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19 April 2024

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Kinetic Study on Effect of Novel Cationic Dimeric Surfactants for the Cleavage of Carboxylate Ester

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Kinetic studies have been performed to understand the reactivity of novel cationic gemini surfactants viz. alkanediyl-α-ω-bis(hydroxyethylmethylhexadecylammounium bromide) (C_{16}-s-C_{16} MEA, $2Br^-$ (where s = 4, 6) in the dephosphorylation of p-nitrophenyl benzoate (PNPB) with N-phenylbenzohydroxamic acid (PBHA) and butane 2, 3-dione monoxime (BDMO). Rate-surfactant concentration profiles are in accord with the pseudophase model with increasing concentrations of surfactants under the reaction conditions. It was observed that the C_{16}-s-C_{16} MEA, $2Br^-$ surfactants are efficient in promoting carboxylate ester cleavage in presence of α nucleophiles to attack on C=O Centre of triester. The catalytic activities of C_{16}-s-C_{16} MEA, $2Br^-$ surfactants are compared with those of N, N'-dihexadecyl-N,N,N',N'-tetramethyl-1,n-dodecanediammonium dibromide C_{16}-s-C_{16}, $2Br^-$ (where s = 10, 16) and also cetyldimethylethanol ammonium bromide (CDMEABr) and $C_nH_{2n+1}N^+Me_2 (CH_2)_3 SO_3^-$ (n=10; SB3-10) surfactants. The micellar effects were analyzed by pseudophse model.

Keywords: Kinetics, Hydrolysis, α-Nucleophile, Dimeric Surfactants

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INTRODUCTION

Micelle-forming surfactants have been widely used as reaction media for many important organic reactions [1-9]. Micelles provide different reactive sites/microenvironments for different parts of reactant molecules [10]. In general, observed rate increases have been referred to as micellar catalysis but this assignment needs particular attention in a kinetic analysis [11] since the micellar effects are critically determined by the ability of micelles to take up the reactants [12, 13]. Studies on the effects of surfactants on reaction rates have been subject of significant interest. Catalytic micellar effects have been analyzed quantitatively in terms of the pseudophase model (PM), pseudophase ion-exchange model (PIE), or Poisson Boltzmann model (PBE) [14, 15]. The relation between surfactant structure and morphology of the aggregate as well as the different molecular interactions determining the properties of the aggregate has been discussed [16, 17]. Kinetic models have been successfully applied to a wide range of chemical reactions in micellar solution [18], including mixed micelles [19] and other types of association colloids such as microemulsions [20] and vesicles [21]. However, the lack of a perfect micellar model for quantitative analysis of the kinetic rate data of micellar-mediated reactions appear to be due to an incomplete understanding of the fine details of the dynamics and structural features of the micelles. Nevertheless, previous kinetic studies helped to understand several complex aspects of micelles [22]. Different surfactants have been used because micelles can act as a microreactor which can both accelerate and inhibit the rates of wide variety of uni- and bimolecular reactions and shift the equilibrium constants of many indicators [23]. The α-nucleophiles such as hydroxamic acids, oximes, hydrogen peroxide, imidazoles, iodosoarenoic acids are among the most powerful reactants in cleavage of carboxylate, phosphate and sulphonate esters [24, 25]. They have proved to be very efficient in promoting acyl, phosphoryl and sulfuryl transfer processes [26]. However it has long been known that cationic micellar media enhance the reaction rates, much effort have been made to the study of novel surfactant systems that are required in drug delivery, stabilization of nanoparticles, gene delivery, find tools for tuning reactivity and for enhancing the solubility of sparingly soluble substrates [27]. Kinetic study of esters are the most challenging and interesting areas of research worldwide.

