Colloid Polym Sci (2005) 284: 214–217
DOI 10.1007/s00396-005-1359-5

SHORT COMMUNICATION

Christian Lange
Thomas Wolff

Calorimetric effects in rapidly frozen micellar solutions below the macroscopic melting point

Received: 30 March 2005
Accepted: 24 May 2005

C. Lange · T. Wolff (✉)
Technische Universität Dresden,
Institut für Physikalische Chemie,
01062, Germany
E-mail:
thomas.wolff@chemie.tu-dresden.de
Tel.: +49-351-46333633
Fax: +49-351-46333391

Abstract Small samples of aqueous solutions of three cetyltrimethylammonium (CTA) salts and of sodium dodecyl sulfate (SDS) were rapidly frozen by plunging into liquid Nitrogen. The frozen samples were heated and recooled in a differential scanning calorimeter between −50 and −5°C, i.e., below the macroscopic melting point. Upon first heating an exothermic process was observed in CTA salts (but not in SDS) at between −20 and −30°C. The process was assigned to crystallization of micellar microdomains that had not taken place upon rapid freezing. The mobility for crystallization in the frozen environment was possible because of local melting point depression. In the presence of sufficient sodium chloride the local melting was proven by according endo- and exothermic DSC peaks upon heating and recooling, respectively.

Keywords Cetyltrimethylammonium salts · Frozen micelles · Differential scanning calorimetry · Local phase transition

Introduction

The question of whether or not aqueous surfactant micellar structures may be conserved upon rapid freezing has been discussed for more than twenty years. Initially Kevan et al. presented evidence from photoionization experiments, which were successful in frozen micellar solutions but not in surfactant-free frozen water [1]. At approximately the same time, Bachmann et al. published freeze-fracture electron micrographs, which directly pictured the contours of small micelles in frozen solution [2]. This technique later allowed the investigation of structures of more complex surfactant systems such as microemulsions [3]. In any material, however, the equilibrium structure of the frozen, crystalline state necessarily differs from the equilibrium structure of molecules or aggregates in the liquid state or in solution, which moreover allows thermal fluctuations. Upon sufficient rapid freezing it is expected that the liquid structure is retained. But the observation of micellar entities in electron micrographs does not ensure that the micelle–water interface region as well as the oil-droplet-like micellar interior has not been transformed to a crystalline microphase, especially when specific care for avoiding the Leidenfrost phenomenon was not taken. This can be done by quickly plunging samples of small dimensions into liquid propane at 77 K, cf. [4]. However, often the necessary equipment is not available and the samples have to be frozen by dipping them into liquid Nitrogen, where the heat transfer is restricted since evaporating gaseous Nitrogen is just around the sample to be frozen.

Here we present calorimetric evidence for an exothermic crystallization process in frozen aqueous cetyltrimethyl ammonium micelles which had been cooled down in liquid Nitrogen. The effect occurs upon heating frozen samples at temperatures well below the macroscopic melting point and indicates a nonequilibrium structure of the frozen micelles. To our knowledge, calorimetric investigations in frozen micellar solutions of common surfactants are not covered in the literature.

Experimental

Chemicals and solutions

Recrystallized cetyltrimethylammonuim salts were available from previous studies [5, 6]. Aqueous solutions at room temperature were prepared using doubly distilled water.

Apparatus

Differential scanning calorimetry was performed using a Setaram DSC 121 apparatus. Enthalpies calculated from DSC curves vary by ±5% at NaCl concentrations below 0.05 mol/dm^3 and by ±10% at higher salt concentrations.

Sample preparation

Stainless steel DSC-crucibles of 0.15 dm^3 volume were filled with between 0.07 and 0.13 g of the liquid samples. The sealed crucibles were thrown into liquid Nitrogen for rapid cooling. The cooled samples were placed in the DSC apparatus set at −50°C. DSC diagrams then were recorded between −50°C and −5°C in both directions.

