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Salt Effect on Interfacial Properties of Cetyltrimethylammonium Bromide and Triton X-102 Mixed Surfactant System

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Micellar and surface properties of cationic surfactants octyl phenolethoxylate (Triton X-102) and cetyltrimethylammonium bromide were investigated with both contact angle measurements and surface tension measurements in the presence of sodium halide (NaF, NaCl and NaBr) solutions at 300 K. Surface tension data were used to compute the critical micelle concentration and interfacial parameters, such as the minimum area per molecule (A_{min}), the maximum surface excess (Γ_{max}) and surface pressure at the critical micelle concentration (Π_{CMC}). Micellar and surface properties of mixed surfactants were evaluated both with and without salts. The critical micelle concentration and degree of the micellar ionization values were found to decrease with an increased salt concentration were proportional to decreased micellar ionization and critical micelle concentration, in the order NaBr < NaCl < NaF.

Keywords: Contact angle, Surface tension, Nonionic surfactant, Cationic surfactant, Wettability.

INTRODUCTION

The surface tension, critical micelle concentration (CMC), adsorption on various interfaces and contact angles of mixed solutions are not additive functions of the corresponding properties of individual surfactant solutions [1-7]. The overwhelming majority of published data deals with the influence of the composition of surfactant mixtures on the CMC and surface tension of their aqueous solutions. There is markedly less information about the wetting of solid surfaces and their absorptive properties [8-17]. A wide range of applications, including detergency [18], liquid surface coating [19-21], flotation [22,23] chemical reactions at solid-liquid interface [24], agrochemistry reservoir flow [25-28] and mass transfer [29] are influenced by the wetting properties of solid surfaces. Wetting of a solid surface by a liquid is associated with molecular attractions at the solid-liquid interface. The surface molecules of a liquid with low surface tension have a stronger attraction to molecules of a solid surface than to each other, resulting in surface wetting and lower contact angles. In recent years, there has been an increasing interest in the study of superhydrophobic surfaces due to their potential applications in, for example, self-cleaning, nanofluidics and electrowetting. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and a liquid interact. Small contact angles (< < 90°) correspond to high wettability, while large contact angles (> > 90°) correspond to low wettability [30].

Two types of surfaces exist *e.g.*, low energy or hydrophilic surfaces and high energy or hydrophobic surfaces. Young's equation can be applied to calculate the contact angle (θ) in terms of interfacial energy [31]. The mechanical equilibrium of the drop under the action of three interfacial energies determines the contact angle on a solid surface [32].

A mixture of surfactants delivers a better result in improving wetting characteristics than pure single surfactant in most practical applications. In fact, commercial surfactants designated as pure surfactants are in some cases mixtures of surfactants due to non-homogeneous raw materials, the presence of unreacted raw materials, or the formation of by products.

In many industrial applications additives are used along with surfactants to improve wetting properties. Additives can have a significant influence on the wetness of the surface. Alcohols and electrolytes are the most common additives to be used [33]. Classic experiments established the Hofmeister series of ions, demonstrating that the log Z solubility of most proteins depends directly on electrolyte concentration and composition. Anions have a stronger effect than cations [34].

The presence of electrolyte as an additive on single or mixed ionic surfactants solutions affect the adsorption density of the surfactant molecules through the reduction in electrostatic repulsive force among the head groups of the surfactant molecules at air-liquid and solid-liquid interfaces, which in turn influence the surface tension of the solution as well as the contact angle on a solid surface [35].

Our goal was to investigate the effect of salts upon the critical micelle concentration and contact angle values of surfactant solutions. Consequently, a systematic investigation of the effects of salts upon the critical concentrations of surfactants has been undertaken.

EXPERIMENTAL

Octylphenolethoxylate (Triton X-102), cetyltrimethyl ammonium bromide (CTAB), NaCl, NaBr and NaF were used as received from Sigma-Aldrich. As surface was used stainless steel. Stainless steel is easy to clean with soap, detergent or dilute (1 %) ammonia solution in warm clean water. Apply with a clean sponge, soft cloth or soft-fibrebrush then rinse in clean water and dry [36]. All the sodium halides *i.e.*, NaCl, NaBr and NaF were used as received from Sigma-Aldrich. Stainless steel surfaces were used as the measurement surface in contact angle measurements. Dynamic surface tension measurement was used to evaluate the purity of the surfactant solution. The minimum surface tension isotherm at the CMC (critical micelle concentration) was also measured.

Aqueous solutions of Triton X-102 and CTAB and mixtures at different ratios of CTAB to Triton X-102 were mixed in deionized water (GFL-2102). Prior to the preparation of the solution, water surface tension was measured. All measurements were made at 298 ± 0.001 K.

