RESEARCH ARTICLE

INFLUENCE OF TTAB/14-s-14 MICELLES ON THE RATE OF THE CONDENSATION BETWEEN NINHYDRIN AND MERCURY-DIPEPTIDE COMPLEX IN ABSENCE AND PRESENCE OF SALTS AND ORGANIC SOLVENTS: A KINETIC APPROACH

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Abstract

The interaction of mercury(II)–glycyl-L-alanine [Hg(II)–Gly-L-Ala]$^+$ complex with ninhydrin has been studied kinetically both in aqueous as well as micellar media (cationic conventional/gemini surfactants) using UV-vis spectrophotometer at 70 ℃ and a particular pH 5.0. The study was carried out as functions of [Hg(II)–Gly-L-Ala]$^+$, [ninhydrin], [surfactant] [salts], and solvents (%v/v). The first-order-rate is observed concerning [Hg(II)–Gly-L-Ala]$^+$, whereas fractional-order-rate dependence for [ninhydrin]. It has been found that 14-s-14 geminis enhance the rate of reaction more effectively than related cationic conventional surfactant tetradecyltrimethylammonium bromide (TTAB). The effect of additives such as salts (inorganic/organic) and organic solvents on the rate was also investigated. The reaction rate was explained in terms of the modified pseudo phase model (considering the association/adsorption of both the reactants on the micellar surface) and changes in micellar morphology occurring at higher [geminis]. The Eyring equation is valid for the reaction over the range of temperatures used. Various thermodynamic parameters and binding constants between reactants with the micelles have been evaluated.

Keywords: Catalytic effect, [Hg(II)–Gly-L-Ala]$^+$, Ninhydrin, Gemini surfactants, Salts, Organic solvents.

1. Introduction

All surfactant molecules are amphiphilic and they exhibit hydrophilic and hydrophobic properties. A chemical structure for their molecules makes it particularly favorable for them to reside at interfaces. As in aqueous detergent solutions, it has become customary to distinguish ionic (cationic or anionic), nonionic and amphoteric surfactants. In a cationic surfactant molecule, the surface-active portion of it bears a positive charge and this charge can be mono (e.g., in TTAB) or di (e.g., in 14-s-14 (where s = 4, 5, 6)). At critical concentration, the surfactant molecules begin to organize by ordering themselves in structures called micelles, a Latin term meaning "small bit" which was first assigned by J. W. McBain.[1] Micelles have become a subject of great interest to the organic chemist and the biochemist because of their unusual catalysis of organic reactions [2] and of their similarity to biological membranes and globular proteins.[1]
Amino acids/peptides coordinated with metal ions are of intrinsic interest as a part of the chemistry of complex ions

in environmental, biochemistry, bioinorganic, bioanalytical, and forensic fields. J. Bjerrum and coworkers [3] reported several metal ions complexation including those for amino acids and peptides.

In recent decades, many scientists have taken care of the changes on Earth according to the environmental impacts of several pollutants and the exposure to them, which destroy our life slowly or quickly depending upon the kind of pollutant. These pollutants find their way to our bodies and cause serious diseases. The most important inorganic/organometallic pollutants are trace metals such as mercury, arsenic, cadmium, lead, cobalt, zinc, copper... etc. Mercury (Hg) is a metal from Subgroup IIB and is related to zinc (Zn) and cadmium (Cd). In the environment, all are toxicological and environmental concerns. Mercury is the most environmentally concerning of the three because of the neurotoxin species methylmercury produced in our biosphere systems through the accumulation and magnification of its concentration levels by aquatic microorganisms.[4] In general, mercury(II) has the greatest binding power for

nitrogen ligands of any of the metal ions (Brooks and Davidson, 1960). [5] Mercury has been known to form strong binding with several ligands such the binding of Hg(II) by natural organic matter (NOM) and protein derivatives and the order within the Subgroup IIB is: Hg(II) > Zn(II)> Cd(II). [6-9] For Metal(II)-glycine binding, the order of stability among various metal complexes has been found to be: Hg(II) > Cu(II) > Ni(II) > Zn(II) > Co(II) > Cd(II).[10]

A well-known reagent, ninhydrin gives a purple-colored product (DYDA) when reacts with amino acids/dipeptides. As the color (DYDA) fades with time at room temperature, several attempts were made to increase the stability and sensitivity of the ninhydrin colorimetric method, metal ion coordination being one of them.

From this view of point, mercury attracts interest both from workers using simulated or model systems and from others using biological materials to explore (1) the mode of interaction of mercury with proteins, dipeptides, amino acids and nucleotides in the hope of elucidating the mechanisms of transport of such a metal either in plants, in blood, or across cell membranes, and (2) the possible mechanism of methylmercury toxicity in mammals.[11]

2. Experimental Section

2.1 Materials and methods

Mercuric nitrate extra pure (s.d. fine, Hg ≥ 58.0%), glycyl-L-alanine (Gly-L-Ala, Aldrich, ≥99%), ninhydrin (Merck, 99%), tetradecyltrimethylammonium bromide (TTAB, Sigma, ≥99%), sodium acetate trihydrate extra pure (s.d fine, 99-102%), acetic acid glacial (Merck, 99-100%), ferric ammonium sulfate (Sigma, 99%), ammonium thiocyanate (Merck, ≥98.0%), 1,6-dibromohexane (Fluka, ≥97.0%), 1,5-dibromopentane (Fluka, ≥98.0%), 1,4-dibromobutane (Aldrich, >99.0%), N,N-dimethyltetradecylamine (Fluka, ≥95.0%), ethyl acetate (Merck, 99.0%), hexane (Merck, ≥95.0), ethanol absolute (Merck, 99.8%), acetonitrile (AN, Merck, ≥99.0%),1,4-Dioxane (DO, Merck, ≥99.0%), dimethyl sulfoxide (DMSO, Merck, ≥99.0%), sodium benzoate (NaBenz, Merck, 99.5%), sodium tosylate (NaTos, Fluka, 70-80% (HPLC)), sodium nitrate purified (Merck, 99 %), sodium sulphate (Merck, ≥ 98%), nitric acid (Rankem, >98%), sodium hydroxide (Fisher, >97.0%) and calcium hydroxide (Sarabhai M. chemicals, >95.0) were used as supplied. The water used to prepare the solutions was demineralized and double distilled in an all-glass (Pyrex) distillation set up. The specific conductivity of water was in the range $1-2 \times 10^{-6}$ S cm^{-1}. Special care was taken while cleaning the glassware (by immersing successively in 1M NaOH-ethanol and 1M nitric acid baths and then by rinsing with double-distilled water. Conductivity and pH measurements were examined and viscosity measurements were made by Ubbelohde viscometer at 70 ± 0.1 °C.

To prepare 0.01M of mercuric nitrate about 0.35g of Hg(NO$_3$)$_2$•H$_2$O was weighed using SHIMADZU-AUY220 analytical balance (±0.2mg) from Kyoto-Japan.

