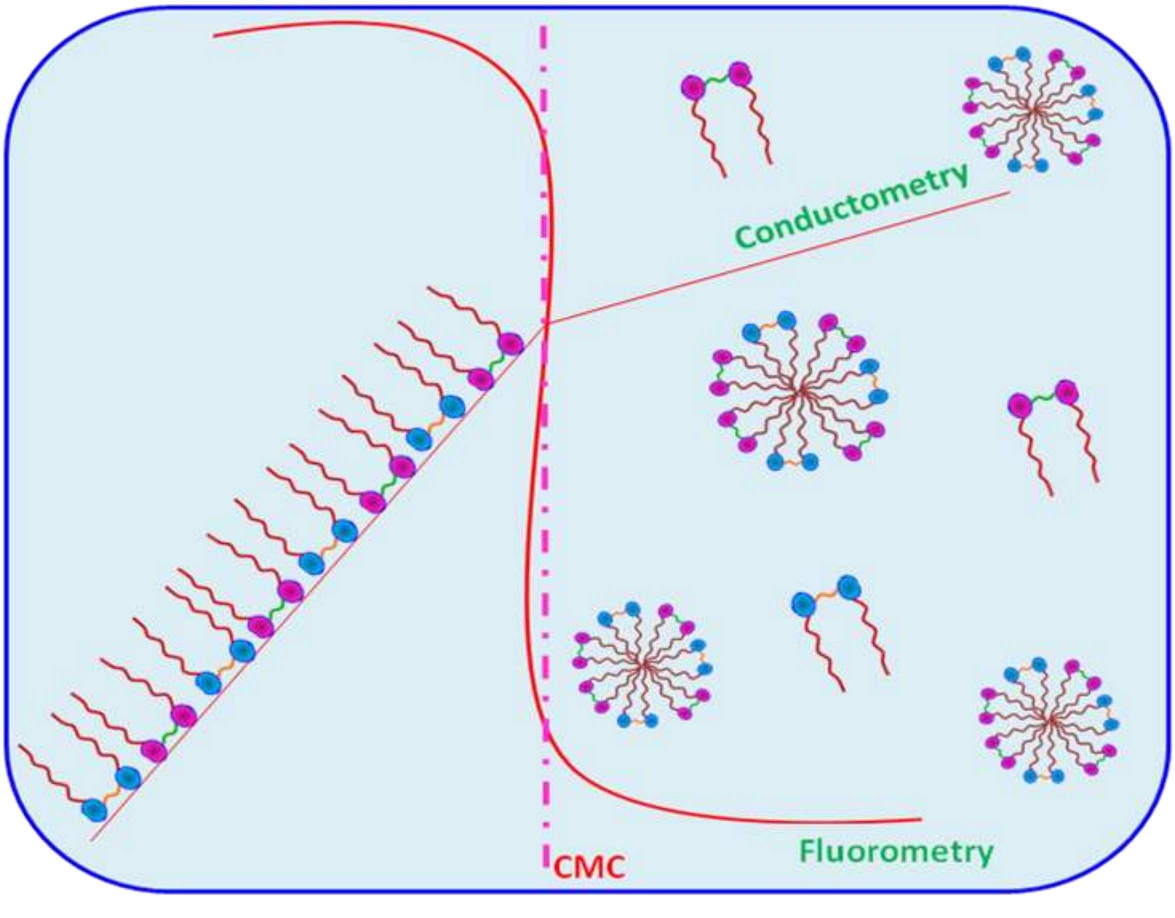
Chapter 3

Association Behaviour and Interaction of Oppositely Charged Gemini Surfactants in Aqueous Solution



3.1. Introduction

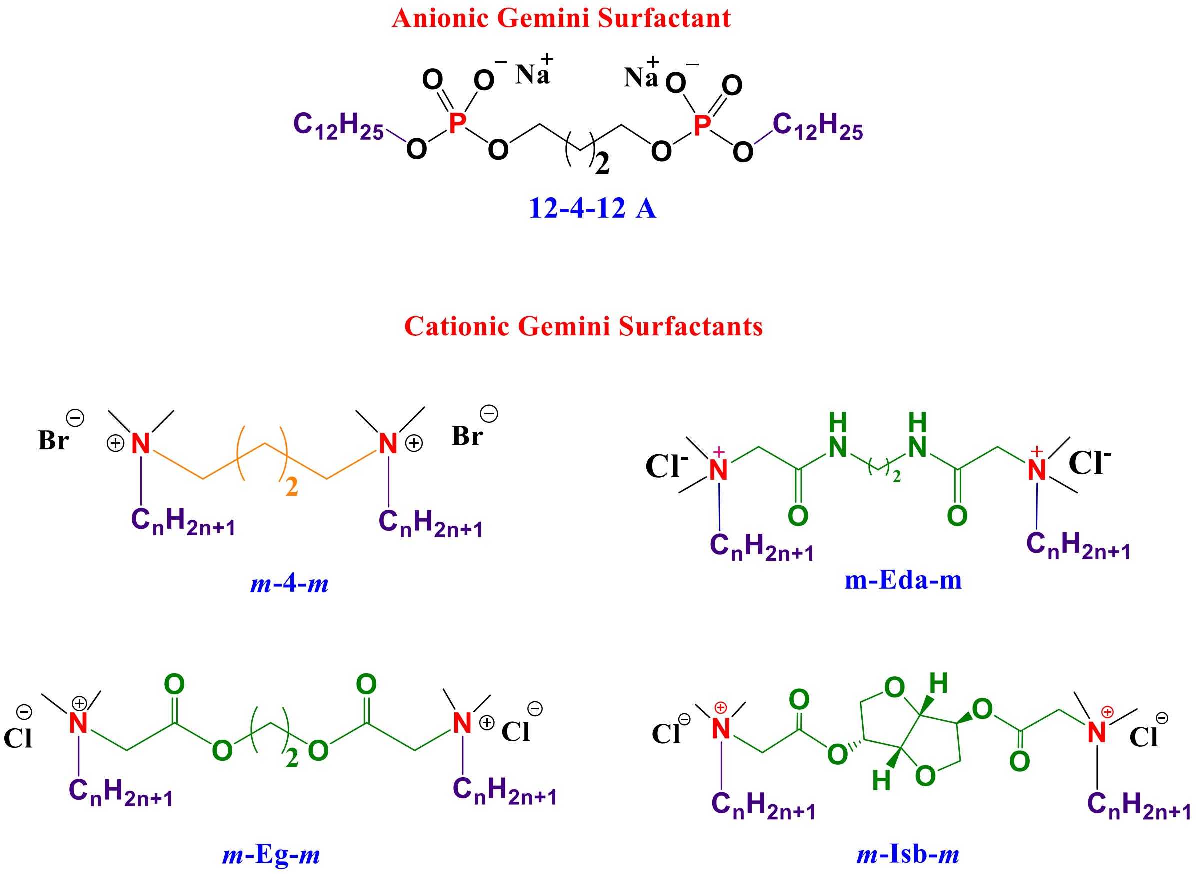
CMC values are first and foremost data needed to establish the appropriatness of the given surfactant or surfactant mixtures or blends. In this direction, present chapter addresses micellization/mixed micellization phenomena and micro-environment existing in the so formed association structures just above the CMC. For the purpose, various combinations of anionic and cationic geminis were taken. Cationic geminis of different chain lengths ($C_{10} – C_{14}$) are used to search chain length compatibility effect in blended mixtures of varied compositions. Additonally, nature of spacers on the interaction behaviour has also been seen in order to evaluate spacer effect on chain length compatibility. The study was initiated from the inspiration that mixed systems performed better than their individual counterparts in the case of conventional surfactants/amphiphiles [1–5].

To derive the above-mentioned information, two methodologies are used (namely, coductometry and fluorometry) to acquire micellization parameters and the polarity of the resultant aggregate above the CMC. Various regular solution theories have been used to derive data related to interactions between components of the gemini blends [6–9]. Thermodynamic data for mixed micellization have also been computed together with mole fractions of individual components in ‘co-micelle’ or blended micelle [10,11]. Micro-polarity and ideal/experimental dielectric constant data were acquired using turro treatment [12].

The material utilised in this study has been compiled in Scheme 1. The mixing composition was varied from 0-1. Stock solutions of individual geminis were prepared, and the requisite volume of each component has been mixed with the other component (requisite amount) in order to prepare the stock solution of the blend to be used for CMC determination.

The method was adopted for every combination prepared for the conductometric study (at 303 K) embodied in this chapter.

For fluorescence measurements, several mixed samples were prepared by taking a fixed amount of the probe (pyrene, 0.002 mM) in each sample for the particular sets of the experiment. The CMC data obtained from both the studies are compared. However, CMC obtained from fluorescence measurements are used to derive interaction and thermodynamic parameters. This technique has also been used to unravel the micro-environment present and experienced by the probe. Further, data are compared with earlier studies conducted on other gemini and conventional blends [13–15].



Scheme 1. Chemical structures with abbreviation of anionic and cationic gemini surfactants (n= 14,12 or 12).

