SOLVENT EXTRACTION OF VANADIUM (IV) FROM SULFURIC ACID SOLUTION BY BIS (2,4,4-TRIMETHYLPENTYL)PHOSPHINIC ACID IN EXXSOL D80

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The distribution equilibrium of vanadium (IV) between solution of bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA, HR) dissolved in EXXSOL D80 and weakly acidic sulfate solution was investigated as functions of the concentration of extractant, vanadyl ion, hydrogen ion and sulfate ion in the aqueous phase.

The stoichiometry and the chemical structure of the extracted species of vanadium (IV) were determined on the basis of slope analysis and IR spectra. The extraction reaction proceeds according to a cation exchange mechanism, in which vanadyl ion VO^{2+} replaces hydrogen ions of P-O-H and coordinates with oxygens in P=O in the BTMPPA and forms the complex $\text{VOR}_2 \cdot 2\text{HR}$ with a possible structure containing eight-membered chelating rings.

Temperature dependence of the extraction equilibrium constants was examined to estimate the apparent thermodynamic functions of extraction reaction (ΔH , ΔS and ΔG).

Introduction

Bis(2,4,4-trimethylpentyl)phosphinic acid (henceforth, abbreviated as BTMPPA), the active component of commercial extractant CYANEX 272, is one of the three kinds of organophosphorus acids which have been extensively studied for cobalt and nickel separation (Danesi *et al.*, 1984(a); 1985(b); Richelton *et al.*, 1984). Owing to the high cobalt/nickel selectivity and ability to reject calcium, CYANEX 272 have found extensive use for the recovery and separation of cobalt and nickel. Although CYANEX 272 was originally developed as a cobalt extractant, recent studies have concerned with the applications on extractive separation of other metals, such as the selective extraction of zirconium and hafnium from an aqueous sulfate solution containing titanium and other metallic impurities (Witte and Frey, 1985), the extraction of cadmium, copper and zinc from aqueous nitrate solutions (Sastre *et al.*, 1990), that of silver from nitrate media (Sole *et al.*, 1994), that of molybdenum from mineral acid solutions (Cao and Nakashio, 1989; Fu *et al.*, 1993), separation of rare earths (Sabot and Rollat, 1985; Komatsu and Freiser, 1989) and that of scandium from thorium, iron and lutetium (Wang and Li, 1994) as well as the gallium recovery from Bayer liquors using CYANEX 272 + Kelex 100 (Bauer *et al.*, 1985). Nevertheless, basic observations

concerning the extraction equilibrium of vanadium(IV) by CYANEX 272 are very few (Fu *et al.*, 1993). Recently, as CYANEX 272 exhibits a good selectivity for molybdenum (VI) and vanadium (IV) over aluminum (III) at relatively low pH, a solvent extraction process was developed in our laboratory for recovery of molybdenum (VI) and vanadium (IV) from a weakly acidic sulfate solution in the presence of a large amount of aluminum (III), a certain amount of cobalt (II), nickel (II) and a small amount of iron (III), resulting from sulfuric acid leaching of spent hydrodesulfurization catalysts as reported in previous paper (Zhang *et al.*, 1995). In this work, quantitative studies on extraction mechanism of vanadium (IV) from acidic aqueous sulfate solution with BTMPPA in EXXSOL D80 and the chemical structure of the complex formed in the organic phase have been conducted based on slope analysis and IR spectral measurements. Furthermore, the effects of sulfate concentration and temperature on extraction of vanadium (IV) with BTMPPA have been also discussed in detail.

1. Experimental

The extractant, CYANEX 272, was kindly supplied by Cyanamid Canada Inc., and purified by the use of the precipitation method as copper salt described as follows. The reagent dissolved in hexane (approx. 0.9M) was mixed and stirred with a solution of 0.5M copper (II) sulfate

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whose pH was adjusted to 4.3 by addition of 20% sodium hydroxide solution. After the copper (II) complex was formed and the hexane was evaporated off, it was washed with acetone to remove impurities. After drying at room temperature, the solid of complex dissolved in hexane was shaken with 1M hydrochloric acid to strip copper. The regenerated extractant solution was washed with water and evaporated in vacuo. The final product BTMPPA was a colorless, moderate viscous oily liquid. The purity of BTMPPA was determined as higher than 99% (molecular weight 290.45) by potentiometric titration in 75% 2-propanol aqueous solution with 0.1M sodium hydroxide solution as well as by an elementary analysis (EA).

