Cationic Micellar Effect on the Kinetics of Interaction between Dipeptide (Glycyl–Alanine) and Ninhydrin with and without Salts Additives

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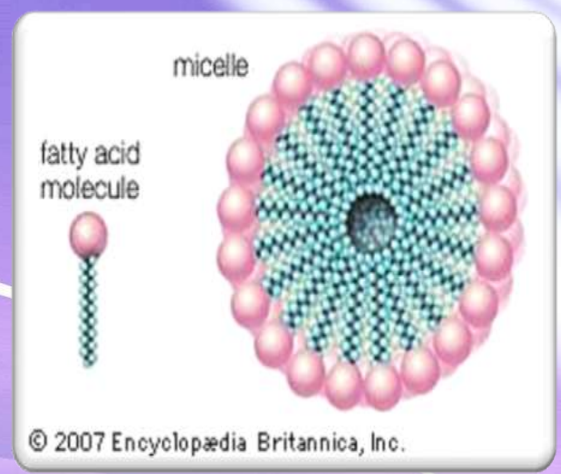
▪Surfactants are amphiphilic molecules, consisting of both a hydrophilic polar head group and a hydrophobic hydrocarbon chain, which decrease the surface as well as the interfacial tension at the interface and form aggregates called micelles at a threshold concentration known as the critical micelle concentration (cmc).

▪The word micelle was coined by J.W. McBain in 1920 to describe colloidal sized particles of detergents and soaps, and the phenomenon of self-association of monomers into micelles was called micellization.



•Glycyl-Alanine is a dipeptide, where the two amino acid molecules, glycine and alanine, bind together by means of dehydration reaction and is one of the important constituent which gets released on protein hydrolysis.

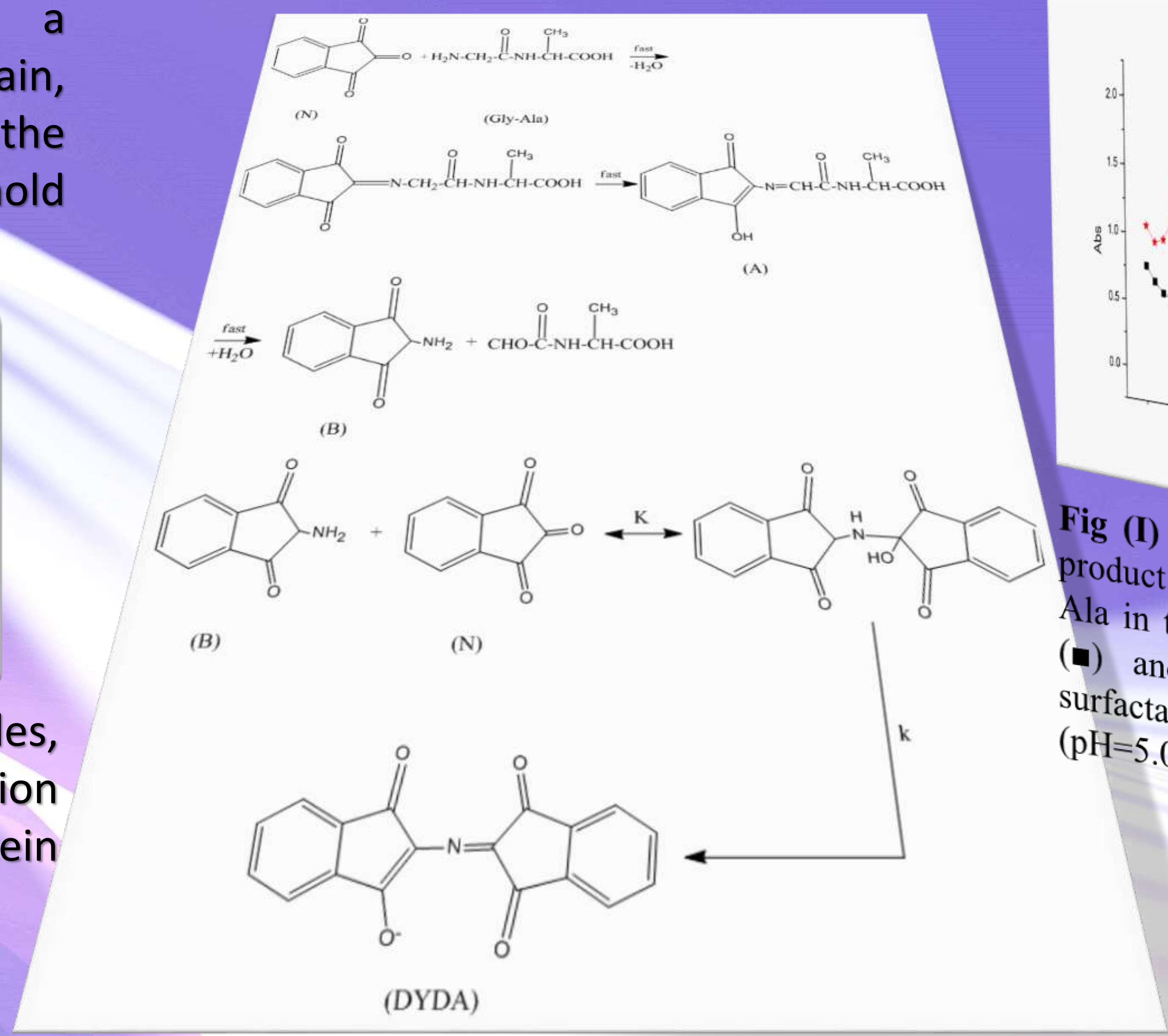
•Catalytic kinetic methods are based on chemical reactions where the rate is influenced by the reaction conditions. That is why the development, optimization and achievement of these methods rely mainly on application of modern theories on chemical kinetics, catalysis and coordination chemistry.

