Synergism in the Extraction of Vanadium: Studies on the Extraction of Vanadium(IV)-Thiocyanate Complex in the Presence of Some Neutral Nitrogen Bases

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Marked synergism is observed in the extraction of vanadium(IV)-thiocyanate complex into benzene in the presence of some neutral nitrogen donors (pyridine, 3-picoline, 4-picoline, quinoline and isoquinoline). These ligands act synergistically by displacing the remaining coordinated waters and thus producing hydrophobic species. The equilibrium constants of the mixed complexes have also been determined. The effectiveness of the bases as synergists follows the order: 4-picoline > 3-picoline > pyridine > isoquinoline > quinoline.

Rao and Sarma have reported that vanadium(IV)-thiocyanate complex extracts only into coordinating solvents like n-butanol and isobutyl methyl ketone, although not quantitatively. They observed a synergistic effect in the presence of o-phenanthroline, a bidentate ligand, the extraction being only into n-butanol. This prompted the present authors to investigate the effect of pyridine and quinoline bases which are unidentate nitrogen containing ligands. Preliminary experiments have shown that in the presence of pyridine or quinoline base, even non-polar solvents like benzene, chloroform, carbon tetrachloride quantitatively extract V(IV) monooxo complex which is not extracted by these solvents in the absence of these nitrogen bases. A detailed study of these bases as synergists has been carried out and the results are incorporated in this note.

Solutions of V(IV), thiocyanate and other bases were prepared as reported earlier. A 0.1M solution of 2,2′-bipyridyl (BDH, Analar) was prepared in doubly distilled water acidified with sulphuric acid. All other chemicals used were of Analar grade.

The optimum conditions for the extraction of V(IV)-thiocyanate complex into benzene are given in Table I. The composition of the extracting species is established by slope analysis. A plot of log q versus log [thiocyanate]aq,total has a slope of 2 indicating a 1:2 [V(IV)-thiocyanate] stoichiometry for the extracting species. Similarly, the plot of log q versus log [base]org,total indicates a slope of 3 and hence the ratio of vanadium to base is 1:3. These results permit the designation of the extracting species as VO(NCS)2B3, where B is pyridine or quinoline base. This composition satisfies the hexacoordination of V(IV) which is also supported by the quantitative extraction of vanadium in all the cases indicating that the extracting species are completely hydrophobic.

In the presence of thiocyanate and base, the following reaction takes place:

\[ VO_{aq}^{2+} + 2SCN_{aq} + 3B_{org} = VO(NCS)_{2B_3} \]

The mixed equilibrium constant and the distribution ratio of these mixed complexes are given by Eqs. (2) and (3) respectively:

\[ \beta_{2,3} = \frac{[VO(NCS)_{2B_3}]}{[VO^{2+}]_aq[SCN^-]_aq[B]^3} \]

\[ q = \frac{[VO^{2+}]_aq^2[SCN^-]^2[B]^3 + \sum_{i=0}^{3} [VO(B)^{3i}]_aq [VO(NCS)_{2B_3}]_aq}{[VO(B)^{3i}]_aq + [VO(NCS)_{2B_3}]_aq} \]

The mixed equilibrium constant and the distribution ratio of these mixed complexes are given by:

\[ \beta_{2,3} = \frac{[VO(NCS)_{2B_3}]}{[VO^{2+}]_aq[SCN^-]_aq[B]^3} \]

\[ q = \frac{[VO^{2+}]_aq^2[SCN^-]^2[B]^3 + \sum_{i=0}^{3} [VO(B)^{3i}]_aq [VO(NCS)_{2B_3}]_aq}{[VO(B)^{3i}]_aq + [VO(NCS)_{2B_3}]_aq} \]

Taking logarithms and rearranging we get

\[ \log q = \log \beta_{2,3} + 2 \log [SCN]_aq + 3 \log [B]_aq \]

By substituting the equilibrium concentrations of thiocyanate and the base, the mixed equilibrium constants log \( \beta_{2,3} \) can be calculated. It is found that thiocyanate does not distribute into benzene under the experimental conditions either alone or in the presence of a base. The partition data for pyridine, 3-picoline and 4-picoline, which are determined by the authors, are 3.2, 8.7 and 9.9 respectively between water and benzene under the experimental conditions (pH 5).

\[ \beta_{2,3} = \frac{[SCN]^2[B]^3}{[VO^{2+}]_aq^2[SCN^-]_aq} \]

References


coefficients for quinoline and isoquinoline are taken as 110 and 114 respectively. The amount of base in aqueous phase is calculated as suggested by Irving and Al-Niami and Akiwa and Kawamoto. The equilibrium constants obtained by substituting the equilibrium concentrations of the ligands are given in Table 1.

