Interactions between Cationic Gemini Surfactants and Nonionic Surfactant in Aqueous Solutions

Halide Akbaş, Mesut Boz and Aylin Dinç

Abstract---In this study, we have investigated mixed micelle formation in mixtures of cationic gemini and nonionic surfactant by conductivity at a certain micellar concentration range and certain temperature. The gemini surfactant of type alkanediyl-α-ω-bis (alkyldimethyl ammonium) dibromide with different alkyl groups referred as ‘’m-2-m” [C_mH_{2m+1} $(CH_2)_2$ N^+ $(CH_2)_2$ $N^+(CH_2)_2$ C_mH_{2m+1}, $2Br^-$] (m = 12 and 16) have been synthesized, purified and characterized in our laboratory. Brij-35 (polyoxyethylene 23 lauryl ether) was used as the nonionic surfactant in experiments. Using the conductance measurements , we have been obtained the values of critical micelle concentrations (CMC) of the binary gemini–nonionic surfactant mixtures having different compositions. The composition of mixed micelles and the micellar interaction parameters, (β), were evaluated from the critical micelle concentration values for different mixtures using the approach of Rubingh`s regular solution theory. Mixed systems were exhibited negative synergism due to positive β values. The β values were found between about zero and 3.5. This indicates that the mixed micelle formation is ideal for Brij 35-(16-2-16) mixtures (β=0.087). Antagonistic interactions were observed in the case of Brij35 - (16-2-16) dimeric cationic surfactant.

***Keywords*—**Cationic Gemini surfactants, critical micelle concentration, micellar interaction parameters, nonionic surfactant, regular solution theory.

I. Introduction

NOW-A-DAYS new classes of surfactants, the dimeric surfactants (also known as Gemini surfactant) have attracted increasing attention due to their superior surface activity comparing that of the corresponding conventional (monomeric) surfactants [1]-[3]. Gemini surfactants have better solubilizing ability, wetting, foaming, stronger biological activity and lime-soap dispersing properties which are compared to conventional surfactants [4[,[5]. They are amphiphilic molecules with hydrophobic tails and two polar head groups covalently to be linked by a spacer group [6], [7]. The various micellar properties of these compounds, such as degree of ionization, aggregate morphology, phase behavior, rheological properties and area per molecule adsorbed at the air/water interface have been studied by a range of experimental techniques [8],[9].

On the other hand, nonionic surfactants which consist of an alkyl chain as hydrophopic moiety and polyoxyethylene ether (POE) chain as hydrophilic moiety are widely used as an agent to solubilize and emulsify processes in the textile, detergent and cosmetic industries. The solubility of non-ionic surfactants in aqueous solution is due to the high hydration of oxyethylene chains [10], [11]. Brij series are widely used in many practical applications. [12], [13].

An industrial surfactants system is typically mixtures of different chemical species such as ionic and nonionic surfactants, electrolytes, dyes and filters [14], [15]. In theory, desirable surface properties for specific applications can be obtained by adjusting the compositions of these systems. The addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsions between the charged surfactant head groups, greatly faciliting micelle formation. The nonideal behavior of mixtures of an ionic and a nonionic surfactant can also be influenced by the structural characteristics of the two surfactants, such as the relative size of head groups and the lengths of their tails. Various theoretical models are available to interpret the formulation of mixed micelles. Rubingh [16] proposed a treatment based on regular solution theory (RST) for nonideal mixed systems which have been extensively used. In the phase separation approach, micelles and monomers in bulk are assumed to be in equilibrium. Both the surfactant composition and spacer length are found to influence the properties of mixed micelle markedly by Wang and co-worker [17].

Perusal of the literature on mixed micellization shows that although there is some work on cationic gemini-conventional mixed systems [18], reports of cationic gemini-nonionic systems is scarce. Keeping all these facts in mind we have studied the mixtures of cationic Geminis of m-2-m type and nonionic surfactants conductometricaly at 30 ^oC. These Geminis are alkanediyl-α-ω-bis (dimethyl ammonium) bromide with m=12 and 16. Brij-35 is used as polyoxyethylene nonionic surfactants.

