JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2007; **20:** 440–447
Published online 9 May 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/poc.1171

Role of cationic gemini surfactants toward enhanced ninhydrin–tryptophan reaction

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Received 14 July 2006; revised 15 January 2007; accepted 25 January 2007

ABSTRACT: In this paper we report the effect of dicationic 'gemini' surfactants $(CH_3)_2C_{16}H_{33}N^+$—$(CH_2)_m$—$N^+C_{16}H_{33}(CH_3)_2$, $2Br^-$ (where $m = 4$, 5, 6) on the reaction of ninhydrin with DL-tryptophan. The gemini surfactant micellar media are comparatively more effective than their conventional monomeric counterpart cetyltrimethylammonium bromide (CTAB) micelles. Also, whereas typical rate constant (k_ψ) increase and leveling-off regions, just like CTAB, are observed with geminis, the latter produce a third region of increasing k_ψ at higher concentrations. These subsequent increases are ascribed to changes in micellar morphologies, consistent with changes in ^{1}H NMR line widths. Quantitative kinetic analysis of the rate constant–[surfactant] data has been performed on the basis of modified pseudophase model. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: micellar kinetics; cationic gemini surfactants; ninhydrin; tryptophan

INTRODUCTION

Ninhydrin is the well known fingerprint developing agent and is widely used reagent for estimation of amine functionality.[1–5] Since its use depends on the formation of purple-colored diketohydrindylidenediketohydrindamine (DYDA, also known as *Ruhemann's purple*, $\lambda_{max} = 400$ and 570 nm)[2], several attempts, that include coordination of amino acids with metal ions, change of solvent, pretreatment of enzymes, addition of surfactants, etc.,[6] have been made in order to enhance the usefulness of the method.[7] Regarding the effect of surfactants we have successfully demonstrated that both the ninhydrin–amino acid and ninhydrin–metal amino acid complex reactions are catalyzed by the surfactant micelles. In the studies we used traditional (single hydrocarbon chain/single polar head group) surfactants, the so-called 'conventional' ones. Recently, a new class of surfactants called 'dimeric' or 'gemini', consisting of two hydrophobic alkyl tails and two polar, or ionic, head groups covalently linked through a flexible or rigid spacer,[8–10] has been introduced which are attracting current attention in the area of surfactant science because of displaying a number of unique properties (e.g., very low critical micelle concentration (cmc), high viscoelasticity, superior surface activity, better wetting, unusual morphologies, etc.). Micellar morphologies and properties of the gemini surfactants are found to be significantly dependent on the nature of the hydrophobic tail, head group, and spacer. Surprisingly, despite a large body of information being available on the physico-chemical aspects of gemini surfactants and the assemblies they form, studies of their effects upon reaction rates have not attracted due attention. For this reason we have performed kinetic studies of the ninhydrin–DL-tryptophan reaction in the presence of three dicationic gemini micelles (Fig. 1). For comparison, the effect of the cationic surfactant cetyltrimethylammonium bromide (CTAB), which can be considered as 'monomeric' counterpart of the above geminis, has also been examined under similar kinetic conditions.[6c] The reason for choosing this particular reaction is that the mechanism in water,[11] in different solvent media,[6h] and in the presence of CTAB surfactant[6c] system is well established. It is important to mention here that under the same reaction conditions no color developed in the absence of gemini surfactants or in the presence of CTAB micelles,[6c] whereas a small concentration (below cmc) of the geminis was sufficient to accelerate the rate of the reaction. The work was undertaken in the hope that the use of gemini surfactants may allow the use of low concentrations of the reactants (ninhydrin and amino acid) as well as maximize the rate, thus, enhance the sensitivity of the technique/reaction.

RESULTS AND DISCUSSION

Though the general mechanism of the *ninhydrin reaction* is well known, it is necessary to describe its salient

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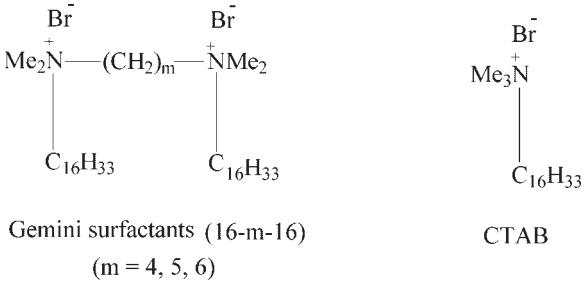


