Effect of Cationic Micelles on the Kinetics of Interaction of [Cr(III)-Gly-Gly]²⁺ with Ninhydrin

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Abstract： The effect of cationic micelles of cetyltrimethylammonium bromide (CTAB) on the interaction of chromium dipeptide complex ([Cr(III)-Gly-Gly]²⁺) with ninhydrin under varying conditions has been investigated. The rates of the reaction were determined in both water and surfactant micelles in the absence and presence of various organic and inorganic salts at 70 ℃ and pH 5.0. The reaction followed first- and fractional-order kinetics with respect to [Cr(III)-Gly-Gly²⁺] and [ninhydrin]. Increase in the total concentration of CTAB from 0 to 40×10^{-3} mol·dm⁻³ resulted in an increase in the pseudo-first-order rate constant (k_ψ) by a factor of ca 3. Quantitative kinetic analysis of k_ψ−[CTAB] data was performed on the basis of the pseudo-phase model of the micelles. As added salts induce structural changes in micellar systems that may modify the substrate-surfactant interactions, the effect of some inorganic (NaBr, NaCl, Na₂SO₄) and organic (NaBenz, NaSal, NaTos) salts on the rate was also explored. It was found that the tightly bound counterions (derived from organic salts) were the most effective.

Key Words： Micelle; Ninhydrin; Kinetics; Salts; [Cr(III)-Gly-Gly]²⁺; CTAB

The use of ninhydrin (N) for the detection and estimation of amino acids and peptides has great potential in revealing latent fingerprints[1]. The use depends on the formation of Ruhemann′s purple[2]. The method, though useful, still has considerable scope for improvements. Continuous efforts are, therefore, being made to improve the method[1,3].

Metal ion complex formations are among the prominent interactions in the nature. To understand metal ion complexation in biological systems, considerable research has been carried out on modeling binary and mixed ligand complexes[4–6].

Chemical reactivity in ionic colloidal self-assemblies (e.g., micelles, microemulsion droplets, and vesicles) has obtained importance owing to similarities in action with the enzymatic reactions. The similarities between the enzymatic reactions and the catalysis or inhibition by micelles include shape and size, polar surfaces, and hydrophobic cores. The micelles provide different microenvironments for different parts of the reactant molecules: that is, a nonpolar hydrophobic core can provide binding energy for similar groups while the outer charged shell can interact with the reactant′s polar groups. This inherent microheterogeneity of the micellar solubilization environment can play an important role in the catalysis of a reaction. The ionic micelles enhance the rate of bimolecular reactions by increasing the concentration of the reactants within the small volume of its Stern layer. The consideration of electrostatic and hydrophobic interactions between the reactants and micelles can account qualitatively for the ki-

netic effect on the reactions in micellar media. Micelle catalyzed reactions as models for electrostatic and hydrophobic interactions in biological systems should provide information regarding the mechanism of tuning of reactions occurring on biological surfaces because micelles are simpler and more easily modified. We have studied the effects of surfactants, salts, and temperature on ninhydrin interaction with different amino acids[7,8] and their metal complexes[9,10] with a view that the studies may prove useful in forensic sciences in enhancing the stability of fingerprints. The present study contributes experimental evidence of the catalytic effect of the CTAB cationic micelles on the reaction of a chromium (III) peptide complex with ninhydrin.

1 Experimental

1.1 Materials

Gly-Gly (LOBA Chemie, 99%), ninhydrin (Merck, 99%), CTAB (BDH, 99%), chromium sulfate (Merck, 99%), sodium benzoate (NaBenz, Merck, 99.5%), sodium salicylate (NaSal, CDH, 99.5%), sodium tosylate (NaTos, Fluka, HPLC, 70%−80%), sodium bromide (LOBA Chemie, 99%), sodium chloride (BDH, 99.9%), sodium sulphate (Qualigens, 99%), sodium acetate (Merck, 99%), and acetic acid (Merck, 99.9%) were used as received. The chromium dipeptide complex, [Cr(III)-Gly-Gly]²⁺, was prepared according to the literature method[11]. A 1:1 molar ratio solution (2×10^{-4} mol·dm⁻³) of the two reactants was taken in a graduated standard flask, boiled for 1 min, and heated in a

controlled manner at 90 ℃ for 1 h (the flask was fitted with a double-surface condenser to prevent evaporation). After reaction, the flask was brought to room temperature and loss in volume, if any, was maintained with the buffer. The complex was then stored in dark. Demineralized and double-distilled water (specific conductance: $(1-2)\times10^{-6}\ \Omega^{-1}\cdot cm^{-1}$) was used throughout. Sodium acetate-acetic acid buffer (pH=5.0) was used as a solvent for preparing the stock solutions.

An ELICO model LI-122 pH meter was used for the pH measurements.

