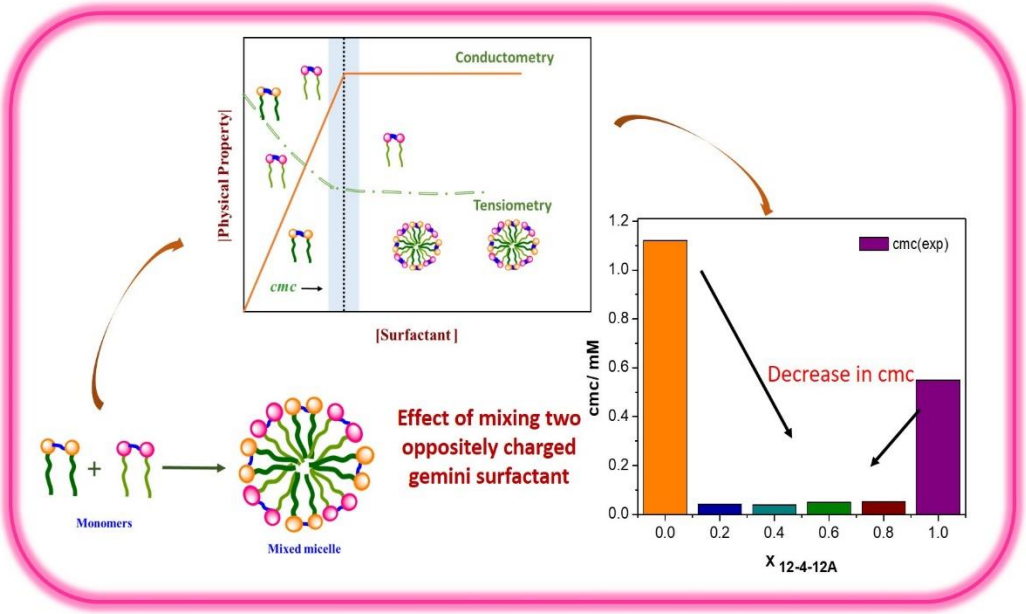
Chapter 5

Mixed Micellization and Interaction of Oppositely Charged Gemini Surfactants



Part of work published in *J. Phys. Chem. B*, *2017, 121, 8756−8766.*

& J. Mol. Liq. 2019, 279, 108-119.

5.1. Introduction

cmc gives fundamental information regarding surface activity and potential use of a typical surfactant.

cmc can be tuned by molecular architecture of the surfactant system(s). As can be seen from the literature survey (please see Chapter 1, 1.3), gemini surfactant micellization is extensively studied in the last two decades [1-7]. Gemini aqueous micellization process has been found to be dependent on spacer nature (*vide supra*), counter-ion and alkyl chain length of both spacer and hydrocarbon tail [1]. In many practical application, mixing of more than one surfactants proved advantageous from the application point of view (*e.g.*, solubilization, clouding, lower *cmcs*, surface activity etc). Mixing of surfactants results in mixed micelles with added advantages. Recently, the gemini surfactant has been regularly used as one of the components of mix micelle to achieve the desired potential of mixing of two surfactants. It has been mention that synergism of mixture follows the order: ionic/non-ionic < ionic /zwitterionic < anionic/cationic. It has been reported that when cationic geminis are mixed with opposite charge conventional anionics, mixture shows better solubilization potential for hydrophobic organic compounds [8]. However, very limited studies are available related to mixed micellization of oppositely charged gemini surfactants [9-12].

Above facts inspired to perform a detailed study of mix micellization involving oppositely charged gemini surfactants. The investigation has been designed to show *cmc* and interaction variations by the mutual presence of oppositely charged gemini surfactants. Effects of alkyl chain length and spacer nature (in cationic geminis) have been checked to draw information of structure-property relationship. These studies would help in selecting the mixed system for their potential solubilization applications.

