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Viscometric Study of the Effects of Added Electrolytes on the Critical Micelle Concentration of Triton X-100 in Aqueous Medium

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Abstract

Viscometric study of the effect of five electrolyte additives (HCl, $HClO_4$, HNO_3, Na_2SO_4 and NaCl) on the critical micelle concentration of a nonionic surfactant, Triton X-100, was investigated at 30 ^{0}C using U-type Ostwald viscometer. Density measurements of Triton X-100 solutions in the presence of varying electrolyte concentrations were carried out using pycnometer. The electrolytes were studied in the concentration range 0 0.1 mol dm^{-3}. All the electrolytes were observed to lower the critical micelle concentration (CMC) of TritonX-100 significantly in the concentration range studied with HCl having the highest CMC decreasing effect up to a factor of over 400. The results have been explained based on *salting-out effect*. The observed trend of the CMC lowering effect of the acids: $HClO_4 < HNO_3 <$ HCl followed the Hofmeister series while greater CMC reducing effect of Na_2SO_4 than that of NaCl can be attributed to ionic strength effect.

Key words: additives, critical micelle concentration, electrolyte, salting-out, viscosity

Introduction

Surfactant applications are wide spread with significant relevance in biological, environmental and industrial processes [1-5]. Surfactants are soluble in aqueous solution. On saturation, the molecules cluster together as aggregates and the concentration at which this begins to occur is referred to as critical micelle concentration (CMC); and CMC is one of the most important physical parameters of surfactants [5]. Solute-solute and solute-solvent interactions between the surfactant monomers and electrolyte additives can significantly alter the micellar properties of the surfactant. The influence of additives on the process of micelle formation in surfactant solution is of considerable interest from both the fundamental and the applied view points since application of surfactants in many physico-chemical and interfacial phenomena largely depend on it [6-7]. Solubilizing capacity, surface and micellar characteristics and detergency of amphiphilic compounds are sensitive to the nature of added co-solute or solvent such as electrolytes [8]. Various physico-chemical properties of surfactants such as specific conductance, viscosity, osmotic pressure, density, polarity, refractive index, surface tension, fluorescence, dye solubilization, etc. have been widely investigated in understanding the interactions between added additives and surfactants [9-13]. There are several reports on the effects of electrolytes on the micellisation of Triton X-100 involving the use of physicochemical techniques such as surface tension, partial molar volume and electron paramagnetic resonance (EPR). However, only few studies have been reported on the use of viscometric method to characterize the micellization of Triton X-100 in electrolyte solutions. This work reports the effects of electrolyte additives (acids and salts) on the critical micelle concentration of a nonionic surfactant, Triton X-100, using viscometic method.

Materials and Methods

Materials: Triton X-100 (Fluka, 100%), Hydrochloric acid (Rieldel-deHaën, specific gravity = 1.19g/mL, 37%v/v), Perchloric acid (Karmel, specific gravity = 1.67g/mL, 70%v/v), Nitric acid (Saarchem, specific gravity = 1.84g/mL, 70% v/v), anhydrous Sodium sulphate (Sigma-Aldrich, >99%), Sodium chloride was a product of British Drug House (BDH) and Glacial acetic acid was purchased from Qualikem (Qualikem). All reagents were used without further purification.

Density Measurements: Densities of the various surfactant-electrolyte solutions were measured using 25 mL pycnometers. These were determined from the difference in mass between the empty pycnometer and when filled with the surfactant-electrolyte solutions after reaching thermal equilibrium in a water bath at 30 ^{o}C. Temperature was controlled with a Grant thermostatic water bath within ± 0.1^{0}C. Mettler Toledo balance with an accuracy of ± 0.001g was used for weighing.

Viscosity Measurements: U-type Ostwald viscometer (Sigma-Aldrich) with sufficiently long efflux time to avoid kinetic energy correction was used to measure the viscosities. The viscometer was calibrated using triply-distilled water. All viscosity measurements were done in triplicate; and the average flow times (reproducible to within ± 0.1s), recorded with a stopwatch were used to calculate viscosity values. A thermostatically controlled Grant water-bath was used to keep the temperature within ± 0.1^{0} C. Viscosity ( ) values, were calculated using the Paulis equation,

$$= kt, \qquad (1)$$

where *t* is the flow time of the surfactant in solution, is the density of the solution, and k is the viscometer constant.

