

Surface Tension Study of the Micellization of the Nonionic Surfactant Triton X-100 in H₂O and H₂O-Ethanolamine Solvents

Sameer H. Kareem and Ayat Monther Noaman

Department of Chemistry, College of Science for Women, University of Baghdad.

Abstract

The critical micelle concentration (cmc) of aqueous solutions of Triton X-100 surfactant and binary mixture of water + ethanolamine solutions have been determined by tensiometry technique in aqueous at different temperatures in the range from 293 to 323 K. The interfacial parameters $\Gamma_{\max}$, $A_{\min}$, Π_{cmc} and $\Delta G^{\circ}_{\text{ads}}$ for the two system were calculated. The results indicate that the cmc increases as the temperature and the percentage of ethanolamine increases. The standard thermodynamic functions, such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of micellization were estimated using the change of cmc with temperature. The effect of addition of ethanolamine to the aqueous solution on the cmc, the adsorption parameters and micellization have been studied.

Keywords: Surfactant, Triton X-100, Thermodynamic micellization, Ethanolamine, Surface Tension.

Introduction:

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, plastics[1,2,3]. The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants. Triton X-100 (TX-100) is a nonionic surfactant which has a hydrophilic polyethylene oxide chain [4]. TX-100 can be found in several types of cleaning compounds, ranging from heavy-duty industrial products to gentle detergents. TX-100 appears as a final ingredient in several yearly influenza vaccines worldwide [5].

Thermodynamic parameters indicate to the hydrophobic interaction of surfactants with water have been the aim of many studies. Ruiz C.C et al.^[6] studied thermodynamic and structural of TX-100 micelle in ethylene glycol-water mixed solvents. It was found that the surface activity of the surfactant decreases slightly with increasing concentration of ethylene glycol at a given temperature. Molina-Bolivar J.M. et al.^[7] investigated the surface activity, Micelle formation, and growth of non ionic surfactant in aqueous solution at different temperature. Fernandes R.M.F. et al.^[8] reported the micellization behavior of a surfactant with high solubility mismatch: composition, temperature, and salt effects. Batigoc. C. et al.^[9] studied thermodynamics of T X-100-cationic gemini

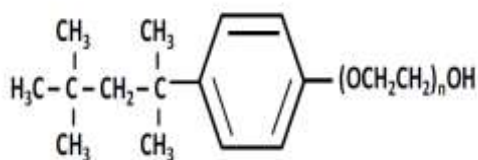
surfactants mixtures at the cloud point. This study investigated the effects of gemini surfactant on the cloud point of the non-ionic surfactant TX-100 in aqueous solutions. Lu S. et al.^[10] studied the micellar evolution in mixed nonionic/ anionic surfactant systems using a range of techniques including surface tensiometry, fluorescence spectroscopy, ultra filtration, and analytical ultra centrifugation.

In this paper, we report study on the micellar properties of the nonionic surfactant TX-100 in Water and Ethanolamine-water mixtures using surface tensiometry technique. This surfactant was selected because of its extensive use in industrial and pharmaceutical formulations and in biochemical research.

Materials and Methods

Materials

The Triton X-100 surfactant of the highest purity was obtained from the BDH Chemicals Ltd poole England. It has formula $(C_{14}H_{22}O(C_2H_4O)_n)$ where $n=10$, its IUPAC name is polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether or octyl phenol ethoxylate, and molecular mass is 646 g/mol. Ethanolamine (EA)(99.0%) was purchased from BDH with formula $CH_2(OH)CH_2NH_2$ and molecular mass is 61.08 g/mol.



Triton X-100

Methods

Determination of Surface Tension

The surface tension of the solutions of surfactant in water and its mixtures with EA was measured using Du-Nouy type tensiometer with Pt ring was made with the DST 30-SEO-Korea.

Preparation of Solutions

1. A stock solution (0.022M) of TX-100 and diluted solutions of different concentration ranged (0.025-0.300) mM (mmol/L) were

prepared in volumetric flask and stored at room temperature until use.