In past decade, extensive efforts have been made to study the mechanisms involved with nucleophilic-assisted hydrolysis of esters. The experimental and computational work has provided a wealth of knowledge on the dynamics, energetic and steric factor inherent to bimolecular nucleophilic substitution (S_N^2) reactions [28]. In recent years, renewed interests arouse with the newly established mass-spectrometric technique and the quantum chemical methods, which explore the α-effect of the bimolecular nucleophilic substitution reactions in the gas phase [29].The significant contributions of Fountain, Buncel, Um, Bierbaum, McAnoy and Nome et al. deserve special mention in this context [30]. The significance of α-nucleophiles such as hydrazines, hydroxylamines with acyl and alkyl halide have been presented by Mayr and research groups [31]. Simanenko and co-workers [32] have investigated a detailed kinetic study of nucleophilic cleavage of some phosphate and sulphonate esters in the presence of imidazolium surfactants bearing moieties of alpha-nucleophiles, namely oximate hydroxamate, amidoximate group. The reactivity of gemini surfactants towords the cleavage of esters with anionic nucleophiles have been reported by Bhattacharya et al. [33]. In order to obtain more reactive systems, gemini aggregates were extensively investigated by Moya and co-workers. [34]They reported that dimeric surfactants are more effective in accelerating the rate of reaction compared to cationic monomeric surfactants. Buurma and research groups [35] have discussed the effects of anionic micelles for the hydrolysis of a series of substituted 1-benzoyl-1, 2, 4-triazoles.
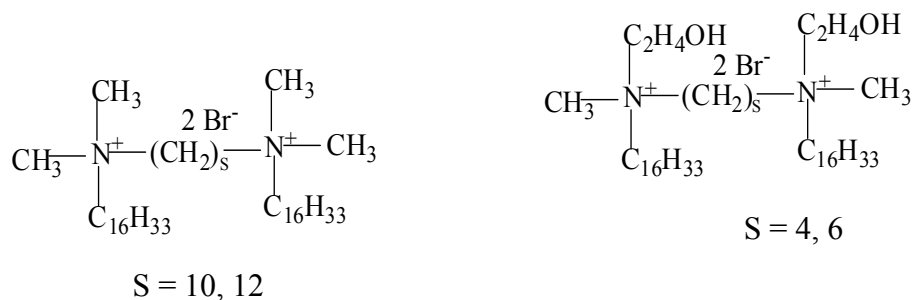

Chart - 1 The structure of the dimeric surfactants

Our research groups [36] have also previously carried out extensive studies of reactivity in micellar media and other colloidal aggregates.

In the present article, a kinetic study has been measured to understand the reactivity of novel cationic gemini viz. alkanediyl-α-ω-bis(hydroxyethylmethylhexadecylammounium bromide)

(C$_{16}$-s-C$_{16}$ MEA, 2Br$^-$ (where s = 4, 6) and conventional N, N'-dihexadecyl-N,N,N',N'-tetramethyl-1,n-dodecanediammonium dibromide C$_{16}$-s-C$_{16}$, 2Br$^-$ (where s = 10, 16) surfactants (Chart 1) in the cleavage of *p*-nitrophenyl benzoate (PNPB) with conventional α-nucleophiles. The catalytic activities of novel and convetional gemini surfactants are compared with those of cetyldimethylethanol ammonium bromide (CDMEABr) and also C$_n$H$_{2n+1}$N$^+$Me$_2$ (CH$_2$)$_3$ SO$_3^-$ (n=10; SB3-10) surfactants. The micellar effects were analyzed by pseudophse model.

MATERIALS AND METHOD

Materials

p-Nitrophenyl benzoate (PNPB) was obtained from Lancaster (Lancashire, England). N-phenylbenzohydroxamic acid (PBHA) was prepared at the Vertox laboratory of Defence Research Development Establishment, Gwalior (India). The dimeric surfactants were synthesized previously [37] Cetyldimethylethanolammonium bromide (CDMEAB) was a gift of Prof. R.M. Palepu, Canada. The butane 2, 3-dione monoxime and zwitterionic surfactant (SB3-10) were procured from Sigma-Aldrich, USA. All the solutions were prepared in triple-distilled water.

Kinetic Measurements

The reactions were studied spectrophotometrically using a Varian Cary 50 spectrophotometer and Systronics (Type-118) UV-Vis spectrophotometer by monitoring the appearance of the leaving *p*-nitrophenoxide ion at 400 nm and at 27±0.2ºC. All kinetic experiments were performed at an ionic strength of 0.1 M (KCl). Phosphate buffers were employed. All reactions were conducted under pseudo-first-order conditions. For all kinetic runs, the absorbance/time results fitted very well to the first-order rate equation:

$$\ln (A_\infty - A_t) = \ln (A_\infty - A_o) - kt. \qquad (1)$$

The pseudo-first-order rate constants were determined by least squares fits. Each experiment was repeated at least twice, and the observed rate constant was found to be reproducible within a precision of 3% or better.