3.2. Results and Discussion

3.2.1. Micellization Process and CMC Values

Micellization process has been studied by using conductometry and fluorometry. Variation of physical property (specific conductance (κ) or micro-polarity) *vs* [Gemini(s)] are depicted in Figures 1-8. This variation gives CMC values of individual gemini surfactants and their blended mixtures. Figure 1 depicts the variations of κ with increasing concentration of surfactant in aqueous solution for individual gemini. So-obtained CMCs are compiled in Tables 1-3.

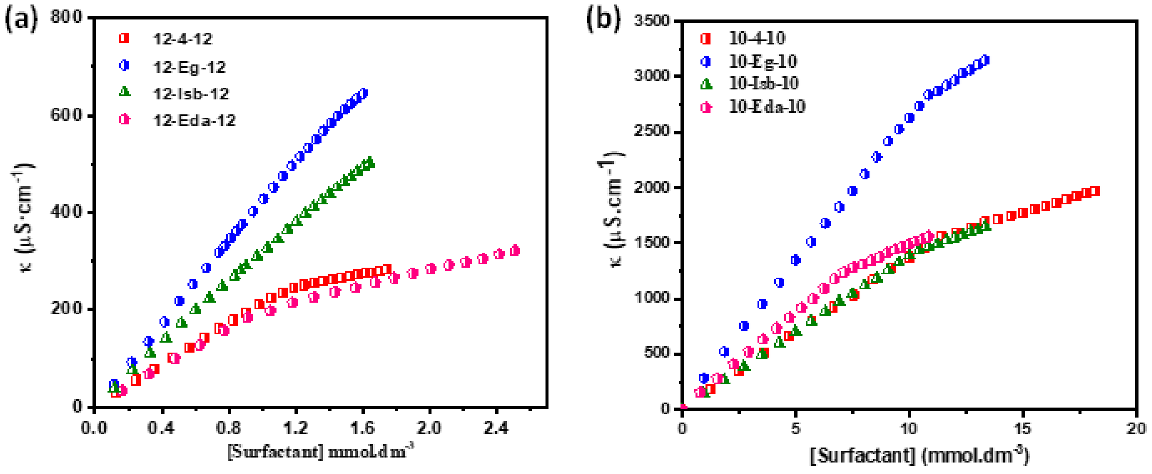


Figure 1. Plots of specific conductance (κ) *vs* [Gemini] of individual cationic gemini with different spacers in aqueous solution at 303 K: (a) n=12, (b) n=10.

Fluorescence data from a probe can be used to extract information regarding micellar association and its internal microenvironment. Pyrene has been used regularly to obtain such information using fluorescence technique. A few typical plots related to intensity *vs* wavelength are given in Figure 2.

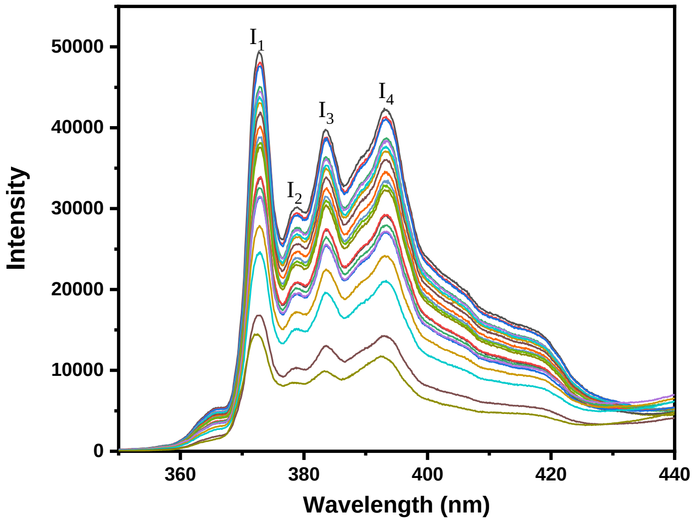


Figure 2. Representative intensity *vs* wavelength plots for pyrene in 0.2 $x_{12\text{-}4\text{-}12}$ + 0.8 $x_{12\text{-}4\text{-}12A}$ at 303 K.

The micellar environment can be represented in the form of I_1/I_3 ratio (I_1 represents the intensity of the solvent responsive peak and I_3 corresponds to the solvent irresponsive peak). Various such graphs (e.g., Figure 2) are used to obtain I_1/I_3 *vs* [Gemini] sigmoid type curves are depicts in Figure 3.This sigmoidal shape of curve indicates the formation of micelle [16]. Data show three regions in which the middle region is flanked between nearly two I_1/I_3 regions (below CMC and above CMC). The later region, in which I_1/I_3 remain nearly unchanged with higher [Surfactant], is indicative of the micellar region [11,17–19].

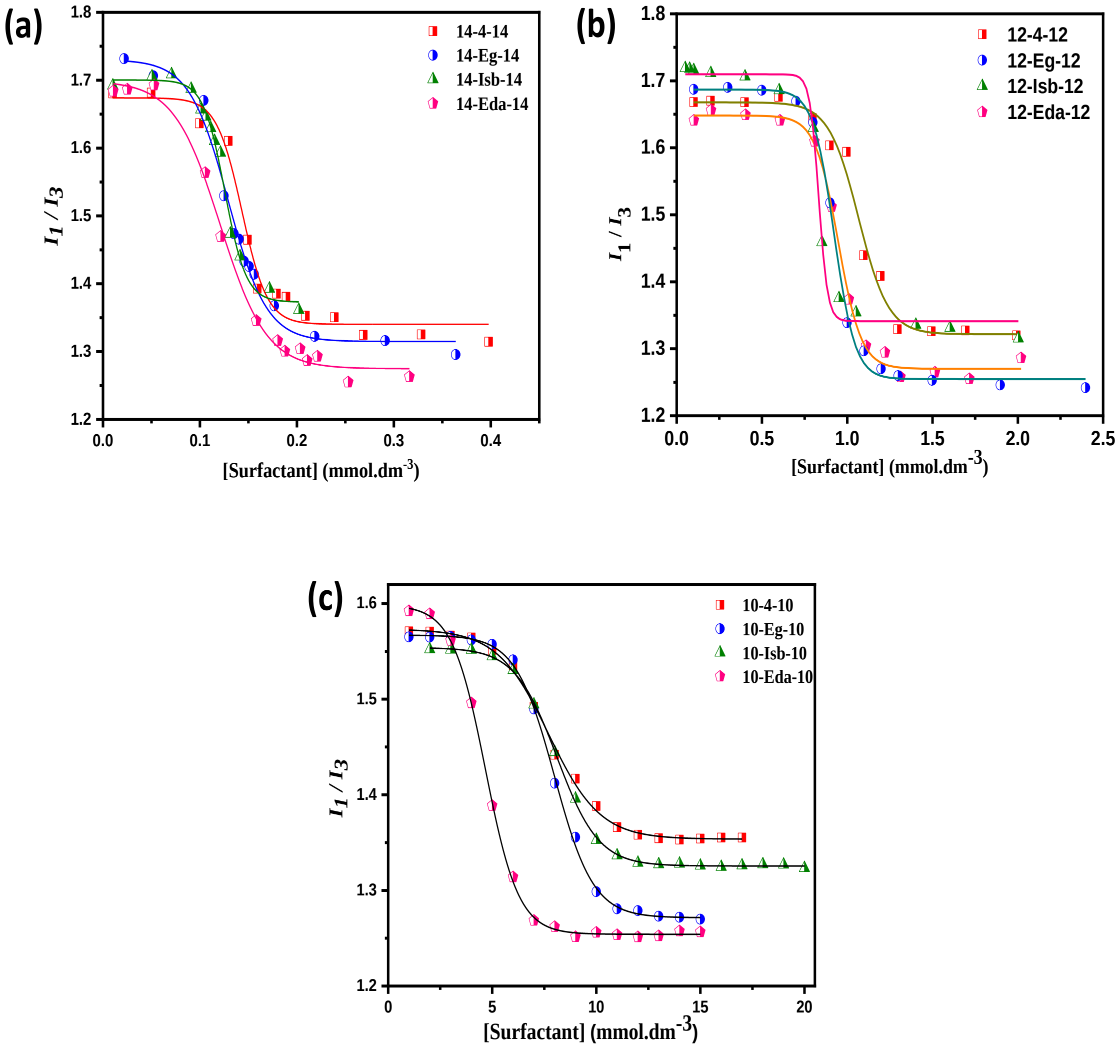


Figure 3. Plot of I_1/I_3 (ratio of vibrational peaks of pyrene) *vs* [surfactant] at 303 K: (a) n=14, (b) n=12 and (c) n=10.

Both techniques gave nearly similar CMC values with narrow concentration differences which indicates the validity of the experiment. However, the small differences in CMC values are mainly because of the physical property whose response to the phenomenon: Conductivity responses the macro-ion (micelle) formation while, fluorescence probe (pyrene) responses to the environment resulted from micellization. Tables 1-3 show lower CMCs of the blended mixtures in comparison to the individual components of the blend. In general, CMCs of the individual components were found in close agreement with the literature reported on similar gemini systems [20–24]. It may be mentioned here that CMC data of individual geminis (with all spacers) varies linearly with alkyl tail length as depicted in Figure 4. Similar practices of plotting CMC data are reported in the past for both conventional and gemini surfactant [25–29]. The linearity of CMC with carbon chain again established the fact that hydrophobic portion variation causes CMC changes and CMC increases with reducing alkyl chain length. For gemini surfactants linearity behaviour has been reported with n=14 or above [30]. However, the linearity in the present case has been observed even with n=10 (Figure 4).