Results

Pure aqueous cetyltrimethylammonium bromide (CTAB)

Aqueous solutions containing CTAB at 0.2 mol/dm^3 in sealed DSC-crucibles (volume 0.15 dm^3) were rapidly frozen in liquid nitrogen, placed in the DSC apparatus and slowly (1–3 K/min) heated. An according DSC curve is shown in Fig. 1. It exhibits an exothermic peak around −22°C. Depending on the individual sample the peak may occur between −20 and −30°C.

The enthalpy of the exothermic peak increases linearly with the CTAB concentration as shown in Fig. 2, which excludes any dirt effect. As samples below and above a CTAB concentration of 0.3 mol/dm^3 fit in the line, there is no difference in the behavior of small spherical and rod-like micelles, respectively. Blank samples of pure water did not show any significant peak.

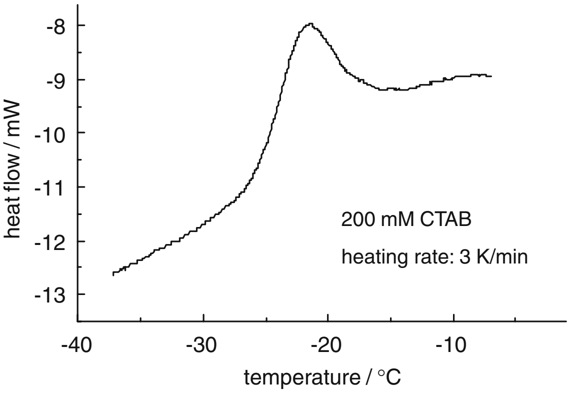

Fig. 1 DSC curve recorded upon heating a rapidly frozen aqueous CTAB solution

When the pure CTAB solutions were recooled after the heating procedure, no peak was found in the temperature range investigated (Fig. 3).

Upon slow cooling of liquid aqueous CTAB solutions crystals of the surfactant precipitate below the Krafft point of the system. In DSC curves this causes an exothermic peak setting on at 10°C (cooling rate 1 K/min). The enthalpy of this peak is 4.9 J/g for 200 mmol/dm^3 CTAB, i.e., it is in the same order of magnitude as the values in Fig. 1 and Fig. 2.

Pure aqueous cetyltrimethylammonium chloride (CTAC) and pure cetyltri-n-butylammonium bromide (CTBAB)

In order to show that the observed exothermic peak upon heating is not a peculiarity of CTAB we included aqueous CTAC and CTBAB solutions in the study. Qualitatively the same results as in CTAB were obtained. At 200 mmol/dm^3, however, the enthalpy of the exothermic peak is only 1.7 J/g for CTAC and 1.6 J/g for CTBAB to be compared to 2.8 J/g in the case of CTAB.

CTAB in the presence of salt

In the presence of sufficient (>0.05 mol/dm^3) sodium chloride an endothermic peak appears in 0.2 molar CTAB upon heating right at the temperature, at which the exothermic peak was found in the absence of NaCl. As revealed by Fig. 4, the endothermic peak is accompanied by an exothermic one, which appears at ca. −38°C upon recooling the sample. The enthalpies of exo- and endothermic peaks are complimentary as shown in Fig. 5, which comprises the results. As without salt, slow cooling of liquid CTAB solutions results in an exothermic DSC peak of 4.9 J/g (for 0.2 molar CTAB and 0.043 molar NaCl) due to the crystallization of CTAB.

