A Kinetic Investigation of Metal-Dipeptide Complex with Ninhydrin in the Absence and Presence of CTAB Micelles

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Abstract: This paper presents the results of a kinetic study performed between ninhydrin and a Ni(II) dipeptide complex under various conditions. The rate of formation of the imine adduct was measured spectrophotometrically both in plain aqueous media and in aqueous micellar media in which CTAB (cetyltrimethylammonium bromide) is used as the surfactant. These studies were carried out at pH 5 and over a temperature range of 50 to 70°C. Studies were also conducted to elucidate the effect of some organic sodium salts on the rate of this reaction. In these studies, it was found that the formation of imine adduct followed a first-order kinetics with respect to [Ni(II)-Gly-Leu]+ in both aqueous and micellar medium. A fractional-order kinetics was observed with respect to ninhydrin, again in both aqueous and micellar media. Increase in the total concentration of CTAB from 0 to 40×10⁻³ mol dm⁻³ resulted in approximately two folds increase in the pseudo-first-order rate constant (kₚ). The rate constant (kₑ) in micellar medium first increased with increase in CTAB concentration, reached a maximum value, and finally, with further increase in CTAB concentration, a decreasing effect was observed. Quantitative kinetic analysis of kₑ−[CTAB] data was performed on the basis of the pseudo-phase model of the micelles. The rate profile in presence of CTAB suggests a cooperative effect in the enhanced formation of the imine adduct as is commonly found in enzyme catalyzed reactions. Addition of organic sodium salts (such as benzoate, salicylate and tosylate) enhanced the rate at lower concentrations but rates start to decrease at higher concentrations. This suggests that tightly binding organic counter-anions were the most effective. Viscosity of the reaction media seems to affect the kinetic behavior in micellar media.

Key words: micelle, kinetics, [Ni(II)-Gly-Leu]+, CTAB, peptide, ninhydrin, Ruhemann’s purple

1 Introduction

Formation of Ruhemann’s purple is widely used to detect amino groups in simple organic compounds, proteins and peptides. For these purposes usually, a spray reagent is prepared in situ in a laboratory environment. A variety of commercial spray reagents are available and these contain ninhydrin, one or more metal ions and surfactants in aqueous and non-aqueous media. Such sprays are used for developing TLC plates and in detecting finger prints for forensic work. The response to these reagents depended upon its formulation and a quicker color development is essential especially for forensic work. The purpose of such formulations is to improve the response time of Ruhemann’s color development. Therefore, reac-

tion kinetics of color development in the use of such mixtures is important. Therefore, it is important to know the role and effectiveness of the various components in these reagents.

Typical steps in the formation of Ruhemann’s color is shown in Scheme 1. The formation of color depends upon the formation of an imine intermediate. Quantitative liberation of carbon dioxide during the formation of the imine intermediate is used to estimate free amino acids¹. However, formation of Ruhemann’s color is not always quantitative. Therefore, to enhance the formation of Ruhemann’s color metal ions such as Sn^{2+} and Cu^{2+} have been incorporated into spray reagents³. Another important factor is the solubility of organic substances in aqueous media. Therefore,
Anionic surfactants like sodium dodecyl sulfate have been studied in mimicking catalysis\(^{11,14}\). However, these can strongly bind to metal ions and for inverted micelles like structures around metal ions with an external hydrophobic environment. Whereas, a cationic surfactant like CTAB can form micelles without coordinating to metal ions. Cationic micelles have not been shown exhibit catalytic effect in the Lewis acid catalysis of condensation reactions\(^{11}\). However, studies on ninhydrin-peptide reaction are scanty and, therefore, in search of enhanced utility, we have studied the Gly-Leu–ninhydrin reaction in a micelle mediated aqueous medium under varying experimental conditions. This study was undertaken to study whether cationic micelles change the course of reaction in anyway compared to reaction of [Ni(II)-Gly-Leu]\(^+\) complex with ninhydrin. The use of this application depends on the formation of Ruhemann’s purple that shows a high intensity band at 550 nm\(^{10}\). The use of this method still has much room for improvements as color formation is a slow process and is not always quantitative. Continuous efforts are, therefore, being made to improve the response time of this reagent\(^{11,12}\). Sn(II) and Cu(II) is one of the most commonly used metal ions in commercially available reagents. Sn(II) is a mild reducing agent and is suggest to prevent formation of indanehydantin from the imine intermediate. The Cu(II) is a mild oxidizing agent and coordinates strongly to amino groups as well as oxo-ligands. These are also good electrophiles and Lewis acid catalysts\(^{13}\) and highly susceptible to redox reactions. While most kinetically inert metal ions are useless, Ni(II) complexes are kinetically labile and only moderate Lewis acids and exhibit neither reducing nor oxidizing properties. Therefore, it seemed an appropriate metal ion to study in this system.