1.2 Kinetic measurements

The required solution of $[Cr(III)-Gly-Gly]^{2+}$, without or with surfactant was taken in a three-necked reaction vessel fitted with a double-surface condenser to prevent evaporation, which was placed in an oil bath thermostated at the desired temperature (±0.1 ℃). To maintain an inert atmosphere, pure nitrogen gas (free from CO_2 and O_2) was passed through the reaction mixture. The reaction was started with the rapid addition of a required volume of thermally equilibrated ninhydrin solution. The progress of the reaction was monitored spectrophotometrically by measuring the absorbance of the reaction product at different intervals of time at 310 nm by a UV-Vis spectrophotometer (SHIMADZU-model UV mini 1240). The pseudo-first-order conditions were maintained by keeping the $[ninhydrin]_T$ (total concentration of ninhydrin) in excess. Values of pseudo-first-order rate constants were evaluated from plots of $lg((A_\infty-A_0)/(A_\infty-A_t))$ vs time (t) (where, A_0, A_t, A_∞ are the absorbances at the indicated times) by a least-squares regression analysis of the data, which showed excellent linearity well up to 80% completion of the reaction. Other details regarding pH measurements and kinetic methodology were the same as described elsewhere[7–10].

1.3 Determination of cmc by conductivity measurements

Conductivity measurements were used to determine the critical micelle concentration (cmc) values (bridge: ELICO, TYPE CM, 82T, cell constant=1.02 cm^{-1}). The conductivity of the solvent was first measured. Then, small volumes of the stock solution of surfactant were added. After complete mixing, the conductivities were recorded. The specific conductance was then calculated by applying solvent correction. The cmc values of CTAB in the absence and presence of reactants were obtained from the break points of nearly two straight lines of the specific

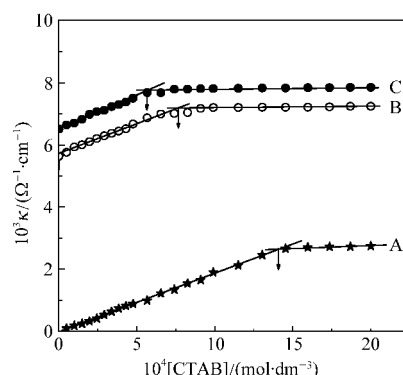**Fig.1** Variation of specific conductivity (κ) with CTAB concentration in (A) water, in (B) the presence of 2.0×10^{-4} mol·dm^{-3} [Cr(III)-Gly-Gly]$^{2+}$, and (C) 2.0×10^{-4} mol·dm^{-3} [Cr(III)-Gly-Gly]$^{2+}$+6×10^{-3} mol·dm^{-3} ninhydrin at 70 ℃

conductivity vs [surfactant] plots[12]. The experiments were carried out at 30 and 70 ℃ under varying conditions, i.e., solvent being water, water+[Cr(III)-Gly-Gly]$^{2+}$, water+[Cr(III)-Gly-Gly]$^{2+}$+ninhydrin, and the respective cmc values were recorded in Table 1. The conductivity curves are depicted in Fig.1.

In ionic surfactants, the cmc decreases with the addition of salts[13] because the screening action of the simple electrolytes lowers the repulsive forces between the polar head groups. In the present system, the additives are hydrophobic in nature and therefore will exist in the Stern layer (head group region). This will decrease the repulsion between surfactant monomers in micelles and will lower the cmc (Table 1).

2 Results and discussion

2.1 Spectra and composition of the product

The UV-Vis spectra of product formed by the reaction between [Cr(III)-Gly-Gly]$^{2+}$ (2.0×10^{-4} mol·dm^{-3}) and ninhydrin (6×10^{-3} mol·dm^{-3}) in aqueous as well as in micellar media are shown in Fig.2. It can be seen that the absorbance increases with the concentration of CTAB micelles with no shift in λ_{max}, i.e., the
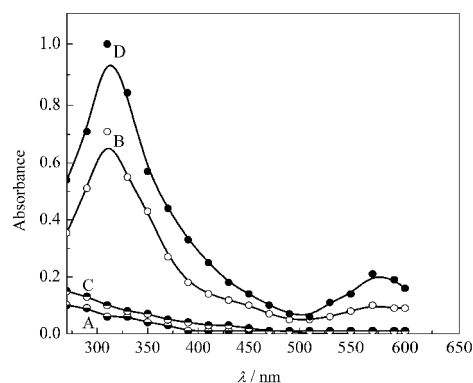
Table 1 Values of cmc of CTAB under different experimental conditions determined by conductivity measurements

Solution[a]	$10^4\times$cmc (mol·dm^{-3})	
	30 ℃	70 ℃
water	9.5(9.80[b])	14.2(15.0[c])
water+[Cr(III)-Gly-Gly]$^{2+}$	3.4	7.6
water+[Cr(III)-Gly-Gly]$^{2+}$+ninhydrin	2.3	5.5

[a][Cr(III)-Gly-Gly^{2+}]=2.0×10^{-4} mol·dm^{-3}, [ninhydrin]=6×10^{-3} mol·dm^{-3}; [b]value of Ref.[12] at 25 ℃; [c]value of Ref.[12] at 70 ℃; Uncertainities in cmc are estimated to be less than or equal to ±0.1×10^{-4} mol·dm^{-3}.

