CHAPTER 7

ANALYTICAL APPLICATION OF SURFACTANTS
ANALYTICAL APPLICATION OF SURFACTANTS

7.0 INTRODUCTION

Hydroxamic acids possessing the functional grouping (I) are ideally suited to form

\[ \text{\text{C} = \text{O}} \]

\[ \text{\text{N - OH}} \]

stable 5-membered chelates (or inner complex compounds) with metal ions.

\[ \text{M}^{n+} + n \left( \frac{R' \text{N} \text{- OH}}{R \text{C} = \text{O}} \right) \rightarrow \left( \frac{R' \text{N} \text{- O} \rightarrow}{R \text{C} = \text{O}} \right) \text{M} + n\text{H}^+ \]

The water insolubility, deep colour and preferential solubility in water immiscible solvents of the metal-chelates of hydroxamic acids have been widely employed for developing gravimetric, colorimetric and solvent extraction methods. Hydroxamic acids have, therefore, found numerous analytical applications. The analytical and complexation chemistry of metal ions have kept pace with the growth of interest in them. There was however a growing tendency in the recent past to employ organic compounds, especially hydroxamic acids which are usually more sensitive as well as selective for analytical purpose. They give colour reactions with metal ions which are very rapid and detectable, estimation can be carried out in a span of very short time. Hydroxamic acids are selective and give reproducible results.

Vanadium is distributed widely in nature and exists up to 300 ppm in the earth crust. Vanadium exhibits positive valency of 2 to 5. The compounds of pentavalent form are most stable in solutions. Vanadium, in microamounts, is present in biological, e.g. blood, steels.

Several spectrophotometric methods for determination of vanadium have been reported. Hydroxamic acids have widely been used as reagents for solvent extraction of metals. N-Phenyl benzohydroxamic acid (PBHA) forms a violet complex with vanadium(V) in mineral acid medium (HCl), readily extractable in
chloroform. Many N-substituted hydroxamic acids have recently been reported as excellent analytical reagents for the determination of vanadium(V) and due to their successful application in determining microgram quantities of vanadium(V) these were used to determine vanadium in different samples of known or unknown composition.

In this chapter a spectrophotometric investigation for the determination of vanadium with PBHA in the presence of surfactant has been reported. The main goal of the present work is to achieve a simple sensitive and selective procedure for spectrophotometric determination of vanadium in the presence of surfactant. The preliminary work on the effect of addition of surfactants (CTAB, CPC, TX-100, Brij-35) to the Vanadium-Hydroxamic Acid complex shows a considerable increase in the absorbance, when surfactant solution is added. The purpose of the addition of surfactants is to enhance the colour reaction of the metal towards hydroxamic acid. The addition of metal ion in the presence of reagents and surfactants has much greater molar absorptivity and stability in comparison to the complex formed in the absence of surfactants. Some blood and steel samples are analysed for determining the vanadium content using the proposed procedure. The experimental procedure is given in chapter II.

7.1 RESULTS AND DISCUSSION

A new, rapid and selective procedure for spectrophotometric determination of vanadium(V) is described. It is based on the complexation reaction of V(V) with N-phenylbenzohydroxamic acid at 3.0-4.5 M hydrochloric acid, in the presence of a non-ionic surface active agent i.e. TX-100. The violet coloured complex of pentavalent vanadium exhibits a wavelength of maximum absorption at 520 nm with the molar absorptivity value of $4.4 \times 10^3$ l mol$^{-1}$ cm$^{-1}$. The coloured system is stable and obeys Beer's law upto 8.0 µg ml$^{-1}$.

The precision, in terms of relative standard deviation, of this system is ± 1.1%. The method is highly selective as many of the common ions do not interfere in the determination of V(V). Highly satisfactory results have been obtained in applying the system to a variety of complex materials for determination of V(V).

7.1.1 The Absorption Spectra

The absorption spectra, plotted for the complex formed in chloroform among V(V), TX-100 and N-phenylbenzohydroxamic acid against the respective
Fig. 7.1 ABSORPTION SPECTRA OF V(V)-TX-100-PBHA COMPLEX AND THE REAGENT BLANK IN CHLOROFORM.

(a) $[V(V)] = 50 \mu g / 10$ ml; $[PBHA] = 0.007$ M
$[HCl] = 0.04$ M; $[TX-100] = 0.05$ M

(b) $[HCl] = 0.04$ M; $[PBHA] = 0.007$ M
$[TX-100] = 0.05$ M.
Fig. 7.2  ABSORPTION SPECTRA OF V(V) - TX-100 - PBHA COMPLEX AND THE REAGENT BLANK IN CHLOROFORM.