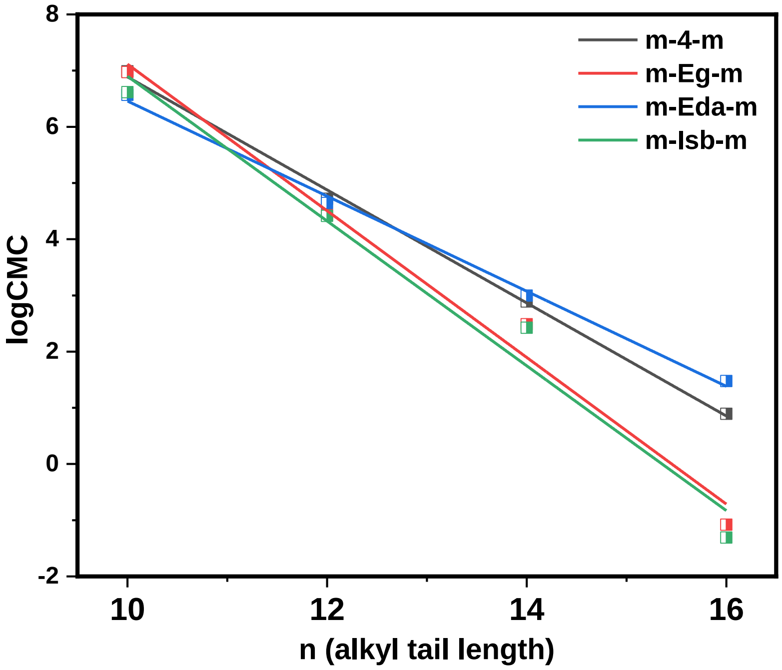


Figure 4. Variation of CMC with alkyl chain carbon number of cationic gemini surfactants with different spacer (CMC data for 16-s-16 are taken for comparison from J. Mol. Liq. 2019, 279, 108-119.).

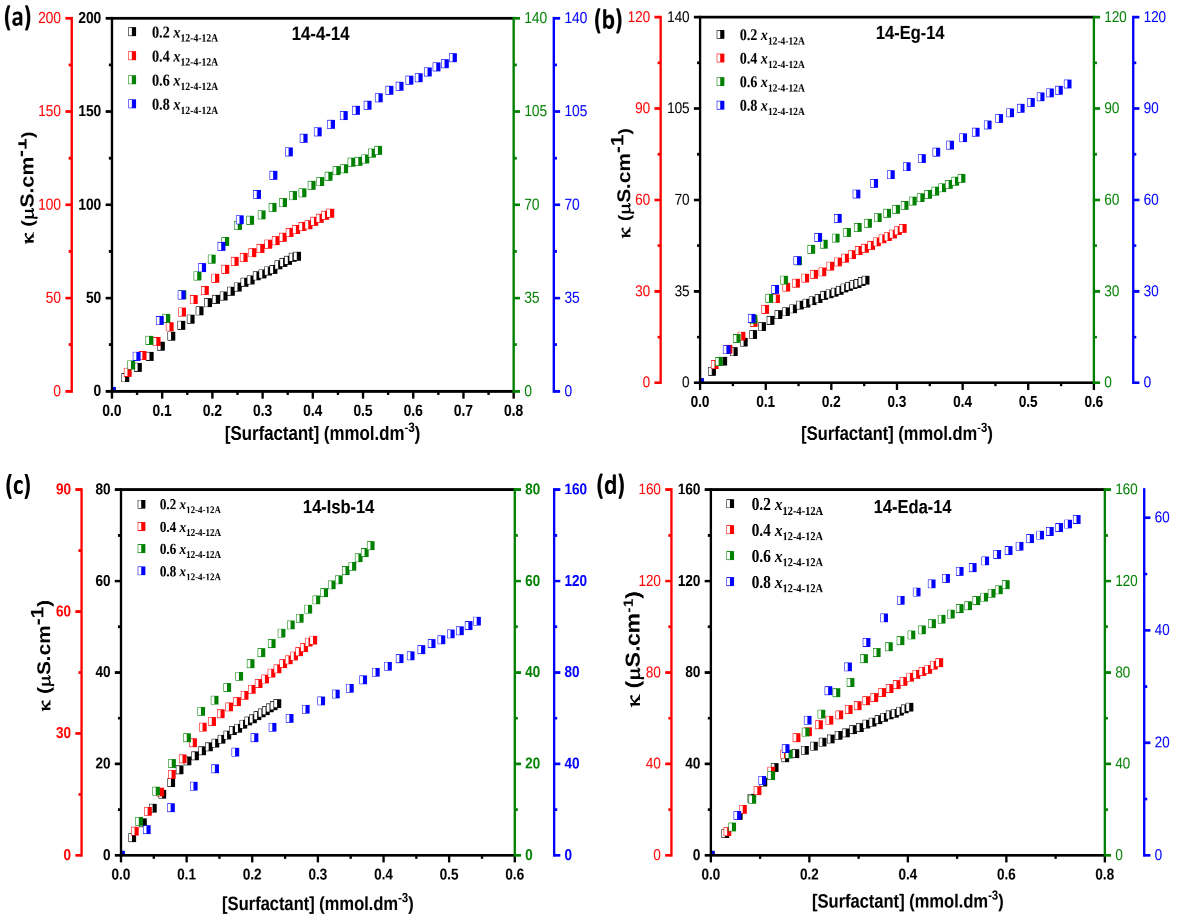


Figure 5. Plot of specific conductance (κ)) vs [surfactants], of mixed gemini surfactants at different mole fractions of anionic gemini (12-4-12A) in aqueous solution at 303 K: (a) 14-4-14, (b) 14-Eg-14, (c) 14-Isb-14 and (d) 14-Eda-14.

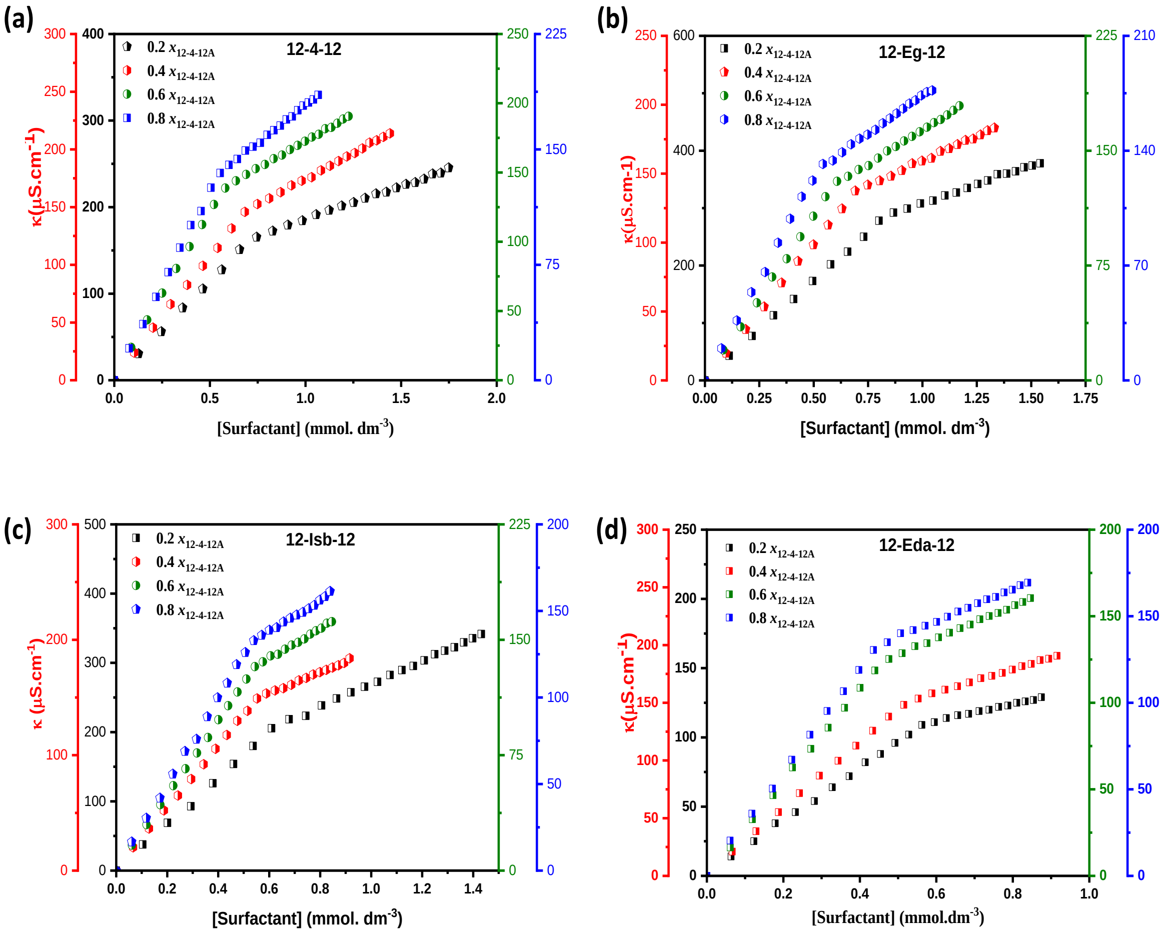


Figure 6. Plot of specific conductance (κ)) vs [surfactants], of mixed gemini surfactants at different mole fractions of anionic gemini (12-4-12A) in aqueous solution at 303 K: (a) 12-4-12, (b) 12-Eg-12, (c) 12-Isb-12 and (d) 12-Eda-12.

