

THE KRAFFT TEMPERATURE OF SURFACTANT SOLUTIONS

by

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Our main motivation to revisit the solution properties of cetyltrimethylammonium bromide is related to the clear requirement for better control of the adsorption parameters to form uniform self-assembled monolayers on muscovite mica substrates. To readily monitor the temporal evolution of structural details in cetyltrimethylammonium bromide solutions, we realized a rather simple conductivity experiment. Conductivity measurements were carried out as a function of temperature, to look closer into the Krafft temperature behavior of this surfactant. We measured the electrical conductivity of different concentrations of aqueous cetyltrimethylammonium bromide solutions, below and above the critical micelle concentration.

Key words: *nanotechnology, surfactants, the Krafft temperature, conductivity measurements*

Introduction

One of the most elegant ways to make ultrathin organic films of controlled thickness is to prepare self-assembled monolayers (SAM). Interest in SAM formation and structure has been increasing recently because self-assembly is a promising approach for the generation of atomically structured devices. There is also special interest in the possibility of manufacturing molecular layers with particular properties. Molecular self-assembly is recognized as a powerful strategy for the fabrication of nanoscale structures [1]. With the development of a number of powerful techniques in surface analysis, such as atomic force microscopy (AFM), academic interest in SAM has revived because of the possibilities to investigate the growth and the structure of such layers on the nanometer scale [2, 3].

Self-assembled monolayers can be prepared using different types of molecules and different substrates. Our aim was to produce homogeneous monolayers of quaternary ammonium surfactants (primary cetyltrimethylammonium bromide – CTAB) on muscovite mica. The adsorption of quaternary ammonium surfactants onto mica substrates has frequently been studied [4-8]. Nevertheless, the interactions between mica surface and alkylammonium ions have not yet been studied in detail. CTAB was the object of the research very often. Depending on the conditions it has been reported that CTAB adsorbs on mica as a compact monolayer [9], as a stable hydrophobic surface [10], as a bilayer [11] or forms aggregates [12]. For the preparation of CTAB self-assembled films on mica numerous adsorption proto-

cols have been proposed in the literature. The applied procedures include the variation of many parameters, such as different temperatures in SAM preparation [10,13-16], or the post-adsorption sample treatment [17, 18].

The role of the temperature in CTAB adsorption on mica is usually under-emphasized in the literature as a factor in surfactant solution preparation or adsorption. A significant number of adsorption experiments have been carried out at temperatures around 25 °C [14, 16], while a few authors have suggested adsorption at 5 °C (in the refrigerator) [13], but in most of experiments this parameter has been neglected [17, 19], both below [20] and above the critical micelle concentration (CMC) [19], or the conditioning during self-assembly have not been mentioned [15, 19]. Different conclusions about adsorption theories and the existence of numerous mechanisms underline this broadness. On the other hand, the Krafft temperature is a very important quantity for CTAB/water solutions [11, 21, 22]. Due to the important structural changes in CTAB solution above the CMC at and above the Krafft temperature, this surfactant transition is still an area of research interest. From the literature review, it is apparent that it is difficult to draw a simple picture of CTAB adsorption, and a standard protocol, which can produce a well defined and reproducible hydrophobic CTAB film on mica, does not exist.

Namely, numerous studies of CTAB adsorption on various substrates, have suggested that the behavior of CTAB is more complex than the behavior of other cationic surfactants [11, 12, 23-25], but the reason for this singularity has not been clearly determined. Low-concentration aqueous solutions of ionic surfactants essentially consist of solvated, dispersed monomers. Around the Krafft temperature T_k , micelles start to form in the saturated solution, as the concentration of dissolved molecules reaches the CMC. The aggregation number commonly lies between 50 and 100 [26] for spherical micelles. Slightly above the CMC, micelles in CTAB solution are usually spherical and made of ~95 monomers, as reported by Ekwall *et al.* [27].

Micelles can exhibit not only spherical, but also cylindrical or lamellar shape. In a CTAB solution of 27 °C, only spherical micelles are known to exist over a rather wide concentration range (below 100 CMC) [22, 28]. In numerous studies, micelles are treated as spherical at concentrations below 300 CMC [27, 29, 30]. Nevertheless, significant changes in micellar shape to rod-like [27] or threadlike [30] have been reported at higher concentrations. Along these lines it is possible to define one CMC for spherical micelles and another CMC for micelles of other shapes.

