In our study, three gemini dicationic surfactants with different methylene group spacer (16-6-16, 16-5-16 and 16-4-16) have been synthesized and characterized in solution by $^1$H NMR spectroscopic technique. The implications of gemini micellar solution on ninhydrin and metal amino acid complex ([Cu(II)-Trp]$^+$) were performed by the means of single-beam UV–visible spectroscopy. The absorbance was noted at regular time intervals and values of rate constant ($k_\psi$) were determined by using a computer-based program. Synthesized surfactants proved as an efficient catalyst on the interaction of ninhydrin with metal amino acid complex as compared with conventional surfactant and aqueous systems. The required description regarding the implications of gemini dicationic surfactants are provided in the text in detail. The conductivity technique was applied in order to get critical micelle concentration (cmc) of geminis in the presence and absence of reactants. Catalytic results developed in gemini dicationic surfactant system were explained effectively by pseudo-phase model. Various thermodynamic quantities, viz., activation energy, $E_a$, activation enthalpy, $\Delta H^\circ$, and activation entropy, $\Delta S^\circ$, were obtained on interaction of ninhydrin with [Cu(II)-Trp]$^+$ in gemini systems by applying Eyring equation. A detailed explanation about these evaluated parameters was also made.

© 2020 The Authors. Published by the Royal Society under the terms of the Creative Commons Attribution License http://creativecommons.org/licenses/by/4.0/, which permits unrestricted use, provided the original author and source are credited.
1. Introduction

Surfactant, referred to as a surface-active material, is capable of reducing interfacial tension. They have polar and non-polar moieties called head group and hydrophobic tail, respectively. Their strength of interaction depends significantly on the nature of hydrophilic heads and hydrophobic tail. So, surfactants have been used in various industrial applications, such as catalyst, cosmetics, oil exploration, daily chemical and pharmaceutical needs, textile industries, dying and painting [1–8]. Commonly, the efficacies of surfactants in uses depend upon critical concentration known as concentration (cmc). It is defined as a minimum range of concentration at which surfactant monomer initiates to self-associate that can be obtained as an inflection point by plotting any of the physico-chemical properties against surfactant concentration [9–14]. Surfactants self-aggregate and turn into several morphological aggregates above cmc, e.g. bilayers, vesicles, micelles and nanostructures. Therefore, surfactants play several important roles in diverse physico-chemical properties [15,16].

Gemini quaternary ammonium surfactants, attached by two hydrophilic head groups and two hydrophobic chains at or close to heads through a spacer, have received the great consideration by several investigators for their outstanding features [17]. Both the hydrophilic head and hydrophobic chain have special chemical structures and are responsible for their excellent uses in numerous purposes (industrial and commercial applications) [18]. Gemini surfactants are a unique class of surfactants and there are great significances for their excellent interfacial properties [19]. In contrast to conventional monoalkyl cationic surfactants, they have a wide range of chemical and structural morphologies and exhibit properties such as good viscoelasticity, better solubilizing capacity, low cmc value, excellent wettability and so on [20–25].

Being dependent on alkyl head group, hydrophobic chain and length of spacer as well as structures of consisting species, studies of gemini surfactants and their aggregates provide several valuable applications in the field of surface and interfacial sciences [26–30]. Most of the current reports available are also focused on the micellar and surface-active properties of gemini surfactants [31–34]. Authors have investigated and reported that gemini surfactants were found to be superior as drug delivery agents in medical and pharmaceutical sciences [35–38]. Even though a large number of scientific reports are existing on surface behaviour of gemini and their aggregates that they form, the reports on the studies of their influences on rates have not received the considerable attraction. However, the complexity in the synthesizing and purifying of gemini surfactants hinders the usage and applications in most domestic and industrial areas.

Therefore, in order to fulfil the growing requirements of several industries and commercial utilization, three dicationic gemini surfactants having various methylene spacer chain length (e.g. 16-6-16, 16-5-16 and 16-4-16) have been synthesized and characterized by using $^1$H NMR spectroscopy. Influences of these synthesized gemini materials on the rates of interaction of ninhydrin with metal amino acid complex have been studied in sufficient manner. We believe that the outcome of the present study will increase the awareness in regard of the use of gemini surfactants and will expand their scope of application to large scale. The findings of study in gemini are also compared with that obtained in aqueous system.

Ninhydrin, an effective colour-generating chemical compound, is used largely to classify the amine functional group in the several domains, e.g. biochemical studies, chemical works and forensics [39,40]. Studies of interaction relating ninhydrin with amine functional group offer a number of biological significances related to living organism (such as, transpeptidation and deamination) [41,42]. Reaction of ninhydrin and amino group yields the diketohydrindylidene-diketohydrindamine (DYDA) commonly called to Ruhemann’s purple. As the DYDA destabilizes at room temperature, many developments (e.g. effect of traditional monoalkyl surfactants, role of various salts, impact of different solvent media, and so on) were made to stabilize the DYDA [43–47]. Whereas, effects of gemini surfactants on amino group and ninhydrin are scanty and have not obtained essential attention. Investigators/scientists working in similar or allied arenas are still awaiting the better outcomes and significances.