RESULTS AND DISCUSSION

Surfactants are characterized by a variety of physical and chemical properties, including the critical micelle concentration (CMC), counterion binding (for ionic micelles), thermodynamics of formation, interfacial adsorption of the constituent monomers, and their aggregation numbers [37].

Kinetic study

The kinetic data for hydrolysis of *p*-nitrophenyl benzoate (PNPB) with N-phenylbenzohydroxamic acid (PBHA) and butane 2, 3-dione monoxime (BDMO) in the absence/presence of novel cationic dimeric (C_{16}-6-C_{16}, MEA Br$^-$ and C_{16}-4-C_{16}, MEA Br$^-$), conventional dimeric (C_{16}-12-C_{16}, Br$^-$ and C_{16}-10-C_{16}, Br$^-$), monomeric cationic (CDMEAB), zwitterionic (SB3-10) surfactants were used. First-order rate constants, k_{obs}, for reaction of PNPB with PBHA were measured at 27 °C and pH 8.0. The effect of nucleophile, pH and formation of phenoxide ion at 400 nm is shown in Fig. 1. The experimental kinetic rate data of PNPB at different concentrations of C_{16}-6-C_{16}, MEA Br$^-$, C_{16}-4-C_{16}, MEA Br$^-$, C_{16}-12-C_{16}, Br$^-$, C_{16}-10-C_{16}, Br$^-$, CDMEAB and SB3-10 with PBHA are shown in Table S1. These results show that C_{16}-6-C_{16}, MEA Br$^-$, C_{16}-4-C_{16}, MEA Br$^-$ compared to C_{16}-12-C_{16}, Br$^-$, C_{16}-10-C_{16}, Br$^-$ play a more dominating role in the hydrolytic cleavage of PNPB with PBHA. We observed that the k_{obs} value for the reaction of PNPB with PBHA increases sharply with an increasing concentration of C_{16}-6-C_{16}, MEA Br$^-$, C_{16}-4-C_{16} MEA Br$^-$, C_{16}-12-C_{16}, Br$^-$, C_{16}-10-C_{16}, Br$^-$ and CDMEAB up to 2.0×10^{-3} M in the solution and then decreases (Fig. 2). This trend can be explained by considering that both PNPB and PBHA are distributed between the micellar and aqueous pseudo phases. The variation of the k_{obs} values of the reactions appears to depend on the size of the head groups of the surfactants. The rate increases in micellar solution are, in addition to hydrophobic effects, due to favourable electrostatic attraction of the positively charged head groups of the cationic micelles with the negatively charged nucleophiles [24]. As a result, the contribution of the reaction occurring in the micellar pseudophase increases with surfactant concentration. For comparison, we have used butane 2, 3-dione monoximate ion (BDMO$^-$) in novel and conventional cationic dimeric surfactants for the cleavage of PNPB (Table S2). Recently, Das et al. [50] have investigated that the nucleophilic reactions of a variety of oxygen nucleophiles

