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SOME PHYSICOCHEMICAL PROPERTIES OF OCTYLPHENOL ETHOXYLATE NONIONICS (TRITON X-100, TRITON X-114 AND TRITON X-405) AND THE TEMPERATURE EFFECT ON THIS PROPERTIES

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ABSTRACT

Surface tensions and condutvities of aqueous solutions of nonionic surfactants at various concentrations were measured at diffferent temperatures.

The critical micelle concentration (CMC) of aqueous solutions of three different octylphenol ethoxylate nonionics(Triton X-114, Triton X-100 and Triton X-405) are determined at different temperatures.

The effect of the ethylene oxide chain length and temperature on the CMC is also determined.

Keywords: Surface tension, conductivity, critical micelle concentration, nonionic surfactants

INTRODUCTION

Surfactants which are known as surface-active matters reduce surface tension in water and other liquids. The surface activity of surfactants derives from their amphiphilic structure that posses both hydrophilic and hydrophobic parts in one molecule. Surfactants are classified into four groups depending on the charge of the hydrophilic part: nonionic (0), anionic (−), cationic (+) and zwitterionic (±) [1,2]**.** Synthetic surfactants are economically important organic chemicals. They are used in many industrial applications such as metal processing, textile, food, pharmaceuticals and paper industries. They are also found in many household cleaning detergents and personal care products [3,4,5].

The interactions between surfactant molecules in aqueous solution have been extensively investigated because of their technological relevance in interfacial systems allowing for a better control of stability, flotation and rheology of dispersed system in different technological processes. Many hypothesis have been developed in order to predict the ideal behavior of surfactants in aqueous solution regarding equilibrium surface tension and adsorption at fluid interface[6].

Nonionic surfactants represent a class of surfactants which are inexpensive and have many potential applications, including cosmetics, detergency, pharmaceuticals, ore flotation, cloud point extraction methods, drilling fluids, and enhanced oil recovery processes [7-10].

Nonionic surfactants have been extensively used in the area of the laundry detergents and personal-care formulations in combination with anionic surfactants. The nonionic surfactants are represented mostly by linear alcohol ethoxylates, with the alcohols being derived from either petrochemical raw materials or natural resources. Different from anionic surfactants, the detergency of compositions containing nonionic surfactants is not sensitive to hard water since no precipitation occurs in the presence of divalent ions. Furthermore, nonionic surfactants can be used to deterge animal fibers such as silk and wool,to avoid the ionic adsorption of surfactant on the amino groups in the fibers since electrostatic force does not work for nonionic surfactants.[11]

Nonionic surfactants have a wide applicability theoretically and technologically. The mechanism of adsorption of nonionic surfactants, especially at the liquid-air interface, and the orientation and interaction of their molecules in the interface region have been the subject of study over recent decades .[12]

Although polyoxyethylenated nonionic surfactants are extensively used, both in industrial and in fundamental research applications, there is little reliable information on the surface and thermodynamic properties of well characterized, highly purified compounds of this type. [13] Investigation of these materials has been hampered by the difficulty of separating individual compounds from the product mixture obtained in the usual method of synthesizing these surfactants, the reaction of ethylene oxide with the hydrophobe, and by the tedium of the alternative method for their synthesis, the addition of the oxyethylene groups one or two at a time. [14]

These are prepared by reaction of ethylene oxide with the appropriate alkyl phenol. The most common such surfactants are those based on nonyl phenol. These surfactants are cheap to produce, but suffer from biodegradability and potential toxicity(the by-product of degradation is nonyl phenol, which has considerable toxicity). Despite these problems, nonyl phenol ethoxylates are still used in many industrial properties, owing to their advantageous properties, such as their solubility both in aqueous and non-aqueous media, good emulsification and dispersion properties etc. [15].

As the concentration of a surfactant in an aqueous solution is increased so called micellization takes place at a concentration referred to as the Critic Micelle Concentration or cmc. The cmc is most often detected in practice by the variation of some property, e.g. the solubilization, or by a change in trend of variation of other property, e.g. electrolytic conductivity or tension. [16]

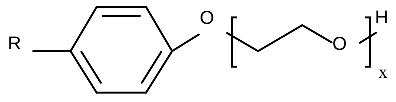
APEs such as nonylphenol ethoxylates are efficient cost effective versatile products which have been used widely in detergent compositions for over forty years. They have a better detergency performance than alcohol ethoxylates (AE). They meet the primary biodegradability but the metabolic products resulting from the degradation process do not readily degrade further and may have undesirable side effects on aquatic life[17].