Results and Discussion

CMC of Triton X-100 was determined from the plot of viscosity against concentration in the absence and presence of the electrolytes. Effect of electrolytes on CMC of Triton X-100 was investigated in the electrolyte concentration range 0.0005-0.10 mol dm^{-3}. Generally, viscosity of Triton X-100 increases with increase in its concentration until a certain point where the viscosity decreases and then increases again. This minimum in the plot where the viscosity shows abrupt change represents the CMC (Figure 1) [14-16].

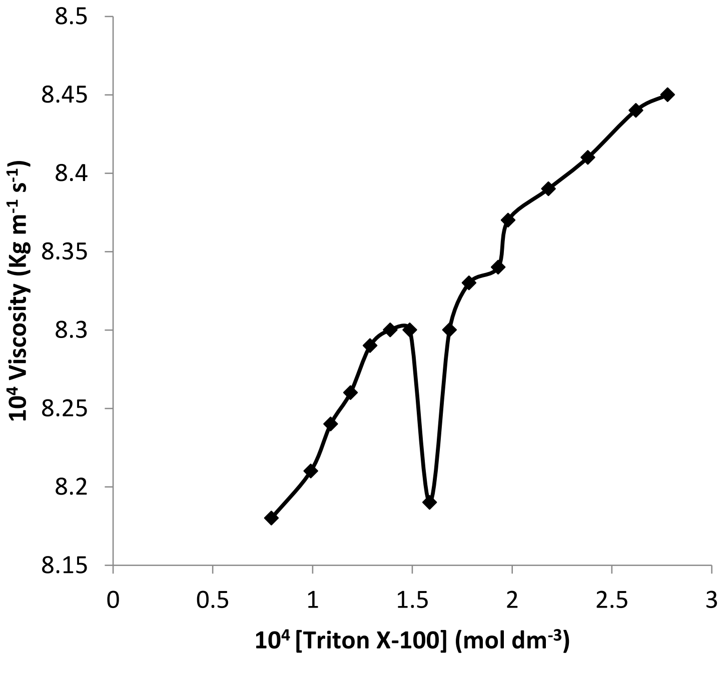

Figure 1: Typical plot of viscosity *versus* Triton X-100 concentration showing minimum point in the graph. T = 30 ^{o}C, [$HClO_4$] = 0.07 mol dm^{-3}.

From the result in Table 1, it can be seen that CMC of Triton X-100 decreases as the concentration of the electrolyte increases. In this work, CMC values of pure aqueous Triton X-100 solution were determined at two temperatures, 25 ^{0}C and 30 ^{o}C. The CMC values were found to be 2.2 × 10^{-4} and 2.4 × 10^{-4} mol dm^{-3} respectively. These values agree well with the reported literature values for CMC values of Triton X-100 using some other methods [17-19]; and therefore validates the results obtained in this work. All the electrolytes studied were found to lower the CMC of Triton X-100 in the studied electrolyte concentration range (Figure 2).

Table 1: CMC of Triton X-100 in the absence and presence of electrolytes at 30 ^{o}C

[Electrolyte] (mol dm^{-3})	10^4 CMC of Triton X-100 (mol dm^{-3})				
	$HClO_4$	HNO_3	HCl	Na_2SO_4	NaCl
0.0000	2.400	2.400	2.400	2.400	2.400
0.0005	2.379	2.387	2.380	2.110	2.260
0.0010	2.182	1.617	1.488	1.680	1.820
0.0020	1.980	1.201	1.091	1.200	1.540
0.0030	1.930	0.809	0.595	1.060	1.430
0.0050	1.785	0.504	0.396	0.500	1.100
0.0070	1.587	0.102	0.099	0.402	0.900
0.0100	1.389	0.083	0.079	0.210	0.380
0.0200	1.289	0.060	0.050	0.107	0.200
0.0500	1.091	0.042	0.020	0.040	0.090
0.1000	0.496	0.010	0.006	0.011	0.030