(conventional and α-effect nucleophile) at the phosphorus and carbon centers of fenitrothion in vacuum and in water by computational methods. They observed that the aqueous-phase reaction is energetically, more favorable than the gas-phase one for all the nucleophiles investigated. The α-effect nucleophile HOO⁻ is found to be the most reactive for the reaction at the phosphorus center in fenitrothion than normal nucleophiles.
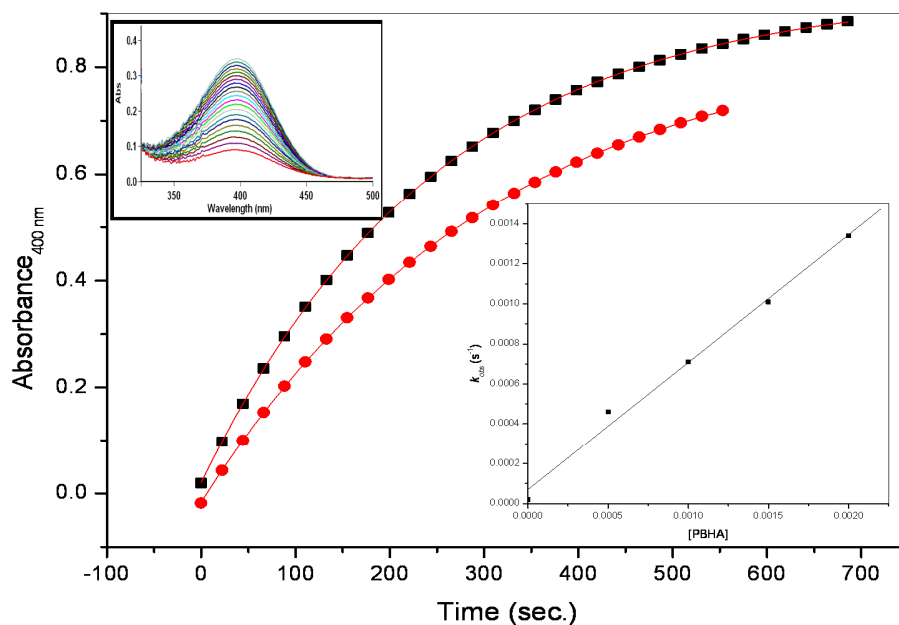

Fig. 1. Effect of α-nucleophile and time-dependent increase of absorbance at 400 nm upon hydrolysis of (●) PNPB (at pH 8.0) and (■) at pH 9.0 by N-phenylbenzohydroxamic acid (PBHA) in the presence of 16-10-16, 2Br-. Conditions: 27 °C, [PBHA] = 0.5 x 10^{-3} M, [16-10-16] = 0.5 x 10^{-3} M, [PNPB] = 0.5 x 10^{-4} M.
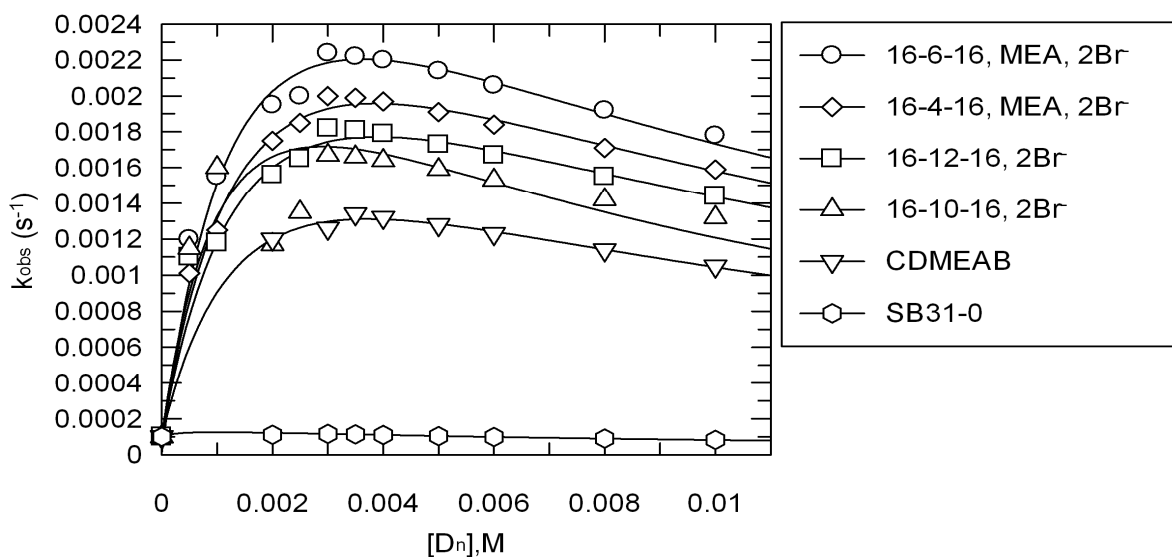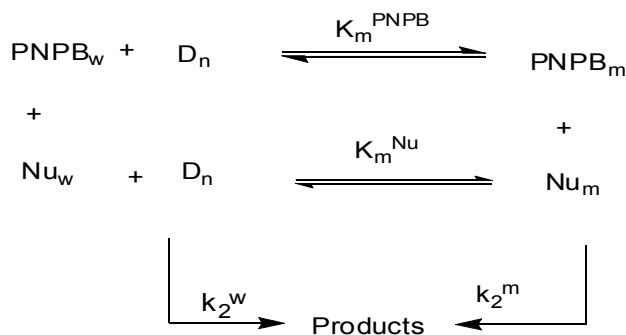
Fig. 2. Rate surfactant profiles for the reaction of PNPB with PBHA in various cationic surfactants (lines are predicted values with model).