Figure 1. The surfactants used in the present study

features. Carbon dioxide, aldehyde, ammonia, hydrindantin, and *Ruhemann*'s *purple* are the products of the reaction[5] that proceeds through the formation of a Schiff base which is unstable and undergoes decarboxylation and hydrolysis to yield 2-amino-indanedione (A) as a stable intermediate (Scheme 1). This intermediate acts as a reactant in the formation of ammonia and *Ruhemann*'s *purple* and the two reactions (i.e., hydrolysis by route (i) and condensation by route (ii)) occur simultaneously. Reactions of both the routes strongly depend upon conditions like pH, presence of atmospheric oxygen, temperature, etc. A yellowish-colored product is formed (instead of *Ruhemann*'*s purple*) in the presence of atmospheric oxygen, as A is highly sensitive to molecular oxygen. At low pH, chiefly route (i) is followed and ammonia is evolved almost quantitatively with no *Ruhemann*'s *purple* formation while route (ii) predominates at $pH \geq 5.0$.

Relevant equilibria involving the reactant species are also shown in Scheme 1. As regards the reactive species of DL-tryptophan (as a matter of fact, any α-amino acid), it has been argued on several occasions[6] that, toward nucleophilic attack on the >C═O group of ninhydrin (N), it is $RCH(NH_2)COOH$, which is in equilibrium with the zwitterionic form $RCH(N^+H_3)COO^-$ (Scheme 1).

Rate–[surfactant] profiles for kinetics of ninhydrin with DL-tryptophan

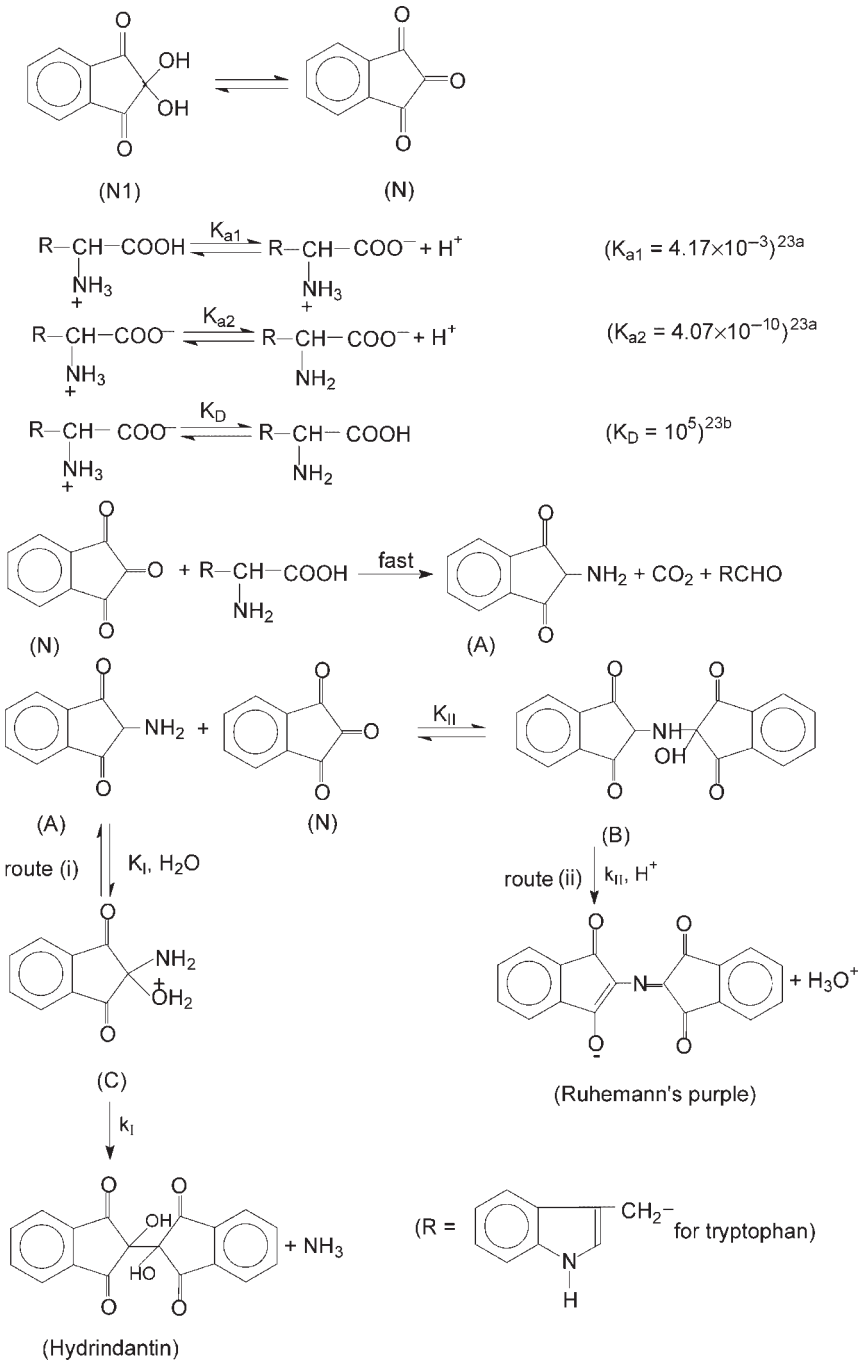
As already mentioned, no purple color developed with $[\text{ninhydrin}] = 5.0 \times 10^{-3}\,\text{mol dm}^{-3}$ and $[\text{tryptophan}] = 1.0 \times 10^{-4}\,\text{mol dm}^{-3}$ at $pH = 5.0$ and temp. = 70 °C either in pure aqueous or $[\text{CTAB}] = 20.0 \times 10^{-5}\,\text{mol dm}^{-3}$ (however, the reaction did occur at $[\text{CTAB}] \geq 5.0 \times 10^{-3}\,\text{mol dm}^{-3}$ (cmc of CTAB = $13.7 \times 10^{-4}\,\text{mol dm}^{-3}$ at 70 °C) and it had been studied in detail[6c]). With the 16-*m*-16 geminis the reaction occurred at a surfactant concentration as low as $20.0 \times 10^{-5}\,\text{mol dm}^{-3}$; therefore, detailed kinetic investigations were made with the three geminis ($m = 4, 5, 6$) only.