2. Water-Ethanolamine mixture media was prepared with four percentage 5%, 10%, 15%, 20% (v%) of EA.

Results and Discussion

The cmc of TX-100 was determined by measure the surface tension (γ) of the prepared aqueous solutions and plotted against their concentrations at constant temperature. When concentration increased the surface tension decreased until reach to cmc where no further change in surface tension. This was presented in Fig.(1) at 20°C and at the four temperatures used in this work, while the values of cmc at the different temperatures are reported in Table (1).

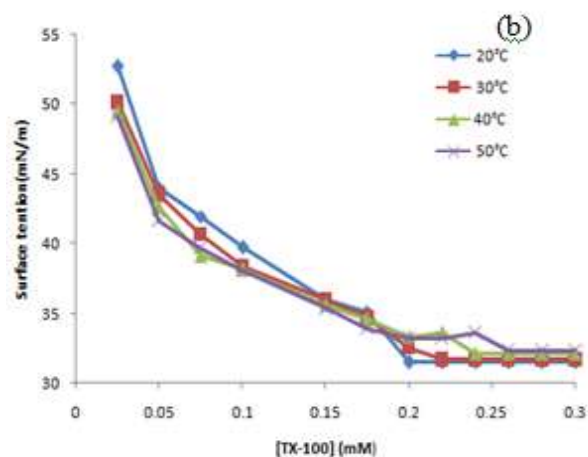
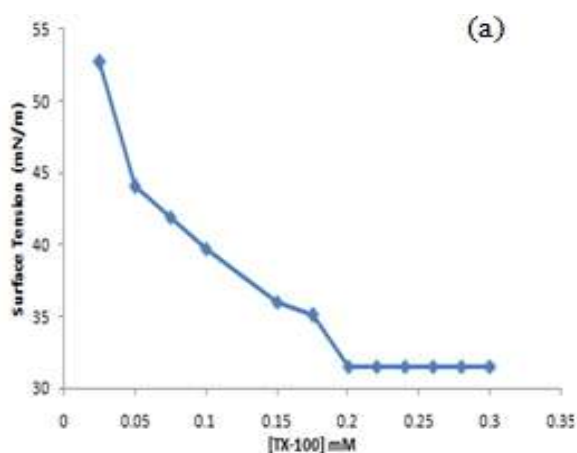


Fig. (1) Variation of surface tension against concentration in aqueous solution for TX-100. (a) at 20°C (b) at different temperature.

The cmc value obtained at 20°C is 0.22 mM, which is in agreement with the published data in the literature, and slight differences can be attributed to the different methods employed for cmc determination [6,11].

The results of Figure 1 and Table 1 show that the cmc of TX-100 surfactant in aqueous solution increases as the temperature increased. This may be due to that the surfactants molecules dissolved in water due to a larger probability of hydrogen bond formation at higher temperature, the hydrophobic group distorts the water structure [12].

Table (1)

Thermodynamic parameters of micellization and adsorption for TX-100 in H₂O and H₂O-EA media at different temperatures.

V% of EA	T (K)	CMC (mM)	Π_{cmc} (mN/m)	$\Gamma_{max} \times 10^3$ (mmol/m ²)	A_{min} (Å ² /molecule)	$-\Delta G_{ads}^{\circ}$ (KJ/mol)	$-\Delta G_m^{\circ}$ (KJ/mol)	ΔH_m° (KJ/mol)	ΔS_m° (J/mol.K)	ΔG_M° (KJ/mol)
0%	293	0.20	43.238	3.80	43.7	41.83	30.45	-4.99	87.03	-
	303	0.22	40.746	3.20	51.9	44.07	31.34	-5.43	85.80	-
	313	0.24	36.23	2.70	61.5	45.54	32.14	-5.70	84.35	-
	323	0.26	32.839	2.60	63.8	45.58	32.95	-6.07	83.28	-
5%	293	0.26	31.553	2.79	59.5	40.37	29.82	1.43	106.60	0.63
	303	0.24	31.081	2.82	58.9	42.46	31.04	1.53	107.50	0.30
	313	0.22	30.263	2.96	56.1	42.49	32.27	1.63	108.30	0.13
10%	293	0.28	28.219	2.79	59.5	39.65	29.54	2.14	108.12	0.91
	303	0.27	28.190	2.80	59.4	40.70	30.63	2.29	108.64	0.71
	313	0.26	27.560	2.90	57.2	41.60	31.75	2.44	109.23	0.39
15%	293	0.30	26.374	2.69	61.7	39.09	29.28	2.85	109.66	1.17
	303	0.29	26.621	2.70	61.5	39.86	30.36	3.05	110.26	0.98
	313	0.28	26.459	2.75	60.4	41.08	31.46	3.26	110.93	0.68
20%	293	0.33	24.613	2.32	72.2	39.98	28.93	3.57	110.96	1.15
	303	0.31	24.993	2.46	67.5	40.24	30.08	3.82	111.88	1.26
	313	0.30	24.659	2.57	64.6	40.77	31.18	4.07	112.62	0.97