In this work, we investigated some surface properties and the temperature effect on this properties Triton X-100, Triton X-114 and Triton X-405 in aqueous solution by means of surface tension, electrical conductivity. The temperature effect on this properties was investigated.

Our goal was to understand the effect of oxyethylene chain length and temperature on the micelle formation of Triton X-100, Triton X-114 and Triton X-405 in aqueous solution.

2.EXPERIMENTAL

2.1 MATERIALS AND METHOD



R = Octyl (C8)
x = 7.5(avg) Triton X-114
x = 9.5(avg) Triton X-100
x = 35(avg) Triton X-405

Scheme 1. Nonionic surfactans structure of Triton X-114, Triton X-100 and Triton X-405

Triton X-100 (polyoxyethylene *p*-*t*-octylphenol), 114(Octylphenol Ethoxylate) and 405(Octylphenol ethylene oxide condensate) were used as received from Aldrich. The surface tension of water was always controlled before the solution preparation.

All the solutions were prepared in doubly distilled water and measured under the thermostated conditions at 298 K with an accuracy of ± 0,001 K.

SURFACE TENSION MEASUREMENTS

Surface tensions of aqueous solutions of surfactants at various concentrations were carried out on the KSV SIGMA 702 with a ring method. The value of surface tension was the average of the three separate measurements.

The surface tension measurements were made at 293, 303, 313, 323, 333, 343 and 353 K with KSV SIGMA 702 tensiometer under the atmospheric pressure by the ring method. The platinum ring was thoroughly cleaned, and the flame was dried before each measurement. The measurements were taken in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension. It was then subsequently pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension, γ (mN/m). The measurements of the surface tension of pure water at 293, 303, 313, 323, 333, 343 and 353 K were performed to calibrate the tensiometer and to check the cleanliness of the glassware.

Since it was found that the surface tension decreases with time, the measurements were carried out until an equilibrium was established. This phenomenon took more than 10 h reach the equilibrium. I is mainly due toy he slow rearrangement of surfactant molecular configuration at the interface.

In all cases more than 10 successive measurements were carried out, and the standard deviation did not exceed ±0.2 mN/m. The temperature was controlled within ±0.1 K.

CONDUCTOMETRIC MEASUREMENTS

The conductometric measurements were taken with a Jenway conductometer conductometer using a cell of cell constant 0.92 cm-1. Accuracy of the measured conductance was within 0.01 µS. The surfactant conductance was measured after thorough mixing and temperature equilibration. The break point in the plot of either the equivalent conductivity versus the square root of the total surfactant concentration or the molar conductivity versus the total surfactant concentration was taken as cmc at the mole fraction.

CMC DETERMINATIONS

TABLE 1. Experimental results of CMC and surface tension at CMC for surfactant TRİTON X-114

t (^{0}C)	cmc values from surface tension (mmol/L)	cmc values from conductivity (mmol/L)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)
20	0,200	0,177	27,73	27,16
30	0,200	0,189	27,78	23,3
40	0,219	0,238	27,07	18,68
50	0,224	0,244	26,79	17,23
60	0,303	0,337	26,92	16,44
70	0,468	0,375	26,81	10,96
80	0,480	0,395	26,62	8,55

TABLE 2. Experimental results of CMC and surface tension at CMC for surfactant TRİTON X-100

t (^{0}C)	cmc values from surface tension (mmol/L)	cmc values from conductivity (mmol/L)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)
20	0,485	0,355	30,65	24,24
30	0,393	0,326	29,70	21,38
40	0,279	0,227	29,46	16,29
50	0,293	0,243	29,07	14,95
60	0,427	0,420	28,45	14,91
70	0,439	0,429	28,14	9,63
80	0,501	0,454	27,82	7,35

