Kinetics of Interaction of Histidine and Histidine Methyl Ester with Ninhydrin in Micellar Media

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ABSTRACT: Kinetics of the interaction of histidine and histidine methyl ester with ninhydrin under varying concentrations of reactants, anionic (sodium dodecyl sulphate, SDS), cationic (cetyltrimethylammonium bromide, CTAB) and non-ionic (Triton X-100, TX-100) micelles have been carried out. Rate of the reaction was found to be independent of the initial concentration of histidine (and histidine methyl ester) but was dependent on [Ninhydrin]. The SDS micelles had no effect on the rate of the reaction. In the presence of the CTAB micelles a small enhancement in the rate was observed. The rate − [CTAB] profile showed that the increase in [CTAB] increased the rate up to a maximum value and a further increase had a decreasing effect on the rate. The rate was enhanced by TX-100 also but, unlike CTAB micelles, TX-100 possessed a curve without peak for the rate − [TX-100] profile. The following rate equation was obeyed by the reaction in CTAB and TX-100 micelles:

$$k_\Psi = \frac{k_w\,[\mathrm{N}]_T + (k_m\,\mathrm{K_S} - k_w)\,[\mathrm{D}_n]\,\mathrm{M_N^S}}{1 + \mathrm{K_S}\,[\mathrm{D}_n]}$$

Values of k_w, k_m, and K_S were evaluated and are reported herein. Int J Chem Kinet 31: 103–111, 1999

INTRODUCTION

Chemical reactivity in ionic colloidal self-assemblies (*e.g.*, micelles, microemulsion droplets, and vesicles) has got 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 could 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

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reactants and micelles can account qualitatively for the kinetic effect on the reactions in micellar media; for example, cationic micelles may accelerate the rates of reactions between neutral molecules and anionic nucleophiles while anionic micelles may inhibit such reactions.

Histidine is an important amino acid which plays an active role in biological systems [1,2] and also provides binding sites for metal ions [3,4]. To understand the behavior of histidine in enzymatic environments the reaction between ninhydrin and histidine have been carried out in aqueous as well as in micellar media of anionic (SDS), cationic (CTAB), and non-ionic (TX-100) surfactants. To elaborate the role of binding of carboxylate group with these micelles, kinetic studies between histidine methyl ester and ninhydrin have also been performed. The results are reported in this paper.

EXPERIMENTAL

L-Histidine (BDH, England), histidine methyl ester (Fluka AG), ninhydrin (SRL), sodium dodecyl sulphate (SDS, 99%, CPC, USA), cetyltrimethylammonium bromide (CTAB, 99%, Loba Chem), and Triton X-100 (TX-100, 99%, Fluka AG) were used as received. Solutions of L-histidine, ninhydrin, and histidine methyl ester were prepared in acetic acid-sodium acetate buffer (pH = 5.0). All other chemicals used were of reagent grade and doubly distilled and deionized water was used throughout.

The reaction vessel, fitted with a double-surface condenser to prevent evaporation, was kept in a thermostated oil-bath. The reaction was started with the addition of thermally equilibrated ninhydrin solution of required volume to the solution containing histidine or histidine methyl ester, the surfactant, buffer, and KNO_3. Zero time was taken when half of the required volume of the ninhydrin solution had been added. Purified nitrogen gas was bubbled through the reaction mixture for stirring as well as to maintain an inert atmosphere. Progress of the reaction was followed spectrophotometrically by measuring the absorbance at 570 nm with a Bausch and Lomb spectrophotometer (Spectronic-20).

