## 5.1. Introduction

The interactions involved in observing clouding phenomenon and hence morphological transitions in the anionic quaternary surfactants are not well explored. The development of attractive interactions among aggregates to observe clouding is also not well documented. In the last two chapters (Chapters 3 and 4), efforts were devoted in observing clouding phenomenon in variety of systems together with collecting information related to morphological transitions when an anionic surfactant solution is heated to cloud point. Some key questions still need to be addressed in order to understand the rationale behind the onset of attractive interactions, morphology and solution behaviour.

To focus on several surprising and unexplained features of the temperature dependence of self-assembly of ionic surfactants like i) decrease in ionic surfactant solubility with increasing temperature ii) the influence of counterion and alkyl headgroup on the solution behaviour, iii) evaluation of temperature effect on micellar growth in single ionic micelles as the system approaches CP, iv) role of grown micelles on the CP and v) the mechanism of clouding, further studies using 2D NMR and optical imaging, are performed and included in the present chapter. The above effects are opposite to the convention existing in the vast literature. It is known that increase in temperature causes faster molecular motions to raise the solute solubility and micellar disintegration. NMR is a unique and promising technique for obtaining intrinsic molecular-level structural information. The binding of quaternary counterion to the head groups and micellar interior can be studied using various 2D NMR techniques. A direct imaging technique like POM can be helpful in monitoring various changes in micellar morphology when the solution is heated. The availability of heating stage assembly with the optical microscope allows capturing micrographs (or even movies for specific temperature interval) at desired stage of the solution. The objectives of the study performed in this chapter are:

***To get further insight in the mechanism of clouding.***

***To explore the interaction of surfactant headgroup and counterion at the molecular level.***

***To provide the experimental evidence for the mechanism of clouding phenomenon resulted by above interactions.***

## 5.2. Results and Discussion

### *5.2.1. 2D NMR measurements*

To examine the mechanism with the scarce information on growth of aggregates and the presence of two populations of different sizes and explore the interactions involved typical 2D NMR studies (COSY and NOESY) are carried out for quaternary anionic surfactants at room temperature (18 °C) and near CP. The 2D COSY and NOESY spectra of TBADS solution are shown in Figures 1 and 2, respectively. Intermolecular interaction is clearly reflected from the cross peaks in NOESY spectra near CP (Figure 2b). Such peaks are absent in Figures 1 and 2b. This may due to the dehydration of $TBA^+$ which predominantly assists in hydrophobic interactions as well as electrostatic interactions, at higher temperature, with the micellar surface/ interior. The $TBA^+$ of the bulk phase may have a tendency to interact with water facing butyl chains of micelle bound $TBA^+$. However, micelle bound $TBA^+$ may be comparatively in favourable environment than the one present in bulk water. The formation of giant aggregates caused by micelle linking can be thus understood in terms of the dependence of hydration of the butyl chains. Near ambient conditions, the driving force will get stronger with increasing temperature. This can add upon the clouding in charged micellar solutions discussed in earlier chapters. Cross peaks between N1-N4, N1-N3, N1-N2 and S1-N4, S1-N2 protons are indicate about the intercalation of the counterion butyl chains. This finds an agreement with the broadening of $^1$H NMR peaks presented and discussed in Chapter 4.

Similar results have been obtained with 0.005M TBPDS (CP= 27.0°C, Figure 3 and 4) and 0.25M TBAMES (CP= 65.0 °C, Figures 5 and 6) solutions. However, with TBAMES a difference in sign of the cross peaks near the CP (Figure 6b), has been observed. The signs of nuclear overhauser effects (NOE) of all the diagonal and the cross peaks in TBADS and TBPDS solutions at 20 °C and near CP are positive, whereas the cross peaks for TBAMES solution near the CP showed the opposite (negative NOE) to that at 18 °C. In the context of clouding, water interacts with counterion, headgroup, micellar interior in addition to the interaction among bulk water molecules. The increase of temperature may affect above water interactions to different extent. This means for TBADS and TBPDS solutions near CP (lower than the CP for TBAMES) the $TBA^+$/ $TBP^+$ counterions are less dehydrated and hence the tumbling rate of the intercalated counterion chain in this case may be faster and hence will be responsible for positive NOE [148]. However, for TBAMES solution near the CP at 64°C, the motion of the alkyl part and the TBA$^+$ counterion is restricted at such high temperature due to the increased dehydration. This may be responsible for deeper insertion of butyl chains TBA$^+$ into the hydrophobic core. Also, the distinct cross peaks S2-S15, S2-N4 and more intense N1-N4, N1-N3 and N1-N2 (Figure 6b) are in agreement to the dominating hydrophobic effects. Though it is difficult to determine the precise inter-proton distances between each individual proton from the cross-peak intensities of the NOESY spectrum, the hydrophobic interactions can easily be explained through the cross peaks. Thus, NOESY results corroborate the proposition that dehydrated TBA$^+$/ TBP$^+$ ions associate with alkyl heads via hydrophobic interactions to form grown micelles at higher temperature (near CP). TBA$^+$/ TBP$^+$ ions first attach to the surface of the anionic micelle and then on further dehydration at higher temperature become inserted into the hydrophobic core. However, there is no such provision in SDS. Hence no cross peaks are seen in spectra with SDS solutions (Figure 7 and 8).

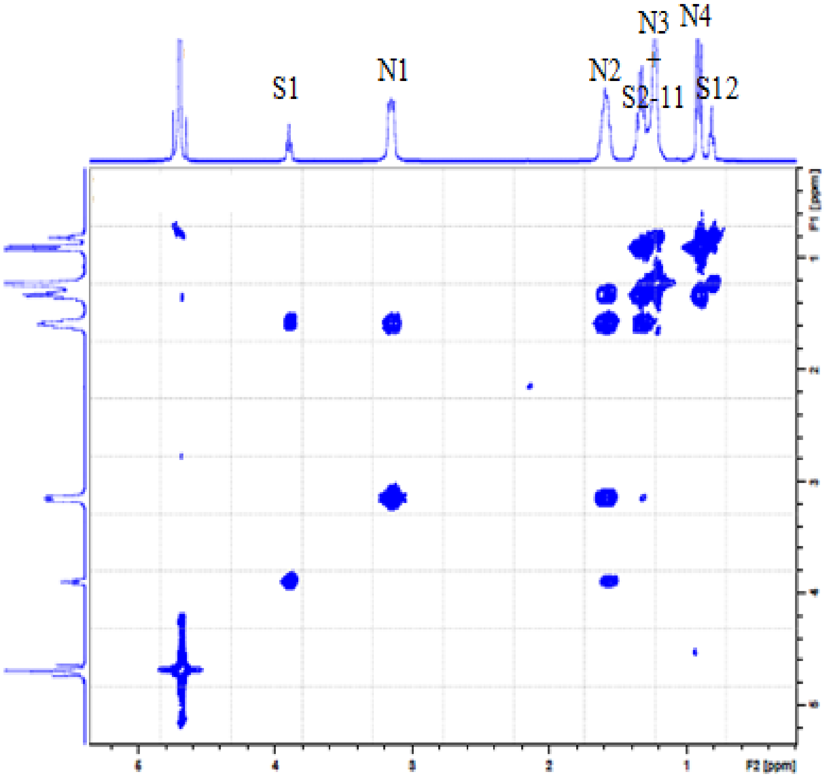
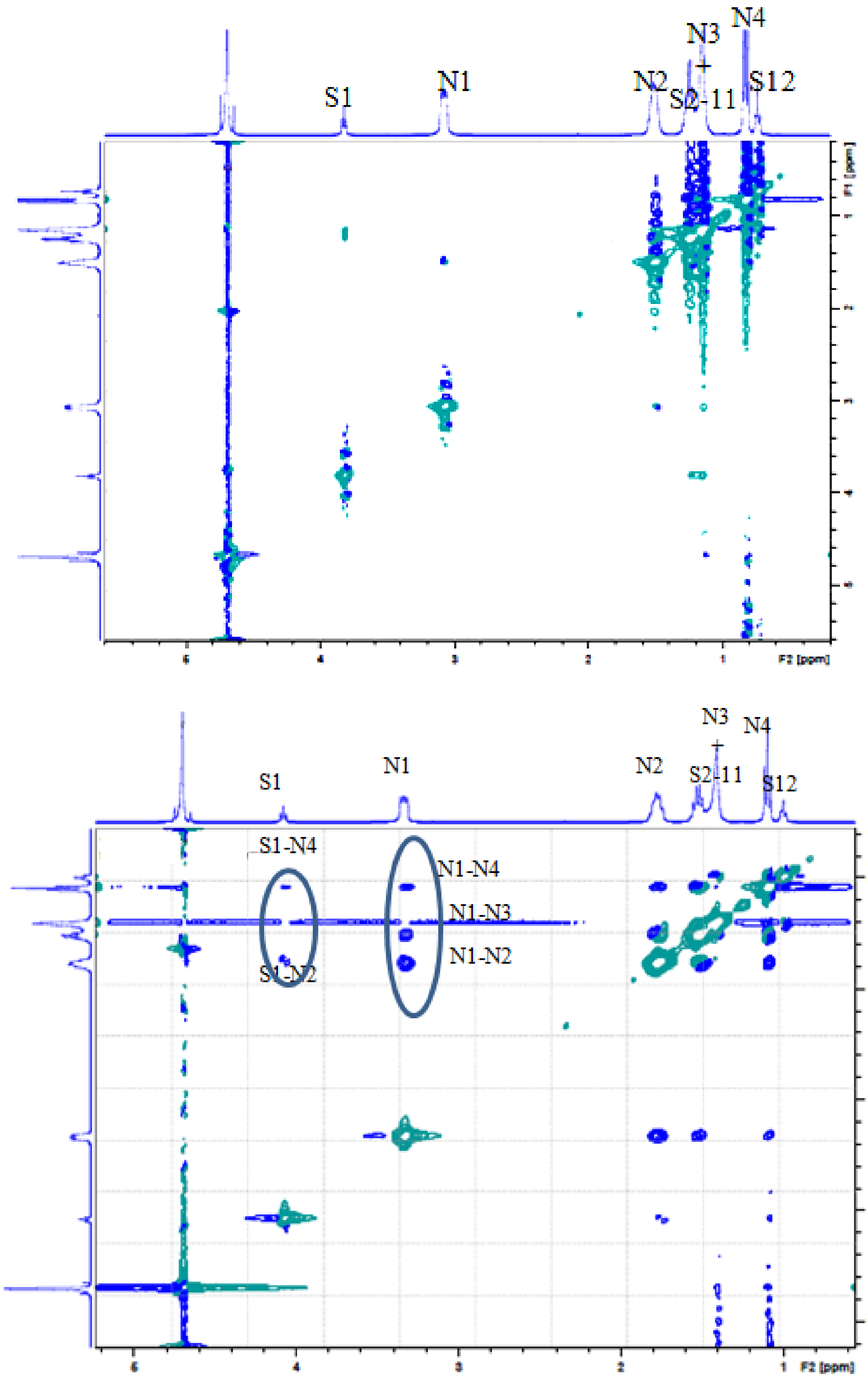


