Microemulsions As Reaction Media For Acid Hydrolysis of Hydroxamic Acids
6.0 INTRODUCTION

A phenomenon closely related to the formation of micelles is the building up of thermodynamically stable emulsions, so-called microemulsions. In the preceding chapters acidic and alkaline hydrolysis of a trihydroxamic acid, desferal have been discussed. It is observed that micelles are quite capable of modulating the reaction kinetics. Rate of reaction is accelerated or inhibited depending upon the nature of interactions among substrate, the acid and the surfactant. In the present investigation it is planned to study reactivity of hydroxamic acids in microemulsions and to explore the effectiveness of its catalysing ability. A brief summary of different types of chemical reactions in microemulsion media have already been presented in Chapter I of this thesis.

Microemulsions are transparent dispersions containing water, oil, a surfactant, and a cosurfactant, which is usually a medium chain length alcohol. The structure and properties of microemulsions were investigated by Schulman et al., who employed various techniques such light scattering, X-ray diffraction, electron microscopy, ultracentrifugation, electrical conductivity, and viscometry. There has been much debate about the use of the term microemulsion to describe such systems and various workers have proposed many other terms. The formation and physical properties of microemulsions are influenced by the alkyl chain length of alcohol and hydrocarbons. Four component systems of surfactant, cosurfactant, oil and water have many

* a part of this work is communicated to Journal of Dispersion Science & Technology, paper under revision
* a part of this work is communicated to Journal of Molecular Liquids
important features and are most studied microemulsion systems. The reason for the significance of these systems is that the introduction of cosurfactant greatly extends the isotropic solution region, especially with single-chain ionic surfactants. In many cases microemulsions can be regarded as rather monodisperse droplets of oil-in-water (o/w) or water-in-oil (w/o). Microemulsions without the addition of cosurfactant are also prepared. Best example in this category are AOT (sodium bis (2-ethyl-1-hexyl) sulfosuccinate)/hydrocarbon/water microemulsions.

In the last few years the interest appears to have strikingly shifted towards w/o microemulsions. The main reason for this is probably the opportunity to investigate the structure of water in the hydrocarbon environment in the presence of surfactant: in particular its dependence on water concentration, influence on the micellar membrane by the hydrophobic hydration and the sensitivity of the water structure on additives (salt and hydrocarbon). Moreover, the discovery of a remarkable catalytic activity has considerably fostered the research on this type of emulsion.

The interest in the structure of water in microemulsions is due to its possible effects on the reactivity of dissolved molecules and the possible applications of these simple systems as models of complex biological structures containing trapped water. The studies on the structure of water in microemulsions have used numerous techniques: electron solvation measurement, NMR and ESR spectroscopy, UV-vis spectroscopy, small angle neutron, X-ray, and light scattering, fluorescence decay, microcalorimetry, and IR and Raman spectroscopy.

Water-in-oil (w/o) microemulsions contain aqueous microdroplets trapped in a film of surfactant and dispersed in a low-polarity bulk solvent. The reagents present in the medium may be separated in different microscopic phases or may share the same phase, and the kinetics of their reactions will
reflect their various distributions. On these premises, the prediction or interpretation of the kinetic influence of these media is relatively easy when both reagents congregate in the aqueous microdroplets, which act as variable size nanoreactors concentrating the reagents. Less attention has been paid to reactions in which the reagents are distributed in aqueous and apolar phases and at their interface.

From the viewpoint of chemical reactivity, owing to the existence of large internal interfaces and the unusual state of water in the droplets, the w/o microemulsions have attracted great interest because they can be used as substitutive novel media capable of significantly altering the rates of chemical and biochemical reactions compared with their rates in bulk water.

Among the surfactants capable of forming reversed micelles and microemulsions, Aerosol OT has a remarkable ability to solubilize large amounts of water, up to water-to-surfactant mole ratios of 40-60, according to the surrounding non-polar medium. The most often used microemulsion is the AOT/water/isooctane system, in which droplet size is controlled by water/AOT mole ratio. Depending on the water/AOT mole ratio, the size of the water pool in microemulsions can be altered and they can be made to acquire properties much different from the bulk water.