The transition in CTAB solution around the Krafft temperature, T_k , clearly occurs and many physical properties of the surfactant solution, such as the solution surface tension, the osmotic pressure or the conductivity reflect this [26]. Although the Krafft temperature is a well-established concept, reported values of T_k for CTAB in water vary considerably, from 20 °C [11, 31] to 25 °C [22, 32], which is inconvenient for research or application at room temperature [21]. It is important to note that many SAM preparation protocols involve solutions around 25 °C without explicit control of thermal history [10, 23]. The rather wide range of reported Krafft temperatures, together with the variety of existing adsorption preparation protocols, around [14] or below [33] 25 °C, with solution concentration above or below the CMC, may be considered a key reason for the incongruent monolayer morphologies reported in the literature.

The properties of aqueous CTAB solution have been investigated by several methods, such as conductivity measurements [34], viscosity, density and light scattering measurements [27] or by adsorption on various substrates [11]. Conductivity measurement is a widely applied and very simple method. Several important aspects have been considered by conduc-

tometry, such as solubility, the CMC, detection of the 2nd CMC as the reflection of some structural changes in the micelle, thermodynamics of micellization and the Krafft temperature.

With the aim to produce homogeneous monolayers CTAB films on mica substrates, self-assembled monolayers were prepared using different methods already proposed in the literature, as well as using newer protocols that we established [35]. Homogeneous hydrophobic monolayers on mica were difficult to realize. The remarkable variety of film morphologies spurred us to go back even one more step and to study the properties of CTAB solutions, to show that the factors such as the temperature during solution preparation, frequently neglected, can be potentially detrimental to surfactant adsorption from solution. In this study we carried out systematic conductivity experiments to monitor structural changes in CTAB/aqueous solutions and to look closer to the Krafft temperature. These results gave valuable information about the structures present in the solution. In heating-cooling cycles below and above the Krafft temperature a significant and reproducible conductivity hysteresis was found. We examined the conditions leading to this hysteresis.

Experimental part

Solution preparation

Single-chained cetyltrimethylammonium bromide CTAB (CTA^+Br^-), $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ was purchased from Fluka and used without further purification. Ultra pure water was prepared using a Barnstead EASYpure™ batch-fed water purification system (resistivity 18.3 MΩcm). The glassware and bottles used in the experiments were cleaned with piranha solution and then rinsed with purified water, to minimize organic contamination.

The surfactant solutions, below and above the CMC ($\text{CMC} = 8.9 \cdot 10^{-4} \text{ M}$ [36]), were prepared from ultra pure water, previously equilibrated at different temperatures. Care was taken to maintain the nominal temperature at all steps of the preparation and subsequent measurements with an accuracy of ± 0.5 °C or better, by controlling the ambient temperature in the laboratory. To achieve reproducible starting conditions of the stock-solutions after storage, some of them were kept in a refrigerator at 5 °C for at least 12 hours prior to heating them up to the temperature used in the experiment.

Conductivity instrument

To monitor the number and mobility of ionic species in solution, the conductivity of CTAB solutions was measured using a Portamess 913 instrument (Knick, Germany), with an operating range between 0.1 μS/cm to 1 S/cm and -20 °C to +120 °C. Before measurement, the instrument was calibrated using 0.1 M KCl solution (purchased from Fluka). The solution for the calibration was taken fresh to avoid any contamination. The cell constant (~1.130 per cm) changed very little over time, but it was usually determined before every experiment.

With calibration, the instrument was adjusted to the cell constants of the sensor (the type of the sensor we used is 4-electrode cell model ZU 6985). This cell was ready for measurement without special preparation after putting it into the liquid. The level of the liquid had to be high enough, marked on the protecting sleeve tube, to immerse all electrodes in the solution for accurate conductivity indication, realized by choosing the appropriate volume of solution. Conductivity was measured between the electrode support and sleeve tube, with an error < 0.5% of measured conductivity value.