This work was supported the Scientific Research Fund of Trakya University (Project No: TÜBAP -2011/43).

Halide Akbaş is with Department of Chemistry, Faculty of Scence, Trakya University (e-mail: hakbas34@yahoo.com).

Mesut Boz is with Department of Chemistry, Faculty of Scence, Trakya University (e-mail: mesutboz@hotmail..com)mesutboz@hotmail.com)

Aylin Dinç is with Company: Mebant Isolation and Band (e-mail: aylinn4@gmail.com).

II. Material And Methods

A. Materials

Cationic surfactants: The cationic gemini surfactants, N,N'-didecyl-N,N,N',N'-tetramethyl N,N'-ethanediyl-diammonium dibromide (12-2-12) and N,N'-dihexadecyl-N,N,N',N'-tetramethyl N,N'-hexanediyl-diammonium dibromide (16-6-16) have been synthesized, purified and characterized in our laboratory. Surfactant purity was checked by nuclear magnetic resonance (NMR) and surface tension, all with excellent results. ^{1}H NMR spectra were recorded in $CDCl_3$ solution with a Varian Mercury Plus 300 MHz spectrometer. ^{13}C NMR spectra were recorded at 75 MHz.

Nonionic surfactants: Polyoxyethylene (23) lauryl ether (Brij 35) has the chemical formula $[C_{12}H_{25}(OCH_2CH_2)_{23}OH]$. Non-ionic surfactant was supplied from Aldrich–Sigma and used as received.

B. Methods

Conductance measurements:

The conductivity of the solutions was measured as a function of concentration by using a conductometer WTW Terminal 740 with cell constant 0.433 cm^{-1}. The conductometer was initially calibrated with standart KCl solutions in appropriate concentration range. The experiments were performed at constant temperature by circulating water through a jacketed cell holding the solution under study. The experimental error in the temperature was minimized to ±0.2 K.

Preparation of mixed surfactant solutions:

Using CMC values which were found for pure surfactant solution, a certain total concentration was selected. At this selected concentration, micellization was present for all surfactant solutions and so, stock solutions were prepared at this concentration. The mixed solutions were prepared by mixing two pure solutions and were kept for at least 30 minutes for equilibrium in a thermostat bath at certain temperature before measuring conductivity. All solutions were prepared with double distilled water in an all-glass distillation apparatus. Specific conductivity of this water was in the range of $(1\text{-}2)\times10^{-6}$ Scm^{-1}.

Regular solution theory of surfactant mixtures:

Rubingh [16] proposed a treatment based on regular solution theory (RST) for non-ideal mixed systems which have been extensively used. According to Rubingh, if the surfactants are mixed, the mixed CMC (C*) is given by Equation [1]:

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2} \qquad [1]$$

Where α_1 is the molar fraction of surfactant 1in the mixed solution, C_1 and C_2 are the CMC values of pure surfactants 1 and 2 respectively. Mixed CMC (C*) values were calculated using the above equation for ideal behavior and plotted against the mole fraction of surfactants. The composition of the mixed micelles, (X_1), at the CMC and the interaction parameter, β, were calculated by iterative resolution of the following equation [2] and [3].

$$\frac{x_1^2 \ln(\alpha_1 C^* / x_1 C_1)}{(1-x_1)^2 \ln[(1-\alpha_1)C^* / (1-x_1)C_2]} = 1 \qquad [2]$$

$$\beta = \frac{\ln(\alpha_1 C^* / x_1 C_1)}{(1-x_1)^2} \qquad [3]$$

It is noted that these calculations are only valid at mixed CMC(C*).

II. Result And Discussion

Gemini surfactant-nonionic surfactant interactions: For gemini cationic surfactant-nonionic surfactant mixtures, the conductance values were measured for aqueous solutions containing (12-2-12)-Brij-35 and (16-2-16)-Brij-35 mixtures with various surfactant mole fractions ranging from zero (pure gemini surfactant) to one (pure nonionic surfactant). (12-2-12)-Brij 35 and (16-2-16)-Triton X-100 mixtures are shown in Fig. 1(a) and Fig. 1(b). The CMC values of surfactant solutions were determined at sharp break points in specific conductivity against concentration curves at 303.15 K and are given Table 1. CMC values were found as 3.30×10^{-5} M for (16-2-16) and between 9.60×10^{-4} M for (12-2-12). Conductivity against concentration curves at 303.15 K and are given Table 1. CMC values were found as 3.30×10^{-5} M for (16-2-16) and between 9.60×10^{-4} M for (12-2-12).