Fig.2 Absorption spectra of the reaction product of [Cr(III)-Gly-Gly]$^{2+}$ (2.0×10^{-4} mol·dm^{-3}) and ninhydrin (6×10^{-3} mol·dm^{-3}) in the absence and presence of CTAB at pH 5.0

(A) immediately after mixing the reactants; (B) after heating solution (A) at 70 ℃ for 2 h; (C) same as solution (A) in the presence of 20×10^{-3} mol·dm^{-3} [CTAB]; (D) after heating solution (C) at 70 ℃ for 2 h
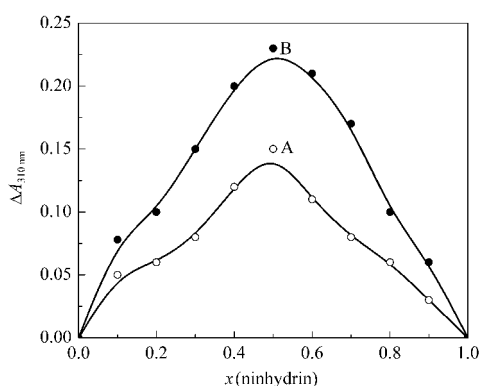
Fig.3   Plots of $\Delta A_{310\,nm}$ *versus* mole fraction (x) of ninhydrin for determination of the composition of the product formed by the interaction of [Cr(III)-Gly-Gly]²⁺ complex with ninhydrin in the absence (A) and presence (B) of 20×10^{-3} mol·dm⁻³ CTAB

wavelength of maximum absorbance (λ_{max}=310 nm) remains the same as in aqueous medium. This indicates the product of [Cr(III)-Gly-Gly]²⁺/ninhydrin reaction to be the same both in aqueous and micellar media. To determine the composition of the reaction product formed, Job′s method of continuous variations was employed in the absence and presence of micelles. The stoichiometry of the complex formed was found to be the same in both media. This is illustrated in Fig.3, in which the stoichiometry can be deduced from the position of the absorption maximum. It is found that one mole of ninhydrin reacts with one mole of [Cr(III)-Gly-Gly]²⁺ complex to give the product.

2.2   Dependence of reaction rate on [Cr(III)-Gly-Gly]²⁺ complex concentration

To determine the order of reaction with respect to [Cr(III)-Gly-Gly²⁺], the rate constants were determined at different initial concentrations of [Cr(III)-Gly-Gly]²⁺ complex ranging from 1.0×10^{-4} to 3.5×10^{-4} mol·dm⁻³. The concentration of ninhydrin was kept constant (6×10^{-3} mol·dm⁻³) at fixed temperature (70 ℃) and pH (5.0). The first order rate constants (k_{obs} and k_{Ψ}, the respective rate constants in water and micellar media) were calculated upto completion of three half-lives using rate constant equation($2.303/t$) lg $((A_\infty-A_0)/ (A_\infty-A_t))$, with the help of computer program. The k_{obs} values are recorded in Table 2. Similar studies were performed in CTAB micelles. As the values of rate constants (k_{obs} and k_{ψ}) were found to be independent of the initial concentration of [Cr(III)-Gly-Gly]²⁺ complex, the order with respect to [Cr(III)-Gly-Gly²⁺] is unity in both media (Eq.(1)).

$$\text{rate}=d[P]/dt=(k_{obs} \text{ or } k_{\Psi})[\text{Cr(III)-Gly-Gly}^{2+}]_T \qquad (1)$$

where, P is product, [Cr(III)-Gly-Gly²⁺]$_T$ is the total concentration of [Cr(III)-Gly-Gly]²⁺.

2.3   Dependence of reaction rate on ninhydrin concentration

The effect of ninhydrin concentration was determined by carrying out the kinetic experiments at different concentrations of ninhydrin keeping [Cr(III)-Gly-Gly²⁺]$_T$ constant (2×10^{-4} mol·dm⁻³) at temperature 70 ℃ and pH 5.0 (Table 2). Experiments were also performed in the presence of CTAB (20×10^{-3} mol·dm⁻³) micelles.

We see that the plots of the rate constants *versus* [ninhydrin]$_T$ pass through the origin (Fig.4), indicating the order to be fractional with respect to [ninhydrin]$_T$ in both media.

