

Clouding Phenomenon of Ionic Surfactant (+TBAB) in Deep Eutectic Solvents

Contents

5.1 Introduction

5.2 Experimental section

5.3 Results and Discussion

5.3.1 Clouding of SDS in water in reline and reline in water

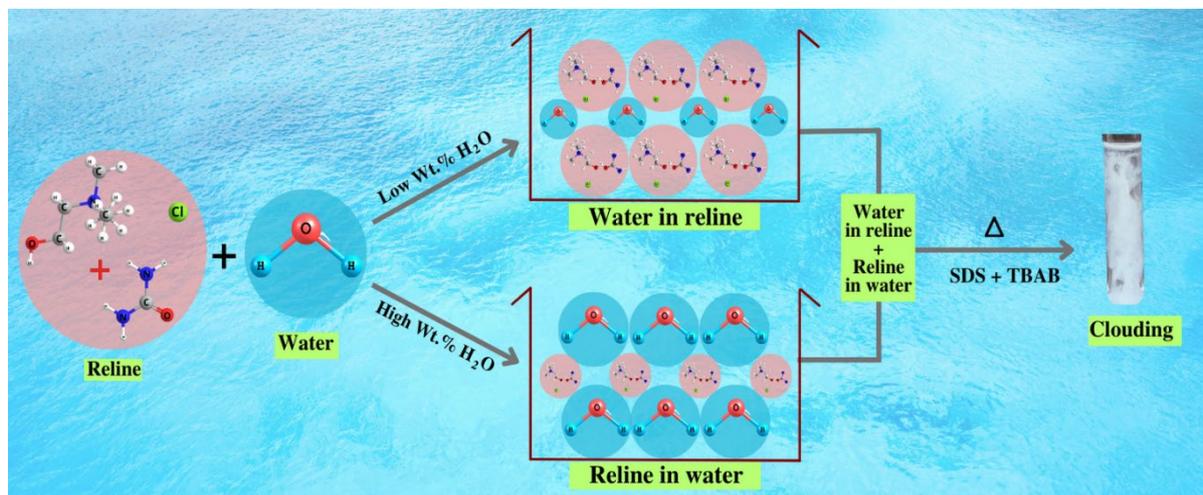
5.3.2 CP measurement of SDS + TBAB in ternary DES -water system

5.3.3 CP variation with $ZnCl_2/CdCl_2$ for 0.1M SDS + 0.1M TBAB in water in reline

5.4 Conclusion

5.5 References

This chapter mainly focused on the clouding behaviour of the anionic surfactant (SDS) (+TBAB) in DESs (reline and ternary DES) with water. Variations of cloud point (CP) against [metal salt] for 0.1M SDS + 0.1M TBAB in 40 wt.% water in water in reline region were also described in this chapter.



5.1 Introduction

It is commonly known that at higher temperatures, the behaviour of ionic and nonionic surfactant solutions is distinct [1,2]. The cloud point (CP) of a surfactant is the temperature at which the surfactant solution undergoes phase separation, resulting in the formation of a cloudy or turbid appearance [3]. The occurrence of clouding is a prominent characteristic in solutions containing non-ionic surfactants, but it is less frequent in solutions containing ionic surfactants in water. There have been recent reports of clouding occurring in ionic surfactant solutions under various experimental conditions, such as different pH, specific counter ions (quaternary), specific head groups, and molecular structure [4–6].

The clouding phenomena appear to be significantly influenced by the dehydration of the head group and counterion, which is a result of their mutual presence. Under specific conditions, numerous amphiphilic drugs exhibit a clouding phenomenon [7,8]. The clouding phenomena in a charged micellar solution occur as a result of the bonding between counterions with opposite charges and the headgroup [4,8]. Thus, the formation of cloudiness in ionic surfactant systems primarily requires the existence of a quaternary salt (tetra-n-butyl ammonium bromide; TBA⁺ counter ion), which covers the charge of the micelles. Another function of this salt is to bind micelles collectively through short hydrocarbon chains.