The pseudo-first-order rate constants (k_ψ, s^{-1}) for the title reaction were determined in micellar media at several gemini surfactant concentrations. Figure 2 shows the variation of k_ψ with surfactant concentrations. With conventional surfactants, k_ψ had been found to increase monotonically and after the substrates completely bind the micelles, it attained constant values (for monomolecular reactions) or passed through a maximum (for bimolecular reactions) with increasing [surfactant].[12–16] In the present case, however, with the gemini surfactants, k_ψ first increases with surfactant concentration (part I), remains constant upto certain concentration (part II – parts I and II behavior is akin to conventional surfactant micelles),[12–16] and then again increases (part III). In part I, at concentrations lower than the cmc, k_ψ should remain constant. The observed catalytic effect may, therefore, be due to (i) presence of premicelles and/or (ii) preponement of micellization by reactants[17] (as is also confirmed by cmc decrease at reaction conditions, Table 2).

Whereas no reaction has been observed in range II with conventional surfactant (CTAB),[6c] k_ψ remains constant upto $40.0 \times 10^{-4}\,\text{mol dm}^{-3}$ for gemini surfactants. This undoubtedly shows better catalyzing power of the gemini surfactants over the corresponding single chain surfactants. This could be due to the presence of spacer in the geminis which decreases the water content in the aggregates making the environment less polar and thus causing rate increases (see Scheme 1 – route (i) may get suppressed). Menger *et al.* [18] have already concluded that due to proximity of positive charges in gemini micelles anion binding at surfaces is increased at the expense of binding of H_2O. The behavior in part II is same for all the three geminis but values of k_ψ at all concentrations are in the order: $m = 4 > 5 > 6$ (Fig. 3). This is not for the first time but best results with 16-4-16 were obtained earlier also.[20] It is well known that, to minimize its contact with water, a spacer longer than the 'equilibrium' distance between two $-\overset{+}{N}Me_2$ head groups (the 'equilibrium' distance occurs at $m = 4$ in 16-*m*-16 geminis) tends to loop towards the micellar interior.[20,21] This increased looping of the spacer (for $m > 4$) will progressively make the Stern layer more wet (in comparison with the $m = 4$ gemini) with a resultant decrease in k_ψ. Thus the results are consonant with the earlier findings that increase in the water content of the reaction environment has an inhibiting effect.[6e,f,g,22]