The effect of the presence of another solvent in addition to surfactant solution, such as EA in the range 5-20% and the effect of the temperature in the range (20-40°C), on the cmc values and another micellization parameters have been studied. The results

obtained are tabulated in Table (1) and a typical plots of γ versus concentration for different percentage of EA at 30°C and at different temperature for 5% EA were presented in Fig.(2).

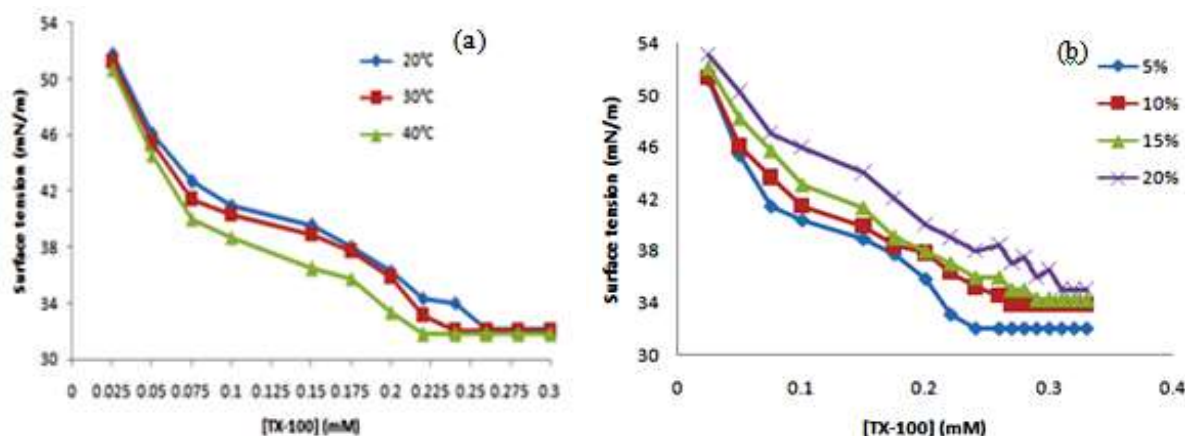


Fig.(2) Surface tension of TX-100 as a function of surfactant concentration:

(a) 5% of EA at different temperature.

(b) 30°C at different percentage f EA.

There is a sharp breakpoint in these plots and the cmc values were taken to be the point of intersection of the lines drawn through the points of the graphs and given in Table (1).

The results obtained show that the cmc values of TX-100 are increases as the percentage of EA increased and that is a result

of the presence of a structure-breaking solute and can be attributed to the increase in solubilization of the nonpolar chain of the surfactant by EA. The decrease in cmc values with the increasing temperature at all given concentration of EA is attributed to the less

disruption of the solvent structure with the increase in temperature⁽¹³⁾.