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### 2 Experimental Procedures

#### 2.1 Materials

Water with a conductivity of \((1-2) \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}\) was obtained by distilling deionized water. The double-distilled water was used throughout the study. Gly-Leu (LOBA Chemie, 99%), NiSO\(_4\) (Merck, 99%), ninhydrin (Merck, 99%), CTAB (BDH, 99%), sodium benzoate (NaBenz, Merck, 99.5%), sodium salicylate (NaSal, CDH, 99.5%), sodium chloride (BDH, 99.9%), sodium sulphate (Qualigens, 99%), sodium acetate (Merck, 99%) and acetic acid (Merck, 99.9%) were used as received. An acetate buffer (pH = 5.0) was used for preparing all stock solutions. The pH of the solutions was measured with an ELICO pH meter (model LI-122, Hyderabad, India) fitted with a combination electrode.

#### 2.2 pH Measurements

For preliminary studies on the interaction of [Ni(II)-Gly-Leu]\(^+\) complex with ninhydrin, solutions were made in the
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2.4 Kinetic Measurements

The reaction vessel was fitted with a double surface water condenser to prevent evaporation. The reaction was started with addition of a thermally equilibrated ninhydrin solution of required volume. Each kinetic run was performed under pseudo-first-order conditions using ≥ 10-fold excess of ninhydrin. It was observed that one mole of ninhydrin reaction with amino acids and peptides is 5.0\(^{11,15,16}\).

2.3 Job’s method of continuous variations

To determine the composition of reaction product formed, Job’s method of continuous variations was employed in the absence and presence of cationic micelles CTAB (20.0 \(\times\) \(10^{-3}\) mol dm\(^{-3}\)) for the determination of the composition of reaction product between [Ni(II)-Gly-Leu]\(^+\) complex and ninhydrin. It was observed that one mole of ninhydrin is required to give the reaction product (Fig. 1).

2.5 Critical micellar concentration

The critical micellar concentration (cmc) values of CTAB were determined under the experimental conditions by measuring the conductivity of surfactant solutions with a Phillips conductivity meter model PR 9500 using platinized electrode. The cmc values of CTAB both in the absence and in the presence of reactants were obtained from the specific conductivity versus [CTAB] plots\(^{20}\). Measurements were carried out under different conditions 1) using plain water; 2) with CTAB in water and 3) with CTAB, [Ni(II)-Gly-Leu]\(^+\) and ninhydrin. The respective cmc values are \((\times 10^3)\) 9.5, 3.4 and 3.3 at 30°C and 14.2, 6.1 and 5.8 mol dm\(^{-3}\) at 70°C.

3 Results and Discussion

The UV-Visible spectra of the products formed by the reaction of Ni(II)-Gly-Leu complex (2.0 \(\times\) \(10^{-4}\) mol dm\(^{-3}\)) with ninhydrin (6.0 \(\times\) \(10^{-3}\) mol dm\(^{-3}\)) in plain water as well as in aqueous CTAB micelles are shown in Fig. 2. Soon after mixing there was no significant product formation. However, after heating for 2 h at 70°C the resulting products showed a prominent band with a wavelength of maximum absorbance (\(\lambda_{\text{max}}\)) at 310 nm. The fact that there was no shift in \(\lambda_{\text{max}}\) confirms that identical products were formed both in the presence and the absence of CTAB. However, a significantly higher absorbance was observed for the reaction in CTAB micelles. This high absorbance noticed in the presence of CTAB suggests that more product has formed within the reaction time in the presence of CTAB.

Another important feature noticeable in the spectrum is a small band around 425 - 450 nm. This band is prominent in presence of CTAB and could represent a square planar complex of the Ni(II) species\(^{20}\). The condensation product resulting from ninhydrin with the complexed dipeptide is a tetradentate ligand and the probability of forming a stable square planar complex is more likely. This species is likely to be in equilibrium with the octahedral species.