$[\text{HCl}] = 0.04 \text{M}; [\text{PBHA}] = 0.007 \text{ M}; [\text{TX-100}] = 0.05 \text{ M}$

(a) $[\text{V(V)}] = 80 \mu\text{g} / 10 \text{ ml}$
(b) $[\text{V(V)}] = 60 \mu\text{g} / 10 \text{ ml}$
(c) $[\text{V(V)}] = 40 \mu\text{g} / 10 \text{ ml}$
reagent blank, exhibited the wavelength of maximum absorbance around 520 nm. Since the reagent blank absorbs at this region, it was used as a reference for all further measurements (Fig. 7.1). No change in the position of $\lambda_{\text{max}}$ of the complex was observed when the metal concentration was varied (Fig. 7.2).

7.12 Effect of Acidity
Varying the concentration of hydrochloric acid of the aqueous phase between 2M and 8M, it is observed that the absorption band of the chloroform extract remains intact ($\lambda_{\text{max}} = 520$ nm) but the absorbance value is affected. For maximum colour development the hydrochloric acid concentration of the aqueous phase should be between 3.0 and 4.5 M (Table 7.01 and Fig. 7.3).

7.13 Effect of Surfactant
Of the various cationic, (CTAB and CPC) anionic (SDS) and non-ionic (TX-100, Brij-35) surfactants used for intensifying the colour reaction of the V(V)-PBHA complex, only the non-ionic surfactant namely Triton X-100 (TX-100) was found to increase the colour of complex. The maximum and full colour development of the ultimate species was obtained when 0.0375 to 0.125 M TX-100 was used. Beyond the upper concentration levels, inseparable froth formation was observed which caused difficulties in absorbance measurements. In practice, 0.05 M TX-100 was used. (Table 7.02 and Fig. 7.4).

7.14 Effect of N-Phenylbenzohydroxamic Acid (PBHA)
The effect of PBHA on the extraction and complete colour formation of the complex was studied. At least 0.0047 M PBHA was necessary for the complete extraction and maximum colour development of the complex and no adverse effect was seen in net absorbance value up to 0.0164 M. In practice, 0.007 M PBHA was used in all further experiments. (Table 7.03 and Fig. 7.5).

7.15 Effect of Temperature, Electrolyte and Dilution
The absorbance of the extract was insensitive to the temperature alteration from 10 to 30°C (Table 7.04 and Fig. 7.6). The effect of presence of various electrolytes on the extraction of metal was also examined. The extraction of the electrolyte was unaffected with 1M KCl/ NH₄Cl/ K₂SO₄ solution, and neither a shift in $\lambda_{\text{max}}$ nor any change in absorbance of the complex was observed. The effect of dilution of the aqueous solution on the extraction of the electrolyte was studied. No adverse effect was observed when the volume ratio of the organic to aqueous phase...
**FIG 7.3 EFFECT OF ACIDITY ON THE FORMATION AND ABSORBANCE OF V(V)-TX-100-PBHA COMPLEX IN CHLOROFORM**

**FIG 7.4 EFFECT OF TX-100 ON THE FORMATION AND ABSORBANCE OF V(V)-TX-100-PBHA COMPLEX IN CHLOROFORM**
**TABLE 7.01**

EFFECT OF CONCENTRATION OF HCl ON THE FORMATION, AND ABSORBANCE OF V(V) - TX -100 - PBHA COMPLEX IN CHLOROFORM.

\[
\begin{align*}
[V^{5+}] & = 9.8 \times 10^{-5} \text{ M (50 µg /10 ml aq. ph.)} \\
[TX - 100] & = 0.05 \text{ M} \\
[PBHA] & = 0.007 \text{ M} \\
\lambda_{\text{max}} & = 520 \text{ nm}
\end{align*}
\]