In this chapter *cmc* data (singly or in combinations) have been acquired for various, gemini(s), using conductivity and surface tension measurements.

cmc data were analyzed using various solution theories as mentioned in **Chapter 4 (4.2.2).** Micellar interaction parameter has been calculated and then correlated with the nature of gemini mixture.

5.2. Results and Discussion

5.2.1. Micellization of Single Gemini Surfactant

cmc values for all the gemini surfactants have been determined by surface tension and conductivity measurements. Figure 1. shows the variation of γ with log C. A well-defined constancy in γ values is observed, after a certain concentration, which is taken as *cmc* of the gemini surfactant. Further, no minimum was observed (Figure 1.) in γ vs log C plots which indicate the high purity of the geminis used in the study. Another point can be noted that *cmc* decreases with a chain length of the alkyl tail which is inline as observed in earlier work [1].

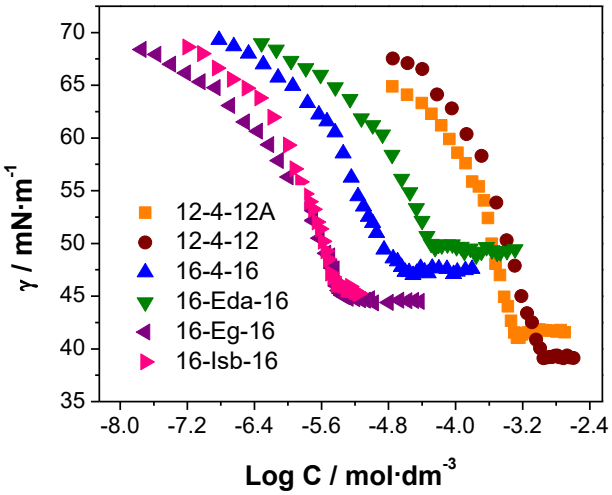


Figure 1. The plot of surface tension (γ) *vs* Log C (logarithm of concentration) of pure gemini surfactants in aqueous solution at 303 K.

However, the nature of spacer and counter-ion play equally important role as gemini of equal chain lengths show different *cmc* values as spacer nature, type of charge or counter-ion were changed.

cmc values of each gemini surfactant have also been determined conductometrically. Representative κ *vs* [Gemini] plots are shown in Figure 2 (a and b). *cmc* values for single geminis by the above two methods are compiled in Table 1. The *cmc* values were in close proximity with each other to validate the measurement.

Table 1. Critical micelle concentration (*cmc*) of various gemini surfactants in aqueous solution at 303 K.

Sr. No.	**Surfactant**	***cmc* / mM**	
		Conductometry	**Tensiometry**
1	12-4-12A	0.53	0.497
2	12-4-12	1.12	1.10
3	16-4-16	0.024	0.021
4	16-Isb-16	0.0027	0.0035
5	16-Eg-16	0.0034	0.0043
6	16-Eda-16	0.044	0.048

Among 12-4-12 (cationic) and 12-4-12A (anionic), former shows higher *cmc* value which is due to the nature of the head group and counter-ion (Figure 2a). This difference may be due to counter-ion/head group and head-group/ head-group interactions.