The weigh then dissolved in a mixture of 0.5 ml concentrated nitric acid (to prevent hydrolysis) and 50 ml water and diluted with water to 100 ml. Standardizing the solution was done by transferring an accurately measured volume of about 20 ml of the solution into Erlenmeyer flask, and adding 0.5 ml of nitric acid and 1ml ferric ammonium sulfate. The titration of Hg(II) solution started by adding 0.02N ammonium thiocyanate up to the first appearance of a permanent brown color, then the calculation was done to find the exact molarity.[12] The standard solution of Hg(II) was used as a stock to prepare [Hg(II)–Gly-L-Ala]$^+$ complex by mixing a desired volume of Hg(II) with an equal molar of Gly-L-Ala (i.e., one mole to one mole in the ratio) in a 250 ml three-necked reaction vessel (fitted with a condenser to prevent evaporation).[13-20] The complexion started at a controlled temperature for 30 min then the 1:1 complex (1 Hg(II):1 (Gly-L-Ala) in the ratio) was used to react with a required volume of known ninhydrin concentration. This process was achieved throughout all kinetic sets.

To examine the effect of organic solvents (i.e., dimethyl sulfoxide (DMSO), 1,4-dioxane (DO), and acetonitrile (AN)) sample solutions were made by taking requisite volumes of solvents in standard volumetric flasks (cleaned/dried) and making up the volumes with the stock solution. When required, more samples were prepared by dilution. After proper mixing, the sample solutions were kept overnight for equilibration. To avoid evaporation, the containers were kept properly stoppered during equilibration and measurements.

The gemini alkanediyl-α,ω-bis(dimethyltetradecylammonium bromide) surfactants (i.e., 14-s-14, where s = 4, 5, 6) were synthesized by refluxing the corresponding α,ω-dibromoalkane with N, N- dimethyltetradecylamine in the ratio 1:2.1, respectively in absolute ethanol with continuous stirring at 80 ℃ for 48 hours. The solid was obtained after recrystallization using ethyl acetate/hexane several times. The purity was checked by characterization using ^{1}H NMR (300 MHz Bruker Avance NMR spectrometer) and C, H, N analysis.

Solutions of surfactants were prepared by weight in buffer solution (pH 5.0). Other stock solutions [Hg(II)–Gly-L-Ala]$^+$ complex and ninhydrin) were prepared freshly to use in the whole experimental sets. To find out the critical micelle concentration (cmc) values of TTAB and geminis 14-s-14 (s = 4, 5, 6) solutions in the absence and presence of organic solvents, the conductivity of solutions was recorded at 30 °C and 70 °C by a calibrated cell conjugated with a conductivity meter (Systronics-306, Hyderabad-India), having a sensitivity of 0.1 μS cm^{-1} and an accuracy of 0.4%. The temperature was maintained constant within ±0.1℃ using a constant temperature oil bath. The cmc values were obtained from the intersection of two tangents drawn on the pre- and post- micellar slopes of specific conductance vs. concentration plots [21] and the cmc values were recorded in Tables 1 and 2.

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Influence of TTAB/14-S-14 Micelles on the Rate of the Condensation between Ninhydrin and Mercury-Dipeptide Complex in Absence and Presence of Salts and Organic Solvents: A Kinetic Approach

Table 1: Cmc values of TTAB/14-s-14 in the absence and presence of reactants at 30 ºC and 70 ºC.

Solution	10^3 cmc (mol dm^{-3})	
	30 ºC	70 ºC
TTAB		
Water	3.900	5.110
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	4.187	5.420
14-6-14		
Water	0.162	0.296
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.166	0.323
14-5-14		
Water	0.145	0.287
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.152	0.311
14-4-14		
Water	0.137	0.273
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.146	0.304

Experimental conditions: [Hg(II)–Gly-L-Ala]$^+$ = 2.0 x 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, [TTAB]$_T$ =20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ =50.0 x 10^{-5} mol dm^{-3}(s = 4, 5, 6), 10.0 % organic solvent (DMSO, AN, DO).

Table 2: Cmc values of TTAB/14-s-14 in the absence and presence of reactants at 30 ºC and 70 ºC with the composition of organic solvents (% v/v).

Solution	10^3 cmc (mol dm^3)					
	In H$_2$O-DMSO		In H$_2$O-DO		In H$_2$O-AN	
	30 ºC	70 ºC	30 ºC	70 ºC	30 ºC	70 ºC
TTAB						
Water+ org. Solvent	4.500	8.121	5.648	11.892	6.108	12.561
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	4.624	8.301	5.778	12.139	6.266	12.812
14-6-14						
Water+ org. Solvent	0.401	0.750	0.485	1.028	0.503	1.128
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.410	0.768	0.498	1.245	0.561	1.353
14-5-14						
Water+ org. Solvent	0.383	0.735	0.391	0.932	0.402	0.967
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.392	0.755	0.423	0.966	0.459	1.190
14-4-14						
Water+ org. Solvent	0.322	0.687	0.336	0.701	0.355	0.755
[Hg(II)–Gly-L-Ala]$^+$ + ninhydrin	0.342	0.714	0.353	0.733	0.404	0.806

Experimental conditions: [Hg(II)–Gly-L-Ala]$^+$ = 2.0 x 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, [TTAB]$_T$ =20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ =50.0 x 10^{-5} mol dm^{-3}(s = 4, 5, 6), 10.0 % organic solvent (DMSO, DO, AN).

2.2 Kinetic procedures

All the kinetic sets were achieved at constant temperatures controlled within ±0.1 ºC in a paraffin oil-bath, which was designed and assembled in the laboratory with commercially available components. A mixture containing appropriate amounts of all the reactants (except ninhydrin) was taken in a three-necked reaction vessel equipped with a double-walled water condenser to prevent evaporation. The reaction vessel was then immersed in the oil-bath at the chosen temperature and the solution was left to stand for 15-20 min to attain equilibrium. The reaction was initiated by adding the requisite volume of thermally equilibrated ninhydrin solution. Purified N$_2$ gas was bubbled through the reaction mixture for stirring as well as to maintain an inert atmosphere. The zero-time was recorded when half of the ninhydrin solution has been added and the reaction was usually followed up to not less than 80% completion. As pH 5.0 gives an optimum reaction rate when using for ninhydrin-metal ions coordinated amino acids/dipeptides all subsequent kinetic sets were done at this pH. **[17-20]**