<table>
<thead>
<tr>
<th>HCl, M</th>
<th>ABSORBANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.145</td>
</tr>
<tr>
<td>2.0</td>
<td>0.275</td>
</tr>
<tr>
<td>3.0</td>
<td>0.430</td>
</tr>
<tr>
<td>3.5</td>
<td>0.430</td>
</tr>
<tr>
<td>4.0</td>
<td>0.430</td>
</tr>
<tr>
<td>4.5</td>
<td>0.430</td>
</tr>
<tr>
<td>5.0</td>
<td>0.399</td>
</tr>
<tr>
<td>5.5</td>
<td>0.350</td>
</tr>
<tr>
<td>6.0</td>
<td>0.320</td>
</tr>
<tr>
<td>6.5</td>
<td>0.275</td>
</tr>
<tr>
<td>7.0</td>
<td>0.234</td>
</tr>
<tr>
<td>8.0</td>
<td>0.150</td>
</tr>
</tbody>
</table>
TABLE 7.02
EFFECT OF CONCENTRATION OF TX - 100 ON THE FORMATION, 
AND ABSORBANCE OF V(V) - TX -100 - PBHA COMPLEX IN CHLOROFORM.

\[ \left[ \text{V}^{5+} \right] = 9.8 \times 10^{-5} \text{ M (50 \mu g /10 ml aq. ph.)} \]
\[ [\text{HCl}] = 4.0\text{M} \]
\[ [\text{PBHA}] = 0.007\text{M} \]
\[ \lambda_{\text{max}} = 520 \text{ nm} \]

<table>
<thead>
<tr>
<th>TX - 100, M</th>
<th>ABSORBANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0125</td>
<td>0.200</td>
</tr>
<tr>
<td>0.025</td>
<td>0.301</td>
</tr>
<tr>
<td>0.0375</td>
<td>0.430</td>
</tr>
<tr>
<td>0.05</td>
<td>0.430</td>
</tr>
<tr>
<td>0.075</td>
<td>0.430</td>
</tr>
<tr>
<td>0.0875</td>
<td>0.430</td>
</tr>
<tr>
<td>0.1</td>
<td>0.430</td>
</tr>
<tr>
<td>0.125</td>
<td>0.430</td>
</tr>
<tr>
<td>0.14</td>
<td>Turbidity</td>
</tr>
</tbody>
</table>
FIG 7.5 EFFECT OF AMOUNT OF PBHA ON THE FORMATION AND ABSORBANCE OF V(III)-TX-100-PBHA COMPLEX IN CHLOROFORM.

FIG 7.6 EFFECT OF TEMPERATURE OF AQUEOUS PHASE ON THE EXTRACTION AND ABSORBANCE OF V(III)-TX-100-PBHA COMPLEX IN CHLOROFORM.
TABLE 7.03
EFFECT OF CONCENTRATION OF N-PHENYL BENZO
HYDROXAMIC ACID ON THE FORMATION, AND ABSORBANCE
OF V(V) - TX - 100 - PBHA COMPLEX IN CHLOROFORM.

\[
\begin{align*}
[V^5+] &= 9.8 \times 10^{-5} \text{ M (50 } \mu\text{g} / 10 \text{ ml aq. ph.)} \\
[HCl] &= 4.0 \text{ M} \\
[TX - 100] &= 0.05 \text{ M} \\
\lambda_{\text{max}} &= 520 \text{ nm}
\end{align*}
\]

<table>
<thead>
<tr>
<th>PBHA x 10^{-3} M</th>
<th>ABSORBANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>0.284</td>
</tr>
<tr>
<td>4.7</td>
<td>0.430</td>
</tr>
<tr>
<td>7.0</td>
<td>0.430</td>
</tr>
<tr>
<td>9.3</td>
<td>0.430</td>
</tr>
<tr>
<td>14.0</td>
<td>0.430</td>
</tr>
<tr>
<td>16.4</td>
<td>0.430</td>
</tr>
<tr>
<td>18.7</td>
<td>0.332</td>
</tr>
<tr>
<td>23.4</td>
<td>0.150</td>
</tr>
</tbody>
</table>
TABLE 7.04
EFFECT OF TEMPERATURE OF AQUEOUS PHASE ON THE FORMATION, AND ABSORBANCE OF V(V) - TX - 100 - PBHA COMPLEX IN CHLOROFORM.

\[
\begin{align*}
[V^{5+}] &= 9.8 \times 10^{-5} \text{ M (50 } \mu\text{g/10 ml aq. ph.)} \\
[HCl] &= 4.0\text{ M} \\
[TX - 100] &= 0.05\text{ M} \\
[PBHA] &= 0.007\text{ M} \\
\lambda_{\text{max}} &= 520 \text{ nm}
\end{align*}
\]