TABLE 3. Experimental results of CMC and surface tension at CMC for surfactant TRİTON X-405

t (^{0}C)	cmc values from surface tension (mmol/L)	cmc values from conductivity (mmol/L)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)
20	0,873	0,908	38,15	16,74
30	0,754	0,798	37,17	13,91
40	0,726	0,750	36,28	9,47
50	0,595	0,578	37,21	6,81
60	0,660	0,650	35,04	8,34
70	0,101	0,870	30,22	7,55
80	0,101	0,908	29,22	5,95

The surface tension of aqueous solutions of single surfactants at various concentrations were determined using the Du Nouy ring method at constant temperature. The cmc values were determined by break points in surface tension against logarithm of concentration curve. The cmc values were found to be in agreement with the measured solution conductivity and density.

The break point in the plot of either the equivalent conductivity versus the square root of the total surfactant concentration or the molar conductivity versus the total surfactant concentration was taken as cmc at the mole fraction.

3.RESULTS

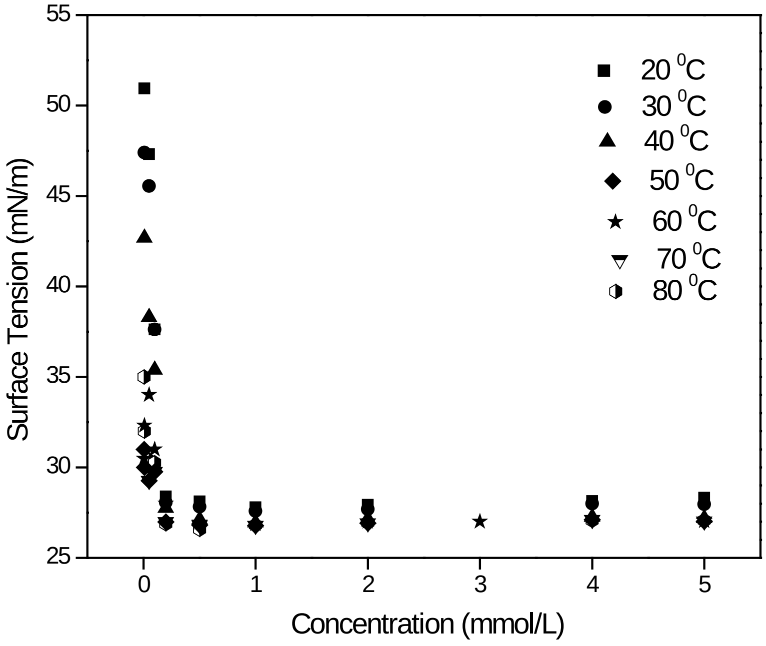


Fig.1 The variation of surface tension as a function of surfactant concentration in aqueous solution at different temperatures for Triton X-114

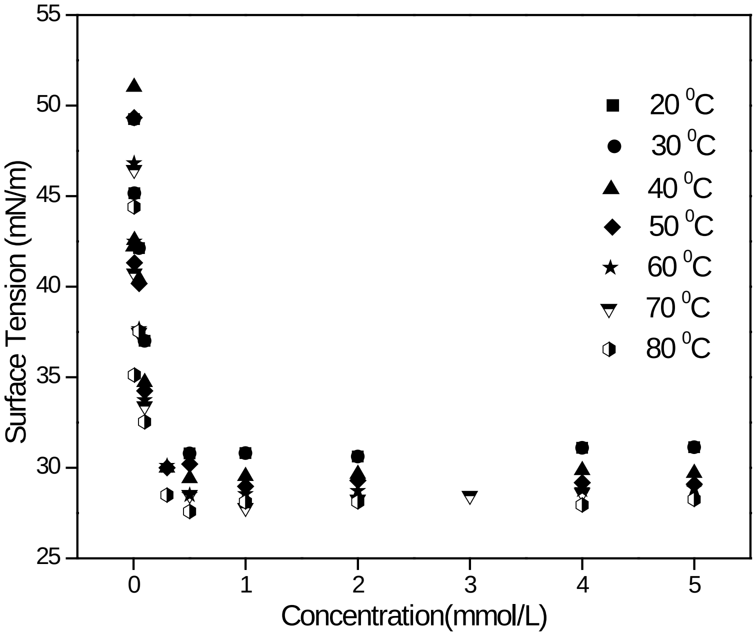


Fig.2 The variation of surface tension as a function of surfactant concentration in aqueous solution at different temperature for Triton X-100