2. Experimental section

2.1. Materials and methods

All the materials applied in the present work is listed in table 1.
Gemini dicationic surfactants (16-6-16, 16-5-16 and 16-4-16) were synthesized in the laboratory and the detailed methods were mentioned in the published articles [48,49]. Synthesized surfactants were characterized by $^1$H NMR technique and were matched in close agreement to results reported formerly [48,49]. Water used throughout the experiment was demineralized double-distilled from alkaline KMnO$_4$. The specific electrical conductivity of water employed was $1 - 2 \mu \text{s cm}^{-1}$ at 298 K.

Standard solutions of complex, ninhydrin and surfactants were made by accurate weighing of required quantity using an acetate buffers. All the solutions were stirred well to be homogenized and kept for a day to attain equilibrium at room temperature. To measure the solution of pH, a digital Elico pH meter (Hyderabad, India) was used.

2.2. Electrical conductivity measurements

Electrical conductivities were measured on conductivity meter (Systronics model 306, Ahmedabad, India) in order to get cmc at required experimental temperatures (i.e. 303 K and 343 K). Solutions of gemini and the mixed additives were left at room temperature to ensure stabilization. For cmc evaluation, [ninhydrin] and [complex] were fixed at 6 and 0.2 mmol kg$^{-1}$, respectively. Each run was repeated at least in triplicate to get reproducible results. Before starting the study, apparatus was calibrated with a solution of potassium chloride at different concentrations. For determining cmc, specific conductivities were plotted against different concentrations of gemini surfactants and the inflection point in the plot corresponds to the cmc value [50–55]. An effective enhancement in conductivity was noted in premicellar region owing to free cations and anions but not in post region due to formation of micelle. In our study, cmc of pure gemini obtained is consistent at 303 K with outcomes published formerly [56]. The cmc values at various reaction situations (i.e. water and water + ninhydrin + [Cu(II)-Trp]$^+$) are existing down.

(a) [16-6-16]: 0.043 and 0.039 mmol kg$^{-1}$ at 303 K; 0.058 and 0.049 mmol kg$^{-1}$ at 353 K.
(b) [16-5-16]: 0.034 and 0.030 mmol kg$^{-1}$ at 303 K; 0.055 and 0.043 mmol kg$^{-1}$ at 353 K.
(c) [16-4-16]: 0.032 and 0.025 mmol kg$^{-1}$ at 303 K; 0.043 and 0.033 mmol kg$^{-1}$ at 353 K.

2.3. Spectra of product formed

Spectra were obtained in aqueous system as well as gemini micellar system. Single-beam Shimadzu model spectroscope (UV mini 1240, Kyoto, Japan) was used to note the absorbance at different wavelengths ranged from 340 to 620 nm. Absorbance of product was drawn against varying wavelength and demonstrated graphically in figure 1. Absorbance values are developed more in surfactant system compared with aqueous system with unaffected absorption maximum (=370 nm).
These results can be seen visually in figure 1. Consequently, figure 1 confirms that product formation is same in the two systems.

2.4. Kinetic measurements

In this study, the experiments were made under pseudo-first-order reaction circumstances fixing concentration of ninhydrin in excess compared with complex concentration. Requisite volumes of gemini surfactant, acetate buffer, metal salt and amino acid were placed in a round-bottomed three-necked reaction pot. The pot was fixed in thermostated water bath at desired experimental temperature. The solution was left 30 min to ensure equilibrium. Kinetic experiments were performed by pouring a known volume of ninhydrin into the pot. So, the kinetic data were acquired under pseudo-first-order reaction circumstances at regular time intervals on UV–visible spectroscopy with identical quartz cuvettes of path length 1 cm. The rate constant ($k_\psi$) values were estimated as an average of at least triplicate runs. A detailed procedure in regard of kinetic measurements is available in the literature published previously [57–63].

2.5. Job’s method

Job’s method was used to inspect composition of product prepared on interaction of metal-amino acid complex and ninhydrin by heating complex and ninhydrin at 368 K for 2 h. Subsequently, absorbance was noted at $\lambda_{\text{max}}$ (= 370 nm) at the end by the means of UV–visible spectrophotometer (figure 2). It was observed that ninhydrin (1 mol) reacted with complex (1 mol) to yield the product.

3. Results

3.1. Influence of pH on $k_\psi$

Interaction of ninhydrin with metal amino acid complex at different pH was studied in the presence of gemini dicationic surfactants, keeping other parameters constant. The resultant values of rate constant obtained at different pH are mentioned in table 2. Also, rate constants are plotted at varying pH and

Figure 1. Spectra obtained in aqueous system as well as gemini micellar system on [Cu(II)-Trp]$^+$ and ninhydrin reaction at 353 K after heating 2 h: (rectangle) aqueous, (circle) 16-6-16, (triangle) 16-5-16 and (inverted triangle) 16-4-16. Experimental conditions: [ninhydrin] = 6 mmol kg$^{-1}$, [Cu(II)-Trp]$^+$ = 0.2 mmol kg$^{-1}$, [16-s-16] = $30 \times 10^{-2}$ mmol kg$^{-1}$ and pH = 5.0.
shown graphically in figure 3. Figure 3 reveals that rate increases up to pH 5, then becomes approximately constant. This behaviour confirms formation of Schiff base in vicinity of pH 5. As a consequence, studies were made at pH 5.