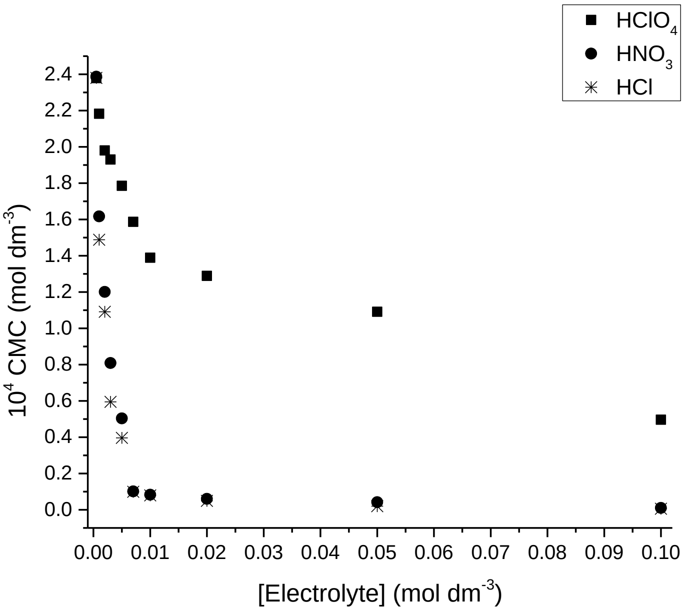

Figure 2: Plots of Critical Micelle Concentrations of Triton X-100 *versus* the concentrations of the various electrolytes in aqueous solution at 30 °C

The presence of electrolytes in the aqueous environment of the non-ionic surfactant is suspected to be the primary factor responsible for the shift in the CMC values when compared to their values in pure surfactant-water solutions. This effect may be attributed to two major possible factors; namely: modification of water structure and salting-out effect.

***Modification of water structure*:** Ions that tighten the structure of water and increase surfactant viscosity are designated as structure promoters. In the absence of charged head group as in the case of Triton X-100, the driving force of micellization is the hydrophobic force and the van der Waals attraction. The presence of these ions can however, affect the water structure in the surfactant environment and enhance micellization of surfactants [20]. Also, hydrogen bonds formed by Triton X-100 with water molecules through the oxyethylene unit require high energy to break. Hence, micelles are formed at high concentrations; but in the presence of the structure maker electrolytes, the hydrogen bonds break easily and so the higher the concentration of electrolytes present, the easier it is for the hydrogen bonds to break [20-21].

Salting-out effect: The presence of electrolyte additives causes dehydration of nonionic micellar aggregates in aqueous solutions. It has been proposed that the total effect of an electrolyte in nonionic surfactant is approximately the sum of its effect on the hydrophobic and hydrophilic parts of the surfactant molecule in contact with the aqueous phase [22]. This dehydration facilitates the expansion of the hydrophobic microenvironment of the nonionic micelle and consequently, the CMC is lowered [23]. Also, the salting-out of hydrophilic part of the surfactant is produced when the anions from the electrolytes compete with surfactant for hydration thereby reducing the amount of water available in the micelle for polar chain hydration. Thus, micelles are formed at lower surfactant concentration [24]. EPR study of surface hydration of Triton X-100 with univalent electrolytes [25] suggests that the solubility of Triton X-100 reduces when the concentration of the electrolyte is increased.

This behavior was attributed to a decrease in concentration of water around the micellar polar shell. The number of hydrogen bonds formed with the ether groups will therefore decrease, thus reducing barrier for micelle-micelle interactions, and hence, enhance micelle formation. Many studies [26-27] have previously classified the electrolytes used in this work as water-structure makers. Electrolytes that are water-structure makers have been reported to show salting-out effect in nonionic surfactants which is in agreement with our findings. For salting-out effect, factors to be considered are: (1) size of anion (ionic charge/radius ratio and (2) ionic strength of the solution.