**Figure 1**: 2D COSY NMR spectra of TBADS at 18 °C



(a)

(b)

**Figure 2**: 2D NOESY NMR spectra of TBADS at a) 18 °C b) at 40 °C

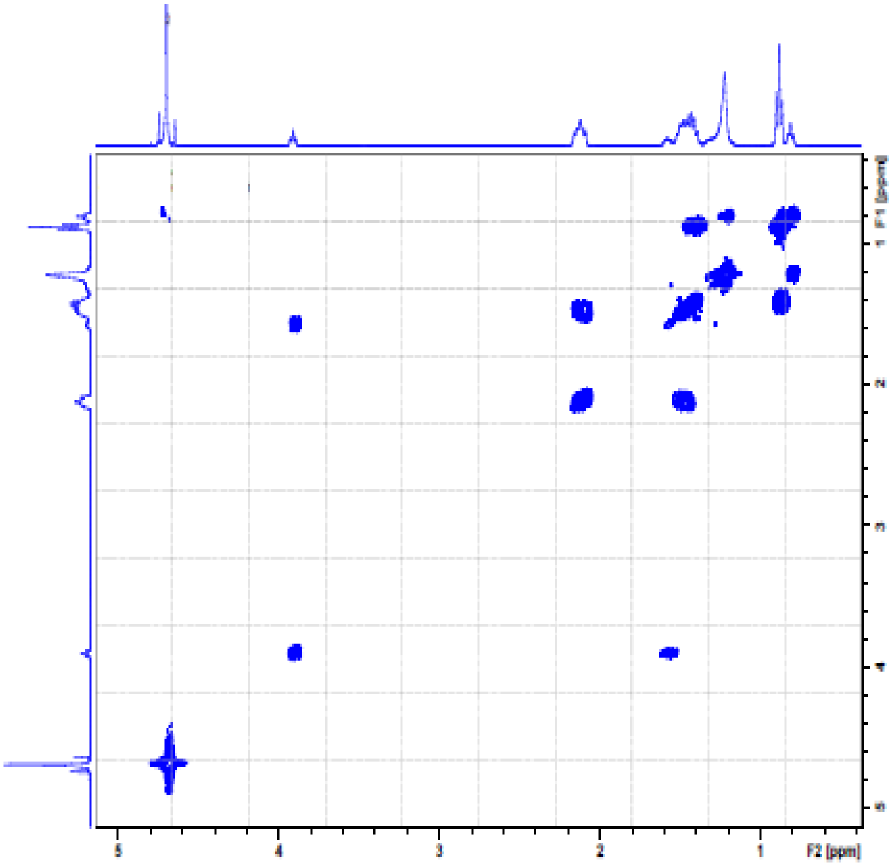
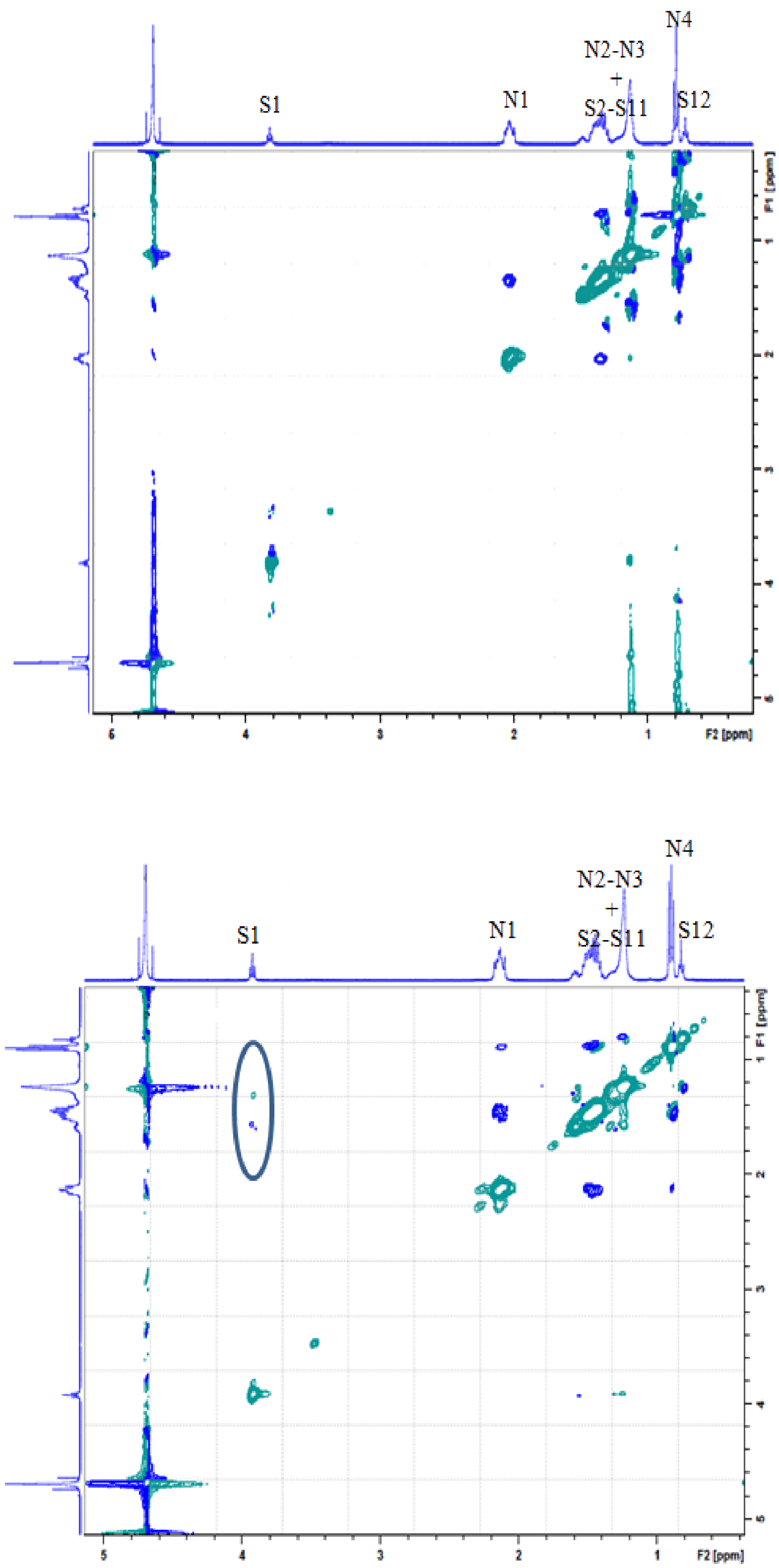


**Figure 3**: 2D COSY NMR spectra of TBPDS at 18 °C



(a)

(b)