Table 2. Implications of different factors on \( k_{\psi} \) on \([\text{Cu(II)-Trp}]^+\) and ninhydrin reaction in geminis (30 × 10^{-2} mmol kg^{-1}) at [ninhydrin] (6 mmol kg^{-1}). Standard uncertainties are in \( k_{\psi} = \pm 0.1 \times 10^{-5} \text{ s}^{-1} \).

| [Cu(II)-Trp]^+ (mmol kg^{-1}) | pH | temp. (K) | \(10^5 k_{\psi} \) (s^{-1}) |
|-----------------------------|----|-----------|-----------------|
|                            |    |           | 16-6-16 | 16-5-16 | 16-4-16 |
| 0.1                        | 5.0| 353       | 9.4   | 10.4   | 12.2   |
| 0.15                       | 5.0| 353       | 9.4   | 10.5   | 12.0   |
| 0.2                        | 5.0| 353       | 9.5   | 10.5   | 12.0   |
| 0.25                       | 5.0| 353       | 9.6   | 10.5   | 12.1   |
| 0.3                        | 5.0| 353       | 9.5   | 10.4   | 12.2   |
| 0.2                        | 4.0| 353       | 5.5   | 6.1    | 6.6    |
| 0.2                        | 4.5| 353       | 6.2   | 7.2    | 8.5    |
| 0.2                        | 5.0| 353       | 9.5   | 10.5   | 12.0   |
| 0.2                        | 5.5| 353       | 9.5   | 11.0   | 13.0   |
| 0.2                        | 6.0| 353       | 11.4  | 12.1   | 13.2   |
| 0.2                        | 5.0| 348       | 6.8   | 7.7    |        |
| 0.2                        | 5.0| 348       | 7.0   | 8.5    | 9.4    |
| 0.2                        | 5.0| 353       | 9.5   | 10.5   | 12.0   |
| 0.2                        | 5.0| 358       | 11.0  | 12.8   | 14.2   |
| 0.2                        | 5.0| 363       | 13.2  | 15.6   | 17.8   |

Figure 2. Plots of \( A_{370} \) versus mole fraction of ninhydrin for estimation of product composition prepared on \([\text{Cu(II)-Trp}]^+\) and ninhydrin reaction by heating complex and ninhydrin at temperature 368 K for 2 h: (rectangle) 16-6-16, (circle) 16-5-16 and (triangle) 16-4-16. Experimental conditions: [16-s-16] = 30 × 10^{-2} \text{ mmol kg}^{-1}.
3.2. Influence of metal amino acid concentration on $k_{\psi}$

To check role of concentration of metal amino acid complex on rate constant, experiments were run at several initial concentrations of complex under pseudo-first-order reaction condition by fixing other experimental ingredients constant. The varied range of complex concentration was 0.1–0.3 mmol kg$^{-1}$. The evaluated values of $k_{\psi}$ at different initial complex concentrations are given in table 2. Evaluated results of table 2 confirmed that the study suggested a first-order dependence of rate in [complex]. Then rate equation can be expressed as equation (3.1).

$$\frac{d[\text{product}]}{dt} = \text{rate constant} \times [\text{complex}],$$

where $[\text{complex}]$ refers to $[\text{Cu(II)-Trp}]+$.

3.3. Influence of ninhydrin concentration on $k_{\psi}$

Influence of ninhydrin concentration was carried out by varying ninhydrin ranging from 0 to 40 mmol kg$^{-1}$ in gemini micellar condition at fixed [complex], temperature and pH. Rate constant increases on increasing ninhydrin concentration. Rate values are plotted against several ninhydrin concentrations (figure 4). Plot of rate constant versus [ninhydrin] clearly demonstrates a nonlinear curve crossing through origin. This confirms order to be fractional in ninhydrin concentration.

3.4. Influence of temperature on $k_{\psi}$

In order to see the behaviour of temperature on the study, kinetic runs were made at five different temperatures, viz., 343, 348, 353, 358 and 363 K at fixed concentration of reactants (ninhydrin and metal-amino acid) and pH in gemini surfactant system. The outcome of rates noted in the study are presented in tabular form in table 2. Rates increase with increasing temperature. Thermodynamic quantities such as $\Delta H^\circ$, $\Delta S^\circ$ and $E_a$ have been determined using Eyring equation in geminis. These thermodynamic quantities are reported in table 3.
4. Discussion

4.1. Reaction mechanism

The proposed reaction mechanism of present study between ninhydrin and metal amino acid complex is shown as scheme 1. This is familiar previously that lone pair of nitrogen of amino group is mandatory for attack on middle carbonyl group of ninhydrin [64–67]. But, electrons of lone pair are connected to metal ion. Under such reaction condition, ninhydrin forms a complex with metal-amino acid. This is known as characteristic of combination-of-two-ligands-attached-to-the-same-metal-ion (CLAM) reaction mechanism [68–71].

4.2. Influence of gemini dicaticionic surfactants on the study

To determine the influence of geminis on the study, rate constants were calculated at several amounts of gemini surfactant concentration keeping other reaction factors fixed. These values of rate constant are summarized in electronic supplementary material, table S1.
Rate constant increases steadily with increasing gemini at concentration below cmc value (Zone I) and levelling-off zones achieve at gemini concentration up to $400 \times 10^{-2}$ mmol kg$^{-1}$ (Zone II). Plots of Zone I and Zone II, figure 5, are detected the same as conventional monomeric surfactants [72–74]. At later stage, geminis result in a Zone III of increasing rate at higher surfactant concentration. Results suggested that the similar kinetics of rate with respect to ninhydrin and metal-amino acid complex, i.e. fractional and first-order, respectively, were attained in gemini micellar medium as that to pure water medium.