•The nature of a surfactant plays a very important role in micellar catalysis. In addition to this, a small change in surfactant architecture can induce changes in the surface properties and rigidity of the micelles which markedly affect the reactivity of substances.

•The requisite volumes of Glycyl-Alanine (Gly-Ala), buffer and surfactant solutions were taken in a reaction vessel. The reaction was started by adding a requisite volume of thermally equilibrated ninhydrin solution. Pseudo-first-order conditions were maintained in all kinetic runs.

•The amount of the reaction products depend upon temperature, pH and reactant concentrations. In the present case, the condensation between carbonyl group of ninhydrin and amino group of Gly-Ala takes place. The reaction starts through the attack of lone-pair of electrons of amino nitrogen (of Gly-Ala) to the carbonyl carbon (of ninhydrin) to give Schiff base A. This Schiff base is unstable and hydrolyses to give 2-amino indanedione, B, which reacts slowly with another ninhydrin molecule to yield the product P named diketohydrindylidenediketohydrindamine (DYDA). (Scheme (I)).

•The absorbance of the product DYDA, (also called Ruhemann's purple) was measured at λmax =570nm (Fig. I).



Scheme (I)

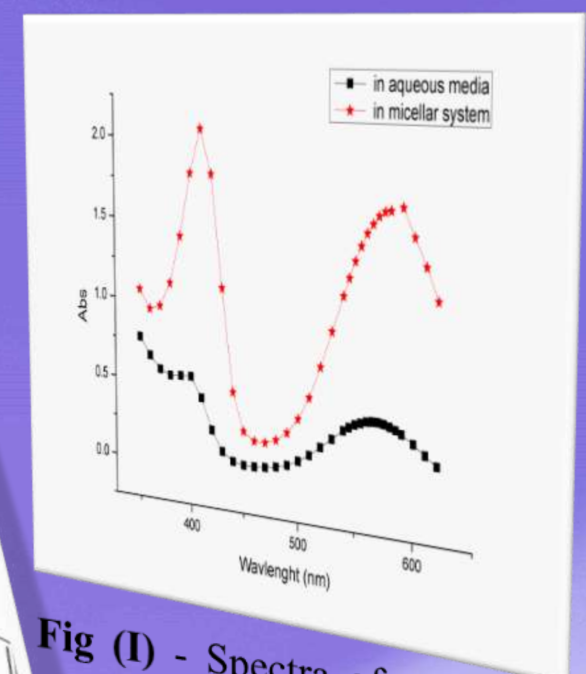


Fig (I) - Spectra of reaction of product of ninhydrin with Gly-Ala in the absence of surfactant (■) and in the presence of surfactant (•) in buffer solution (pH=5.0) at 70ºC