3.1 Effect of varying [Ni(II)-Gly-Leu]\(^+\) concentration

To investigate the effect of [Ni(II)-Gly-Leu]\(^+\) complex on the reaction rate, kinetic experiments were performed at different initial concentrations of [Ni(II)-Gly-Leu]\(^+\)
3.2 Dependence on Ninhydrin concentration

The dependence of the reaction constant on ninhydrin was determined by carrying out a series of kinetic runs at different concentrations of ninhydrin. The results of these experiments are shown in Fig. 2. The reaction was carried out at a constant temperature of 70°C and at a pH of 5.0. The rate constant values were obtained in the presence of CTAB micelles. It was found that the value of rate constant was independent of the initial concentration of the [NI(II)-Gly-Leu]+ in micellar media indicating the order with respect to ninhydrin is fractional both in absence and presence of CTAB micelles.

3.3 Effect of temperature variation on the reaction rate

The rate constant values were obtained by conducting these kinetic studies at various temperatures within the temperature range of 60 to 80°C, both in plain aqueous as well as in CTAB micelles media with fixed reactants concentration. The activation parameters were obtained using Arrhenius and Eyring equation and these data are presented in Table 2.

Table 1 Effect of [NI(II)-Gly-Leu]+ on pseudo-first-order rate constants (kobs/kp) for the reaction of [NI(II)-Gly-Leu]+ with ninhydrin.

| Reaction conditions: | 10⁻¹[Ni(II)-Gly-Leu]+ (mol dm⁻³) | 10⁻⁵kobs (s⁻¹) | 10⁻⁵kp (s⁻¹) |
|----------------------|---------------------------------|----------------|--------------|
| [ninhydrin] = 6.0 × 10⁻³ mol dm⁻³ | 1.0 | 3.7 | 6.3 |
| [CTAB] = 2.0 × 10⁻² mol dm⁻³ | 1.5 | 3.5 | 6.3 |
| pH = 5.0 | 2.0 | 3.5 | 6.1 |
| Temperature = 70°C | 2.5 | 3.6 | 6.0 |
| | 3.0 | 3.5 | 6.2 |
| | 3.5 | 3.5 | 6.1 |

Table 2 Effect of temperature on pseudo-first-order rate constants (kobs/kp) for the reaction of [NI(II)-Gly-Leu]+ with ninhydrin.

| Reaction conditions: | 10⁻¹[Ni(II)-Gly-Leu]+ (mol dm⁻³) | 10⁻⁵kobs (s⁻¹) | 10⁻⁵kp (s⁻¹) |
|----------------------|---------------------------------|----------------|--------------|
| [ninhydrin] = 6.0 × 10⁻³ mol dm⁻³ | 60 | 1.6 | 2.6 |
| [CTAB] = 2.0 × 10⁻² mol dm⁻³ | 65 | 2.5 | 3.9 |
| pH = 5.0 | 70 | 3.5 | 6.1 |
| | 75 | 5.0 | 6.8 |
| | 80 | 7.6 | 9.1 |

Parameters

- E (kJ mol⁻¹) = 79.4, 65.0
- ΔH° (kJ mol⁻¹) = 76.6, 62.2
- ΔS° (JK⁻¹ mol⁻¹) = 151.0, 156.0
3.4 Reaction in aqueous medium

Detailed investigations reveal that the rate of formation of the product is first-order with respect to Ni(II)-Gly-Leu complex concentration. Rate expression (1), as confirmed by (i) the initial rate being \(v_i = k_{obs}[\text{Ni(II)-Gly-Leu}^+]\) directly proportional to the initial concentration of [Ni(II)-Gly-Leu\(^+\)]\(\_T\) complex, and (ii) constancy of \(k_{obs}\) values obtained at different initial concentrations of [Ni(II)-Gly-Leu\(^+\)]\(\_T\) (Table 1). Plots of \(k_{obs}\) versus [ninhydrin]\(\_T\) show a fractional-al-order with respect to [ninhydrin]\(\_T\).

On the basis of the above results, the following mechanism is proposed for the reaction of [Ni(\text{-Gly-Leu})\(^+\)] (Scheme 2).