Effect of electrolyte anion size: The work required for the association of any surfactant with water changes in the presence of an electrolyte due to water ion interactions. If this work increases by the addition of an electrolyte, surfactant monomers are salted-out and micellization is enhanced. Electrolyte effects depend upon the radius of the hydrated ion. The smaller the radius, the greater the salting-out effect, and the more the value of CMC decreases [28]. The order of decreasing ability of the acid electrolytes to enhance micellization of Triton X-100 as observed in this study is HCl > HNO_3 > $HClO_4$ (Figure 2) showing strong dependence on the size of the anions. acccording to Hofmeister series [24]. Salting-out effect influences solubility and depends on the hydration energy of the ions. The Hofmeister series is the arrangement of ions according to their ability to salt out, and orders ions with decreasing salting out potency from left to right shown below:

SO_4^{2-}, HPO_4^{2-},OH^-,F^-,$HCOO^-$,CH_3COO^-,Cl^- ,Br^-,NO_3^-,I^- , SCN^-,ClO_4^-

Effect of ionic strength: In the case of the inorganic salts, Na_2SO_4 shows greater salting out ability than NaCl (i.e, SO_4^{2-}> Cl^-). Since both salts are known to be structure-making electrolytes [29], the result suggests that the ionic strength of the electrolytes contribute significantly to lowering of the CMC of Triton X-100. Salting-out utilizes changes in solubility based on ionic strength [30]. The ionic strength of an electrolyte solution, I is the sum of the ionic strength of the individual ions in the solution, mathematically expressed as

$$I = \frac{1}{2} \quad {}_i z_i^2 \qquad (2)$$

where m_i = concentration of the ion and z_i = charge on the ion

In determining the effect of electrolytes on the CMC of a surfactant, the anion and cation contribute to the overall decrease or increase in CMC of the surfactant. For nonionic surfactant solutions, the salt effect on CMC is given in equation 3 [31]

$$\log CMC = - KC_s + \text{constant} \ (C_s<0.1) \qquad (3)$$

where K is a constant for a particular surfactant in a given electrolyte solution and temperature. C_s is the concentration of electrolyte in moles per liter.

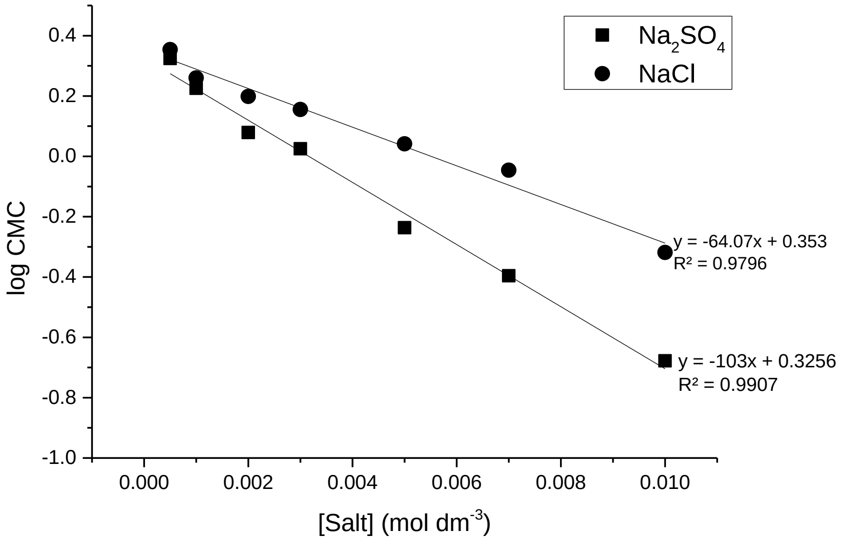

Figure 3: Plots of logarithm of Triton X-100 CMC versus salt concentration at 30 °C

Linear plots of logCMC versus salt concentration (0.0-0.01 mol dm^{-3}) are shown in Figure 3. The values of K for Triton X-100 in solutions of Na_2SO_4 and NaCl at 30 ^{0}C are 103.00 and 64.07 respectively. The salt constant of a surfactant molecule is also based on the sum of two opposing contributions [32-33]: One which results from its hydrophobic tail and the other from its hydrophilic head group [26]. The salting-out effect of the hydrocarbon moiety has been found to lower the CMC of the surfactant to a greater extent than the hydrophilic head group. In addition to this, the stronger water-structure making salt gives the greater value of salt effect parameter [33].