Experimental procedure

The conductivity measurements were realized with the set up shown in fig. 1. After at least 12 hours in the refrigerator, a CTAB solution (3) was placed in the double-walled solution container (4) on the magnetic stirrer plate (5). The temperature was controlled using an external thermostat (6) connected to a double-walled solution container (4). A mechanical stirrer (a small magnetic stirring bar) was used to prevent precipitation of the crystals and to produce a uniform solution. The rate of stirring was maintained constant during the measurements. During the conductivity measurements, the temperature was ramped up and down in the range between 15 °C and 40 °C while continuously stirring the solution.

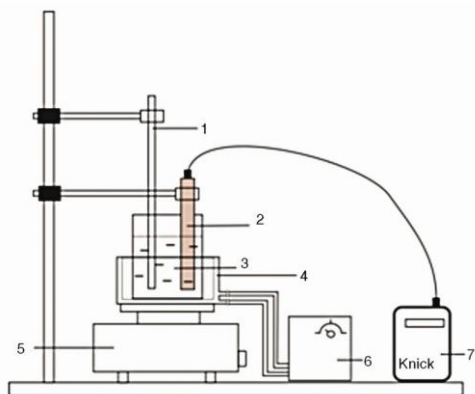


Figure 1. The set-up for the conductivity measurements;

1 – thermometer, 2 – conductivity probe,
3 – CTAB-aqueous solution, 4 – double/walled
container, 5 – magnetic stirrer, 6 – thermostat,
7 – conductometer

Typically, the temperature set-point was manually incremented in 2 °C steps at intervals of 30 minutes, while the temperature of the solution was monitored by a thermometer (1)-(mercury thermometer $\pm 0.5^\circ$). In the temperature range very close to T_k , *i. e.* 20 °C to 28 °C, the temperature was increased only in one-degree steps to better resolve the conductivity transition. The reproducibility of all measurement was verified both in the same solution, as well as in newly prepared solutions.

Results

We followed conductivity as a function of temperature. The results will be divided into several groups according to the characteristic phenomena observed in the measurements.

Conductivity as a function of temperature

The electrical conductivity of an ionic surfactant solution was determined by the concentration and mobility of dissolved ions therein. We carried out conductivity measurements below and above the CMC, at nominal concentrations between $5 \cdot 10^{-4}$ M (≈ 0.5 CMC) and 0.163M (≈ 180 CMC). The characteristic increase in conductivity observed at the Krafft temperature is illustrated in fig. 2 for different molar ratios of the simple CTAB/water system.

The nominal concentration accounted for both the dissolved and the crystalline CTAB in the solution (*e. g.* saturated solution below T_k). The prominent transition of conductivity seen here is commonly used to define the Krafft temperature of a surfactant solution [34, 37].

For all nominal concentrations above the CMC there was a significant change in conductivity around $T = 24.5 \pm 1$ °C (point A in fig. 2). Below this transition, the conductivity was low and independent of the amount of coexisting CTAB crystals, cf. fig. 2(a) and 2(b). Due to constant stirring, the crystals were prevented from sedimenting and the solutions were thus turbid.

At $T = 24.5 \pm 1$ °C, the crystals dissolved and the solutions became transparent (around the point B in fig. 2). This readily visible optical effect was paralleled by the dramatic increase in the solution conductivity mentioned above.

Hysteresis in conductivity measurements

To follow the solution properties with decreasing temperatures, we ramped the temperature down, over the same range (from 40 °C to 15 °C). The complete thermal cycle for solution at 30 CMC is illustrated in fig. 3. We observed a significant hysteresis for concentrations above the CMC.

For more concentrated solution, especially at higher temperatures, hysteresis had a more complex character (fig. 4).

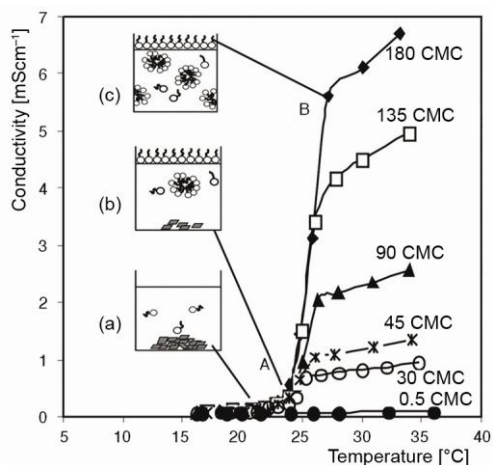


Figure 2. Conductivity of CTAB solutions at nominal concentrations below and above the CMC with insets schematically showing molecular details of the solution composition at different temperatures