2.3 Stoichiometric measurements using a method of continuous variations (MCV)

A simple sensitive spectrophotometric method (Job's method of continuous variation) were performed in the absence and presence of cationic micelles TTAB (20.0 x10^{-3} mol dm^{-3}), 14-s-14 (50 x 10^{-5} mol dm^{-3}) (where, s = 4, 5, 6) and 10.0% organic solvents for the determination of the composition of the reaction product between [Hg(II)–Gly-L-Ala]$^+$ complex and ninhydrin. It was found that one mole of [Hg(II)–Gly-L-Ala]$^+$ complex associates with one mole of ninhydrin to give the final product (Fig. 1.(A), (B)).
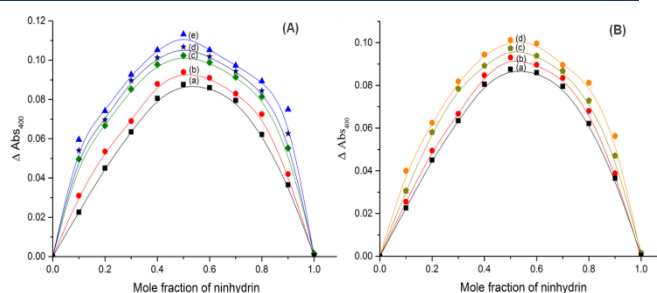

Figure 1 (A) Plots of ΔAbs_{400} *vs.* mole fraction of ninhydrin for determination of the composition of the product formed by the interaction of [Hg(II)–Gly-L-Ala]$^+$ complex with ninhydrin: in aqueous media (a); (b) in presence of 14-6-14 (b); 14-5-14(c); TTAB (d); 14-4-14 (e) without organic solvents. **(B)** Plots of ΔAbs_{400} *vs.* mole fraction of ninhydrin for determination of the composition of the product

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formed by the interaction of [Hg(II)–Gly-L-Ala]$^+$ complex with ninhydrin without surfactants: in aqueous media (a); in presence of DMSO (b); DO (c); AN (d). *Experimental conditions*: [14-s-14]$_T$ = 50.0 x10^{-5} mol dm^{-3}, [TTAB]$_T$ = 20.0 x10^{-3} mol dm^{-3} (**1.(A)**), 10.0 % organic solvent (v/v) (**1.(B)**), Temperature =70 ℃, *p*H=5.0

3. Results

3.1 *Spectra*

The progress of the reaction was monitored spectrophotometrically by following the appearance of the product of [Hg(II)–Gly-L-Ala]$^+$ complex–ninhydrin reaction at 400 nm (the λmax of a product) with UV-mini 1240 spectrophotometer, SHIMADZU (Tokyo-Japan) (Fig. 2.(A),(B)). In comparison with aqueous media, the absorbance is higher in presences of TTAB/14-s-14 which becomes highest when organic solvents are present. Further, no shift in the absorbance maxima was observed concluding that the same product is formed in both media (i.e., aqueous and TTAB/14-s-14 micellar systems in the absence and presence of organic solvents).
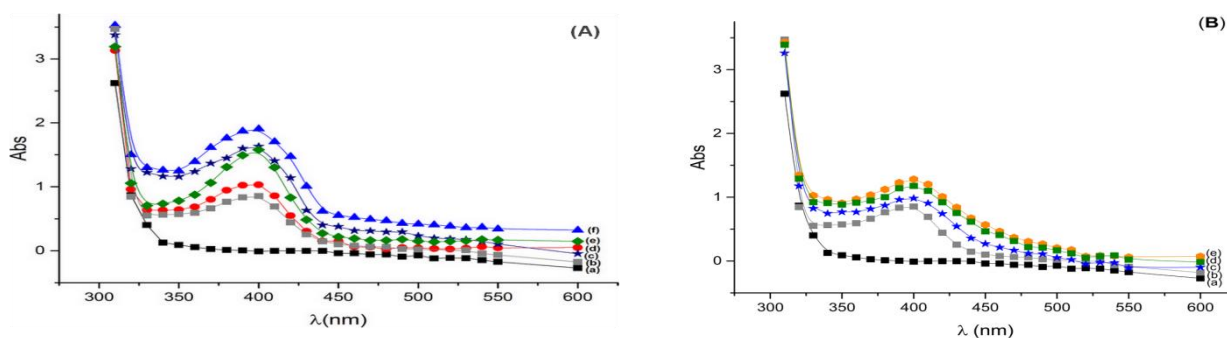

Figure 2 Absorption spectra of the reaction product of [Hg(II)–Gly-L-Ala]$^+$ complex with ninhydrin **(A)** in (a, b) the absence and (c-f) presence of surfactants: (a) represents absorbance when the reaction was tried in the absence of surfactant at 70 ℃ showing the absence of any reaction under the conditions at zero time; (b) aqueous medium after completion the reaction; (c) in presence of TTAB after completion the reaction; (d) in 14-6-14 ; (e) in 14-5-14 and (f) in 14-4-14. **(B)** in (a, b) the absence and (c-e) presence of organic solvents: (a) represents absorbance when the reaction was tried in the absence of organic solvents at 70 ℃ showing the absence of any reaction under the conditions at zero time; (b) aqueous medium after completion the reaction; (c) in presence of 10.0 % (v/v) DMSO after completion the reaction; (d) in 10.0 % (v/v) DO; (e) in 10.0 % (v/v) AN. *Experimental conditions*: [Hg(II)–Gly-L-Ala]$_{IT}^+$ = 2.0 × 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x10^{-3} mol dm^{-3}, [TTAB]$_T$ = 20.0 x10^{-3} mol dm^{-3}, [14-s-14]$_T$ = 50.0 x10^{-5} mol dm^{-3} (s = 4, 5, 6), temperature = 70 ℃, *p*H= 5.0. Lines are drawn as a guide to the eye

3.2 *Influence of [Hg(II)–Gly-L-Ala]$^+$ on the reaction rate*

To find out the order of reaction with respect to metal ion coordinated-dipeptide concentration, the rate constants were determined at different initial concentrations of [Hg(II)–Gly-L-Ala]$^+$ complex ranging from 1.0 x 10$^{\square\square}$ to 3.5 x 10$^{\square\square}$ mol dm$^{\square\square}$. The concentration of ninhydrin was kept constant at fixed temperature and pH. The k (k$_{obs}$ or k$_\psi$) values are recorded in Table 3. Similar studies were performed in TTAB/14-s-14 micelles. As the values of rate constants (k$_{obs}$ or k$_\psi$) were found to be independent of the initial concentration of metal-peptide complex, the order concerning [Hg(II)–Gly-L-Ala]$^+$ complex

concentration is unity in both the media. Hence, the rate law is:

rate = k [Hg(II)–Gly-L-Ala]$_T^+$
(1)

where [Hg(II)–Gly-L-Ala]$_T^+$ is the total concentration of Hg(II)–Gly-L-Ala complex.

3.3 *Influence of [ninhydrin] on the reaction rate*

The rate constants were determined by carrying out the kinetic experiments with different concentrations of ninhydrin keeping the [Hg(II)–Gly-L-Ala]$_T^+$, temperature, and pH constant in both the media. The plots of rate constant values (k, s$^{\square 1}$) versus [ninhydrin]$_T$ are curved passing through the origin (Fig. 3). This verifies that the order is fractional with respect to [ninhydrin]$_T$ in aqueous and micellar media.