The dependence of cmc on the temperature was used to calculate the thermodynamic parameters of adsorption and micellization. The surface excess concentration, ($\Gamma_{\max}$), and the minimum area per surfactant molecule, $A_{\min}$, at the air/water interface were obtained using the following equations [6]:

$$\Gamma_{\max} = \frac{-(\partial\gamma/\partial\ln C)}{RT} \dots\dots\dots (1)$$

$$A_{\min} = 1/N_A \Gamma_{\max} \dots\dots\dots (2)$$

where R is the gas constant, N_A is Avogadro's number, γ is the surface tension value, and C is the molar concentration of surfactant in solution. The values of the surface pressure at the cmc (Π_{cmc}) were obtained employing the following equation:

$$\Pi_{\text{cmc}} = \gamma - \gamma_{\text{cmc}} \dots\dots\dots (3)$$

where γ_{cmc} is the surface tension at cmc. The Gibbs free energy of micellization ΔG°_m was calculated using the equation:

$$\Delta G^\circ_m = RT \ln X_{\text{cmc}} \dots\dots\dots (4)$$

Where X_{cmc} is the mole fraction of surfactant at the cmc. The standard free energy of adsorption, $\Delta G^\circ_{\text{ads}}$, was determined using the equation:

$$\Delta G^\circ_{\text{ads}} = \Delta G^\circ_m - \Pi_{\text{cmc}} / \Gamma_{\max} \dots\dots\dots (5)$$

The enthalpies of micellization ΔH°_m were obtained from the temperature variation of the cmc, by employing the equation:

$$\Delta H^\circ_m = -RT^2(\partial \ln X_{\text{cmc}} / \partial T) \dots\dots\dots (6)$$

The entropy values of micelle formation ΔS°_m were evaluated from the calculated enthalpy and free energy values as follows:

$$\Delta S^\circ_m = (\Delta H^\circ_m - \Delta G^\circ_m) / T \dots\dots\dots (7)$$

The effect of the co-solvent on the micelle aggregation process ΔG°_M was calculated from the following equation:

$$\Delta G^\circ_M = \Delta G^\circ_m (\text{EA} + \text{water}) - \Delta G^\circ_m (\text{water}) \dots\dots\dots (8)$$

The $\partial\gamma/\partial\ln C$ in equation 1 was determine from the slope of the plot of γ versus $\ln C$, and the $\partial \ln X_{\text{cmc}} / \partial T$ in equation 6 was determine from the slope of plot of $\ln X$ versus T shown in Fig.(3).

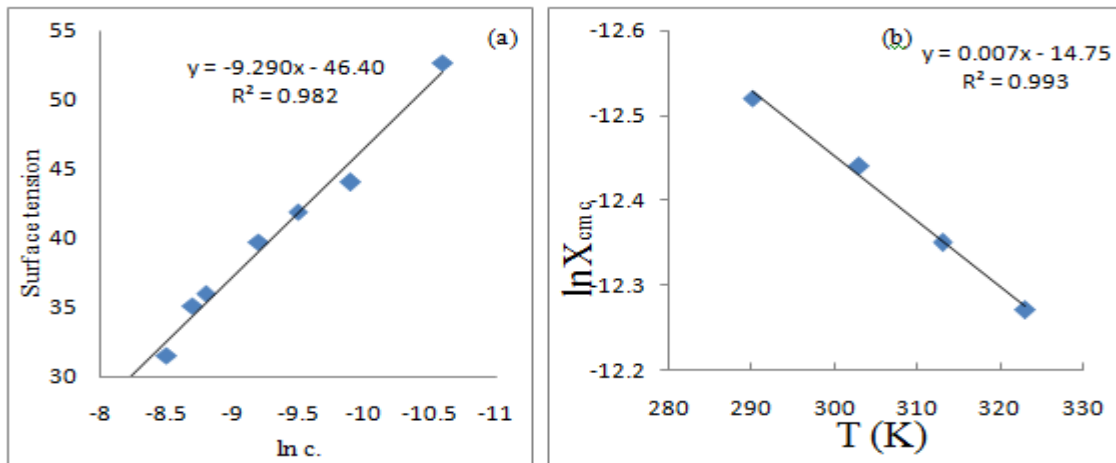


Fig.(3) Typical plot of a) surface tension versus $\ln C$ at 293 K; b) $\ln X_{\text{cmc}}$ versus temperature, for aqueous solution of TX-100.

The results obtained by applying the above procedure are reported in Table 1 for the

thermodynamic parameters of micellization and adsorption.