2.4   Dependence of reaction rate on temperature

A series of kinetic runs was carried out at different temperatures with fixed reactant concentrations both in the absence and presence of [CTAB]$_T$ (Table 2). The linear least-squares regression technique was used to calculate the activation parameters using Arrhenius and Eyring equations.

Table 2   Dependence of pseudo-first-order rate constants (k_{obs} or k_{Ψ}) on [Cr(III)-Gly-Gly²⁺], [ninhydrin], and temperature in the absence and presence of CTAB micelles[a] at pH 5.0

$\dfrac{10^4[\text{Cr(III)-Gly-Gly}^{2+}]}{(\text{mol·dm}^{-3})}$	$\dfrac{10^3[\text{ninhydrin}]}{(\text{mol·dm}^{-3})}$	$T/℃$	$10^5 k_{obs}/\text{s}^{-1}$	$10^5 k_{\Psi}/\text{s}^{-1}$
1.0	6	70	2.4	4.5
1.5			2.4	4.4
2.0			2.4	4.5
2.5			2.3	4.4
3.0			2.4	4.5
3.5			2.3	4.5
2.0	6	70	2.4	4.5
	10		4.7	7.7
	15		6.9	12.1
	20		9.4	19.0
	25		12.5	24.5
	30		21.2	33.2
	35		27.5	39.5
	40		28.9	41.6
2.0	6	60	1.2	2.5
		65	1.9	3.1
		70	2.4	4.5
		75	4.5	6.8
		80	5.1	9.4

[a] [CTAB]=20×10^{-3} mol·dm⁻³; Uncertainties in k_{obs} and k_{Ψ} values are estimated to be less than or equal to $\pm0.1\times10^{-5}$ s⁻¹.

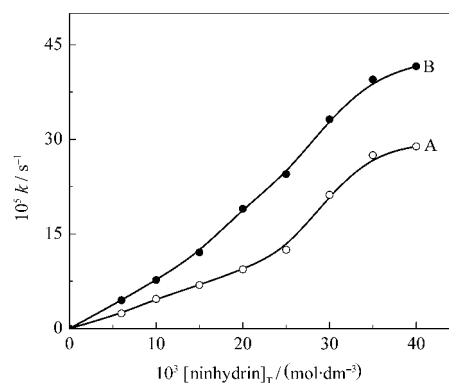**Fig.4   Plots of k *versus* [ninhydrin]$_T$ for the interaction of [Cr(III)-Gly-Gly]²⁺ with ninhydrin in the absence (A) and presence (B) of surfactant CTAB**

reaction conditions: [Cr(III)-Gly-Gly²⁺]=2.0×10^{-4} mol·dm⁻³,
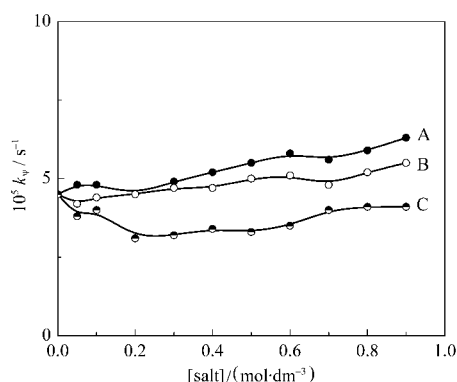[CTAB]=20×10^{-3} mol·dm⁻³, pH=5.0, T=70 ℃

Fig.5 Effect of inorganic salts on the reaction rate for the interaction of [Cr(III)-Gly-Gly]²⁺ with ninhydrin in the presence of surfactant CTAB

(A) NaBr, (B) NaCl, (C) Na₂SO₄; reaction conditions: [Cr(III)-Gly-Gly²⁺]=2.0×10⁻⁴ mol·dm⁻³, [ninhydrin]=6×10⁻³ mol·dm⁻³, [CTAB]=20×10⁻³ mol·dm⁻³, pH=5.0, T=70 ℃

$$k=A\exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

$$k=\left(\frac{k_B T}{h}\right)\exp\left(\frac{\Delta S^{\#}}{R}\right)\exp\left(\frac{-\Delta H^{\#}}{RT}\right) \tag{3}$$

where, the quantities in Eqs.(2) and (3) are the frequency factor A, the energy of activation E_a, enthalpy change $\Delta H^{\#}$, entropy change $\Delta S^{\#}$, the Boltzmann constant k_B, the Planck constant h, and the gas constant R.

2.5 Dependence of reaction rate on salt concentration

The effects of added salts on the reaction rates were also explored because salts, as additive, in micellar systems acquire a special place owing to their ability to induce structural changes, which may, in turn, modify the substrate-surfactant interactions[14]. The salt effects on the reaction rate were studied at fixed [ninhydrin]$_T$, [CTAB]$_T$, and temperature. The values of k_ψ are depicted graphically in Figs.5 and 6.

