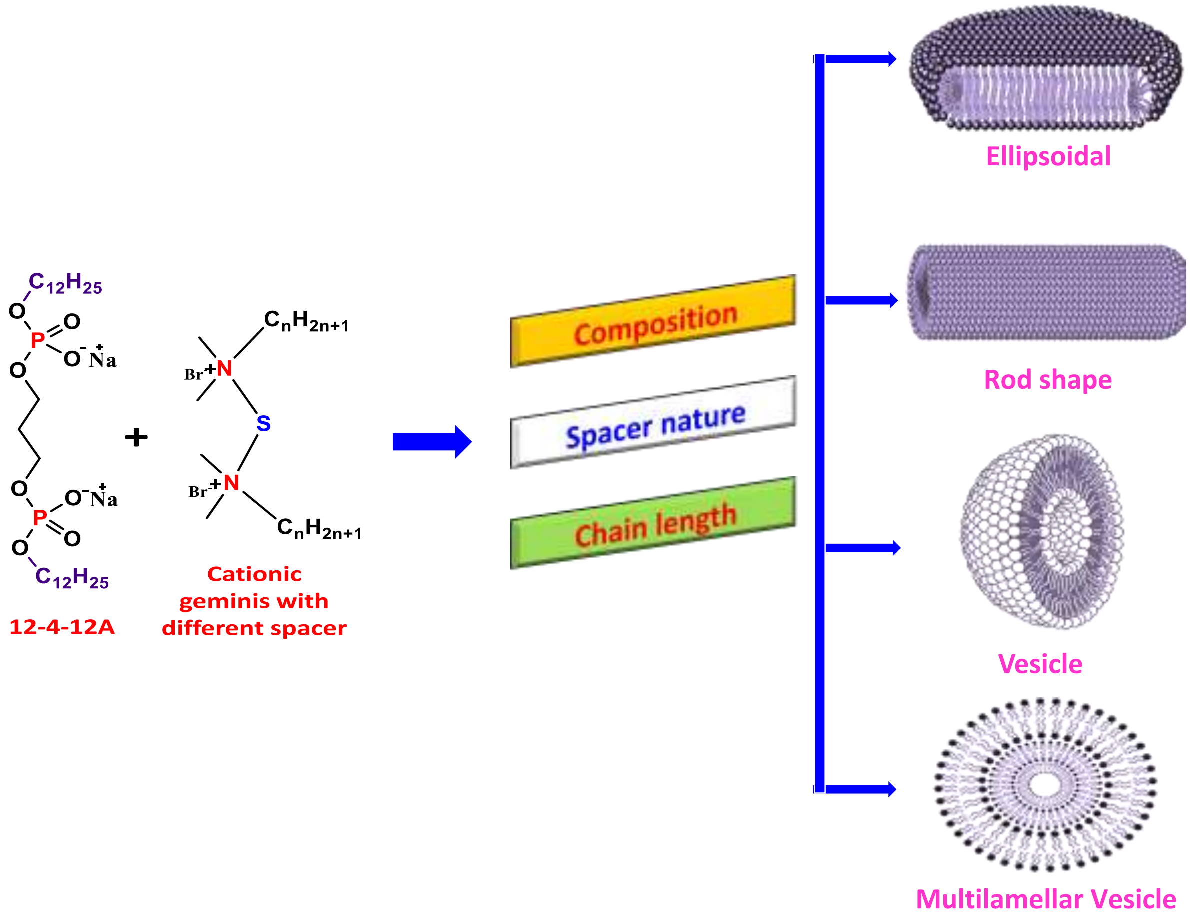
Chapter 4

Composition Triggered Morphologies of Mixed Oppositely Charged Geminis having Different Chain Length and Spacers



4.1. Introduction

Blending of surfactants imparts different variations regarding association and architecture of resulting aggregates just above CMC or much higher than CMC, respectively. Regarding CMC variations, the results are provided and interpreted in Chapter 3. Present Chapter deals with structural modifications (sphere-rod transition (*s* → *r*), rod - worm like micelle, or vesicle formation from lower order aggregate) due to compositional changes within blended geminis. Blending or mixing of surfactant can cause additional features regarding their solution properties (e.g.; viscosity) or applications (e.g.; increase aqueous solubility of hydrophobic material). Blending of various conventional surfactant of all types of charges are reported in the current literature.

In recent time, there are number of publications about the solution behaviour of blended gemini surfactants with their conventional analogues [1–4]. However, scanty reports are found on mixtures of gemini surfactants [5–7]. On the micellar morphology front, only a few reports are available [5,8,9]. The presence of a spacer is prime difference between conventional and gemini surfactant other than number of alkyl tails and head groups. Researches on gemini surfactants revolved around changes in alkyl tail, spacer nature or electrostatics of the head group [10,11]. In case of spacer nature, only one variation of changing polymethylene length of the spacer tried many times [12–17]. Only few reports are related to bio-degradable spacer [18–23].

Looking at the facts mentioned above, not many studies are conducted with blending of gemini surfactants. Among gemini blending, counter charged geminis co-micellization and morphological investigations are clearly lacking in the current literature [5,24]. Therefore, this gemini mixing and resultant morphological changes are of genuine interest in order to exploit solution morphologies and their modified interior environment for further exploitation related to solubilization, delivery or targeting vehicles in pharmaceutical research [25–27]. Keeping above view in mind, this chapter deals with blended gemini aqueous mixtures of counter charges and their resultant impact on micellar architectural changes.

Here, cationic gemini surfactants of various chain lengths and spacers are blended with 12-4-12A. Structures and chain length are already depicted in Scheme 1 of Chapter 3. When oppositely charged geminis are mixed together, not only the morphology but surface charge which also modifies. Nowadays, morphologies are studied either by scattering techniques (dynamic light scattering (DLS), small angle neutron scattering (SANS) or small angle x-rays scattering (SAXS)) or by optical microscopy (transmission electron microscopy (TEM), polarising optical microscopy (POM) or atomic force microscopy (AFM)) [28–32]. To draw information related to morphology or their variations and magnitude of charge, DLS, zeta-potential and TEM are used. Various variations related to composition, chain length or spacer nature are tried to know about optimum mixed micellar system for further applications.

4.2. Results and Discussion

In this chapter, for blending of various geminis of opposite charges, a fixed concentration of the mixture was taken (10 mM). A typical appearance of such mixture has been shown in Figure 1 (12-4-12A + 12-4-12, scheme 1 of Chapter 3). The appearances of other blended systems were also similar but not shown here.