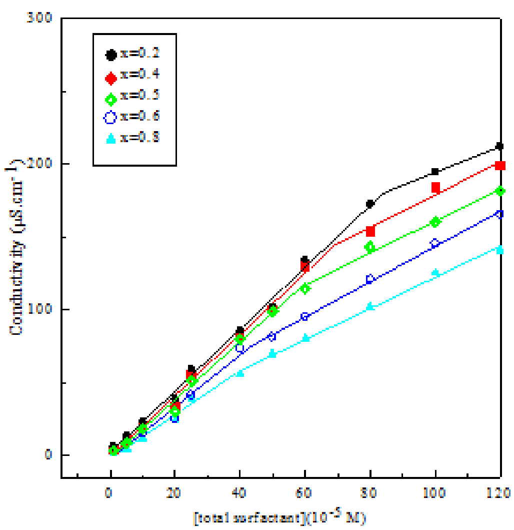
Gemini surfactants have low CMC values compared with corresponding conventional surfactants of equivalent chain length.[2]. The CMC values of 16-2-16 are about 28 times less than that of CTAB (CMC of CTAB is 9.09×10^{-4} M). Doubling surfactant molecular weight decreases CMC values.

This indicates that the studied dimeric species have a much better micelle-forming ability than single tail-single head ones, probably because the two hydrophobic chains of gemini surfactants break the water structure earlier and thus increase the tendency to form micelles. From Table 1, it can be seen that mixed CMC values decrease with the increasing in mole fraction of the Brij 35 in (12-2-12)-Brij-35 binary system. This indicate that the added Brij 35 assist cationic gemini surfactant in the micelle formation. Also, in (16-2-16)-Brij 35 binary system, CMC values increase with the increasing in mole fraction of the Brij 35. So that, added Brij 35 delays micellization process.

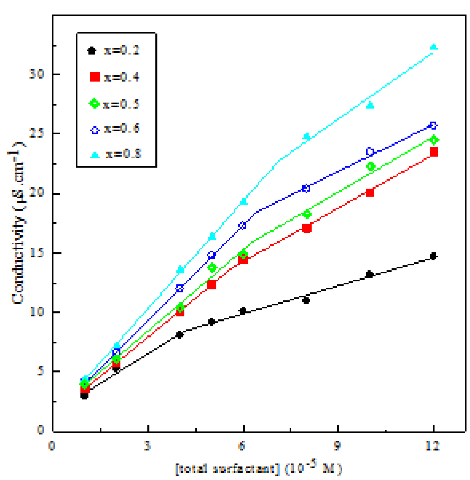
Mixed micelle formation may be ideal or nonideal. Fig. 2 (a) and Fig. 2 (b) were plotted using these critical points against to mole fraction of Brij 35. Furthermore, mixed critical point values calculated using the Equation [2] for ideal behavior are also plotted against the mole fraction of Brij 35 and are shown as dotted line in same figure. Using an iterative solution of Equations [2] and [3] for each composition, the interaction parameter (β) and the composition of the mixed micelles (X_1) were calculated. These values were given in Table 1.

The β values demostrate the extent of interaction between the two surfactant which leads to the deviation from ideality. Negative β values indicate that the attractive interaction (synergism) between the two different surfactants is stronger than the attractive interaction between each type of surfactant. A positive value β indicates that the repulsive interaction (antagonism) between the two different surfactants is stronger than the self-repulsion between two individual surfactants of the same type.