In the absence of the additive, the free energy of micellization becomes more negative with an increase in temperature indicating that the formation of micelles becomes more spontaneous with increasing temperature. The data of ΔH_m° , that we have obtained indicate that the micellization process is exothermic ($\Delta H_m^\circ < 0$). The entropy of micellization ΔS_m° is positive in all temperature range and decreases with increase in temperature. This is due to fact that the head group is more hydrated than the hydrophobic tail with increasing temperature which leads to an overall ordering of the system hence, the lowering of the entropy with increase in temperature⁽¹⁴⁾.

The results also show that the values of surface excess decrease with temperature increased. As the temperature increases, the hydration of the ethoxy segments of TX-100 is increased so the $\Gamma_{\max}$ decreased. The $\Delta G_{\text{ads}}^\circ$ values are more negative than the corresponding ΔG_m° values. This indicates that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric state at the surface to the micelle through the aqueous media. The values of $\Delta G_{\text{ads}}^\circ$ become more negative with respect to temperature, implying that the dehydration of the hydrophilic group is a necessary condition for the adsorption to take place. At higher temperatures, the surfactant is less hydrated and requires less energy for the adsorption process⁽⁶⁾. The effectiveness of a surface-active molecule is measured by the value of surface pressure, π_{cmc} . The values of π_{cmc} were found to be lower at high temperatures, indicating slightly less adsorption at the air/liquid interface at higher temperatures.

In the presence of EA, the ΔG_m° free energy of micellization was still negative but the values became less than the ΔG_m° in the absence of EA which indicate that spontaneous of the micellization process is decreased. This may be due to the fact that the hydrophobic group is more solvated. The enthalpy of micellization values in the presence of EA is positive which indicate that the process in the presence of EA become endothermic. The entropy of micellization is also positive in the presence of EA and increased as the amounts of EA increased. The values of $\Delta G_{\text{ads}}^\circ$ in the

presence of EA are more negative than the corresponding $\Delta G_{\text{ads}}^\circ$ values in aqueous media. The values are decreased when the EA is added and more decreased when the percentage of EA increased, but the sign is still negative. This indicate that the work done to transfer the surfactant molecules to the surface micelle through the H₂O–EA media is smaller than in the aqueous media.

The ΔG_M° values that were found are positive in all cases and increased with increasing EA percentage. This can be understood on the basis of a reduction of the hydrophobic interactions caused by improved solubility⁽¹⁵⁾. The ΔG_M° values increased when the temperature increased which indicate the reduction of the hydrophobic interactions increased with temperature. $\Gamma_{\max}$ values are decrease and $A_{\min}$ values are increase in the presence of EA and the effect increased as the percentage of EA increased. As the EA percentage increases the solubility increased and the $\Gamma_{\max}$ decreased. The values of $\Gamma_{\max}$ were increase and minimum area per surfactant molecules was decrease with temperature. This can be attributed to several factors, namely; a change in the water structure due to the addition of EA, the interaction between the EA and the surfactant, and the presence of the EA at the interface⁽¹⁶⁾.

References

- [1] Tharwat F. Tadros "Applied Surfactants", Wiley-Vch Verlag GmbH & Co. KGaA, Weinheim, Germany, Ch.1, P.1, 2005.
- [2] Aboulhassan M. A. Souabi S., Yaacoubi A. and Baud M. "Removal of surfactant from industrial wastewaters by coagulation flocculation process", J. Environ. Sci. Tech., france, 327-332, 2006.
- [3] Drew Myers "Surfactant Science and Technology", Third Edition, John Wiley & Sons, INC., Publication, Canada, Ch.1, P.7, 2006.
- [4] Jean-Louis Salager: "Surfactants types and uses", Mérida-Venezuela Versión, Ingeniería, 2002.
- [5] Jonges, M.; Liu, W. M.; Van Der Vries, E.; Jacobi, R.; Pronk, I.; Boog, C.; Koopmans, M.; Meijer, A. et al. "Influenza Virus Inactivation for Studies of Antigenicity and Phenotypic Neuraminidase Inhibitor