<table>
<thead>
<tr>
<th>TEMPERATURE OF AQUEOUS PHASE, °C</th>
<th>ABSORBANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.390</td>
</tr>
<tr>
<td>10</td>
<td>0.430</td>
</tr>
<tr>
<td>15</td>
<td>0.430</td>
</tr>
<tr>
<td>20</td>
<td>0.430</td>
</tr>
<tr>
<td>25</td>
<td>0.430</td>
</tr>
<tr>
<td>30</td>
<td>0.430</td>
</tr>
<tr>
<td>35</td>
<td>0.350</td>
</tr>
<tr>
<td>40</td>
<td>0.320</td>
</tr>
<tr>
<td>45</td>
<td>0.300</td>
</tr>
</tbody>
</table>
was varied from 2.1 to 1.5. Hence, in all extraction work an equi volume of each phases (10 ml) was kept.

7.16 Extraction Period, Stability of The Extract and Order of Addition of Reagents

A shaking period of 2 min. was sufficient for complete colour development of the extract. No change in absorbance of the extract was observed upto an extraction time of 10 minutes. The colour of the extracted complex remained unchanged for atleast 2 hrs. at room temperature (28 ± 2 °C). The sequence, in which the reagents were added, was not critical.

7.17 Beer’s Law and Its Correlation Coefficient, Molar Absorptivity, and Detection Limit

The coloured V(V) -TX100-PBHA complex in chloroform adhered to the Beer’s law up to 80 μg of the metal in a 10 ml ultimate solution at $\lambda_{max}$ 520 nm, with a correlation coefficient value of 0.999 (Table 7.05, Fig.7.7). This method is applicable for detection of V(V) down to a concentration level of 0.1 μg V(V) ml⁻¹ aqueous solution.

7.18 Precision of The Method

In order to have the knowledge of precision of the method, ten independent determinations each containing 50.0 μg of V(V)/10 ml organic phase were taken. The mean absorbance value, 0.430 and a standard deviation value ± 0.0047 was achieved which gave a relative standard deviation of ± 1.1%. The confidence limit of the system at 95% probability was found to be 4400± 30 l mol⁻¹ cm⁻¹.

7.19 Effect of Diverse Ions

The effect of various diverse ions, which may associate with the analyte, on the extraction of 50.0 μg V(V) was studied. Almost all anions and cations examined did not interfere. The only interference caused by Fe(III) was minimised by the addition of trisodium phosphate prior to the extraction of V(V). The tolerable amount of various diverse ions is summarised in Table 7.06.

7.2 APPLICATION OF THE PROPOSED METHOD

An attempt was made to determine vanadium in human blood and steel samples by the proposed method. The standard addition method was used for determination of vanadium(V) in these samples.
FIG. 7.7 PLOT OF BEER'S LAW DATA FOR V(V) AS V(V) - TX-100-PBHA COMPLEX IN CHLOROFORM.
TABLE 7.05
BEER'S LAW FOR THE DETERMINATION OF V(V) WITH TX-100 AND PBHA

\[
\begin{align*}
[HCl] & = 4.0 \text{M} \\
[TX-100] & = 0.05 \text{M} \\
[PBHA] & = 0.007 \text{M} \\
\lambda_{\text{max}} & = 520 \text{ nm}
\end{align*}
\]

<table>
<thead>
<tr>
<th>V(V) / μg</th>
<th>ABSORBANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.043</td>
</tr>
<tr>
<td>10</td>
<td>0.08</td>
</tr>
<tr>
<td>30</td>
<td>0.26</td>
</tr>
<tr>
<td>50</td>
<td>0.430</td>
</tr>
<tr>
<td>70</td>
<td>0.61</td>
</tr>
<tr>
<td>80</td>
<td>0.69</td>
</tr>
</tbody>
</table>
### TABLE 7.06

**EFFECT OF DIVERSE IONS**

\[ [V^{5+}] = 9.8 \times 10^{-6} \text{M} \ (50 \mu g / 10 \text{ ml aq. ph}) \]