Microemulsion droplet can be considered as a minireactor where certain chemical reactions take place within the very small domain provided by the droplet. The presence of the droplet can enhance or retard chemical reaction rates by large factors. In recent years, microemulsions, therefore, have found increasing uses as potential reaction media both for kinetic and equilibrium studies.

The results obtained for reactions in microemulsion media has been quantitatively explained by applying the pseudophase model generally
used for reactions in micellar systems. The microemulsions are assumed to be divided into three regions corresponding to the oil-rich domain, central aqueous core, and the surfactant interfacial region. The reagents are distributed between the three pseudophases according to their solubilities, and the global rate of reaction will be the sum of the rates in the different pseudophases.

A large number of publications available describing organic, inorganic and biochemical reactions in microemulsions. Hydroxamic acids are the derivatives of carboxylic acids and has enormous use in the field of chemical, biological and medicinal sciences. Many works appeared on the hydrolysis of the hydroxamic acids in aqueous and in micellar media catalyzed by acids or bases. It is for the first time that an effort has been taken to study its hydrolytic behaviour in microemulsion media. No publication has appeared on hydrolysis of such compounds in microemulsions, as per author's knowledge.

This Chapter has been divided into two parts; (A) and (B). Part (A) describes the acid hydrolysis of N-hydroxyphthalimide (I) or phthalamohydroxamic acid (PHA) in AOT/isooctane/water microemulsions and in part (B) acid catalysed hydrolysis of salicylhydroxamic (II) in microemulsions of AOT/isooctane/water is discussed. The hydrolyses have been carried out at constant acid concentration ([HCl] = 0.1 mol dm$^{-3}$) for both the compounds. It is tried to study the reactivity of hydroxamic acids in Cetyltrimethylammonium bromide/sodium dodecyl sulphate – n-butanol–n-hexane microemulsions but kinetics was not successful.

$\text{H-N-OH}$

$\text{N-hydroxyphthalimide (I)}$

$\text{OH}$

$\text{Salicylhydroxamic acid (SHA) (II)}$
6.1 PART (A) : ACID CATALYZED HYDROLYSIS OF N-HYDROXYPHTHALIMIDE IN AOT/ISOOCTANE/WATER MICROEMULSIONS:

6.11 Present Investigation

Microemulsion may show certain unique solvent properties. They can influence both reaction kinetics and reaction equilibria\textsuperscript{83-85}. It has been proved that the presence of the microemulsion droplets can enhance or retard chemical reactions\textsuperscript{46-54} depending on the nature of the surfactant, the nature of the oil phase and the size of the water pool present in the medium. In this work, the results obtained for the acid catalyzed hydrolysis of N-hydroxyphthalimide (PHA) in AOT - isoctane - water microemulsions are presented. The dependence of rate constant on the surfactant concentration and water concentration has been investigated. The choice of AOT as surfactant was based on the fact that it allows the solubilization of a considerable amount of water in the bulk of different organic compounds without necessity of adding a cosurfactant\textsuperscript{\textsuperscript{12}}. Iso-octane (2,2,4 trimethylpentane) has a structure similar to the tail structure of AOT and thus has the best penetration into AOT tails\textsuperscript{\textsuperscript{85}}. (Fig. 6.1).

(a) Iso-octane (2, 2, 4-trimethylpentane)

(b) AOT (Aerosol-OT, Sodium bis (2-ethyl hexyl) sulfo succinate)

Figure 6.1
N-hydroxyphthalimide (PHA) has recently been recognized as a valuable catalyst for the oxidation of various organic compounds. To date no kinetic data for the hydrolysis of hydroxamic acids in microemulsions has been reported in the literature.

PHA shows $\lambda_{\text{max}} = 300$ nm in aqueous and neutral microemulsion media (Fig. 6.2) but in acidic microemulsion medium a hypsochromic shift was observed. The reaction was followed at 284 nm. The $\lambda_{\text{max}}$ of the PHA in microemulsions in acidic condition. Surfactant, oil, water ratio were varied to study the impact of these components on reaction rate. Pseudo first order rate constants have been obtained with a standard deviation below 0.5% (Fig. 6.3). All measurements were carried at 55°C and the microemulsion is quite stable at high temperature. The reactions were carried out in 0.1 mol dm$^{-3}$ HCl concentration and concentration of PHA was $2.5 \times 10^5$ mol dm$^{-3}$ in all experiments.