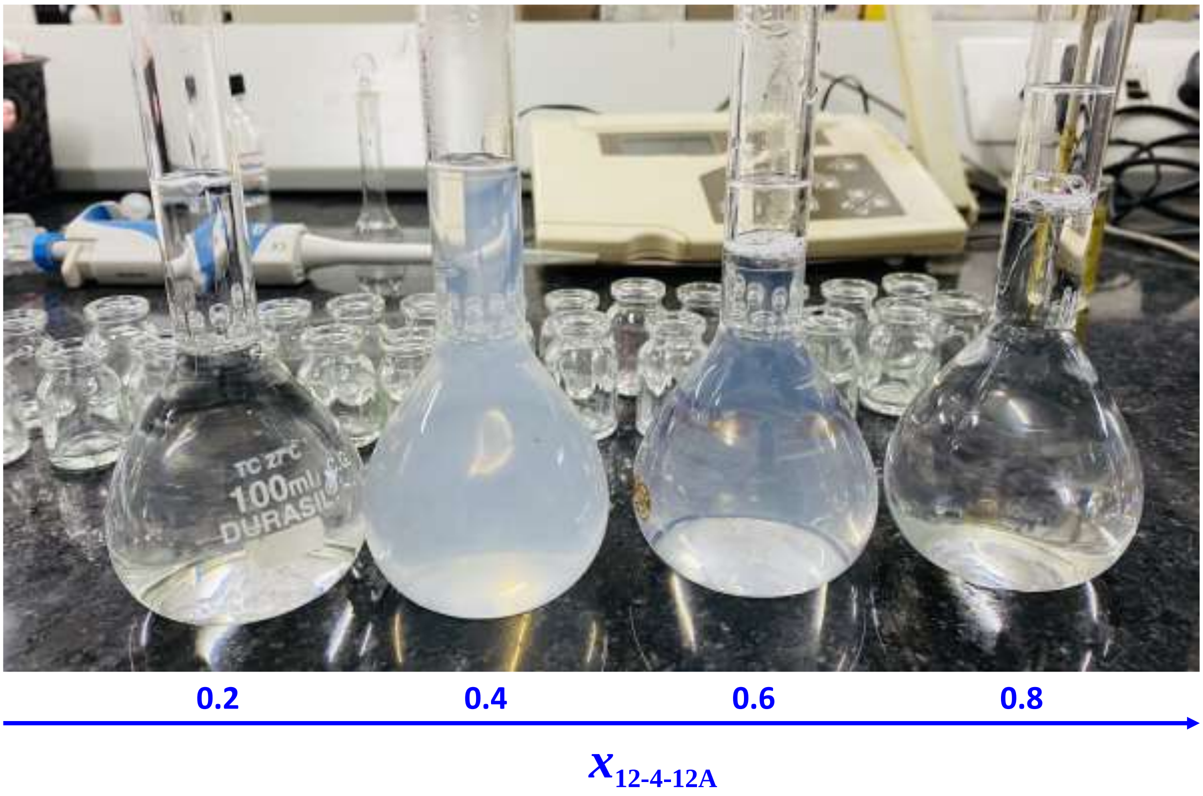


Figure 1. Appearance of 12-4-12A + 12-4-12 aqueous mixtures as a function of composition (total [Geminis] = 10 mM).

As can be seen from Figure 1, appearance passes from clear to bluish to clear as mole fraction of 12-4-12A increases from 0.2-0.8. It may be mentioned here that pure 10 mM 12-4-12A or 10 mM of cationic gemini solutions appears clear or transparent. Above appearance changes hints towards structural modification in micellar morphologies which has been studied using DLS and TEM [33].

4.2.1. DLS Studies on Blended Gemini Systems

When oppositely charged amphiphiles mixed in a typical system, two possibilities arise: (1). Phase separation and (2). Structural modifications. Structural modifications can be understood in the light of surfactant packing parameter or Mitchell Ninham parameter (***P***) [34].The peak can be related with surfactant architecture (head group area (a_0) and alkyl tail volume (V) and length (l)) by the previously given expression (equation 1, section 1.5 of Chapter 1). When two geminis mixed, it is expected that length of the alkyl tail (l) has slight modification in a typical mixed micelle. However, a_0 or V affected drastically and contribute towards variation in P. In an earlier study, variation in P has been used to obtain micellar aggregates of varied morphologies in aqueous solution [35]. In the present case, variation in P seems more distinct due to the presence of two alkyl tails in each component of the mixture. Similarly, due to the presence of opposite charges on the head groups of the two components of the mixture, a_0 expected to decrease drastically [8,36,37]. Therefore, increase in V and decrease in a_0 cause an enhancement in the value of P and provided a bases for the formation of higher order aggregates at some compositions of the mixture. This indeed was observed from our DLS data shown in Figures (2-4). The nature of spacer (hydrophilic or hydrophobic) has also shown some overall effect on micellar architecture. From the DLS data, it is clearly seen that larger morphologies are formed in the solution when mole fractions of the two components are nearer to each other (x = 0.4 or 0.6). Such morphologies can be vesicles which is further confirmed by other studies such as TEM. DLS data also show that the sizes are dependent on the chain length of cationic gemini of the blended system. This observation can be interpreted in terms of chain length compatibility of the two component of the mixture (12-4-12A and 12-s-12). It may be mentioned here that larger aggregates were formed in the solution when oppositely charged conventional surfactant of equal chain length were present in the solution [38]. Similar chain length compatibility effect was observed in micro-emulsion systems by Shah *et al.* [39].