2.6 Reaction in aqueous medium

Detailed investigations reveal that the rate of formation of the product shows first-order kinetics with respect to [Cr(III)-Gly-Gly²⁺] in Eq.(1), as confirmed by: (i) the initial rate being directly proportional to the initial concentration of the complex, and
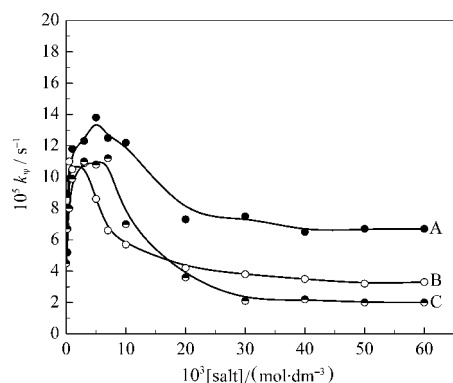

Fig.6 Effect of organic salts on the reaction rate for the interaction of [Cr(III)-Gly-Gly]²⁺ with ninhydrin in the presence of surfactant CTAB

(A) NaBenz (sodium benzoate), (B) NaSal (sodium salicylate), (C) NaTos (sodium tosylate); Reaction conditions are the same as that in Fig.5.

(ii) constancy of k_{obs} values obtained at different initial concentrations of [Cr (III)-Gly-Gly]²⁺ (Table 2). The plots of k *versus* [ninhydrin]$_T$, as shown in Fig.4, indicate a fractional-order with respect to [ninhydrin]$_T$.

On the basis of the above results and previous observations, the mechanism shown in Scheme 1 has been proposed for the reaction of [Cr(III)-Gly-Gly]²⁺ complex and ninhydrin.

It is well known that lone pair electrons of amino group are necessary for nucleophilic attack on the carbonyl group of ninhydrin[15–19]. In complex (S), this lone pair is not free, and therefore, nucleophilic attack is not possible. The reaction, therefore, proceeds through condensation of coordinated carbonyl group of ninhydrin (N) within the coordinated coordination sphere of Cr (III) (B to P). The coordination of both reactants (ninhydrin and Gly-Gly) with the same metal ion (Cr(III)) is an example of template mechanism[11a].

On the basis of the mechanism in Scheme 1, the following
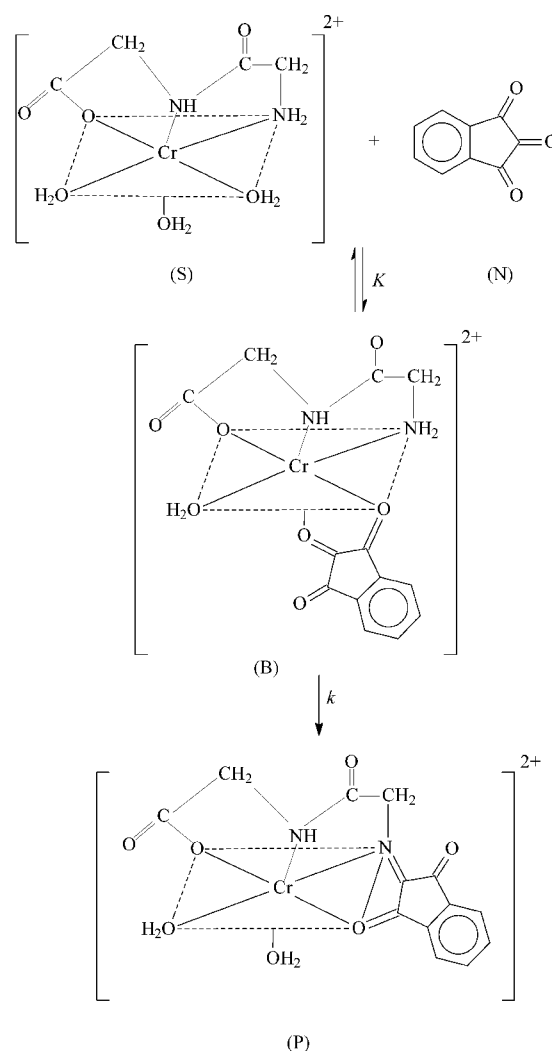
Scheme 1 Mechanism of reaction of [Cr(III)-Gly-Gly]²⁺ complex and ninhydrin

rate equation is derived:

$$\frac{d[P]}{dt}=\frac{kK[\text{ninhydrin}]_T[\text{Cr(III)-Gly-Gly}^{2+}]_T}{(1+K[\text{ninhydrin}]_T)} \qquad (4)$$

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

$$k_{\text{obs}}=\frac{kK[\text{ninhydrin}]_T}{(1+K[\text{ninhydrin}]_T)} \qquad (5)$$

Rearrangement of Eq.(5) gives

$$\frac{1}{k_{\text{obs}}}=\frac{1}{k}+\frac{1}{kK[\text{ninhydrin}]_T} \qquad (6)$$

Accordingly, a double reciprocal plot of $1/k_{\text{obs}}$ *versus* $1/[\text{ninhydrin}]_T$ should yield a straight line with an intercept (=$1/k$) and a positive slope ($1/kK$). Indeed, it was found so and the values of k and K were found to be 6.6×10^{-4} s⁻¹ and 8.3 mol⁻¹·dm³, respectively.