6.12 Results and Discussion

The size of the water pool has pronounced effect in controlling reaction rates. It has been found that the physical properties of solubilized water are quite different from the properties of bulk water especially at the low levels of hydration of the head groups. At higher concentrations the water in the micellar interior behaves like bulk water. In the present study reaction has been carried out at low $\omega$ [$\text{Water}$/ [AOT] values to investigate the indifferent catalytic properties of water pool of microemulsion. The aqueous core radius ($r$) has been calculated by using the equation (1).

$$r \ (\text{Å}) = 36.65 \frac{\nu}{g}$$

where $\nu$ and $g$ are weight percentages of water and AOT respectively (Table 6 1). There are instances where such differences of the properties of water pool at low
Fig. 6.2  UV spectra of PHA in aqueous (A) and in neutral microemulsion (B) media.
Fig. 6.3 - Successive spectral scans during the hydrolysis of PHA \((2.5 \times 10^{-5} \text{ mol dm}^{-3})\) in the presence of HCl \((0.1 \text{ mol dm}^{-3})\) in the microemulsion medium. \((\omega = 4.9)\)

1. After mixing
2. after 10 min.
3. after 25 min.
4. after 45 min.
5. after 65 min.
6. after 85 min.
7. after 100 min.
water/surfactant mole ratio have distinct effect on the reaction studied in them compared to the high water/surfactant mole ratios.

**Table 6.1**: Observed rate constant for the hydrolysis of PHA at different \( \omega \) values.

<table>
<thead>
<tr>
<th>( \omega )</th>
<th>( z )</th>
<th>( r(A^+) )</th>
<th>( k_{obs} \times 10^6 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>8.5</td>
<td>6.1</td>
<td>14.4</td>
</tr>
<tr>
<td>4.9</td>
<td>8.3</td>
<td>7.33</td>
<td>16.6</td>
</tr>
<tr>
<td>6.6</td>
<td>8.1</td>
<td>9.77</td>
<td>18.8</td>
</tr>
<tr>
<td>8.2</td>
<td>7.8</td>
<td>12.2</td>
<td>19.2</td>
</tr>
<tr>
<td>10.7</td>
<td>7.4</td>
<td>15.9</td>
<td>19.3</td>
</tr>
<tr>
<td>12.3</td>
<td>7.1</td>
<td>18.3</td>
<td>19.6</td>
</tr>
</tbody>
</table>

\( k_w = 5.06 \times 10^{-6} \text{s}^{-1} \) \( \omega = [\text{H}_2\text{O}]/[\text{AOT}] \) \( z = [\text{isoctane}]/[\text{AOT}] \)

The possible mechanism of acid catalyzed hydrolysis of PHA in the aqueous phase can be represented by Scheme I. The reaction rate is controlled by the rate

![Scheme I](image-url)
limiting attack of water on protonated substrate and the reaction is first order each in substrate and [acid]. Further, the values of $k_{\text{obs}}$ are independent of the initial [PHA]. Since PHA is highly soluble in water, the hydrolysis is expected to take place in water phase of the microemulsion or in the interfacial region. The observed rate constant at different $\omega$ values are given in Table 6.1.

A pseudophase model, analogous to that widely used in micellar catalysis and which assumes competition between possible reaction in three microphases (oil, water and the interface) has been proposed\textsuperscript{34}. However, its scope is presently limited to reaction occurring a prion in one microphase only\textsuperscript{55-56}. This is, in particular, the situation when the two reagents are hydrophilic so that they can react together only in water phase\textsuperscript{38} or when a hydrophilic substrate reacts with a hydrophobic reagent so that the reaction must necessarily occur at the interphase\textsuperscript{34,55,56}. The local reagent concentrations and rate constants are, therefore, readily obtained from a single-phase model since the complete kinetic equation is greatly simplified. In the present work problem is oversimplified because the reagent (H\textsuperscript{+} ion) and the substrate (PHA) both are hydrophilic. Hence the reaction is supposed to occur in water core and in the interface. $\omega = 12.3$ has been chosen as the higher limit of the investigated microemulsion range. Therefore, in this system there is no bulk water because it is generally agreed that below $\omega = 13$ there is no bulk water but only bound water\textsuperscript{85}. Secondly, as shown in Scheme 1, both transition state and the reagent H\textsuperscript{+} ion are positively charged, so they are greatly adsorbed at the interface by the negatively charged head groups of AOT. It is therefore believed that the interfacial region has got key role to control the kinetics of such hydrolysis reaction. In the second step of the mechanism there is an attack of water molecule on transition state to form product. Hence activity of water molecule also plays a vital role in this kinetic study. Since both the reagents and the substrate are highly water soluble, the pseudophase model can not be constructed here\textsuperscript{85}. Furthermore, absence of bulk water ($\omega < 13$) rejects the possibility of exchange of reagent and PHA from bulk aqueous phase to interfacial region. It is therefore believed that the only factor influencing the rate
of reactions are encased water and AOT. Fig. 6.4 shows a model of the reaction conditions prevailing in AOT microemulsions.