- Resistance" Influenza Virus Inactivation for Studies of Antigenicity and Phenotypic Neuraminidase Inhibitor Resistance Profiling *Journal of Clinical Microbiology*, 48, 3, 28–40, 2010.
- [6] Carnero Ruiz C., Molina-Bolívar J. A., and Aguiar J., "Thermodynamic and Structural Studies of Triton X-100 Micelles in Ethylene Glycol-Water Mixed Solvents", *Langmuir* 17, 6831-6840, 2001.
- [7] Molina-Bolivar J. A., Aguiar J., Peula-Garcia J. M., and Carnero Ruiz C., Surface Activity, "Micelle Formation, and Growth of n-Octyl- β -D-Thioglucoopyranoside in Aqueous Solution at Different Temperatures", *J. Phy. Chem. B*, 108, 12813-12820, 2004.
- [8] Ricardo M.F. Fernandes, Eduardo F. Marques, Bruno F.B. Silva, Yujie Wang, "Micellization behavior of a catanionic surfactant with high solubility mismatch: Composition, temperature, and salt effects" *Journal of Molecular Liquids* 157, 113–118, 2010.
- [9] Cigdem Batigoc, Halide Akbas , Mesut Boz, "Thermodynamics of non-ionic surfactant Triton X-100-cationic surfactants mixtures at the cloud point" *J. Chem. Thermodynamics* 43, 1800–1803, 2011.
- [10] Shaohua Lu, Jun Wu, Ponisseril Somasundaran, "Micellar evolution in mixed nonionic/ anionic surfactant systems" *Journal of Colloid and Interface Science* 367, 272–279, 2012.
- [11] Ray, A.; Ne'methy, "Micelle Formation by nonionic detergents in water-ethylene glycol mixture", *G. J. Phys. Chem.*, 75, 809, 1971.
- [12] Li-Jen che, shi-yow lin, chiung-changhuang and En-Ming Chem. "Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants", *colloids and surfaces A: physicochem. Eng. Aspects*, 135, 175-181, 1998.
- [13] Carnero Ruiz, "Thermodynamics of micellization of tetradecyltrimethylammonium bromide in ethylene glycol-water binary mixture", *C. Colloid Polym. Sci.* 277, 1999.
- [14] Del Rio, J. M.; Prieto, G. Sarmiento, F.; Mosquera, "Thermodynamics of Micellization of N-octyltrimethylammonium bromide in different Media", *V. Langmuir*, 11, 1511, 1995.
- [15] Sulthana, S. B.; Bhat, S. G. T.; Rakshit, "Thermodynamic of micellization of non-ionic surfactant my rj us: effect of additives", *A. K. Colloids Surf.* 111, 57, 1996.
- [16] Sulthana, S. B.; Bhat, S. G. T.; Rakshit, "studies of the effect of additives on the surface and thermodynamic properties of (oxyethylene(10) Lauryl Ether) in Aqueous solution", *A. K. Langmuir*, 13, 4562, 1997.

الخلاصة

في هذا البحث تم إيجاد التركيز الحرج لتكوين الميسل (cmc) للمادة الفعالة سطحيا Triton X-100 في محلولها المائي ومحلول مزيج ماء - إيثانول أمين باستخدام قياسات الشد السطحي في مدى من درجات الحرارة تراوحت بين 293 و 323 كلفن. تم حساب كل من معاملات السطح البينية $\Gamma_{\max}$ و $A_{\min}$ و Π_{cmc} و ΔG_{ads} لكل من المحلول المائي والمحلول الثنائي. ودلت النتائج التي تم الحصول عليها بان التركيز الحرج للميسل يزداد بزيادة كل من درجة الحرارة ونسبة الإيثانول أمين في المزيج. كذلك تم حساب كل من الدوال الترمودينمكية القياسية ΔG° و ΔH° و ΔS° لتكوين الميسل بالاعتماد على تغير التركيز الحرج مع تغير درجة الحرارة. ودرس تأثير اضافة الإيثانول أمين الى المحلول المائي على كل من التركيز الحرج ومعاملات الامتزاز وتكوين الميسل.