The purified BTMPPA was used after dissolved as necessary in EXXSOL D80, one kind of commercial aliphatic diluent similar to kerosene.

Aqueous solution of vanadium (IV) was prepared by dissolving vanadyl sulfate n -hydrate ($\text{VOSO}_4 \cdot n\text{H}_2\text{O}$, $n = 3\sim 4$) in sulfuric acid solution. The ionic strength of the aqueous phase was kept at constant ($I = 1.5$) using reagent grade sodium sulfate except for the experiments of the sulfate effect on distribution equilibria. The initial vanadium (IV) concentration in the aqueous phase was maintained at approx. $9.5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ except for the experiments of the effect of metal concentration.

1.1 Extraction and Analytical Procedures

Distribution equilibria of vanadium (IV) were measured batchwise in which equal volumes (10 cm^3) of the aqueous and organic phases were shaken for 40 hours in 50 cm^3 stoppered flasks immersed in a thermostated air bath at 303 K, except for the experiments of temperature effect on distribution equilibria. A shaking time of 40 hours was found in the preliminary experiments to attain the equilibration. The pH of the aqueous phase was measured by a BECKMAN Ø45 pH meter.

The vanadium concentration in aqueous phase before and after equilibrium was analyzed by a Shimadzu ICPS-2000 multi-spectrometer. Since the phase separation occurred rapidly in all the cases, and the volume changes after contact were negligible, vanadium concentration in the organic phase was calculated by mass balance.

1.2 IR Spectral Measurement

IR spectra of the extracted complexes of vanadium (IV) were recorded on a Jeol JIR-AQS 20M FT-IR spectrophotometer.

2. Theory

It is well known that BTMPPA exists predominantly as a dimeric species in nonpolar diluents (Sole *et al.*, 1994) and vanadium (IV) do as the vanadyl ion VO^{2+} in aqueous phase in a wide range of acidity (Rossotti and Rossotti, 1955). Assuming that the overall extraction of vanadium (IV) from an acidic sulfate solution by BTMPPA in EXXSOL D80 may be represented by the cation exchange reaction expressed by Eq. (1), the equilibrium constant, K_{ex} , can be described by Eq. (2)

$$K_{\text{ex}} = \frac{[(\text{VO})_m \text{R}_{2m} \cdot 2(n-m)(\text{HR})][\text{H}^+]^{2m}}{[\text{VO}^{2+}]^m [\text{H}_2\text{R}_2]^n} \times f(\gamma) \quad (2)$$

in which $f(\gamma)$ refers to the equilibrium ratio of activity coefficients of species. Assuming $f(\gamma)$ is a constant, the apparent equilibrium constant is given as:

$$K'_{\text{ex}} = \frac{[(\text{VO})_m \text{R}_{2m} \cdot 2(n-m)(\text{HR})][\text{H}^+]^{2m}}{[\text{VO}^{2+}]^m [\text{H}_2\text{R}_2]^n} = \frac{K_{\text{ex}}}{f(\gamma)} \quad (3)$$

Taking into account the equilibria of the complexation of vanadyl ion with sulfate ion and the dissociation of H_2SO_4 in aqueous solution described by Eqs.(4) (Hogeltdt, 1982(a)) and (5) (Hogeltdt, 1982(b)), the total concentrations of vanadium (IV) and sulfate ions in the aqueous phase, $[\text{V(IV)}]_{\text{a}}^{\text{total}}$ and $[\text{SO}_4^{2-}]_{\text{a}}^{\text{total}}$ are expressed by Eqs. (6) and (7), respectively.

$$[\text{V(IV)}]_{\text{a}}^{\text{total}} = [\text{VO}^{2+}] + [\text{VOSO}_4] = \text{VO}^{2+} (1 + \beta [\text{SO}_4^{2-}]) \quad (6)$$

$$[\text{SO}_4^{2-}]_{\text{a}}^{\text{total}} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{VOSO}_4] \\ = [\text{SO}_4^{2-}] (1 + K_{\text{H}} [\text{H}^+] + \beta [\text{VO}^{2+}]) \quad (7)$$

The concentration of vanadium (IV) in aqueous phase used in this work is sufficiently low so that $\beta[\text{VO}^{2+}]$ is much less than $(1 + K_{\text{H}}[\text{H}^+])$ and therefore Eq. (7) is reduced to

$$[\text{SO}_4^{2-}]_{\text{a}}^{\text{total}} = [\text{SO}_4^{2-}] (1 + K_{\text{H}} [\text{H}^+]) \quad (7')$$