![Fig. 6.4 - A schematic model of the AOT/iso-octane/water microemulsion system protonated PHA is shown to be entrapped in aqueous core.]

The rate of reaction is about three to four times greater in microemulsion medium compared with aqueous medium. Increase in observed rate constant is not linear with $\omega$. A sharp jump in $k_{obs}$ has been observed from $\omega = 4.0$ to $\omega = 8.2$ after that this increase becomes insignificant. Water activity values, $a_w$, in various AOT-oil-water microemulsion have been determined. In all cases, a decrease of water activity by decreasing the molar ratio, $\omega$, was found and this diminution was related to the interaction of water molecules with the ions which come from the surfactant.

In the case of AOT–iso-octane–water microemulsion, $a_w = 0.82$ for $\omega = 5.86$ and $a_w = 0.97$ for $\omega$ from 20 to 54. In the microemulsion of lower $\omega$ value having low water activity reagent molecules are easily available to substrate for the reaction to take place. Therefore, a large increase of the reaction rate was observed compared with the reaction in aqueous phase at the lower $\omega$ values. A jump in the rate constant from $\omega = 4.0$ to 8.2 may be explained by the fact that by increasing molar ratio of water availabilities of water molecules increases at the interface due to increase of water activity. This increase at the $\omega$ values greater than 8.2 is not sharp due to decrease of reactant effective concentration.
The effect of surfactant concentration on reaction rate has been studied by varying the concentration of AOT at constant $\omega = 12.3$. The results have been shown in Table 6.2.

Table 6.2: Effect of [AOT] on the rate at constant $\omega = 12.3$ at 55°C

<table>
<thead>
<tr>
<th>Water/AOT/Iso-octane</th>
<th>% of AOT</th>
<th>$k_{\text{obs}} \times 10^5$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/30/55</td>
<td>30</td>
<td>19.6</td>
</tr>
<tr>
<td>17.5/35/47.5</td>
<td>35</td>
<td>15.3</td>
</tr>
<tr>
<td>20/40/40</td>
<td>40</td>
<td>14.5</td>
</tr>
<tr>
<td>22.5/45/32.5</td>
<td>45</td>
<td>11.7</td>
</tr>
<tr>
<td>25/50/25</td>
<td>50</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The pseudo first order rate constant decreases linearly with [AOT] at constant $\omega$. (Fig. 6.5). It is often reported that the reaction rate influencing effect in microemulsion medium depends on $\omega$ but is independent of the concentration of amphiphile. The results presented in Table 6.2 are contradictory to this.

![Graph showing the variation of $k_{\text{obs}}$ with [AOT] at constant $\omega = 12.3$.]
expectation. The following arguments can be made to explain this decrease of \( k_{\text{obs}} \) at constant \( \omega \). Since majority of reaction takes place at interface the concentration of reagent is diluted by increasing the concentration of AOT. Furthermore, at the \( \omega = 12.3 \) where interaction between counterions and water is considerably lowered, the concentration of counterions near the interfacial region increases and the \( \text{H}^+ \) ions concentration is effectively lowered at this region. The ratio of \( \text{Na}^+ \) to \( \text{H}^+ \) in the interfacial region is getting larger and the \( \text{H}^+ \) concentration within the totality of the micelles is going down.