**Figure 4:** 2D NOESY NMR spectra of TBPDS at (a) 18°C and (b) near CP

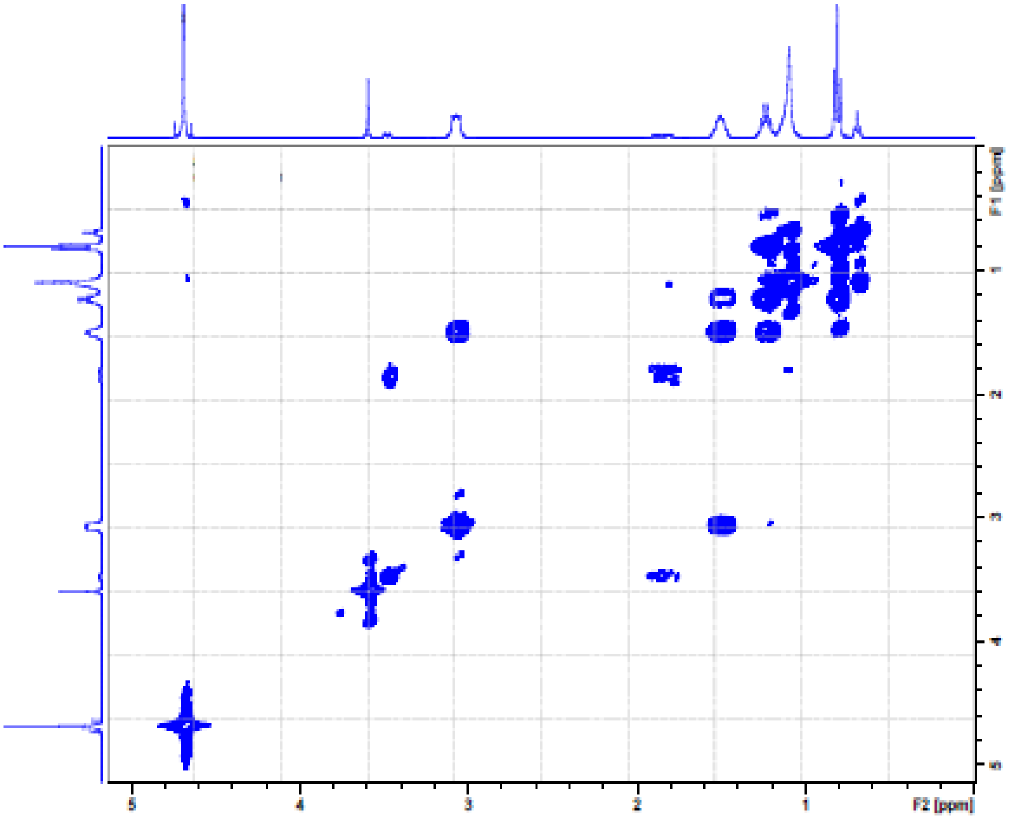
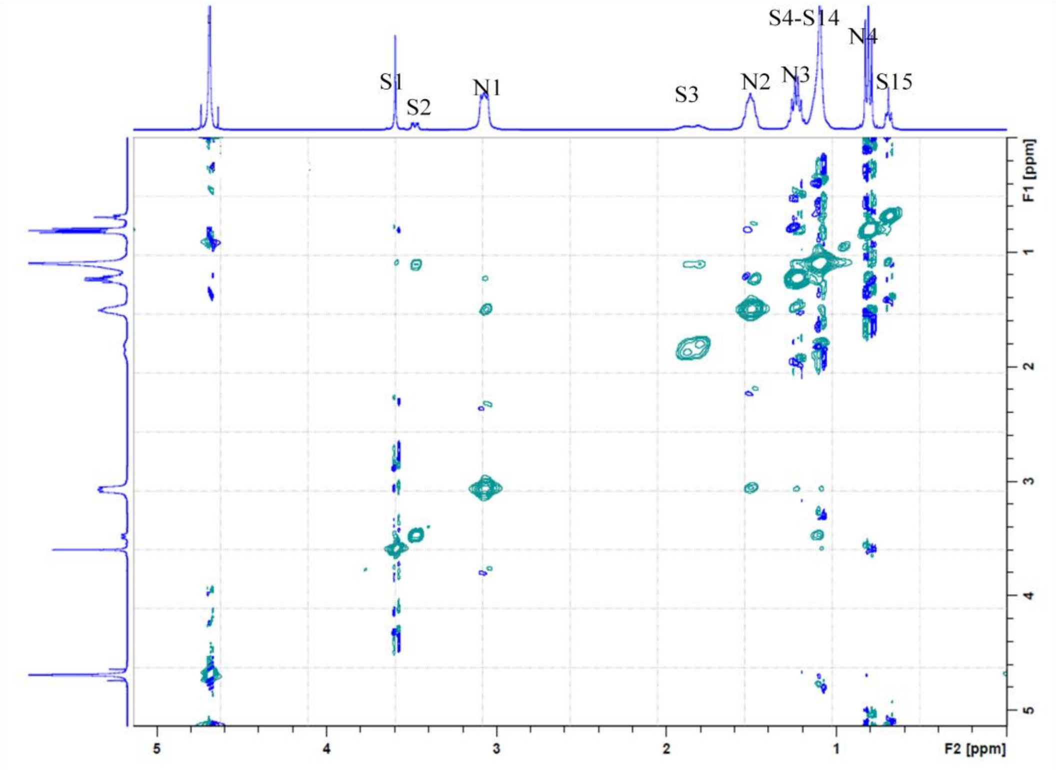
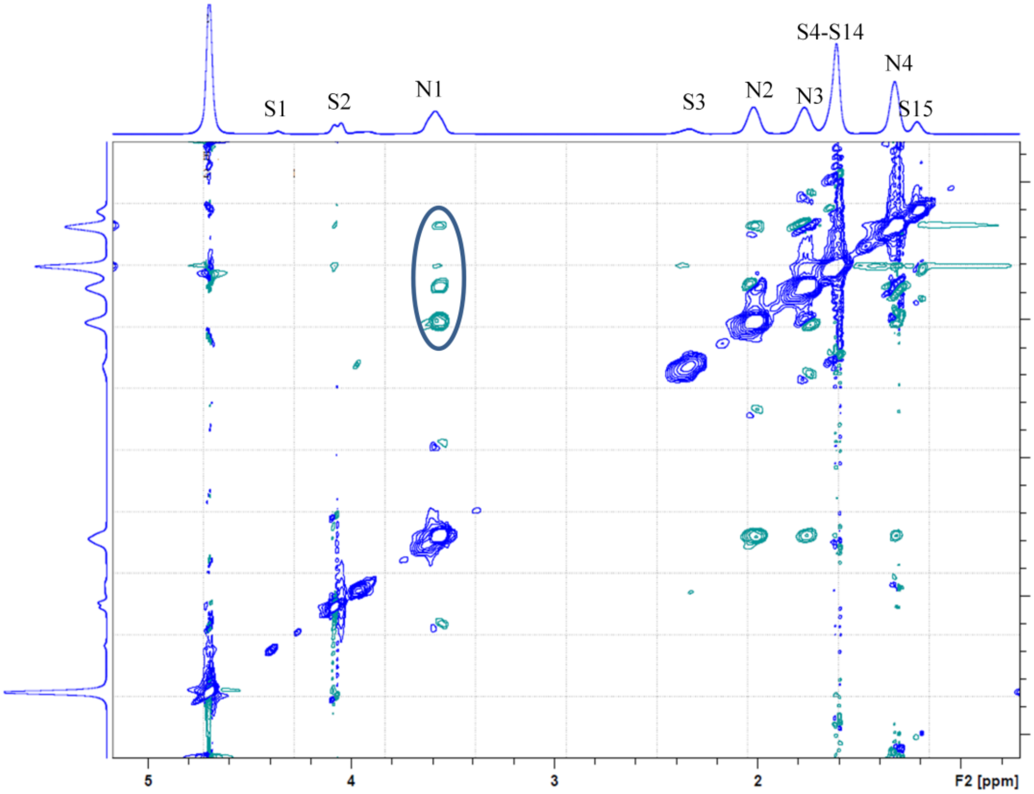


**Figure 5**: 2D COSY NMR spectra of TBAMES at 18 °C



(a)



(b)