It is well known that the lone pair electrons on amino group is necessary for nucleophilic attack on the middle carbonyl group of ninhydrin\(^{10, 21-23}\). In complex A, this lone pair electron is not free, therefore, nucleophilic attack is not possible. However, Ni(II) complexes are somewhat labile and therefore the lone pair is available and the reaction proceeds through template assisted condensation on Ni(II) center itself. Such reactions are very common in kinetic labile complexes and particularly, it is well known in Ni(II) macrocyclic chemistry\(^{24, 25}\). The proximity of the coordinated carbonyl group of ninhydrin close to the primary amino group in Gly-Leu dipeptide enhances the reaction\(^{26}\). The presence of metal ion brings the reaction groups together and provides a better chance for their combination within the coordination sphere. In such cases where there is no free carboxyl group adjacent to the reacting amine and in the presence of metal ions where there is a complex, CO\(_2\) is not eliminated\(^{3, 27}\). The mechanism (Scheme 1), proposed on the basis of above, involves two kinetically distinguishable steps: (i) a rapid ternary labile complex formation between [Ni(II)-Gly-Leu\(^+\)] complex and ninhydrin, and (ii) a slower condensation of amino group to carbonyl group. Accordingly, the following rate equation.

\[
\frac{dP}{dt} = \frac{kK[N][A]_T}{(1 + K[N])} \tag{2}
\]

which, on comparison with eq. (1), gives,

\[
k_{obs} = \frac{kK[N]}{1 + K[N]} \tag{3}
\]

A double-reciprocal plot between \(k_{obs}\) and [N] resulted in a straight line (as envisaged by eq. (2)) which allowed us to obtained the values of \(k\ (16.3 \text{ s}^{-1})\) and \(K\ (79.5 \text{ mol}^{-1} \text{ dm}^3)\) in

| Parameters and Constants | Values |
|--------------------------|--------|
| \(10^9 k_d\ (s^{-1})\) | 16.3 |
| \(10^5 k_1\ (\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1})\) | 18.8 |
| \(10^5 k_2\ (\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1})\) | 13.5 |
| \(k_3/k_2\) | 10.4 |
| \(K_s\ (\text{mol}^{-1} \text{ dm}^3)\) | 43.2 |
| \(K_m\ (\text{mol}^{-1} \text{ dm}^3)\) | 79.5 |

\(^{\_T}\) second-order rate constants \((k_{1\_T})\) are based on eq. (3.5).

### Table 3

| Values of rate parameters \((k_{0\_obs}, k_1, k_2, k_s, k_m, k_{1\_T})\) and binding constants \((K_s, K_m)\) for the reaction of [Ni(II)-Gly-Leu\(^+\)] and ninhydrin in micellar media. |
|---------------------------------------------|
| Reaction conditions: |
| [Ni(II)-Gly-Leu\(^+\)] | 2.0 \times 10^{-4} \text{ mol dm}^{-3} |
| [ninhydrin] | 6.0 \times 10^{-7} \text{ mol dm}^{-3} |
| pH | 5.0 |
| Temperature | 70°C |

### Scheme 2

Formation of imine complex from [Ni(II)-Gly-Leu\(^+\)]\(\_T\) ninhydrin.
the aqueous medium. The calculated values of rate constants ($k_{\text{obs}}$, Table 3, obtained by substituting $k$ and $K$ in eq. (3)) are in closed agreement with the $k_{\text{obs}}$ which supports the proposed mechanism and confirms the validity of the rate eq. (3).

3.5 Reaction in presence of CTAB

Preliminary experiments indicate that absorbance of end product increases as the concentration of CTAB micelles increases from 0 to $60.0 \times 10^{-3}$ mol dm$^{-3}$ (Fig. 3). The observed rate increased from 3.5 to 6.2 (nearly doubled) but the wavelength of maximum absorbance ($\lambda_{\text{max}}$) remained unchanged (vide-supra); this confirms that the product of the reaction remains the same as in aqueous medium.

To find out the role of cationic surfactant on the reaction rate, the effect of varying [CTAB] was studied at constant [Ni(II)-Gly-Leu]$^+$ ($2.0 \times 10^{-3}$ mol dm$^{-3}$), [ninhydrin] ($6.0 \times 10^{-3}$ mol dm$^{-3}$) and pH 5.0 at 70°C. The observed rate constant is affected by [CTAB] changes and the maximum rate enhancement is ca. two fold. A plot of $k_v$ versus [CTAB] shows a rate maximum at [CTAB] = $40.0 \times 10^{-3}$ mol dm$^{-3}$ (Fig. 3), a very common characteristics of bimolecular reactions catalyzed by micelles$^{26, 27}$. It has been established$^{30}$ that micelles can cause a change in aqueous reaction mechanism. Therefore, in order to confirm the mechanism proposed in Scheme 2, the effect of reactant concentrations and temperature was studied in presence of CTAB ($20.0 \times 10^{-3}$ mol dm$^{-3}$). The results are given in Table 2. Just the same first-and fractional-order in [Ni(II)-Gly-Leu]$^+$ and [ninhydrin], respectively, being followed. Thus, we can safely conclude that the reaction mechanism remains the same in presence of cationic CTAB micelles with all possible intermediary situations.