Conclusion

We have studied the effects of HCl, $HClO_4$, HNO_3, Na_2SO_4 and NaCl electrolytes on the micellization behavior of Triton X-100 using viscosity measurements. The results obtained in this work show that the lowering of the CMC of Triton X-100 by the electrolytes is not only due to the modification of the water structure but significantly due to salting-out effect. The observed trends for the Triton X-100 CMC lowering effect of the acids and salt electrolytes are: $ClO_4^- < NO_3^- < Cl^-$ and $Cl^- < SO_4^{2-}$ respectively. The results agree with the Hofmeister series on salting-out potency of electrolytes.

References:

[1] Y. Chen, H. Yang and G. Gu (2001), Effect of acid and surfactant treatment on activated sludge dewatering and settling, *Water Research*, **35**(11), 2615-2620.

[2] I. Kralova and J. Sjöblom (2009), Surfactants Used in Food Industry: A Review. *Journal of Dispersion Science and Technology,* 3**0**(9), 1363-1383.

[3] Y. Zhang, Z. Zeng, G. Zenga, X. Liu, Z. Liu, M. Chen, L. Liu, J. Li and G. Xie (2012), Effect of Triton X-100 on the removal of aqueous phenol by laccase analyzed with a combined approach of experiments and molecular docking. *Colloids and Surfaces B*: Biointerfaces, **97**, 7 12.

[4] N. Kumar and R. Tyagi (2013), Dimeric Surfactants: Promising Ingredients of Cosmetics and Toiletries. *Cosmetics*, **1**(1), 3-13.

[5] K. Staszak, D. Wieczorek and K. Michocka (2015), Effect of Sodium Chloride on the Surface and Wetting Properties of Aqueous Solutions of Cocamidopropyl Betaine. *Journal of* Surfactants *and* Detergents, **18**, 321 328.

[6] M. C. Hoener and S. Varon (1997), Effects of sodium chloride, Triton X-100, and alkaline pH on the measurable contents and sedimentability of the nerve growth factor (NGF) antigen in adult rat hippocampal tissue extracts. *Journal of Neuroscience Research,* **49**(4), 508-514.

[7] K. Holmberg, B. Jonsson, B. Kornberg annd B. Lindman (2003), Surfactants and Polymers in Aqueous Solution, 2nd Edition. John Wiley & Sons, New York, pp.121-124.

[8] N. Dubey (2008), Conductometrics study of interaction between Sodium Dodecyl Sulfate and1-propanol, 1-butanol, 1-pentanol and 1-hexanol at different temperatures, Journal of Surface Science and Technology. Journal of *Surface Science* and *Technology***,** **24**, 139-148.

[9] T. S. Singh and S. Mitra (2010), Interaction of charge transfer fluorescence probe with nonionic surfactants: Estimation of physic chemical properties and association constant. *European Journal of Chemistry*, **1**(4), 341-347.

[10] G. P. Jones, S. Regismond, K. Kwetkat and R. Zana (2001), Micellization of Nonionic Surfactant Dimers and of the Corresponding Surfactant Monomers in Aqueous Solution. *Journal* of *Colloid* and *Interface Science*, **243**, 496 502.

[11] Y. Shi, H. Q. Luo, and N. B. Li (2011), Determination of the critical premicelle concentration, first critical micelle concentration and second critical micelle concentration of surfactants by resonance Rayleigh scattering method without any probe. *Spectrochimica Acta Part A*: Molecular Spectroscopy, **78**, 1403-1407.

[12] N. Kolishetti, and S. Ramakrishnan (2007), Effect of surfactants on the fluorescence spectra of water soluble MEHPPV derivatives having grafted polyelectrolyte chains. *Journal* of *Chemical* Sciences, **119**(2), 185 193.

[13] K. Szymczyk, and A. Taraba (2016), Aggregation behavior of Triton X-114 and Tween 80 at various temperatures and concentrations studied by density and viscosity measurements, *Journal of Thermal Analysis and* Calorimetry, **126**, 315 326.

[14] W. Chunhung, J. L. Neng, C. C. Kuan and H. Hsiu-Fu (2014), Determination of critical micelle concentrations of ionic and nonionic surfactants based on relative viscosity measurements by capillary electrophoresis, *Research* on *Chemical* Intermediates, **40**, 2371-2379.