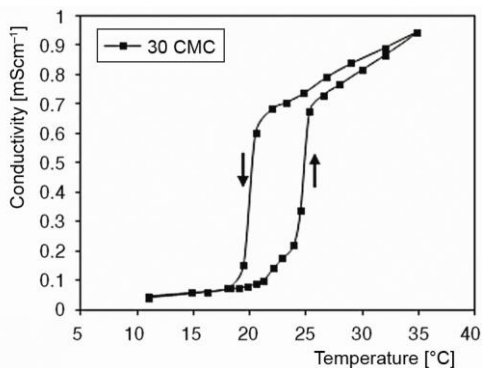


Figure 3. Typical hysteresis behavior in conductivity for a concentration of 30 CMC; the points were measured at intervals of 30 minutes

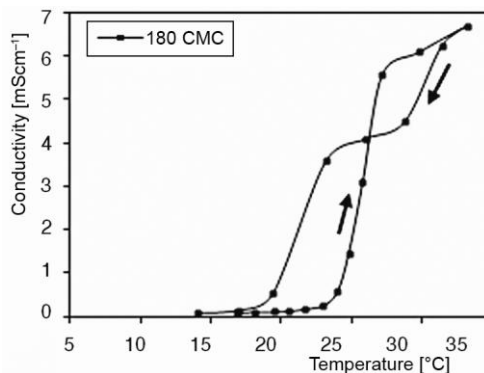


Figure 4. More complex hysteresis in the conductivity results for the solution concentration of 180 CMC

To assess the stability of the micelles above T_k we further increased the solution temperature up to 70 °C at a concentration of 30 CMC. The observed monotonic and featureless increase of conductivity at high temperatures indicated that there were no further qualitative structural changes occurring in the solution.

Discussion

The shape of the conductivity curves, *i. e.* significant increase of conductivity around the Krafft temperature (very well known in the literature), suggests a division of the underlying transport mechanism into two qualitatively distinct regimes.

Below the transition, the conductivity barely depends on temperature. Within the experimental error, the dependence appears to be linear and charge transport is essentially provided by hydrated ions, including the CTA^+ cations. In this first regime, the CTAB solubility slowly increases. Only for concentrations above the CMC can a significant rise in conductivity be observed around the Krafft temperature.

The occurrence of a transition can be understood as follows: at the Krafft temperature the concentration of the surfactant monomers becomes equal to the CMC and micelles form spontaneously. The observation that the concentration of surfactants solutions exhibits a drastic increase around T_k was the historical indicator that led to the discovery of this transition [38, 39]. Beyond T_k the conductivity of the solution is determined not only by monomeric surfactant ions and counterions but also by micelles in great numbers, figs. 2(b) and 2(c). Taking into account the fact that the solubility of monomers is only slowly increasing, it is clear that most of the additionally dissolved molecules are now in the form of micelles [40], as schematically illustrated in fig. 2(c). A further temperature increase produces a smaller increase in conductivity, which can be due to an increase in the thermal energy of the charged species [41].

There are different explanations in the literature as to how exactly the conductivity changes as a function of temperature, within the Krafft temperature phenomenon. One viewpoint [34] proposes the existence of two characteristic points on the conductivity curve, the Krafft point and the Krafft temperature. The Krafft point is defined as the point where the concentration of the monomers becomes equal to the CMC and the micelles start to form. Upon temperature rise, CTAB crystals have dissolved completely when the Krafft temperature is reached [34].

Instead of a distinction between a Krafft point and a Krafft temperature, some authors suggest the existence of a temperature range between them, the so-called *micelle temperature range* [42], claiming that this is a term that can more precisely explain the behavior of surfactant solutions. But, from the literature overview of the Krafft temperature phenomenon, the difference between the Krafft point and the Krafft temperature is still a matter of debate.