3.1 Quantitative Treatment of the Rate Data

Micellar catalysis has usually been interpreted in terms of the pseudophase ion exchange model and pseudophase model [38]. Menger and Portnoy [39] proposed a model for the treatment of the micellar-mediated reactions which was further developed by Bunton [40] and Romsted [41]. Micelles are dynamic structures which are influenced by counterions, ionic strength, polarity of the medium, temperature, etc [42]. The effects of structural variation of the surfactants have been analyzed by various models and theories [24]. The interfacial ion exchange and the binding constant of the substrate are the key factors for the efficiency of micellar catalysis. It seems reasonable to expect that a factor of importance for the relative rates in the aqueous and micellar pseudophase would be the orientation of the substrate molecule within the surfactant aggregate. The overall kinetic behavior of the surfactants is described in the framework of the psuedophase model. It was observed that the rate enhancement is mainly due to the reagent concentration in the micellar pseudophase. In this system substrate, is distributed between the bulk and micellar phases are given in Scheme 2.

7

$$K_m^{PNPB}$$

PNPB$_w$ + D$_n$ $\rightleftharpoons$ PNPB$_m$

\+ \+

Nu$_w$ + D$_n$ $\rightleftharpoons$ Nu$_m$

$$K_m^{Nu}$$

k_2^w $\longrightarrow$ Products $\longleftarrow$ k_2^m

Scheme 2

In Scheme 2, subscripts w and m indicates aqueous and micellar pseudophases, in which substrate (PNPB) and α-effect nucleophiles, PBHA, BDMO are rapidly partitionated. The cleavage of PNPB by PBHA and BDMO with cationic gemini surfactants is main route at pH 8.0. So, using pseudophase model (Eq. 2) allows us to estimate approximate parameters of the micellar effect on the raction rate.

$$k_{obs} = \frac{k_2^W + (k_2^m/V_m)\, K_m^{PNPB}\, K_m^{Nu}\, [D_n]}{(1 + K_m^{PNPB}[D_n])(1 + K_m^{Nu}[D_n])} [Nu]_T \qquad (2)$$

In the Eq. 2, k_2^w and k_2^m is the second order rate constants in the aqueous and micellar pseudophases (in mol^{-1} dm^3 s^{-1}), K_m^{PNPB} and K_m^{Nu} is the equilibrium and association binding constant of the PNPB and nucleophile to micelles, $[D_n]$ is the micellized surfactant concentration. The V_m is equal to the partial molar volume of the interfacial reaction volume in the micellar pseudophase. The local morality of some ions can be determined by trapping, or estimated by solving the Poisson-Boltzmann equation (PBE) [43] and it is convenient to write second-order rate constants as $k_2^m = k_m V_m$. These values seem reasonable when compared to those obtained for monomeric alkyltrimethylammonium bromide surfactants as well as for dimeric alkanediyl-α-ω-bis (dodecyldimethylammonium) bromide, 12-s-12,2Br− surfactants [34]. The V_m may depend on the head group and the value of 0.63 M^{-1} was used in fitting data for reactions in dimeric micelles because the extended head group structure of the dimeric surfactants indicates that the interfacial region will be larger than that for the dicationic head group micelle [44] The CMC values were taken from the literature [37]. The calculated

