

Effects of Sodium Bromide Salt and Temperature on the behaviour of Aqueous Solution of Cetyltrimethylammonium Bromide

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Abstract: *The effects of sodium bromide (NaBr) salt and temperature on the aggregation behaviour of cetyltrimethylammonium bromide (CTAB) have been studied using conductivity data. Conductivity was observed to vary increasingly with both temperature and salt concentration. The critical micelle concentration (CMC) of CTAB decreased with increase in the concentration of NaBr but increased as temperature increased. For example, the CMCs of CTAB in 0.0 and 10.0 mM solutions of NaBr at 30 °C were 1.68 and 1.50 mM respectively while those of the same concentrations at 35 °C were 1.84 and 1.63 mM respectively. It was also found that both salt and temperature influenced the degree of micelle ionization as well as the free energy of micellization. Results also showed that the stability of CTAB micelles was enhanced by adding NaBr molecules. These observations have been discussed in terms of the electrostatic repulsion of charged CTAB head group.*

Key words: *Conductivity, micellization, cetyltrimethylammonium bromide, sodium bromide, temperature and CMC.*

I. Introduction

A surfactant molecule is a surface-active agent with two distinct moieties- the polar head group and the non-polar alkyl chain part. Whereas the polar head group may or may not be charged, the non-polar tail group usually comprises of hydrocarbon chains (Bidyut et al, 2009 and Tyowua et al, 2012) though fluorocarbon units also exist. The dual molecular architecture of surfactant molecules distinguishes them from other surface-active agents in that at low concentrations, they drastically reduce the unusual high surface tension of water through adsorption of the molecules at the air-water interface. Secondly and more significantly, surfactant molecules usually arrange themselves in bulk solutions into aggregates called micelles. Micelle formation is driven by hydrophobic effect but opposed by electrostatic repulsion of ionic head groups (Jiang et al, 2005).

In addition to extensive industrial and household applications of surfactants such as in oil recovery, cosmetics, pharmaceutical, food, detergency, water treatment and micellar solubilisation (Briscoe et al, 2006, Briscoe and Klein, 2007, Sehgal et al, 2008 and Patil et al, 2008), surfactants are also very indispensable in Analytical Chemistry such as in spectrophotometry, electrochemistry and liquid chromatography (Němcová et al, 2009). For instance in spectrophotometry, surfactants influence the absorption spectra of dyes and their complexes with metals. They are also able to influence acid-base equilibria by altering pK_a values of acid-base media since the pH of pseudophase micelles is different from that of the aqueous phase (Němcová et al, 2009). In chemical kinetics, they play a vital role in influencing rates of chemical reactions as well as the stability of reaction products. Such effects have been shown to be strongly dependent on the nature of the surfactant head group, the initial counterion present, and the total ionic content of the system (Quina and Chaimovich, 1979).

Surfactants can only function effectively above a certain solution concentration called critical micelle concentration (CMC) i.e., the concentration above which they form aggregates or micelles. It is only above this concentration that significant changes in both physical and performance properties of surfactants take place. The CMC is influenced by a number of parameters including the nature of surfactant head group and alkyl chain, temperature, pressure, pH and ionic strength. For ionic surfactants, micelle formation is greatly affected by temperature as hydrophobic chain and head group interactions change relatively with temperature (Miller et al, 1990 and Noudehet al, 2007). In other words, inhibition or catalysis by micelles in chemical reactions is a function of the surfactant head group. This dependence is greatly influenced by the presence of a common ion from an added salt. Salts bearing the same counterion as that of a surfactant will tend to decrease the fraction of charged sites on micellar headgroup and so reduce the electrostatic interactions on the charged head group resulting in reduced CMC (Bunton C.A. and Cerichelli G., 1980).

The relevance of ionic micelles in the inhibition and/or catalysis of reaction rates in aqueous solutions has been widely studied particularly in view of the analogies drawn between micellar and enzyme catalysis (Katre et al, 2010). The focus has been on the effect of added salts bearing an ion with the counterion of the

surfactant ion since salts increase the concentration of counterions and thus reduce the number of charged sites on a charged micelle surface. Jones and Jandik, 1991 have shown that for inorganic anions, the addition of a cationic surfactant in a concentration above the critical micelle concentration affects the electrophoretic mobility of the analytes and makes it possible to fine-tune the selectivity of the separation. This effect was attributed to the electrostatic interaction of the anions with the cationic micelles and corroborated by Orentaite and Pyell, 2011. Although the literature is replete with studies that have been conducted on the thermodynamic properties of surfactants with varying head groups (Noudeh et al, 2007, Bidyut et al, 2009, and Katre et al, 2010) and at different temperatures, there are however, no recorded studies on the effects of temperature and sodium bromide salt on the thermodynamic properties of CTAB- an important and widely employed surfactant. This study thus attempts to investigate the effects of these parameters on the micellization of CTAB through conductivity measurements.