It is clear from the constants given in Table 1 that the effectiveness of these bases as synergists in the extraction of V(IV)-thiocyanate complex into benzene follows the order: 4-picoline > 3-picoline > pyridine and isoquinoline > quinoline. 2-Picoline is found ineffective in forming a mixed complex due to probable steric hindrance caused by the methyl group in the ortho-position. Similar studies were also made into n-butanol, a coordinating solvent, where the extent of synergism is much less than in benzene and the extracting species is found to be VO(NCS)₂B₂ROH where ROH is n-butanol. The same order of the bases is observed in this solvent also.

2,2'-Bipyridyl, a bidentate ligand, was also studied. The results obtained are similar to those obtained by Rao and Sarma in the case of o-phenanthroline. Of these two bases o-phenanthroline is found to be more effective as synergist, the stability constants (log K) being 6.0 and 4.25 for o-phenanthroline and 2,2'-bipyridyl complexes respectively.

It is very interesting to observe that the equilibrium constants for the o-phenanthroline and 2,2'-bipyridyl bases, which are bidentate ligands, are lower than those for pyridine and quinoline bases which are unidentate ligands. This may be attributed to the fact that the extracting species of bipyridyl and o-phenanthroline complexes do contain a molecule of n-butanol, an oxygen donor VO(NCS)₂B₂ROH whereas the pyridine and quinoline complexes are formed from only pure nitrogen donors VO(NCS)₂B₂. The introduction of an oxygen donor might have reduced the stability of the mixed complex by changing the environment of the central metal ion.

**Procedure** — Aqueous phase (20 ml) containing V(IV) (overall conc. 5 x 10⁻⁴ M) and the ligand was equilibrated with organic phase (20 ml) for 2 min maintaining the ionic strength constant at 1 M with potassium chloride. The amount of vanadium in the aqueous phase was determined by the methods described by Rao and Sastry.

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**References**


**2-Hydroxy-1-naphtaldioxide as an Analytical Reagent for Pd(II)**

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2-Hydroxy-1-naphtaldioxide is proposed as a new selective and sensitive reagent for the gravimetric determination of Pd(II). The complex having the composition 1:2 (metal-ligand) can be dried to a constant weight at 105-110° and the conversion factor is 0.2223. It is stable up to 280° and the weight loss from 285° to 470° corresponds to the complete loss of ligand molecules. IR studies reveal that the complex is formed by the replacement of the hydrogen of phenolic OH by Pd(II) which coordinates through oxime nitrogen. A square planar structure is suggested for the diamagnetic (ESR) complex.

Amongst the gravimetric reagents for Pd(II), oximes occupy an important place. However, even amongst the oximes the claims for superiority over the long established dimethylglyoxime method have not been confirmed.

In the course of our work on the use of several organic compounds as possible gravimetric reagents for Pd(II), it was noted that 2-hydroxy-1-naphtaldioxide gave a bright yellow precipitate with Pd(II) in the cold at pH 0-5-3-0 and no precipitate with Ni(II), Co(II), Zn(II), Mn(II), U(VI), Rh(III) and Pt(IV). The limits of identification and dilution determined by Feigl's method were 2-0 μg and

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**NOTES**

Table 1 — Optimum Conditions for the Extraction of V(IV)-SCN⁻ Complex in the Presence of Various Bases and the Stability Constants of the Mixed Complexes

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>pH</th>
<th>[SCN⁻]_aq,total (M)</th>
<th>[Base]_org,total (M)</th>
<th>log β_{2,3} (at 28°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>Benzene</td>
<td>4-5-5-5</td>
<td>0·0492</td>
<td>0·500</td>
<td>6-63</td>
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<tr>
<td>3-Picoline</td>
<td>do</td>
<td>4-5-5-5</td>
<td>0·0274</td>
<td>0·250</td>
<td>8-12</td>
</tr>
<tr>
<td>4-Picoline</td>
<td>do</td>
<td>4-5-5-5</td>
<td>0·0219</td>
<td>0·200</td>
<td>8-82</td>
</tr>
<tr>
<td>Quinoline</td>
<td>do</td>
<td>4-0-5-0</td>
<td>0·2670</td>
<td>1·4678</td>
<td>7-96</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>do</td>
<td>4-0-5-0</td>
<td>0·3666</td>
<td>0·3786</td>
<td>10-39</td>
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<tr>
<td>2,2'-Bipyridyl</td>
<td>n-Butanol in benzene</td>
<td>1-0-3-0</td>
<td>0·3377</td>
<td>0·0075†</td>
<td>4-25</td>
</tr>
<tr>
<td>o-Phenanthroline*</td>
<td>n-Butanol in benzene</td>
<td>1-0-3-3</td>
<td>0·0625</td>
<td>0·0050†</td>
<td>6-00</td>
</tr>
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