The quaternary counterion appears to have a dual function, resulting in an atypical clouding effect in aqueous ionic surfactants. Firstly, it gradually discharges the micelle, causing the system toward a pseudo-nonionic state. Secondly, it interacts with the micellar surface through hydrophobic interactions [9]. The phenomenon of counterion effect involving quaternary counterions is currently receiving increased attention in micellar systems [10,11]. A clouding behavior of surfactants with and without salts in an aqueous medium is common and it has been studied for the last five decades [12–15]. Nowadays, researchers are working on the determination of CP in non-aqueous media like ionic liquids and DESs [3,16–18].

The nano-structure of DES, with or without water, can influence the aggregation/association behaviour of surface-active agents (Surfactants). Surfactants, due to their solution behaviour, are of immense importance in different applications of the colloidal field [19]. The synergy between surfactants and DES can boost their application in different areas of biomedical sciences [20,21]. An upward trend has been seen in recent times in studying the physicochemical/association behaviour of surfactants and their interconnection with DES [22–25].

Presently, metals are separated from their complex mixtures via an electrochemical route [26–28]. Reline has been shown to dissolve different metal oxides and ligands [29]. Due to the miscibility of reline with water, it cannot be used for extraction purposes. However, surfactants are known to form biphasic systems at elevated temperatures (CP) [30]. At CP, the surfactant solution shows liquid-liquid phase separation (LLPS) with surfactant-rich and surfactant-lean phases [31]. This fact can be used to develop extraction methodologies for metals from complex mixtures or matrices. On the downside, LLPS is usually shown by non-ionic surfactants, which cannot bind charge moieties/ions [32]. The problem can be solved if an ionic surfactant can show LLPS individually or in the presence of some additives. It has been demonstrated that anionic surfactants can show clouding or LLPS in the presence of specific quaternary ammonium bromides (TBAB) [33].

The above facts inspired us to study the clouding behaviour of sodium dodecyl sulphate (SDS) with and without TBAB in reline or the reline-water mixture in both ranges of composition [34,35] i.e., water in reline or reline in water. Additionally, the CP of SDS is also determined in the ternary DES system (ChCl: urea: glycerol; 1:1:1(CUG I) and 1:1.5:0.5 (CUG II)) with water. The influence of DES components (ChCl and urea) on the CP of the SDS+TBAB system was also checked in the present work and it is observed that there is no

effect of DES components on the CP of the SDS + TBAB system. Further, the effect of the addition of metal salt (zinc sulphate, $ZnSO_4$ or Cadmium chloride, $CdCl_2$) has also been seen on the clouding behaviour of SDS (0.1M) + TBAB (0.1M) in water in reline (40% water). The purpose of the present study is to explore clouding in reline(+water) based surfactant solutions and their potential use for cloud point extraction methodologies (CPEM) for metal extraction.

5.2 Experimental section

The materials and methods used are discussed in chapter 2.

5.3 Result and discussion

5.3.1 Clouding of SDS in water in reline and reline in water

Clouding behaviour (or LLPS) in aqueous SDS solutions has been reported with TBAB in the last two decades [36–38]. It is known that organic counter ions (e.g., TBA^+) interact with the sulphate head group via close ion pair interaction. TBA^+ (having four n-butyl alkyl chains together with N atom having a positive charge) can interact solvophobicly (via butyl chains) and electrostatically (due to opposite charges) with the anionic micellar surface [4,39]. This causes an increase in surfactant packing parameter (P) [40] and the formation of larger aggregates. These aggregates of higher hydrophobicity are sufficient to produce clouding followed by phase separation (on standing, LLPS) [5]. Various micellar architectural structures formed in an aqueous solution were reported and interpreted in terms of increasing P [41–43]. CP is dependent directly on [SDS] and inversely on [TBAB] [44].