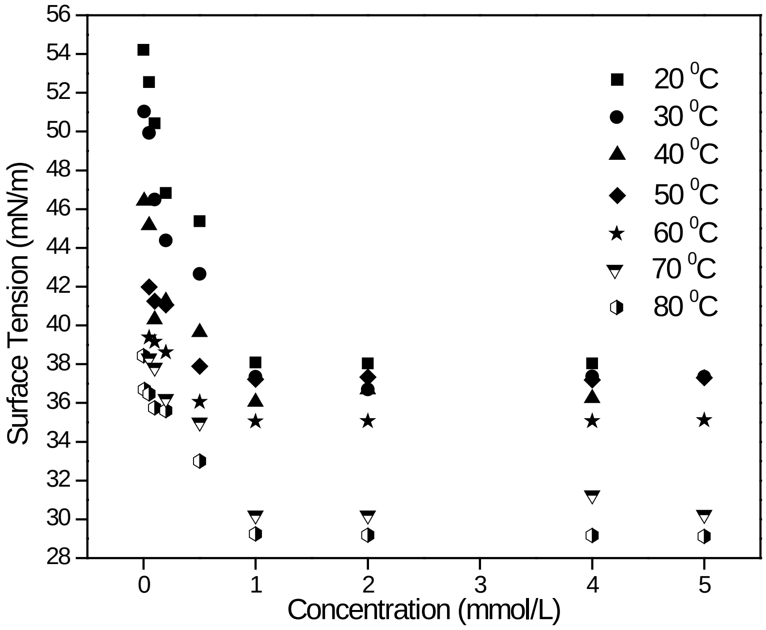


Fig.3 The variation of surface tension as a function of surfactant concentration in aqueous solution at different temperature for Triton X-405

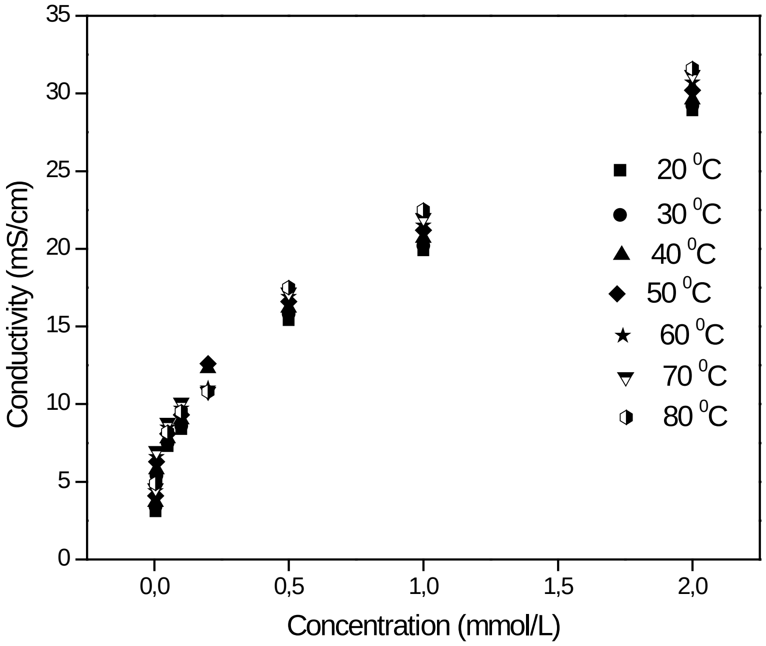


Fig.4 The variation of conductivity as a function of surfactant concentration in aqueous solution at different temperatures forTriton X-114