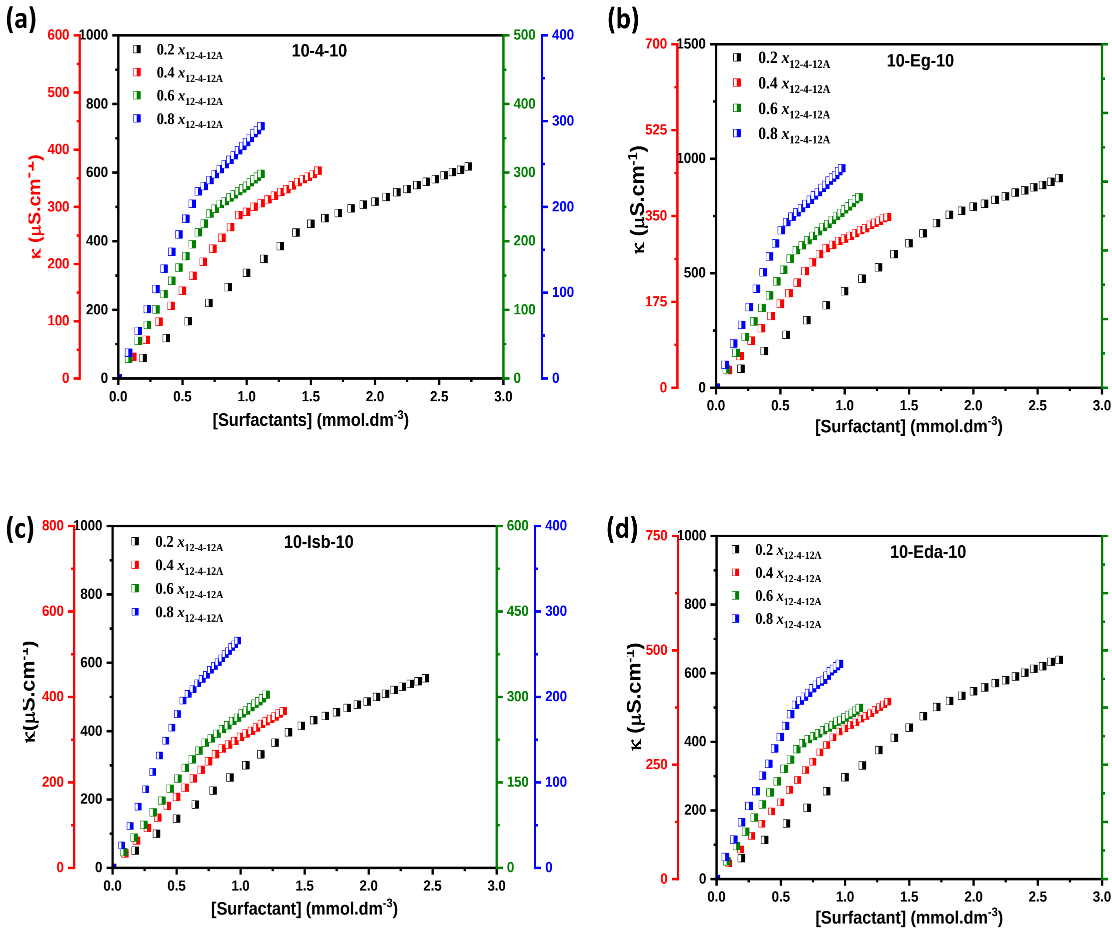


Figure 7. Plot of specific conductance (κ)) vs [surfactants], of mixed gemini surfactants at different mole fractions of anionic gemini (12-4-12A) in aqueous solution at 303 K: (a) 10-4-10, (b) 10-Eg-10, (c) 10-Isb-10 and (d) 10-Eda-10.

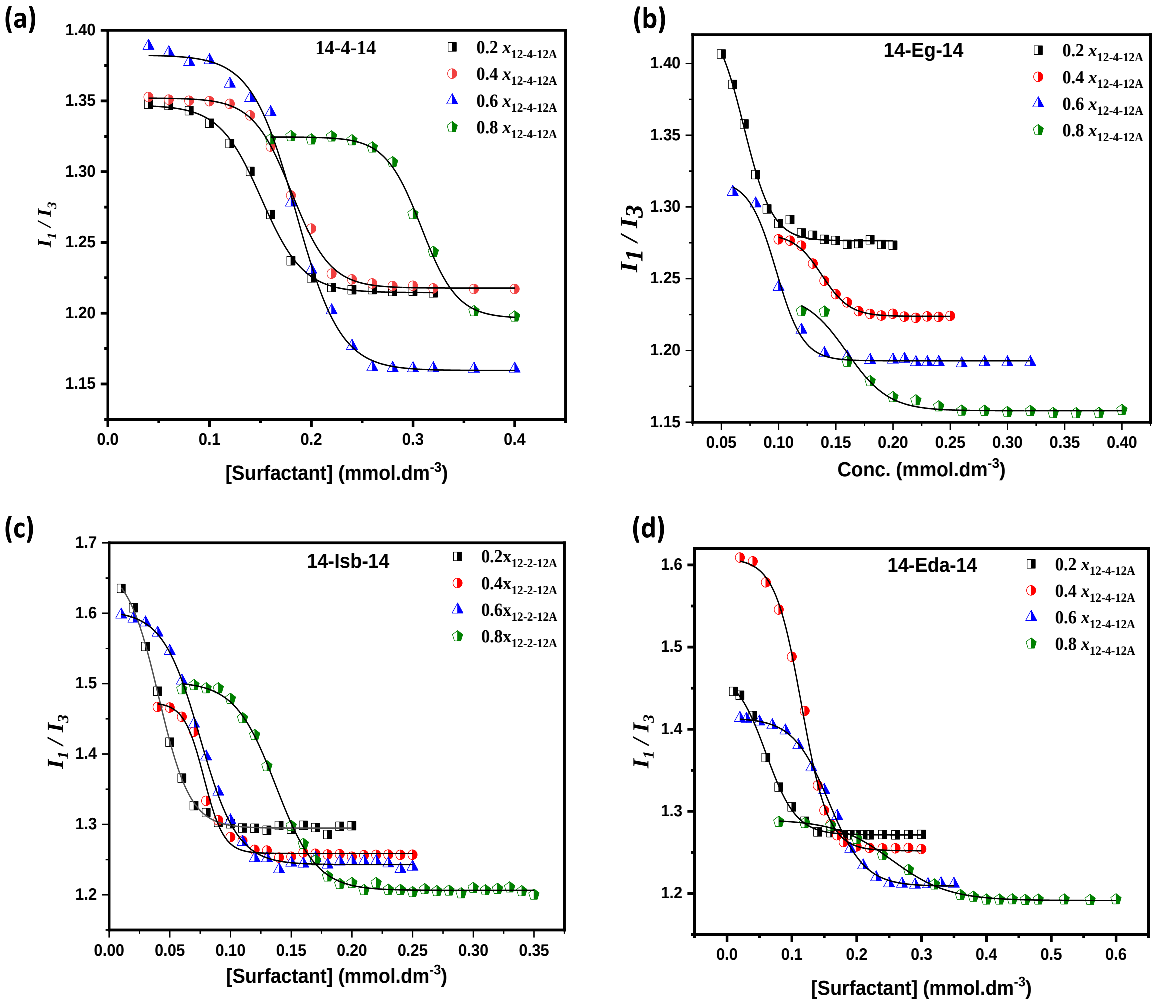


Figure 8. Variation of I_1/I_3 *vs* [Gemini mixture] in aqueous solution at 303 K: (a) 14-4-14, (b) 14-Eg-14, (c) 14-Isb-14 and (d) 14-Eda-14.