In recent reports, it has been mentioned that SDS can form cylindrical micelles in reline due to Ch^+ binding with sulphate head group of SDS [25,45]. This binding may decrease in the presence of water and replacement with a more hydrophobic cation (TBA^+) is expected in the present SDS + TBAB system. In a separate study on counter ion binding on the micellization process, it was observed that the organic counter ion of dodecyl sulphate species (DS^-) shows lower CMC than the inorganic counter ion [46]. Extending this analogy, one can expect the preferred binding of TBA^+ over Na^+ or Ch^+ . Since counter ion binding or solvation (hydration) depends upon the nature of the solvent and hence can influence clouding phenomenon observed in the present case. In another study, the effect of addition of quaternary counter ion to the SDS solution showed micellar growth which was explained based on $TBA^+ - DS^-$ interactions. The present clouding phenomenon could be a result of the replacement of Na^+ or Ch^+ by TBA^+ which can contribute toward micellar growth, in forming hydrophobic and dehydrated aggregates resulting in clouding and phase separation [10,47].

In the present study, SDS showed clouding behaviour with TBAB both in water in reline and reline in the water region. CP data of SDS + TBAB (with different concentrations) in both regions are compiled in **Table 5.1**. It may be mentioned here that clouding was not observed above 66% of reline in the reline-water mixture in water in reline. Further, SDS + TBAB was not soluble in higher reline content in the water in the reline region which restricted the CP studies below this composition.

Table 5.1: Compilation of CP (K) data of SDS + TBAB in water in reline and reline in the water region.

Wt.% of water	CP (K)					
	0.1M TBAB + 0.1M SDS	0.1M TBAB +0.05M SDS	0.1M TBAB +0.075M SDS	0.1M TBAB +0.125M SDS	0.1M SDS + 0.075M TBAB	0.1M SDS+ 0.125M TBAB
100	315	305	309	325	326	306
90	322	315	315	329	329	314
80	325	319	319	330	338	317
70	334	323	327	333	341	320
60	333	324	328	332	346	319
50	327	322	327	328	338	318
40	329	322	324	328	333	322
38	327	322	325	329	340	316
36	-	321	325	320	339	315
33.3	327	-	-	-	-	-

A perusal of data shown in **Figure 5.1** dictates that the dependence of CP in DES (reline-water mixtures) shows a similar trend as observed in the aqueous system (i.e., $CP \propto [SDS]$ and $CP \propto 1/[TBAB]$) [48–50]. However, CP values are found to be higher than the values obtained in an aqueous solution. In a separate study, it has been reported that DES clusters remain (between 2w-10w or ~12-25 weight% of water) but are separated by added water [51]. This water can interact both with reline and the micellar surface of the SDS + TBAB system.