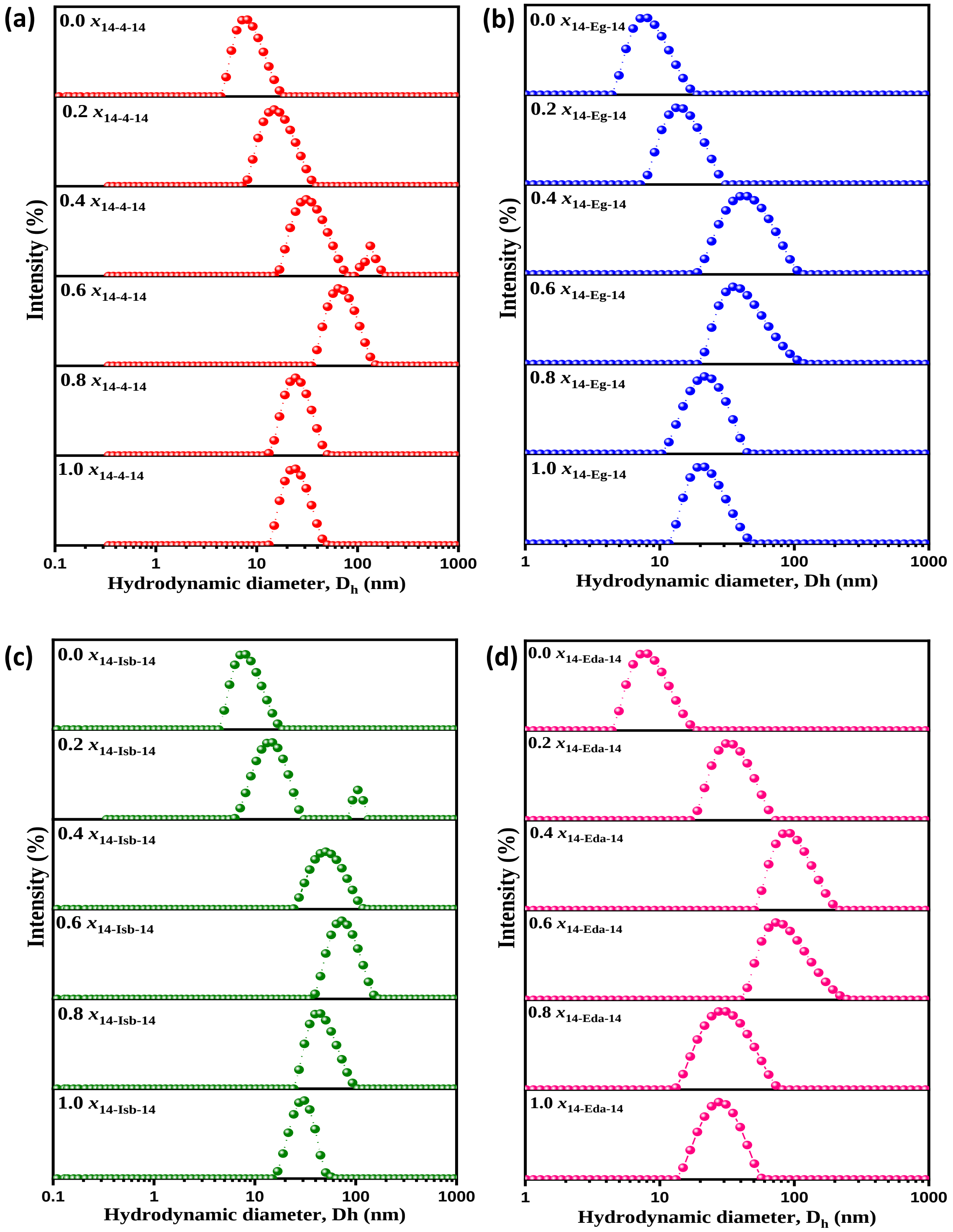


Figure 2. DLS data of 10 mM aqueous mixed gemini surfactant systems at varies mole fractions of 12-4-12A at 303 K: (a) 14-4-14, (b) 14-Eg-14, (c) 14-Isb-14 and (d)14-Eda-14.

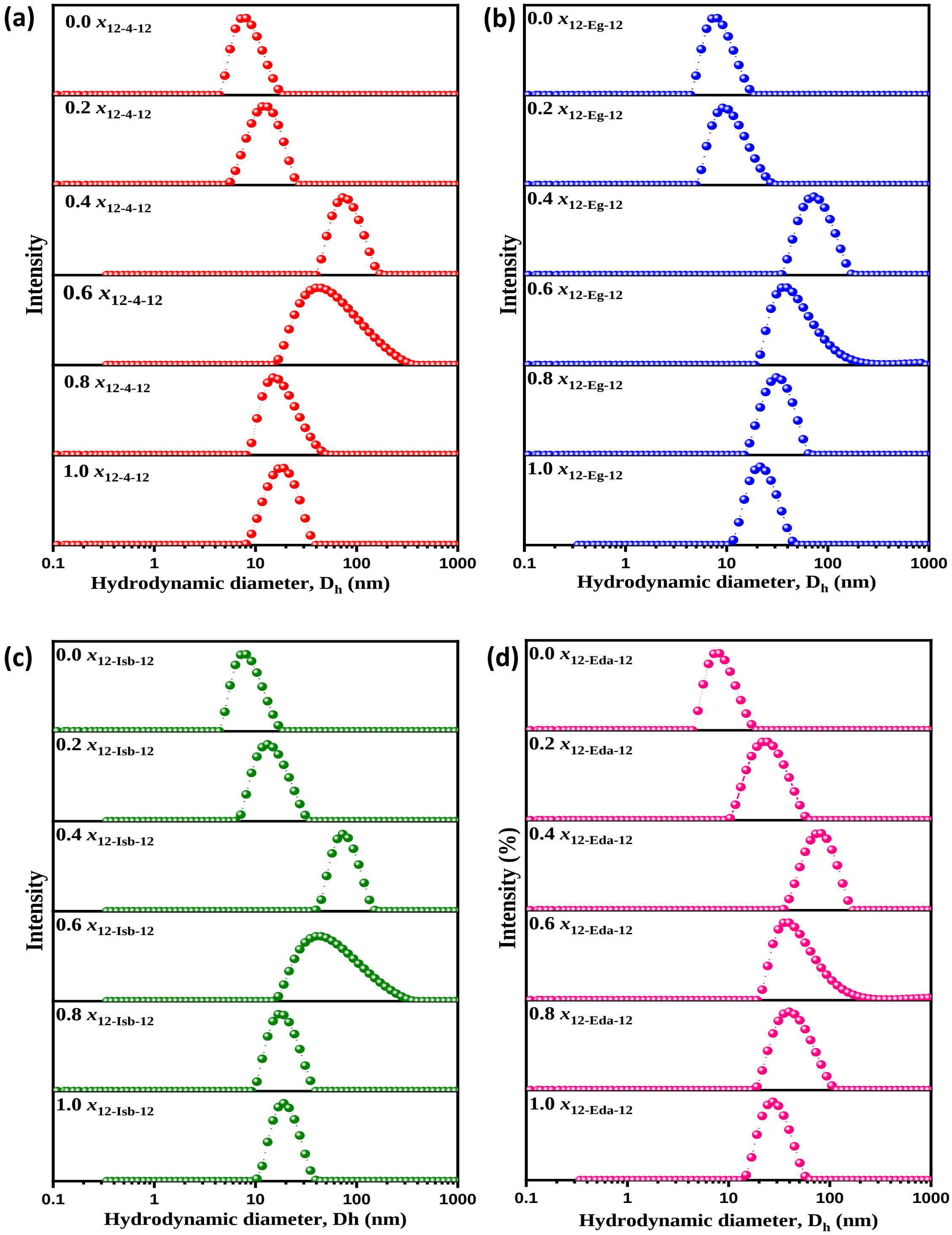


Figure 3. DLS data of 10 mM aqueous mixed gemini surfactant systems at varies mole fractions of 12-4-12A at 303 K: (a) 12-4-12, (b) 12-Eg-12, (c) 12-Isb-12 and (d)12-Eda-12.