**Figure.6**: 2D NOESY NMR spectra of TBAMES at (a) 18°C and (b) near CP.

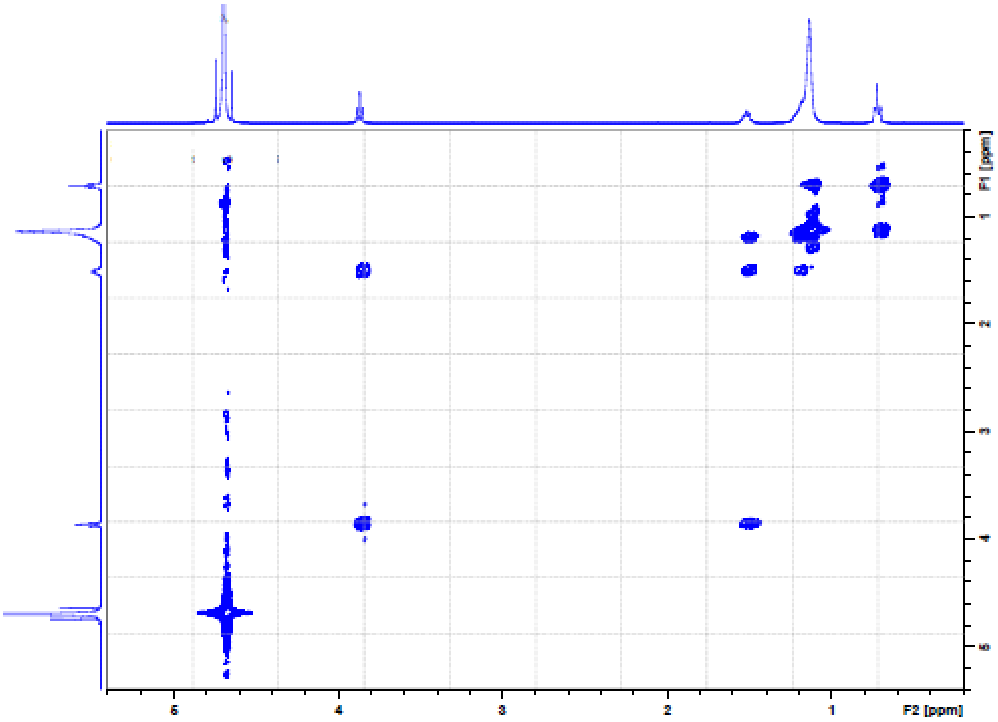


**Figure 7**: 2D COSY NMR spectra of SDS at 18 °C

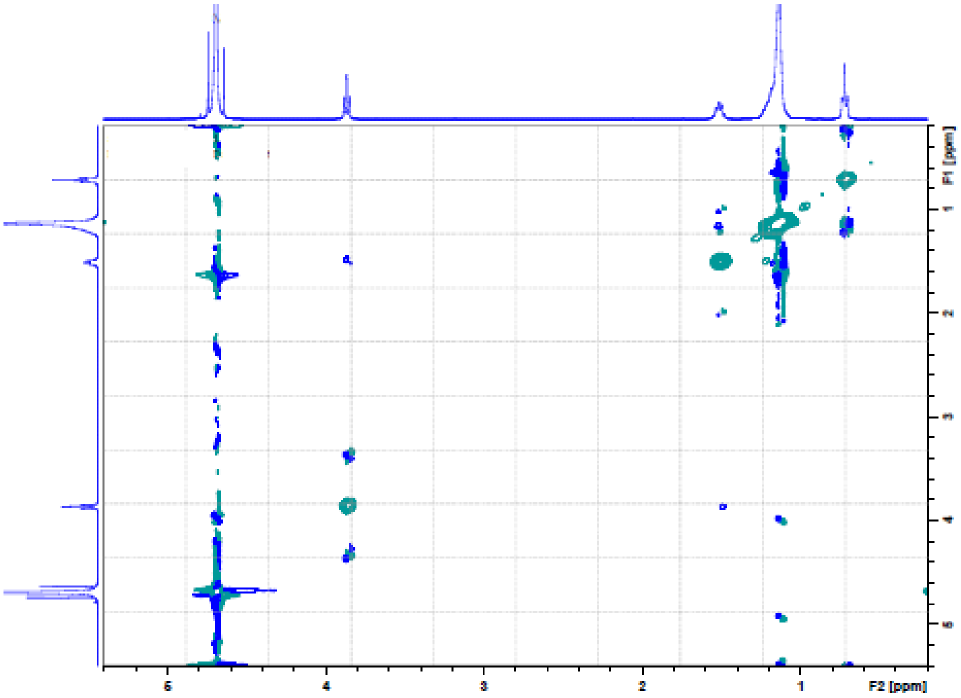
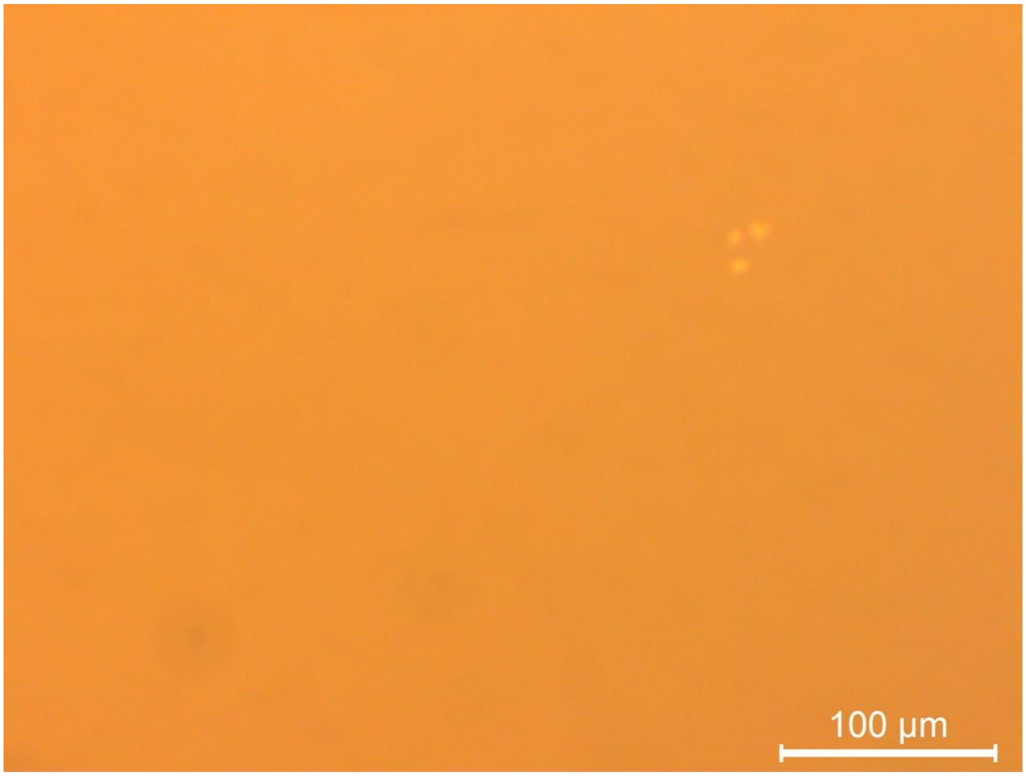


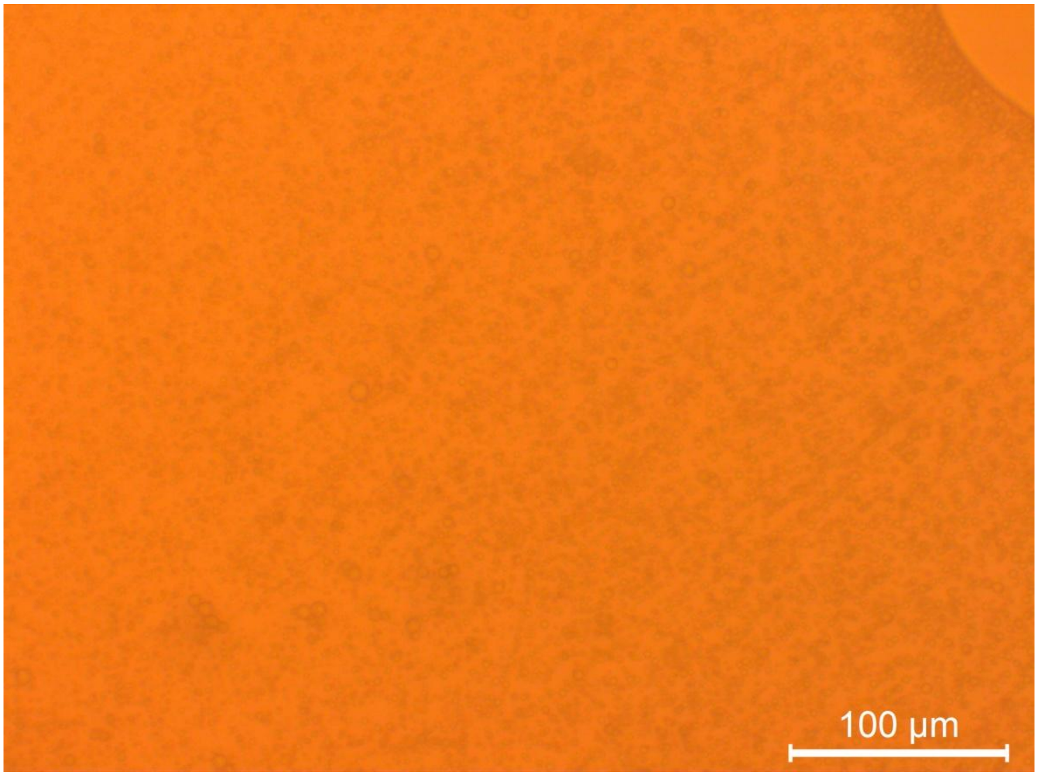
**Figure 8**: 2D NOESY NMR spectra of SDS at 18°C

### 5.2.2. POM Studies

To get insight about the morphology present at ambient temperature and near/ at the CP, POM micrographs have been recorded. The typical micrographs for TBADS, TBADBS and TBAMES are shown in (Figures 9-11). As evidenced from the micrographs at room temperature (Figures 9a, 10a, 11a), aggregates may be of very small sizes (below the lower detection limit of the polarising microscope). However near the CP, each surfactant solution shows distinct bigger morphologies (easily seen by the POM. To get clear insight, the two phases at CP in 0.1M TBADS solution were separated and then analysed at RT. It was found that even at RT the rich phase showed the presence of bigger aggregates (Figure 12a), unlike that with the lean phase. However, when the rich phase was further heated again from RT, aggregates of even higher sizes are seen (Figure 12). Another observation was the fusion of above higher sized aggregates in the vicinity of CP. This observation clearly demonstrates that the fusion of many grown micelles is responsible for macroscopic phenomenon of clouding and phase separation. This is in agreement with the Langer-Schwartz theory [44] that predicts: the nucleated phase may appear as a cloud of small droplets that grow slowly beyond the critical droplet size or it may form as an isolated droplet that rapidly grows to a very large size. Same analogy is drawn to the present surfactant solutions in which it has been found that probably a cloud of small droplets grows beyond the critical droplet size and responsible for clouding and liquid-liquid immiscibility. Also the reversibility of the phenomenon on cooling was observed.



(a)