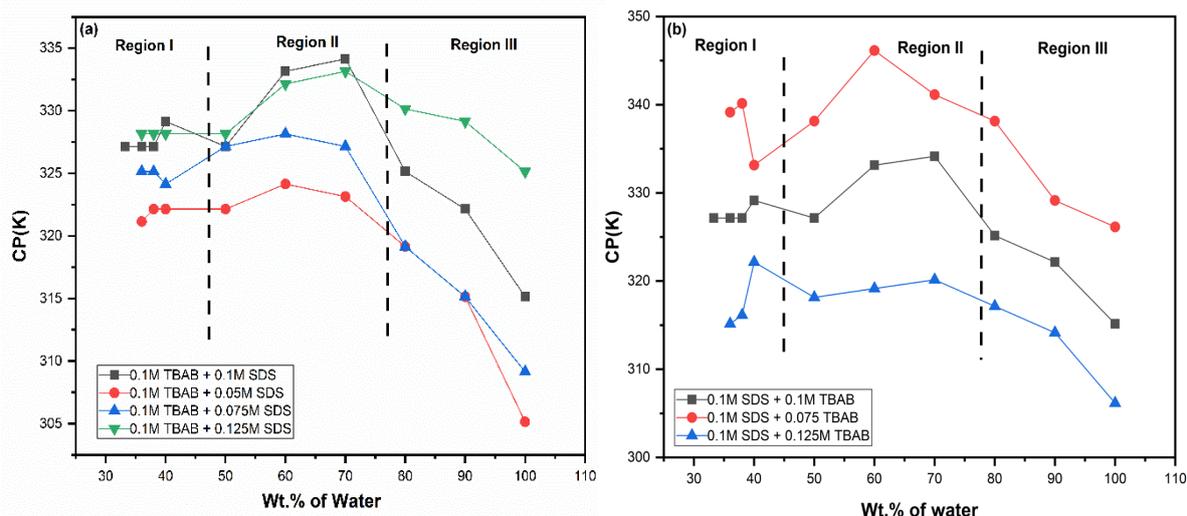


Figure 5.1: Variation of cloud point (CP) of SDS+TBAB against wt.% of water: (a) effect of [SDS], (b) effect of [TBAB].

Above water and micellar surface interaction strength is expected to be higher than without reline in the system and seems responsible for higher CP. TBAB is known to form DES with HBD (e.g., alkanolic acid) [52] and, therefore, one can expect the interaction of TBAB with HBD (urea). Latter interaction results in decreased partitioning of TBAB towards the micellar surface and is responsible for the increase in CP. This trend of CP increase persists in region I, where water in reline solvent is present. However, once a sizable amount of water is added to reline, then the distribution of TBAB between water in reline and the micellar surface is shifted solely to the micellar surface. These two effects compensate for each other and show a level-off behaviour. However, in region III, both TBAB and ChCl compete for the site at the anionic micellar surface with a simultaneous gradual decrease in CP in region III (reline in water region).

It may be mentioned here that CP values are always higher than those observed in the pure aqueous system of SDS + TBAB. Both Ch^+ and TBA^+ compete for anionic micellar surface; therefore, effective [TBAB] will be lesser at the micellar surface. Moreover, Ch^+ ion is expected to be more hydrophilic than the TBA^+ ion. The above two inter-related factors may increase the water content of the micellar surface, which requires a higher temperature to remove this water and to observe the clouding phenomenon (reason for the observance of higher CP in region III).

5.3.2 CP measurement of SDS + TBAB in ternary DES -water system

The CP data of SDS + TBAB (with varying concentrations of both) in ternary DESs made up of ChCl, urea, and glycerol at different eutectic ratios (ChCl:U:G; 1:1:1 (CUG I) and ChCl:U:G; 1:1.5:0.5 (CUG II)) in the presence of water, are summarized in **Table 5.2** and **Table 5.3** respectively. The micellar head group region is commonly associated with a specific amount of water molecules for hydration. In ionic micellar solutions, counterion condensation plays a crucial role in determining the effective charge on the micelle. This, in turn, affects the micelle's formation, structure, and interaction. The SDS solution in its pure form does not exhibit any cloudiness, however, the introduction of TBAB into the system is the cause of the observed clouding effect.

Table 5.2: CP (K) data of SDS + TBAB in Ternary DES (CUG I)-water system.

Wt.% of water	CP (K)			
	0.1M TBAB + 0.1M SDS	0.1M TBAB +0.075M SDS	0.1M TBAB +0.125M SDS	0.1M SDS + 0.075M TBAB
33.3	296	291	299	308
30	326	331	318	345
20	328	351	358	335
10	348	342	341	328

It is observed that CP increases as the water content decreases and ternary DES content increases. It may be due to the interaction between surfactant micelles and network of DES.

Table 5.3: CP (K) data of SDS + TBAB in Ternary DES (CUG II)-water system.