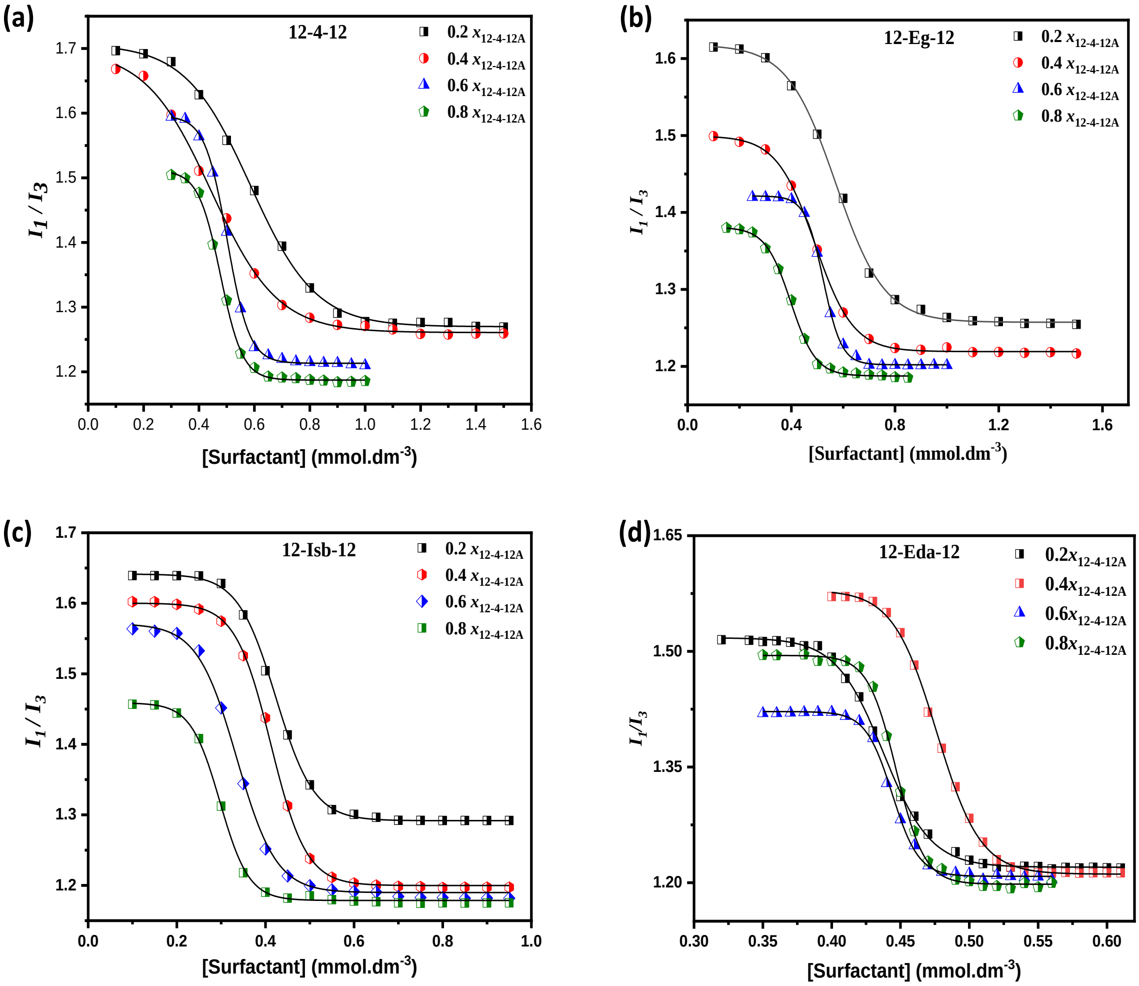


Figure 9. Variation of I_1/I_3 *vs* [Gemini mixture] in aqueous solution at 303 K: (a) 12-4-12, (b) 12-Eg-12, (c) 12-Isb-12 and (d) 12-Eda-12.

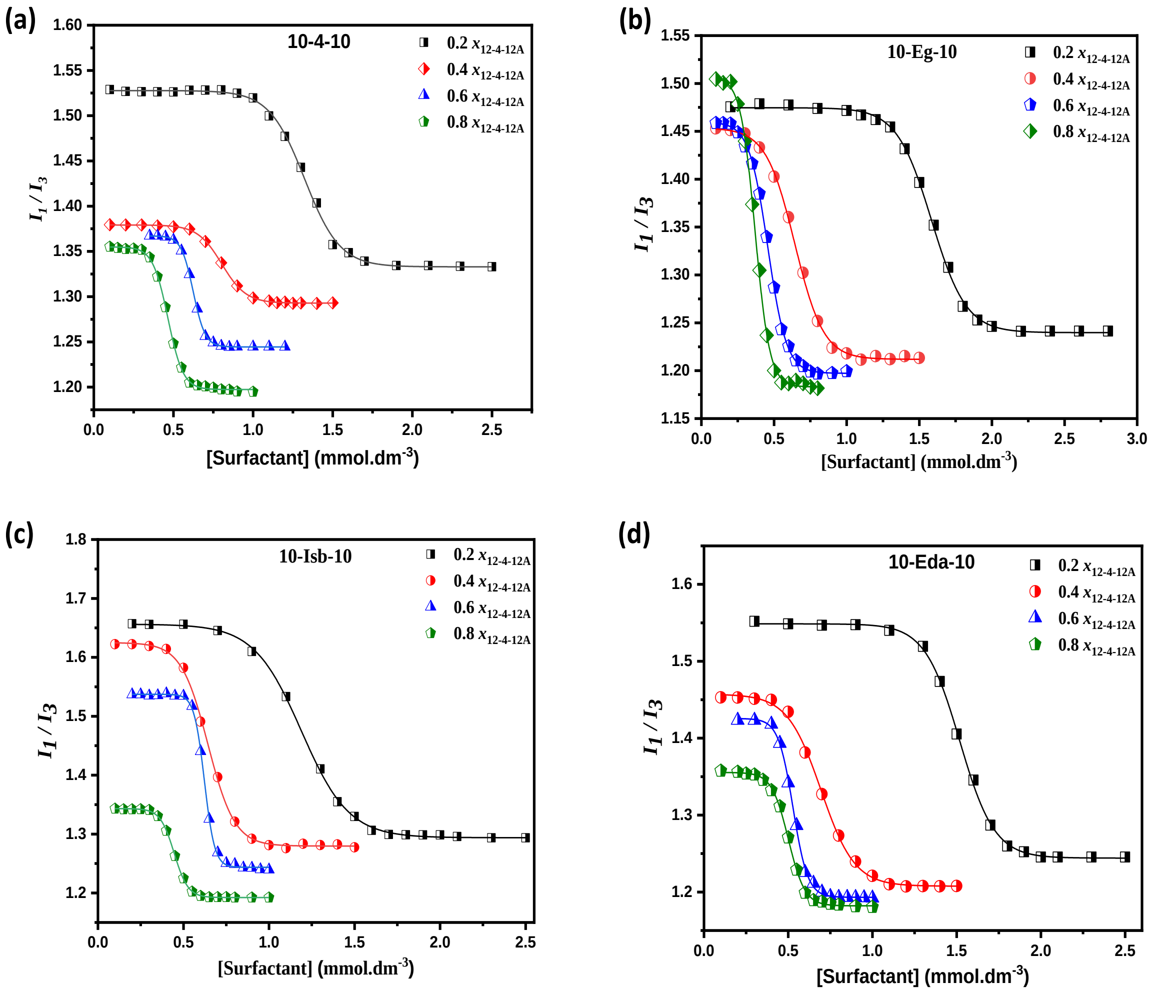


Figure 10. Variation of I_1/I_3 *vs* [Gemini mixture] in aqueous solution at 303 K: (a) 10-4-10, (b) 10-Eg-10, (c) 10-Isb-10 and (d) 10-Eda-10.

Table 1. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	CMC_{exp} (mmol.dm^{-3})		CMC_{ideal} (mmol.dm^{-3})	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG_{ex} kJ mol^{-1}
	Fluorometry	**Conductometry**							
				14-4-14					
0	0.180	0.168							
0.2	0.196	0.189	0.207	0.120	0.078	-0.631	0.613	0.991	-0.164
0.4	0.237	0.229	0.244	0.201	0.184	-0.183	0.889	0.992	-0.072
0.6	0.253	0.241	0.298	0.376	0.337	-0.704	0.733	0.923	-0.409
0.8	0.364	0.348	0.382	0.569	0.575	-0.187	0.965	0.941	-0.113
1.0	0.531	0.550							
				14-Eg-14					
0	0.120	0.154							
0.2	0.106	0.112	0.141	0.207	0.053	-2.619	0.192	0.893	-1.059
0.4	0.121	0.128	0.173	0.279	0.131	-2.142	0.328	0.845	-1.061
0.6	0.159	0.165	0.224	0.352	0.253	-1.598	0.511	0.820	-0.897
0.8	0.228	0.234	0.315	0.484	0.474	-1.281	0.711	0.740	-0.787
1.0	0.531	0.550							

Table 2. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	CMC_{exp} (mmol.dm^{-3})		CMC_{ideal} (mmol.dm^{-3})	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG_{ex} kJ mol^{-1}
	Fluorometry	**Conductometry**							
14-Isb-14									
0	0.113	0.154							
0.2	0.074	0.097	0.134	0.273	0.050	-4.322	0.102	0.723	-2.113
0.4	0.109	0.121	0.164	0.287	0.124	-2.454	0.287	0.816	-1.236
0.6	0.118	0.122	0.214	0.379	0.241	-2.695	0.354	0.678	-1.561
0.8	0.182	0.194	0.305	0.480	0.459	-0.161	0.957	0.963	-0.098
1.0	0.531	0.550							
14-Eda-14									
0	0.213	0.200							
0.2	0.126	0.138	0.227	0.309	0.091	-3.935	0.153	0.686	-2.069
0.4	0.165	0.177	0.261	0.357	0.211	-2.549	0.348	0.723	-1.439
0.6	0.229	0.311	0.337	0.429	0.376	-1.546	0.604	0.753	-0.931
0.8	0.361	0.377	0.418	0.593	0.616	-0.521	0.917	0.833	-0.348
1.0	0.531	0.550							

