Extraction of Vanadium (IV) with Acetic, Propionic, Butyric, Valeric & Caproic Acids in Presence of Some Neutral Donors

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Received 5 June, 1978; revised 6 September 1978; accepted 4 October 1978

Extraction of vanadium(IV) with aliphatic carboxylic acids (acetic, propionic, butyric, valeric and capric acids) in the presence and absence of neutral donors (antipyrine and pyridine bases) has been studied. Caproic acid extracts vanadium(IV) into solvents like benzene and nitrobenzene unlike other acids. The species extracted is found to be monomeric VO(H$_2$O)$_3$R$_2$. It is demonstrated that neutral donors, when used as synergists, are also incorporated into the extracted species by replacing water molecule. The effectiveness of these carboxylic acids as extractants of vanadium(IV) in the presence of neutral donors is found to increase with increase in number of carbon atoms in the carboxylic acid (i.e.) caproic acid $>$ valeric acid $>$ butyric acid $>$ propionic acid $>$ acetic acid. The effectiveness of pyridine bases is found to be 4-picoline $>$ 3-picoline $>$ pyridine $>$ 2-picoline in the extraction of vanadium(IV)-caproate system.

Materials and Methods

Beckman DU2 spectrophotometer and Philips pH meter were used. Vanadium(IV) and antipyrine solutions were prepared as reported earlier.

Solutions (2M) of acetic, propionic, butyric, valeric and capric acids were prepared by dissolving the required amount of freshly distilled acid in the organic solvent.

Pyridine (AR, BDH), 2-picoline (E. Merck), 3-picoline (E. Merck), 4-picoline (E. Merck) and the solvents were freshly distilled before use. All other chemicals used were of AR (BDH) grade.

General procedure — Vanadium(IV) solution (2.5 x 10$^{-4}$M) was diluted to 20 ml, pH being adjusted to the appropriate value and then shaken with the organic solvent (20 ml) containing the required amount of carboxylic acid and the neutral donor (antipyrine was taken in the aqueous phase). pH of the aqueous phase was noted after separation. Vanadium content in both the phases was determined by the oxine-alcohol method.

A two minute shaking is sufficient for maximum recovery of vanadium in all these systems.

The composition of the extracting species in all the systems was determined by the method of slope analysis. In order to overcome the limitations of this technique, the investigations were carried out at two different anion concentrations and at two different pH values. In these experiments, the ionic strength was kept constant at 0.25M with sodium sulphate in the aqueous phase as sulphate is found to be without influence in the extraction of vanadium(IV) in the presence of the neutral donors used in these investigations.

Results and Discussion

Vanadium(IV)-caproate binary system — Caproic acid extracts vanadium(IV) into solvents like benzene, chloroform, nitrobenzene, carbon tetrachloride unlike the other acids. Benzene was found to be the best solvent for the extraction of vanadium(IV)-caproate complex (60%) at pH 5-6. Plot of log $q$ vs log [HR] (Fig. 1) indicates that two carboxylate ions are associated with vanadium in the extracting species. No polynuclear species is formed in the concentration range employed in these investigations. The formation of vanadium(IV)-caproate complex can be represented as:

\[
\text{VO}(	ext{H}_2\text{O})_3\text{R}_2 + 2\text{HR} \rightarrow \text{VO}(	ext{H}_2\text{O})_3\text{R}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} \quad \quad (1)
\]

The equilibrium constant 'K' of equilibrium (1) is given by Eq. (2)

\[
K = \frac{[\text{VO}^2\text{HR}^2]}{[\text{VO}(	ext{H}_2\text{O})_3\text{R}_2] [\text{H}^+]^2} \quad \quad (2)
\]
The distribution ratio \( q \) of vanadium is given by Eq. (3)
\[
q = \frac{C_{v,o}}{C_{o,v}} = \frac{[\text{VO(H}_2\text{O)}_3\text{R}_2]}{\sum^n_{i=1} [\text{VO}^{2+}]_{n} + [\text{VOR}^{2-} - n] + [\text{VOR}^{3+}]_{n} + [\text{VO(H}_2\text{O)}_3\text{R}_2]} \quad \ldots (3)
\]

\( \text{VOR}^n \) complexes have not so far been reported. As assumed by Tanaka and coworkers, the existence of charged complexes in the aqueous phase is ignored. The absence of anionic complexes \((\sum^n_{i=1} [\text{VOR}^{2-} - n])\) is confirmed by the fact that the extent of extraction remains unaffected even though the concentration of the ligand is enormously increased.