parameters are shown in Tables 1 and 2. Result shows that the effect of nuclephiles is more pronounced in C_{16}-6-C_{16}, MEA Br⁻ than in C_{16}-12-C_{16}, Br⁻ and C_{16}-10-C_{16}, Br⁻. The experimental data shows that BDMO is more reactive compared to PBHA in dimeric micellar media (see Tables S1 and S2). Tables 1 and 2 show that the association binding constants, K_m^{Nu} of PBHA and BDMO are larger for the C_{16}-s-C_{16}, MEA Br⁻ (s = 4, 6) than for the conventional cationic dimeric C_{16}-s-C_{16}, MEA Br⁻ (s = 10, 12) micelles. The measured value of binding constant for PNPB with BDMO and PNPB in cationic micellar media was estimated, and we observed that the ethanol group of the dimeric surfactants has a large effect on the binding constant. This can most likely be attributed to the hydrogen bonding ability of the ethanol moiety of the cationic head groups that can help to stabilize the micelles [45]. Surfactants are capable to influence rate and equilibrium constants of numerous chemical processes [46] because micelles are able to concentrate the reactants at the micelle–water interface called the Stern layer [47]. Hydrogen bonding can play a significant role here, which agrees with literature data [37]. The lower polarity of the interfacial region as compared with that of water can also contribute to the rate acceleration since charge is dispersed in the transition state [48] and, as a consequence, the reduction in the polarity of the reaction site will favour the reaction. This could explain that the dimeric surfactants are better catalysts than the momomeric surfactants. It is known from the literature that the reactivity in the presence of dimeric surfactants is much higher than that of the corresponding monomeric surfactants. The reason is that the critical micelle concentrations (cmc) of the cationic dimeric surfactants are 10-100 times lower than those of the conventional surfactants [49]. This is likely to provide additional hydration at the head group level resulting in screening of repulsion Columbic forces between charged heads and also enforcing a connection among head groups, helping C_{16}-s-C_{16}, MEA Br⁻ surfactants to form aggregates at a lower concentration than those of C_{16}-s-C_{16}, Br⁻ and monomeric surfactants. So, the hydrogen bonding ability of the ethanol moiety at the surfaces could explain this unusual behaviour, helping the molecules to stay adsorbed at the surface.

Table 1. Kinetic parameters obtained by applying pseudophase model for the nucleophilic reaction of *p*-nitrophenyl benzoate (PNPB) with N-phenylbenzohydroxamic acid in the presence of cationic surfactants.

Surfactant	k^2_w ($M^{-1}s^{-1}$)	K_m^{PNPB}	k^2_M ($M^{-1}s^{-1}$)	$K_m^{Nu}(M^{-1})$	k_M/k_w
C_{16}-6-C_{16}, MEA, $2Br^-$	0.020	700	0.04977 ± 0.0052	106 ± 9	31
C_{16}-4-C_{16}, MEA $2Br^-$	0.020	700	0.0456 ± 0.0051	102 ± 10	30
C_{16}-12-C_{16}, $2Br^-$	0.020	800	0.044 ± 0.0003	89 ± 0.55	26
C_{16}-10-C_{16}, $2Br^-$	0.020	800	0.0309 ± 0.0099	134 ± 39	23
CDMEAB	0.020	900	0.0077 ± 0.0038	84 ± 9	19
SB3-10	0.020	4000	0.00056 ± 0.0003	74 ± 8	1

Reaction Conditions: Temp. = 27 °C, pH = 8.0, [Substrate] = 0.5×10^{-4} M, [PBHA] = 0.5×10^{-3} M, [KCl] = 0.1 M.

Table 2. Kinetic parameters obtained by applying pseudophase model for the nucleophilic reaction of *p*-nitrophenyl benzoate (PNPB) with butane 2,3-dione monoxime in the presence of cationic surfactants.