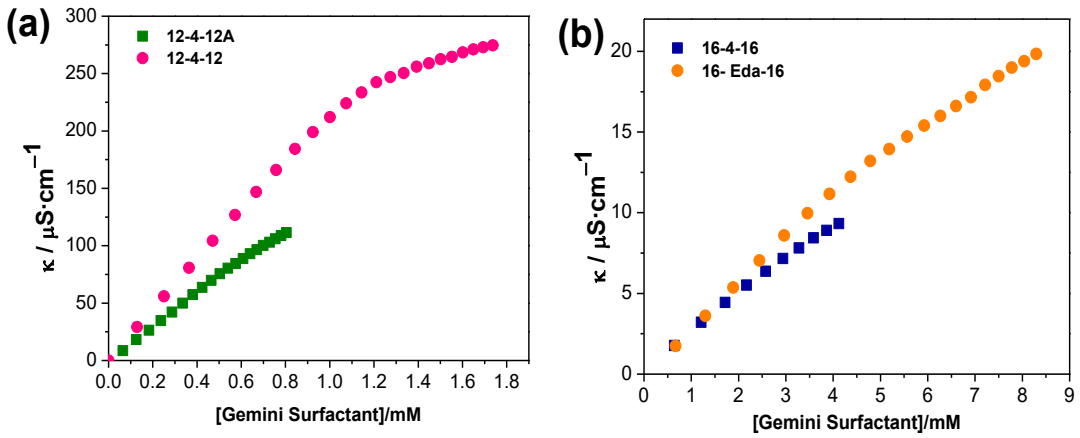


Figure 2. Representative plots of specific conductance (κ) vs [surfactant], single gemini surfactants (a) 12 C cationic gemini 12-4-12 and anionic gemini 12-4-12A (b) 16 C cationic geminis.

5.2.2. Mixed Micellization of Gemini Surfactant Systems

Various cationic geminis-12-4-12A combinations were used to study mixed micellization phenomenon by mixing two components at various compositions. Again both (conductometry and tensiometry) techniques were used to determine *cmc*, at each composition, for different systems. Relevant plots for the variation of γ (or κ) with a mole fraction of added 12-4-12A, to cationic gemini surfactant (16-4-16, 16-Eda-16, 16-Eg-16 16-Isb-16 or 12-4-12), have been shown in Figures 3-5. The relevant *cmc* data on mixed micellization have been compiled in Tables 2 and 3. The typical *cmc* value of the mixed system has been found lower than that of the individual component (with higher *cmc*) and higher than the one having lower *cmc*.

γ at *cmc* of the mixture (γ_{cmc}) ranges from 30-50 m**N**.**m**$^{-1}$ depending upon composition and nature of the mixture formed by two different types of gemini surfactants. Probably, competition for the air-water interface can affect the accumulation of the components of the mixture, their interactions, and hence overall surface activity.

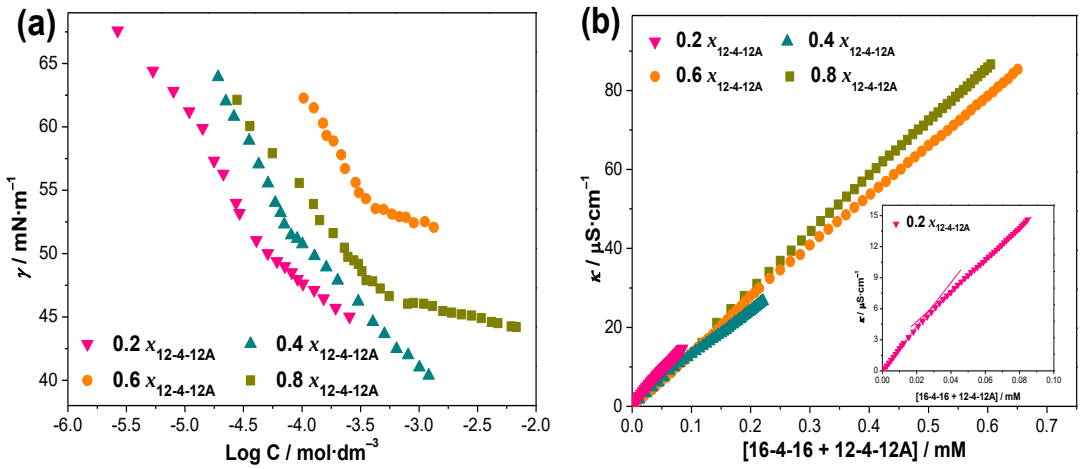


Figure 3. (*a*) Representative plot of surface tension (γ) *vs* log C (logarithm of concentration) and (*b*) Plot of specific conductance (κ)) *vs* [surfactants], of mixed gemini surfactants (16-4-16 + 12-4-12A) at different mole fractions (x) of anionic gemini (12-4-12A) in aqueous solution at 303 K.