The results of part III are most interesting: instead of k_ψ remaining constant, it increases (though slowly) in the surfactant concentration range 40.0×10^{-4}–$300 \times 10^{-4}\,\text{mol dm}^{-3}$. After leveling-off, further increase at higher [gemini] is probably associated with a change of micellar structure. That structural changes indeed occur at higher [gemini] are confirmed by examining the ^{1}H NMR spectra of the surfactants. Whereas chemical shifts with increase in concentration of surfactants remain almost invariant, increases of line width at half-height (lw) signals of hydrogens of $—N^+CH_3$ segment are seen (Fig. 4). The broadening is consonant with the

DOI: 10.1002/poc

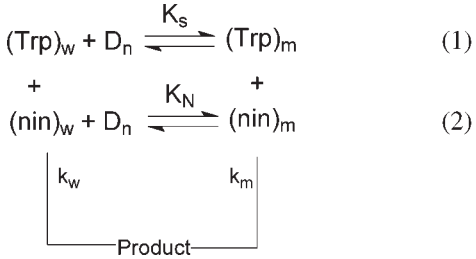


Scheme 1

literature evidence for transition to larger aggregates.[24,25] Obviously, changes in aggregate morphology provide different reaction microenvironments (less polar), hence the k_ψ increases at higher [gemini] (Fig. 2).

Analysis of k_ψ – [gemini] data

The observed catalytic role of gemini micelles (upto range II) can be explained in terms of the modified pseudophase model[14,26,27] (Scheme 2) originally proposed by Menger and Portnoy.[28]



Scheme 2

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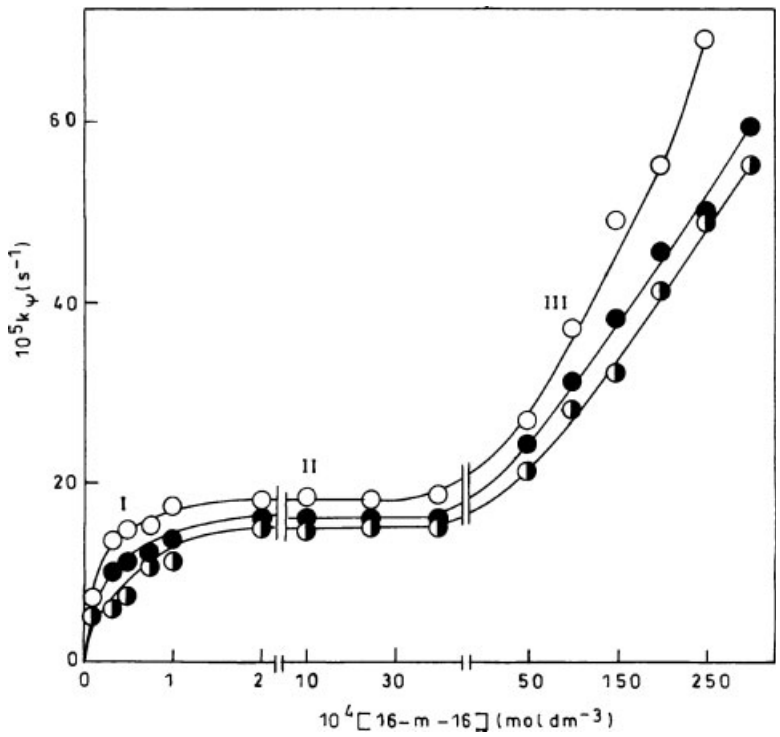

Figure 2. Variation of k_ψ for the reaction of DL-tryptophan (1.0×10^{-4} mol dm^{-3}) with ninhydrin (5.0×10^{-3} mol dm^{-3}) in the presence of 16-*m*-16 gemini micelles at 70 °C. $m = 6$ (◑), 5 (●), 4 (○)

Table 1. Values of binding constants (K_S, K_N) and k'_m for the reaction of ninhydrin (5.0×10^{-3} mol dm^{-3}) with DL-tryptophan (1.0×10^{-4} mol dm^{-3}) in presence of CTAB and gemini surfactants at 70 °C

	Parameter		
Surfactant	K_S (mol^{-1} dm^3)	K_N[a] (mol^{-1} dm^3)	$10^2 k'_m$ (s^{-1})
CTAB[6c]	59	100	0.055
16-6-16	68	70	6.44
16-5-16	70	75	6.82
16-4-16	72	79	7.20

[a] For calculation details see Ref. 6i.