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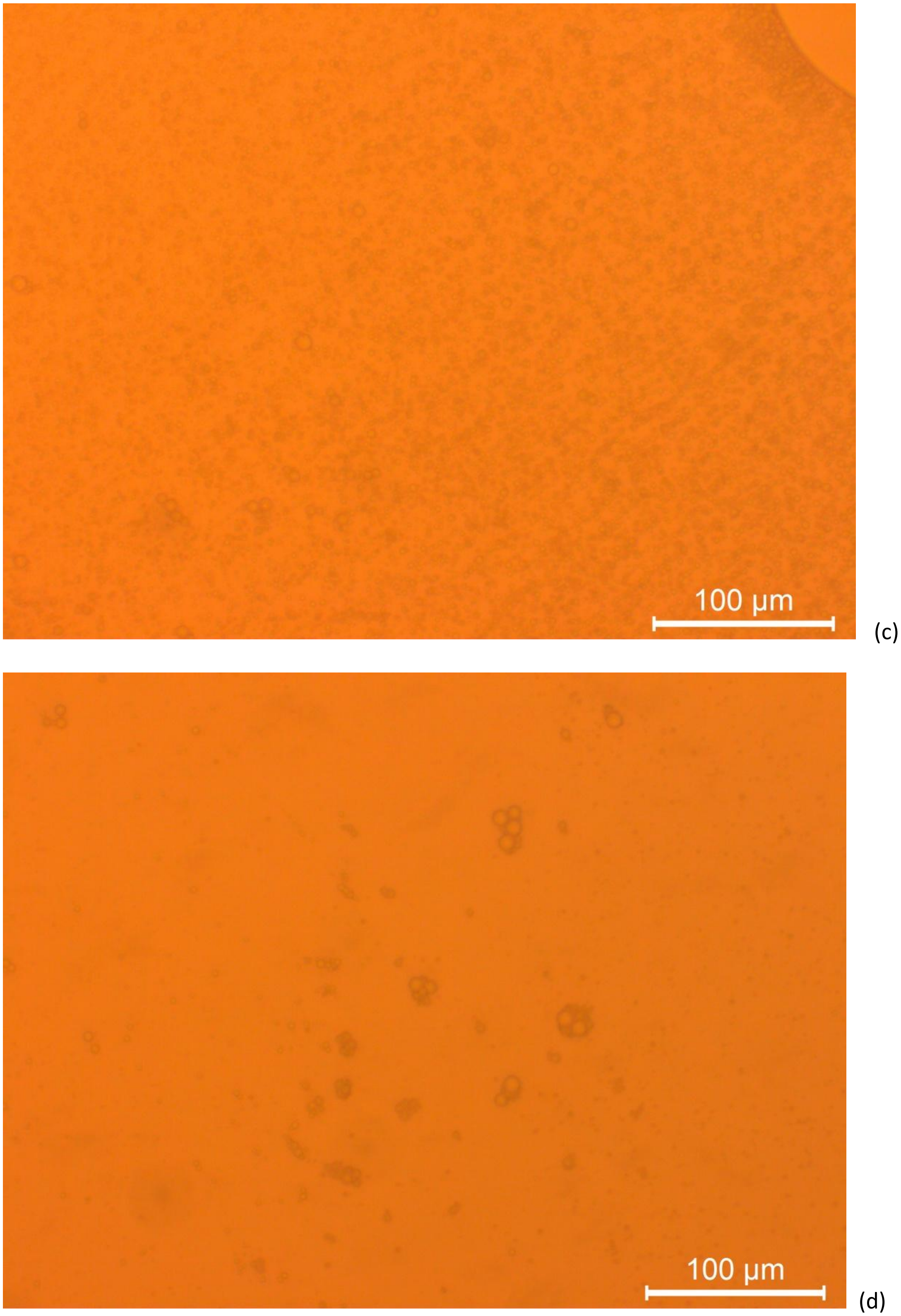
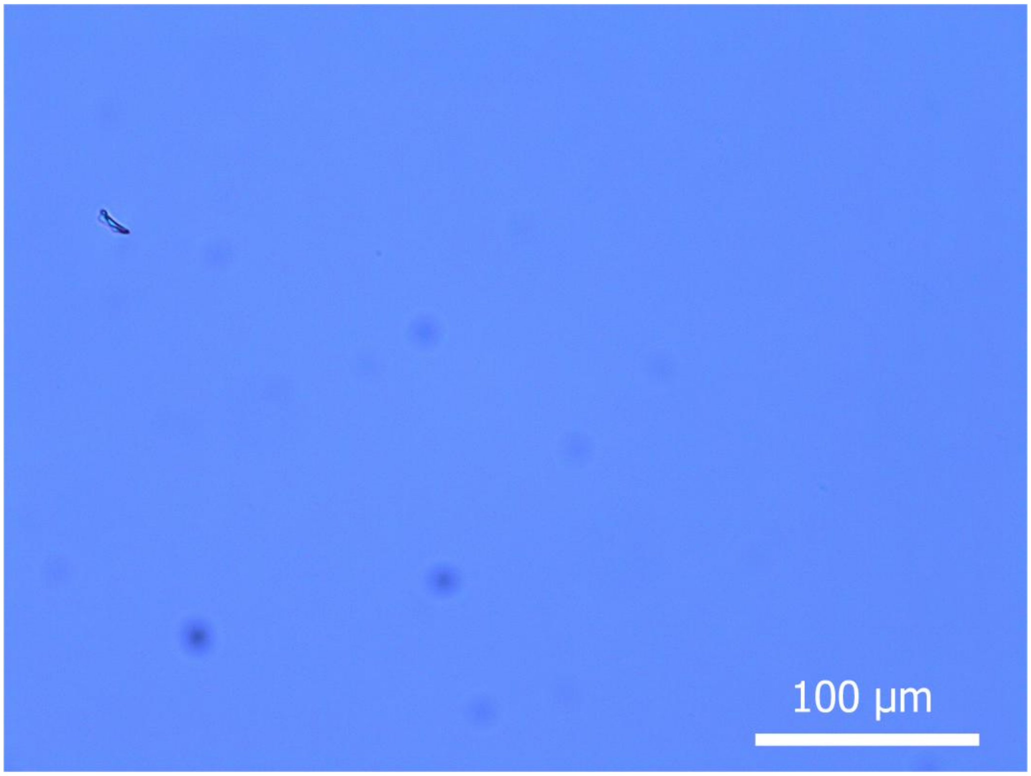
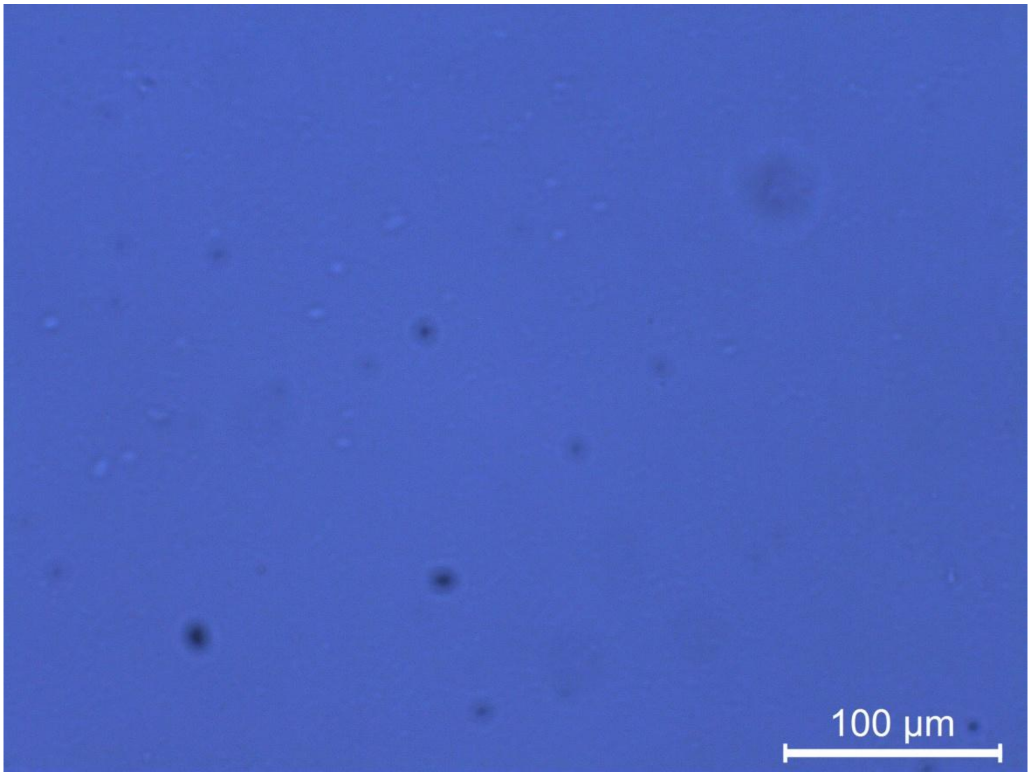


**Figure 9:** Optical micrographs of 0.03M TBADS at (a) 20 °C, (b) 41.8 °C, (c) 42.0 °C, (d)  CP=42.5 °C



(a)