Thus
\[
q = \frac{[\text{VO(H}_2\text{O)}_3\text{R}_2]}{[\text{VOR}^{2+}] + [\text{VO(H}_2\text{O)}_3\text{R}_2]} \quad \ldots (4)
\]

From Eq. (4) we get
\[
1 = \frac{p_c [\text{VOR}^{2+}] + 1}{p_c [\text{VO(H}_2\text{O)}_3\text{R}_2]} \quad \ldots (5)
\]

where \( p_c \) is the partition of the complex species.

From Eqs (2) and (5), it follows that
\[
1 = \frac{1}{p_c} - \frac{1}{K_{\text{HR}}} + \frac{1}{[\text{HR}]} \quad \ldots (6)
\]

from which \( K_{\text{HR}} \), the equilibrium constant of vanadium(IV)-caproate complex is determined. For the determination of this constant, the equilibrium concentration of carboxylic acid is determined making use of mass balance equation derived as follows:

The total concentration of carboxylic acid is given by
\[
[\text{HR}]_{\text{total}} = [\text{HR}]_{\text{aq}} + [\text{HR}]_{\text{aq1}} + [\text{HR}]_{\text{aq2}} + [\text{R}^-] + [\text{VO(H}_2\text{O)}_3\text{R}_2] + [\text{VO(H}_2\text{O)}_3\text{R}_2] \]
\[
= 1 + \frac{p_c}{[\text{HR}]_{\text{aq}}} + k_2 \frac{[\text{HR}]_{\text{aq2}}}{[\text{HR}]_{\text{aq}}} + k_3 \frac{[\text{HR}]_{\text{aq3}}}{[\text{HR}]_{\text{aq}}} + [\text{H}]^{2+} K_{\text{HR}} \left( 1 + \frac{1}{p_c} \right) [\text{VO(H}_2\text{O)}_3\text{R}_2] \quad \ldots (7)
\]

From Eq. (7)
\[
\frac{1 + \frac{1}{[\text{HR}]_{\text{aq}}} + k_2 \frac{[\text{HR}]_{\text{aq2}}}{[\text{HR}]_{\text{aq}}} + k_3 \frac{[\text{HR}]_{\text{aq3}}}{[\text{HR}]_{\text{aq}}} + [\text{H}]^{2+} K_{\text{HR}} \left( 1 + \frac{1}{p_c} \right) [\text{VO(H}_2\text{O)}_3\text{R}_2]}{[\text{HR}]} = 2k_4 \beta^2 \quad \ldots (8)
\]

where \( p, k_2 \) and \( K_{\text{HR}} \) are the distribution coefficient, dimerization constant and association constant of carboxylic acid respectively which are taken from literature.

Vanadium(IV)-neutral donor-carboxylate systems — In the presence of neutral donors like antipyrine (oxygen donor) and pyridine bases (nitrogen donors) synergism is observed which can be attributed to the formation of mixed complexes. Acetic acid is found to be ineffective in the extraction of vanadium(IV) even in the presence of the neutral donors. From the point of percentage extraction and easy separation, nitrobenzene and benzene were chosen for vanadium(IV)-antipyrine-carboxylate and nitrogen base systems respectively as solvents. Plots of log \( q \) vs log [HR] (Figs. 1 and 2) at constant concentration of neutral donor and log \( q \) vs log [neutral donor] (Figs. 3 and 4) at constant concentration of carboxylic acid, show that the ratio vanadium:neutral donor:carboxylate is 1:1:2 in all the cases, except with propionic acid system.