w and m represent the aqueous and micellar pseudophase, respectively, and D_n is the micellized surfactant. Neglecting k_w (as no purple color developed in the aqueous medium[6c]), the first-order rate equation according to Scheme 2 is given by

$$k_\psi = \frac{k_m K_S [D_n]}{1 + K_S [D_n]} \tag{3}$$

The first-order rate constant in micellar (k_m) pseudophase is related to the second-order rate constant in the micellar (k'_m) pseudophase by

$$k_m = \frac{(k'_m[(nin)_m])}{[D_n]} = k'_m M_N^S \tag{4}$$

Table 2. Critical micelle concentration (cmc) values of gemini surfactants in absence and presence of DL-tryptophan (1.0×10^{-4} mol dm^{-3}) and ninhydrin (5.0×10^{-3} mol dm^{-3})

	10^5cmc (mol dm^{-3})					
	16-6-16		16-5-16		16-4-16	
Solution	30 °C	70 °C	30 °C	70 °C	30 °C	70 °C
Water	4.37(4.46)[a]	5.55	3.63(3.60)[a]	5.40	2.83(2.63)[a]	4.75
DL-Tryptophan	4.10	5.0	3.0	3.40	2.40	2.50
Ninhydrin	2.55	4.85	2.45	2.80	1.25	1.50
Tryptophan + ninhydrin	2.35	4.40	2.00	2.40	1.00	1.25

[a] Determined from surface tension measurements.

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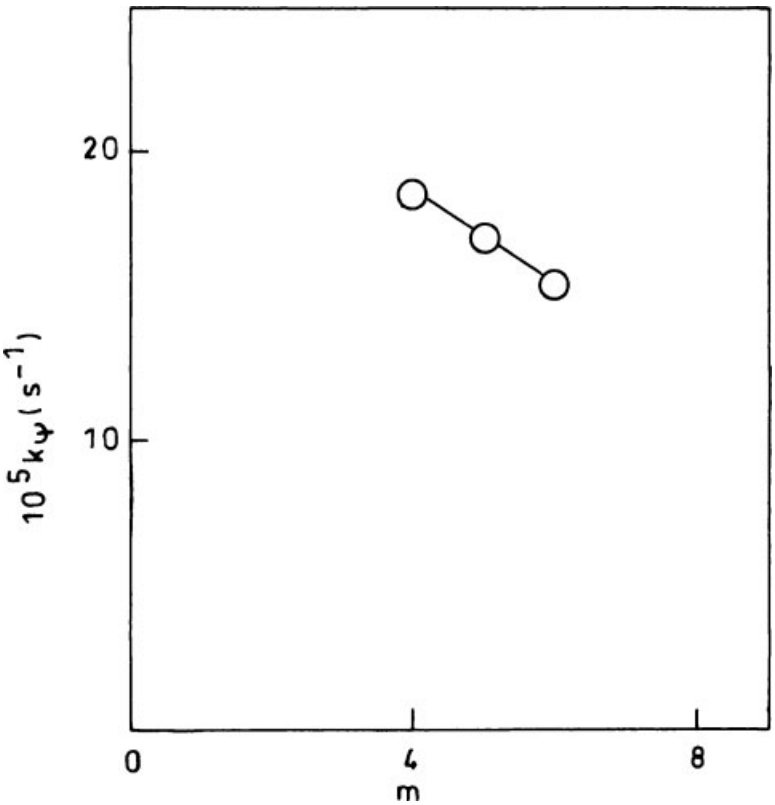

Figure 3. Dependence of k_ψ as a function of the spacer chain length (*m*-value) of 16-*m*-16 gemini micelles for the reaction of DL-tryptophan (1.0×10^{-4} mol dm^{-3}) with ninhydrin (5.0×10^{-3} mol dm^{-3}) at 70 °C. [geminis] = 2.5×10^{-3} mol dm^{-3}

where M^S_N (=[(nin)$_m$]/D$_n$) is the mole ratio of ninhydrin bound to micellar head group.

Equation (3) can be written as Eqn (5) when k_m value is substituted from Eqn (4)

$$k_\psi = \frac{k'_m K_S [D_n] M^S_N}{1 + K_S [D_n]} \quad (5)$$

Values of k'_m and binding constant K_S were obtained using a computer-based program[6b] and are given in Table 1. The data in Table 1 reveal that the binding constant (K_S) for the substrate is larger with 16-4-16 gemini micelles compared to that with 16-5-16, 16-6-16, and CTAB. The second-order rate constants in the micellar pseudophase, k'_m, are also higher in the 16-4-16 gemini micelles. Taken together, these results confirm significantly enhanced reaction rates in 16-*m*-16 gemini micelles for the ninhydrin–DL-tryptophan reaction.

