

Solvent Extraction of Ti(IV) From Aqueous Sulphate Solution By Cyanex301 Dissolved in Kerosene : Equilibrium Studies.



Chemistry

KEYWORDS : Titanium, Solvent extraction, cyanex301, equilibrium.

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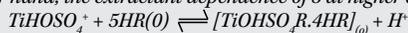
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ABSTRACT

Cyanex301 dissolved in kerosene is found to be a good extractant for the extraction of Ti(IV) from aqueous sulphate medium. The equilibration time has been determined to be ~30 min. The extent of extraction is found to increase with increasing Ti(IV) concentration in the aqueous phase, though the extraction ratio is decreased with increasing Ti(IV) concentration. The extraction is found to increase with increasing pH and cyanex301 concentration. The sulphate ion concentration has little effect on the extraction of Ti(IV) by Cyanex301. The system is found to be endothermic in the lower temperature region (<30° C) and exothermic over 30° C. The pH dependence of 1 and the Cyanex301 dependence of 1 in its lower concentration region as well the sulphate ion dependence of almost zero suggests the following reaction for extraction at lower concentration region of Cyanex301(HR):



On the other hand, the extractant dependence of 5 at higher concentration region of the extractant suggests the following mechanism:



satisfying the dependences of other parameters. Finally the equilibrium constants for the extraction reactions suggested have been calculated to be 54.97 and 282.50 respectively.

Introduction: Titanium is known as a space-age metal because it has high tensile strength and its weight is comparatively low. Moreover, metal titanium is inert to many corrosive media. Presently, the applications of titanium include canister for nuclear plant waste, casing for pace maker, medical implant, high performance automobile and ordnance armor. Though highly pure TiO₂ is mainly being utilized as a white pigment, it can also be used as a photocatalyst for the treatment of anthropogenic compounds present in water. Titanium is an important constituent for various alloys and catalyst and that's why- the future applications of titanium could include single-crystal electrode of TiO₂, catalyst for flu-gas denitrication, and for the manufacture of thermistor such as barium- titanate. As titanium is being used frequently for many purposes, the primary sources of titanium are going to be finished and efficient methods should be developed to recover titanium from low-grade secondary sources. For this reason, to get high purity and quantity, solvent extraction is attractive and a good alternative.

Solvent extraction of Ti (IV) by Cyanex301 has been reported Biswas et al (1) as well as with Cyanex302 (2) from sulphate solution. Sole (3,4) also reviewed the extraction of Ti(IV) from sulphate medium using some acidic and neutral organo-phosphorus extractants, concluding tri-octylphosphine oxide as the best for Ti(IV) extraction. Some other researchers have also reviewed the extraction of Ti (IV) from sulphate solution (5-7), on the other hand, Some other reported its extraction procedure from chloride solution (8-17).

Cyanex301(bis-2,2,4-trimethylpentyl)dithiophosphinic (C₁₆H₃₄PS₂H) acid is an acidic extractant produced by American Cyanamide Co. The supplied sample contains 77.2 % of Cyanex301 having pK_a in water = 2.61, viscosity = 7.8 kg m⁻¹ s⁻¹, molar mass = 322 g mol⁻¹, density = 950 kg m⁻³, aqueous solubility = 7 mg dm⁻³, flash point = 146 °C, auto ignition temperature = 297 °C and decomposition temperature = 220 °C and it is monomeric in nature [18] Cyanex301 as a good extractant is also being used for the extractions of Zn(II) by Rickelton et al(19); In(III) by Avila et al(20); Fe(III), Zn(II), Cu(II), and Ni(II) by Sole et al (21); Co(II) and Ni(II) by Tait (22); Sb(III), Bi(III),

Pb(II), and Sn(IV) by Facon et al (23) Cu(II) by Sole and Hiskey(18); Ag(I) by Sole et al(24).

EXPERIMENTAL

Apparatus

A Mettler- Toledo 320 pH meter (England), Stuart Flask Shaker machine (220V, 50Hz), Mettler- Toledo balance (AB 204-S) and WPA5104 Spectrophotometer (UK) were used for experimental techniques.