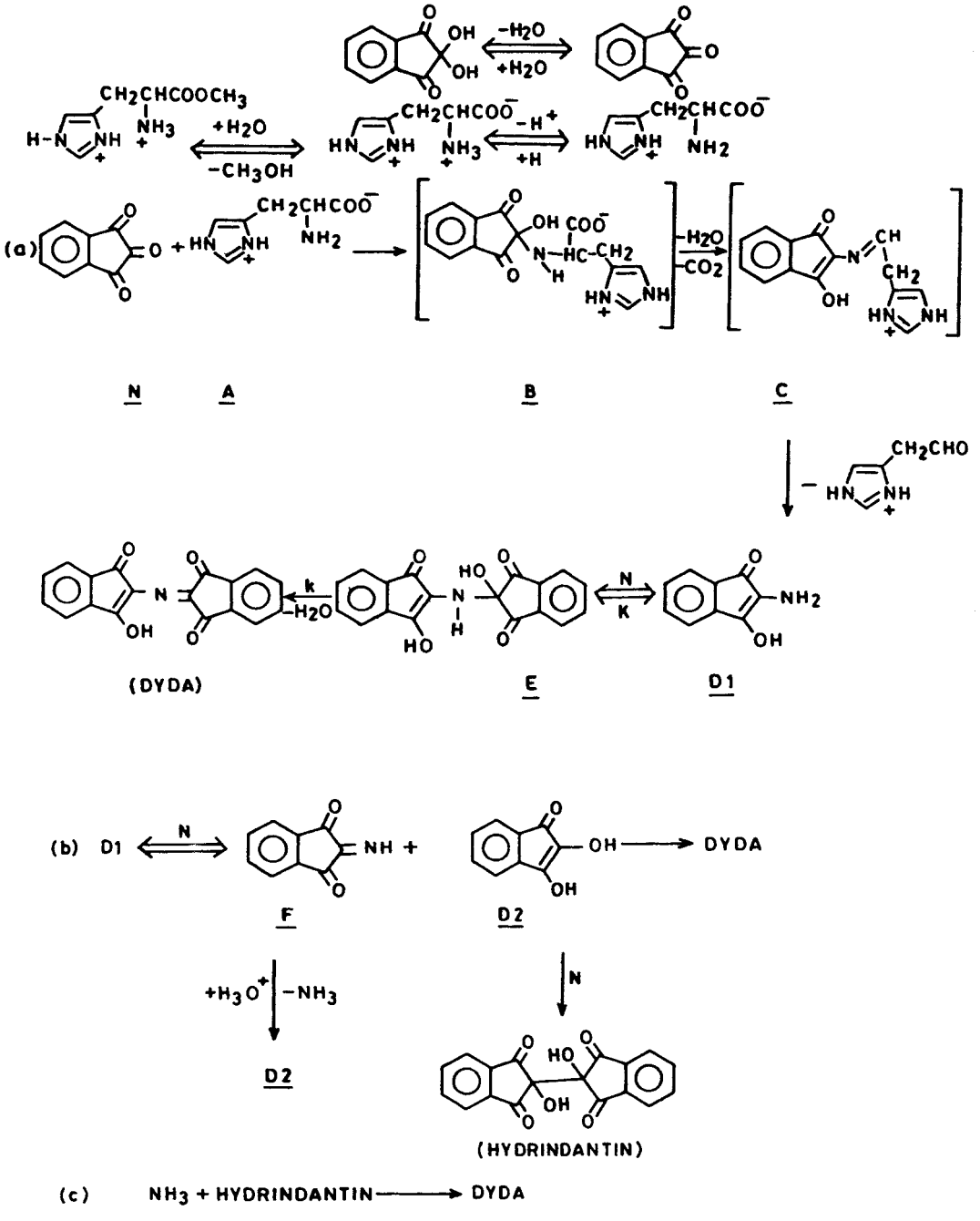
In the experiments, pseudo-first-order conditions were maintained by keeping the ninhydrin in excess (60×). The pseudo-first-order rate constants were calculated for completion of 80% of the reaction by using a program run on a VAX-11/780.

The critical micellar concentration (cmc) values of SDS, CTAB, and TX-100 in the buffer solution (pH = 5.0) containing the substrate and KNO_3 (μ = 1.0 mol dm^{-3}) were determined conductimetrically at 70°C. The values were 6.25×10^{-3} (SDS), 8.25×10^{-4} (CTAB), and 2.8×10^{-4} mol dm^{-3} (TX-100). The respective values in water are 1.14×10^{-2} (SDS, 70°C). 1.32×10^{-3} (CTAB, 55°C) and 3.00×10^{-4} mol dm^{-3} (TX-100, 65°C) [5,6].

