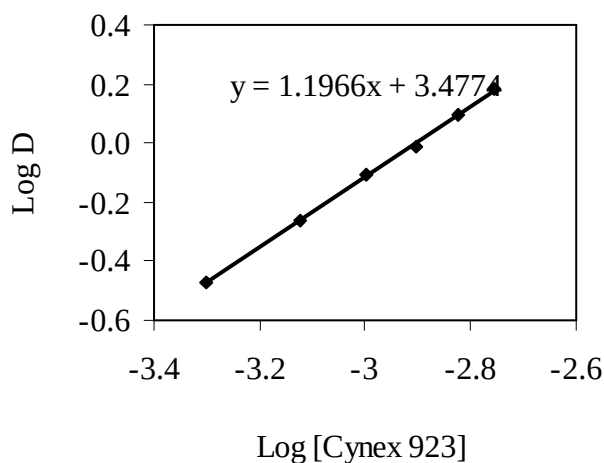
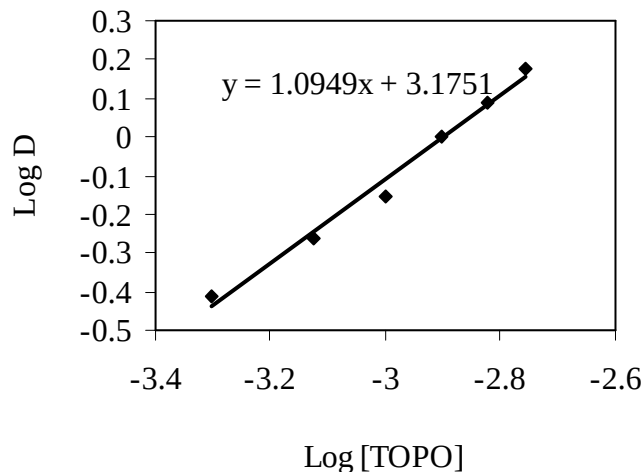
In the present investigation the potentiality of Cyanex-923 as extractant and also as a synergistic agent has been tried and verified. The present results show that disolvates such as UO₂(NO₃)₂.2TRPO.2S and UO₂(NO₃)₂.2TRPO.S exist in the extraction of U(VI) by Cyanex-923 and S (where S= Cyanex-272, TOPO, TPBD, TNBD). The synergistic effect increases with increase in the concentration of the extractant. The association of anionic ligands with metal along with molecules of extractants employed is noticed when Cyanex-923 is employed as one of the extracting agents. The nature of different metal species transferred into the organic phase has been clearly established.

References

1. WWW Table of Radioactive Isotopes, <http://ie.lbl.gov/toi/nucSearch.asp>
2. *American Mineralogist*; January; v. 96; no. 1; p. 188-196; DOI: 10.2138/am.2011.3610
3. Siddall III, T.H.: J. Inorg. Nucl. Chem. 13, 151 (1960)
4. Mason, G. W., Griffin, H.E.: in Actinide Separations, ACS Symp. Ser. 177, J. D. Navratil and W. W. Schulz, Eds. (1980), p. 89
5. Suresh, A., Subramaniam, S., Srinivas, T.G., Vasudeva Rao, P.R.: Solv. Extr. Ion Exch. 13, 415 (1995)
6. Kolarik, Z.: Gmelin Handbook of Inorganic Chemistry, Uranium Suppl. Vol. 2 Solvent extraction of Uranium, Springer-Verlag, Berlin (1982), p. 95.
7. Reddy, M. L. P., Luxmi Varma, R., Rammohan, T.R., Sahu, S. K., Chakravorty, V., Solv. Extr. Ion Exch. 16, 795 (1998)
8. Saji John, K., Saji, J., Reddy, M. L. P., Rammohan, T. R., Rao, T.P.: Hydrometallurgy 51, 9 (1999)
9. Jun, Lu., Zhenggui, Wei., Dequian, Li., Gengxiang, Ma., Jiang Zucheng.: Hydrometallurgy 50, 77 (1998)
10. Journal of radioanalytical and Nuclear Chemistry, Vol. 254, No.3(2002) 479-483
11. J.Radioanal Nucl Chem(2010) 258;301-308

Table 1: Characteristic FTIR Spectral data of the extracted complex of Uranium (VI).

TRPO	U + TRPO	U + TRPO + Cyanex 272	U + TRPO + TNBD	U + TRPO + TPBD	U + TRPO + TOPO	Probable assignment
2926-2857	2927-2855	2929-2862	2927-2858	2928-2858	2926-2859	ν_{C-H}
1647	1646	1649	1609	1628	1643	ν_{P-O-P}
1461	1460	1465	1452	1524	1461	ν_{CH_3}
1153	1108	1102	1100	1144	1113	P=O stret.
808	858	819	794	824	816	P-C stret.
---	926	924	923	924	925	O=U=O stret.