Analytical

The stock solution was prepared by digesting appropriate 50g of TiO₂ in concentrated H₂SO₄ with continuous heating and constant stirring and then filtered to remove insoluble residue dissolving it in 15% H₂SO₄. The standard solution was prepared roasting 0.50g of TiO₂ with 10g of KHSO₄ and calibration line was fitted (30% 1 ml H₂O₂ and 1 ml H₃PO₄). The extractant Cyanex301 (bis-(2,2,4-trimethylpentyl)-di thiophosphinic acid) was analytical grade and 2.0M solution was prepared using kerosene as a diluent and all other chemicals used were analytical grade.

General Extraction Procedure

Extraction experiments were carried out by taking 20ml of aqueous solution containing TiOHSO₄⁺ with 20ml of Cyanex301 solution dissolved in kerosene at an O/A ratio of one and shaken for 40 min to reach equilibrium state at room temperature and then the aqueous phase was separated to determine the concentration of aqueous phase by spectro photometer and the value of distribution co-efficient (D) was determined.

Result and discussion:

The experimental data and graph shows that the value of concentration ratio increases almost exponentially with increasing the phase contact time up to 30 min and then the curve levels off when Ti(IV) is extracted from SO₄²⁻ medium by analytical grade Cyanex301. It is therefore concluded that the equilibrium time for this system is 30 min. In subsequent experiments phase contact time of 40 min have been used to ensure equilibration for other parameters. Previously, the equilibration time of about 3 hours and 2 hours have been reported for extractions of Ti(IV) by

D2EHPA from sulphate (5) and chloride (13) medium, respectively. So, Cyanex301 can extract Ti(IV) faster than does D2EHPA.

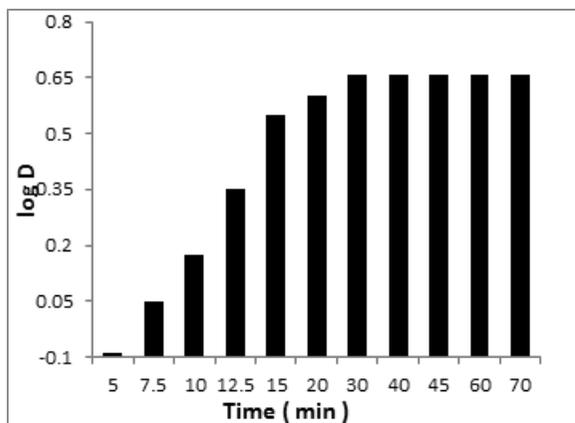


Fig-1: Dependence of extraction ratio on time for the extraction of Ti(IV) by Cyanex301. pH = 1.60, Temperature = 25°C, [Ti(IV)] = 0.5 g dm⁻³, [SO₄²⁻] = 1.0 mol dm⁻³ [Cyanex-301] = 0.05 mol dm⁻³

Effect of Ti(IV) concentration in the aqueous phase on the extraction ratio(D) of Ti(IV) during extraction by Cyanex301 shows that plot is a straight line with slope equaling to -1.0. This is contrary to the general principle of solvent extraction of metal ions. The Eq. (4) deduced latter shows that the values of D should be independent of metal ion concentration provided the equilibrium pH and extractant concentration are kept constant. The deviation from this statement indicates the non ideality of phases in the system. The log D vs. log [Ti(IV)]_{eq} plot is also shown in Fig.2. This plot is also a straight line but with a slope of -0.5. One reason for this dependency may be due to the change of equilibrium pH to different extent from the initial pH value and also the change in equilibrium extractant concentration.