RESULTS AND DISCUSSION

Reaction in the Absence of Micelles

Kinetics of interaction of amino acids with ninhydrin in aqueous medium has been studied under varying conditions of temperature, hydrogen ion, and reactant concentrations, and the role of metal ions thereby has been well established [7–11]. It is known that amino acids [12], on interaction with ninhydrin, produce a purple colored product, called diketohydrindylidenediketohydrindamine (DYDA). Different amino acids (except proline) react with different rates but all produce the same final product [7–14]. Histidine exists in zwitterionic form with imidazole and amino groups having positive charges and carboxylate group bearing negative charge. The condensation between the carbonyl group of ninhydrin and deprotonated amino group (which exists in equilibrium with its protonated form) of histidine takes place. The reaction starts through the attack of lone-pair of electrons of amino nitrogen to the carbonyl carbon (of ninhydrin) to give a Schiff's base (after decarboxylation). This Schiff's base is unstable and hydrolyses to give 2-amino indanedione (D_1) and an aldehyde. D_1, in turn, reacts slowly with another ninhydrin molecule to yield DYDA. A side product, hydrindantin, may also be obtained depending upon reaction conditions (low pH and low temperature). If formed, hydrindantin reduces the yield of DYDA (Scheme-I). The 2-iminoindanedione(F), upon hydrolysis, gives ammonia which may react with hydrindantin to give DYDA (route c). To our knowledge, detailed studies on kinetics of histidine-ninhydrin interaction in aqueous solutions are yet to be made. To clarify certain points, experiments were carried out, such that reactions of alternate routes (b) and (c) were suppressed (almost completely) by performing the studies at elevated temperature (≥ 70°C) and pH = 5.0 (formation of ammonia is negligible at pH ≥ 5.0) [7]. The results show (Table I) that the rate constants are independent of the initial concentration of histidine, indicating the order of the reaction with respect to histidine to be unity. The observed pseudo-first-order rate constant vs. [Ninhydrin] plots show a nonlinear behavior (Figure 1A), thus indicating fractional order in [Ninhydrin].



Scheme 1

On the basis of the observed rate law ($d[P]/dt = k_{obs}$ [Histidine]$_T$ and the mechanism (Scheme 1), the rate equation (1) is derived:

$$k_{obs} = \frac{k\,K\,[N]_T}{1 + K\,[N]_T} \qquad (1)$$

where $[N]_T$ = total ninhydrin concentration. The data treatment was carried out by an alternative method using equation (2). The double-reciprocal plots resulted in straight

$$1/k_{obs} = 1/k + 1/k\,K\,[N]_T \qquad (2)$$

lines (Figure 1B), and thus confirmed the validity of the proposed mechanism. From the intercepts and

Table I Values of Rate Constants at Varying Concentrations of Histidine and Ninhydrin at $[H^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, temperature = 70°C

10^4 [Histidine]$_T$ mol dm^{-3}	10^3 [Ninhydrin]$_T$ mol dm^{-3}	$10^4 k_{obs}$ s^{-1}
1.0	6.0	1.67
1.5	6.0	1.68
2.0	6.0	1.69
2.5	6.0	1.68
1.0	10.0	3.04
1.0	15.0	4.46
1.0	20.0	5.39
1.0	25.0	6.11
1.0	30.0	6.56
1.0	35.0	6.80
1.0	40.0	7.10

slopes, the respective values of k and K were evaluated, which are: 1.77×10^{-3} s^{-1}, 12.67 (70°C); 3.64×10^{-3} s^{-1}, 16.48 (80°C); 5.00×10^{-3} s^{-1}, 23.81 (90°C).

In order to elaborate the role played by the intermediate (i.e., the Schiff's base) in the development of purple color and also to stabilize the DYDA, the effects of anionic, cationic and non-ionic micelles on the histidine- and histidine methyl ester-ninhydrin interaction under similar kinetic conditions were studied.

Reaction in the Presence of Anionic SDS Micelles

The rate constants for the interaction of ninhydrin with histidine obtained at varying concentrations of SDS micelles were the same while those with histidine methyl ester were slightly higher as compared to the aqueous medium values (Table II).