**Figure 1: Effect of concentration of $NaNO_3$** **Figure 2: Effect of concentration of Cyanex-923****Figure 3: Effect of Cyanex-272 in presence of Cyanex-923****Figure 4: Effect of Cyanex-923 in presence of Cyanex-272****Figure 5: Effect of Cyanex-923 in presence of TOPO****Figure 6: Effect of TOPO in presence of Cyanex-923**

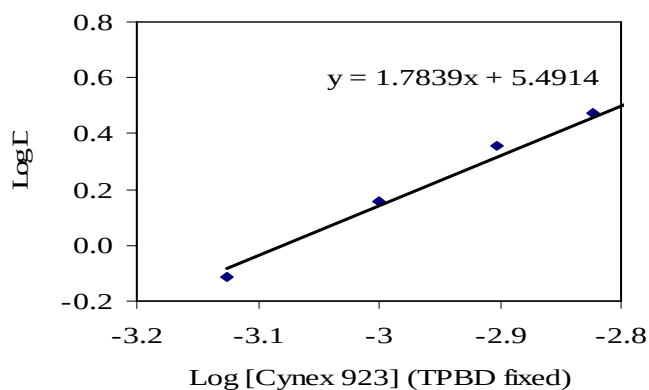


Figure 7: Effect of Cyanex-923 in presence of TPBD

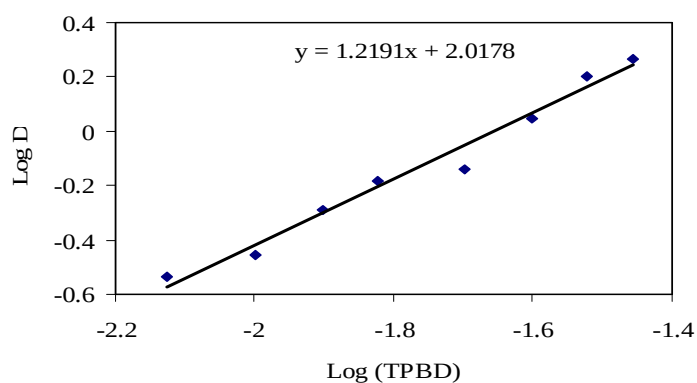


Figure 8: Effect of TPBD in presence of Cyanex-923

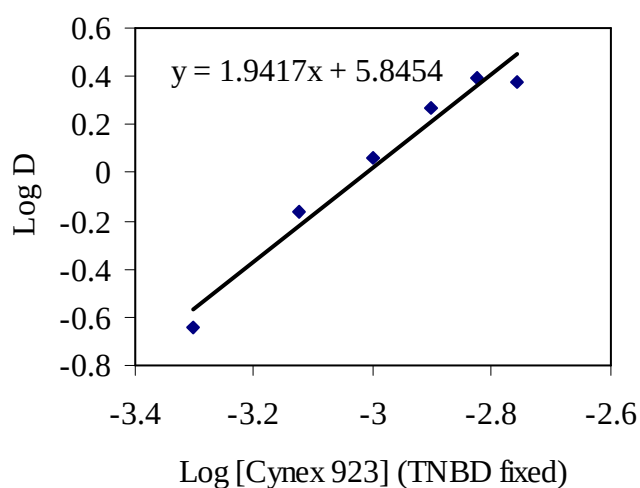


Figure 9: Effect of Cyanex-923 in presence of TNBD

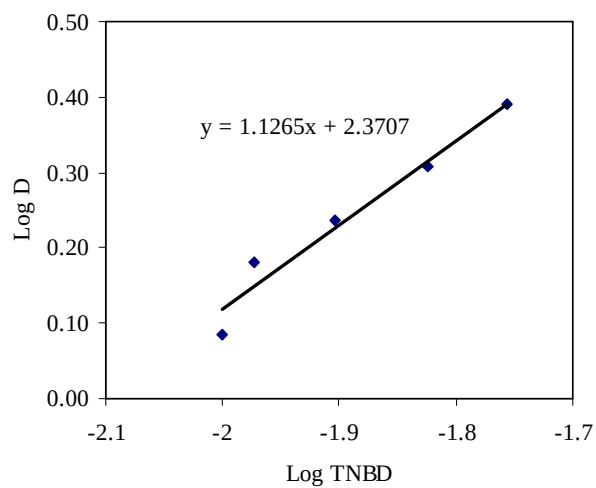


Figure 10: Effect of TNBD in presence of Cyanex-923