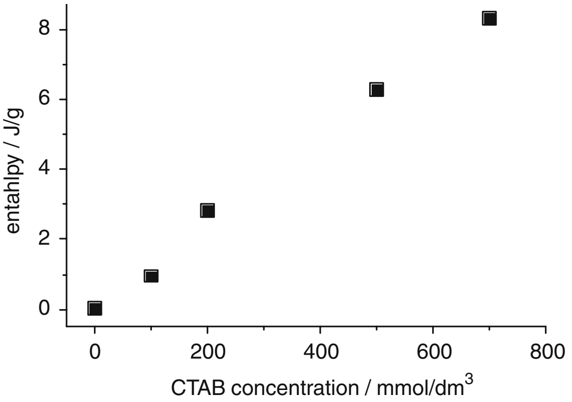

Fig. 2 Enthalpy of the exothermic peak in DSC diagrams of rapidly frozen aqueous CTAB solutions below the macroscopic melting point as a function of CTAB concentration

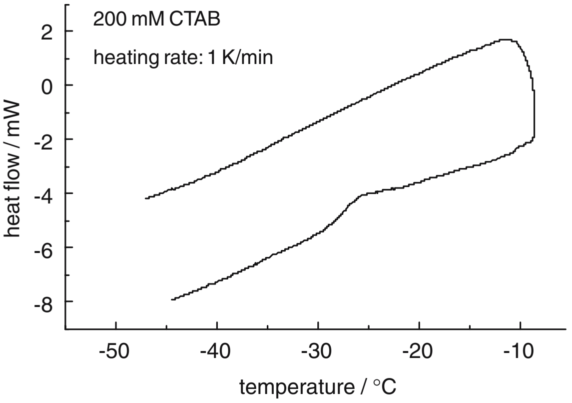

Fig. 3 DSC diagram recording heating (lower branch) and recooling (upper branch) of a rapidly frozen aqueous CTAB solution

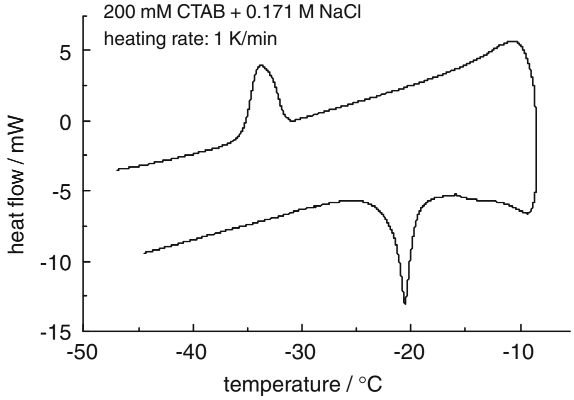

Fig. 4 Example of a DSC diagram recording heating and recooling a rapidly frozen CTAB solution in the presence of NaCl

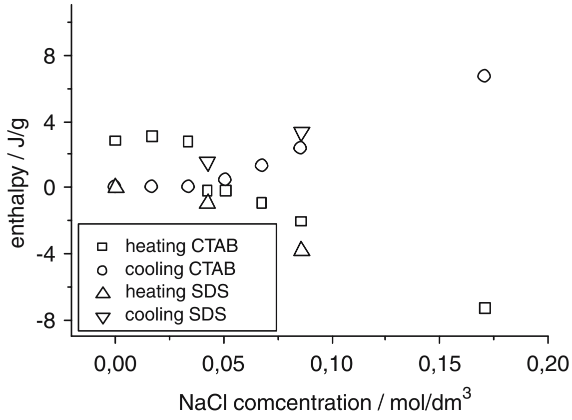

Fig. 5 Enthalpy of peaks appearing in rapidly frozen 0.2 molar aqueous surfactant solutions below the macroscopic melting point as a function of NaCl concentration (exothermic positive)

Sodium dodecyl sulfate (SDS) in the presence and absence of salt

Experiments with aqueous solutions (0.2 mol/dm^3) of the anionic surfactant SDS lead to different results. The exothermic process occurring upon heating of rapidly frozen solutions of all the cetyltrimethylammonium salts investigated cannot be detected in pure aqueous SDS solutions. In the presence of NaCl, however, we observe the endothermic and exothermic local melting peaks upon heating and recooling frozen samples as in the CTAB case (in the presence of salt). The SDS results are included in Fig. 5.