Surface tension measurements: The surface tensions of aqueous solutions of surfactants at various concentrations were measured from a series of aqueous solutions with a platinum ring: a KSV SIGMA 702 Tensiometer. The surface tension of double distilled water, 72 ± 0.3 mN/m, was used for calibration purposes. The flame was dried and the platinum ring was thoroughly cleaned prior to each measurement. Surface tension measurements were taken by dipping the vertical ring into the liquid surface and subsequently extracting the ring. The maximum force needed to remove the ring was expressed as γ (mN/m). The tensiometer was calibrated with pure water at 303 K.

Since surface tension decreases over time, measurements were collected up to the point of equilibrium. This phenomenon took more than 10 min to reach the equilibrium. The surface tension was calculated as the average of three independent measurements. The temperature was controlled within ± 0.1 K.

Contact angle measurements: Contact angle of the sessile drops was measured at 25° using a KSV CAM 101 goniometer microscope. Goniometry determines the contact angle using an image of the drop, drawing a tangent and the liquid interface across the drop profile. This method is very crude and the obtained angle is dependent on the judgment of the user and is generally not suitable for scientific applications. The mean drop size was 50 µL. Different regions of stainless steel surface were used to measure the contact angle.

Determination of critical micelle concentration (CMC): Both mixed and single surfactants were evaluated for surface tension properties at various concentrations with a platinum ring a KSV SIGMA 702 Tensiometer at a constant temperature. The CMC values were determined by the break points in the surface tension against the logarithm of the concentration curve.

RESULTS AND DISCUSSION

The surface tensions relative to surfactant concentration of the cationic surfactants octylphenolethoxylate (Triton X-102) and cetyl trimethyl ammonium bromide (CTAB) at 298 K (Fig. 1). The CMC values of the various binary mixtures (Triton X-102/CTAB systems) were determined from the surface tension-[surfactant] plots (Table-1). The results were consistent with other reports in the literature regarding nonionic and single cationic surfactants. The surface tension of the surfactant and mixed surfactant systems changes in the presence of sodium halide (NaF, NaCl and NaBr) as shown in Figs. 1-4. The CMC of the cationic and nonionic surfactant mixture, CTAB and Triton X-102 in aqueous media containing sodium halides (NaCl, NaBr and NaF), has been determined from surface tension measurements as shown Table-1.

TABLE-1
SURFACE PROPERTIES OF CTAB/TRITONX-102 SYSTEM WITH DIFFERENT MOLE FRACTION AND ELECTROLYTES AT 298 K

	CTAB/TX-102 mole fraction	CMC (mmol/L)	Π_{cmc} (mN/m)	$10^6\ \Gamma_{max}$ (mol/m^2)	A^o_{min} (10^{20} m^2 mol^{-1})
Water	0	0.36	35.50	0.59	2.80
	0.2	0.42	32.89	0.38	4.38
	0.4	0.57	31.93	0.28	4.18
	0.6	0.58	31.93	0.39	5.84
	0.8	0.72	32.96	0.69	2.40
	1.0	0.64	35.42	0.03	4.86
NaF	0	0.16	34.82	0.08	20.61
	0.2	0.16	33.91	0.07	21.54
	0.4	0.19	31.84	0.42	39.55
	0.6	0.34	30.38	0.73	22.75
	0.8	0.34	32.11	0.08	20.61
	1.0	0.18	35.87	0.06	28.29
NaCl	0	0.19	33.10	0.24	6.97
	0.2	0.09	35.60	0.19	8.42
	0.4	0.10	35.51	0.26	6.48
	0.6	0.19	35.04	0.19	8.83
	0.8	0.33	34.49	0.89	1.86
	1.0	0.20	35.60	0.31	5.40
NaBr	0	0.17	37.35	0.12	13.54
	0.2	0.08	35.95	0.08	20.61
	0.4	0.07	36.82	0.05	27.88
	0.6	0.16	37.12	0.08	20.17
	0.8	0.16	37.61	0.03	43.08
	1.0	0.23	33.90	0.04	39.49

It can be inferred from Table-1 that for this mixture the CMC value decreases in the presence of salts. At the air-water interface, the cationic surfactants form an ionic monolayer, anion addition results in a reduction in thickness and potential electrostatic interactions among opposing charges and the formation of an electric double layer [37]. As a result, electrostatic repulsion between polar head groups is reduced, reducing CMC relative to the salt-free system. Micellation tendencies are countered by the repulsion among polar head groups of surfactants.