From the mechanism of the reaction (Scheme 1), we can see that SDS (as it is an anionic micelle having negatively charged surface) cannot bind either with an electron-cloud-rich ninhydrin molecule or with a histidine bearing, negatively charged carboxylate group and amino nitrogen having a lone pair of electrons towards its surface. Therefore, it can be safely said that the presence of SDS micelles will not affect the rate of the reaction. The slight increase in rate for histidine

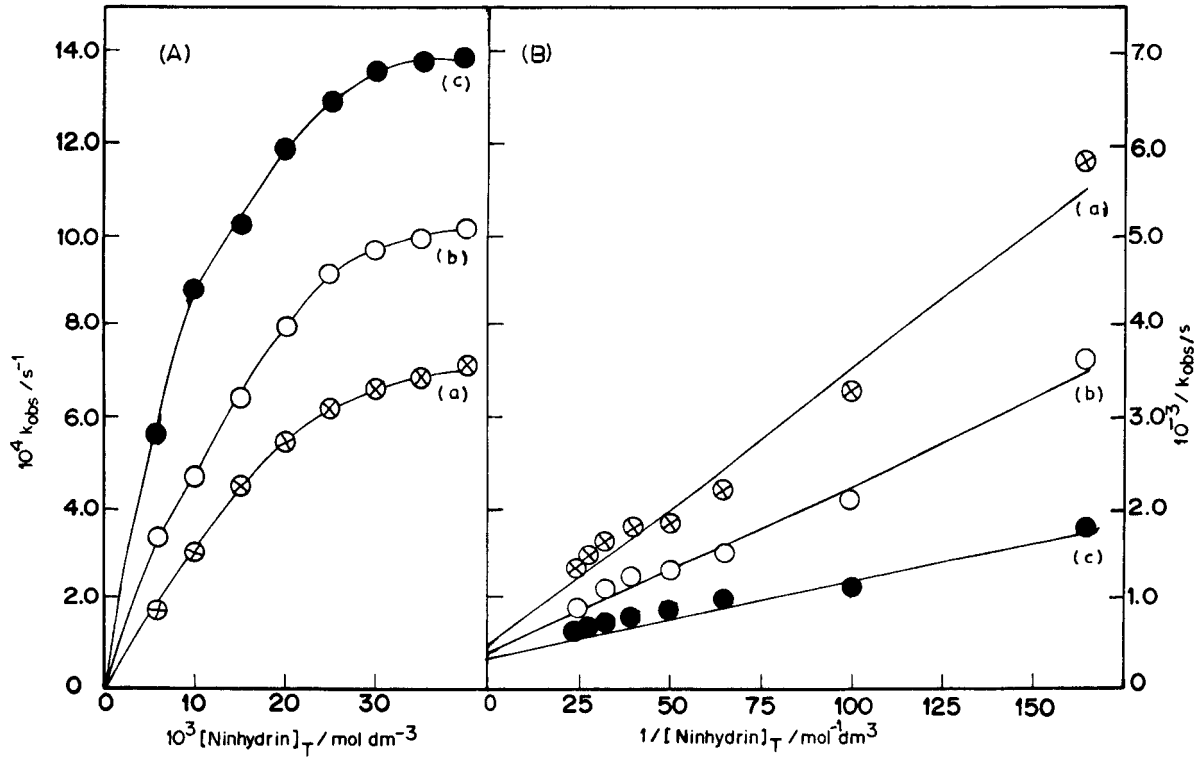


Figure 1 (A) Plots of k_{obs} vs. [Ninhydrin]$_T$ for the interaction of ninhydrin with histidine at (a) 70°C, (b) 80°C, and (c) 90°C. [Histidine] = 1.0×10^{-4} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-5}$ mol dm^{-3}. (B) Double-reciprocal plots of $1/k_{obs}$ vs. 1/[Ninhydrin]$_T$. [Histidine] = 1.0×10^{-4} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-5}$ mol dm^{-3}.

Table II Values of the Observed Pseudo-First-Order Rate Constants, k_ψ, for the Interaction of Ninhydrin with Histidine/Histidine Methyl Ester Showing Dependence upon [SDS].
[Ninhydrin] = 6.0×10^{-3} mol dm^{-3}, [H$^+$] = 1.0×10^{-5} mol dm^{-3}, temperature = 70°C

10^2 [SDS] mol dm^{-3}	10^4 k_ψ/s^{-1}	
	Histidine	Histidine Methyl Ester
0.0	1.67 ± 0.62	0.53 ± 0.04
0.5	1.74 ± 0.54	0.62 ± 0.04
1.0	1.70 ± 0.63	1.02 ± 0.05
2.0	1.68 ± 0.58	1.02 ± 0.05
5.0	1.68 ± 0.44	1.02 ± 0.05
10.0	1.68 ± 0.57	1.02 ± 0.05