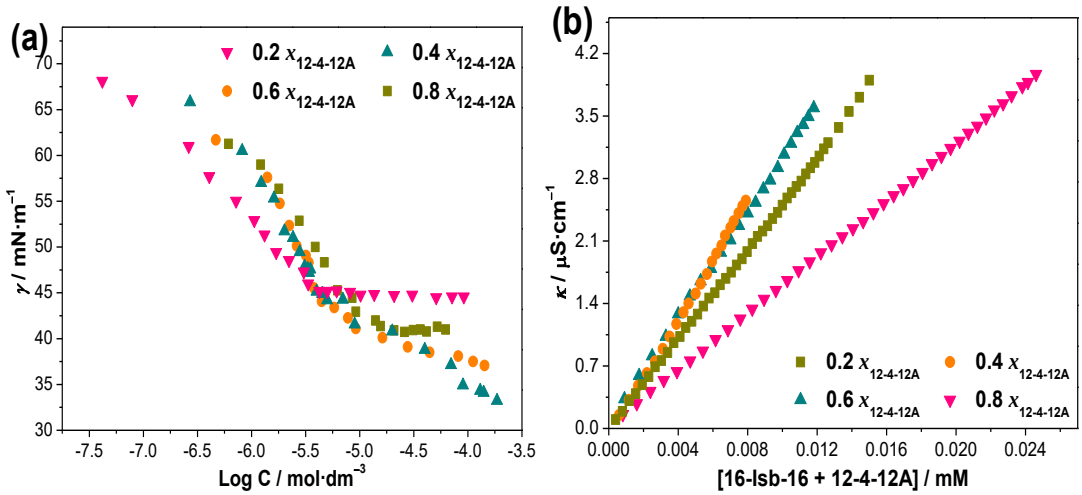


Figure 4. (*a*) Plot of surface tension (γ) *vs* log C (logarithm of concentration) and (*b*) Plot of specific conductance (κ)) *vs* [surfactants], of mixed gemini surfactants (16-Isb-16 + 12-4-12A) at different mole fractions (x) of anionic gemini (12-4-12A) in aqueous solution at 303 K.