2.7   Reaction in the presence of CTAB

Preliminary experiments indicate that absorbance of the end product increases as the concentration of CTAB micelles increases from 0 to 20×10^{-3} mol·dm⁻³(Fig.2), whereas the wavelength of maximum absorbance remains unchanged (*vide supra*); this confirms that the product of the reaction remains the same as in aqueous medium. These observations suggest a strong association/incorporation of the product into/at the CTAB micelles. Seemingly, the hydrophobic moieties present in the end product, i.e., indandione and indole are responsible for incorporation of the product into reactive region of the CTAB micelles.

To determine the effect of CTAB micelles on the reaction rate, the kinetic experiments were performed in the presence of varying [CTAB] at constant [Cr(III)-Gly-Gly²⁺] (2.0×10^{-4} mol·dm⁻³), [ninhydrin] (6×10^{-3} mol·dm⁻³), and pH 5.0 at 70 ℃. The observed rate constant (k_{ψ}) increased from 2.4×10^{-5} to 7.3×10^{-5} s⁻¹ (ca three-fold) with increase in [CTAB] from 0 to 40×10^{-3} mol·dm⁻³. A plot of k_{ψ} *versus* [CTAB] shows a rate maximum at [CTAB]=40×10^{-3} mol·dm⁻³ (Fig.7), a very common characteristic of bimolecular reactions catalyzed by micelles[14,20]. A further increase in [CTAB] ($>40\times10^{-3}$ mol·dm⁻³) results in a decrease in the reaction rate.

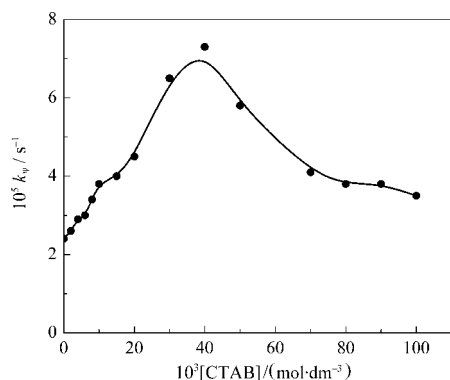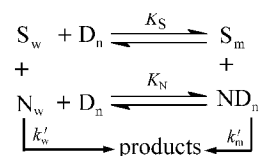The catalytic behavior of cationic surfactant (CTAB) can be rationalized in terms of the pseudo-phase model (Scheme 2) proposed by Menger and Portnoy[21] for the incorporation/association of one reactant into the micellar phase.

Scheme 2   Menger and Portnoy pseudo-phase model for the reaction of [Cr(III)-Gly-Gly]²⁺ (S) with ninhydrin (N)

S_w and S_m denote [Cr(III)-Gly-Gly]²⁺ in aqueous and micellar media, respectively; N_w denotes ninhydrin in aqueous medium.

In Scheme 2, D_n represents the micellized surfactant (i.e., [D_n]= [CTAB]$_T$−cmc).

The rate equation for Scheme 2 is given by

$$\frac{-d([S_w]+[S_m])}{dt}=\frac{-d[S]_t}{dt}=\frac{d[P]}{dt}=k'_w[S_w]+k'_m[S_m] \qquad (7)$$

where, [S]$_t$ is the stoichiometric concentration of the metal-peptide complex at time t. The observed rate constant for the product formation, k_{ψ}, is given by:

$$k_{\psi}=\frac{-d[S]_t}{dt}/[S]_t=k'_wF_w+k'_mF_m \qquad (8)$$

where, F_w and F_m are the fractions of the uncomplexed and complexed substrates, respectively. Often, for a pseudo-first-order process [D_n]≫[S_m] and F_m is constant. The equilibrium constant, K_S, can be expressed in terms of the concentrations and in terms of the fractions of the complexed and uncomplexed substrates:

$$K_S=\frac{[S_m]}{([S]_t-[S_m])[D_n]}=\frac{F_m}{[D_n]F_w}=\frac{F_m}{[D_n](1-F_m)} \qquad (9)$$

Combination of Eqs.(8) and (9) and rearrangement leads to:

$$k_{\psi}=\frac{k'_w+k'_mK_S[D_n]}{1+K_S[D_n]} \qquad (10)$$

Eq.(10) can be modified as Eq.(11) by substituting the values of second-order rate constants $k_w(=k'_w/[N_w])$, k_m ($=k'_m/M_N^S$, $M_N^S=[N_m]/[D_n]$), and the mass balance to ninhydrin [N]$_T$=[N_w]+[N_m]

$$k_{\psi}=\frac{k_w[N]_T+(K_Sk_m-k_w)M_N^S[D_n]}{1+K_S[D_n]} \qquad (11)$$

In order to obtain the values of k_m and K_S, the non-linear regression technique was adopted for Eq.(11). In the calculation, the cmc of CTAB used was 5.5×10^{-4} mol·dm⁻³ (as determined conductometrically under the experimental condition). The best fit values are given in Table 3.