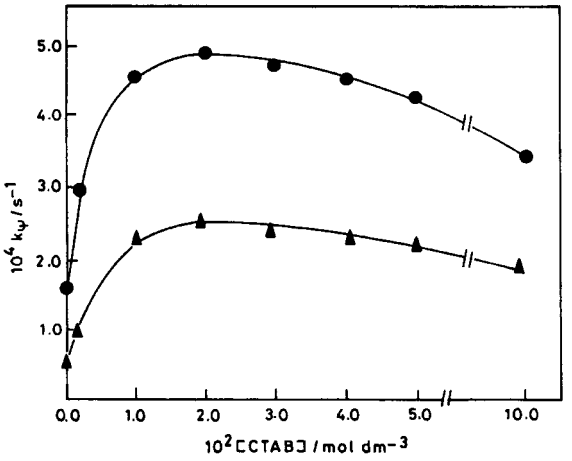


Figure 2 Plots of k_ψ vs. [CTAB] for the interaction of ninhydrin with histidine (●)/histidine methyl ester (▲) at 70°C. [Histidine] = 1.0×10^{-4} mol dm^{-3}, [Histidine Methyl Ester] = 1.0×10^{-4} mol dm^{-3}, [Ninhydrin] = 6.0×10^{-3}, [H$^+$] = 1.0×10^{-5} mol dm^{-3}.

methyl ester-ninhydrin reaction (Table II) may be due to the catalytic effect of SDS on the rate of hydrolysis of ester group to produce carboxylate group. This is in conformity with several studies made in the presence of an ionic micelle which, in most cases, have catalytic effect on the rate of hydrolysis of esters [15].

Reaction in the Presence of Cationic CTAB Micelles

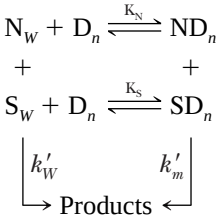
The pseudo-first-order rate constants for the development of purple color by the interaction of ninhydrin with histidine or histidine methyl ester reached a maximum value at 2×10^{-2} mol dm^{-3}. Further increase in [CTAB] leads to a slow decrease in the observed rate. Detailed studies were carried out in the presence of 2×10^{-2} mol dm^{-3} CTAB. All the results are given in Table III. The values of the rate constants were independent of the initial concentration of histidine/histidine methyl ester but were dependent on the ninhydrin concentration. Typical results are shown in Figure 2.

Ionic and polar reagents bind close to the micellar surface and reactions take place in this region. Nin-

Table III The Dependence of Pseudo-First-Order Rate Constants on [CTAB] for Histidine/Histidine Methyl Ester-Ninhydrin Reaction.
[Histidine] = 1.0×10^{-4} mol dm^{-3}, [Histidine Methyl Ester] = 1.0×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-5} mol dm^{-3}, temperature = 70°C

	10^4 k_ψ/s^{-1}			
	10^3[Ninhydrin]/mol dm^{-3}			
10^3 [CTAB] mol dm^{-3}	6.0	10.0	6.0	10.0
	Histidine		Histidine Methyl Ester	
0.0	1.67 ± 0.04	2.55 ± 0.21	0.53 ± 0.04	0.96 ± 0.06
0.5	2.13 ± 0.12	3.06 ± 0.18	0.86 ± 0.07	1.27 ± 0.11
1.0	2.49 ± 0.08	3.81 ± 0.22	0.99 ± 0.08	1.66 ± 0.12
5.0	3.85 ± 0.15	5.62 ± 0.31	2.01 ± 0.12	2.74 ± 0.08
10.0	4.68 ± 0.09	7.14 ± 0.41	2.32 ± 0.13	3.61 ± 0.14
20.0	4.94 ± 0.11	7.65 ± 0.46	2.45 ± 0.11	3.84 ± 0.13
30.0	4.71 ± 0.10	7.39 ± 0.38	2.39 ± 0.08	3.75 ± 0.11
40.0	4.48 ± 0.12	7.23 ± 0.42	2.28 ± 0.09	3.68 ± 0.09
50.0	4.22 ± 0.30	6.89 ± 0.33	2.17 ± 0.11	3.45 ± 0.12
100.0	3.41 ± 0.12	6.32 ± 0.29	1.85 ± 0.09	3.22 ± 0.14