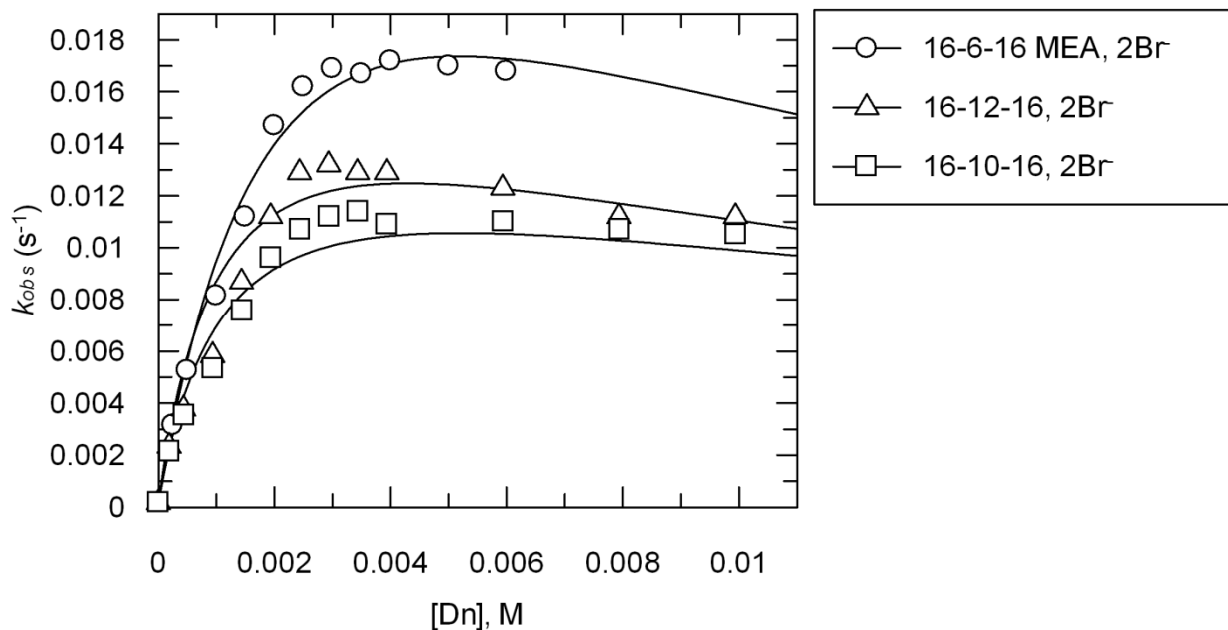| Surfactant	k^2_w $(M^{-1}s^{-1})$	K_m^{PNPB}	k^2_M $(M^{-1}s^{-1})$	$K_m^{Nu}(M^{-1})$	k_M/k_w
C_{16}-6-C_{16} MEA, 2Br⁻	0.36	200	0.455±0.0225	184±9	100
C_{16}-12-C_{16}, 2Br⁻	0.36	800	0.378±0.1424	65±19	76
C_{16}-10-C_{16}, 2Br⁻	0.36	800	0.3526±0.133	60±19	71
Reaction Conditions: Temp. = 27 °C, pH = 8.0, [Substrate] = 0.5×10^{-4} M, [BDMO] = 0.5×10^{-3} M, [KCl] = 0.1 M.					

Fig. 3. Rate surfactant profiles for the reaction of PNPB with BDMO in various cationic surfactants (lines are predicted values with model).

Figs 2 and 3 show that the rates of reaction increase with increasing surfactant concentration which reflect a further incorporation of the organic substrate molecules into the micelles where a high interfacial bromide ion concentration is present. Once the substrate molecule is wholly incorporated into the micelles, no further increase in k_{obs} is expected. We observed that the butane 2, 3-dione monoxime ion show higher nucleophile reactivity compared to that of N-phenylbenzohydroxamate ion with the novel cationic dimeric surfactants. Literature values [50, 51] show that N-phenylbenzohydroxamate (PBHA$^-$), salicylhydroxamate (SHA$^-$) and benzohydroxamate (BHA$^-$) ions are very reactive in the hydrolysis of p-nitrophenyl acetate (PNPA), p-nitrophenyl benzoate (PNPB) and p-nitrophenyl diphenyl phosphate (PNPDPP) in the presence of cationic micellar media.

Table 2 shows that the k_2^w and k_2^m values for the hydrolysis of PNPB with BDMO in the absence and presence of C$_{16}$-6-C$_{16}$, MEA, 2Br$^-$, C$_{16}$-12-C$_{16}$, 2Br$^-$, and C$_{16}$-10-C$_{16}$, 2Br$^-$. The results show that the second-order rate constant is higher in micellar media compared to aqueous media. Thus, the reaction is faster in the cationic micellar solutions investigated than in water, the dimeric aggregates being more efficient as catalysts than the monomeric micelles. The second-order rate constants of micelles with nucleophilic anions for many reactions are similar to or slightly lower than the second order rate constant in water k_2^w depending upon on the nature of the reaction [52]. Recently, Moya et al. [34] have successfully analyzed rate effects of dimeric micelles by using pseuophase model in which the micellar interface acts as an unusual reaction region. For PBHA, the second-order rate constants of CDMEAB and SB3-10 do not differ very much in aqueous and at micellar surfaces. The catalytic efficiency of the various micelles (viz. k_m/k_w) increases with increasing spacer chain length for C$_{16}$-s-C$_{16}$ MEA, 2Br$^-$ (where s = 4, 6) 31, 30 and C$_{16}$-s-C$_{16}$, 2Br$^-$ (where s = 10, 12) [24]. Tables 1 and 2 show that the binding constant is much higher for C$_{16}$-6-C$_{16}$ MEA, 2Br$^-$ than other cationic surfactants and that k_m^2 is higher for dimeric than for monomeric surfactants. But k_m^2 value difference is very little for all gemini