Discussion

Since considerable local melting point depression in the Stern layer region of small ionic micelles was established previously by means of spin probe investigations [6], calorimetric effects well below the macroscopic melting point might have been expected. These effects being due to local phase transitions (of water mainly), however, should be exothermic upon cooling and endothermic upon heating, as was found for loosely related microemulsion and vesicle systems [7]. Our results agree with this in the presence of sufficient NaCl for both CTAB and SDS solutions. As we observe single peaks in both temperature directions, we cannot discriminate different states of interfacial water as was found in nonionic microemulsions [8].

In rapidly frozen aqueous CTAB, however, we observe exothermic peaks upon the first heating. A possible cause for this arises when it is accepted that the disordered oil-droplet-like solution structure of the micellar interior is retained upon rapid freezing. The exothermic peak then reflects the crystallization of this region (including the hydration layer), which becomes possible upon heating at temperatures, at which a local softening of the micelle region starts (below the macroscopic melting point due to local melting point depression [6]). As this is a crystallization process it can be expected to be exothermic. In keeping with this explanation are the facts that (i) upon recooling, the samples do not show calorimetric effects and that (ii) the enthalpy of CTAB crystallization from liquid solutions is in the same order of magnitude. The latter enthalpy exceeds that observed in frozen solutions by 30–40%. A perfect agreement of the value in frozen solution cannot be expected since the dissociated counterions (residing in the still frozen aqueous surrounding) cannot find the cetyltrimethylammonium moieties. Fractions of counterions dissociated from aqueous surfactant micelles were found to be between 20 and 40%, depending on surfactant, temperature, and concentration [9, 10].

The missing of the exothermic process upon heating frozen SDS solutions might be a consequence of the shorter alkyl chain and the smaller micelle size, which allows crystallization while the sample is cooled down in liquid Nitrogen. The lower enthalpy of the exothermic process measured for CTAC and CTBAB (as compared to CTAB) might reflect differences in the degree of counter-ion binding and in the extent of the micellar hydration layer, cf. [11, 12].

Conclusion

Freezing small samples (Ø 1–2 mm) of micellar solutions of cetyltrimethylammonium salts in liquid nitrogen is fast enough to retain noncrystalline structures of micelles. Local melting in the micellar Stern-layers below the macroscopic melting point allows crystallization in the frozen environment at ca. −25°C.

Acknowledgements We thank Mrs. A. Göpfert for excellent technical assistance in the DSC measurements.

References

1. Narayana PA, Li ASW, Kevan L (1981) J Am Chem Soc 103:3603–3604
2. Bachman L, Dasch W, Kutter P (1981) Ber Bunsenges Phys Chem 85:883–887
3. Jahn W, Strey R (1988) J Phys Chem 92:2294–2301
4. Wolff T, Emming C-S, von Bünau G, Zierold K (1992) Colloid Polym Sci 270:822–824
5. Yu X, Wolff T (2003) Langmuir 19:9672–9679
6. Weber S, Wolff T, von Bünau G (1996) J Colloid Interface Sci 184:163–169
7. Senatra D, Guarini GGT, Gabrielli G (1985) In: De Giorgio V, Corti M (eds) Physics of Amphiphiles: Micelles, Vesicles, Microemulsions. North Holland Physics Publishing. Amsterdam, pp 802–829
8. Ezrahi S, Nir I, Aserin A, Kozlovich N, Feldmann Y, Garti N (2002) J Dispers Sci Technol 23:351–378
9. Bežan M, Malavašič M, Vesnaver G (1993) J Chem Soc Faraday Trans 89:2445–2449
10. Ruiz CC (1999) Colloid Polym Sci 277:701–707
11. Lindmann B, Wennerström H (1982) In: Mittal KL, Fendler FJ (eds) Solution behaviour of surfactants. Plenum Press, New York, p 10
12. El Seuod OA, Blaskó A, Bunton CA (1994) Langmuir 10:653–657