The catalytic behavior of cationic surfactant (CTAB) can be rationalized in terms of pseudo-phase model (Scheme 3), proposed by Menger et al.$^{26, 29}$ and developed by Bunton$^{30}$ and Romsted$^{31}$. 

Here subscripts "w" and "m" represent the aqueous pseudo-phase and micellar pseudo-phase, respectively. $K_s$ is the binding constant of the [Ni(II)-Gly-Leu]$^+$ complex to the cationic micelles, and $[D_m] = [\text{CTAB}] - \text{CMC}$. The pseudo-first-order rate constants in aqueous and micellar pseudo-phases are represented by $k_w$ and $k_m$ respectively. The observed rate law (eq. (1)) and Scheme 3 lead to eq. (4).

$$k_v = \frac{k_m K_s [D_m]}{1 + K_s [D_m]}$$

Eq. (4) can be modified into eq. (5)

$$\frac{1}{k_w - k_v} = \frac{1}{k_m - k_w} + \frac{1}{k_m - k_w}K_s [D_m]$$

According to eq. (5), a plot of the left-hand side versus 1/[D$_m$] should give a straight line with an intercept equal to 1/($k_m - k_w$) and slope equal to 1/($k_m - k_w$)$K_s$. Interestingly, linearity in the plot of (1/$k_w$ - $k_v$) versus 1/[D$_m$] was observed, implying that Scheme 3 model is adequate.

The decrease in rate constant beyond [CTAB] > $40.0 \times 10^{-3}$ mol dm$^{-3}$ (Fig. 3) could be explained as follows. At [CTAB] > $40.0 \times 10^{-3}$ mol dm$^{-3}$ practically, $K_s$ has reached the saturation value for the distribution of the substrate complex of [Ni(-Glu-Lys)(ninhydrin)]. Once, this saturation is attained, any further addition of CTAB that generates more cationic micelles can take up only the hydrophobic ninhydrin molecules into new micelle and this should not react with the complex in another micelle$^{31}$. Another reason for the decrease in rate constant could be a result of counter ion inhibition. Micelles mediated reactions occur either inside the stern layer or at the interface between micellar and bulk water solvent$^{36, 37}$. However, micellar mediated reactions are also found to occur at the interfacial juctural region of stern and Gouy-Chapman layers$^{38, 39}$. Micellar surfaces are water-rich$^{40}$. Due to different properties of micellar pseudo-phase, it is not possible to precisely locate the site of reaction. But, at least the localization of the reactants can be considered. The main factor involved in the kinetic micellar effects on bimolecular reactions is

$$\text{(Ni(II)-Gly-Leu)$_w$ + D}_n \xrightleftharpoons{K_s} \text{(Ni(II)-Gly-Leu)$_m$}$$

$$\text{N}_w + \text{D}_n \xrightarrow{K_s} \text{ND}_n$$

Scheme 3

$$\text{Products} \xrightarrow{k_m'}$$
the increased concentration of reactants into a small volume through electrostatic and hydrophobic interactions. Based on purely electrostatic considerations, ninhydrin having electron cloud will be located predominately in the Stern layer and to a lesser extent in the counter ion diffuse layer surrounding the cationic micelles. That Gly-Leu forms part of the inner co-ordination shell of a cationic nickel(II) complex (which gives the complex some hydrophobic character), it may, at least partly, remain embedded (partly because electrostatic repulsion occurs between the metal ion and the micellar surface). While discussing the nature of interaction, it is worth considering kinetic lability and the various coordination geometrical isomers of the Ni(II) complex, that may exist in solution. Ni(II) being a kinetically labile, the water exchange rates are of the order of $10^4$ and are even higher in complexes with multidentate ligands$^{42}$. Of these (shown in Scheme 2) the octahedral mer-[Ni(II) (Gly-Leu) (H$_2$O) ]$^+$ and fac-[Ni(II) (Gly-Leu) (H$_2$O) ]$^+$ isomers are more hydrophilic in nature and may be the dominant species in aqueous phase. But they are also in equilibrium with the square planar Ni(II) species, [Ni(II) (Gly-Leu) (H$_2$O) ]$^+$. As this square planar species has only one aqua-ligand and two freely available coordination sites for ninhydrin to bind, there is a higher probability that this species is bound within micellar Stern layer. The negative entropy of activation is also a characteristic of the formation of a well-structured activated state in which the reactive groups are closely associated with less of a degree of freedom. In addition, a lower value of activation energy clearly suggests the catalytic role of CTAB (catalysts lower the activation energy and enhances the reaction rate).