### 4.3. Quantitative analysis of rate constant against gemini surfactants plot

Quantitative analysis of enhanced rate constant against [gemini] in the study can be interpreted successfully with model led by Menger & Portnoy [75] and established by Bunton [76,77].

In current study, the model is shown as scheme 2 below.

Equation (3.1) and scheme 2 gave equation (4.1)

$$k_\psi = \frac{k_W + k_m K_E[Y]}{1 + K_E[D_n]}$$  \hspace{1cm} (4.1)

Then, equation (4.1) can be converted to equation (4.2)

$$k_\psi = \frac{k_W[N] + (K_E k_m - k_w) M_N^S[D_n]}{1 + K_E[D_n]}$$  \hspace{1cm} (4.2)

where $k_w$ and $k_\psi$ denote rate constants in pure water and gemini surfactants, respectively. $K_E$ and $K_F$ specify the respective binding constant of M-AA complex to micelle and ninhydrin to micelle. $M_N^S = [(Nin)_m]/[D_n]$ is concentration of ninhydrin in molar ratio of the micellar head group.
In order to get $k_E$ and micellar rate constant ($k_m$), we need cmc values under existing kinetic study. So, cmc values have been determined by the means of conductometric technique. For known cmc, $k_E$ and $k_m$ were calculated from equation (4.2) by a computer process. The values of $K_E$ and $k_m$ are provided in table 3. Putting of $K_E$ and $k_m$ in equation (4.2) results in the calculated $k_{cal}$ which is in consistent with the observed $k_w$ (electronic supplementary material table S1). Electronic supplementary material, table S1 confirms the good matching between the observed $k_w$ and calculated $k_{cal}$ within experimental errors, authenticating the proposed mechanism of present study.

Considering the consequences of Zone I (figure 5), [geminis] are lower than their cmc, $k_w$-values should be remained constant. Rate profile of $k_w$ versus [geminis] (figure 5) has confirmed an increment in rate constant. This may be owing to existence of premicellar aggregates between substrate and surfactant molecules even though at surfactant concentrations lower than that of their cmc values. It is approved well that gemini surfactants can form various morphological aggregates, such as vesicles, micelles and bilayers with different additives. It has also been noted that the surfactant molecules with substrate molecules formed premicellar aggregates and catalysed the reaction even at concentration lesser than cmc value [78–81].

**Scheme 2.** Metal-amino acid and ninhydrin reaction in pure water and gemini micellar systems. $k_w (= k_w/[(Nin)_w])$ and $k_m (= k_m/k_m^0)$ refer to second rate constant in pure water and geminis. $D_m (= [total surfactant] - cmc)$ signifies micellized surfactant.

Figure 5. Implication of varying [geminis] on $k_w$ for [Cu(II)-Trp]$^{2+}$ and ninhydrin reaction: (rectangle) 16-6-16, (circle) 16-5-16, (triangle) 16-4-16. Experimental conditions: [ninhydrin] = 6 mmol kg$^{-1}$, [Cu(II)-Trp]$^{2+}$ = 0.2 mmol kg$^{-1}$, temperature = 353 K and pH = 5.0.
According to multiple equilibrium models, the partition of surfactant between different states is governed by a several dynamic association and dissociation equilibrium. The smaller aggregates, such as dimer, trimer, tetramer etc. can be present at the concentration of surfactants below their cmc values

$$D + D \rightarrow D_2 + D \rightarrow D_3 \cdots D_{n-1} + D \rightarrow D_n.$$  

Rate constants become almost constant in Zone II. This happens when reactants are totally micellar bound with the micellar structure reflected to persist intact [82]. It was found that gemini surfactants were more functioning to catalyse the reaction than corresponding monomeric surfactant (cetyltrimethylammonium bromide, CTAB). This was the benefit of gemini surfactants used in the present kinetic study.

Gemini surfactants result in a Zone III of increasing rate at higher surfactant concentrations. Enhancement in rate occurs at higher gemini concentrations caused by changes in micellar structure and are a good match to $^1$H NMR spectral consequences stated previously [48,83]. Henceforward, an intensification in rate constant $k_\psi$ at higher surfactant concentrations follows as a result of modifications in morphological aggregates that delivers different experimental microenvironment, i.e. less polar.

All categories of micellar-mediated organic reactions (ionic, polar and neutral) are commonly believed to happen into small volume of a micelle (i.e. Stern layer) of an ionic surfactant.

Rate enhancement in positively charged micelles could be attributed to the stabilization of Schiff base intermediate on a positively charged micellar surface increasing the concentration of intermediate in the Stern layer. From electrostatic considerations, $\pi$-electrons existing in ninhydrin assist its possibility of partitioning between aqueous and positively charged micelles [84]. Hydrophobic interactions bring about incorporation of [Cu(II)-Trp]$\textsuperscript{1+}$ into micelles. Therefore, both reactants ninhydrin and [Cu(II)-Trp]$\textsuperscript{1+}$ get associated/incorporated into the aqueous surface of the micelles (i.e. the Stern layer) [76]. Therefore, the concentration of reactants increases into a small volume, that is, the Stern layer of the micelles (scheme 3), catalysing the reaction and resulting in an increase in the observed rate ($k_\psi$).