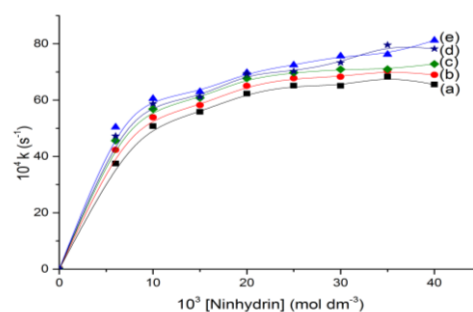**Figure 3** Influence of [ninhydrin] on the reaction rate of Hg(II)–Gly-L-Ala complex with ninhydrin in (a) aqueous (a) and (b-e) presence of surfactants: (b) 14-6-14; (c)14-5-14; (d)TTAB (e) and 14-4-14. *Experimental conditions*: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [TTAB]$_T$ = 20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ = 50.0 x 10^{-5} mol dm^{-3} (s = 4, 5, 6), temperature = 70 °C, *p*H = 5.0

3.4 *Influence of [surfactant] on the reaction rate*

The effect of cationic surfactants on the reaction rate was studied under varying concentrations of TTAB/geminis (Fig. 4.) at constant [Hg(II)–Gly-L-Ala]$_T^+$, [ninhydrin]$_T$, temperature (70 ℃) and pH (5.0). The study showed that the reaction follows first- and fractional-order kinetics concerning concentrations of metal ion-dipeptide complex and ninhydrin, respectively. Hence, the order is the same with respect to [Hg(II)–Gly-L-Ala]$_T^+$ and

[ninhydrin]$_T$ as that in aqueous media. In a conventional surfactant (TTAB), the values of rate constant (k) for spontaneous reactions generally increase monotonically with increasing surfactant concentration and after the substrates completely bind with the micelles, k_ψ values decrease. The plot of k_ψ vs. [TTAB] has a perfectly common characteristic of bimolecular reactions catalyzed by micelles (Fig. 4. (A)).[22-28] However, with gemini surfactants, the k_ψ–[14-s-14] profile follows a special phenomenon: at low [14-s-14] below cmc (part I) the k_ψ values increases due to reaction in so-called premicelles. After that (part II) there is no critical change in $k\psi$ up to definite concentration then $k\psi$ values increases again (part III) (Fig. 4.(B)).
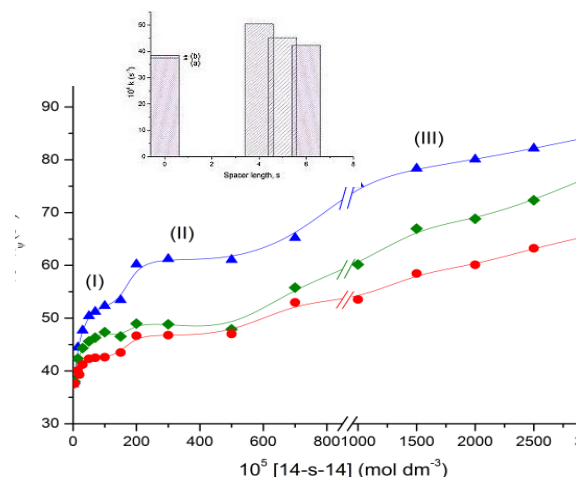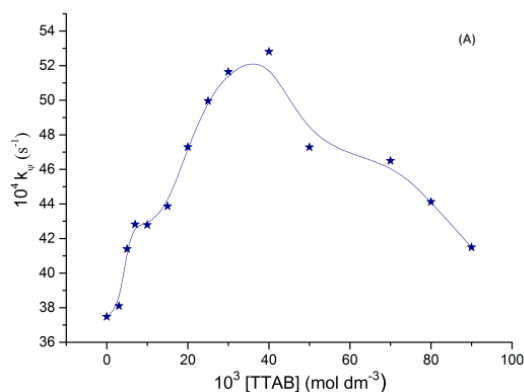

Figure 4 Effect of surfactant (**(A)** TTAB and **(B)** (14-s-14) concentration on the reaction rate of Hg(II)–Gly-L-Ala complex with ninhydrin. (**B**) (inset) spacer length (s = 4, 5, 6) effect on the reaction rate of Hg(II)–Gly-L-Ala complex (2.0 x 10^{-4} mol dm^{-3}) with ninhydrin (6.0 x 10^{-3} mol dm^{-3}) in: (a) aqueous, and (b) [TTAB]$_T$ = 50.0 x 10^{-5} mol dm^{-3}, at *p*H=5.0 and 70 ℃. Others are for [14-s-14]$_T$ = 50.0 x 10^{-5} mol dm^{-3} with the respective s values. *Experimental conditions*: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, *p*H = 5.0, temperature = 70 ℃. (a) 14-6-14; (b) 14-5-14; (c) 14-4-14

Table 3: Effect of [Hg(II)–Gly-L-Ala]$_T^+$ on *pseudo*-first-order rate constants (k$_{obs}$/k$_\psi$) for the reaction of Hg(II)–Gly-L-Ala complex with ninhydrin.

10^4 [Hg(II)–Gly-L-Ala]$_T^+$ (mol dm^{-3})	10^4 k$_{obs}$ (s^{-1})	10^4 k$_\psi$ (s^{-1})			
	Aqueous	TTAB	14-6-14	14-5-14	14-4-14
1.0	36.6	46.4	41.3	44.8	49.5
2.0	37.5	47.3	42.3	45.6	50.4
2.5	36.8	46.2	42.1	46.3	51.3
3.0	37.8	47.5	43.4	46.0	50.7
3.5	36.8	46.9	42.4	46.2	51.1

Experimental conditions: [TTAB]$_T$ = 20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ = 50.0 x 10^{-5} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, *p*H = 5.0 , Temperature = 70 °C.

3.5 *Influence of salts additives and organic solvents composition on the reaction rate*

Effect of several salts (inorganic; NaNO$_3$, Na$_2$SO$_4$ and organic; NaBenz, NaTos) were seen on Hg(II)–Gly-L-Ala–ninhydrin reaction in presence of [TTAB]$_T$ = 20.0 x 10$^{□□}$ mol dm$^{□□}$ to check the acceleration/inhibition effect on the rate of the reaction studied. The results were evaluated in Fig. 5.