### 3.6 Effect of added salts in the presence of CTAB

Salts, as additives, in micellar systems acquire a special place due to their ability to induce structural changes in micelles as well as to the Ni(II)-Gly-Leu complex. This may, in turn, modify substrate-surfactant interactions$^{43}$. With this viewpoint, the effect of added salts on the reaction was also studied. The results are shown graphically in Figs. 4 and 5. At very low concentrations, the rate increases with the addition of sodium salts of organic acids. With increasing concentrations, the rate continues to increase only for sodium benzoate. For sodium salicylate and tosylate, the rate decreases as their concentration is increased$^{40}$. Coordination geometry around Ni(II) ion is influenced by solvents, environments and also ionic strength. Usually an increase in ionic strength increases the square planar species unless the counter anion is strongly coordinating. Tosylates, sulfate, and perchlorate in aqueous media are poor coordinating agents$^{46}$. Salicylate anion on the other hand is a strong bidentate ligand in basic media but relatively weaker at pH 5 under which these studies were performed.}

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**Fig. 4**  Effect of NaBenz(A), NaSal(B), and NaTos(C) on the reaction rate of [Ni(II)-Gly-Leu]$^+$ complex with ninhydrin. Reaction conditions: [Ni(II)-Gly-Leu]$^+$ = $2.0 \times 10^{-4}$ mol dm$^{-3}$, [ninhydrin] = $6.0 \times 10^{-3}$ mol dm$^{-3}$, [CTAB] = $2.0 \times 10^{-2}$ mol dm$^{-3}$, pH = 5.0, temp. = 70°C.
carried out. This is due to protonation of the phenolate anion. While tosylate can form ion pair, salicylate can bind via hydrogen bonding and benzoate can coordinate to the Ni(II) centers and also interact with the micellar phase.

Rate enhancement or inhibition of micellar catalysis by added organic sodium salts can be due to the change in shape and size of micelles and or exclusion of the reactants from the micellar pseudo-phase. The organic anions used in this study are having hydrophobic character. Such anions will be solubilized in the micelle palisade layer with the acidic group exposed close to the head group region. Therefore, in addition to neutralization of micellar positive charge, they will restrict solubilization sites to hydrophobic substrate. Thus, they catalyze the reaction initially by virtue of increased concentration of the reactants in the Stern layer of micelle. As we increase the concentration, the above site will be saturated. Once this site is fully occupied, additional salts will try to get adsorbed at the micellar surface and will thus compete for a site with reactants. The unique behavior of the benzoate could only be accounted by its tendency to bind to the square planar Ni(II) species. This would produce a neutral Ni(II) species which could enter the micellar phase much more easily.

Another factor which could inhibit the rate is the possible micellar growth at higher salts concentration as reflected by the viscosity data (Fig. 5). In our case, the change in morphology from spheroidal micelles to rod shaped (as indicated by increase in viscosity) would have changed the binding characteristics of the substrate and thereby, suppress the Ni(II) complex concentration at the micellar surface with a concomitant decrease in the rate.

4 Conclusion

The kinetics of the interaction of [Ni(II)-Gly-Leu]$^{+}$ and ninhydrin has been studied in aqueous and cationic micelles of CTAB. Contrary to previous observations in metal Lewis acid catalyzed reactions, we find an increase in the rate in the CTAB micellar phase for formation of the imine-intermediate needed for Ruhemann’s purple color development. Quantitative treatment of the kinetic data seems justified as observed and calculated rate constant values were in close agreement within experimental errors. The fast exchange rates in Ni(II) complexes and formation of small quantities of square planar Ni(II) species as evidenced in the UV-Visible spectra, is proposed to enhance the rate of formation in micellar media. The effect of salts on micellar catalysis seems to depend on the nature of salt which could accelerate or inhibit the reaction. Finally, we can conclude that molecule-molecule interactions in micellar media could successfully be treated using the pseudo-phase model.

Acknowledgments

The authors are thankful to UGC (India) for providing financial assistance in doing this research work.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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