Finally, we can conclude that unlike conventional single chain surfactants which show a constancy in k_Ψ, it again increases with the 16-*m*-16 type gemini surfactants. ^{1}H NMR spectra show a broadening in peaks at these later concentrations. Both kinetic and ^{1}H NMR results indicate that larger aggregates are forming at these surfactant concentrations due to which a less polar environment is available for the reaction to proceed. Hence, k_Ψ increases at high gemini surfactant concentrations.

EXPERIMENTAL SECTION

Materials

Ninhydrin (E. Merck, India, 99%), DL-tryptophan (SISCO, India, 99%), CTAB (BDH, England, ≥99%), 1,6-dibromohexane (Fluka, ≥97%), 1,5-dibromopentane (Fluka, ≥98%), 1, 4-dibromobutane (Fluka, ≥98%), *N*, *N*-dimethylhexadecylamine (Fluka, ≥95%), ethyl acetate (HPLC and spectroscopy grade, 99.7%), *n*-hexane (HPLC and spectroscopy grade, 99.0%), and ethanol absolute (E. Merck, Germany, 99.8%) were used as received. The stock solutions of tryptophan, ninhydrin, and geminis were prepared in CH_3COONa–CH_3COOH buffer solution (pH 5.0) which was prepared by mixing 30 cm^3 of 0.2 mol dm^{-3} acetic acid and 70 cm^3 of 0.2 mol dm^{-3} sodium acetate.[29] D_2O (99.9%) was an Aldrich product.

Synthesis

The gemini surfactants were synthesized by refluxing the corresponding α, ω-dibromoalkanes ($m = 4$, 5, 6) with *N*, *N*-dimethylhexadecylamine (molar ratio 1:2.1) in dry ethanol at 80 °C for 48 h. The solvent was removed under vacuum and the solid thus obtained was recrystallized four to five times from hexane/ethyl acetate mixture to

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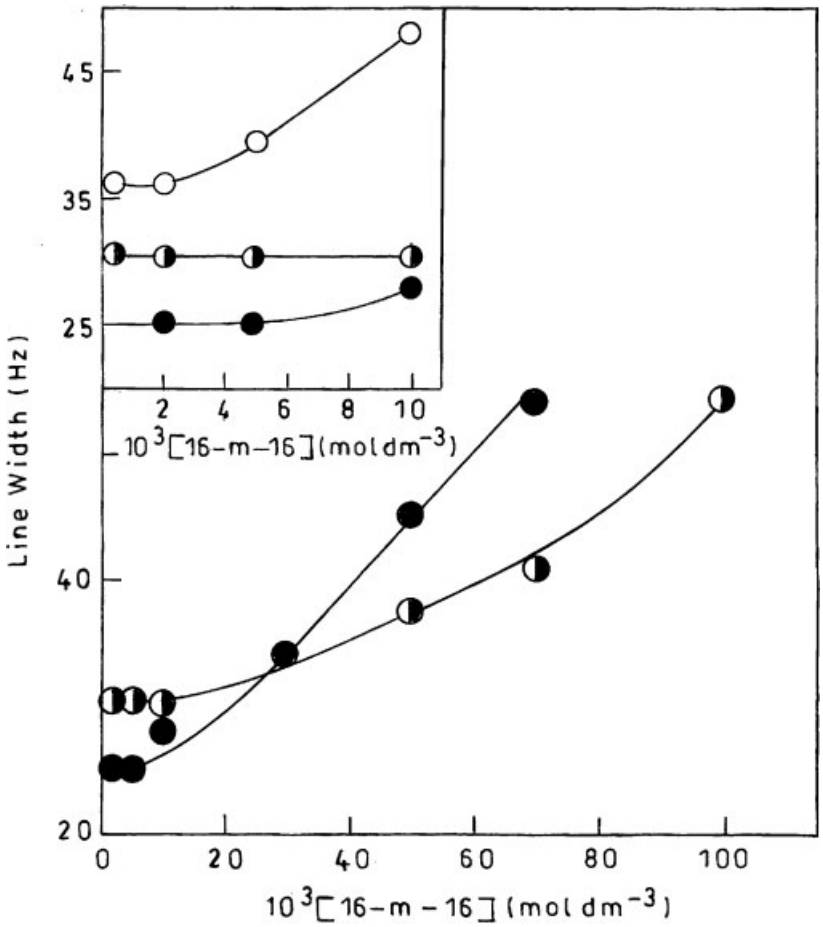