<table>
<thead>
<tr>
<th>IONS</th>
<th>ADDED AS</th>
<th>TOLERABLE AMOUNT / mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>CuSO(_4).5H(_2)O</td>
<td>20</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>Pb (CH(_3) COO(<em>2</em>))</td>
<td>35</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>NiSO(_4).6H(_2)O</td>
<td>18</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>K(_2) CrO(<em>4</em>)</td>
<td>12</td>
</tr>
<tr>
<td>Mn(^{7+})</td>
<td>KMnO(<em>4</em>)</td>
<td>50</td>
</tr>
<tr>
<td>Mn(^{6+})</td>
<td>(NH(_4))(_6) Mo(_2)O(_4).4H(_2)O</td>
<td>5</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>Fe (NO(_3))(<em>3</em>)</td>
<td>10*</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>Al (NO(_3))(<em>3</em>) 9H(_2)O</td>
<td>10</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>Ba (NO(_3))(<em>2</em>)</td>
<td>5</td>
</tr>
<tr>
<td>Bi(^{3+})</td>
<td>Bi (NO(_3))(<em>3</em>) 5H(_2)O</td>
<td>5</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>3 CdSO(_4).5H(_2)O</td>
<td>10</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>CoSO(_4).7H(_2)O</td>
<td>7</td>
</tr>
<tr>
<td>SO(_4)(^{2-})</td>
<td>Na(_2)SO(<em>4</em>)</td>
<td>10</td>
</tr>
<tr>
<td>NO(_3)(^{-})</td>
<td>NaNO(<em>3</em>)</td>
<td>10</td>
</tr>
<tr>
<td>PO(_4)(^{3-})</td>
<td>Na(_3)PO(<em>4</em>)</td>
<td>10</td>
</tr>
</tbody>
</table>

* Masked with 2 mg trisodium phosphate

* Causing error in absorbance of ±< 2%
### Table 7.07
**Recovery of Vanadium(V) from Blood and Steel Samples**

<table>
<thead>
<tr>
<th>Sample and Source</th>
<th>Weight of Sample</th>
<th>Vanadium(V), µg</th>
<th>Relative Error %</th>
<th>Relative Standard Deviation of Present Method ±%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blood, obtained from Medical Coll. Ripur</td>
<td>5g</td>
<td>50, 51.0</td>
<td>+1.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Steel, obtained from Bhilai Steel Plant, Bhilai</td>
<td>1g</td>
<td>50, 51.5</td>
<td>+2.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

n = 5 determinations were performed

Normal vanadium content of sample was negligible
7.21 Procedure For Determination of V(V) In Blood samples

About 5 gm. of blood sample was transferred to a 100 ml kjeldahl flask with a small funnel in its mouth. 0.5 gm. of potassium sulphate and 5 ml of concentrated nitric acid was added into it, and heated gently for guarding against too vigorous initial reaction. Digestion was then proceeded moderately rapidly by increasing the temperature without too greater loss of nitric acid. The solution was evaporated to dryness and cooled, and then 1 ml of sulphuric acid and 5 ml of nitric acid was added and evaporated gently to fumes. This procedure was repeated for three times. About 2 ml of nitric acid, 1 ml of 5 ml sulphuric acid and 25 ml of water was added to the ash and digested on a water bath for 30 minutes. Then the flask is transferred to hot plate and evaporated to fumes. A light yellow clear solution was obtained after cooling and adding 25 ml of water to it.

7.22 Procedure For Determination of V(V) In Steel Sample

About 1 gm. of steel sample was transferred to a 500 ml beaker with 3 ml nitric acid and heated. For evaporation of NO₃ ions more 2-3 ml HCl were added and heated up to dryness. It was dissolved in distilled water in a 25 ml volumetric flask. For the analysis of vanadium, after filtration portions of solutions were taken from volumetric flask.

7.23 Procedure For Blank Test

For each determination of vanadium, a blank digestion is carried out at the same time with the same amount of sample and oxidising agents as are needed for digesting the bio sample to which vanadium is added externally.

7.3 CONCLUSION

The present method described above is the modification made over the classical PBHA method. The introduction of a non-ionic surfactant i.e. Triton X-100 intensifies the colour reaction of V(V)-PBHA complex to 2-folds. The method is highly selective as most of the common ions tested do not interfere. The molar absorptivity of the complex is $4.4 \times 10^3$ l mol⁻¹ cm⁻¹. The method followed Beer's law upto 8.0 μg ml⁻¹ of final organic phase. The present method has been found suitable for the determination of vanadium(V) in a variety of complex materials.