Thus, Eq. (3) can be rewritten as follows:

$$K'_{\text{ex}} = \frac{[(\text{VO})_m \text{R}_{2m} \cdot 2(n-m)(\text{HR})][\text{H}^+]^{2m}}{\{[\text{V(IV)}]_{\text{a}}^{\text{total}}\}^m [\text{H}_2\text{R}_2]^n} \times \frac{1}{(\alpha_{\text{VO}^{2+}})^m} \quad (8)$$

where, $\alpha_{\text{VO}^{2+}}$ is a fraction of vanadium (IV) present as cationic species VO^{2+} in the aqueous phase, calculated in terms of the stability constant of vanadyl sulfate:

$$\alpha_{\text{VO}^{2+}} = \frac{1}{(1 + \beta [\text{SO}_4^{2-}])} \quad (9)$$

If $\overline{(\text{VO})_m \text{R}_{2m} \cdot 2(n-m)(\text{HR})}$ is only extracted species, then, the distribution coefficient can be expressed by Eq. (10):

$$D = \frac{[\text{V(IV)}]_{\text{o}}^{\text{total}}}{[\text{V(IV)}]_{\text{a}}^{\text{total}}} = \frac{m [(\text{VO})_m \text{R}_{2m} \cdot 2(n-m)(\text{HR})]}{[\text{V(IV)}]_{\text{a}}^{\text{total}}} \quad (10)$$

and Eq. (8) can be changed as:

$$K'_{\text{ex}} = \frac{D}{m} \times \frac{[\text{H}^+]^{2m}}{[\text{H}_2\text{R}_2]^n \{[\text{V(IV)}]_{\text{a}}^{\text{total}}\}^{m-1}} \times \frac{1}{(\alpha_{\text{VO}^{2+}})^m} \quad (11)$$

Fig. 1 Dependence of extraction of vanadium (IV) on vanadium (IV) concentration in aqueous solutions

Fig. 2 Effect of extractant concentration on extraction of vanadium (IV)

(○) : $\text{pH}_{\text{eq}} = 1.01 \pm 0.00$; (●) : $\text{pH}_{\text{eq}} = 1.17 \pm 0.00$;
 (□) : $\text{pH}_{\text{eq}} = 1.34 \pm 0.01$; (◇) : $\text{pH}_{\text{eq}} = 1.43 \pm 0.01$;
 (△) : $\text{pH}_{\text{eq}} = 1.69 \pm 0.02$.

or rearranged as follows after taking logarithm:

$$\log D = \log m + \log K'_{\text{ex}} + m \log \alpha_{\text{VO}^{2+}} + n \log [\overline{\text{H}_2\text{R}_2}] + 2m \text{pH} + (m-1) \log [\text{V(IV)}]_{\text{a}}^{\text{total}} \quad (12)$$

In the above equations, $[\overline{\text{H}_2\text{R}_2}]$ represents the free dimeric reagent concentration in the organic phase and can be calculated using the following formula:

$$[\overline{\text{H}_2\text{R}_2}] = \frac{C_{\text{HR}} - \frac{n}{m} [\text{V(IV)}]_{\text{o}}^{\text{total}}}{2} \quad (13)$$

where, C_{HR} represents the analytical concentration of the

Fig. 3 Effect of pH on extraction of vanadium (IV)

(○) : $[\overline{\text{H}_2\text{R}_2}] = 0.05 \text{ M}$; (●) : $[\overline{\text{H}_2\text{R}_2}] = 0.075 \text{ M}$;
 (□) : $[\overline{\text{H}_2\text{R}_2}] = 0.10 \text{ M}$; (◇) : $[\overline{\text{H}_2\text{R}_2}] = 0.15 \text{ M}$;
 (△) : $[\overline{\text{H}_2\text{R}_2}] = 0.20 \text{ M}$.

monomeric BTMPPA and $[\text{V(IV)}]_{\text{o}}^{\text{total}}$ is the total concentration of vanadium in the organic phase.

3. Results and Discussion

3.1 Stoichiometry of Extracted Species

The experimental data of distribution equilibrium was analyzed by means of conventional slope analysis on the basis of the above-mentioned stoichiometry.

In order to determine whether the extracted species of vanadium (IV) by BTMPPA is mononuclear or polynuclear, the dependence of the distribution coefficient on the concentration of vanadium (IV) in the aqueous solutions was first examined by varying the initial vanadium (IV) concentration in aqueous phase. **Figure 1** shows the logarithmic relationship between D and $[\text{V(IV)}]_{\text{a}}^{\text{total}}$. Obviously, since the distribution coefficient is independent of vanadium (IV) concentration, the value of $(m-1)$ in Eq. (12) is equal to 0, i.e., $m = 1$, indicating that the extracted species is mononuclear in the whole region of the experimental conditions.