To discover the effect of solvents on Hg(II)–Gly-L-Ala–ninhydrin reaction, a number of organic solvents; dimethyl sulfoxide (DMSO), acetonitrile (AN), 1,4-dioxane (DO) have been used for the purpose. It has been observed that the addition of small quantities of water-soluble organic solvents significantly increases the rate as well as the intensity of the color in micellar systems (Fig. 2. (B), Fig. 6).
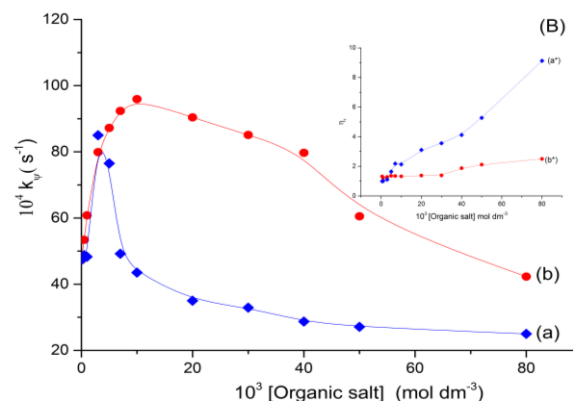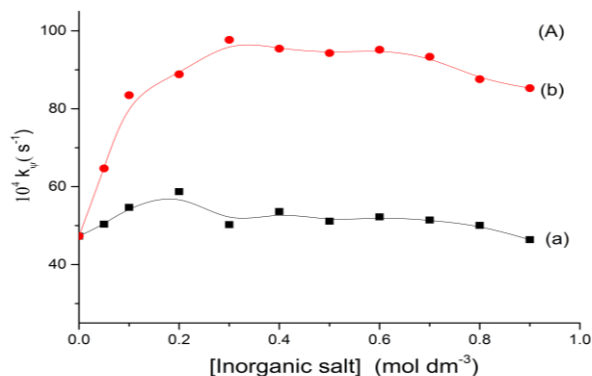
Figure 5 (A) Effect of [inorganic salt] ((a) NaNO$_3$, (b) Na$_2$SO$_4$) on the rate constant (k) of Hg(II)–Gly-L-Ala complex with ninhydrin in the presence of TTAB. **(B)** Effect of [organic salt] (NaTos (a,a*), NaBenz (b,b*), (a, b) for concentration and (a*, b*) for viscosity (inset)) on the rate constant (k) for the reaction of Hg(II)–Gly-L-Ala complex with ninhydrin in the presence of TTAB. *Experimental conditions*: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, [TTAB]$_T$ = 20.0 x 10^{-3}mol dm^{-3}, pH = 5.0, temperature = 70 °C
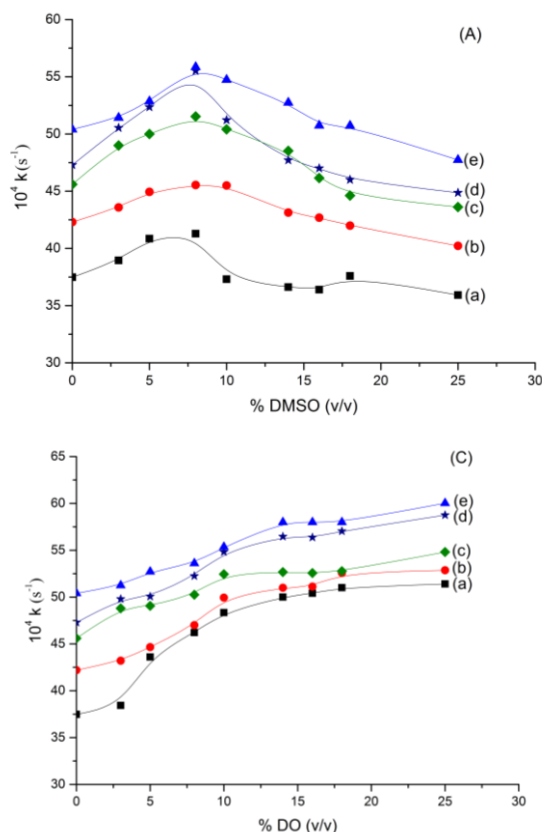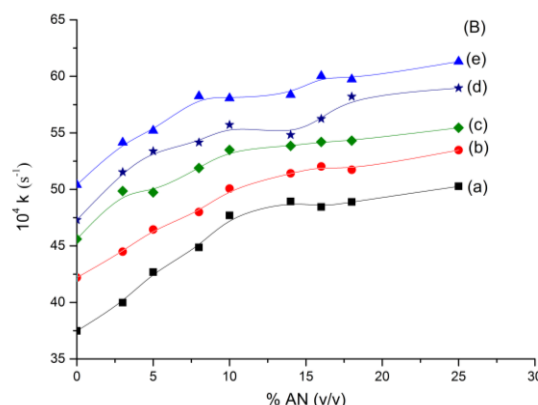

Figure 6 Effect of composition of organic solvents DMSO **(A)**, AN **(B)**, DO **(C)** (% v/v) on the rate reaction of Hg(II)–Gly-L-Ala complex with ninhydrin in: aqueous (a); 14-6-14 (b); 14-5-14 (c); TTAB (d); 14-4-14 (e). *Experimental conditions*: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, [TTAB]$_T$ =20.0 x10^{-3} mol dm^{-3}, [14-s-14]$_T$ =50.0 x10^{-5} mol dm^{-3}, pH = 5.0, temperature = 70 °C

3.6 *Influence of temperature on the reaction rate*

The influence of temperature on the rate of Hg(II)–Gly-L-Ala–ninhydrin reactions was studied at several

temperatures with five-degree interval (range 60–80 °C) in absence and presence of TTAB/14-s-14 surfactants. The pseudo-first order rate constants increased with a rise in temperature from 60 to 80 °C in both media. The pseudo-first order rate constants (k, s^{-1}), as summarized in Table 4, were used to calculate free energy (E$_a$), activation entropy ($\Delta S^{\neq}$) and activation enthalpy ($\Delta H^{\neq}$) from the Eyring equation by plotting of log k vs. 1/T (which was

found to be linear with a negative slope in both the media) and the values of these activation parameters are recorded in Table 4.

4. Discussion

4.1 *Reaction in water*

As regards the reaction in water, the amount of reaction products of Hg(II)–Gly-L-Ala–ninhydrin reaction and the intensity of colored-product were found to depend on the conditions of reaction medium i.e., pH, temperature, and [ninhydrin], etc.[29,30] The studies also confirmed that it is not possible to react with ninhydrin through nucleophilic addition to give Schiff's base because the lone-pair of electrons of an amino group of dipeptide is not free and bounds with Hg(II) takes place by condensation of the coordinated amino group to carbonyl group within the coordination sphere of Hg(II). This coordination of ninhydrin and Gly-L-Ala with the same Hg(II) to give the ternary labile complex of [Hg(II)–Gly-L-Ala]+–ninhydrin reaction is an example of kinetic

template mechanism. Under our experimental conditions (pH 5.0) unoccupied coordinated positions of Hg(II) could be filled by water molecules. Based on the above discussion, and the reaction rate data, the following mechanism (Scheme 1) has been proposed. Carbon dioxide gas test was performed to investigate the cleavage of –COOH group of Gly-L-Ala with Hg(II). A negative result indicates no CO_2 is evolved in the present case. Thus, Hg(II) reduces the escaping tendency of –COOH and enhances the electrophilic character of >C=O group.

Table 4 Effect of temperature on *pseudo*-first-order rate constants (k_{obs}/k_ψ) and thermodynamic parameters for the reaction of Hg(II)–Gly-L-Ala complex with ninhydrin.