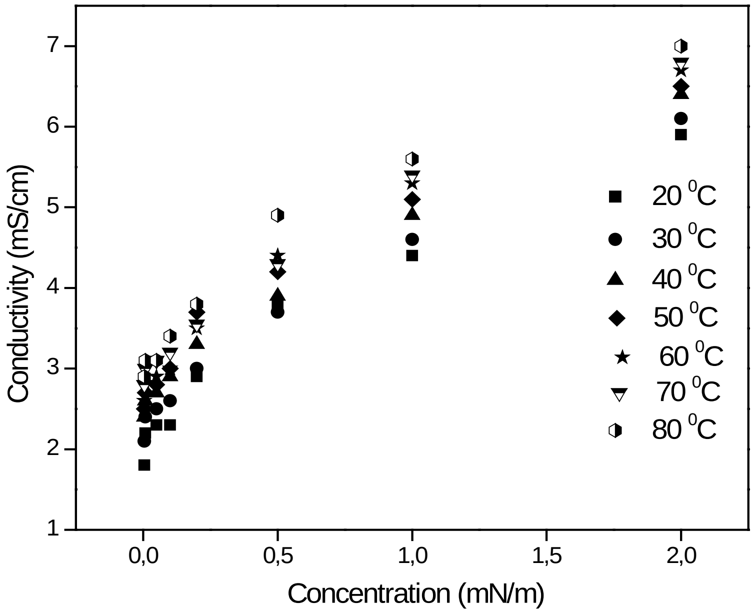


Fig.5 The variation of conductivity as a function of surfactant concentration in aqueous solution at different temperatures for Triton X-100

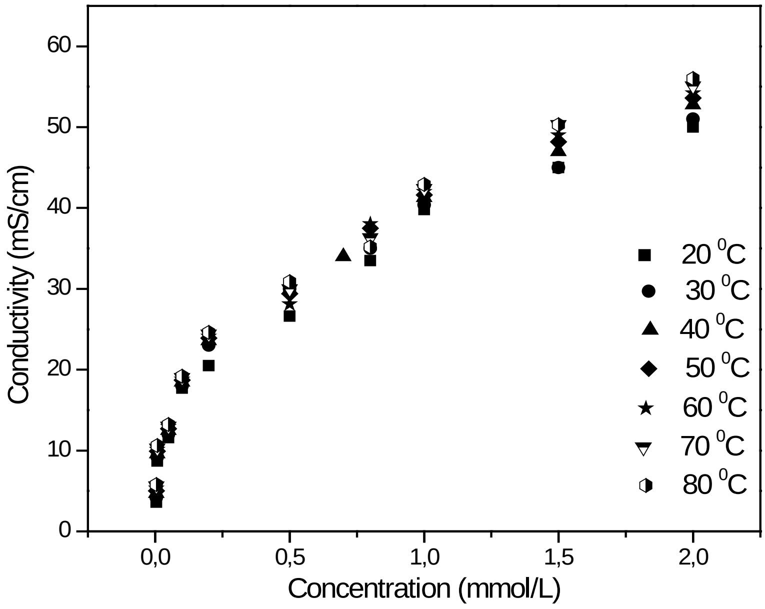


Fig.6 The variation of conductivity as a function of surfactant concentration in aqueous solution at different temperatures for TritonX-405

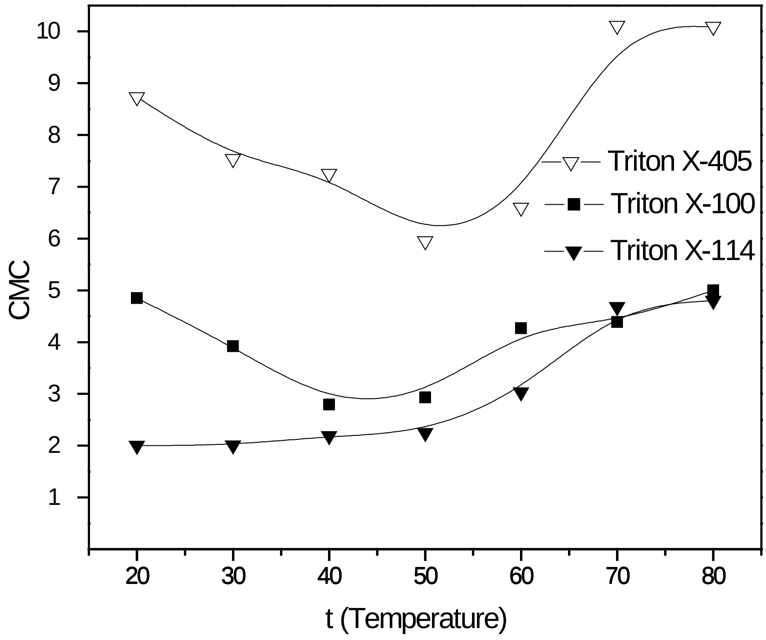


Fig.7 The varition of critic micelle concentration as a function of temperature for three surfactants