6.13 Effect of Temperature on Reaction Rates

Effect of temperature on reaction rate has been studied by carrying out reaction both at high and low temperatures at \( \omega = 4.9 \). Table 6.3 summarizes the kinetic activation parameters obtained from the temperature dependence of the rate constant. In higher temperature the systems remain stable, microemulsion showing perfect transparency.

Table 6.3: Activation parameters for the acid hydrolysis of PHA in AOT/isoctane/water

<table>
<thead>
<tr>
<th>( \omega = [\text{H}_2\text{O}/\text{AOT}] )</th>
<th>Temp. (°C)</th>
<th>( k_{\text{obs}} \times 10^5 \text{ s}^{-1} )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta G^\circ )</th>
<th>( \Delta S^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td>45</td>
<td>2.60</td>
<td>58.9</td>
<td>56.4</td>
<td>102.9</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>5.06</td>
<td>58.9</td>
<td>56.4</td>
<td>102.9</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>9.72</td>
<td>58.9</td>
<td>56.4</td>
<td>102.9</td>
</tr>
<tr>
<td>4.9</td>
<td>45</td>
<td>10.8</td>
<td>30.1</td>
<td>25.6</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>16.8</td>
<td>30.1</td>
<td>25.6</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>20.2</td>
<td>30.1</td>
<td>25.6</td>
<td>97.3</td>
</tr>
</tbody>
</table>

The large negative value of entropy confirms the bimolecular mechanism as given in Scheme I. The difference in entropy of activation in the aqueous and
microemulsion media also gives hint that the transition state might be undergoing some structural modification in the microemulsion medium. The lowering of $E_a$ and $\Delta H^*$ values in microemulsion medium supports the catalysis of the reaction through preferential incorporation of PHA in the microdroplets of water to favorably react with $H^+$.

6.14 Conclusion

The results presented led to the following conclusions:

I Reaction rate for the acid hydrolysis of PHA is three to four times higher in microemulsions compared to reaction in pure water.

II Pseudo-first order rate constant increases appreciably up to $\omega = 8.8$, and at higher values of $\omega$ its increases becomes insignificant.

III Reaction rate decreases linearly with the increasing percentage of AOT.

IV Large negative value of entropy confirms bimolecular mechanism as suggested in Scheme 1.

V Reaction is assumed to take place at interface. Pseudophase model is not applied because of least possibility of exchange of ions at the selected range of $\omega$. 
6.2 PART (B) : ACID CATALYZED HYDROLYSIS OF SALICYLHYDROXAMIC ACID IN AOT/ISOOCTANE/WATER MICROEMULSIONS :

6.21 Present Investigation

In part (A) of this Chapter acid hydrolysis of a cyclic hydroxamic in most widely used three component AOT/isooctane/water microemulsions has been discussed. The microemulsion media proved to be an excellent catalyst for the hydrolysis reaction. The profound impact of this medium on reaction rate encourages repeating the same experimental procedures with same ternary microemulsion system for a linear hydroxamic acid. The compound selected for this study is salicylhydroxamic acid (SHA). Salicylhydroxamic acid is an antitubercular agent. Urbanski\(^3\) found salicylhydroxamic to be equivalent (by percent survival index) at 250 mg/kg (route unspecified) against an experimental infection mice to PAS at 500 mg/kg.

The SHA has \(\lambda_{\text{max}} = 296\) nm in aqueous and neutral microemulsion media which is very close to the \(\lambda_{\text{max}}\) of PHA (Fig. 6.6). A hypsochromic shift was observed in acidic microemulsions. The reaction was followed at 284 nm, the \(\lambda_{\text{max}}\) of SHA in microemulsions, in acidic conditions. The dependence of rate constant on the surfactant concentration and water concentration has been investigated. Pseudo-frist order rate constants have been obtained with a standard deviation below 0.5% (Figs. 6.7 and 6.8). All measurements were carried at 55°C. 0.1 mol dm\(^{-3}\) HCl concentration was maintained in all measurements. The reactions were carried out at different water/AOT mole ratio (\(\omega\)) to study the impact of water core on reaction rate. Effect of AOT concentration has also been studied by varying AOT concentration at a fixed \(\omega\). Effect of temperature on reaction rate is investigated by carrying out reaction at 45 and 55°C. System was found to be more stable at 45°C.
Fig. 6.6 - UV spectrum of SHA in aqueous medium.
Fig. 6.7 - Successive spectral scans during the hydrolysis of SHA in the presence of HCl (0.1 mol dm$^{-3}$) in the microemulsion medium. ($\omega = 4.9$)