hydrin is a polar molecule with a π-electron cloud around it, which has the likelihood of coming closer to the cationic micellar surface [16]. Histidine, being in the zwitterionic form with its negatively charged carboxylate and protonated amino groups, binds and gets accumulated in the Stern layer of the cationic CTAB micelles (the effect will be slightly diminished in the histidine methyl ester due to the presence of an ester group). Thus, the CTAB micelles help in bringing the reactants in the Stern layer and the reaction takes place in this region. This reaction of ninhydrin with histidine/histidine methyl ester in the presence of a surfactant can be explained by considering the pseudo-phase kinetic model with micelles and water regarded as distinct reaction regions [17,18]. The mechanism of the reaction is presented in Scheme 2



Scheme 2

where S_w is the substrate (histidine/histidine methyl ester) in water and SD_n is the subtrate complexed with the micellized detergent D_n ($[D_n]$ = [surfactant] − cmc) with an association constant K_S, k'_w, and k'_m are the first-order rate constants for the reaction taking place in aqueous and micellar pseudo-phases. The pseudo-first-order rate constant, k_Ψ, for overall reaction, consistent with the Scheme-II, is given by [18]

$$k_\Psi = \frac{k'_w + k'_m K_S[D_n]}{1 + K_S[D_n]} \tag{3}$$

The respective pseudo-first-order rate constants in aqueous (k'_w) and micellar (k'_m) pseudo-phases are defined as

$$k'_w = k_w\,[N_w], \quad k'_m = k_m\,M_N^S \tag{4}$$

M_N^S is the molarity of ninhydrin bound to the micellar head groups, given as

$$M_N^S = [ND_n]/[D_n] \tag{5}$$

Table IV Parameters that Best Fit the Kinetic Results for the Interaction of Ninhydrin with Histidine/ Histidine Methyl Ester in the Presence of CTAB Micelles [see equation (9)]

Parameters	Histidine	Histidine Methyl Ester
K_S	4	2
$10^2\,k_m$ (s^{-1})	3.33 ± 0.81[a]	3.34 ± 0.92[a]
	3.36 ± 0.82[b]	3.39 ± 0.86[b]
$10^3 k_2^m$($mol^{-1}dm^3s^{-1}$)	4.65 ± 1.13[a]	4.67 ± 1.29[a]
	4.71 ± 1.15[b]	4.74 ± 1.21[b]

K_N = 100, $10^3\,k_w$ = 27.60 $dm^3\,mol^{-1}\,s^{-1}$ and 10.12 $dm^3\,mol^{-1}\,s^{-1}$ for histidine and histidine methyl ester, respectively.
[a] [Ninhydrin] = 6.0×10^{-3} mol dm^{-3}
[b] [Ninhydrin] = 1.0×10^{-2} mol dm^{-3}

Values of M_N^S were estimated by considering the equilibrium

$$N_w + D_n \overset{K_N}{\rightleftharpoons} ND_n$$

$$K_N = \frac{[ND_n]}{[N_w]([D_n] - [ND_n])} \tag{6}$$

and the mass balance

$$[N]_T = [N_w] + [ND_n] \tag{7}$$

Upon solving equations (6) and (7), a quadratic equation (8) results which was solved for $[ND_n]$ with the help of a computer program where K_N was an adjustable parameter. M_N^S was then calculated with the help of equation (5). Equation (3) takes the form of equation (9) as developed by Rodenas et al. [18], when values of k'_w and k'_m are substituted from equation (4)

$$K_N[ND_n]^2 - (1 + K_N[D_n] + K_N[N]_T)[ND_n] + K_N[D_n][N]_T = 0 \tag{8}$$

$$k_\Psi = \frac{k_w[N]_T + (K_S k_m - k_w)\,M_N^S[D_n]}{1 + K_S[D_n]} \tag{9}$$

The value of K_N for the binding of ninhydrin with CTAB micelles was assumed as 100 (see our earlier paper [11].) In order to find k_m and K_S, the nonlinear least squares technique was used for equation (9). This process gave a value of least squares; that is, $\sum d_i^2$ where $d_i = k_{obsi} - k_{cali}$ at ith K_S. The calculation was repeated for different values of K_S ranging from 0.2 to 20 and the best value was the one for which $\sum d_i^2$ was minimum. The K_S, thus obtained, was used to obtain the value of k_m. These values are given in Table IV.