Wt.% of water	CP (K)			
	0.1M TBAB + 0.1M SDS	0.1M TBAB +0.075M SDS	0.1M TBAB +0.125M SDS	0.1M SDS + 0.075M TBAB
33.3	309	305	311	320
30	342	336	359	358
20	338	355	362	355
10	355	361	369	365

CP value is higher in CUG II compared to CUG I. As the urea content increases and glycerol content decreases in ternary DES, the CP value for SDS + TBAB increases. It may be due to less hydrogen bonding in CUG II.

5.3.3 CP variation with ZnCl₂/CdCl₂ for 0.1M SDS + 0.1M TBAB in water in reline

The effect of the addition of ZnCl₂ and CdCl₂ on the CP behaviour has been depicted in **Figure 5.2**. It has been seen that CdCl₂ causes CP to increase while ZnSO₄ causes a reverse effect (decreasing). Both Zn⁺² and Cd⁺² will compete with TBA⁺ for DES-water motive and SDS micellar surface. Zn⁺² has a lower crystal radius than Cd⁺². However, the hydration capacity of Zn⁺² will be higher than Cd⁺². These interdependent effects may affect the metal ion interaction with the micellar surface. Zn⁺² may remove the solvent (water) from the head group site of the micelle and cause a decrease in CP, as observed in **Figure 5.2**. However, such effects are weaker in the case of Cd⁺² ion and responsible for the weak dependence of CP on [CdCl₂].

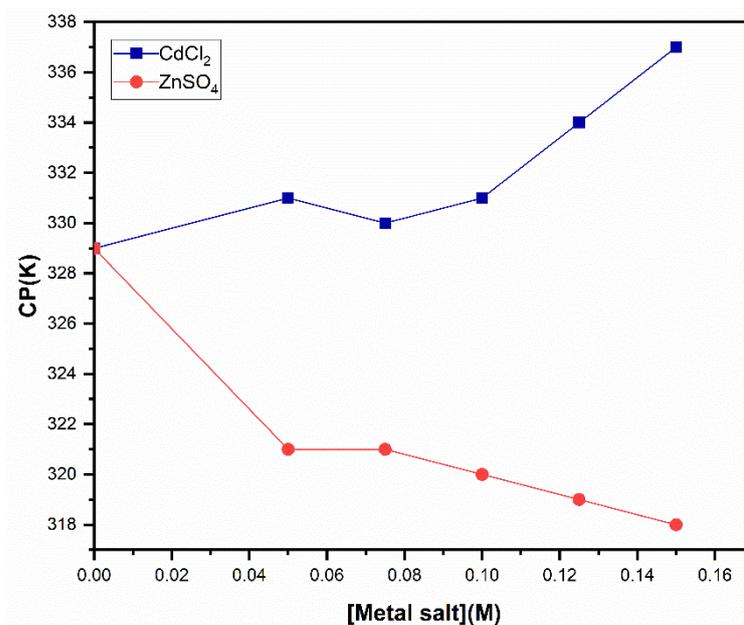


Figure 5.2: Variation of cloud point (CP) against [metal salt] for 0.1M SDS + 0.1M TBAB in 40 wt.% water in water in reline region: ■ CdCl₂, ● ZnSO₄.

5.4 Conclusion

From the data presented here, it can be concluded that the clouding phenomenon can be observed in the reline-water mixtures as in an aqueous solution. The CP data show that water in reline converts to reline in water through the medium region (region II). CP values have been found dependent on [SDS] and [TBAB] in reverse fashion, respectively. CP values increase as the glycerol content decreases in ternary DES. Further, CP values were consistently higher than observed in pure water. In a selective system effect of the addition of CdCl₂ and ZnSO₄ shows opposite CP variation, which can be correlated with hydrated and crystal radii of metal ions. The study can open new extraction strategies for obtaining metal from various matrices [53]. CP data presented here help in finding other surfactant salt combinations for CP studies in DES solvents.