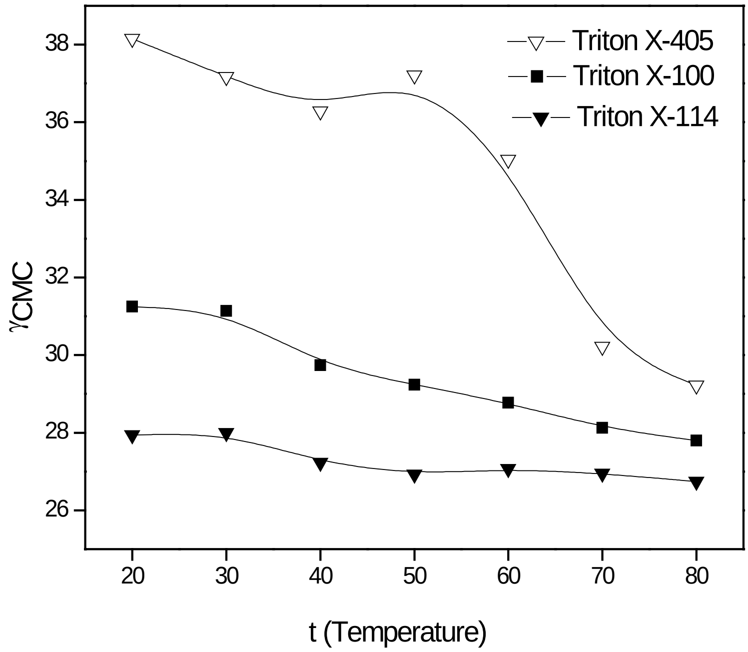


Fig.8 The varition of surface tension as a function of temperature for three surfactants

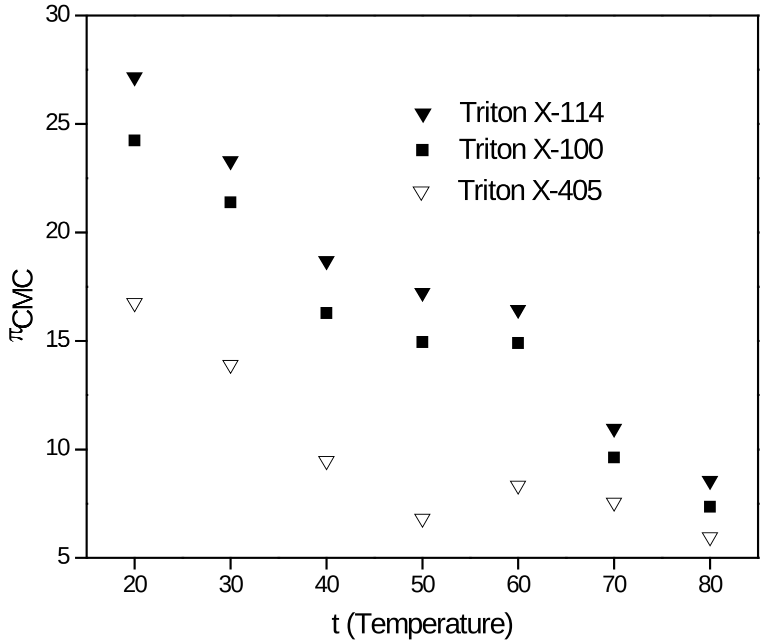


Fig.9 The varition of pressure as a function of temperature for three surfactants

The surface tensions were measured as a function of surfactant concentration at several different temperatures, as shown in Fig.1, Fig.2, Fig.3, Fig.4, Fig.5and Fig.6 . The cmc was then taken as the concentration at the sharp break, as listed in tables 1-3 for three surfactants. The cmc values from the surface tension-[surfactant] and conductivity-[surfactant] plots and are presented in Tables 1-3. Obviously, the curves corrobarated each other. Our results in the case of single nonionic surfactants have corroborated literatures. It was observed a constant temperature the cmc increases as the number of oxyethylene groups increases. [18]

Such behavior is directly related to the increase of hydrophilicity of the molecules with increasing oxyethylene chain length. For each surfactant, as the system temperature increases, the cmc initially decreases and then increases, as shown in Fig.7.