Table V Values of Pseudo-First-Order Rate Constants for Ninhydrin-Histidine/Histidine Methyl Ester Reaction Showing Dependence upon [TX-100].
[Histidine] = 1.0×10^{-4} mol dm^{-3}, [Histidine Methyl Ester] = 1.0×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-5} mol dm^{-3}, temperature = 70°C

10^2[TX-100] mol dm^{-3}	$10^4\ k_\psi$/s^{-1}			
	10^3[Ninhydrin]/mol dm^{-3}			
	6.0	10.0	6.0	10.0
	Histidine		Histidine Methyl Ester	
0.0	1.67 ± 0.04	2.55 ± 0.21	0.53 ± 0.04	0.94 ± 0.06
1.6	2.82 ± 0.08	5.17 ± 0.11	1.09 ± 0.05	2.13 ± 0.07
4.0	6.02 ± 0.12	9.32 ± 0.22	1.94 ± 0.08	3.74 ± 0.09
6.0	10.12 ± 0.31	13.46 ± 0.28	2.87 ± 0.11	5.38 ± 0.13
8.0	13.41 ± 0.34	18.38 ± 0.37	4.12 ± 0.09	7.26 ± 0.14
10.0	16.37 ± 0.42	22.51 ± 0.38	5.62 ± 0.18	8.96 ± 0.22
12.0	17.21 ± 0.39	25.19 ± 0.47	6.71 ± 0.22	10.27 ± 0.14
16.0	17.64 ± 0.47	26.43 ± 0.44	7.22 ± 0.22	11.63 ± 0.23

Reaction in the Presence of Non-ionic Triton X-100 Micelles

The effect of TX-100 micelles on the reaction of histidine/histidine methyl ester with ninhydrin at varying concentrations of histidine/histidine methyl ester, ninhydrin, and TX-100 were studied at 70°C and [H$^+$] = 1.0×10^{-5} mol dm^{-3}. It was found that the rate constants were independent of the initial concentrations of histidine (and histidine methyl ester) but dependent on the concentrations of ninhydrin and TX-100. The results are summarized in Table V. The kinetic studies carried out at two different [Ninhydrin] under varying [TX-100] are shown graphically in Figure 3. Unlike the effect of CTAB micelles, the TX-100 micelles gave no peaked behavior for rate vs. [surfactant] profile. At low [surfactant], the rate did show linear dependency but at higher concnetrations it became independent of [TX-100].

TX-100 is a non-ionic polar surfactant and provides an ambient environment for the binding of histidine/histidine methyl ester and ninhydrin. The reaction in the presence of TX-100 too followed Scheme 2 and the rate equation (9). Values of k_m and K_S, evaluated with the help of equations (4–9), are given in Table VI.

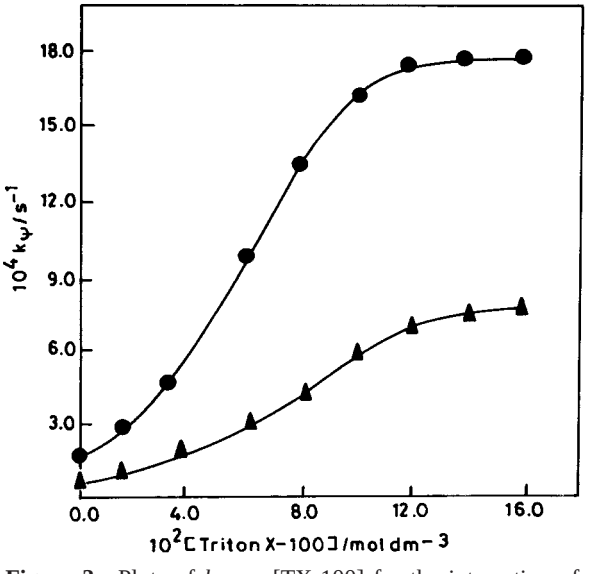


Figure 3 Plots of k_ψ vs. [TX-100] for the interaction of ninhydrin with histidine (●)/histidine methyl ester (▲) at 70°C. Reaction conditions same as in Figure 2.