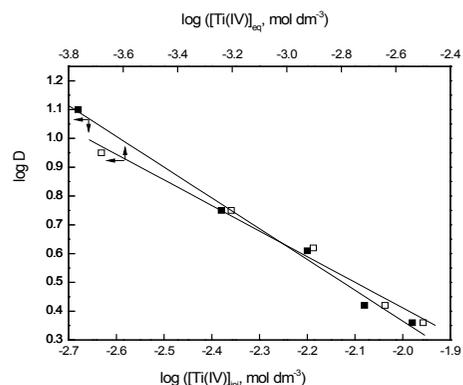


Fig-2: Effect of Ti(IV) concentration in the aqueous phase on the extraction ratio(D) of Ti(IV) during extraction by Cyanex301. pH = 1.60, Time = 40 min, [Cyanex-301] = 0.1 mol dm⁻³ [SO₄²⁻] = 1.0 mol dm⁻³, Temperature = 24° C

The logD vs. pH_{eq} plot in Fig.3 shows that the extraction of Ti(IV) with analytical grade Cyanex301 is a straight line with slope approximately one both for extractant concentration 0.1 mol dm⁻³ and 0.25 mol dm⁻³ (the least squares slopes being 0.95 and 0.965 respectively), so that the extraction ratio (D) increases with increasing equilibrium as well as initial pH values of aqueous solution of Ti(IV). The straight line has least squares intercept of -0.673 and -0.915. In case of extraction with D2EHPA, the pH dependence is about 2 [28]. Consequently Cyanex301 can extract Ti(IV)

over a wide range of aqueous pH than does D2EHPA. However, in the present case, the extraction at higher pH values is often encountered with emulsion formation. It is therefore suggestible to carry out this extraction system in presence of a modifier (higher alcohol-emulsion inhibitor) as done for the ditolylphosphoric acid extraction of Ti(IV) (25).

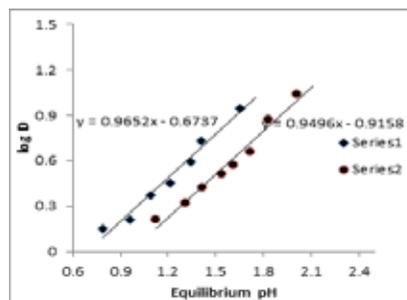


Fig-3: Dependence of extraction ratio (D) on equilibrium pH in the aqueous phase in the case of extraction of Ti(IV) by Cyanex301. [Ti(IV)](ini) = 0.5 g dm⁻³, Shaking time = 40 min, [SO₄²⁻] = 1.0 mol dm⁻³ and series1[Cyanex-301] = 0.1 mol dm⁻³, series2[Cyanex-301] = 0.25 mol dm⁻³, Temperature = 30° C.

The equilibrium pH values in both series of extractions are found to very within ± 0.01 pH units. The data have been displayed in Fig.-4 as log D vs. log [Cyanex301] for pH values of 1.6 and 1.8. In both cases, curves rather than straight line are obtained. The curves have a limiting slope of unity at lower concentration region of Cyanex301, whereas it is increased to about 5 in the higher concentration region.

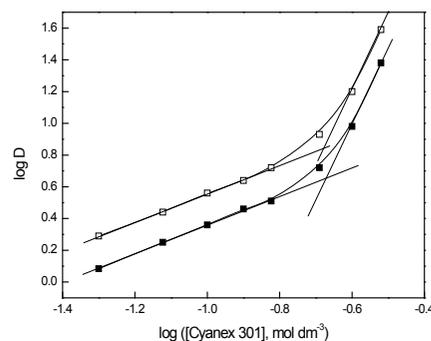


Fig-4: Dependence of extraction ratio (D) on extractant (Cyanex301) concentration in the organic phase. Time = 40 min, Temperature = 24° C, [Ti(IV)] = 0.5 g dm⁻³, [SO₄²⁻] = 1.0 mol dm⁻³ pH = 1.60 and pH = 1.80

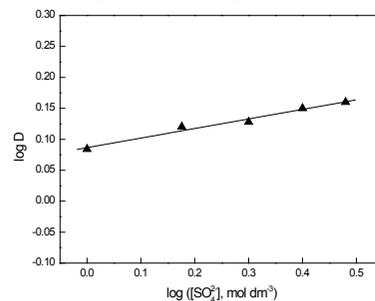
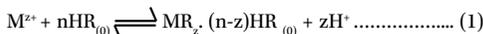


Fig-5 shows log D vs. log [SO₄²⁻] plot. The log D vs. log [SO₄²⁻] plot is a straight line with slope of about 0.16. From this plot, it is clear that there is little effect of sulphate ion concentration in the aqueous phase on the extraction ratio.