### 4.4. Thermodynamic quantities

Numerous thermodynamic quantities viz., activation energy, $E_\psi$, activation enthalpy, $\Delta H^\#$, and activation entropy, $\Delta S^\#$, were evaluated on interaction of ninhydrin with metal amino acid in three gemini dicationic surfactant systems with Eyring equation. Obtained values of these thermodynamic quantities are listed in table 3. A lower value of activation enthalpy ($\Delta H^\#$) in gemini than the absence of surfactant (i.e. aqueous medium [85]) was obtained. This can be ascribed to the fact that an electrostatic attraction occurs between surfactants and reactant molecules when reactant molecules are existing in micellar phase. A reduced
value of activation entropy ($\Delta S^*$) in gemini surfactants with those acquired in aqueous system confirms that the activated complex formed are well order in gemini surfactants.

5. Conclusion

In this present article, three gemic dicationic surfactants were synthesized and characterized consisting of two heads and tails connected covalently through a spacer by $^1$H NMR technique. The implications of their micellar solution on the study were performed with UV–visible spectroscopy. Studies were made at different experimental situations, e.g. temperature, pH, reactants and surfactant concentration. The cmc determination of gemini surfactants with and without additives was done on conductivity meter.

Under a set of varying experimental conditions, gemini micellar systems (even though at gemini surfactant concentrations lower than their cmc) were detected more effective to catalyse and accelerate the reaction over aqueous system. This suggested that the gemini surfactants were proved better surface active materials for the selected study. All the three gemini surfactants showed the order of their catalysing efficacies at each concentration as 16-4-16 > 16-5-16 > 16-6-16. Use of fairly small amounts of synthesized gemini surfactants in the study provides less environmental effect and reduces the catalytic competitions required as a catalyst in several industries. We trust that the specific outcomes of this study simplify an improved understanding of the reaction between ninhydrin and amine functional group. Study may reveal a new platform in intensifying the immense scope of uses of these gemini surfactants for scientific community in future.

Data accessibility. Data that supporting this study have been uploaded to electronic supplementary material. Authors' contributions. D.K. has done the experiments and written the manuscript. M.A.R. and A.M.A. analysed and interpreted data. All authors gave final approval for publication.

Competing interests. The authors declare no competing interest.

Funding. We received no funding for this study.

Acknowledgements. Division of Computational Physics, Institute for Computational Science, Ton Duc Thang University, Ho Chi Minh City, Vietnam are highly acknowledged.