(1) After mixing, (2) after 22 min., (3) after 32 min., (4) after 45 min., (5) after 67 min., (6) after 82 min., (7) after 101 min.
Fig. 6.8 - Successive spectral scans during the hydrolysis of SHA in the presence of HCl (0.1 mol dm$^{-1}$) in the microemulsion medium. ($\omega = 8.2$)

(1) After mixing, (2) after 10 min., (3) after 20 min., (4) after 43 min., (5) after 68 min., (6) after 83 min.
6.22 Results and Discussion

In anhydrous media surfactants form small polydisperse aggregates. Increasing the concentration of surfactant-entrapped water results in the formation of water-in-oil microemulsion. In microemulsions, the polar head group and counterions of the surfactant perturb a significant fraction of the water in the pool. This effect is emphasized in small water pools. It is found that, in small water pools, a fraction of the water molecule solvate Na⁺. These water molecules are considered to be bound. For \( \omega \leq 12 \), in addition to these bound water molecules, interfacial water molecules are present which are held to the sulfonate or carboxyl groups of AOT by ion-dipole or hydrogen bonds. For \( \omega > 12 \), water excess of bound and interfacial molecules forms the central water pool, which has a comparatively higher mobility. The immobilized water pools provide the medium for very large and highly specific rate enhancement, and thus resemble the hydrophilic pockets of enzymes. The size of water pool depending upon the value of \( \omega \) is depicted in Fig. 6.9.

![Diagram](image)

**Fig. 6.9** Size of the water pool in w/o microemulsions depending on \( \omega \)
(a) water pool at \( \omega = 5 \),  (b) water pool at \( \omega = 10 \)
The interesting results obtained with microemulsions in earlier experiments provided an inspiration to probe the anomalous nature of the water present in the core of these microemulsions. The results obtained are shown in Table 6.4. Surprisingly, the hydrolytic behaviour of SHA in microemulsions does not resemble to that of PHA. Selecting the same range of $\omega$, it is observed that rate first increases up to certain optimum value of $\omega$ then decreases. This behaviour is similar to that of hydrolysis of hydroxamic acids and similar compounds in micellar media where occurrence of a rate maxima is quite common. In Table 6.4 rate

Table 6.4: Observed rate constants for the acidic hydrolysis of SHA at different $\omega$ values

<table>
<thead>
<tr>
<th>$\omega^b$</th>
<th>$z^b$</th>
<th>$r(A^c)$</th>
<th>$k_{obs} \times 10^5$, $s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>8.5</td>
<td>6.10</td>
<td>12.2</td>
</tr>
<tr>
<td>4.9</td>
<td>8.3</td>
<td>7.33</td>
<td>13.3</td>
</tr>
<tr>
<td>6.6</td>
<td>8.1</td>
<td>9.77</td>
<td>13.9</td>
</tr>
<tr>
<td>8.2</td>
<td>7.8</td>
<td>12.2</td>
<td>14.6</td>
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<tr>
<td>10.7</td>
<td>7.4</td>
<td>15.9</td>
<td>41.8</td>
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<tr>
<td>12.3</td>
<td>7.1</td>
<td>18.3</td>
<td>29.5</td>
</tr>
</tbody>
</table>

$r_1 = k_{obs}$ at 55°C, $r_2 = k_{obs}$ at 45°C, $\omega = \frac{[H_2O]}{[AOT]}$, $z = \frac{[isooctane]}{[AOT]}$

constant of SHA in aqueous acidic medium is not presented for comparison because reaction is too low to be predicted within a measurable time span.

The presence of a rate maximum in the kinetic investigation in microemulsion media is uncommon. Results of different kinetic studies in these reaction media show that at constant AOT concentration the rate of reaction is inversely proportional to the molar ratio $\omega$. However, Garcia-Rio et al. recently observed
a direct relationship between \( \omega \) and the rate constant for solvolysis of substituted benzoyl chloride in AOT/isoctane/water microemulsions. The reaction is assumed to take place at the interface via dissociative mechanism.