•In aqueous media, a micellar system can serve as a catalyst for organic reactions, but it is also possible for it to retard such reactions. The efficiency of surfactant used in reducing the surface tension of water depends on the structure of surfactant and on its concentration and this can lead to affect the reaction rate (Fig. II).

•Cetylpyridinium chloride (CPC), Cetyltrimethylammonium bromide (CTAB), and trimethyl (tetradecyl) ammonium bromide (TTAB)) were used in pH =5.0 and at 70º C.

•The reaction rates in micelles used are in the order: CTAB ≈ TTAB > CPC

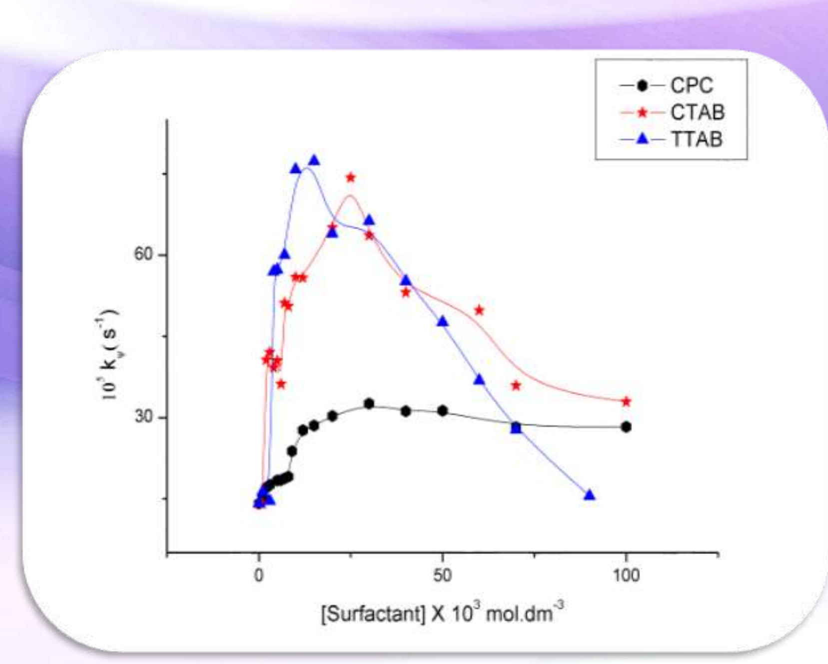
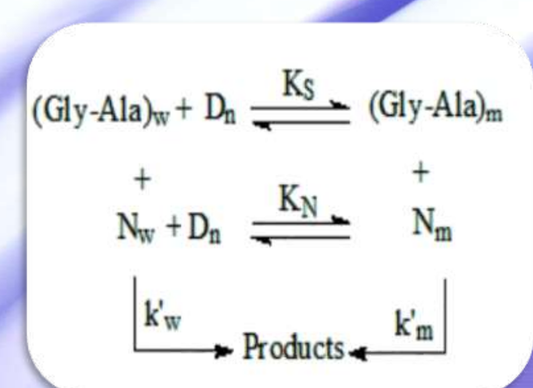


Fig (II) - Effect of surfactant concentration on the reaction rate for interaction of ninhydrin with Gly-Ala

Proposed mechanism for increase in rate of reaction in presence of surfactants has been explained in the light of Menger and Portnoy and developed by Bunton and Romsted.
This model is called pseudo-phase model of the micelles.



•Salts, as additives, in micellar systems acquire a special place due to their ability to induce structural changes which may, in turn, modify the substrate-surfactant interactions.