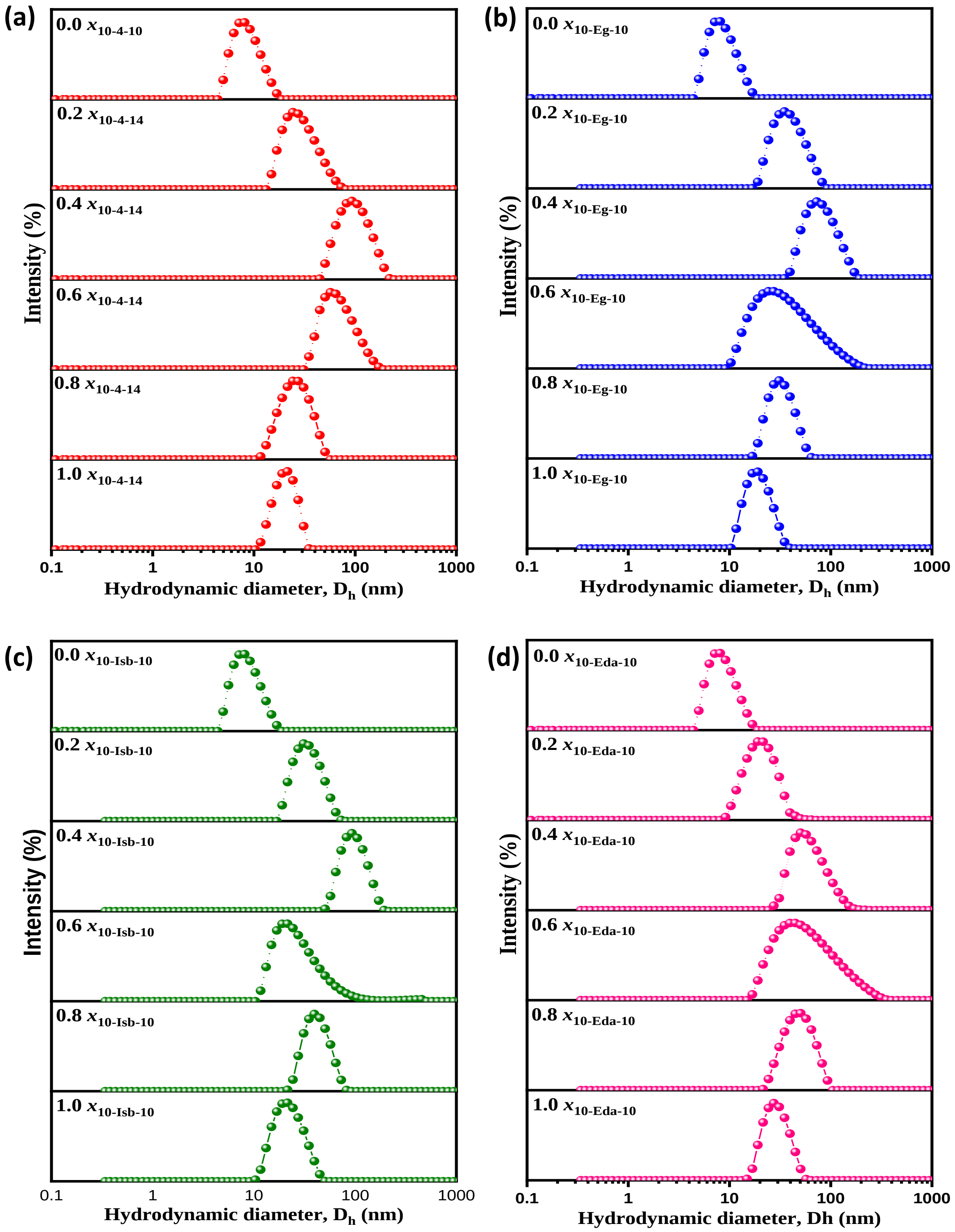


Figure 4. DLS data of 10 mM aqueous mixed gemini surfactant systems at varies mole fractions of 12-4-12A at 303 K: (a) 10-4-10, (b) 10-Eg-10, (c) 10-Isb-10 and (d)10-Eda-10.

4.2.2. Zeta (ζ)-Potential Data

The decrease in a_0 was further provided by zeta-potential data. When oppositely charged amphiphiles are mixed in aqueous solution one can expect head group charge depletion. Figures 5-7 show zeta (ζ) variation with the mole fraction of 12-4-12 ($x_{12\text{-}4\text{-}12A}$). The data show that positively charged micelle has less and less cationic charge as $x_{12\text{-}4\text{-}12A}$ increases in the blended mixture. Further, in the middle range of mole fraction micelle seems nearly uncharged with zeta (ζ)-potential is just around zero (pseudo-non-ionic aggregate). In the region where anionic gemini predominates in the blended mixture, zeta show negative value. With a hint of charge reversal, all these variations in zeta(ζ) and hence a_0 are responsible for the DLS data observed and discussed in above section.