References

1. Rosen MJ. 2004 Surfactants and interfacial phenomena, 3rd edn. New York, NY: John Wiley & Sons.
2. Vance SJ, McDonald RE, Cooper A, Smith BO. 2013 The structure of latherin, a surfactant allergen protein from horse sweat and saliva. J. R. Soc. Interface 10, 20130453. (doi:10.1098/rsif.2013.0453)
3. Åberg C, Spar E, Larsson M, Wennenström H. 2010 A theoretical study of diffusional transport over the alveolar surfactant layer. J. R. Soc. Interface 7, 1403–1410. (doi:10.1098/rsif.2010.0002)
4. Kumar D, Rub MA. 2017 Effect of anionic surfactant and temperature on micellization behavior of promethazine hydrochloride drug in absence and presence of urea. J. Mol. Liquids 238, 389–396. (doi:10.1016/j.molliq.2017.05.027)
5. Kumar D, Hidayathulla S, Rub MA. 2018 Association behavior of a mixed system of the antidepressant drug imipramine hydrochloride and diocyl sulfosuccinate sodium salt: effect of temperature and salt. J. Mol. Liquids 271, 254–264. (doi:10.1016/j.molliq.2018.08.147)
6. Amador GJ, Endlein T, Sitti M. 2017 Soiled adhesive pads shear clean by slipping: a robust self-cleaning mechanism in climbing beetles. J. R. Soc. Interface 14, 20170134. (doi:10.1098/rsif.2017.0134)
7. Harishchandra RK, Saleem M, Galla H-J. 2010 Nanoparticle interaction with model lung surfactant monolayers. J. R. Soc. Interface 7, 515–526. (doi:10.1098/rsif.2009.0329.focus)
8. Rub MA, Azeem N, Kumar D, Khan F, Aasi AM. 2015 Clouding phenomenon of amphiphilic drug promazine hydrochloride solutions: influence of pharmaceutical excipients. J. Ind. Eng. Chem. 21, 1119–1126. (doi:10.1016/j.jiec.2014.05.023)
9. Raj SR, Sarkar A, Pandey A, Dasgupta S, Majumder I, Das D, Bose D, Mukhopadhyay M. 2019 Photometric study of the interaction of zincl(II) complexes of Schiff bases with cetyltrimethyl ammonium bromide. Macromol. Sympos. 388, 1900030. (doi:10.1002/masy.201900030)
10. Sachin KM, Karpe S, Singh M, Bhattarai A. 2018 Physicochemical properties of dodocetyltrimethylammonium bromide (DOTAB) and sodiumdodecyl sulphate (SDS) rich surfactants in aqueous medium, at T = 293.15, 298.15, and 303.15 K. Macromol. Sympos. 379, 1700034. (doi:10.1002/masy.201700034)
11. Amin MR, Mahbub S, Molia MR, Alam MM, Hossain MF, Rana S, Rub MA, Hoque MA, Kumar D. 2019 Phase separation and thermodynamic behavior of triton X-100 in the occurrence of levofloxacin hemihydrates: Influence of additives. J. Chem. Eng. Data 64, 2750–2758. (doi:10.1021/acs.jced.9b00146)
12. Mahbub S, Rub MA, Hoque MA, Khan MA, Kumar D. 2019 Micellization behavior of catonic and anionic surfactant mixtures at different temperatures, effect of sodium carbonate and sodium phosphate salts. J. Phys. Org. Chem. 32, e3967. (doi:10.1002/poc.3967)
13. Rahman M, Anwar SJ, Molia MR, Rana S, Hoque MA, Rub MA, Khan MA, Kumar D. 2019 Influence of alkyls and varying temperatures on the interaction between drug ofloxacin sodium trihydrate and surfactant, a multi-techniques study. J. Mol. Liquids 292, 111322. (doi:10.1016/j.molliq.2019.111322)
14. Hasan MZ, Mahbub S, Hoque MA, Rub MA, Kumar D. 2020 Investigation of mixed micellization study of sodium dodecyl sulfate and tetradecyltrimethylammonium bromide mixtures at different compositions: Effect of electrolytes and temperatures. J. Phys. Org. Chem. 33, e4047. (doi:10.1002/poc.4047)
15. Chattopadhyay P, Karthick RA. 2017 Characterization and application of surfactant foams produced from ethanol-sodium lauryl sulfate-silica nanoparticle mixture for soil remediation. Macromol. Sympos. 376, 1600182. (doi:10.1002/masy.201600182)
16. Gulyuz U, Okay O. 2015 Self-healing poly(acrylic acid) hydrogels: effect of surfactant. Macromol. Sympos. 358, 232–238. (doi:10.1002/masy.201500063)
17. Fredric MM, Jason SK. 2000 Gemini surfactants. Angew. Chem. Int. Ed. 39, 1906–1920. (doi:10.1002/anie.199911040)
18. Lindman B, Astuvus F, Aidarova S, Miguel M, Nylander T. 2014 Polyethylene oxide surfactant association from fundamentals to applications. Colloid J. 76, 385–594. (doi:10.1134/S1069393X14050111)
19. Kamal MS. 2016 A review of gemini surfactants: potential application in enhanced oil recovery. J. Surf. Deterg. 19, 223–236. (doi:10.1007/s11745-015-1776-5)
20. Jobe DJ, Reinsborough VC. 1984 Surfactant structure and micellar rate enhancements: comparison within a related group of one-tailed, two-tailed and headed anionic surfactants. Aust. J. Chem. 37, 1593–1599. (doi:10.1071/CH941593)