Mechanism of extraction:

An acidic extractant, HR can extract a metal ion, M^{z+} according to the following reaction:



The equilibrium constant, K_{ex} of the above reaction can be represented as follows:

$$K_{ex} = \frac{[MR_{z(n-z)}]_{(0)} [H^+]^z}{[M^{z+}] [HR]_{(0)}^n} \dots\dots\dots (2)$$

On taking logarithm of both sides

$$\log K_{ex} = \log D + z \log H^+ - n \log [HR]_{(0)} \dots\dots\dots (3)$$

Where, D = [MR_{z(n-z)}]₍₀₎ / [M^{z+}]₍₀₎ = [M^{z+}]₍₀₎ / [M^{z+}]_(a).

From equation (3)

$$\log D = \log K_{ex} + z \text{pH} + n \log [HR]_{(0)} \dots\dots\dots (4)$$

Equation (4) states that the slope of the plot of log D vs. pH gives the value of z (the number of H⁺ releases due to extraction reaction) and slope of the plot of log D vs. log [HR]₍₀₎ gives the value of n (the number of HR molecule consumes to form the extractable species due to extraction reaction).

In the present case, the value of n (in lower concentration region of Cyanex301) and z are both unity. Therefore, n-z = 0, so that no solvated complex is formed in the lower concentration region of Cyanex301. However in the higher concentration region of Cyanex-301, the value of n becomes almost 5 and so solvated species is formed at higher concentration region of Cyanex301.

TiO²⁺ can form strong complex with bisulphate ion. The acid dissociation constant of H₂SO₄ are K_{a1} ~ 1000 [26] and K_{a2} = 10⁻² at zero ionic strength [27]. These values indicate that if in an acidic solution, sulphate ion is added, all sulphates converts into bisulphate.

The stability constant of TiOHSO₄⁺ is 10^{2.2} [27]. Simple calculation shows that in 0.5 g dm⁻³ Ti(IV) and 1 mol dm⁻³ sulphate medium, the percentage of TiOHSO₄⁺ is 98.88; whereas in 0.5 g dm⁻³ Ti(IV) and 3 mol dm⁻³ sulphate medium, the percentage of TiOHSO₄⁺ is 99.84%. It is therefore obvious that the extractable TiO²⁺ species in the aqueous phase is the TiOHSO₄⁺ and its concentration is not so much varied when sulphate ion concentration is varied within 1 - 3 mol dm⁻³. For this reason, the log D vs. log [SO₄²⁻]₍₀₎ plot has a very low slope.

Considering all these facts, the proposed extraction equilibrium reaction in the case of extraction of Ti(IV) from sulphate medium by Cyanex301 in its lower concentration region is:



On the other hand, the extraction reaction at higher concentration region of Cyanex301 is:



Calculation of Extraction Equilibrium Constant, K_{ex}:

Equation (5) indicates that the intercept of the plot of log D vs. pH will be equal to log K_{ex} + n log [Cyanex301]. The value of n

depends on the Cyanex301 concentration region. It is 1 in the concentration region of 0.05-0.15 mol dm⁻³ and above concentration region up to 2 mol dm⁻³ of cyanex301 for eq-5

$$\text{Intercept} = -0.91 = \log K_{ex} + 1.0 \log 0.1$$

$$\log K_{ex} = 0.09$$

$$\text{So that } K_{ex} = 10^{0.09} = 1.23$$

And also for eq-6

$$\text{Intercept} = -0.673 = \log K_{ex} + 5.0 \log 0.25$$

$$\log K_{ex} = 2.33$$

$$K_{ex} = 217.42$$

Equation (4) also indicates that the intercept of log D vs. log [Cyanex301] plot is log K_{ex} + z pH. Here 'z' is 1. The intercepts at lower Cyanex-301 region of log D vs. log [Cyanex-301] plots are 1.28 and 1.50, respectively, at equilibrium pH 1.5 and 1.7. It follows that

$$(i) \text{ Intercept} = 1.28 = 1.0 \log K_{ex} + 1 \times 1.5$$

$$\log K_{ex} = -0.22$$

$$\text{or, } K_{ex} = 10^{-0.22} = 0.60$$

$$(ii) \text{ Intercept} = 1.5 = \log K_{ex} + 1 \times 1.7$$

$$\text{or, } \log K_{ex} = -0.2$$

$$\text{or, or, } K_{ex} = 10^{-0.2} = 0.63$$

Therefore, the average K_{ex} value for the reaction given in Eq. (4) is 54.97.