Based on the surface tension curves, the Gibbs adsorption eqn. 1 was used to calculate the surface excess concentrations

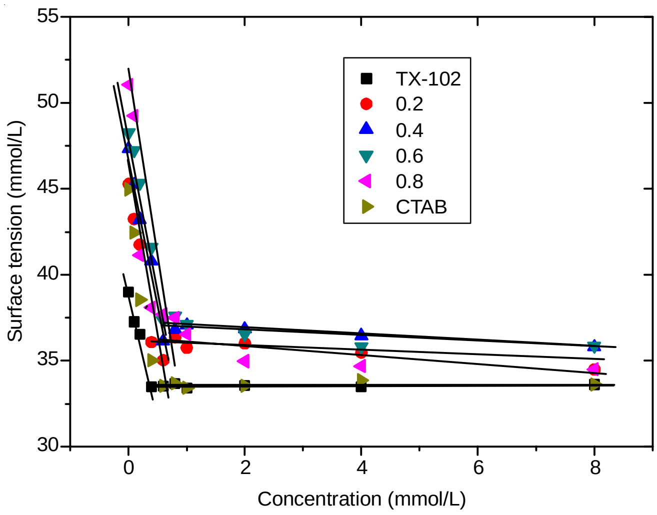

Fig. 1. Plot of surface tension *versus* total surfactant concentration for different mole fraction of CTAB/TX-102 at 298 K

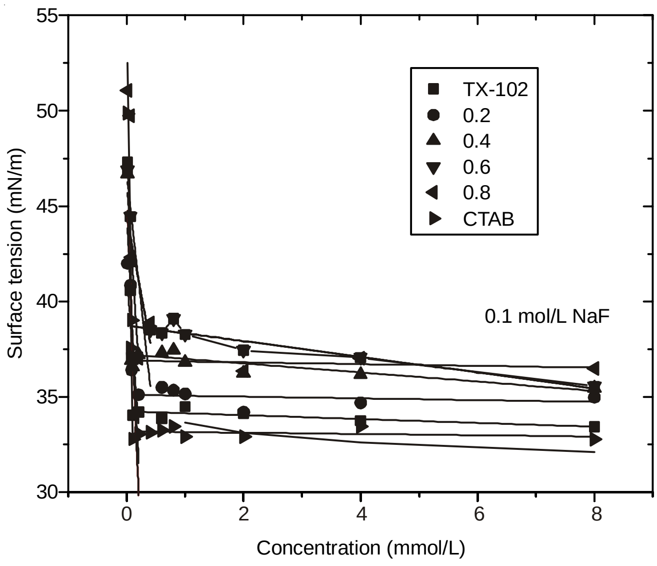

Fig. 2. Plot of surface tension *versus* total surfactant concentration for different mole fraction of CTAB/TX-102 at 298 K

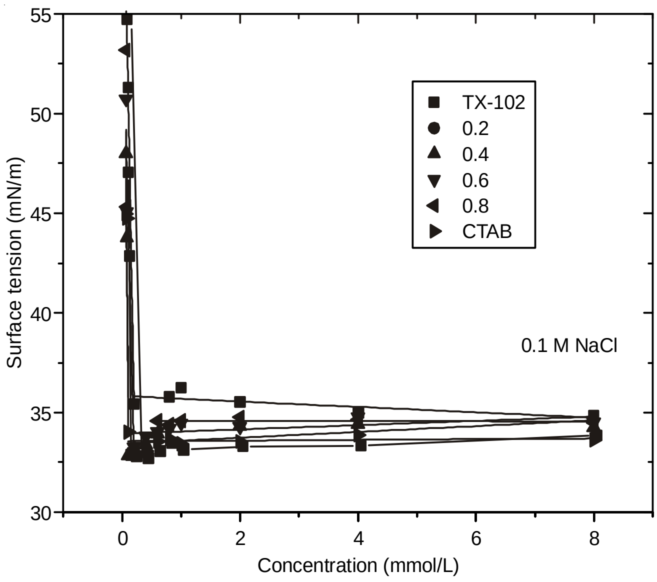

Fig. 3. Plot of surface tension (c) *versus* total surfactant concentration for different mole fraction of CTAB/TX-102 at 298 K

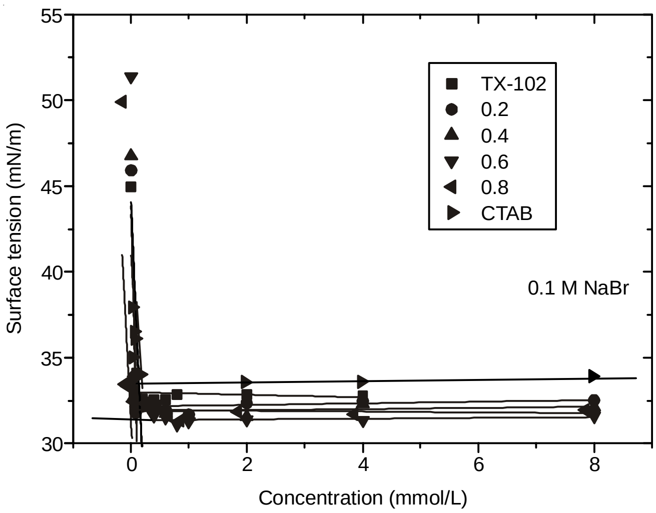

Fig. 4. Plot of surface tension (c) *versus* total surfactant concentration for different mole fraction of CTAB/TX-102 at 298 K