It is relatively easier to explain very high reaction rate in microemulsions of low water content. The substrate SHA and the catalyst \( H^+ \) ion both are hydrophilic. Their effective concentration increase in the aqueous microdroplets, which act as variable size nanoreactors. In the microemulsions of low \( \omega \) value the water molecules are bound to the polar head groups of AOT. Additional water molecules occupy the core of the droplet, and their properties resemble bulk water. The two types of water coexist, but exchange between the two states is fairly rapid. In the hydrolysis of SHA, the rate of reaction is controlled by the rate limiting attack of water molecules on the protonated substrate (Scheme II). The concentration of these positively charged activated molecules becomes higher in the interfacial region due to electrical interactions among the negatively charged head groups of AOT and the positively charged activated substrate. Since water molecules remain bound to the AOT heads in this region, they are readily available to the substrate for their hydrolysis.

\[
\begin{align*}
\ce{C=O} + \ce{H^+} & \text{ (fast)} \rightarrow \ce{C-\text{NH}} + \ce{2H^+} \\
\ce{\text{OH}}^- & \rightarrow \ce{\text{O}^-} \\
\ce{\text{C}} & \rightarrow \ce{\text{C}^+} \\
\ce{\text{NH}_2OH}^- & \rightarrow \ce{\text{NH}_2OH} \\
\ce{\text{OH}}^- & \rightarrow \ce{\text{OH}^-}
\end{align*}
\]

Scheme II
The water pool-size in the microemulsions depends on \( \omega \) value. At low \( \omega \) activity of water molecules are low\(^{38,39} \) due to their interactions with \( \text{Na}^+ \) coming from AOT, sulphonates or carboxyl groups. Hence, the chance of their attack on the activated substrate molecules is also comparatively lower. By the addition of water, pool size of microemulsion increases. The activity of water molecules also increase due to lowered interaction among water molecules and mainly counterions. This increase in water activity facilitates its encounter with the protonated substrate increasing the rate of hydrolysis reaction.

In the hydrolysis of SHA the prediction of a rate maximum with increasing \( \omega \) indicates that microemulsion with \( \omega = 10.7 \) has a maximum reaction turnover. Moulik et al.\(^{98} \) found similar observation for hydrolysis of \( p \)-nitrophenyl phosphate with alkaline phosphatase in AOT/decane/water microemulsions. They observed a maximum for this enzyme catalysed hydrolysis at \( \omega = 18.7 \). In the case of SHA the rate of reaction is not greatly effected upto \( \omega = 8.2 \) but at \( \omega = 10.7 \) nearly a three-fold jump in the reaction rate has been observed. The droplet radius for this microemulsion composition is 15.9 A\(^{\circ} \). It seems quite rational to think that this dimension of microemulsion droplet nicely fits with the structural dimension of SHA molecule. This may be the explanation of highest catalytic efficiency for the microemulsions corresponding to \( \omega = 10.7 \). The high catalytic activity of this composition is confirmed by repeating the experiment with two microemulsion compositions at lower temperature 45°C. In these experiments also composition corresponding to \( \omega = 10.7 \) turned to be most effective (Table 6.4). The successive scans for the hydrolysis are shown in Figs. 6.10 and 6.11.

It is generally observed that the medium properties of the micellar interface do not change much with amphiphile concentration and there is much experimental evidence to support this assumption\(^{34,99} \). This conclusion stems from the general observation that the experimentally estimated rate constants for the reaction within the micellar and microemulsion interface are, for a variety of reactions, basically
Fig. 6.10 - Successive spectral scans during the hydrolysis of SHA in the presence of HCl (0.1 mol dm$^{-3}$) in the microemulsion medium ($\omega = 10.7$) at 45°C.