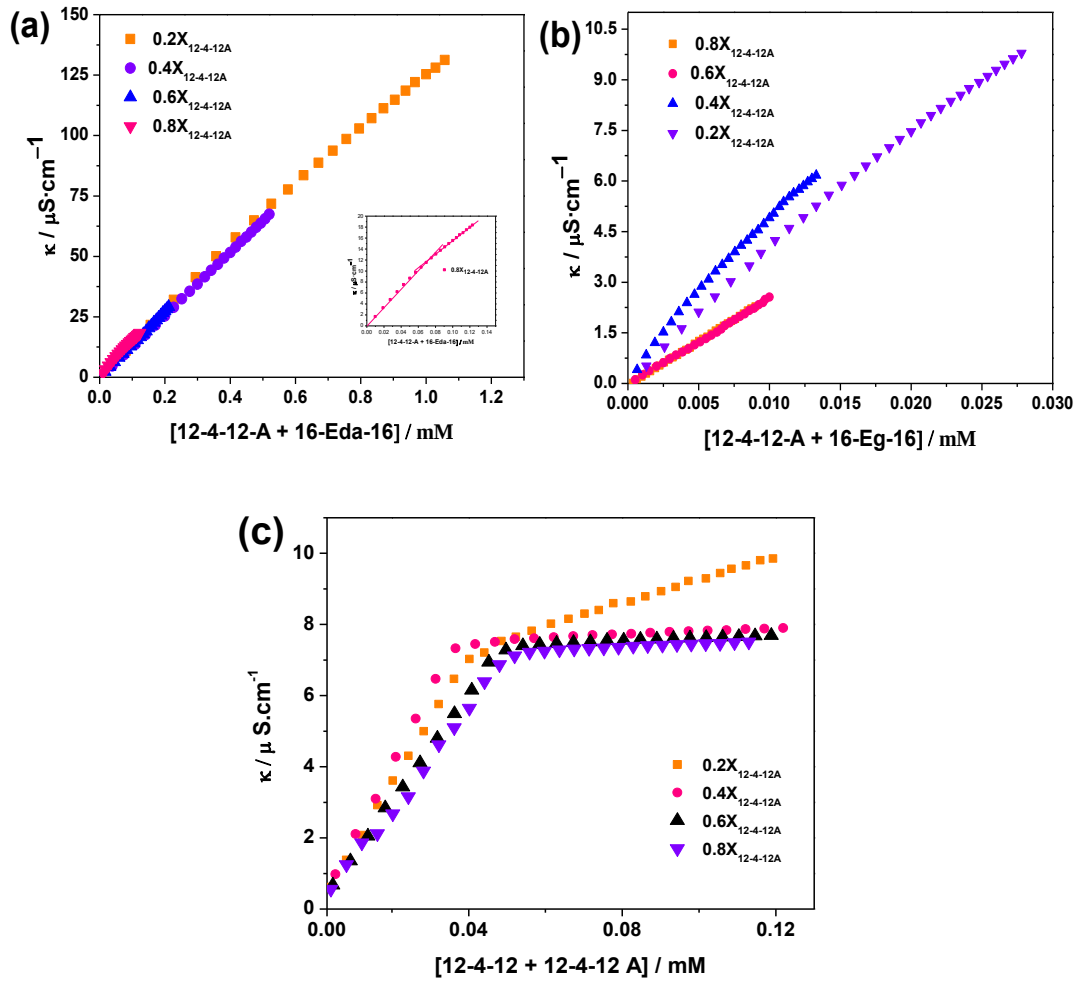


Figure 5. Plot of specific conductance (κ)) *vs* [surfactants], of mixed gemini at different mole fractions (x) of anionic gemini (12-4-12A) in aqueous solution at 303 K. (a) 16-Eda-16 + 12-4-12A (b) 16-Eg-16 + 12-4-12A and (c) 12-4-12 + 12-4-12.

5.2.3. Interaction of Oppositely Charged Gemini Surfactants

The idea of interaction between two components of the mixture can be realized by comparing experimental *cmc* (cmc_{exp}) with *cmc*'s of individual components used in a mixture (cmc_1 and cmc_2, for individual component 1 and 2). Ideal *cmc* of the mixture (cmc_{ideal}) of the mixture has been determined by the same method as given in the previous chapter (**Chapter 4, 4.2.2.**). Interaction parameter (β^m), between two gemini components, can be obtained by using values of cmc_1, cmc_2 and cmc_{exp} as mentioned in

Chapter 4. These data are compiled in Tables 2 and 3. The variation of both cmc_{ideal} and cmc_{exp} has been shown in Figure 6.