Thus, Eq. (12) becomes as follows:

$$\log D = \log K'_{\text{ex}} + \log \alpha_{\text{VO}^{2+}} + n \log [\overline{\text{H}_2\text{R}_2}] + 2\text{pH} \quad (14)$$

or

$$\log D' = \log K'_{\text{ex}} + n \log [\overline{\text{H}_2\text{R}_2}] + 2\text{pH} \quad (14')$$

Fig. 4 Effect of sulfate concentration on extraction of vanadium (IV)

Fig. 5 Effect of temperature on extraction of vanadium (IV)

where $D' = D/\alpha_{VO_2^+}$

Figure 2 shows the relationship between $\log D' - 2$ pH and $\log [H_2R_2]$. The slope of this relationship was obtained as 1.83 which is close to 2, suggesting that two ligands react with one molecule of vanadyl ion.

Figure 3 shows the relationship between $\log D' - 2$ $\log [H_2R_2]$ and pH. The slope of this relationship was obtained as 2.19 which is in good agreement with the predicted value of 2, confirming that two protons were released according to cation exchange reaction.

Summarizing the results, it can be inferred that vanadium (IV) forms the complex of the type, $VOR_2 \cdot 2(HR)$, and the overall extraction reaction can be expressed as follows:

The apparent equilibrium constant was evaluated as $K'_{ex} = 8.7 \times 10^{-1}$ by the least-squares method using the experimental data. This value is greater than that reported by Fu *et al.* ($K'_{ex} = 2.69 \times 10^{-2}$) (1993). It may be attributed to the difference with and without consideration on the complex equilibrium of vanadyl ion with sulfate group in

Table 1 Thermodynamic Functions of Extraction of Vanadium (IV) with BTMPPA in EXXSOL D80

Temperature (K)	$\log K'_{ex}$	ΔG kJ mol ⁻¹	ΔS J K ⁻¹ mol ⁻¹	ΔH kJ mol ⁻¹
283	-0.35	1.89	128.5	38.26
293	-0.12	0.67	128.3	
303	-0.06	0.35	125.1	
313	0.30	-1.80	128.0	
323	0.55	-3.40	129.0	

aqueous phase.

3.2 Effect of Sulfate Concentration

The effect of sulfate ion on distribution coefficient was examined by addition of sodium sulfate to aqueous phase at constant pH ($pH_{eq} = 1.34$). The results shown in Fig. 4 suggested that the distribution coefficient of vanadium (IV) was decreased as increasing the sulfate concentration. Clearly, it is the result of the formation of vanadyl sulfate in the aqueous phase as described in Eq. (4), as a free vanadyl ion (VO_2^+) which is thought to be extractable species by BTMPPA, is decreased with the increase of sulfate concentration.

3.3 Temperature Effect

The change of the apparent equilibrium constant, K'_{ex} , with the temperature is expressed by a van't Hoff equation:

$$\frac{\partial(\log K'_{ex})}{\partial(1/T)} = -\frac{\Delta H}{2.303R} \quad (16)$$

Figure 5 illustrates the plot of $\log K'_{ex}$ against $1/T$. The plot is lying on straight line and enthalpy change of the extraction reaction was evaluated as $\Delta H = 38.26$ kJ·mol⁻¹ which means the endothermic reaction process.

Other values of the observed thermodynamic functions of extraction reaction such as free energy ΔG and entropy ΔS were also calculated from Eqs. (17) and (18), respectively as shown in Table 1.

$$\Delta G = -2.303RT \log K'_{ex} \quad (17)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (18)$$

As the overall changes in the thermodynamic functions reflect the summation of the contributions of the dehydration of the hydrated vanadyl species and the complexation between vanadyl ion and extractants, the positive values of enthalpy and entropy imply that the dehydration is more significant in the process of extraction than the complexation process. In addition, the positive enthalpy also shows that the increase in temperature may be proven favorable to extraction of vanadium (IV).