Temperature (°C)	$10^4 k_{obs}$ (s^{-1}) Aqueous	$10^4 k_\psi$ (s^{-1}) TTAB	14-6-14	14-5-14	14-4-14
60	20.6	27.6	21.2	24.4	30.0
65	25.8	34.3	27.2	28.4	39.0
70	37.5	47.3	42.3	45.6	50.4
75	48.6	58.9	50.2	60.0	67.0
80	66.5	78.4	71.0	84.0	88.0
Parameters					
E_a (kJ mol^{-1})	74.3±0.4	53.7±0.3	65.3±0.4	61.6±0.4	54.8±0.3
$\Delta H^{\neq}$ (kJ mol^{-1})	71.4±0.4	50.9±0.3	62.4±0.3	58.7±0.3	51.9±0.3
$-\Delta S^{\neq}$ (JK^{-1}mol^{-1})	283±4	285±4	284±4	284±3	285±3
$\Delta G^{\neq}$ (kJ mol^{-1}) ^{a}	168±1	149±0.9	160±0.9	156±0.8	150±0.8

Experimental conditions: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [TTAB]$_T$ = 20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ = 50.0 x 10^{-5} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, pH= 5.0.
^{a} Activation free energy was calculated using the relation $\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq}$.

With the help of mechanism (Scheme 1), the rate equation is derived:

$$\text{rate} = kK[S]_T[N]_T/(1 + K[N]_T) \qquad (2)$$

or alternatively,

$$k_{obs} = kK [N]_T /(1+ [N]_T) \qquad (3)$$

where $[N]_T$ is the total concentration of ninhydrin.

On inverting Eq. (3), we get

$$1/k_{obs} = B_1/[N]_T + B_2 \qquad (4)$$

where, $B_1 = 1/kK$ (the gradients), $B_2 = 1/k$ (the intercepts).

Equation (3) on rearrangement gives Eq. (4), which shows a linear dependence of $1/k_{obs}$ on $1/[N]$. The respective values of k, and K were thus evaluated in water ($k = 14.89$ x 10^{-5} s^{-1}, $K = 7.88$ mol. dm^{-3}).

4.2 Reaction in micellar systems

In presence of TTAB/14-s-14 micelles, Hg(II)–Gly-L-Ala complex reacts with ninhydrin similarly to a reaction in water with the same first- and fractional- order kinetics

concerning Hg(II)–Gly-L-Ala complex and [ninhydrin]$_T$, respectively (Fig. 4). Added TTAB/14-s-14 micelles (as well as organic solvents) lead to increase the absorbance as it plotted in Fig. 2. (A), (B). The kinetic results are similar to those obtained in water except the substrate effect in which Michaelis–Menten behavior has been observed i.e., the binding of the substrate with the surfactant. Investigation of thermodynamic parameters (Table 4) shows that the large negative value of activation of entropy ($\Delta S^{\neq}$) and the less value of free activation energy ($\Delta G^{\#}$) in presence of surfactants indicate the formation of more ordered activated complex in surfactant media. The small values of free energy (E_a) and activation enthalpy ($\Delta H^{\#}$) in the presence of micelles imply that the catalytic effect on the reaction is more as compared to aqueous media.

Electrostatic interactions and hydrophobic character are the two main factors in the kinetics micellar catalysis, which increases the concentration of reactants into a small volume. Dipeptide forms part of the inner coordination shell of a cationic metal complex (which give a complex some hydrophobicity), it may, at least partly according to electrostatic repulsion occurs between the complexion and the micellar surface, remain embedded. The micelle thus helps in bringing the reactants together which may now orient in a manner suitable for the condensation. At a higher concentration of TTAB and above the *cmc*, the decreases in k_ψ values can be explained by Berezin's model[31] which involves solubilization of the reactants in both media. Because all the substrate has been incorporated into the micellar phase and when water bulk of the substrate is incorporated into the micelles, the addition of more TTAB generates more cationic micelles, which simply take up the ninhydrin molecules into the Stern layer, and thereby deactivate them; because a reactant molecule in one micelle should not react with the other in another micelle. Other reasons of decrease in k_ψ could be a result of counter ion (Br$^-$) inhibition due to competition with lone pair electrons in nitrogen atom of a dipeptide (in the complex of [Hg(II)–Gly-L-Ala]$^+$–ninhydrin) and/or segregation of the reactants in the different micelles as they are distributed in the increased number of micelle aggregates. Moreover, partitioning a hydrophilic species, between the bulk phase and micellar phase decreases k_ψ.[32] In case of gemini micelles, it can be seen that k_ψ-[gemini] profiles have three parts (Fig.

4(B)). Rate constant (k_ψ) first increases (part I), remains constants up to certain concentration (part II) (parts I and II behavior is like to conventional surfactant micelles) and then increases again (part III). In part I, at concentrations lower than *cmc*, k_ψ increases abnormally. The noticeable catalytic effect may be due to the presence of premicelles. In part II, the k_ψ values remain almost unchanged up to ~ 800 x10^{-5} mol dm^{-3} of gemini surfactants. Within the range of concentrations in part I and II, gemini micelles provide a much better environment for the Hg(II)–Gly-L-Ala–ninhydrin reaction as compared to their analogous monomeric (TTAB) micelles (Fig. 4 (A)). In part (III), k_ψ increases again perhaps due to change in micelles structure (i.e., from spherical to rodlike). The nature of the spacer plays an important role in increasing k_ψ and for 14-s-14 series, the increasing follow the order: 14-4-14 > 14-5-14 > 14-6-14 because of the decrease of the water content in the aggregates that make the environment less polar.

The *pseudo*-phase kinetic model [28,33-36] (Scheme 2) was successfully applied in our study to describe the catalytic effects of [TTAB]/[14-s-14] on Hg(II)–Gly-L-Ala –ninhydrin reaction. The total volume of micelles can be treated as a separate phase and frequently spread in the aqueous phase; the reaction occurs in both phases.
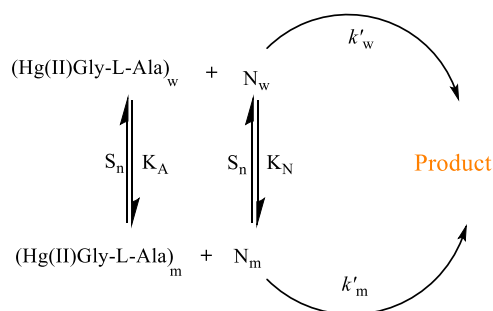
Although several kinetics equations based on this general Scheme have been developed, the most successful appears to be that of Berezin's model for bimolecular and the development of Bunton [34,37] who suggested an Eq. (5), which takes into account both (1) the solubilization of the reactants into the micelles and (2) the mass action model.

$$k_\psi = \{ k_w[N]_T + (K_A k_m - k_w) M_N^S [S_n] \} / 1 + K_A [S_n] \quad (5)$$