of CTAB/Triton X-102 (Γ_{max}) were calculated from and the minimum surface area per surfactant molecule (A_{min}):

$$\Gamma_{max} = -\frac{1}{n2.303RT}\left(\frac{\delta\gamma}{\delta\log c}\right)_T \tag{1}$$

$$A_{min} = \frac{1}{N_A\Gamma_{max}} \tag{2}$$

where R is the gas constant, T is the absolute temperature, N_A is Avogadro's number and c is the concentration of surfactant in solution. For nonionic and zwitterionic surfactant, n = 1 [38-41].

Figs. 5 and 6 show the change in contact angle with the increasing cationic surfactant mole fraction in the cationic nonionic mixed surfactant system with increasing electrolytes (NaCl, NaBr and NaF). By comparing the contact angle data in the absence of electrolyte, it can be observed that even at low surfactant concentration we can achieve a similar or even lower minimum contact angle by adding electrolyte than in the presence of pure surfactant without electrolyte. Figs. 4 and 5 show that adhesion is decreased at all concentrations,

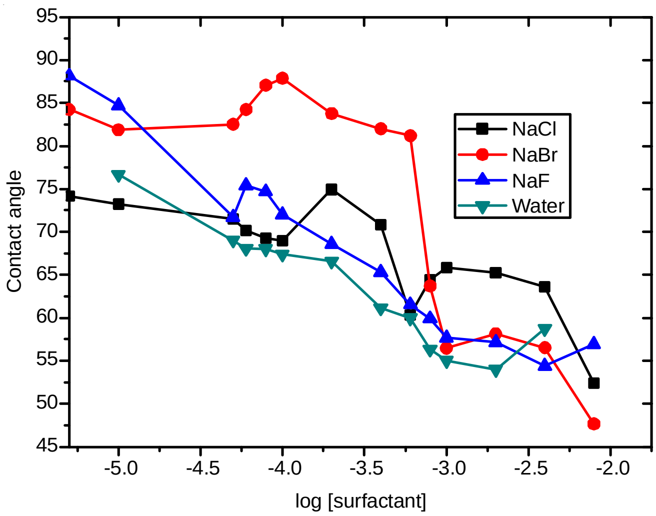

Fig. 5. Plot of contact angle (c) *versus* total surfactant concentration for different electrolytes of Triton X-102 at 298 K

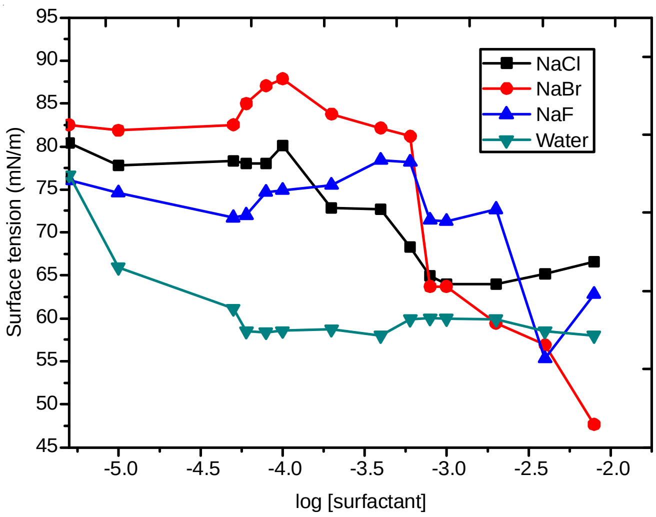

Fig. 6. Plot of contact angle (c) *versus* total surfactant concentration for different electrolytes of CTAB at 298 K

but reaches a plateau at high concentrations of NaBr. The differences are initially more noticeable. Adhesion is dependent on surfactant concentration; increased electrolyte concentrations while maintaining constant surfactant concentrations can achieve similar results. Counter ion and co-ion valence can effect wetting and contact angle. A similar effect influences the contact angle; increasing surfactant concentration reduces contact angle to a known constant value. Contact angle remains constant at high surfactant concentration.

Conclusion

Surface properties and micellar characteristics were evaluated through the measurement of contact angle and surface tensions. Increasing cationic surfactant concentrations result in a decreasing contact angle which approaches a minimum angle constant. Low concentrations of additives decreased surfactant CMC. At the same level of incorporation, the CMC values were found to be NaF > NaCl > NaBr, with the maximum reduction being observed using the additive NaBr.

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