It can be seen from Table 1, the β values for (16-2-16)-Brij 35 mixtures were close to zero, especially at equimolar composition (β = 0.062). If the β values were slightly positive indicating repulsive interaction and the system exhibits negative synergism. If β = 0 then mixed micelle formation is ideal. Actually, all β values for (16-2-16)-Brij 35 system are found ideal with close to zero values of



(a)



(b)

Fig.1 Conductivity as a function of total surfactant concentration for Geminis - Brij 35 mixtures of different compositions at 30°C. (a)-(12-2-12) – Brij 35, (b)- (16-2-16) – Brij 35.

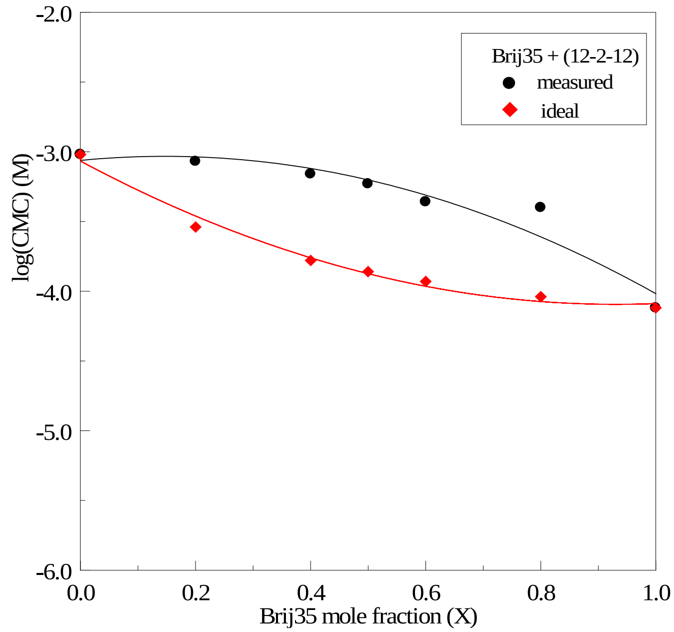


Fig. 2 Experimental and ideal critical misellar concentration of (12-2-12)-Brij 35 mixtures as a function of mole fraction Brij 35 at 30 °C.

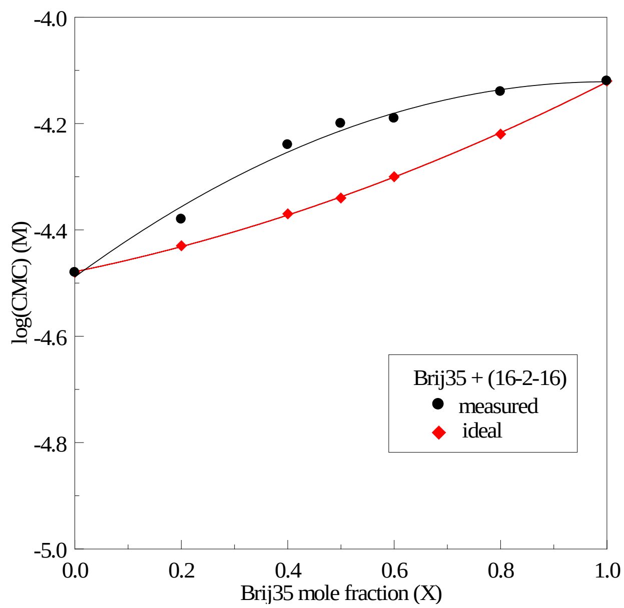


Fig. 3 Experimental and ideal critical misellar concentration of (16-2-16)-Brij 35 mixtures as a function of mole fraction Brij 35 at 30 °C.

TABLE I
MOLE FRACTION OF NONIONIC SURFACTANT IN TOTAL MIXED SOLUTE (α) , MIXED MICELLES (X_1), MIXED CMC, IDEAL VALUES OF CMC*, INTERACTION PARAMETER (β), AVERAGE PARAMETER $\overline{\beta}$, FOR GEMINIS - BRIJ 35 SYSTEM AT 30^{o}C.