5.5 References

- [1] R. Dong and J. Hao, *Chem Rev* **110**, 4978 (2010).
- [2] R. Zana and C. Weill, *Journal de Physique Lettres* **46**, 953 (1985).
- [3] R. Halko, I. Hagarová, and V. Andruch, *J Chromatogr A* **1701**, 464053 (2023).
- [4] S. Kumar, A. Bhadoria, H. Patel, and V. K. Aswal, *Journal of Physical Chemistry B* **116**, 3699 (2012).
- [5] A. Bhadoria, S. Kumar, V. K. Aswal, and S. Kumar, *RSC Adv* **5**, 23778 (2015).
- [6] B. L. Bales and R. Zana, *Langmuir* **20**, 1579 (2004).
- [7] Md. S. Alam, S. Kumar, A. Z. Naqvi, and Kabir-ud-Din, *Colloids Surf B Biointerfaces* **53**, 60 (2006).
- [8] S. Kumar, S. Alam, N. Parveen, and Kabir-ud-Din, *Colloid Polym Sci* **284**, 1459 (2006).
- [9] S. Kumar, Z. A. Khan, and Kabir-ud-Din, *J Surfactants Deterg* **7**, 367 (2004).
- [10] S. Kumar, V. K. Aswal, P. S. Goyalb, and K. -Ud-Dina, *Micellar Growth in the Presence of Quaternary Ammonium Salts A SANS Study*, 1998.
- [11] U. Thapa, J. Dey, S. Kumar, P. A. Hassan, V. K. Aswal, and K. Ismail, *Soft Matter* **9**, 11225 (2013).
- [12] P. Mukherjee, S. K. Padhan, S. Dash, S. Patel, and B. K. Mishra, *Adv Colloid Interface Sci* **162**, 59 (2011).
- [13] A. Z. Naqvi and Kabir-ud-Din, *Colloids Surf B Biointerfaces* **165**, 325 (2018).
- [14] Md. Diluar Hossain, S. Afrin, A. Atiya, K. Anjum, M. Shanimul Hasan, Md. Rafikul Islam, T. Hasan, S. Rana, and Md. Anamul Hoque, *J Mol Liq* **385**, 122334 (2023).
- [15] A. S. Sadaghiana and A. Khan, *J Colloid Interface Sci* **144**, 191 (1991).
- [16] Anjali and S. Pandey, *Langmuir* **40**, 2254 (2024).
- [17] D. Snigur, E. A. Azooz, O. Zhukovetska, O. Guzenko, and W. Mortada, *TrAC Trends in Analytical Chemistry* **164**, 117113 (2023).
- [18] D. Hirpara, B. Patel, V. Chavda, A. Desai, and S. Kumar, *J Mol Liq* **364**, 119991 (2022).

- [19] Janos H. Fendler, Trends Biochem Sci **8**, 225 (1983).
- [20] A. Shishov, A. Bulatov, M. Locatelli, S. Carradori, and V. Andruch, Microchemical Journal.
- [21] A. M. Curreri, S. Mitragotri, and E. E. L. Tanner, Advanced Science **8**, (2021).
- [22] M. Pal, R. Rai, A. Yadav, R. Khanna, G. A. Baker, and S. Pandey, Langmuir **30**, 13191 (2014).
- [23] Komal, G. Singh, G. Singh, and T. S. Kang, ACS Omega **3**, 13387 (2018).
- [24] R. K. Banjare, M. K. Banjare, K. Behera, S. Pandey, and K. K. Ghosh, ACS Omega **5**, 19350 (2020).
- [25] R. S. Atri, A. Sanchez-Fernandez, O. S. Hammond, I. Manasi, J. Douth, J. P. Tellam, and K. J. Edler, Journal of Physical Chemistry B **124**, 6004 (2020).
- [26] A. P. Abbott, G. Capper, D. L. Davies, and P. Shikotra, Transactions of the Institutions of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy **115**, 15 (2006).
- [27] Q. Song, Q. Xia, X. Yuan, and Z. Xu, Resour Conserv Recycl **190**, 106804 (2023).
- [28] C. A. C. Sequeira and D. M. F. Santos, J Braz Chem Soc **20**, 387 (2009).
- [29] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, and P. Shikotra, Inorg Chem **44**, 6497 (2005).
- [30] Milton J. Rosen, *Surfactant and Interfacial Phenomena*, third (2012).
- [31] O. A. Q. Jimenez, J. M. Costa, B. R. de Souza, A. C. Medeiros, E. G. Monteiro-Junior, and R. C. Basso, Processes **10**, 2023 (2022).
- [32] R. Dong and J. Hao, Chem Rev **110**, 4978 (2010).
- [33] S. Kumar, H. Patel, and S. R. Patil, Colloid Polym Sci **291**, 2069 (2013).
- [34] H. Zhang, M. L. Ferrer, M. J. Roldán-Ruiz, R. J. Jiménez-Riobóo, M. C. Gutiérrez, and F. Del Monte, Journal of Physical Chemistry B **124**, 4002 (2020).
- [35] M. J. Roldán-Ruiz, R. J. Jiménez-Riobóo, M. C. Gutiérrez, M. L. Ferrer, and F. del Monte, J Mol Liq **284**, 175 (2019).