Table VI Parameters that Best Fit the Kinetic Results for the Interaction of Ninhydrin with Histidine/Histidine Methyl Ester in the Presence of Triton X-100 Micelles [see equation (9)].

Parameters	Histidine	Histidine Methyle Ester
K_S	11	7
$10^2\ k_m$ (s^{-1})	4.67 ± 0.94[a]	2.15 ± 0.92[a]
	4.74 ± 0.89[b]	2.17 ± 0.93[b]
$10^2 k_2{}^m$(mol^{-1}dm^{3}s^{-1})	3.18 ± 0.63[a]	1.46 ± 0.62[a]
	3.22 ± 0.60[b]	1.48 ± 0.63[b]

K_N = 50, $10^3\ k_w$ = 27.60 dm^3 mol^{-1} s^{-1} and 10.12 dm^3 mol^{-1} s^{-1} for histidine and histidine methyl ester, respectively.
[a] [Ninhydrin] = 6.0×10^{-3} mol dm^{-3}
[b] [Ninhydrin] = 1.0×10^{-2} mol dm^{-3}

General

The values of *cmc* of surfactants are sensitive to the nature of the reactants and also depend upon reaction conditions. Therefore, the "kinetic" *cmc* is often taken as an adjustable parameter, with the proviso that it must be lower than that in water. In our study the variation in values of the kinetic *cmc* did not significantly affect the results and, therefore, all the calculations for k_m and K_S were made using the *cmc* values given in the experimental part.

Histidine and histidine methyl ester are highly soluble in water and due to their hydrophilic nature the values of K_S are quite low [19]. The higher values of K_S for histidine rather than histidine methyl ester with micelles of both CTAB and TX-100 may be because histidine is more polar and hence more suitable for solubilization in the Stern layer of CTAB/outer shell of TX-100 micelles. As regards higher values of K_S in TX-100 rather than in CTAB, the positive charge on imidazole moiety of A (cf. Scheme 1) seems to play a role, as there will be less objection for solubilization in the non-ionic TX-100 than in the cationic CTAB.

The rate constants in micellar pseudo-phase, k_m (whose unit is reciprocal seconds), cannot be compared directly with the second-order rate constant in water, k_w (having the unit $dm^3\ mol^{-1}\ s^{-1}$). The comparison can be made by considering the volume element of reaction in the micellar pseudo-phase; that is, volume of the reactive region. Thus, the second-order rate constant in the micellar pseudo-phase, k_2^m, is given by

$$k_2^m = V_m k_m \tag{10}$$

where V_m is the volume element in dm^3 per mol of micellised surfactant. The value of $V_m = 0.14\ dm^3$ for CTAB micelles (i.e., the volume of the Stern layer) as found by Bunton and coworkers [20]. However, the value of V_m for non-ionic TX-100 was estimated by using an oblate ellipsoid [21,22] instead of a spherical micellar model [20]. In this model the total volume of the micelle is determined by using the semi-major axis (a = 47.5 Å) and semi-minor axis (b = 22.5 Å) [22]. For an oblate ellipsoid, the radius of a sphere of equal volume is $(a^2b)^{1/3}$. From this the volume of hydrophobic region (a = 35 Å, b = 10.0 Å) of the micelle was substracted to determine the volume element available per micelle. Using 143 as the aggregation number of TX-100 micelle [21] and number of molecules per gm mole of TX-100, the value of V_m was obtained as 0.68 dm^3 (this being the molar volume of the outer shell reactive region).

The values of k_2^m in the micelles of CTAB and TX-100 are quoted in Tables IV and VI. The second-order rate constants for histidine-ninhydrin reaction in CTAB and TX-100 micelles are, respectively, 5.93 and 0.87 times than the second-order rate constants in water (k_w/k_2^m). The k_w/k_2^m values for histidine methyl ester-ninhydrin in CTAB and TX-100 micelles are 2.17 and 0.69, respectively. Thus, the second-order rate constants (for both histidine and histidine methyl ester) in the CTAB micellar pseudo-phase are lower than the second-order rate constants in aqueous phase, whereas a reverse case is observed in TX-100: but the highest reaction rate was obtained in micellar media.

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