The kinetic results in CTAB solutions are considered with the assumption that the mechanism of the reaction does not change in the presence of surfactant. Simply based on electrostatic considerations, the ninhydrin (owing to the presence of electron cloud on it[1]) comes closer to the CTAB micellar surface, which increases the local molarities in the Stern layer. The removal of water molecule from the inner solvation shell of Cr(III) by the coordinated Gly-Gly gives the complex some hydrophobic character. Owing to the hydrophobic nature (inspite of bearing a positive charge), the complex gets incorporated into the micelles. The micelles thus help in bringing the ninhydrin and the complex close together, which may now orient in a suitable manner for the reaction (Fig.8).

The decrease in k_{ψ} beyond [CTAB] 40×10^{-3} mol·dm⁻³ can be

Fig.7   Effect of [CTAB] on the reaction rate for the interaction of [Cr(III)-Gly-Gly]²⁺ with ninhydrin

reaction conditions: [Cr(III)-Gly-Gly²⁺]=2.0×10^{-4} mol·dm⁻³, [ninhydrin]=6×10^{-3} mol·dm⁻³, pH=5.0, T=70 ℃

Table 3   **Thermodynamic parameter, rate, and binding constant values for the reaction of metal-Gly-Gly complexes with ninhydrin**

Parameters and constants	Cr(III)[a]		Ni(II)[a]		Cu(II)[b]	
	aqueous	micellar	aqueous	micellar	aqueous	micellar
E_a/(kJ·mol^{-1})	71.2	63.8	58.4	45.6	74.6	60.3
$\Delta H^{\#}$/(kJ·mol^{-1})	68.4	60.9	55.5	42.8	71.8	57.4
$-\Delta S^{\#}$/(J·K^{-1}·mol^{-1})	122.6	135.7	177.9	203.6	133.6	156.0
$10^4 k_m$/s^{-1}	–	6.6	–	1.5	–	3.0
K_N/(mol^{-1}·dm^3)	–	67	–	84	–	65.3
K_S/(mol^{-1}·dm^3)	–	18.7	–	5.3	–	4.0
$10^5 k_2^m$/(mol^{-1}·dm^3·s^{-1})[c]	–	9.2	–	2.1	–	4.2
$10^5 k_w$/(mol^{-1}·dm^3·s^{-1})	–	2.4	–	3.1	–	5.2

[a][metal-Gly-Gly]$_T$=2.0×10^{-4} mol·dm^{-3}, [ninhydrin]$_T$=6×10^{-3} mol·dm^{-3}, pH=5.0 (sodium acetate-acetic acid), T=70 ℃, Ref.[14]; [b][metal-Gly-Gly]$_T$=1.5×10^{-4} mol·dm^{-3}, Ref.[15]; [c]k_2^m (=$V_m k_m$) is the second-order rate constant in the micellar medium, (Bunton, C. A. In Mittal, K. L.; Shah, D. O. Eds. Surfactants in solution. New York: Plenum, 1991, Vol. 1). Uncertainties in thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, and E_a are less than or equal to ±0.1 kJ·mol^{-1}, ±0.1 J·K^{-1}·mol^{-1}, and ±0.1 kJ·mol^{-1}, respectively.

explained as follows. At [CTAB] ≥40×10^{-3} mol·dm^{-3}, practically all the substrate has been incorporated into the micellar phase. When bulk of the substrate is incorporated into the micelles, addition of more CTAB generates more cationic micelles, which simply take up the ninhydrin molecules into the Stern layer, and thereby deactivate them, because a ninhydrin molecule in one micelle should not react with the complex in another micelle[22]. Another reason of decrease in k_{ψ} could be a result of counter ion inhibition.