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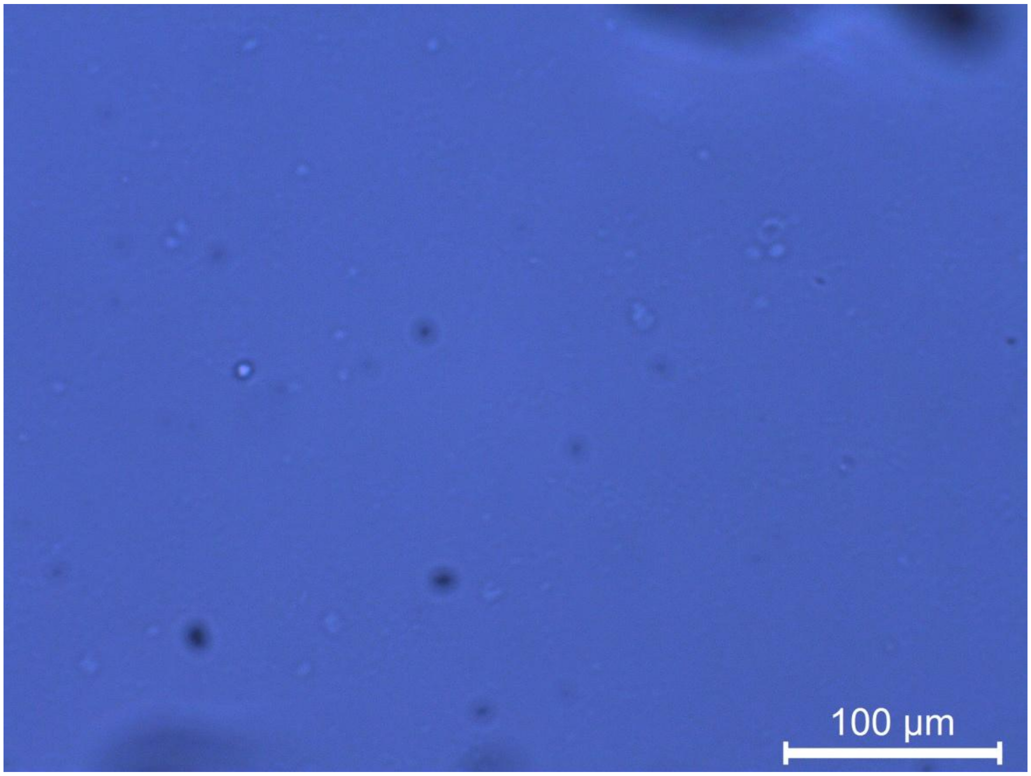
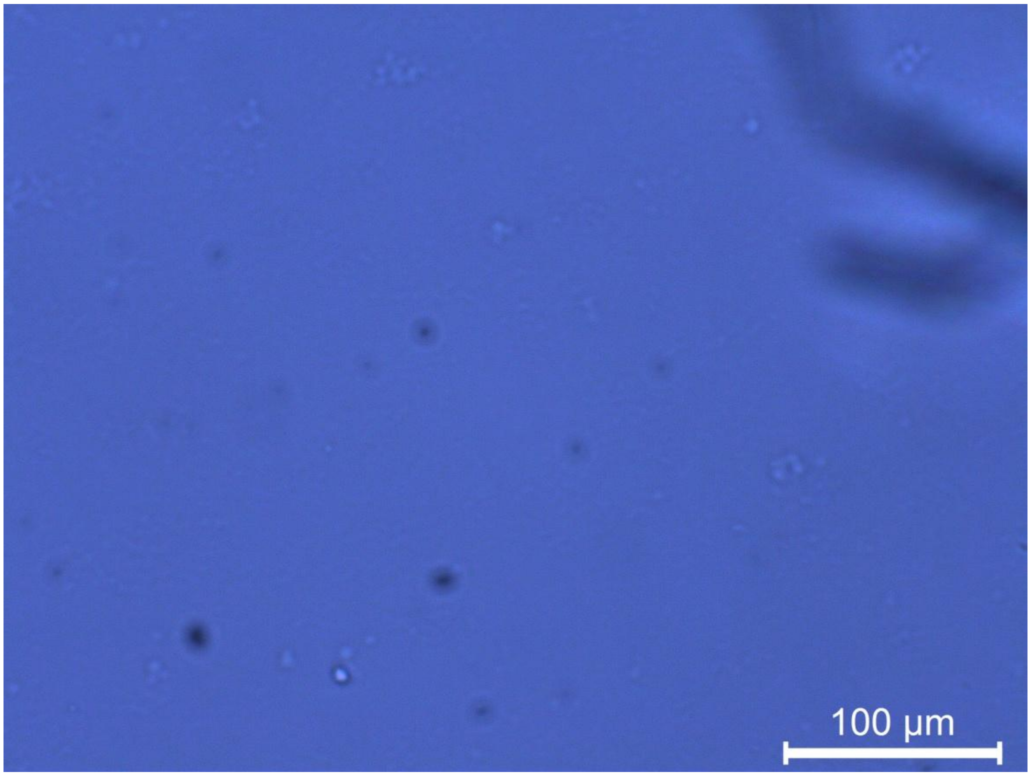
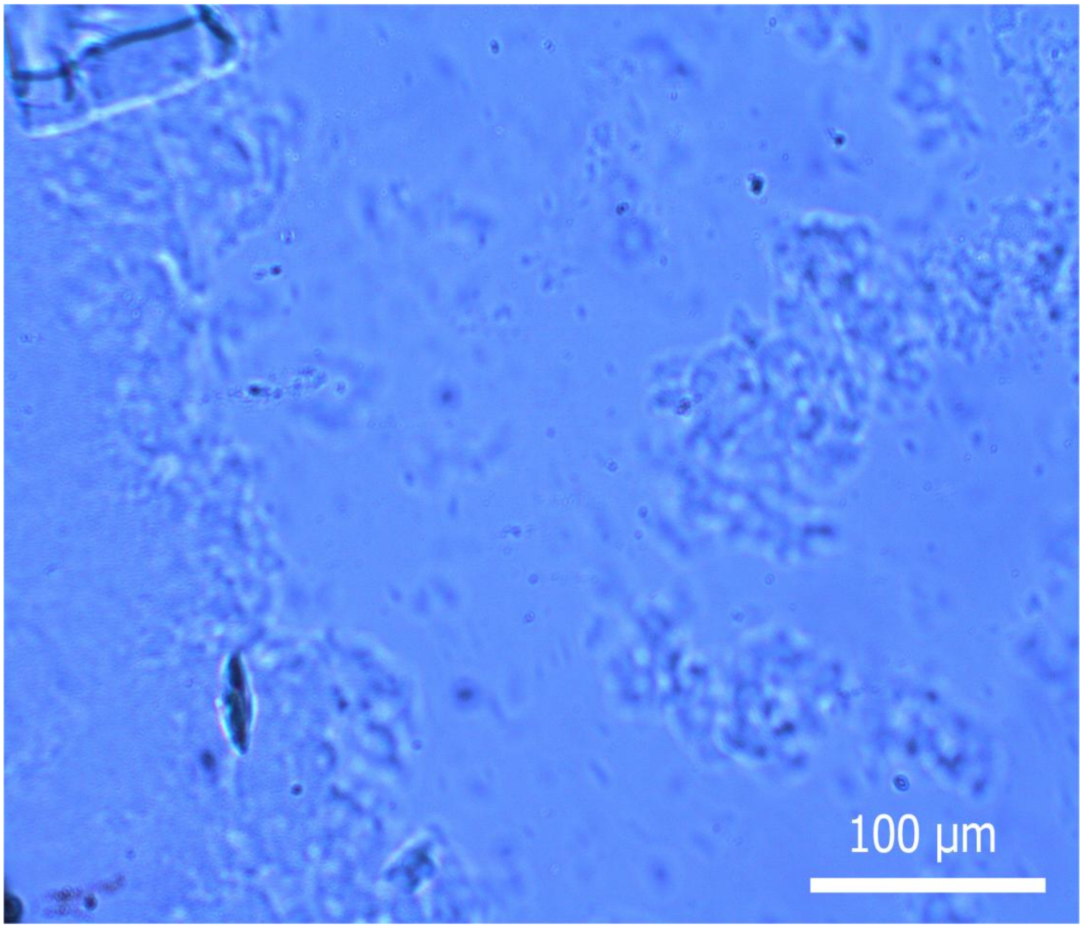


(c)

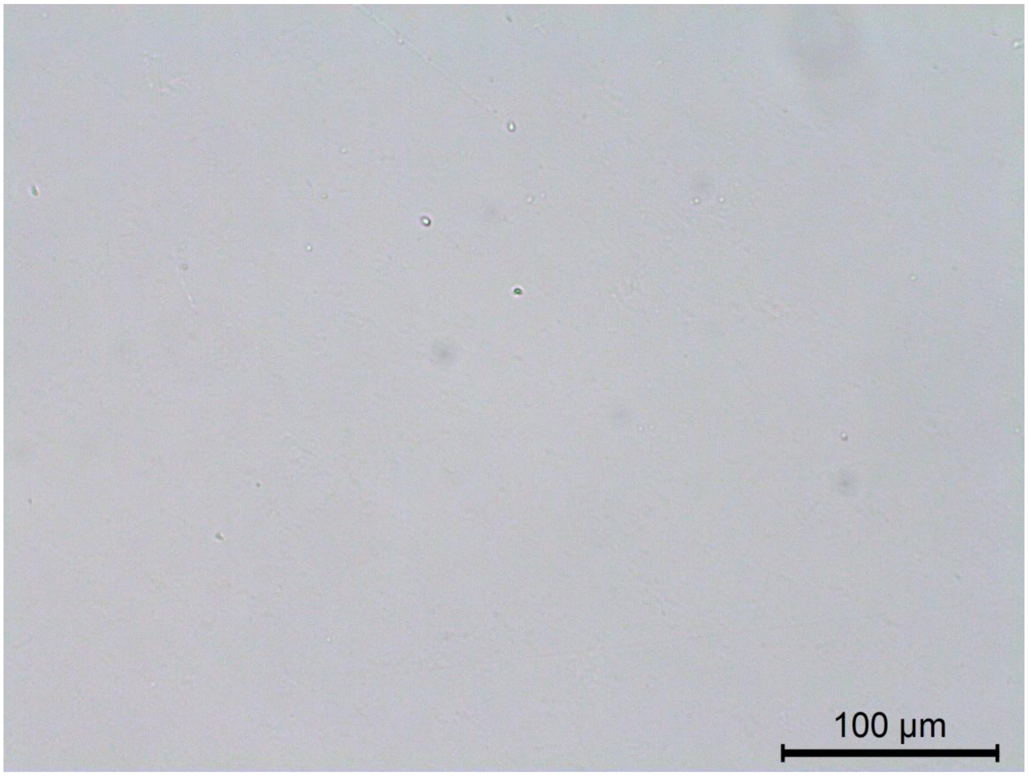


(d)

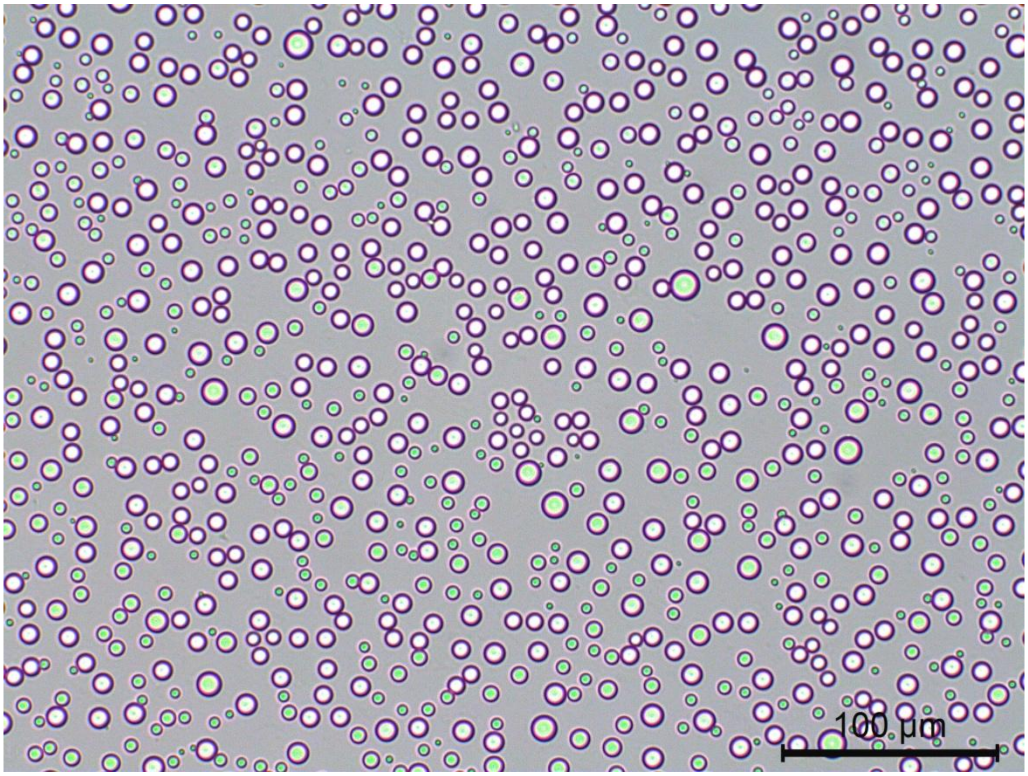


(e)

**Figure 10 :** Optical micrographs of 0.03M TBADBS at (a) 20 °C, (b) 40.0 °C, (c) 40.5 °C, (d) 40.8 °C and (e) CP=41°C)



(a)