II. Materials and Methods

Cetyltrimethylammonium bromide (98% purity) and sodium bromide were purchased from Sigma Aldrich. Deionized water was prepared in our laboratory. The reagents were used as received without further purification. Stock aqueous solutions of CTAB were prepared at concentrations approximately ten times the literature value of its CMC (Azum et al, 2008). Stock solutions of CTAB were prepared in 0.0 mM and 10.0 mM concentrations of NaBr. Conductivity measurements of all the solutions were carried out with a JENWAY 4510 conductivity meter at 30, 35, 40 and 45 °C. The conductance of a known volume of deionized water was first measured. Subsequently, a precise volume of a stock solution was added into the deionized water using an Eppendorf pipette. This addition was repeated severally and in each case, the conductivity of the solution was measured. Concentrations of CTAB were calculated from the volumes of the stock solutions used for each measurement.

III. Results And Discussion

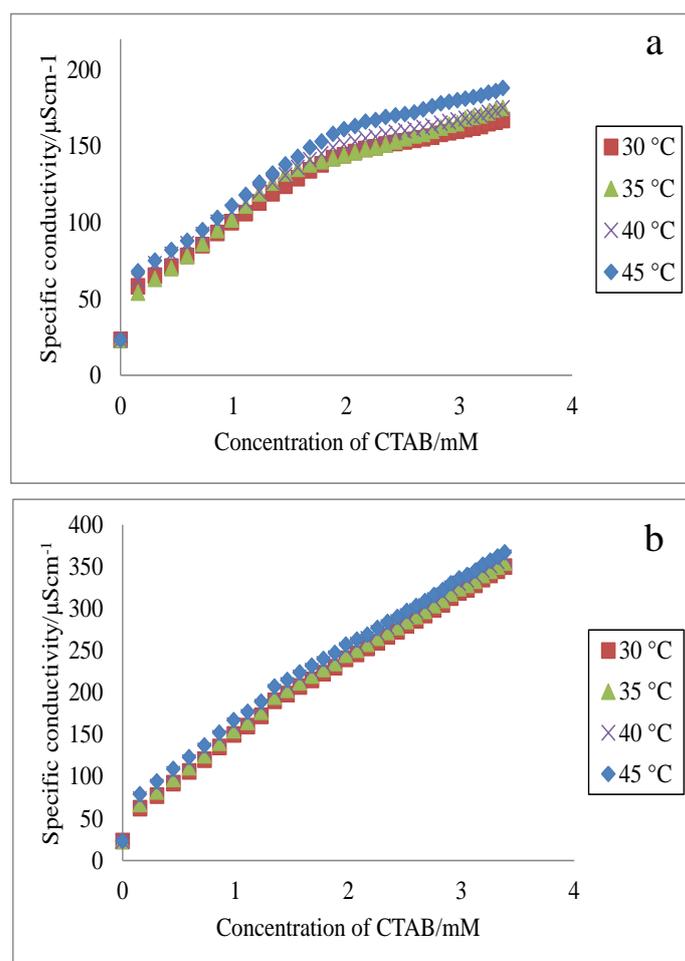


Figure 1: Specific conductivity versus concentration of CTAB, at (a) 0.0 mM and (b), 10.0 mM of NaBr at different temperatures.

Figures 1 (a) and (b) show the variation of specific conductivity with CTAB concentration in the presence (10.0 mM) and absence (0.0 mM) of NaBr at 30, 35, 40 and 45 °C. These curves show that the specific conductivity of CTAB increased as the total surfactant concentration increased with a corresponding increase in gradient until an inflection point (the CMC) was observed. Above this point, the specific conductivity still increased with concentration but with a decrease in slope. This abrupt change at the CMC has been reported in several literatures (Domínguez et al, 1997 and Kroflic et al, 2012) as due to different degrees of ionization of surfactants below and above the CMC. Below the CMC, ionic surfactants behave as strong electrolytes and dissociate completely into their ions. At CMC, aggregates begin to form and mobility of ions is slowed down. Above the CMC, dissociation becomes weaker thus micelles are partially ionized and electrical conductivity then depends on the degree of micelle ionization. These curves also illustrate the dependence of specific conductivity on the concentration of NaBr salt with specific conductivity increasing as the concentration of the salt increased. This behaviour may be attributed to increased counterion content in the solution. The cluster of the plots (b) at different temperatures indicates that in the presence of NaBr, temperature has little effect on the specific conductivity of CTAB.