3.4 IR Spectra and Structure of Complex

The infrared spectra of free BTMPPA and its organic complexes with vanadium (IV) prepared by contacting equal volumes of aqueous vanadyl sulfate solutions (0.02, 0.1, 0.5, 1.0 M) at pH 2.0 with an organic solvent of 0.1M BTMPPA in EXXSOL D80 were examined. It can be seen from Fig. 6 that the absorption bands

Fig. 6 IR spectra of BTMPPA and the extracted complexes of vanadium (IV) by 0.10 M BTMPPA in EXXSOL D80 (1, BTMPPA; 2, 3, 4 and 5, solvent loading of vanadium (IV) at 0.0097, 0.0183, 0.0274 and 0.0329 M, respectively.)

in the region of $2730\sim 1700\text{ cm}^{-1}$ in BTMPPA spectrum of 1 are considered to be relative to aggregative P-O-H vibrations between intermolecular hydrogen bonding in the dimer; the absorption band at 964 cm^{-1} is assigned to the P-O-H stretching vibration and the band at 1170 cm^{-1} is assigned to the P=O stretching vibration in hydrogen bonding aggregation, whilst the bands at 1470 and 1380 cm^{-1} arise from alkyl C-H vibrations. Comparing with the spectra of the complexes of 2 - 5, some obvious changes are observed. As the vanadium content in the organic complexes increases, the intensities of OH stretching and bending bands at $2730\sim 1700\text{ cm}^{-1}$ decrease to some extent; P=O absorption band at 1170 cm^{-1} shifts to the lower frequency by 32 cm^{-1} for the complexes containing the high loading of vanadium (IV); P-OH stretching band at 964 cm^{-1} becomes weaker significantly; and two new absorption bands at 1045 and 1004 cm^{-1} which are ascribed to the P-O-V and V=O stretching frequencies (Selbin *et al.*, 1963), respectively, appear and they become

Fig. 7 Probable structure of the vanadium (IV) complex formed with BTMPPA in EXXSOL D80

stronger and wider with increasing the loading of vanadium (IV) by BTMPPA. These results show that when the dimeric BTMPPA forms complex with vanadium (IV), the hydrogen atom of P-OH is substituted by vanadium (IV) and simultaneously, the oxygen atom in P=O group takes part in the coordination with vanadium (IV). These spectra changes confirm the extraction mechanism described previously.

Additionally, the fact that no absorption band of SO_4^{2-} group is observed on the IR spectra supports that the extracted complex does not contain sulfate ion.

Based on the slope analysis, IR spectral measurements and referring to Selbin *et al.*'s studies with respect to structure of vanadyl compounds (1963), a possible structure of the extracted species of vanadium (IV) with the major component $\text{VOR}_2 \cdot 2\text{HR}$ containing eight-membered chelating rings may be postulated as schematically shown in Fig. 7.

Conclusion

The slope analysis and IR spectroscopic measurement have been employed to characterize the stoichiometry and structure of the extracted complex of vanadium (IV) by BTMPPA. The results demonstrate that vanadium (IV) is extracted with BTMPPA by a cation exchange mechanism from sulfate solution into the organic phase as $\text{VOR}_2 \cdot 2\text{HR}$ in which vanadyl ion, VO^{2+} , is exchanged with hydrogen ions of P-O-H and coordinated with oxygens in P=O of BTMPPA to form the structure containing eight-membered chelating rings.

Extraction of vanadium (IV) by BTMPPA is dependent on the sulfate concentration in aqueous phase but the vanadyl sulfate is unextractable by BTMPPA. Apparent equilibrium constants and the thermodynamic functions, ΔH , ΔS and ΔG in the extraction of vanadium (IV) with BTMPPA have been evaluated. The extraction reaction is an endothermic process and increase in temperature is favorable for extraction of vanadium (IV) by BTMPPA.

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Nomenclature

D	= distribution coefficient	[-]
K_{ex}	= extraction equilibrium constant	[-]
K'_{ex}	= apparent extraction equilibrium constant	[-]
HR	= monomer of BTMPPA	
H_2R_2	= dimer of BTMPPA	
$f(\gamma)$	= equilibrium ratio of species activities	[-]
$\alpha_{VO^{2+}}$	= fraction of vanadium (IV) present as VO^{2+} in aqueous phase	[-]
β	= stability constant of vanadyl sulfate	[dm ³ ·mol ⁻¹]
T	= temperature	[K]
ΔH	= enthalpy	[kJ·mol ⁻¹]
ΔS	= entropy	[J·K ⁻¹ ·mol ⁻¹]
ΔG	= free energy	[kJ·mol ⁻¹]
[j]	= concentration of species j	[mol·dm ⁻³]

<Superscript>

- = organic phase species

<Subscripts>

aq = aqueous phase
org = organic phase

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