[15] P. Wiseman, C. A. Kennedy; D. G. Marangoni and R. A. Palepu (1998), Viscometric and Conductometric Investigation of the Micellar and Solution Properties of Two-Headed Surfactant Systems, the Disodium 4-Alkyl-3-sulfonatosuccinates, *Journal of* Solution Chemistry, **27**(3), 217 233.

[16] T. Patel, G. Ghosh, V. Aswal and P. Bahadur (2009), Micellization of sodium dodecyl sulfate and polyoxyethylene dodecyl ethers in solution, *Colloid and Polymer Science*, **287**, 1175 1181.

[17] R. C. Chautmal, T. J. Patil and V. B. Jadhav (2015), Micellar Behavior of Non-ionic Surfactant Triton-X-100 in Presence of Myo-Inositol at Different Temperatures by Surface Tension, International Journal of PharmTech Research, **8**(6), 192-197.

[18] C. C. Ruiz, J. A. Molina-Bolivar and J. Aguiar (2001), Thermodynamic and Structural Studies of Triton X-100 Micelles in Ethylene Glycol-Water Mixed Solvents. *Langmuir*, **17**, 6831-6840.

[19] G. Nemethy and A. Ray. (1971). Micelle formation by nonionic detergents in water-ethylene glycol mixtures, *Journal of Physical Chemistry*, , **75**(6), 809-815.

[20] B. Hribar, N. T. Southall, V. Vlachy and Dill, K. A. (2002), How ions affect the structure of water, *Journal of the American Chemical Society*, **124**(41), 12302-12311.

[21] H. Kanno, K. Yonehama, A. Somraj and Y. Yoshimura (2006), Structure-making ions become structure breakers in glassy aqueous electrolyte solutions, *Chemical Physics Letters*, **427**, 82-86.

[22] M. J. Rosen (2004), Surfactants and Interfacial Phenomena, Third Ed. Wiley-Interscience, New York, p. 145

[23] M. N. Khan (2007), Micellar Catalysis, CRS Press, Surfactant Series, CRC Press Taylor & Francis Group, Volume 133, p. 22

[24] A. A. Taha, H. H. Abdel Rahman and F. M. Abouzeid (2013), Effect of Surfactants on the Rate of Diffusion Controlled Anodic Dissolution of Copper in Orthophosphoric Acid, *International Journal of Electrochemical Science*, **8**, 6744 6762

[25] B. J. Jose, B. L. Bales and M. Peric (2009), An EPR Study of the Surface Hydration of Triton X-100 Micelles in Water with Added Monovalent Alkali Salts, *Journal of Physical Chemistry B*, **113**(40): 13257 13262.

[26] H. Scott and A. E. Royce (1984), Effect of inorganic additives on solutions of Nonionic surfactant VI- further Cloud Point Relations, *Journal of Pharmaceutical Sciences*, **73**(6), 793-799.

[27] S. Miyagishi, K. Okada and T. Asakawa (2001), Salt Effect on Critical Micelle Concentrations of Nonionic Surfactants, N-Acyl-N-methylglucamides (MEGA-n), *Journal* of *Colloid* and *Interface Science*, **238**, 91 95.

[28] H. B. Klevens (1948), Critical micelle concentrations as determined by refraction, *Journal* of Physical and *Colloid Chemistry*, **52**(1),130-48.

[29] S. M. Burkinshaw (2016) Physico-chemical Aspects of Textile Coloration John Wiley & Sons, p 119-120

[30] C. Raymond (2000), Physical Chemistry for the Chemical and Biological Science. 3rd ed. Sausalito, Calif: University Science Books.

[31] A Ray and G. Nemethy (1971), Effects of ionic protein denaturants on micelle formation by nonionic detergents, *Journal of the American Chemical Society*, **93**, 6787 6793.

[32] Carale, T. R.; Pham, T.; Blankschtein, D. (1994), Salt effects on intramicellar interactions and micellization of nonionic surfactants in aqueous solutions, *Langmuir.* **10**(1), 109 121.

[33] N. Nishikido and R. Matuura (1977), The Effect of Added Inorganic Salts on the Micelle Formation of Nonionic Surfactants in Aqueous Solutions, *Bulletin of the Chemical Society of Japan*, **50**, 1690-1694.