21. Aslam J, Siddiqui US, Bhat IA, Kabir-ud-Din. 2014 Molecular interactions of cationic gemini surfactants (m–s–m) with an environmental friendly nonionic sugar-based surfactant (m–s–m): interface, micellar and aggregation behavior. J. Ind. Eng. Chem. 20, 3841–3850. (doi:10.1016/j.jiec.2013.12.088)
22. Kumar D, Rub MA. 2018 Catalytic role of 16-s-16 micelles on condensation reaction of ninhydrin and metal-dipeptide complex. J. Phys. Org. Chem. 32, e3918. (doi:10.1002/poc.3918)
23. Kumar D, Rub MA. 2019 2012 Physicochemical studies of pyridinium Gemini surfactants with promethazine hydrochloride in aqueous solution. Phys. Chem. Chem. Phys. 14, 887–889. (doi:10.1039/C1CP22448D)
24. Han Y, Wang Y. 2011 Aggregation behavior of gemini surfactants and their interaction with macroolecules in aqueous solution. Phys. Chem. Chem. Phys. 13, 1939–1956. (doi:10.1039/C0CP01196G)
25. Kumar D, Rub MA. 2019 Interaction of metal ion-coordinated dipeptide complex and ninhydrin in alkane-diyl-a,-ω-bis(dimethylcetyl ammonium bromide) gemini surfactants. J. Phys. Org. Chem. 32, e3946. (doi:10.1002/poc.3946)
26. Han Y, Wang Y. 2011 2012 Aggregation behavior of gemini surfactants and their interaction with macromolecules in aqueous solution. Phys. Chem. Chem. Phys. 13, 1939–1956. (doi:10.1039/C0CP01196G)
27. Thaloby B, Warri GG. 2004 The selective binding of anions to gemini and trimeric surfactants at air/solution interfaces. Aust. J. Chem. 57, 193–196. (doi:10.1039/C0013000)
28. Blom A, Warri GG, Wanless EJ. 2006 Growth of double-chained cationic surfactant films on mica. Aust. J. Chem. 59, 381–385. (doi:10.1071/CH06069)
29. Wei XL, Wang XH, Sun DZ. 2012 Phase and rheological behavior of a gemini cationic surfactant aqueous system. Soft Matter 8, 10 115–122. (doi:10.1039/C2SM25436G)
30. Mungia MC, Machua LM, Fernandez ME. 2019 Cationic Gemini compounds with antifungal activity and wood preservation potentiality. J. Ind. Eng. Chem. 72, 170–177. (doi:10.1016/j.jiec.2018.12.016)
31. Tawfiq SM, Abd-Elaal AA, Shaban SM, Rosddy AA. 2015 Surface, thermodynamic and biological activities of some synthesized Gemini quaternary ammonium salts based on polyethylene glycol. J. Ind. Eng. Chem. 30, 112–119. (doi:10.1016/j.jiec.2015.05.011)
32. Han LI, Chen H, Luo PY. 2004 Viscosity behavior of cationic gemini surfactants with long alkyl chains. Surf. Sci. 564, 141–148. (doi:10.1016/j.susc.2004.06.172)
33. Pei XM, Zhao JX, Wei XL. 2011 Effect of sodium salicylate on the formation and properties of wormlike micelles in aqueous cationic gemini surfactant solutions. Acta Phys. Chem. Sin. 27, 913–917. (doi:10.3866/PKU.WHXB20101140)
34. Mirkordeskaia AB, Yatskevich EI, Zakharin LV, Konовал AI. 2012 Gemini surfactant – nonionic polymer mixed micellar systems. Colloid J. 74, 91–103. (doi:10.1134/S1069393X10061315)
35. Pei XM, Zhao JX, Wei XL. 2011 Effect of sodium salicylate on the formation and properties of wormlike micelles in aqueous cationic gemini surfactant solutions. Acta Phys. Chem. Sin. 27, 913–917. (doi:10.3866/PKU.WHXB20101140)
36. Panara M, Kamal M. 2017 Interaction of oxy-diester-linked cationic gemini surfactants with nonionic amphiphiles in aqueous solution. Colloid Polym. Sci. 295, 2363–2371. (doi:10.1007/s00396-017-4203-9)
37. Kumar D, Rub MA, Aziz N, Aziz AM. 2018 Micellar mixed stabilization study of ibuprofen sodium salt and cationic surfactant conventional as well as Gemini. J. Phys. Org. Chem. 31, e3730. (doi:10.1002/poc.3730)
38. Kumar D, Aziz N, Rub MA, Aziz AM. 2018 Aggregation behavior of sodium salt of ibuprofen with conventional and Gemini surfactant. J. Mol. Liquids 262, 86–96. (doi:10.1016/j.molliq.2018.04.053)
39. Mahajan RK, Mahajan S, Bhadani A, Singh S. 2012 Physicochemical study of pyridinium Gemini surfactants with promethazine hydrochloride in aqueous solution. Phys. Chem. Chem. Phys. 14, 887–889. (doi:10.1039/C1CP22448D)
40. Rub MA, Kumar D, Aziz N, Khan F, Asiri AM. 2014 Study of the interaction between promazine hydrochloride and surfactant conventional and Gemini mixtures at different temperatures. J. Sol. Chem. 43, 930–949. (doi:10.1007/s10953-014-0174-3)
41. Friedman M. 2004 Applications of the ninhydrin reaction for analysis of amino acids peptides and proteins to agricultural and biomedical sciences. J. Agric. Food Chem. 52, 385–406 and references cited therein. (doi:10.1021/jf030490p)
42. Joullie MM, Thompson TR, Nemeroff NH. 1991 Ninhydrin and ninhydrin analogs syntheses and applications. Tetrahedron 47, 8791–8830. (doi:10.1016/S0040-4020(01)00997–2)
43. Connell GE, Dixon GH, Hanes CS. 1955 Quantitative chromatographic methods for the study of enzymic transpeptidation reactions. Can. J. Biochem. Physiol. 33, 416–427. (doi:10.1139/n55-055)
44. Kalyankar GD, Snell EE. 1957 Differentiation of α-amino acids and amines by non-enzymatic transamination on paper chromatograms. Nature 180, 1069–1070. (doi:10.1038/1801069a0)
45. Akram M, Zaidi NH, Kabir-ud-Din. 2006 Kinetics and mechanism of interaction of dipeptide glycidyl-glycine with ninhydrin in aqueous micellar media. Int. J. Chem. Kinet. 38, 463–650. (doi:10.1016/S0020-7691(05)00105-9)
46. Akram M, Rub MA, Kabir-ud-Din. 2012 Zinc dipeptide complex (Zn(H2-Gly-Tyr))–ninhydrin reaction in presence of Gemini surfactants: a kinetic study. J. Mol. Liq. 188, 61–66. (doi:10.1016/j.molliq.2013.09.018)
47. Akram M, Kabir-ud-Din. 2012 Micelle-catalyzed reaction between ninhydrin and nickel
dipeptide complex [Ni(II)-Gly-Gly]-. Colloids Surf. A 89, 220–225. (doi:10.1016/j.colsurr.2012.01.041)

60. Akram M, Kumar D, Kabir-ud-Din. 2012 Effect of dicaticonic surfactants 16-s-16=4 5 6 on the ninhydrin-dipeptide glycyly-tyrosine reaction. Int. J. Chem. Kinet. 44, 800–809. (doi:10.1002/kin.20731)

61. Kumar D, Rub MA. 2018 Studies of interaction between ninhydrin and gly-leu dipeptide: influence of cationic surfactants m-s-m type gemini. J. Mol. Liquids 269, 1–7. (doi:10.1016/j.molliq.2018.08.002)