The equilibrium constant K_{ex} for the reaction given by Eq. (6) which is valid at higher concentration region of Cyanex301, can be derived as follows:

$$\text{Intercept} = 3.98 = \log K_{ex} + 1.5 \text{ (eq.pH)}$$

$$\text{giving } \log K_{ex} = 2.48 \text{ or } K_{ex} = 301.99$$

$$\text{and intercept} = 4.12 = \log K_{ex} + 1.7 \text{ (eq. pH)}$$

$$\text{giving } \log K_{ex} = 2.42 \text{ or, } K_{ex} = 263$$

Therefore, K_{ex} value at the higher concentration region is 282.50.

Dependence of extraction on temperature:

The log D vs 1/T × 10³ plot is shown in Fig. 6. The extraction of Ti(IV) increases with increasing temperature below 30°C and above 30°C, the reverse trend is observed.

Since the extraction ratio, D is proportional to extraction equilibrium constant, K_{ex}, the Vant Hoff equation in the following modified form can be applied for the solvent extraction study:

$$\log D = - \Delta H / 2.303 RT \dots\dots\dots (7)$$

Where, ΔH is the enthalpy change during extraction and R is the molar gas constant. According to this equation, the slope of the log D Vs 1/T plot should be equal to -ΔH / 2.303 R.

In the present case, the slopes at lower and higher temperature regions are -5236.16 and 4000, respectively which give respective ΔH values of 100.28 kJ and -76.61 kJ mol⁻¹. The extraction process is therefore endothermic at lower temperature region whereas it is exothermic at higher temperature region.

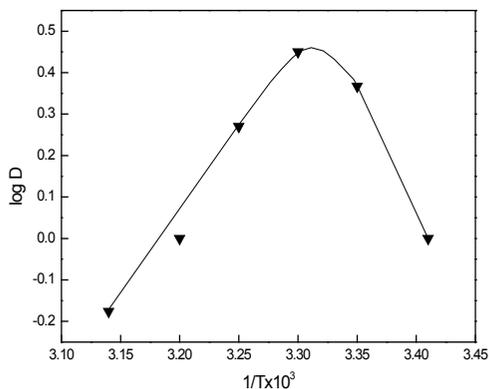


Fig-6: Dependence extraction of Ti(IV) by Cyanex301 on temperature pH = 1.6, Time = 40 min $[SO_4^{2-}] = 1.0 \text{ moldm}^{-3}$, $[Ti(IV)] = 0.5 \text{ g dm}^{-3}$ $[Cyanex-301] = 0.05 \text{ mol dm}^{-3}$

Conclusions

1. The Ti(IV)- SO_4 -cyanex301-kerosene system takes about 30 min for equilibration.
2. The slopes of the logD vs. $\log [Ti(IV)]_{ini}$ and logD vs. $\log [Ti(IV)]_{eq}$ plots are -1 and -0.5 respectively. Although with increasing Ti(IV) concentration in the aqueous phase, D is found to decrease, the amount of Ti(IV) extracted in the organic phase is increased.
3. The slope of logD vs. pH plot shows that the aqueous acidity dependence is minus unity.
4. The logD vs. $\log [cyanex301]$ plots show that extractant dependences are 1 and 5 in the lower and higher concentration regions of extractant respectively.
5. The extraction ratios are varied little with increasing sulphate ion concentration. The slope of logD vs. $\log [SO_4^{2-}]$ plot is 0.16.
6. The temperature dependence study shows that the reaction is endothermic up to 30°C and in the higher temperature region, the extraction process seemed to be exothermic in nature.

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