In the case of vanadium(IV)-neutral donor-caproate system, the composition was determined at a concentration of caproic acid not exceeding 0.2 M overall as at this concentration the extraction of the binary complex is negligible and coextraction is eliminated. The plots of log \( C_{\text{pR}} \) against log \{[\text{VO}^{2+}] - 2 \log [\text{HR}]\} where \( C_{\text{pR}} \) and \([\text{VO}^{2+}]\) represent the concentration of vanadium(IV) in the organic and aqueous phases respectively yield a slope of 1 in all the cases which confirms the absence of polynuclear species in the concentration range used.

Similar treatment was adopted by Tanaka and coworkers in the extraction of carboxylate complexes of scandium, copper and nickel.
The equilibrium constant $K$ of the mixed complex is given by Eq. (10).

$$K = \frac{[\text{VO}(\text{H}_2\text{O})_2\text{BR}_2][\text{H}^+]^2}{[\text{VO}^{2+}][\text{HR}]^2[B]}$$

The equilibrium constant of the ternary complex is determined by adopting the treatment given for vanadium(IV)-caproate system. The final expression is given by Eq. (11).

$$\frac{1}{q} = \frac{1}{P_1} \frac{1}{K_3} \frac{[\text{H}^+]^2}{[\text{HR}]^2[B]} + \frac{1}{P_1}$$

The equilibrium concentration of carboxylate is determined making use of mass balance equation as described by Eq. (8) and that of antipyrine is given by Eq. (12)

$$[\text{ApY}]_{\text{aq}} = \frac{[\text{ApY}]_{\text{total}}}{1+P_1} \frac{[\text{VO}(\text{H}_2\text{O})_2\text{BR}_2]}{}$$

where $P_1$ is the partition of antipyrine between water and nitrobenzene under experimental conditions.

The mass balance equation for pyridine can be expressed by Eq. (13)

$$[\text{B}]_{\text{aq}} = \frac{[\text{B}]_{\text{total}}}{1+P_B} \frac{[\text{VO}(\text{H}_2\text{O})_2\text{BR}_2]}{K_{\text{BH}^+}}$$

where $P_B$ and $K_{\text{BH}^+}$ are the partition coefficient and protonation constant of pyridine base respectively. The $K_{\text{BH}^+}$ and $P_B$ values are taken from literature. The interaction of carboxylic acids either with antipyrine or with pyridine base is found to be negligible under experimental conditions. Similarly the stability of vanadium(IV)-neutral donor complexes is also negligible. The same type of equations are used for vanadium(IV)-antipyrine/pyridine-propionate system also by introducing $2B$ instead of $B$ in Eq. (9). The equilibrium constants obtained from Eq. (11) are included in Table 1.

From these constants, it is observed that the ternary complexes show an increasing tendency in the effectiveness with increasing molecular weight of the acid. It is interesting to note that the optimum concentrations of the carboxylic acids and neutral donors required also decrease with increasing molecular weight of the carboxylic acid, $pH$ being about the same in all the cases. Either on the basis of the concentration of base required for 50% extraction or on the basis of extraction constants, it is observed that the effectiveness of the carboxylic acids investigated follows the order: caproic acid > valeric acid > butyric acid > propionic acid > acetic acid. Similar trend has been reported in the various extraction studies of metals involving these carboxylic acids and neutral donors.

The effectiveness of nitrogen donors as synergists in the extraction of vanadium(IV) is found from the constants determined for vanadium(IV)-neutral donor-caproate system. The order of effectiveness is: 4-picoline > 3-picoline > pyridine > 2-picoline.
2-Picoline is found to be ineffective in the extraction of vanadium(IV) in the presence of caproic acid due to steric hindrance caused from the methyl group present in ortho-position. The above order is further supported by the fact that the concentration of base required to effect 50% recovery of vanadium is in the order pyridine > 3-picoline > 4-picoline. In several other extraction systems also, the same order is established.

Acknowledgement

Two of us (K.V.S.L.V.P. and V.V.S) thank the CSIR, New Delhi, for the award of research fellowships.

References