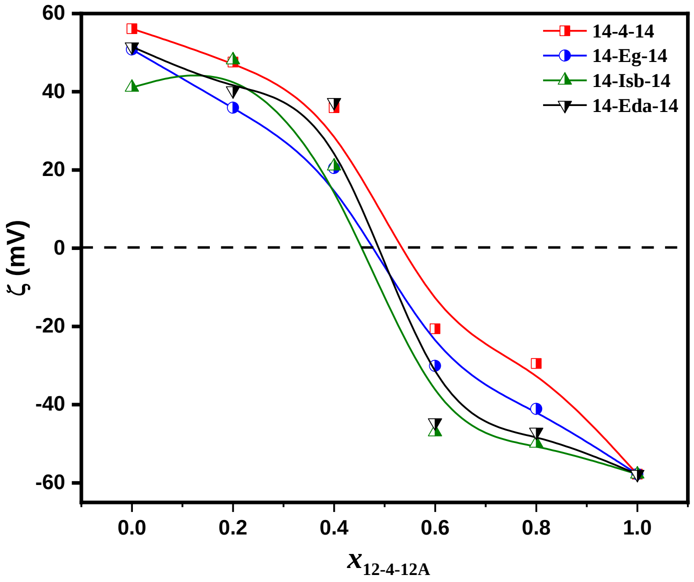


Figure 5. Zeta (ζ)-potential variation of 10 mM mixed aqueous gemini surfactant systems (14-s-14 + 12-4-12A) with change $x_{12\text{-}4\text{-}12A}$ at 303 K.

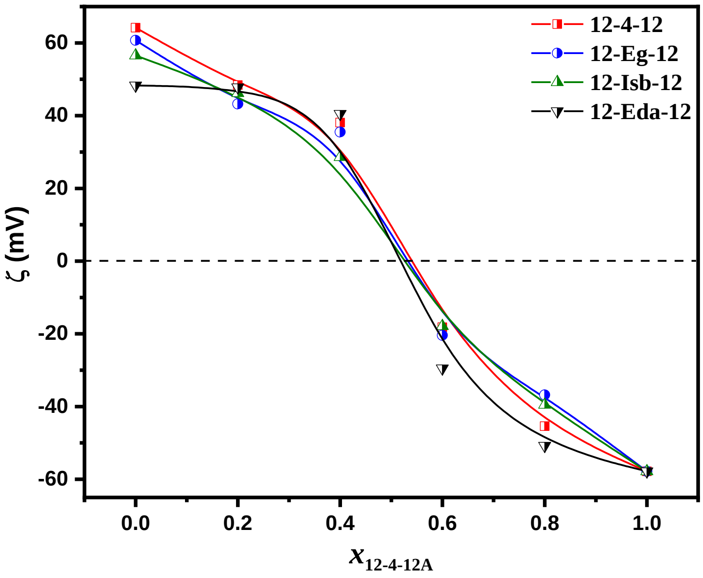


Figure 6. Zeta (ζ)-potential variation of 10 mM mixed aqueous gemini surfactant systems (12-s-12 + 12-4-12A) with change x12-4-12A at 303 K.

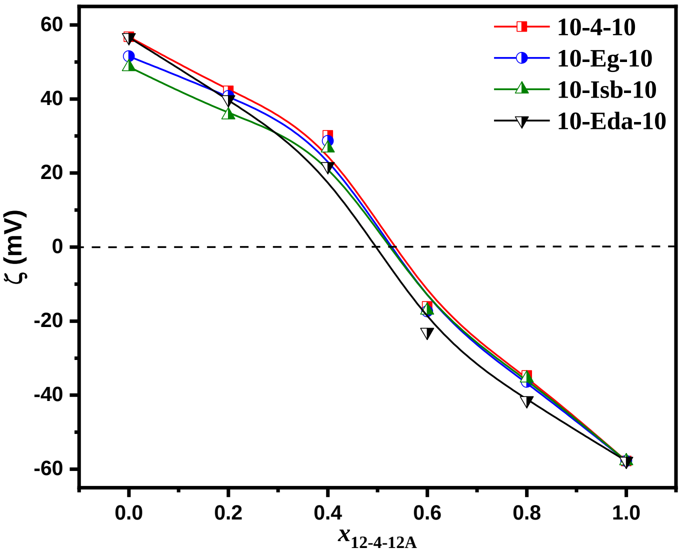


Figure 7. Zeta (ζ)-potential variation of 10 mM mixed aqueous gemini surfactant systems (10-s-10 + 12-4-12A) with change x12-4-12A at 303 K.

4.2.3. TEM Micrographs of Blended Micelles

TEM analyses were also utilised to corroborate the information provided in the above sections. Such studies are conducted to establish aggregate morphologies of the blended mixtures of oppositely charged geminis at different mole fractions. Typical micrographs are provided in Figures 8-12. TEM images were acquired for the systems where compositions of the two individual components are nearly equal (x = 0.4 or 0.6). As observed with DLS studies, bigger aggregates (vesicles) are formed due to blending and the sizes are chain length, nature of spacer and composition dependent. Further, multilamellar vesicles are observed with polymethylene spacer and equal chain length of the gemini (c =12, Figure 9).

From the above studies, one can tune micellar morphology by selecting optimize composition together with chain length and nature of the spacer. Above information can be used to establish structure property-composition relationship for the formation of amphiphilic assemblies.