By proper choice of surfactant systems it is possible to enhance the stability, selectivity and sensitivity of analytical reactions. Thus, the micelles offer a potential system for application in future, although it must be realized that a great deal of study is needed in order to understand their stability and specificity.
7.4 CONCLUSION, PERSPECTIVES AND GUIDELINES FOR FUTURE WORK

Recently hydroxamic acids have attracted curiosity of scientists due to their structural complexity\textsuperscript{31-33} and its potential application as drug delivery agents\textsuperscript{34-35} for the treatment of pathogenic infections. Explosive increment of research activities in biological applications of hydroxamic acids is going on. In addition to their applications in medicine, it is expected that metal complexes of chiral hydroxamic acids may find use in selective DNA cleavage\textsuperscript{36} and stereospecific epoxidation of allylic alcohols.\textsuperscript{37}

Previous work in our laboratory has dealt with the thermodynamics, kinetics\textsuperscript{38-40} of hydrolysis mechanism of hydroxamic acids. The hydroxamic acids which shows high hydrolytic stability in mineral acid media should obviously be preferred for solvent extraction, spectrophotometry and biological applications. Most important reactions occur not in a homogeneous solution but an interface. Many industrially important processes occur on the surfaces of solid catalysts, and nearly all biological reactions take place at gas - liquid interfaces. The high rates and specificities of these reactions has prompted a search for model systems which mimic, at least to some extent, the biological catalysts.\textsuperscript{41-43} The term "Biomimetic Chemistry" has been coined to describe this general subject, and "Membrane Mimetic Chemistry" is that aspect of the subject which is related to reactions at interfaces. Surfactants properties have attracted growing attention for use in biochemistry, biological and chemical research applications. An important characteristics of reactions in micellar systems is that the micellar concentration can be varied to some extent. In a usual solvent it is almost impossible to avoid side reactions. In a micellar system, on the other hand, side reactions can be avoided by adjusting the concentrations of reactants and micelles so that most micelles contain just one reactant molecule.

Therefore, studies in the presence of micelles would be of considerably more relevance. A study of the hydrolysis in the presence of micelles be a better model than studies in water from which to draw conclusions concerning the stability of hydroxamic acids in biological and analytical systems. Our present work then is an attempt to contribute to this field.

The novel feature of this investigation is that it provides a judicious and rational kinetic basis for the choice of an organic analytical reagent from the family of hydroxamic acids. Surfactants in some cases, have been shown to increase the sensitivity of the colour reaction of substrate - metal complexes with greater solubility and higher stability which is much needed property in quantitative spectrophotometric determination of metals. The present study has been one such attempt in this direction when N-phenylbenzohydroxamic acid (PBHA) has been selected to study complexation behaviour with vanadium(V) in the presence of surfactants.
Our main aim was to analyse the acidic and alkaline hydrolysis reaction of hydroxamic acids from a mechanistic point of view, and therefore our most of the results were focused on kinetic and mechanistic aspects of different hydroxamic acids in micelles. We didn't consider analytical application in detail. The structure of micelles was considered only to the extent needed to understand reactivity.

For acidic hydrolysis in the presence of cationic, anionic and non-ionic surfactants at fixed concentrations of HCl and substrate, the reaction rate decreased as the surfactant concentration was increased. This behaviour probably because of the combination of three effects operating in the same direction: (i) the $[H^+]$ is reduced from the micellar region as degree of ionic dissociation $\alpha$ increases; (ii) the increase of the molar reactions volume, which produces a dilution of both reactants in the micellar region; and (iii) a probable change in the apparent dielectric constant of the reaction site in the micelle. The situation is different for the hydrolysis in alkaline medium, because here rate constants increase with concentration of surfactants. The Pseudo-phase model and Pisziewicz model have also been successfully to kinetic data. Salt, solvent and substituent effects have been carefully investigated.

The present work appears to be most systematic and extensive study on the subject. As has been explained earlier about the aim of the present work, the results reported in this thesis show that the goal has been achieved to quite a good extent. These studies have provided answers for old questions and raised new horizons. There are unanswered questions regarding surface and thermodynamic properties, of surfactants, applicability of various models, kinetics in mixed-micelles etc. and calculation of micellar aggregation number by NMR spectroscopy etc. Micellar catalysis have attracted growing attention for use in biochemistry, biological and chemical research applications. Recently a micellar system has been developed that simultaneously destroys environmental contaminants by oxidative and hydrolytic path ways.

More detailed studies are needed which are at present being done in our laboratories by other workers. The present work, therefore may be treated as a part of group research undergoing in our laboratory. Many more generalisation and facts are expected to come out when this project gets completed. The list of possibilities is endless and limited only by imagination. The coming years promise to provide additional exciting and challenging opportunities for the study of micellar hydrolysis of hydroxamic acids. Perhaps one day all chemical reactions will be routinely performed under micellar environment, and the present use of simple mono-component phases will seem a primitive approach.
REFERENCES


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