Mixture of Surfactant	Mole fraction (α)	CMC (measured)	CMC* (ideal)	X_1	β	$\overline{\beta}$
12-2-12 + Brij35	**0.0**	9.60×10^{-4}	9.60×10^{-4}	-	-	3.584
	0.2	8.40×10^{-4}	2.86×10^{-4}	0.753	0.209	
	0.4	6.90×10^{-4}	1.68×10^{-4}	0.886	0.864	
	0.5	5.80×10^{-4}	1.39×10^{-4}	0.917	1.522	
	0.6	4.30×10^{-4}	1.19×10^{-4}	0.942	3.139	
	0.8	3.90×10^{-4}	9.20×10^{-5}	0.972	12.189	
	1.0	7.50×10^{-5}	7.50×10^{-5}	-	-	
16-2-16 + Brij35	**0.0**	3.30×10^{-5}	3.30×10^{-5}	-	-	0.087
	0.2	4.10×10^{-5}	3.72×10^{-5}	0.089	0.131	
	0.4	5.70×10^{-5}	4.25×10^{-5}	0.218	0.064	
	0.5	6.20×10^{-5}	4.58×10^{-5}	0.296	0.062	
	0.6	6.40×10^{-5}	4.97×10^{-5}	0.388	0.065	
	0.8	7.10×10^{-5}	5.98×10^{-5}	0.628	0.113	
	1.0	7.50×10^{-5}	7.50×10^{-5}	-	-	

In this system, the mixed CMC values are greater than the ideal CMC's obtained from Equation [2]. Also, β values in (12-2-12)-Brij 35 binary system, are found positive and this system exhibits nonsynergistic behavior, so that antogonistic interaction. A positive β parameter implies a net repulsive interaction between the surfactants in the mixture.Equal chain of both gemini and nonionic surfactants (12-2-12)-Brij 35 makes it diffucult for these chains, to accumulate in the core. Antogonistic interactions were observed in the mixed micelles of (12-2-12) gemini-Brij 35 ($\overline{\beta}$ =3.584). The magnitude of antogonistic interactions increased with increase in mole faction of Brij 35 . Maximum antagonistic is observed at 0.8 mole fraction of Brij 35 as β = 12.189. Also, similar antagonist interactions were observed for (14-2-14)-Triton X-100 system[19].

On the other hand, antogonistic interaction decreased with the increase in hydrophobicity of the cationic component. As seen as Table 1, in (16-2-16) gemini - Brij 35 system, the average value.of $\overline{\beta}$ is found as 0.087. A positive or negative deviation in CMC from ideality can be explained in terms of unfavorable and favorable mixing, respectivity. among the unlike monomers of binary mixtures.

ACKNOWLEDGMENT

H. Akbaş gratefully acknowledges the financial support of the Trakya University Research Fund (Project No: TÜBAP-2011/43).

REFERENCES

[1] R. Zana, "Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review" Adv.Colloid Interface Sci., vol. 97, pp. 205-253, 2002. http://dx.doi.org/10.1016/S0001-8686(01)00069-0

[2] H. Akbaş, A. Elemenli and M. Boz, "Aggregation and Thermodynamic Properties of Some Cationic Gemini Surfactants" J. Surfact. Deterg., vol. 15, pp. 33-40, 2012. http://dx.doi.org/10.1007/s11743-011-1270-7

[3] K.S. Sharma, P.A. Hassan and A.K. Rakshit, "Self aggregation of binary surfactant mixtures of a cationic dimeric (Gemini) surfactant with nonionic surfactants in aqueous medium" Colloid Surf. A, vol. 289, pp. 17-24, 2006. http://dx.doi.org/10.1016/j.colsurfa.2006.04.004

[4] R. Zana, "Gemini (dimeric) surfactants" Curr. Opin. Colloid Interface Science, vol. 1, pp. 566, 1996. http://dx.doi.org/10.1016/S1359-0294(96)80093-8

[5] H. Akbas and Ç. Batıgöç, "Spectrometric studies on the cloud points of Triton X-405" Fluid Phase Equilibria, vol. 279, pp. 115-119, 2009. http://dx.doi.org/10.1016/j.fluid.2009.02.014

[6] R. Zana and J. Xia, Gemini Surfactants; New York: Marcel Dekker,vol. 117, 2004.

[7] M. J. Rosen "Geminis : A New Generation of Surfactants" Chem. Tech., vol. 23, pp. 30-33, 1993.