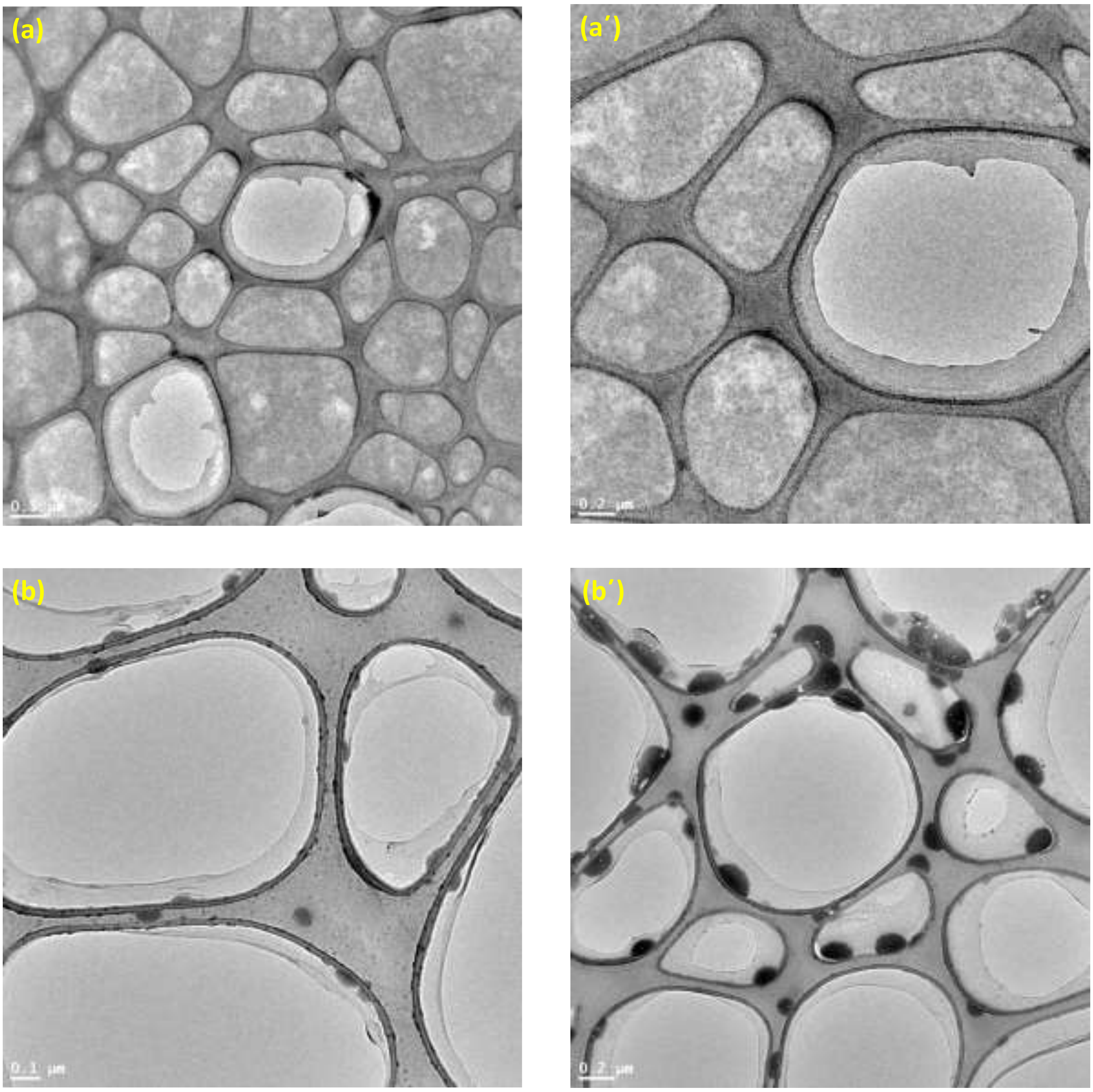


Figure 8. TEM images of 10 mM aqueous mixed gemini surfactant system of 14-Eda-14 + 12-4-12A (a, a′) 0.4 $x_{12\text{-}4\text{-}12A}$ and (b, b′) 0.6 $x_{12\text{-}4\text{-}12A}$.

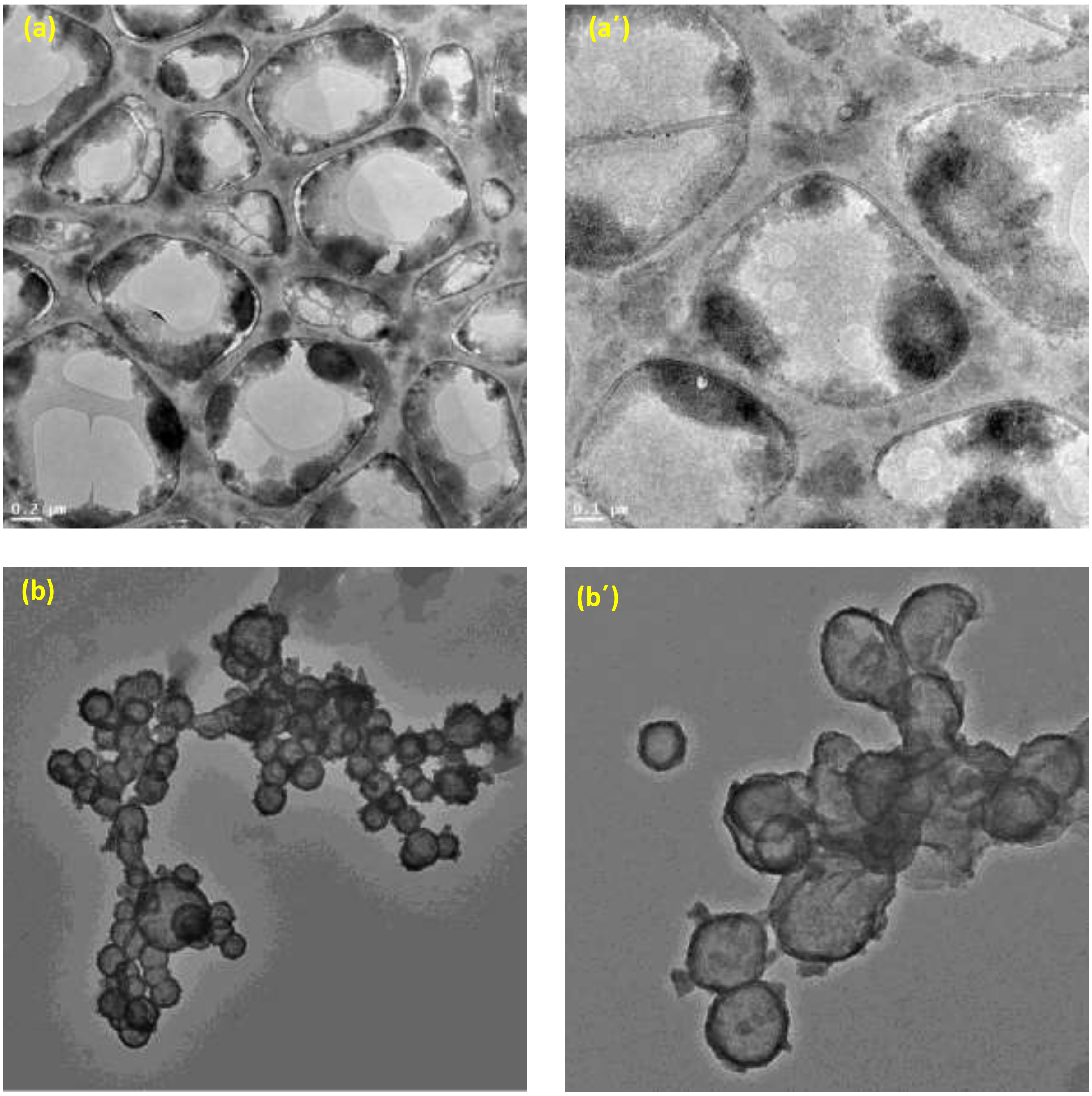


Figure 9. TEM images of 10 mM aqueous mixed gemini surfactant system of 12-4-12 + 12-4-12A (a, a′) 0.4 $x_{12\text{-}4\text{-}12A}$ and (b, b′) 0.6 $x_{12\text{-}4\text{-}12A}$.