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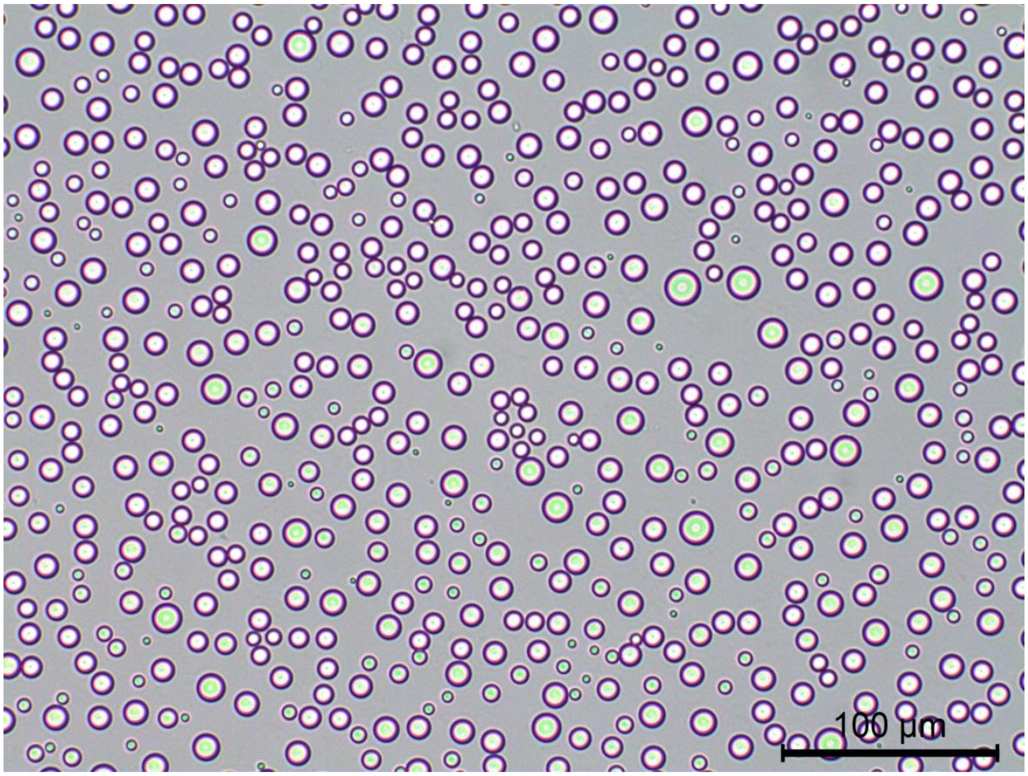

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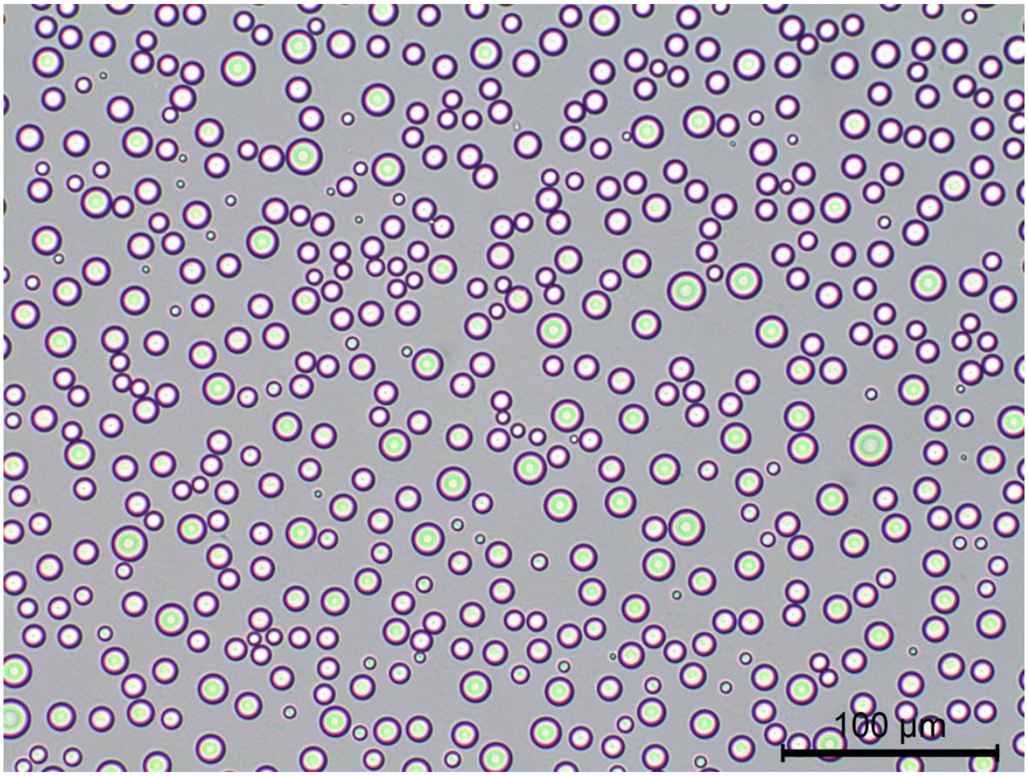

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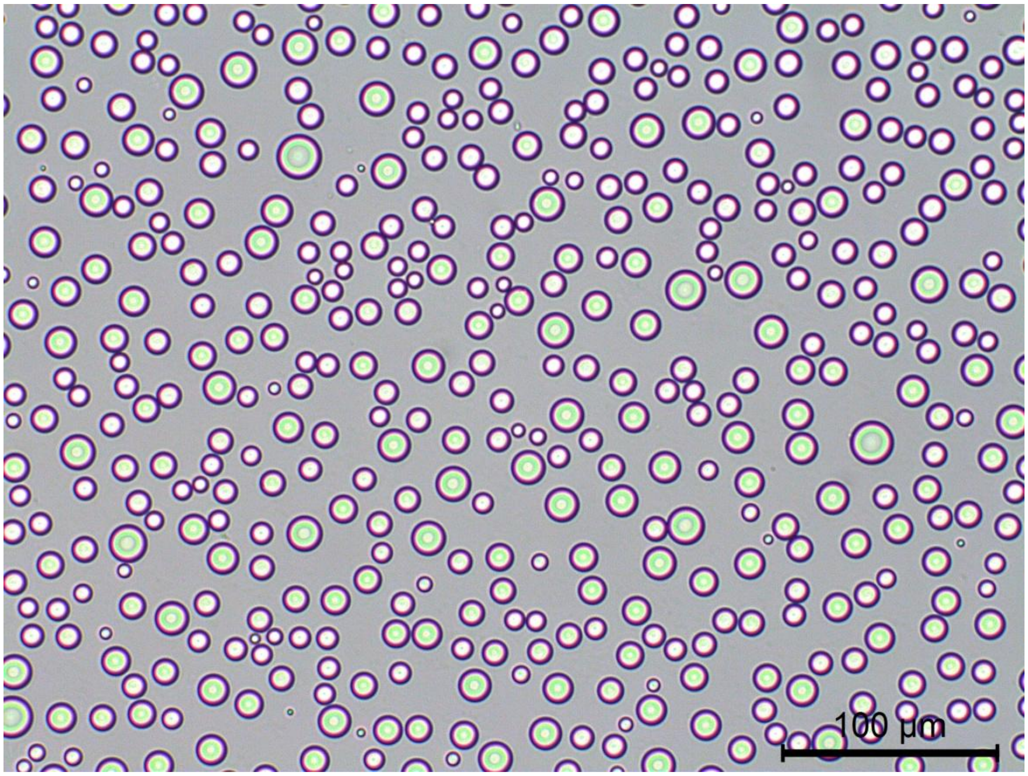