The initial decrease of the cmc with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules, owing to the smaller probability of hydrogen bond formation at higher temperatures. In other words, the increase in temperature causes the decrease in hydration of the hydrophilic oxyethylene group, which favors micellization. Consequently, the onset of micellization occurs at lower concentrations as the temperature increases.

On the other hand, while the surfactant molecules dissolve in water, the hydrophobic group distorts the water structure. The increase in temperature also causes the increase in breakdown of the structured water surrounding the hydrophobic alkyl group, which disfavors micellization. Consequently, the onset of micellization tends to occur at higher concentrations as the temperature increases.

Therefore, as the temperature increases further, the effect of the hydrophobic groups begins to exert an influence and finally predominates as the cmc reaches a minimum value and finally increases with temperature. Our results in the case of Triton X-100, Triton X-114 and Triton X-405 surfactants have corroborated literatures. It can be seen that the surface tension gradually decreased with increasing the concentration of Triton X-100. The decrease of surface tension indicated that Triton X-100, Triton X-114 and Triton X-405 molecules were adsorbed at the air/solution interface [19].

The initial decrease of the surface tension is followed by an abrupt change in the slope of the surface tension vs Triton X-100 concentration. After the breaking point, the surface tension of the solutions no longer changes obviously, suggesting the formation of micelles where the break point corresponds to a cmc, the corresponding surface tension is defined as cmc. The cmcs obtained from surface tension measurements are presented in Tables 1-3. It is obvious that for all three surfactant solutions the surface tension decreases monotonically as the temperature increases, and Triton X-114 of these systems is the most surface active among the three systems over the whole temperature range. It should be further noted that the decrease in surface tension γ_{CMC} is more pronounced for surfactants with a longer oxyethylene chain length, as shown in Fig. 8, due to an increase of the rupture of hydrogen bonds. It is well understood that there exists hydrogen bonding between water and surfactant molecules. While the temperature increases, some of the existing hydrogen bonds would rupture due to thermal fluctuation, which makes the surfactant molecules more hydrophobic, and thus the surface tension decreases. With a longer oxyethylene chain length surfactant, the oxyethylene chain is greatly hydrated. Therefore, the dehydration effect would be somewhat more pronounced for longer oxyethylene chain length surfactants since the surfactant molecule binds considerably more water molecules.

The cmc values of the surfactant solutions at different temperatures are also listed in Tables 1-3. While the temperature increases, some of the existing hydrogen bonds would rupture due to thermal fluctuation, which makes the surfactant molecules more hydrophobic, and thus the surface tension decreases. With a longer oxyethylene chain length surfactant, e.g. Triton X-405, the oxyethylene chain is greatly hydrated. Therefore, the dehydration effect would be somewhat more pronounced for longer oxyethylene chain length surfactants since the surfactant molecule binds considerably more water molecules.

In addition, the surface pressure is also listed in Tables 1-3. Rosen et al. [20] found a decrease of cmc with rising temperature for Tritons with small numbers of oxyethylene groups, whereas with more than five oxyethylene groups remains almost constant for the temperature ranging from 10°C to 40°C. Fig.9 shows the variation of surface pressure over a wide temperature range (10-80°C) for three surfactants. For the three systems, the surface pressure decreases monotonically with temperature.

The cmc values show an increase with increase in the number of oxyethylene groups in the molecule from seven to night and from nine to thirtynine as would be expected from the increase in the hydrophilic character of the molecule resulting from this change.

4.CONCLUSIONS

Surface properties studies of aqueous solutions of Triton X-114, Triton X-100 and Triton X-405 are important for understanding the apolar and polar interactions between Triton X-114, Triton X-100 and Triton X-405 surfactants and water molecules.

As a result the variations in cmc depends on the temperature and oxyethylene chain length of aqueous solution of nonionic surfactants. These observations may be of interest in practical applications of nonionic surfactant combinations.

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