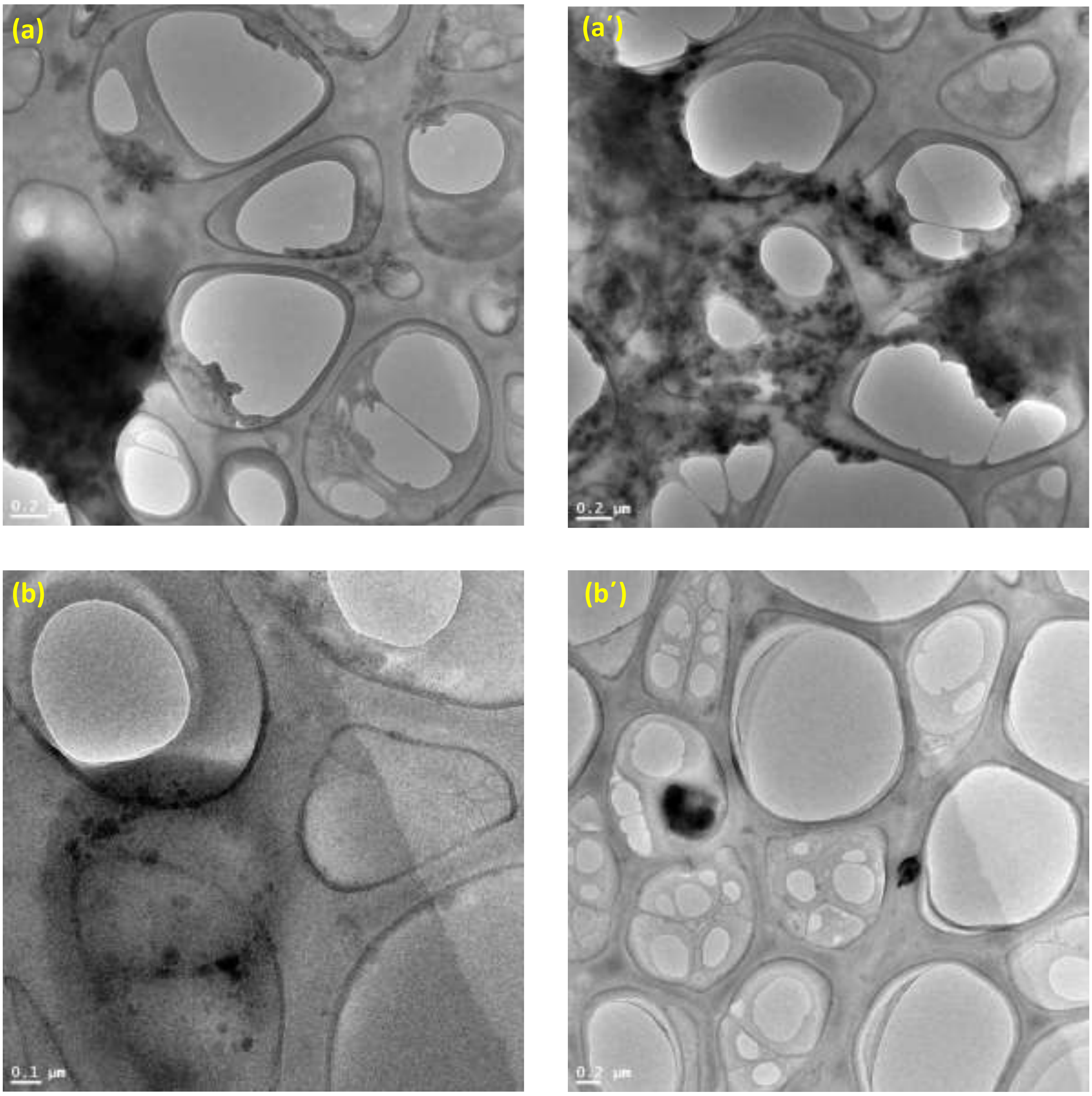


Figure 10. TEM images of 10 mM aqueous mixed gemini surfactant system of (a, a′) 12-Eg-12 + 0.4 $x_{12\text{-}4\text{-}12A}$ and (b, b′) 12-Isb-12 + 0.4 $x_{12\text{-}4\text{-}12A}$.