The CMCs of CTAB extrapolated from the inflection points on the specific conductivity versus concentration curves at the various temperatures and concentrations of NaBr salt are illustrated in Figure 2.

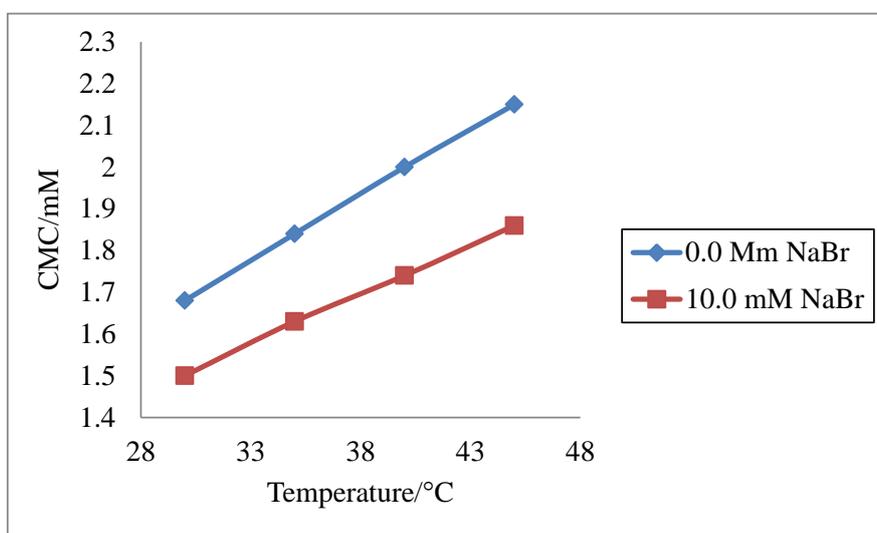


Figure 2: Variation of the critical micelle concentration of CTAB with temperature and concentrations of NaBr.

Figure 2 shows the dependence of the CMC of CTAB on both temperature and salt concentration. At a given concentration of NaBr, the CMC increased with increase in temperature. However, at constant temperature, the CMC decreased with increasing concentration of NaBr. For instance, the CMC of CTAB in 10.0 mM solution of NaBr salt at 30 °C was 1.50 mM while that at 35 °C for same concentration of NaBr was 1.63 mM. At constant temperature of 35 °C, the CMCs were 1.84 and 1.63 for 0.0 mM and 10.0 mM concentrations of NaBr respectively. Thermal agitation (as a result of increase in temperature) is expected to increase the electrostatic repulsion of the ionic head group; hence, the chances of micelle formation are reduced leading to higher CMC. Aggregation of surfactant molecules into micelles is enhanced by attractive interactions of the hydrophobic alkyl chains but opposed by the electrostatic repulsion of charged head groups (Domínguez et al, 1997). A decrease in CMC of CTAB with increasing NaBr concentration may imply that the presence of the salt enhances the formation of CTAB micelles. This is probably because Br⁻ ion of NaBr increases the surfactant's counterion in solution and thus greatly reduces the number of unbound ionic sites on CTAB micellar head group. Subsequently, the degree of electrostatic repulsion on the charged head group reduces leading to increased micelle formation. These observations are in agreement with studies (Noudeh et al, 2007) on the CMC of ionic surfactants at temperatures higher than 25 °C.

Employing the method by Kroflic et al. 2012, values of the degree of micelle ionization at the different temperatures and in the absence and presence of salt addition were calculated. A linear relationship was observed in both cases (Figure 3). It was also observed that the degree of micelle ionization increased with temperature and with salt concentration.