62. Kumar D, Rub MA. 2020 Catalytic influence of 16-s-16 gemini surfactants on the rate constant of histidine and ninhydrin. R. Soc. Open Sci. 7, 191648. (doi:10.1098/rsos.191648)

63. Kumar D, Rub MA. 2019, 2019 Micellenic catalysis of composite reactions — the effect of SDS micelles and premicelles on the alkaline fadning of crystal violet and malachite green. J. Dispersion Sci. Technol. 23, 473–481. (doi:10.101080/03602457098065104)

64. Kumar D, Rub MA. 2019 Kinetic and mechanistic investigations of [Zn(II)-Gly-Gly]+ and ninhydrin in aqueous and cationic CTAB surfactant. J. Mol. Liquids 324, 639–645. (doi:10.1016/j.molliq.2018.11.035)

65. Radoja MZA, Khan Z, Khan AA. 1994 Kinetics of the interaction of ninhydrin with a [Cr(histidine-H2O)3]2+ complex. J. Phys. Org. Chem. 32, 639–645. (doi:10.1002/poc3997)

66. Brinchi L, Germani R, Goracci L, Savelli G, Runton CA. 2002 Decarboxylation and dephosphorylation in new gemini surfactants. J. Mol. Liquids 92, 477–480. (doi:10.1016/S0190-2909(01)00134-6)

67. Brinchi L, Germani R, Goracci L, Savelli G, Runton CA. 2002 Decarboxylation and dephosphorylation in new gemini surfactants. J. Mol. Liquids 92, 477–480. (doi:10.1016/S0190-2909(01)00134-6)

68. Akram M, Kumar D, Kabir-ud-Din. 2013 Influence of cationic gemini and conventional CTAB on the interaction of [Cr(III)-Gly-Tyr]- complex with ninhydrin. Colloids Surf. A 428, 92–99. (doi:10.1016/j.colsurfa.2013.03.042)

69. Akram M, Kumar D, Kabir-ud-Din. 2014 Catalytic behavior of a series of cationic gemini (16-s-16 type, s=4, 5, 6) and CTAB surfactants on the reaction of ninhydrin with [Ni(III)-Gly-Phe]+. J. Solution Chem. 43, 648–660. (doi:10.1007/s10953-014-1049-4)

70. Kumar D, Rub MA. 2019 Role of cetylmethyl ammonium bromide CTAB surfactant micelles on kinetics of [Zn(II)-Gly-Leu]+ and ninhydrin. J. Mol. Liquids 274, 639–645. (doi:10.1016/j.molliq.2018.11.035)

71. Zheng Y, Li X, Liu J, Zeng X. 2002 Micellar catalysis of composite reactions — the effect of SDS micelles and premicelles on the alkaline fadning of crystal violet and malachite green. J. Dispersion Sci. Technol. 23, 473–481. (doi:10.101080/03602457098065104)

72. Wu J, Upadhyay SK. 2005 Effect of cationic micellar aggregates on the kinetics of oxidation of aminoalcohols by N-bromosuccinimide in alkaline medium. J. Colloid Interface Sci. 285, 789–794. (doi:10.1016/j.jcis.2004.01.085)

73. Yang L, Li X, Liu J, Zeng X. 2002 Micellar catalysis of composite reactions — the effect of SDS micelles and premicelles on the alkaline fadning of crystal violet and malachite green. J. Dispersion Sci. Technol. 23, 473–481. (doi:10.101080/03602457098065104)

74. Pandey S, Upadhyay SK. 2005 Effect of cationic micellar aggregates on the kinetics of oxidation of aminoalcohols by N-bromosuccinimide in alkaline medium. J. Colloid Interface Sci. 285, 789–794. (doi:10.1016/j.jcis.2004.01.085)

75. Bhatia N, Upadhyay SK. 2003 Catalytic effect of supported metal ion complexes on the induced oxidative degradation of pyrocatechol violet by hydrogen peroxide. J. Colloid Interface Sci. 263, 228–236. (doi:10.1016/S0021-9797(03)00134-6)

76. Bhatia N, Upadhyay SK. 2003 Catalytic effect of supported metal ion complexes on the induced oxidative degradation of pyrocatechol violet by hydrogen peroxide. J. Colloid Interface Sci. 263, 228–236. (doi:10.1016/S0021-9797(03)00134-6)

77. Bhatia N, Upadhyay SK. 2003 Catalytic effect of supported metal ion complexes on the induced oxidative degradation of pyrocatechol violet by hydrogen peroxide. J. Colloid Interface Sci. 263, 228–236. (doi:10.1016/S0021-9797(03)00134-6)

78. Bhatia N, Upadhyay SK. 2003 Catalytic effect of supported metal ion complexes on the induced oxidative degradation of pyrocatechol violet by hydrogen peroxide. J. Colloid Interface Sci. 263, 228–236. (doi:10.1016/S0021-9797(03)00134-6)

79. Bhatia N, Upadhyay SK. 2003 Catalytic effect of supported metal ion complexes on the induced oxidative degradation of pyrocatechol violet by hydrogen peroxide. J. Colloid Interface Sci. 263, 228–236. (doi:10.1016/S0021-9797(03)00134-6)