•To enhance the reaction between ninhydrin with Gly-Ala in presence of CPC, several inorganic slats (sodium chloride NaCl, sodium bromide NaBr, and sodium sulfate Na_2SO_4) and organic salts (sodium salicylate NaSal, sodium benzoate NaBenz, and sodium tosylate NaTos) were explored. An example of the salts additives effect on the reaction rate are shown in Table (I).

The presence of inorganic salts [NaCl, NaBr, Na_2SO_4] dose not bring any regular effect but using organic salts [NaSal, NaBenz, NaTos] shows an increase in the rate followed by a decrease.(Fig III).

Table(I) – The effect of salts additives on the reaction rate constant (k_ψ)

[Salt]	k_ψ (10^5) s^{-1}
No salts added, [CPC] =$20X10^{-3}$ $mol.dm^{-3}$	30.32
[Inorganic Salt]= 0.9 $mol.dm^{-3}$	
NaCl	50.11
NaBr	46.05
Na_2SO_4	48.41
[Organic Salt]= 5 $X10^{-3}$ $mol.dm^{-3}$	
NaSal	64.11
NaBenz	45.73
NaTos	46.72

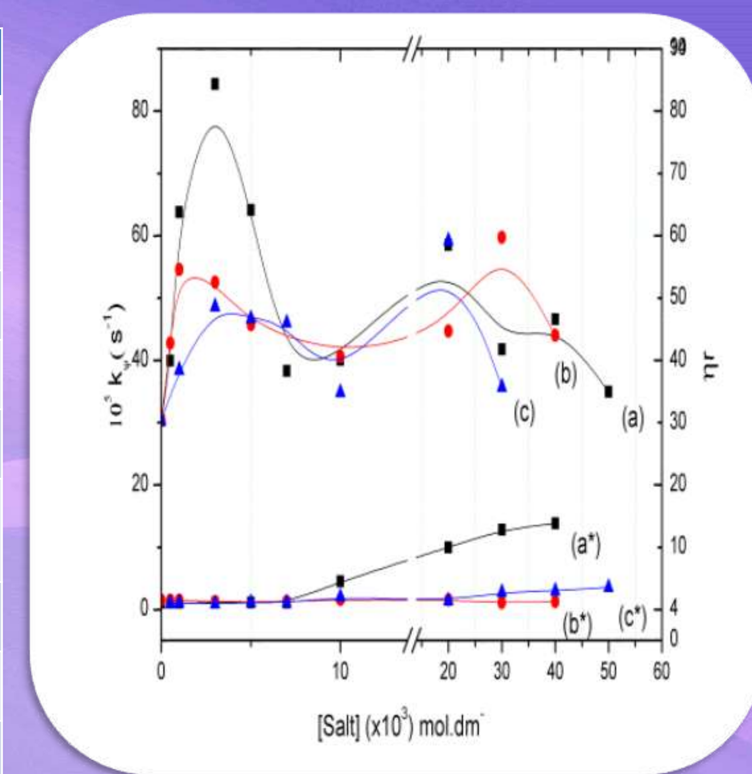


Fig (III) - Effect of [organic salts] on the reaction rate (a,b,c) and on solution viscosity (a*,b*,c*) for the interaction of ninhydrin with Gly-Ala in the presence of surfactant. Reaction Condition: [Gly-Ala] = 2.0 $x10^{-4}$ mol dm^{-3}, [ninhydrin] = 6.0$x10^{-3}$ mol dm^{-3}, [CPC] = 20$x10^{-3}$ mol dm^{-3}, pH = 5.0, temperature = 70 °C.. NaSal (a,a*), NaBenz (b,b*),NaTos (c,c*).

Herein we report, the reaction between dipeptide Gly-Ala and ninhydrin in both aqueous and in micellar media. By comparing the values with those obtained in aqueous medium, we find that the presence of cationic micelles catalyze the reaction with less enhancement for CPC. Adding salts to the micellar media can increase the reaction rate.

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