K_A is the binding constant of the complex to the micelles. The values k_w (aqueous path), k_m (micellar path) and K_A are calculated using a computer-based program (basic dos software) with the help of the non-linear least square technique. For K_N, the best value was considered to be one for which the value of Σd_i^2 (di- $k_{\psi obsi}$- $k_{\psi cali}$) turned out to be minimum. The best fit values are given in Table 5. The validity of the proposed mechanism is confirmed by a close agreement between the observed and calculated k_ψ values.
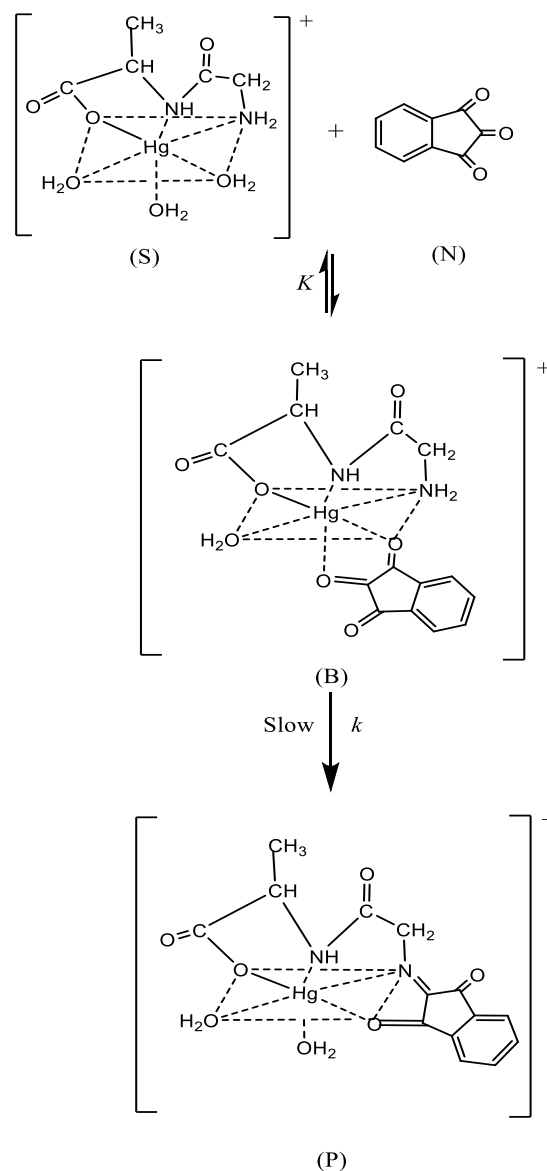
Scheme 1 Proposed mechanism of [Hg(II)–Gly-L-Ala]$^+$ complex (S) –ninhydrin (N) reaction.

Scheme 2 Pseudophase model for the Hg(II)–Gly-L-Ala complex-ninhydrin reaction.

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Table 5 Rate and binding constants for the reaction of ninhydrin with Hg(II)–Gly-L-Ala complex.

Constants	Values			
	TTAB	14-6-16	14-5-14	14-4-14
$10^2 k_m$ (s^{-1})	5.43	7.57	6.85	8.20
$10 k_w$ (mol^{-1}dm^3 s^{-1})	6.25	6.25	6.25	6.25
K_A (mol^{-1}dm^3)	70	142	135	118
K_N (mol^{-1} dm^3)	55.8	58.7	56.4	54.5

Experimental conditions: [Hg(II)–Gly-L-Ala]$_T^+$ = 2.0 x 10^{-4} mol dm^{-3}, [TTAB]$_T$ = 20.0 x 10^{-3} mol dm^{-3}, [14-s-14]$_T$ = 50.0 x 10^{-5} mol dm^{-3}, [ninhydrin]$_T$ = 6.0 x 10^{-3} mol dm^{-3}, Temperature = 70 °C.

In micellar systems and due to the different properties of the micellar *pseudo phase*, the exact site of the reaction is not possible but, at least, localization of the reactants can be considered. Most ionic micelle mediated reactions take place either at the interface between the bulk water solvent and micellar surface or inside the Stern layer's water rich-region close to the surface of the micelle.[28,38] The water activity at the surface of an ionic micelle is similar to that in the aqueous *pseudo phase*.[39] The catalytic effect of TTAB/14-s-14 on the reaction of Hg(II)–Gly-L-Ala complex with ninhydrin can be explained using electrostatic considerations as follows. Ninhydrin as it contains electron clouds can be assumed to reside predominantly in the Stern layer. The micellar surface can repel or attract ionic species due to electrostatic interaction whereas hydrophobic interaction can bring about the incorporation of reactants into micelles. As TTAB/14-s-14 is cationic micelles, their surface attracts ninhydrin closer that increases the local molarities in the Stern layer. For the Hg(II)–Gly-L-Ala complex despite bearing positive charge, the removal of water molecules from the inner solvation shell of metal by coordinated dipeptide gives the complex some hydrophobic character and due to this hydrophobic nature, the complex gets incorporated into the cationic micelles. As a result, the Hg(II)–Gly-L-Ala complex and ninhydrin bring close together into a small volume, i.e. Stern layer by the help of micelles then orient in a manner suitable for the condensation (a possible arrangement- although highly schematic-could be as illustrated in Scheme. 3.

4.2.1 Influence of salts on the reaction rate in the presence of TTAB

Added electrolytes can enhance/inhibit the rate of micellar catalysis due to the change in size and shape of micelles and/or exclusion of the reactants from the micellar *pseudo*-phase.[40-42] Although there is no regular pattern was found in the case of added inorganic salts (i.e. NaNO$_3$ and Na$_2$SO$_4$) (Fig. 5(A) Table 5), it seems there is an enhancement effect at low concentration. This behavior at low concentration can be related to change in solubility of reactants and to drive off them toward the micellar surface. However, with the organic (hydrophobic) salts (NaBenz, and NaTos), rate constant increases, reaches a maximum and then decreases with further increase in salt concentration (Fig. 5.(B), Table 6). With such hydrophobic salts, penetration of the benzene ring into the micellar palisade layer (a few carbon atoms deep toward core) takes place while the negative group on salts (if any) neutralize the micellar surface charge, so restrict interior solubilization of reactants causing an increase in the concentration of the latter in the Stern layer; the reaction is thus catalyzed. In comparison with sodium benzoate (NaBenz), sodium tosylate (NaTos), gives marked rate enhancement at low [NaTos], passing through a maximum as the [salt] is increased then further increasing leads to decrease in the rate constant. While the benzene ring saturates in the palisade layer, the sulfonate group of NaTos remains in the outermost region of the micelle (a case of intercalation).[43] As we increase the [NaTos], the above site will first be saturated and once this site is fully occupied, additional [NaTos] will try to get adsorbed at the micellar surface (a case of adsorption) and will thus compete for a site with reactants (a case of tosylate ion association in the form of adsorption). Consequently, [reactants] is decreased at the reaction site by the latter effect (exclusion of substrate). The progressive withdrawal of the substrate from the reaction site would slow down the rate, as was indeed observed. Possibly the above two effects work together on NaTos addition and the resultant effect is a function of [NaTos]. The inhibition effect for NaTos in comparison with NaBenz could be due to the SO^{-2} group on NaTos which may constrain the lone pair on ninhydrin to react with Hg(II)–Gly-L-Ala complex. Another reason to explain the inhibitory effect of NaTos in comparison with NaBenz is the micellar growth at a higher salt concentration as reflected by viscosity data (Fig. 5. (B) (Inset)).