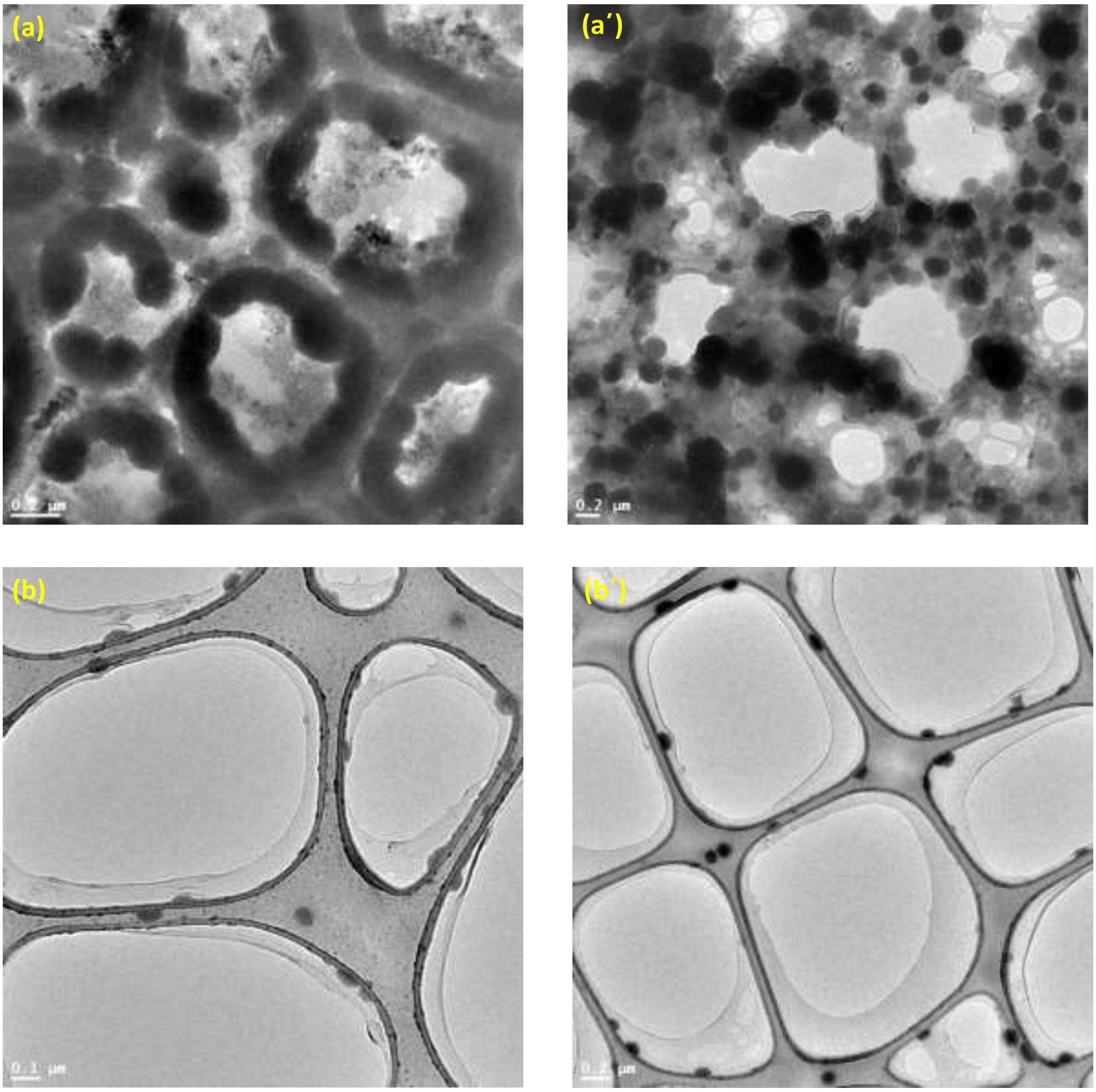


Figure 11. TEM images of 10 mM aqueous mixed gemini surfactant system of (a, a′) 10-4-10 + 0.4 $x_{12\text{-}4\text{-}12A}$ and (b, b′) 10-Eg-10 + 0.4 $x_{12\text{-}4\text{-}12A}$.

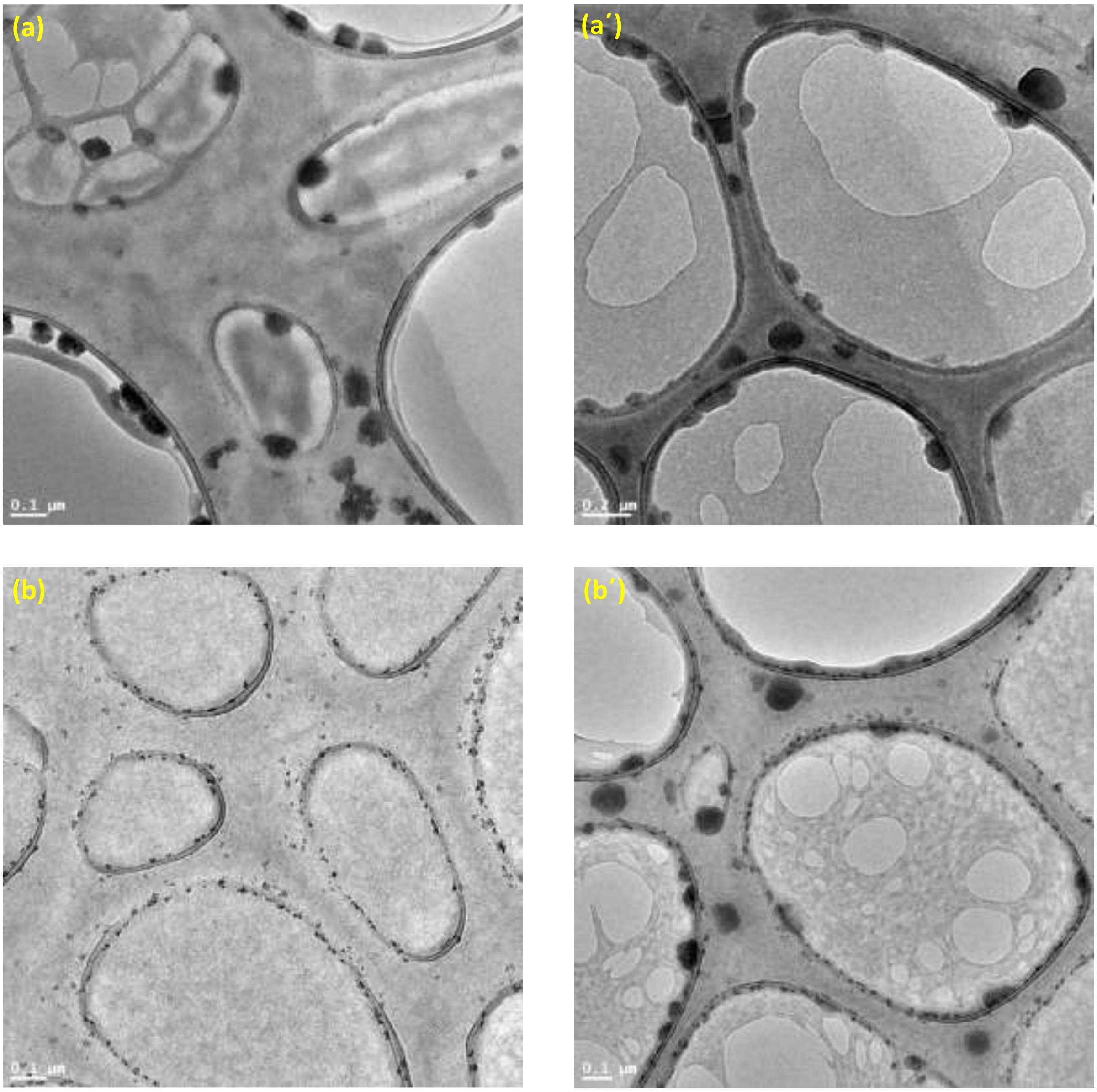


Figure 12. TEM images of 10 mM aqueous mixed gemini surfactant system of (a, a′) 10-Isb-10 + 0.4 $x_{12\text{-}4\text{-}12A}$ and (b, b′) 10-Eda-10 + 0.4 $x_{12\text{-}4\text{-}12A}$.

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