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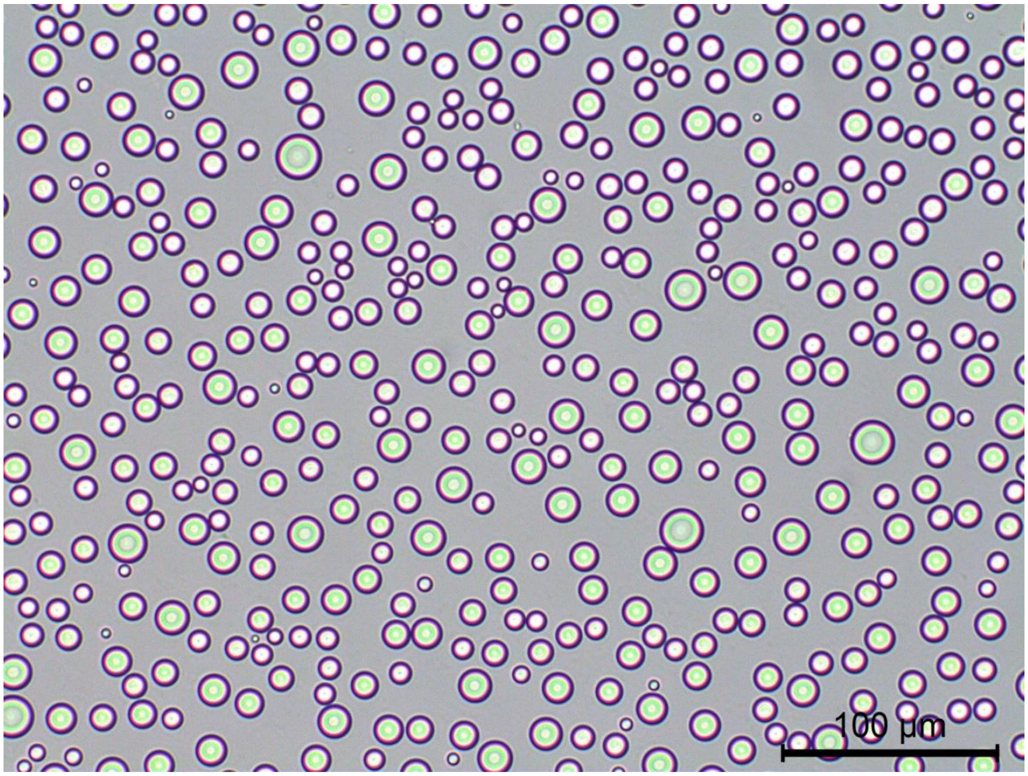
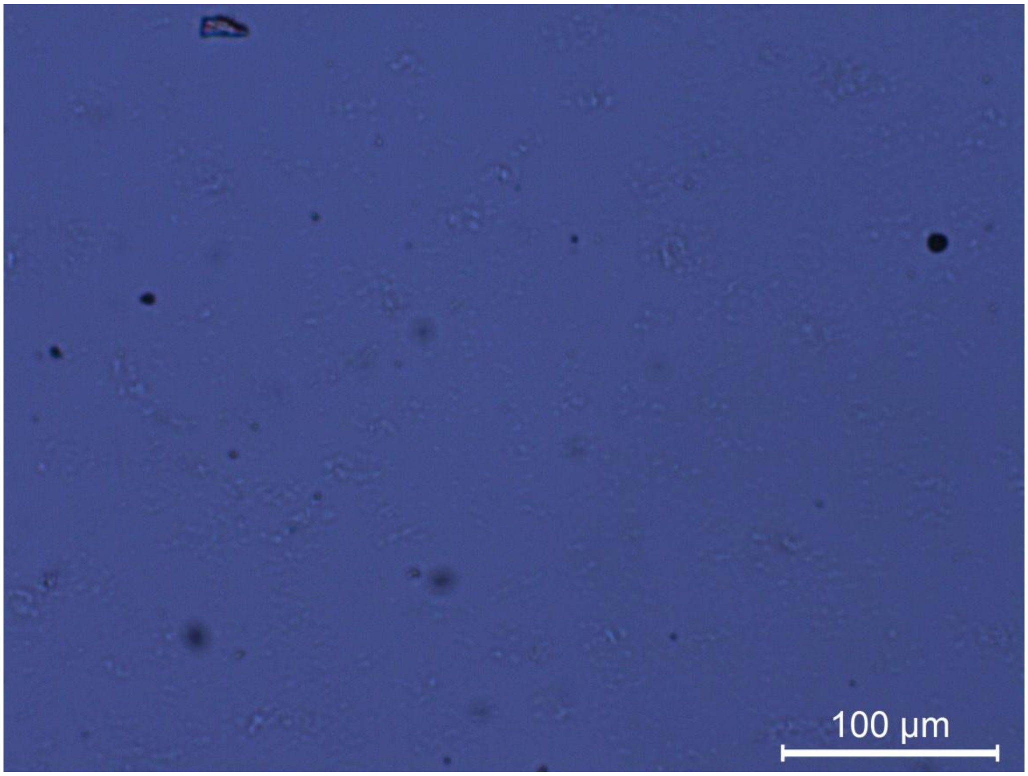
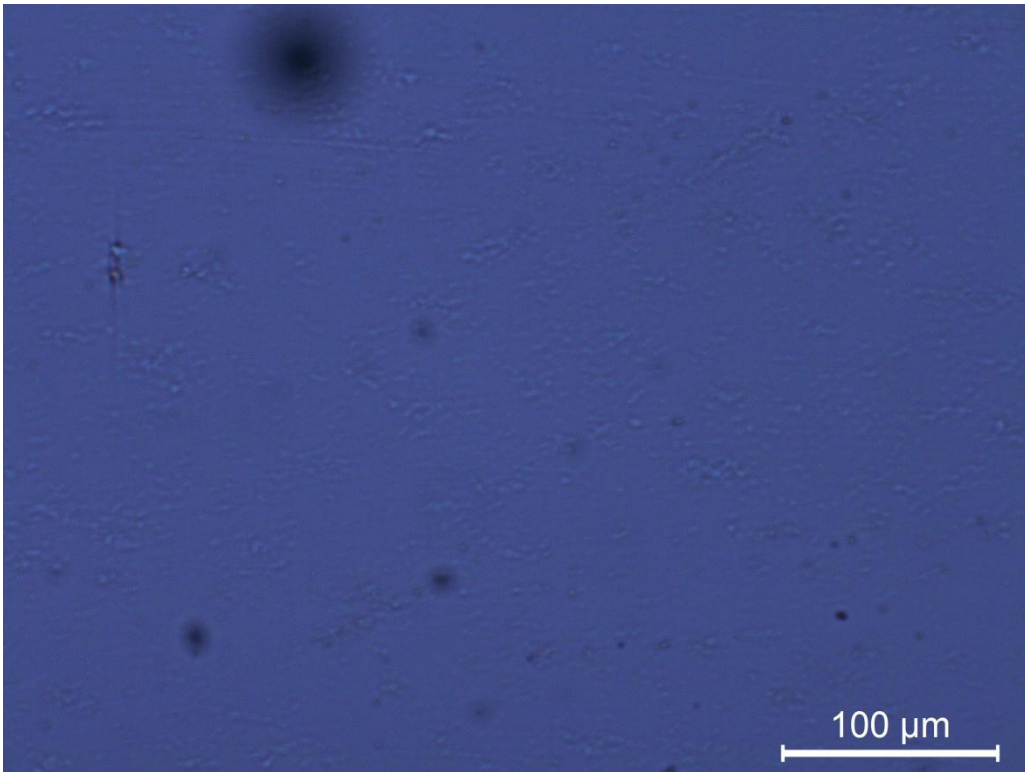


(f)

**Figure 11**: Optical micrographs of 0.25M TBAMES at (a) 60 °C, (b) 63.5 °C, (c) 64.0 °C, (d) 64.4 °C (e) 64.8 °C and (e)  CP=65.0°C)



(a)



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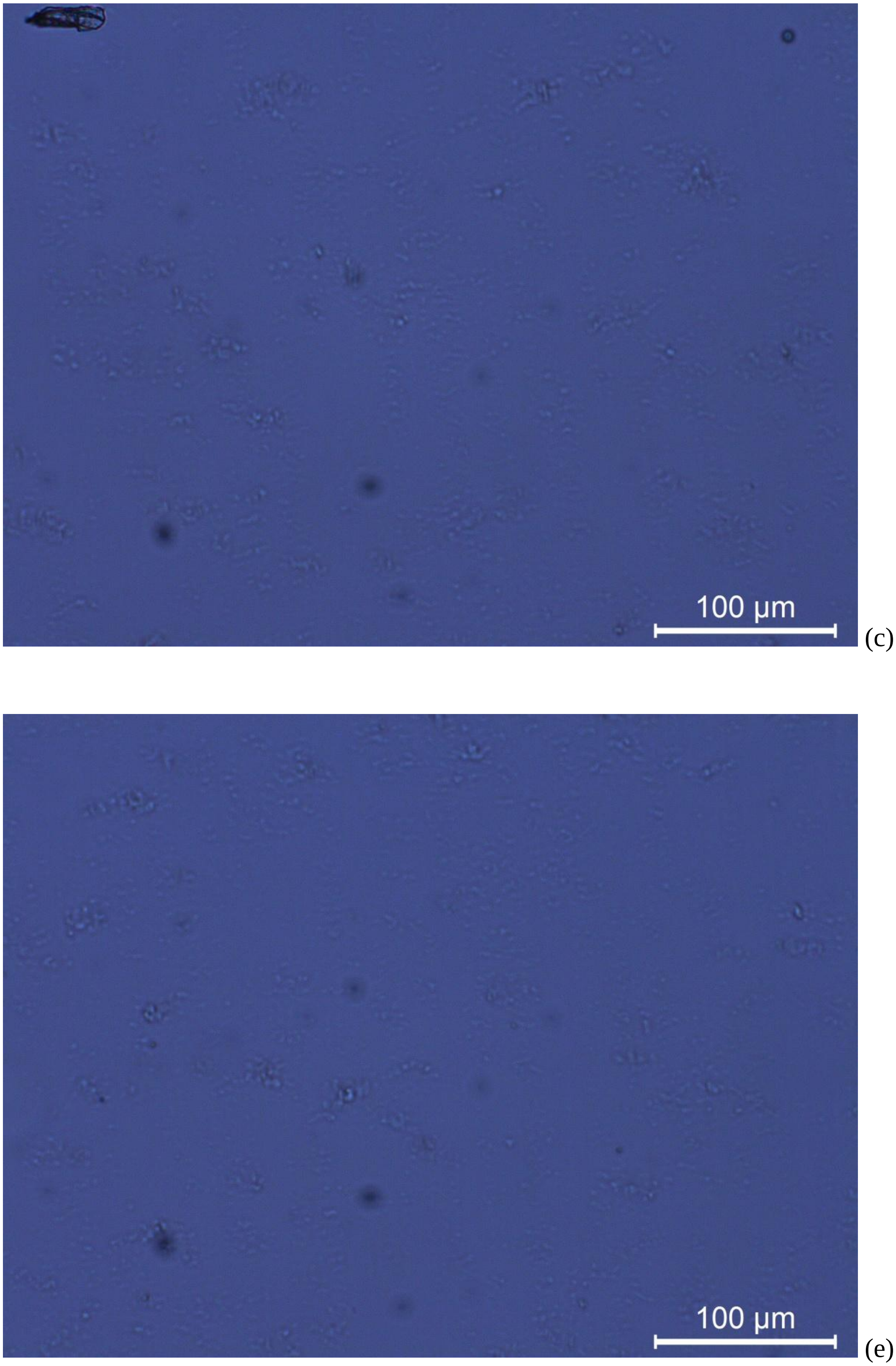

Figure 12: Optical micrographs of the rich phase of 0.1M TBADS at (a) 20 °C, (b) 25.0 °C, (c) 30.0 °C, (d)  32.0 °C

## 5.3. Conclusions

From the 2D NMR data, the prominent temperature effect could be studied and the tumbling rate of butyl chains of the counterion has been found dependent on the nature of surfactant head/ hydrophobic portion. It is confirmed that $TBA^+$ ions associate closely with $DS^-$ to form bigger micelles at higher temperature near CP. Temperature induces both hydrophobic and electrostatic interactions responsible for the approach of aggregates near to each other. This approach is facilitated by the dehydration of both counterion and head group at elevated temperature (near the CP). The increase in attractive interactions and their role in the formation of bigger aggregates are seen visually by POM data. The POM data also provide evidence regarding the formation of cloud of aggregates which grows to a critical limit in order to visualize in the form of clouding or phase separation.