Table 3. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	CMC_{exp} (mmol.dm^{-3})		CMC_{ideal} (mmol.dm^{-3})	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG_{ex} kJ mol^{-1}
	Fluorometry	**Conductometry**							
				12-4-12					
0	1.250	1.120							
0.2	0.826	0.742	0.983	0.404	0.371	-0.733	0.771	0.887	-0.434
0.4	0.729	0.685	0.811	0.591	0.611	-0.439	0.929	0.857	-0.261
0.6	0.641	0.586	0.689	0.744	0.779	-0.401	0.974	0.801	-0.188
0.8	0.553	0.512	0.601	0.849	0.904	-0.737	0.983	0.588	-0.232
1.0	0.531	0.550							
				12-Eg-12					
0	1.030	0.839							
0.2	0.776	0.808	0.867	0.358	0.326	-0.492	0.816	0.938	-0.278
0.4	0.655	0.675	0.748	0.551	0.563	-0.541	0.896	0.647	-0.628
0.6	0.598	0.588	0.658	0.704	0.744	-0.482	0.958	0.787	-0.246
0.8	0.503	0.515	0.588	0.795	0.885	-1.164	0.952	0.478	-0.465
1.0	0.531	0.550							

Table 4. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	CMC_{exp} (mmol.dm^{-3})		CMC_{ideal} (mmol.dm^{-3})	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG_{ex} kJ mol^{-1}
	Fluorometry	**Conductometry**							
				12-Isb-12					
0	0.925	0.826							
0.2	0.605	0.625	0.805	0.374	0.303	-1.271	0.608	0.625	-1.182
0.4	0.564	0.549	0.713	0.525	0.537	-0.942	0.808	0.771	-0.577
0.6	0.555	0.536	0.641	0.674	0.723	-0.675	0.931	0.736	-0.365
0.8	0.508	0.518	0.581	0.796	0.874	-0.967	0.961	0.541	-0.386
1.0	0.531	0.550							
				12-Eda-12					
0	1.040	1.090							
0.2	0.492	0.552	0.873	0.419	0.328	-2.424	0.442	0.653	-1.452
0.4	0.515	0.527	0.752	0.538	0.566	-1.524	0.722	0.643	-0.932
0.6	0.476	0.454	0.661	0.649	0.746	-1.540	0.827	0.522	-0.863
0.8	0.472	0.443	0.588	0.771	0.887	-1.554	0.922	0.397	-0.675
1.0	0.531	0.550							

Table 5. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	**CMC_{exp} (mmol.dm^{-3})**		**CMC_{ideal} (mmol.dm^{-3})**	X_1^m	X_{ideal}	**β^m**	f_1^m	f_2^m	**ΔG_{ex} (kJ mol^{-1})**
	Fluorometry	**Conductometry**							
				10-4-10					
0	11.532	11.182							
0.2	1.578	1.464	2.242	0.756	0.844	-1.986	0.842	0.372	-1.014
0.4	0.995	0.931	1.242	0.807	0.935	-2.014	0.928	0.268	-0.771
0.6	0.747	0.719	0.858	0.873	0.970	-2.088	0.966	0.204	-0.570
0.8	0.599	0.603	0.656	0.917	0.988	-2.463	0.999	0.126	-0.422
1.0	0.531	0.550							
				10-Eg-10					
0	10.632	10.652							
0.2	1.892	1.797	2.212	0.754	0.833	-0954	0.944	0.581	-0.435
0.4	0.879	0.827	1.235	0.766	0.930	-2.643	0.865	0.212	-1.166
0.6	0.618	0.611	0.856	0.799	0.968	-3.356	0.874	0.116	-1.321
0.8	0.499	0.517	0.655	0.837	0.988	-4.056	0.898	0.058	-1.358
1.0	0.531	0.550							

Table 6. Micellization parameters (CMC_{exp} and CMC_{ideal}) and interaction parameters (by using regular solution theory) for individual and mixed gemini surfactant systems in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	**CMC_{exp} (mmol.dm^{-3})**		**CMC_{ideal} (mmol.dm^{-3})**	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	**ΔG_{ex} (kJ mol^{-1})**
	Fluorometry	**Conductometry**							
10-Isb-10									
0	10.125	10.143							
0.2	1.527	1.432	2.194	0.692	0.827	-1.956	0.830	0.392	-1.025
0.4	0.826	0.823	1.231	0.748	0.927	-2.919	0.831	0.195	-1.352
0.6	0.707	0.706	0.855	0.846	0.966	-2.383	0.945	0.182	-0.765
0.8	0.563	0.556	0.655	0.884	0.987	-2.991	0.960	0.097	-0.756
1.0	0.531	0.550							
10-Eda-10									
0	7.198	7.114							
0.2	1.758	1.745	2.050	0.708	0.772	-0.797	0.934	0.670	-0.405
0.4	0.926	0.923	1.195	0.769	0.900	-1.842	0.906	0.336	-0.803
0.6	0.641	0.645	0.843	0.803	0.953	-2.648	0.902	0.181	-1.031
0.8	0.619	0.611	0.652	0.937	0.981	-1.439	0.994	0.282	-0.208
1.0	0.531	0.550							

3.2.2. CMC Data Treatment and Interaction between Geminis

Tables 1-3 also contain CMC data of various mixtures resulted from the blending of different geminis having varied alkyl chain together with variety of spacers (Scheme 1). For a blend of counter charged surfactants, an expression (Equation 1) exists for ideal mixing [6].

$$\frac{1}{CMC_{ideal}} = \frac{x_1}{CMC_1} + \frac{x_2}{CMC_2} \tag{1}$$

where, x_1 and x_2 are mole fractions of 12-4-12A and cationic gemini, respectively.

Above relation results ideal CMCs (CMC_{ideal}) of the blends. Plots of CMCs (both experimental (CMC_{exp}) and CMC_{ideal}) of the mixtures with composition variation are shown in Figures 11-13.

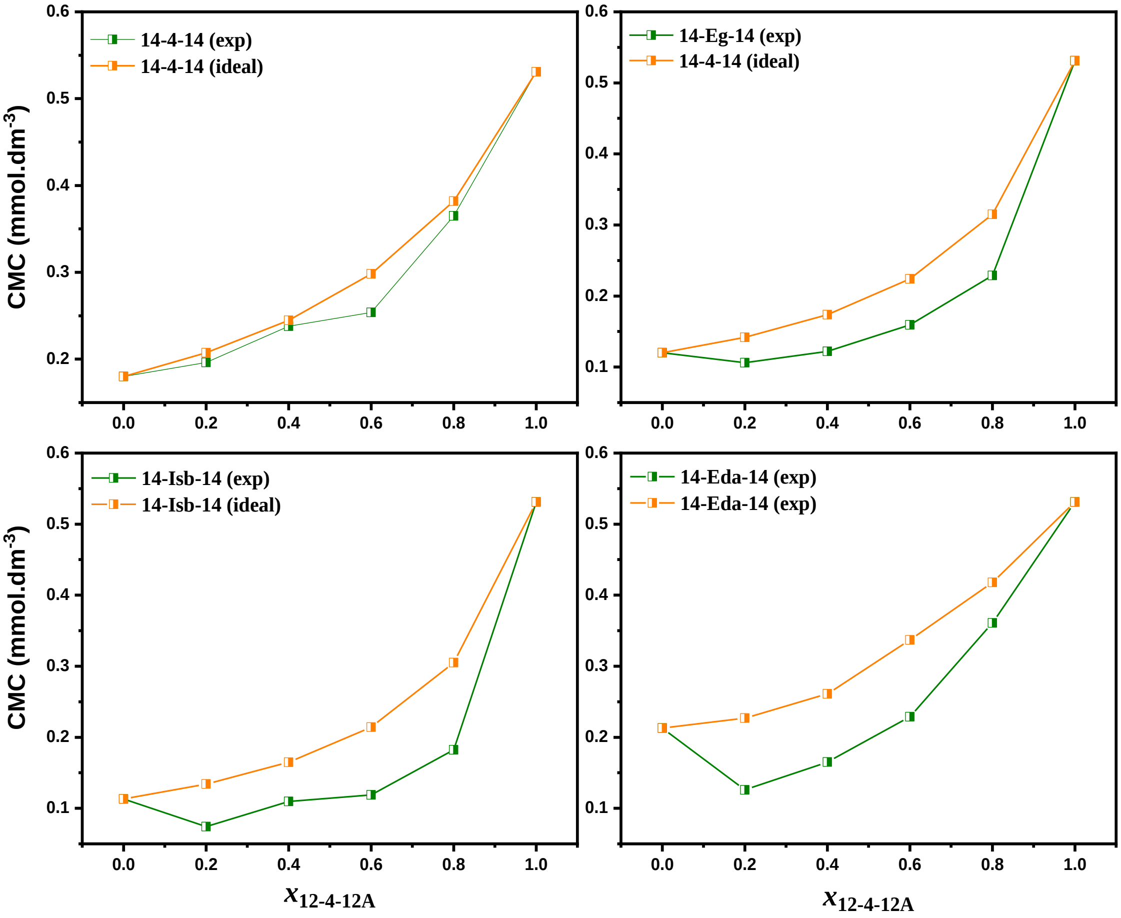


Figure 11. CMC variation of mixed surfactant systems (14-s-14 + 12-4-12A) with mole fraction of anionic gemini surfactant in aqueous solution at 303 K.