(1) After mixing. (2) after 13 min. (3) after 25 min. (4) after 35 min.
(5) after 50 min. (6) after 80 min.. (7) after 93 min.
Fig. 6.11 - Successive spectral scans during the hydrolysis of SHA in the presence of HCl (0.1 mol dm⁻³) in the microemulsion medium (ω = 12.3) at 45°C

(1) After mixing, (2) after 12 min., (3) after 25 min., (4) after 42 min., (5) after 80 min., (6) after 105 min.
Table 6.5: Effect of [AOT] on the rate of hydrolysis of SHA at constant \( \omega = 12.3 \) at 55°C

<table>
<thead>
<tr>
<th>Water/AOT/Isooctane</th>
<th>% of AOT</th>
<th>( k_{obs} \times 10^5 ) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/30/55</td>
<td>30</td>
<td>29.5</td>
</tr>
<tr>
<td>17.5/35/47.5</td>
<td>35</td>
<td>10.3</td>
</tr>
<tr>
<td>20/40/40</td>
<td>40</td>
<td>7.54</td>
</tr>
<tr>
<td>22.5/45/32.5</td>
<td>45</td>
<td>5.4</td>
</tr>
<tr>
<td>25/50/25</td>
<td>50</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Insensitive to amphiphile concentration. However, observed rate constants as shown in Table 6.5 are generally sensitive to amphiphile composition. The probable reason that \( k_{obs} \) goes down as AOT goes up is that the ratio of Na\(^+\) to H\(^+\) in the interfacial region is getting larger and the H\(^+\) concentration, within the totality of the micelles is going down. A sharp inhibition in rate is observed when [AOT] is increased from 30 to 35% but thereafter rate decreases slowly and linearly due to increasing concentration of water in the core. The gradual increase of water percentage compensate rate inhibition due to increasing value of Na\(^+\)/H\(^+\) ratio in the core.

The kinetic data have been analysed in terms of Quantitative model\(^{33,34,54,86}\) by extending the pseudophase model to include three pseudophases (water, isoctane, and AOT), each of which is considered as being uniformly distributed in the total volume of the microemulsion. This model assumes competition between possible reactions in three microphases. However, its scope is presently limited to reactions occurring in one microphase only. This is the situation when the two reagents are hydrophilic so that they can react together only in the water phase, or when a hydrophilic substrate reacts with a hydrophobic reagent so that the reaction must necessarily occur at the interphase.

In the present investigation, the upper range of \( \omega \) is 12.3. Hence water present in the interior of w/o microemulsion are bound water. They remain bound
to the AOT head groups or solvated by Na⁺ in the interfacial region. These water molecules have lower activity and are not normal water. The water-pool size is extremely small and the water molecules present do not behave like bulk water. Secondly the H⁺ ion and the protonated SHA both are water soluble and get attracted by the negatively charged polar head groups of AOT in the interfacial region. Thus possibility of any exchange of reagents within three microphases is ignored. Hence, a quantitative model, as has been applied for reactions in w/o microemulsions, can not be constructed here.

6.23 Effect of Temperature on Reaction Rates

Effect of temperature on reaction rate has been investigated by carrying out reactions at two different temperatures (45 and 55°C) for three microemulsion compositions. Activation parameters are calculated using Eyring equation and are shown in Table 6.6. Enthalpy of activation as well as free energy of activation increases from ω = 4.9 to ω = 12.3 indicating the facilitation of reaction in the

<table>
<thead>
<tr>
<th>ω = [H₂O]</th>
<th>Temp. (°C)</th>
<th>k₁₀⁻⁵ s⁻¹</th>
<th>Eₐ</th>
<th>ΔH°</th>
<th>ΔG°</th>
<th>ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AOT]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.7</td>
<td>45</td>
<td>32.2</td>
<td>22.6</td>
<td>20.0</td>
<td>104.5</td>
<td>-261.4</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>41.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.3</td>
<td>45</td>
<td>19.7</td>
<td>34.9</td>
<td>32.45</td>
<td>105.5</td>
<td>-226.2</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>29.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Further, a high negative value of entropy supports the bimolecular mechanism proposed in Scheme II.
6.24 Conclusion

I When hydrolysis of salicylhydroxamic acid in microemulsions are carried out varying $\omega$ at a fixed composition of AOT (30%), a rate maximum is observed. This indicates a particular microemulsion composition to be most effective for catalysing the hydrolysis reaction.

II Reaction rate decreases with increasing concentration of AOT and at a fixed $\omega$ value (12.3).

III Quantitative model is not applied because there is no exchange of reagents within three microemulsions i.e. oil, water and interface.

IV A very high negative value of entropy of activation supports bimolecular mechanism.
References


86. C. Einhorn, J. Einhorn, C. M. Abbadi, J. L. Pierra, J. Org. Chem. 1996, 64, 4542