[8] S. Zhu, F. Cheng, J. Wang and Jiu-gao Yu, "Anionic Gemini surfactants: Synthesis and aggregation properties in aqueous solutions" Colloid Surf. A, vol. 281, pp. 35, 2005. http://dx.doi.org/10.1016/j.colsurfa.2005.02.045

[9] R. De Lisi, C.Ostiguy,G.Perron and J.E.Desnoyers, "Complete thermodynamic properties of nonyl- and decyltrimethylammonium bromides in water" J.Colloid Interface Sci., vol. 71, pp. 147-166, 1979. http://dx.doi.org/10.1016/0021-9797(79)90229-7

[10] K.S. Sharma, S.R. Patil, A.K. Rakshit, "Study of the cloud point of C12En nonionic surfactants: effect of additives" Colloid Surf. A, vol. 219, pp. 67–74, 2003. http://dx.doi.org/10.1016/S0927-7757(03)00012-8

[11] K. Toerne, R. Rogers and R. von Wandruszka, "Fluctuating clouding behavior in mixed micellar solutions" Langmuir, vol. 16, pp. 2141–2144, 2000. http://dx.doi.org/10.1021/la991046c

[12] H. Akbaş, M. Boz, Ç. Batıgöç, "Study on cloud points of Triton X-100-cationic gemini surfactants mixtures: A spectroscopic approach" Spectrochimica Acta Part A, vol. 75, pp. 671-677, 2010. http://dx.doi.org/10.1016/j.saa.2009.11.038

[13] Ç. Batıgöç and H. Akbaş, "Spectrophotometric determination of cloud point of Brij 35 nonionic surfactant" Fluid Phase Equilibria, vol. 303, pp. 91-95, Apr. 2011. http://dx.doi.org/10.1016/j.fluid.2011.01.004

[14] H. Akbaş, T. Tanzer, "The Effect of Electrolytes on the Interaction of C. I. Reactive Orange 16-Tetradecyltrimethylammonium Bromide" Tenside Surf. Det., vol. 50, pp. 1-6, March 2013. http://dx.doi.org/10.3139/113.110235

[15] C.Carnero Ruiz and J Aguiar , "Mixed micelles of triton X100: interaction, composition, stability and micro -environmental properties of the aggregates" Molecular Physics, vol. 97, pp.1095-1103, sep.1999. http://dx.doi.org/10.1080/002689799163046

[16] D.N.Rubingh, “Mixed micelle solution ” in Solution Chemistry of Surfactant, KL Mittal Plenum Press. vol.1. New York, 1979, pp. 337-354. http://dx.doi.org/10.1007/978-1-4615-7880-2_15
[17] X. Wang, J. Wang, Y. Wang, J.Ye, H. Yan, R.K. Thomas, "Properties of mixed micelles of cationic gemini surfactants and nonionic surfactant triton X-100: Effects of the surfactant composition and the spacer length", J. Colloid Interface Sci., vol. 286, pp. 739-746, 2005. http://dx.doi.org/10.1016/j.jcis.2005.01.084
[18] N. Azum, A.Z.Naqvi, M.Akram, Kabir-ud-Din, " Mixing behavior of conventional and gemini cationic surfactants", J. Dispers. Sci. Technol., vol. 29, pp. 711-717, 2008. http://dx.doi.org/10.1080/01932690701756735
[19] M. S. Bakshi, S.Sachar, K.Singh and A. Shabeen, " Mixed micelle behavior of Pluronic L64 and TritonX-100wșth conventional and dimeric cationic surfactants" , J. Colloid Interface Sci., vol. 286, pp.369-377. http://dx.doi.org/10.1016/j.jcis.2004.12.044

Halide Akbaş was born in Istanbul, TURKEY. She graduated from the Technical University of Istanbul and received her Ph.D. at Trakya University, Edirne in 1993. Since 2013 she is a Professor of Physical chemistry at the Department of Chemistry, Faculty of Science, Trakya University. Her research area focuses on novel surfactants, their thermodynamic properties and interactions, thermodynamic properties. and surface chemistry.