Both micelles and monomers contribute to the conductivity measured in our experiments. The number ratio between these charge carriers, as well as changes of morphology of the micelles (*i. e.* mobility), can affect the conductivity. An interesting question is thus, how the structural composition of this solution changes with concentration above the CMC and at temperatures above T_k . A possible explanation is that a significant change in the micellar shape occurs at higher concentrations. Such shape changes have previously been reported for high concentrations and were sometimes also linked to the existence of a secondary CMC, where micelles change from a spherical into a more complex (*e. g.* threadlike) shape [30, 43]. For CTAB solutions, the concentration above which these effects can be observed is reported differently by different authors in a range of 20-300 CMC [30, 35, 43]. Our conductivity results confirm the existence of such subtle changes in the solution at higher concentrations (>90 CMC) where also the conductivity hysteresis has a more complex character (fig. 4). A more detailed analysis of the structural properties is difficult from conductivity measurements alone [44].

Hysteresis in the conductivity measurements was observed in the temperature range from 15 °C to 40 °C in all CTAB solutions at concentrations above the CMC. One of the results is given in fig. 3. Structural hysteresis is widely known to occur in many different macromolecular systems. Even more generally, hysteresis is common to many self-assembling

systems [45]. The response of the system to an external stimulus thus depends not only on external parameters (*e. g.* temperature, pressure) but also on the previous history of the system.

It is noteworthy that successive heating/cooling cycles yield reproducible conductivity loops. The high reproducibility of our hysteresis measurements (fig. 5) suggests that it is possible to “erase” memory effects either by cooling to very low temperatures or by heating to very high temperatures. As is shown in fig. 5, the exact same conductivity results were observed after storing the solution at 5 °C in a refrigerator for 15 hours.

This implies, for example, that the temperature at which a stock-solution is prepared, especially above the CMC, may be critically relevant for a subsequent experiment. The adsorption experiments [35] show that the temperature of solution preparation, even for subsequently diluted solutions, has a significant effect on the solution structure. The time effects observed in the conductivity measurements provide additional support for this hypothesis.

Conclusions

The wide variety of different adsorbate morphologies obtained with different preparation protocols spurred us to scrutinize the CTAB/water solution properties, since the structure of an adsorbed monolayer is expected to critically depend on the structures present in the solution. We investigated the specific conductivity of aqueous cetyltrimethylammonium bromide solutions below and above the critical micelle concentration to elucidate the structural changes, which allowed us to draw conclusions about their structural properties. Below the Krafft temperature, the solubility of CTAB is relatively low and surfactant monomers are in equilibrium with the solid phase. At the Krafft temperature (≈ 25 °C), the monomer solubility meets the critical micelle concentration and aggregation occurs in solutions above the CMC. Micelle formation in the solution was observed by a significant increase of conductivity. Upon decreasing the temperature of the micellar surfactant solution across the Krafft temperature a significant hysteresis was observed—followed by precipitation of crystals. We scrutinized the conditions leading to this hysteresis and also outlined a simple procedure that allowed the structural memory effects to be “cleared”. It is our conclusion that structural changes in the surfactant solution are reflected in the morphology of the adsorbed films.

The measurements presented above were realized by measuring the conductivity without complete equilibration of the system. A question of practical relevance is how long one has to maintain the solution at an extreme temperature to reach equilibrium and erase any history or structural memory? Time-effects and thermal history are important and from a systematic study of thermal equilibration with the next conductivity measurement, the characteristic time intervals can be determined at different equilibration temperatures. These results can be very relevant for the correct handling of CTAB solutions, especially if they are to be used to prepare monolayers.

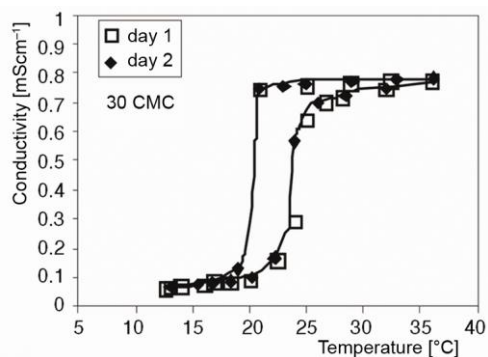


Figure 5. Reproducibility of hysteresis in conductivity of the same CTAB solution in two following days, by storing the solution in the refrigerator (as the possibility to “erase” the memory effects)

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