Activation parameters (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$) in both media were calculated using Arrhenius and Eyring equations. These values are summarized in Table 3. The values of E_a clearly suggest that CTAB acts as a catalyst and provides a new reaction path with lower activation energy. The variation of the activation parameters in CTAB micelles compared in water is as expected because one may expect stabilization of the transition state owing to the presence of micelles that facilitate the occurrence of the reaction. The observed large decrease in $\Delta S^{\#}$ further strengthens the point. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values are associated to the overall reaction. In a complex reaction, each elementary step has its own
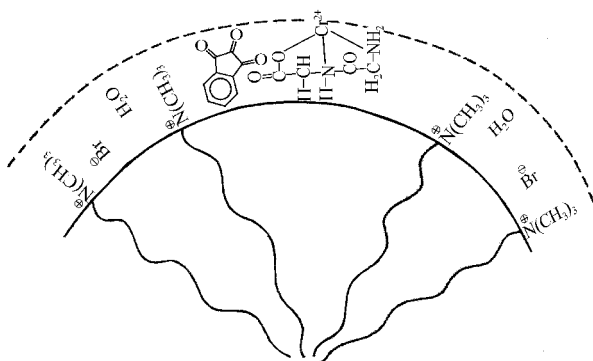

Fig.8   **Schematic model showing probable location of reactants for the cationic micellar catalyzed condensation reaction between [Cr(III)-Gly-Gly]$^{2+}$ complex and ninhydrin**

values of enthalpy and entropy. The observed rate constants are representative of the total rate and are complex functions of the true rate and binding constants. Therefore, for complex reaction path, a mechanistic explanation is not possible on the basis of $\Delta H^{\#}$ and $\Delta S^{\#}$.

Interestingly, the reactivity of Cr^{3+}/Ni^{2+}/Cu^{2+}-Gly-Gly complexes with ninhydrin is of the same order (Table 3). The reported values of the respective ionic sizes are 1.27, 1.24, and 1.28 nm for chromium, nickel, and copper, respectively. Thus, the size of all complexes will approximately be the same, and hence, the approach/penetration/incorporation of the complexes into the respective region of micelles will not differ and will consequently show the same reactivity with ninhydrin.

Direct comparison of the second-order rate constants in water (k_w, mol^{-1}·dm^3·s^{-1}) with k_m (in s^{-1}) cannot be made. The conversion of k_m into second-order rate constant (k_2^m, mol^{-1}·dm^3·s^{-1}) requires the exact value of the volume of the micellar pseudo-phase (V_m). The value of V_m=0.14 dm^3·mol^{-1} has been widely used[23–25]. Therefore, k_2^m was calculated from the relationship k_2^m=$V_m k_m$. The second-order-rate constants k_2^m and k_w are similar in magnitude. Generally, k_w>k_2^m for several bimolecular reactions in aqueous and micellar pseudo-phases[26,27]. However, there are several examples in which k_2^m is similar in magnitude with k_w[28].

2.8   Salt effect

The effect of added electrolytes on the reaction rate at pH=5.0 with constant [CTAB] (20×10^{-3} mol·dm^{-3}), [ninhydrin] (6×10^{-3} mol·dm^{-3}), and temperature (70 ℃) was also studied. The salt effect on micellar catalysis should be considered in the light of its competition with the substrate molecule that interacts with the micelle electrostatically and hydrophobically. Fig.5 shows no regular pattern in the presence of inorganic salts. On the other hand, the hydrophobic salts such as sodium tosylate (NaTos), sodium benzoate (NaBenz), and sodium salicylate (NaSal), produce rate enhancement at low salt concentrations, passing through a maximum as the [salt] is increased (Fig.6). Addition of these hydrophobic salts causes negatively charged counterions to get solubilized in micellar palisade layer with acidic groups exposed near the head group region[29,30]. Owing to neutralization of micellar surface charge, they catalyze the reaction initially by virtue of increased concentration of reactants in the Stern layer. The decreased rate observed at higher [organic salt] is a consequence of the adsorption of hydrophobic anion at the micellar surface and exclusion of substrate from the micellar surface. The progressive withdrawal of the substrate from the reaction site will slow down the rate, as was indeed observed.

3   Conclusions

The rates of reaction between [Cr(III)-Gly-Gly]$^{2+}$ and ninhydrin were determined in both water and micellar media. By comparing the values with those obtained in aqueous medium, we find that the presence of cationic micelles of CTAB catalyzes the reaction. The value of E_a clearly suggests that CTAB acts as a catalyst and provides a new reaction path with lower activation en-

ergy. This indicates the adsorption/incorporation of both reactants on the micellar surface as well as through stabilization of the transition state.

A lower value of K_S (18.7 mol⁻¹·dm³) is observed in the present case of [Cr(III)-Gly-Gly]²⁺ complex as compared to Gly-Gly only (317 mol⁻¹·dm³)[17]. This lower value indicates that hydrophobicity of the Gly-Gly molecule is diminished in the presence of Cr(III) owing to the positive charge on the complex. Does the [Cr(III)-Gly-Gly]²⁺ complex prefer Stern layer of micelles or aqueous phase? The answer to this question lies in the extent of electrostatic repulsion playing an important role in the binding of the metal complex, and thus, a low binding constant is observed.

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