Figure 4. Line widths of the signals from the protons of the *N*-methyl groups of 16-*m*-16 geminis plotted against different concentrations. $m = 6$ (◑), 5 (●), 4 (○). Solutions of 16-4-16 became too viscous at higher concentrations and, therefore, results are compared at lower concentrations (see inset)

obtain pure surfactants. The gemini surfactants were characterized and gave satisfactory ^{1}H NMR and C, H, N data. The main features and peaks were similar as reported previously.[21]

NMR spectra

NMR spectra for characterization of synthesized materials were recorded in $CDCl_3$ on a Bruker Cryomagnet spectrometer working at 300 MHz, with ^{1}H chemical shifts relative to internal TMS. Other NMR spectra in D_2O for different sample solutions were recorded on the same instrument.

Surface tension measurements

The surface tension was measured by a Du Nouy type tensiometer (Hardson and Co., Kolkata) at 35 °C. The cmc values were estimated as intersections of two linear segments, above and below the cmc, of surface tension *versus* log[surfactant] plots. Also, presence of no minimum in the surface tension *versus* log[surfactant] plots was taken as additional evidence regarding the purity of the geminis.[30]

Determination of cmc by conductivity measurements

Conductivity measurements were used to determine the cmc values (bridge: ELICO, Hyderabad, India, 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 and gemini surfactants in the presence and absence of reactants were obtained from the break points of nearly two straight lines of the specific conductivity *versus* [surfactant] plots.[31] The experiments were carried out at 30 and 70 °C under varying conditions, that is, water + tryptophan,

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water + ninhydrin, water + tryptophan + ninhydrin. The results are recorded in Table 2.

Kinetics

The kinetic experiments were performed under nitrogen atmosphere with *pseudo*-first-order reaction conditions of [ninhydrin] > [DL-tryptophan]. The reaction was studied spectrophotometrically by monitoring the appearance of purple color *(vide infra)* as a function of time at 570 nm using a Bausch & Lomb Spectronic 20 spectrophotometer. A three-necked reaction vessel (fitted with double-walled condenser to check evaporation) containing required volumes of DL-tryptophan and surfactant was kept immersed in an oil-bath thermostatted at the desired temperature (±0.1 °C). For stirring and to maintain an inert atmosphere, pure nitrogen gas (free from CO_2 and O_2) was bubbled through the reaction mixture. The reaction was initiated by rapid addition of known amount of thermally equilibrated ninhydrin solution. The *pseudo*-first-order rate constants (k_{Ψ}, s^{-1}) were calculated up to 80% completion by using $k_{\Psi} = (2.303/t)\log\{(A_{\infty} - A_0)/(A_{\infty} - A_t)\}$ with the help of a computer program.