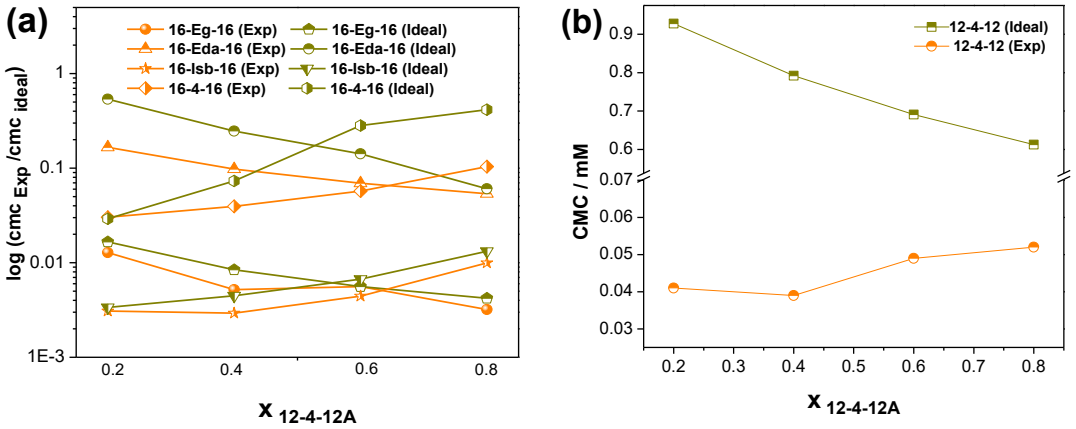


Figure 6. Critical micelle concentration (*cmc*) by conductometry with a variation of mixed surfactant systems (cationic-anionic) with a mole fraction of anionic gemini surfactant ($x_{12\text{-}4\text{-}12A}$) in aqueous solution at 303 K. The plot represents experimental and ideal values (calculated from ideal mixing model).

Mostly, the β^m has been used to show the nature and strength of the interactions between different amphiphilic gemini molecules (constituting the mixture). As cmc_{exp} has been found lower than the cmc_{ideal}, β^m values are expected to be negative in each case (synergistic interaction). This indeed was observed from *cmc* data analysis (Table 2 and 3). The behavior is the result of the packing of each component of the mixture in the mixed micelle (and the resultant cmc_{exp}). Interaction among the two geminis in the mixed micelle is associated with the decrease of energy which is denoted in terms of β^m. This is a measure of the degree of interaction between two gemini component of the mixed micelle and accounts for deviation from ideal mixing (or for cmc_{exp} from cmc_{ideal}). The higher the negative magnitude of β^m, stronger is the synergistic interaction between the two gemini components. The perusal of data of Table 2 indicates that β^m shows a dependency on the nature of the spacer present in the cationic gemini surfactant and hints toward stronger attractive interactions with 16-Isb-16. The strength of

interactions (Table 3), between oppositely charged geminis of equal chain length (12-4-12 and 12-4-12A), has been found nearly equal with 16-Isb-16 combination (Table 2). Further, β^m was found distinctly lower than 16-4-16 combination. These two observations clearly indicate that chain length has a distinct role to play in addition to the magnitude of head group charges. Probably, chain-length compatibility plays a major role in overall interaction and hint towards stronger packing (with equal chain-length) inside the micelle or monolayer (below *cmc*). It has been reported for similar charged (cationic) gemini mixtures that β^m decreases as the chain length of the spacer decrease. This value could not be determined in a few systems due to the absence of convergence of the data in the Mathematica computer program.

Above-trend was not observed when one of the components of the mixture was a non-ionic surfactant (Brij 58) [13]. Moreover, chain length increase in cationic gemini has nearly no effect on β^m when mixed with the Brij 58 [14, 15]. In the case of ester spacer based cationic (12-Eg-12) sodium dodecyl sulfate (SDS) shows higher - β^m than sodium-dodecyl benzo sulphonate (SDBS) [15]. Above observation shows that β^m is governed by the nature of the charge of the surfactants constituting a binary mixture. In this context, β^m data of Table 2 shows not only the charge, spacer length but nature of the spacer can also be one of the governing factors deciding the strength of interaction between the components of gemini mixtures.

Based on interaction studies, various compositions were finalized for the study on morphological changes at a higher total concentration (with similar molar composition). The related data of morphological transitions are compiled in the next chapter (**Chapter 6**).

Table 2. Micellization parameters (cmc_{exp} and cmc_{ideal}) and interaction parameter (β^m, by Rubingh's method) of mixed gemini surfactant systems in aqueous solution at 303 K.

	16-4-16			**16-Isb-16**			**16-Eda-16**			**16-Eg-16**		
$x_{12\text{-}4\text{-}12A}$	cmc_{exp}	cmc_{ideal}	β^m	cmc_{exp}	cmc_{ideal}	β^m	cmc_{exp}	cmc_{ideal}	β^m	cmc_{exp}	cmc_{ideal}	β^m
	(mM)			**(mM)**			**(mM)**			**(mM)**		
0.0	0.0244	-	-	0.0027	-	-	0.044	-	-	0.0034		
0.2	0.0292	0.0306	-11.87	0.0031	0.0034	-12.96	0.059	0.0538	-	0.0128	0.0042	-
0.4	0.0734	0.0395	-	0.0037	0.0045	-7.90	0.141	0.0695	-	0.0052	0.0056	-0.08
0.6	0.2822	0.0570	-	0.0046	0.0067	-8.05	0.265	0.0978	-	0.0056	0.0084	-0.42
0.8	0.4159	0.1036	-	0.0099	0.0132	-9.80	0.518	0.165	-	0.003	0.0165	-7.13
1.0	0.5310	-		0.5310	-	-	0.531	-	-	0.531		