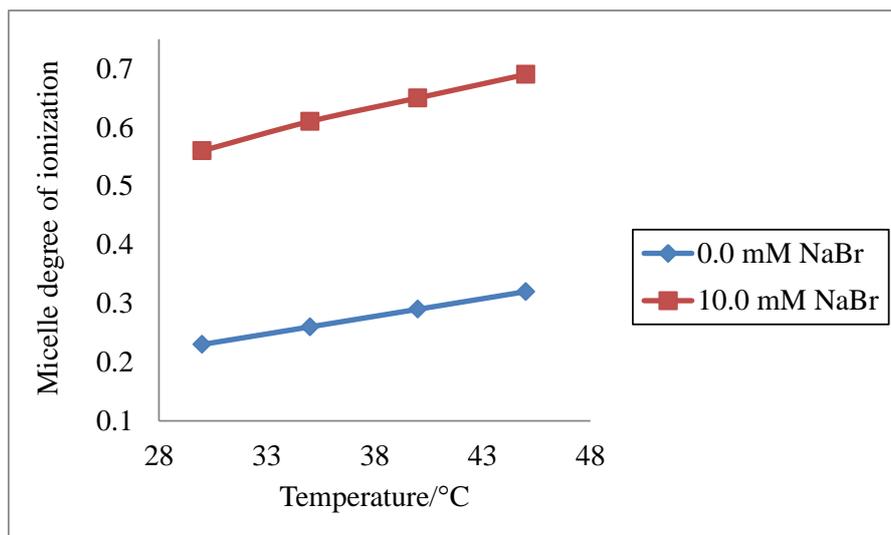


Figure 3: Variation of the degree of micelle ionization of CTAB with temperature in the presence (10.0 mM) and absence (0.00 mM) of NaBr.

This trend agrees with the results obtained by Kroflicet al, 2012 on the study of the degree of ionization of alkyltrimethylammonium chlorides at different temperatures. They noted that increasing temperature increased the degree of ionization of the surfactant but no distinct influence of added salt was actually observed. The increase in degree of ionization with NaBr concentration is an indication that the ionic strength of CTAB solutions increased with increasing concentration of the salt or the presence of NaBr increased the number of unbound counterions in CTAB solution.

The stability of the CTAB micelles formed was evaluated using equation 1 (López-Díaz and Velázquez, 2007).

$$\Delta G_M = RT \ln X_{CMC} \quad (1)$$

where X_{CMC} is the critical micelle concentration in mole fraction unit, R , ΔG_M and T are gas constant, free energy change and absolute temperature respectively.

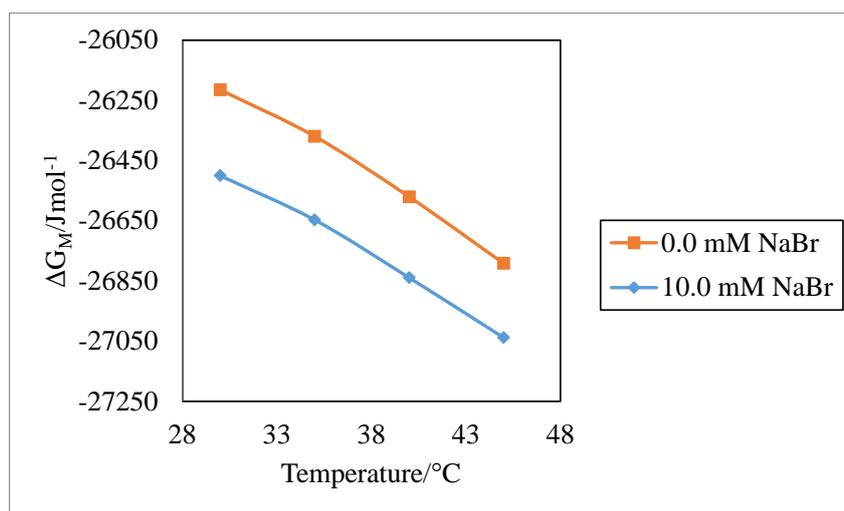


Figure 4: Variation of the change in free energy of micelle formation (ΔG_M) of CTAB as a function of temperature and NaBr concentrations.

The plots in Figure 4 show that at increasing salt concentrations, the magnitudes of the free energy change of micelle formation for CTAB increased with increasing temperature, signifying that CTAB formed more stable micelles in the presence of NaBr salt. The decrease in CMC with NaBr concentration (Figure 2) might imply that NaBr concentration reduced the electrostatic repulsion of charged CTAB head group thereby enhancing micelle formation. Consequently, the free energy required to transfer each CTAB molecule from the bulk solution into

the micelle phase might have been reduced in comparison with that required to do same in the absence of the salt. Although the increase in the negative values of the free energy change of micelle formation with temperature was not very clear, it is possible that the sum of the other competing effects may be greater than the reduced repulsion of ionic head group. For instance, dehydration of the ionic head group of a surfactant will normally increase with increasing temperature which may result in enhanced micelle formation.

IV. Summary And Conclusion

Conductivity measurements on the solutions of CTAB at different temperatures and NaBr concentrations showed that the CMC of CTAB was inversely proportional to NaBr concentration but directly proportional to temperature. The degree of micelle ionization of CTAB increased with increase in both salt content and temperature. It was also found that the overall stability of CTAB micelles estimated from the change in Gibbs free energy of micelle formation could be enhanced by adding NaBr molecules. These results have been attributed to the reduction of the repulsive interactions of CTAB ionic head group in the presence of NaBr salt.

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