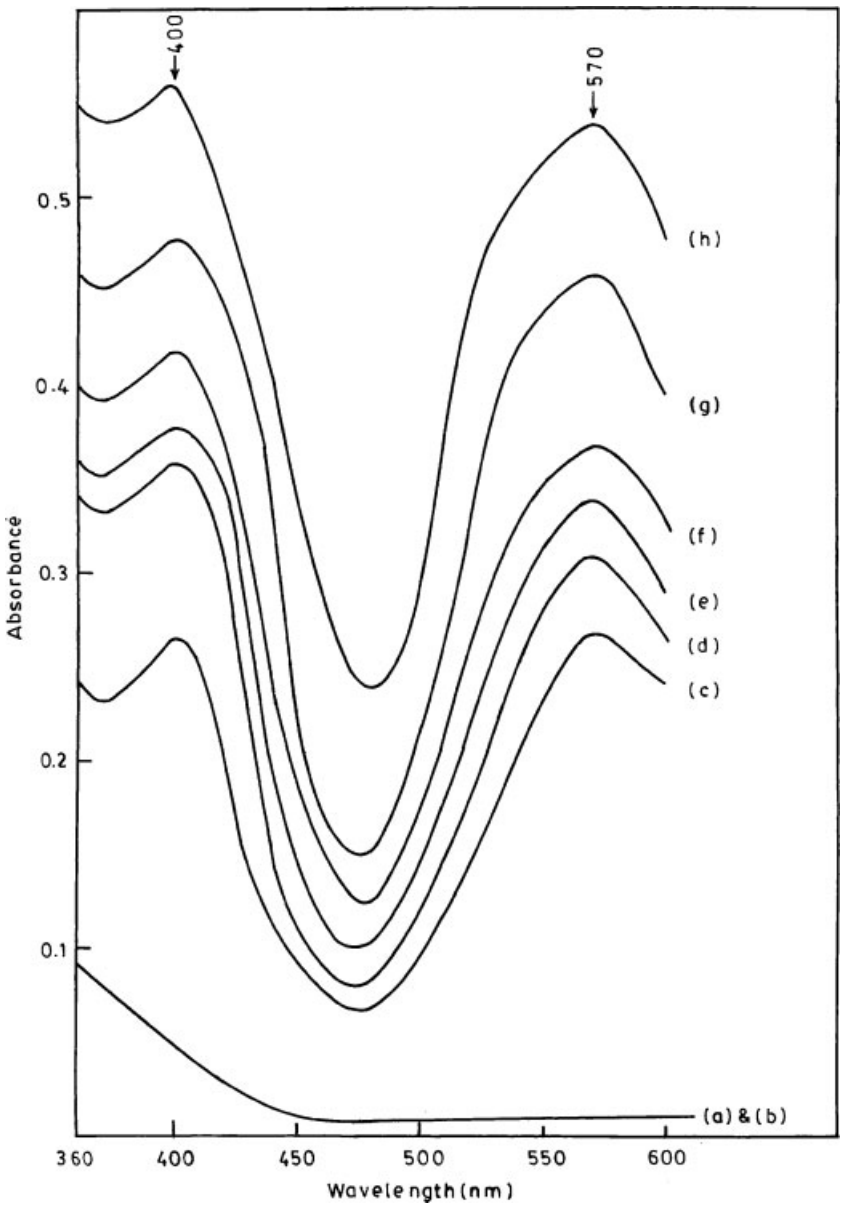

Figure 5. Absorption spectra of the reaction product of DL-tryptophan (1.0×10^{-4} mol dm^{-3}) with ninhydrin (5.0×10^{-3} mol dm^{-3}) in aqueous micellar media at 70 °C. (a) In absence of surfactant, (b) in presence of [CTAB] = 20.0×10^{-5} mol dm^{-3}, (c) in presence of [16-6-16] = 20.0×10^{-5} mol dm^{-3}, (d) in presence of [16-5-16] = 20.0×10^{-5} mol dm^{-3}, (e) in presence of [16-4-16] = 20.0×10^{-5} mol dm^{-3}, (f) after boiling solution (a), (g) after boiling solution (b), (h) after boiling solution (e)

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Identification of the product

In order to confirm whether the same colored product is formed in the absence and presence of surfactants (CTAB, geminis), absorption spectra of the reaction mixture, that is, $[\text{tryptophan}] = 1.0 \times 10^{-4}\,\text{mol dm}^{-3}$, $[\text{ninhydrin}] = 5.0 \times 10^{-3}\,\text{mol dm}^{-3}$, $[\text{gemini}] = 20.0 \times 10^{-5}\,\text{mol dm}^{-3}$, and $\text{pH} = 5.0$ at 70 °C were taken at the end of the reactions. These results are shown as absorbance-wavelength profiles in Fig. 5. The absorption maxima were found at $\lambda_{max} = 400$ and 570 nm, which clearly indicate that the same purple-colored reaction product (*Ruhemann's purple*) is formed in each case due to the strong association between the purple-colored product and gemini micelles. In presence of CTAB micelles no color developed under the similar reaction conditions; however, at increased [CTAB] ($5.0 \times 10^{-3}\,\text{mol dm}^{-3}$), color developed at 70 °C and pH = 5.0 and in this case also the absorption maxima were at the same wavelengths (400 and 570 nm).[6c] No change in the absorption maxima in the absence as well as presence of CTAB/gemini surfactants leads to the conclusion that the same product is formed in each case (Fig. 5).

Acknowledgements

W. F. is grateful to the Council of Science and Technology, UP for obtaining a Research Assistantship (Project No CST/SERC/D-1122). Thanks are due to RSIC, Lucknow, for providing C, H, N analysis data and ^{1}H NMR spectra.

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DOI: 10.1002/poc