Table 3: Micellization Parameters (critical micelle concentration, *cmc*) and interaction parameters (by using Rubingh's method) of Single (pure) and Mixed (binary) GeminiSurfactant System in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	cmc_{ideal} (mM)	cmc_{exp} (mM)	X_1^m	X_1^i	β^m
0.0	-	1.12	-	-	-
0.2	0.9277	0.041	0.4699	0.3373	-12.279
0.4	0.7918	0.039	0.5108	0.5758	-12.079
0.6	0.6906	0.049	0.5426	0.7533	-11.077
0.8	0.6123	0.052	0.5780	0.8906	-11.419
1.0	-	0.55	-	-	-

5.3. Conclusion

Various cationic gemini surfactants have been chosen for micellization study individually or in combination with oppositely charged 12-4-12A. *cmc* data reveal that *cmc* of the mixture is always lower than the component having higher *cmc* in the mixture. Experimental *cmc* value for all combinations was found lower than the theoretical *cmc* (cmc_{ideal}) of the mixture computed by Clints Model. This indicates that mixing follows non-ideal behavior. The interaction parameter (β^m) values were found a negative (for the combinations data allow computation) indicating synergistic interaction between both the surfactants present in the aqueous mixture. It has been found that the strength of interaction is dependent on the chain length and spacer nature of two component.

References

[1] R. Zana, Adv. *Colloid Interf. Sci*. 2002, 97, 205-253.

[2] F.M. Menger, J.S. Keiper, Angew. *Chem. Int. Ed*. 2000, 39, 1909-1920.

[3] N. Kumaraguru, K. Santhakumar *J. Colloid Interf. Sci*. 2009, 252, 290-296.

[4] L. Tavano, M.R. Infante, M.A. Riya, A. Pinazo, M.P. Vinardell, M. Mitjans, M.A. Manresa and L. Perez. *Soft matter*. 2013 9, 306-319.

[5] M.S. Bakshi, F. Possmayer and N.O. Petersen, *J. Phys. Chem. C*. 2008, 112, 8259-8265.

[6] A.R. Tehrani-Bagha and K. Holmberg, *Langmuir*, 2010, 26, 9276-9282.

[7] K. Parikh, S. Singh, A. Desai, S. Kumar, *J. mol. Liq*. 2019, 278, 290-298.

[8] T. Yoshimura, A. Ohno, and K. Esumi, *J. Colloid. Interf. sci*. 2004, 272, 191-196.

[9] S.K. Yadav, K. Parikh, S. Kumar, *Colloid. Surf. A*. 2017, 522, 105-112.

[10] S. Singh, A. Bhadoria, K. Parikh, S.K. Yadav, S. Kumar, V.K. Aswal and S. Kumar, J. Phy. Chem. B, 2017, 121, 8756-8766.

[11] S. Singh, K. Parikh, S. Kumar, V.K. Aswal and S. Kumar, J.Mol. Liq. 2019, 279, 108-119.

[12] Z. Liu, Y. Fan, M. Tian, R. Wang, Y. Han and Y. Wang, Langmuir. 2014, 30, 7968-7976.

[13] M. Panda, J. Mol. Liq. 2013, 187, 106-113

[14] W.H. Ansari, N. Fatma, M. Panda, Soft Matter. 2013, 9, 1478-1487

[15] N. Fatma, M. Panda, W.H. Ansari, Colloid. Surf. A, 2015, 467, 9-17.