4.2.2 Influence of spacer chain length of gemini surfactants on the reaction rate

The spacer chain length (s-values) can increase k_ψ values in the order s = 4 > 5 > 6 under the reaction conditions (Fig. 4. (B)). The variation of spacer chain lengths alters the cmc, morphology, etc. of gemini micellar aggregates and this alteration was supported by microviscosity and SANS data while the length and type of the spacer moiety dictate the conformation of the gemini molecule.[44-50] Thus, because of the spacer greatly affecting the surfactant morphology, the pseudo rate constants values (k_ψ, s^{-1}) obtained in the present studies are consistent with

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the expectation being the highest when using 14-4-14 micelles. The nature of the spacer which decreases the water content in the aggregates making the environment less polar and thus the k_ψ increases.
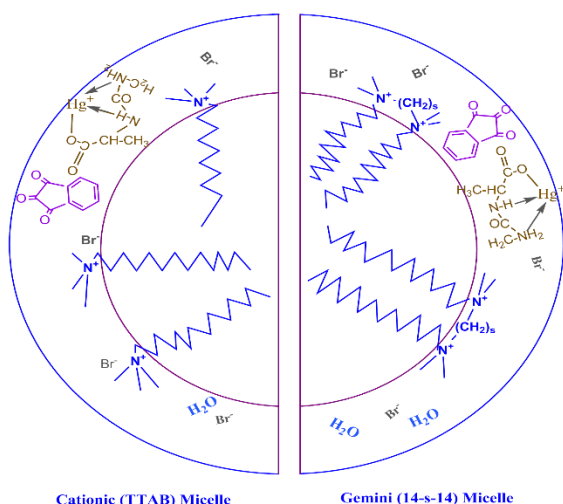
Scheme 3 Schematic model representing the probable location of reactants for the cationic/dicationic (TTAB/14-s-14) micellar catalyzed condensation reaction between Hg(II)–Gly-L-Ala complex and ninhydrin.

4.2.3 Influence of organic solvents on the reaction rate

Solvents can affect the 3D structure of water bulk in several ways. This effect depends on the category of organic solvents: (1) AN (polar) and DO (less polar) which forms hydrogen bonds with water and (2) DMSO which form hydrates with water. Although the studied solvents increase the absorbance and intensity of the Hg(II)–Gly-L-Ala complex–ninhydrin reaction (Fig. 2.(B)), each solvent has been found to postpone micellization of the surfactants (Table 2, due to different reasons. In the case of AN and DO, the decreases in the number of micelles is due to the formation of hydrogen bonds between water and AN or DO molecules. The effect of dimethyl sulfoxide on TTAB/14-s-14 micellization can be explained based on a strong interaction with water and stoichiometric hydrate (DMSO.$2H_2O$) formation which results in increased structuring of the solvent system and the inhibiting effect of DMSO on the formation of micelles. An increase in the orderliness of the DMSO-H_2O-TTAB/14-s-14 system takes place as the composition of DMSO is increased.

Despite all the three solvents inhibiting the micellization in TTAB/14-s-14 micelles, the reaction still shows some catalysis effect in the presence of these solvents especially at low composition concentration (Fig. 6). This can be due to the relative participation of water and organic solvents in acid-base equilibria and hydrogen bonding.

5.   Conclusion

Mercury has been known for about 2000 years and is still used in industrial and medical fields despite its high toxicity. Accumulation of mercury in biosystems has attended a critical attention to study its influence both from researchers using biological materials and from others using simulated or model systems.

This work is the first effort to focus on mercury ion coordinated–Gly-L-Ala–ninhydrin reaction as a model and the kinetics investigation of this reaction was done in several environments i.e. in the absence and presence of micellar medium including solvents and salts effects.

Effect of TTAB/14-s14 surfactants in the absence and presence of added salts and organic solvents on the kinetics of Hg(II)–Gly-L-Ala coordinated–ninhydrin reaction was carried out at pH 5.0 and temperature 70 ℃. Comparing the values with those obtained in aqueous, it was found that gemini micelles catalyze the reaction more. The use of a quite small quantity of the geminis provides less environmental impact when carrying out the reaction. An important point to be noted is that, at present reaction conditions, a small amount of organic solvents was sufficient to accelerate the reaction rate than that of pure water.

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Influence of TTAB/14-S-14 Micelles on the Rate of the Condensation between Ninhydrin and Mercury-Dipeptide Complex in Absence and Presence of Salts and Organic Solvents: A Kinetic Approach

مقالة بحثية

تأثير الميسيلات TTAB/14-s-14 على معدّل الارتباط بين النّهيدرين ومعقّد الزّئبق-ثنائي الببتيد في غياب ووجود الأملاح والمذيبات العضويّة: دراسة حركيّة

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الملخص

تمّ دراسة التّداخل بين معقد الزّئبق (2) - جلايسيل-L-ألانين مع الننهيدرين حركيّاً في الأوساط المائيّة واللامائيّة وأيضا في وجود المواد الفّعالة سطحيّا الأحاديّة والجيمني باستخدام جهاز الطّيف المرئي-فوق البنفسجي عند درجة حرارة 70 °م ودرجة حموضة 5. تمّ تتبّع التّفاعل باستخدام تراكيز كلّ من معقّد الزّئبق-جلايسيل-L-ألانين، النّنهيدرين، المادّة الفعّالة سطحيّاً، الأملاح، وكذا النّسب المئويّة الحجميّة/الحجميّة للمذيبات. أظهرت الدّراسة أنّ رتبة التّفاعل كانت من المرتبة الأولى بدلالة [Hg(II)–Gly-L-Ala]+، بينما كانت الرّتبة كسريّة بالاعتماد على تركيز النّنهيدرين. أدّى استخدام الجيمني 14-s-14 إلى تحسين معدّل التّفاعل بشكل أفضل من استخدام المادّة الكاتيونيّة التّقليديّة TTAB المقابلة للجيميني. أيضاً، تمّ دراسة تأثير المضافات الملحيّة (غير عضويّة/عضويّة) والمذيبات العضويّة. رتبة التّفاعل تمّ شرحها باستخدام النّموذج المعدّل من الرّتبة الوهميّة وظهر هناك تغيّر في الطّبيعة الميسيليّة عند التّراكيز المرتفعة من الجيمني. كانت معادلة إيرينج صالحة للتّفاعل في مدى الحرارة المستخدم. تمّ التّحقّق أيضا من عدد من معلمات ديناميكا الحرارة وثوابت الارتباط بين المتفاعلات مع الميسيلات.

الكلمات الرئيسية: تأثير التحفيز، [Hg(II)–Gly-L-Ala]+، الننهيدرين، المواد الفعّالة سطحيّاً (الجيمني)، الأملاح، المذيبات العضويّة.