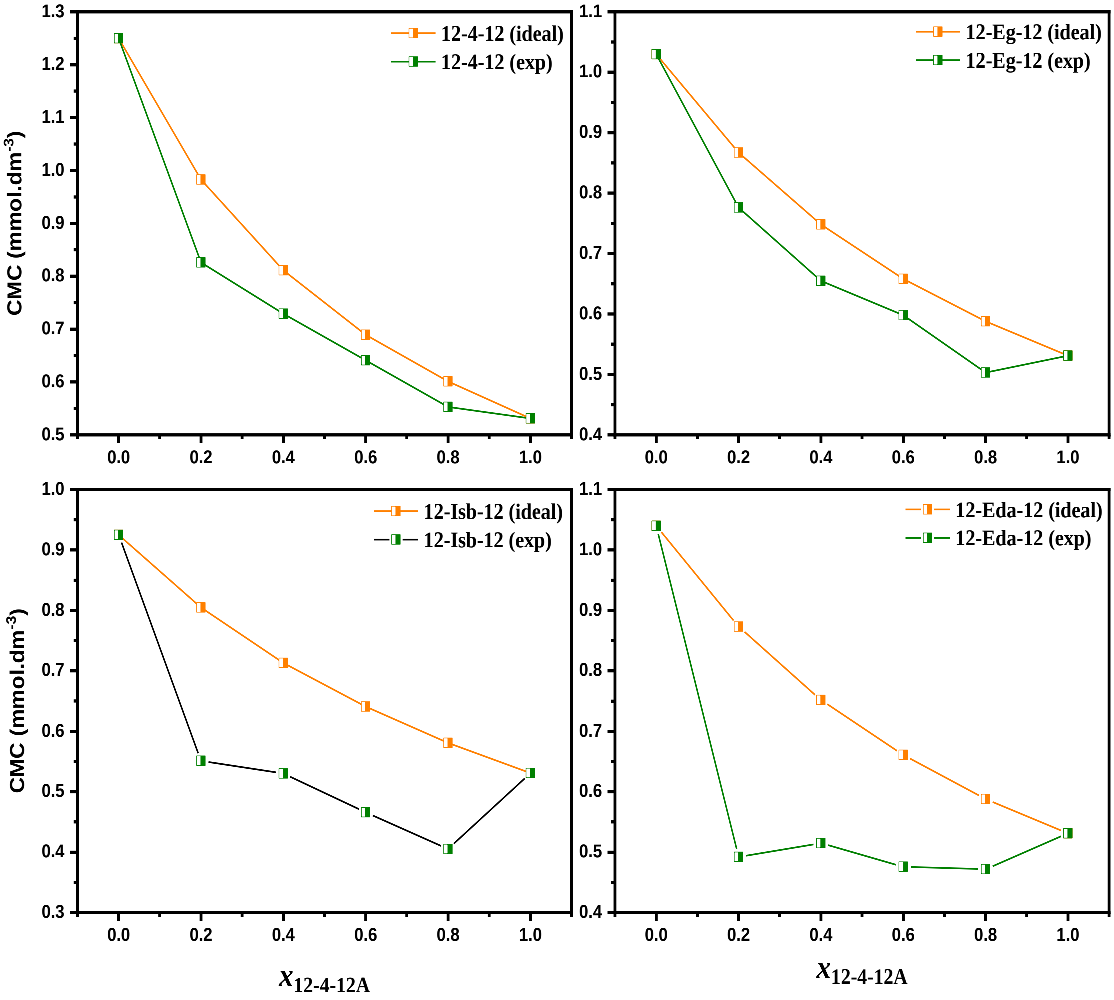


Figure 12. CMC variation of mixed surfactant systems (12-s-12 + 12-4-12A) with mole fraction of anionic gemini surfactant in aqueous solution at 303 K.

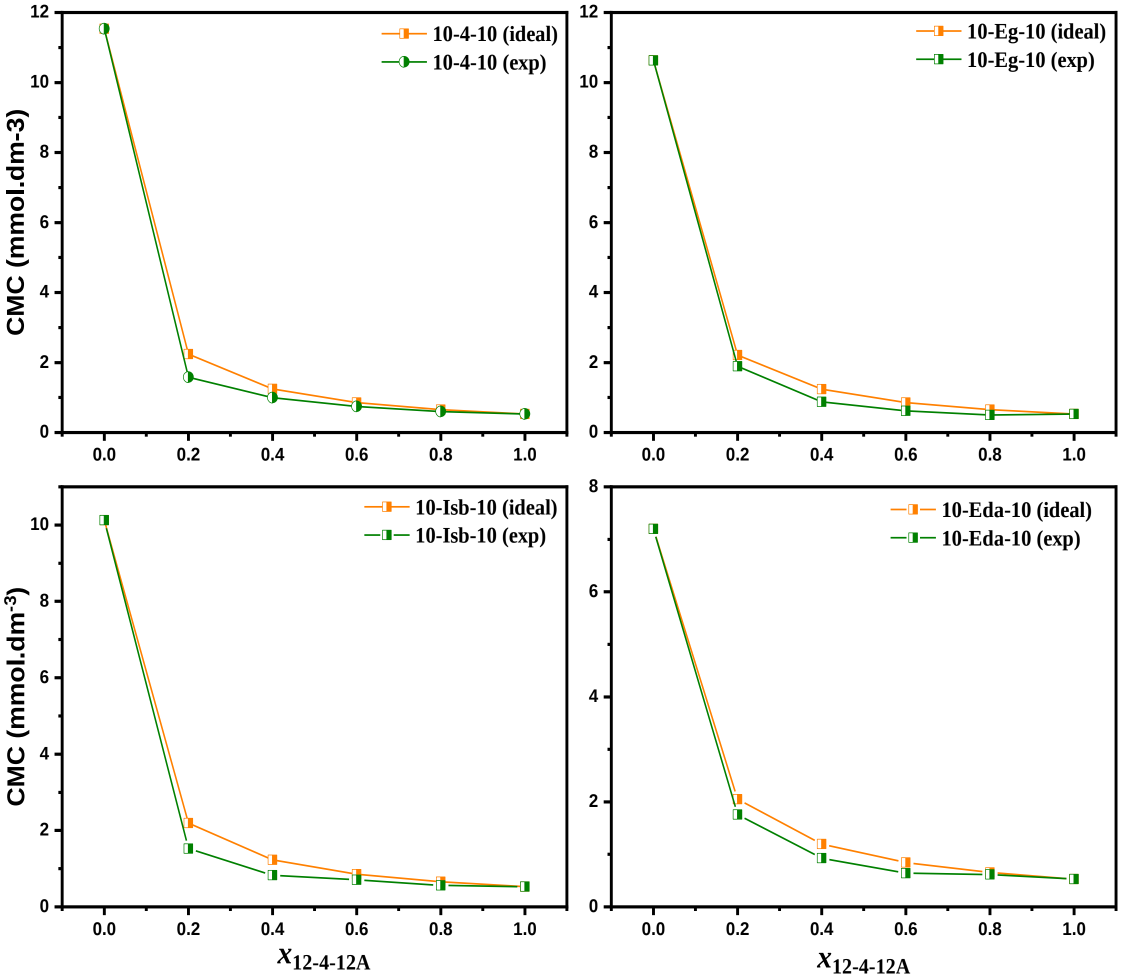


Figure 13. CMC variation of mixed surfactant systems (10-s-10 + 12-4-12A) with mole fraction of anionic gemini surfactant in aqueous solution at 303 K.

By applying pseudo phase separation model, one can evaluate the deviation of above mentioned two kinds of CMCs (CMC_{ideal} and CMC_{exp}). Both CMC_{ideal} and CMC_{exp} are also compiled in Tables 1-6. The lower values of CMC_{exp} from CMC_{ideal} (Figure 11-13) indicates synergistic interaction between two components constituting different gemini mixtures. CMC data have been further treated using following expression (equation 2) based on regular solution theories [31].

$$\frac{[(X_1^m)\ln(CMC_{exp}x_1/CMC_1X_1^m)]}{(1-X_1^m)^2[CMC_{exp}(1-x_1)/CMC_2(1-X_1^m)]} = 1 \qquad (2)$$

Continuation (mole fraction) of 12-4-12A in a typical mixed micelle has been denoted by X_1^m. Motomura's relation [8] has been used to compute ideal mole fraction of 12-4-12A in the mixed micelle (X_1^i).

$$X_1^i = \frac{x_1CMC_2}{x_1CMC_2+(1-x_1)CMC_1} \qquad (3)$$

In general, the inference regarding blending of amphiphilic molecules and the nature of interactions between the components of the mixture can be acquired with the help of down coming mathematical relation (equation 4) [9].

$$\beta^m = [\ln(CMC_{exp}x_1/CMC_1X_1^m)]/(1-X_1^m)^2 \qquad (4)$$

β^m denotes the interaction parameter whose sign will decide the nature of interaction. As can be seen from the data compiled in Tables 1-6, all β^m values are found negative which depict that the synergistic interactions between all combinations of blended gemini mixtures. β^m data are plotted against chain lengths of cationic gemini involved in blended mixture with 12-4-12A (Figure 14). Interactions increases with the chain length of cationic gemini which indicates mixing of surfactant and magnitude of synergies are dependent on carbon chain length as observed with other micellar parameters [25–29].