surfactants. The reason may be…………………….. The relative values of the binding constants indicate that BDMO is more reactive than PBHA and it located more deeply in the interfacial region. These results are qualitatively consistent with the concept that the high concentration of oximate moiety in the interfacial region is the major source of the rate enhancements [44]. On the basis of above explanation the reactions at the interfacial region of dimeric surfactants show larger changes compared to conventional and other surfactants. Therefore, stronger medium kinetic micellar effects would be predicted in C_{16}-s-C_{16}, MEA 2Br$^-$. The micellar binding constants for PNPB binding to C_{16}-6-C_{16}, MEA Br$^-$, C_{16}-4-C_{16}, MEA Br$^-$, C_{16}-12-C_{16}, Br$^-$ and C_{16}-10-C_{16}, Br$^-$ are higher compared to those of CDMEAB, (Table 1). Using the pseudophase model, it is found that the agreement between experimental and the calculated data is good. On the basis of experimental data and data analysis using the pseudophase model,the expected trend would be C_{16}-6-C_{16}, MEA Br$^-$ > C_{16}-4-C_{16}, MEA Br$^-$ > C_{16}-12-C_{16}, Br$^-$ > C_{16}-10-C_{16}, Br$^-$ > CDMEAB > SB3-10 as was found.

CONCLUSION

Kinetic studies can provide information about the occurrence of morphological transitions in dimeric cationic micellar solutions. This article explores the catalytic activity of dimeric micelles in nucleophilic ester hydrolysis. It is evident from results that the observed rate constants for C_{16}-6-C_{16}, MEA Br$^-$ are higher than that of C_{16}-12-C_{16}, Br$^-$. Less spatial obstruction and low CMC of novel dimeric gemini surfactants may be responsible for the better kinetic advantage by these surfactants. The most useful are alpha nucleophilic moieties which are to be deprotonated in their reactive anionic form. Although it has long been known that cationic micellar mediums enhance the reaction rates, much interest have been devoted to the study of novel cationic gemini surfactant systems that are required to enhance solubility of sparingly soluble substrates, and find additional tools for tuning reactivity. Micellar properties of gemini surfactants and anionic nucleophiles being the most sensitive to the micelle composition parameter that can be changed in the kinetic investigations. Novel class of gemini C_{16}-s-C_{16} MEA, 2Br$^-$ (s = 4, 6) surfactants containing ethanol moieties (C_2H_4OH) in the head groups, which show a different reactivity compared to conventional dimeric and monomeric surfactants. It is observed that butane 2,3-dione monoxime shows abnormal reactivity compared to N-phenylbenzohydroxamic acid

(PBHA) for the hydrolysis of p-nitrophenyl benzoate (PNPB) in C_{16}-s-C_{16} MEA, $2Br^-$ (s = 4, 6) compared to C_{16}-s-C_{16}, $2Br^-$ (s = 10, 12) and CDMEAB.

The zwitterionic surfactant is not effective for the hydrolysis of PNPB with both nucleophiles. Novel dimeric surfactants provide better microrganized media for micellar catalysis.

SUPPORTING MATERIALS

Table S1. Kinetic rate data for the reaction of p-nitrophenyl benzoate (PNPB) with p-phenylbenzohydroxamic acid in presence of novel and conventional cationic dimeric surfactants.

Table S2. Kinetic rate data for the reaction of p-nitrophenyl benzoate (PNPB) with butane 2,3-dione monoxime (BDMO) in presence of novel and conventional cationic dimeric, monomeric and zwitterionic surfactants.

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