- [36] R. Zana, M. Benrraou, and B. L. Bales, *Journal of Physical Chemistry B* **108**, 18195 (2004).
- [37] S. Kumar, V. K. Aswal, A. Z. Naqvi, P. S. Goyal, and Kabir-Ud-Din, *Langmuir* **17**, 2549 (2001).
- [38] S. Kumar, A. Bhadoria, H. Patel, and V. K. Aswal, *Journal of Physical Chemistry B* **116**, 3699 (2012).
- [39] N. Vlachy, B. Jagoda-Cwiklik, R. Vácha, D. Touraud, P. Jungwirth, and W. Kunz, *Advances in Colloid and Interface Science*.
- [40] J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*.
- [41] S. R. Raghavan and E. W. Kaler, *Langmuir* **17**, 300 (2001).
- [42] N. Vlachy, A. Renoncourt, M. Drechsler, J. M. Verbavatz, D. Touraud, and W. Kunz, *J Colloid Interface Sci* **320**, 360 (2008).
- [43] L. Sreejith, S. Parathakkat, S. M. Nair, S. Kumar, G. Varma, P. A. Hassan, and Y. Talmon, *Journal of Physical Chemistry B* **115**, 464 (2011).
- [44] S. Kumar, D. Sharma, Z. A. Khan, and Kabir-Ud-Din, *Langmuir* **17**, 5813 (2001).
- [45] T. Arnold, A. J. Jackson, A. Sanchez-Fernandez, D. Magnone, A. E. Terry, and K. J. Edler, *Langmuir* **31**, 12894 (2015).
- [46] A. Sanchez-Fernandez, O. S. Hammond, K. J. Edler, T. Arnold, J. Douth, R. M. Dalgliesh, P. Li, K. Ma, and A. J. Jackson, *Physical Chemistry Chemical Physics* **20**, 13952 (2018).
- [47] S. Kumar, V. K. Aswal, A. Z. Naqvi, P. S. Goyal, and Kabir-Ud-Din, *Langmuir* **17**, 2549 (2001).
- [48] S. Kumar, D. Sharma, and Kabir-ud-Din, *Langmuir* **19**, 3539 (2003).
- [49] S. Kumar, D. Sharma, Z. A. Khan, and Kabir-ud-Din, *Langmuir* **18**, 4205 (2002).
- [50] S. Kumar, D. Sharma, Z. A. Khan, and Kabir-Ud-Din, *Langmuir* **17**, 5813 (2001).
- [51] O. S. Hammond, D. T. Bowron, and K. J. Edler, *Angewandte Chemie - International Edition* **56**, 9782 (2017).

- [52] Y. Marcus, *Deep Eutectic Solvents* (Springer International Publishing, 2019).
- [53] E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chemical Reviews*.