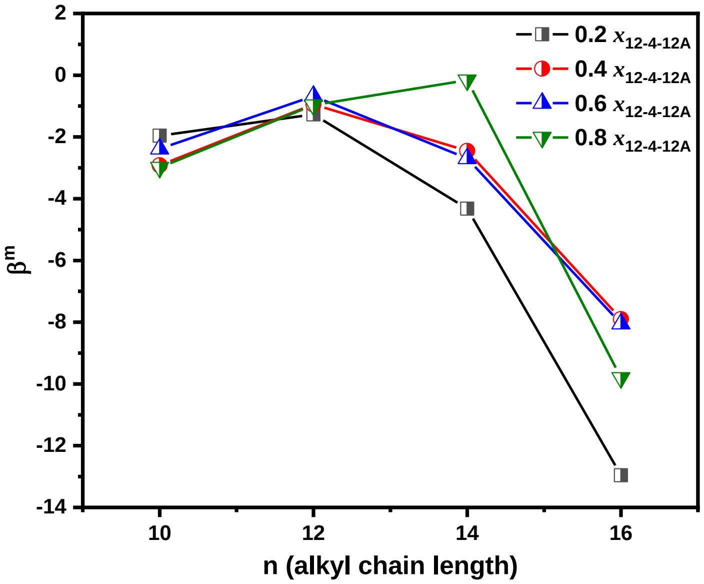


Figure 14. Variation of β^m with alkyl chain carbon number of cationic gemini surfactants (CMC data for 16-s-16 are taken for comparison from J. Mol. Liq. 2019, 279, 108-119.).

β^m can be related with activity coefficients (f_i^m, equations 5&6) of the individual components in the blended micelles [31].

$$f_1^m = \exp[\beta^m(1 - X_1^m)^2] \tag{5}$$

$$f_2^m = \exp[\beta^m(X_1^m)^2] \tag{6}$$

The computed f_1^m and f_2^m (Tables 1-6) are also compiled with other micellization data. One can see that f_i^m values are lower than unity indicating the presence of blended micelle in the system.

f_i^m can be used to compute excess free energy of mixing (ΔG_{ex}) by using following mathematical equation 7.

$$\Delta G_{ex} = RT\ [X_1^m ln f_1^m + (1 - X_1^m) ln f_2^m] \tag{7}$$

From the perusal of ΔG_{ex} data (Tables 1-6), it can be observed that all are negative values indicating the stability of blended micelle. Further, it also indicates that stability is chain length and spacer nature dependent.

3.2.3. Mixed Micellar Microenvironment

Fluorescence data (Figure 2 and similar Figures not shown) can further be exploited to understand microenvironment of the blended micelle. I_1/I_3 is the measure of the environmental polarity of the mixed micelle. Tables 7-9 shows an interplay of chain length and composition with subsequent variation in I_1/I_3. A low value of I_1/I_3 infers a non-polar site like produced by apolar solvents. I_1/I_3 value decrease as the 12-4-12A content increases in a typical mixed micelle. Similarly, polarity decreases as the chain length of cationic gemini increases from 10-14. This means micellar environment, produced by mixing of two geminis, can be tuned by judicious selection of composition and chain length. It can be further be stressed that environment of the mixed micelle is also spacer nature dependent.

Table 7. Micro polarity (I_1/I_3), calculated dielectric constant (D_{exp}) and ideal dielectric constant (D_{ideal}) for aqueous mixed surfactant systems (14-s-14 + 12-4-12A) at 303 K.

$x_{12-4-12A}$	**14-4-14**			**14-Eg-14**			**14-Isb-14**			**14-Eda-14**		
	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}
0.0	1.349	28.507	28.507	1.346	28.275	28.275	1.438	36.240	36.240	1.295	23.507	23.507
0.2	1.225	25.384	17.896	1.281	25.198	22.413	1.309	31.569	24.695	1.271	21.591	21.511
0.4	1.222	22.260	17.672	1.254	22.120	20.227	1.266	26.899	21.200	1.255	20.314	19.516
0.6	1.165	19.136	17.506	1.197	19.043	15.685	1.250	22.229	19.955	1.211	16.803	17.521
0.8	1.202	16.012	16.084	1.159	15.966	12.661	1.219	17.559	17.449	1.192	15.286	15.526
1.0	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888

Table 8. Micro polarity (I_1/I_3), calculated dielectric constant (D_{exp}) and ideal dielectric constant (D_{ideal}) for aqueous mixed surfactant systems (12-s-12 + 12-4-12A) at 303 K.

$x_{12-4-12A}$	**12-4-12**			**12-Eg-12**			**12-Isb-12**			**12-Eda-12**		
	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}
0.0	1.328	26.724	26.723	1.272	21.896	21.896	1.315	25.603	25.603	1.228	18.159	18.159
0.2	1.279	23.957	22.229	1.257	20.094	20.474	1.292	23.060	23.267	1.219	17.233	17.441
0.4	1.259	21.189	20.634	1.218	18.293	17.361	1.197	20.517	15.685	1.212	16.308	16.882
0.6	1.212	18.423	16.883	1.201	16.491	16.005	1.182	17.974	14.488	1.207	15.382	16.483
0.8	1.196	15.656	15.606	1.188	14.690	14.967	1.175	15.431	13.929	1.196	14.456	15.605
1.0	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888

Table 9. Micro polarity (I_1/I_3), calculated dielectric constant (D_{exp}) and ideal dielectric constant (D_{ideal}) for aqueous mixed surfactant systems (12-s-12 + 12-4-12A) at 303 K.

$x_{12-4-12A}$	**10-4-10**			**10-Eg-10**			**10-Isb-10**			**10-Eda-10**		
	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}	I_1/I_3	D_{ideal}	D_{exp}
0.0	1.355	29.051	29.051	1.279	22.499	22.499	1.326	26.551	26.551	1.254	20.345	20.345
0.2	1.337	25.818	26.858	1.257	20.577	19.436	1.296	23.818	23.586	1.219	18.854	19.676
0.4	1.294	22.586	23.427	1.218	18.655	17.042	1.280	21.086	22.309	1.212	17.362	16.723
0.6	1.245	19.353	19.516	1.201	16.733	16.005	1.244	18.353	19.436	1.207	15.871	15.366
0.8	1.197	16.121	15.685	1.188	14.811	14.728	1.193	15.621	15.366	1.196	14.379	14.728
1.0	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888	1.167	12.888	12.888

Additionally, I_1/I_3 ratio can be used to obtain experimental dielectric constant (D_{exp}), of the mixed micellar interior (probe experienced) , using the well-known relation [11,12,32] (equation 8).

$$\frac{I_1}{I_3} = 1.000461 + 0.01253 D_{exp} \tag{8}$$

Based on ideal mixing, Turro and co-workers proposed another correlation (Equation 9) to get ideal dielectric constant (D_{ideal}) of the environment present in a typical mixed micelle.

$$D_{ideal} = \Sigma X_i D_i \tag{9}$$

Both D_{exp} and D_{ideal} are also included in Tables 7-9. As mentioned earlier, mixing of counter charged geminis deviates from ideal mixing, which is further seen from the difference in D_{exp} and D_{ideal} values at each composition of the mixture. However, the mixing of two components causes modification of the environment present in micelles of individual gemini (12-4-12A or any cationic gemini taken for the study).

In a separate study, it has been mentioned that addition of a non-ionic surfactant to an anionic surfactant changes the micellar environment. Moreover, sodium dodecyl sulphate micelle shows Dexp value 19.1 [12]. Pure 12-4-12A micelle gives D_{exp} value 12.89. This may be due to the gemini nature of 12-4-12A, which contains two dodecyl tails. Further, in a fairly recent study the D_{exp} for pure 14-4-14 was found 38.0 (at 298 K) which is quite similar (at 303 K) to the values (Table 2) obtained for the similar alkyl tail geminis [11]. In this study, D_{exp} has been modified with addition of a non-ionic surfactant. This observation was further validated from the present study conducted with counter charged geminis. These micellar environmental changes can be exploited for the loading of hydrophobic material. This information has been used in order to produce mixed micelle of desired polarity. In fact, in the following chapters above information has been exploited for the enhancement of solubility of water insoluble materials such as polyaromatic hydrocarbons and hydrophobic drugs.

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