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I. Introduction

Surfactants sometimes called surface active agents, which contain both hydrophobic group (hydrocarbon chain) and hydrophilic group (polar head) in the same surfactant molecule[1-3].

In aqueous solutions, surfactant molecule starts to aggregate and form micelle in concentration called as critical micelle concentration, and it is one of the most important physical parameters of surfactants. The properties of a surfactant (like conductivity, viscosity, osmotic pressure, density, polarity, specific heat, refractive index and solubilization power etc.) vary markedly when its concentration is higher or lower than its CMC, and the studies and industrial applications of a 2 surfactant are always based on the value of its CMC. Also, micelle formation enables emulsification, solubilisation and dispersion [4-8].

In this study, polyoxyethylene sorbitan fatty acid esters (polysorbate or known as tween), it is a nonionic surfactants that use as a detergent and an emulsifier in a number of domestic, scientific and industrial applications, however the tween surfactant also have found use in cell lysis, nucleic acid isolation and cell fractionation. These surfactants are non-toxic and possess an extremely compatible set of physical properties that allow for widespread use along with other surfactants, for example, used tween surfactants with proteins to stabilize food foams [9-14].

The chemical name and the chemical formula of the tween series surfactants used in this study are presented in table (1), and their structures are shown in figure (1) [15-18].

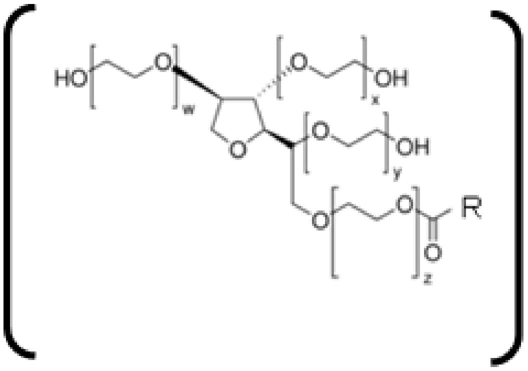

Figure (1) : Structure If Tween series surfactant

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Table (1) : structures of tween series surfactant

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Surfactant	Chemical name	Chemical formula (R)	n	w+x+y+z
Tween20	Polyoxyethylen (20) Sorbitanmono-laurate	C_nH_{2n+1}	11	20
Tween21	Polyoxyethylen (4) Sorbitanmono-laurate	C_nH_{2n+1}	11	4
Tween40	Polyoxyethylen(20) Sorbitanmonopalmitate	C_nH_{2n+1}	15	20
Tween60	Polyoxyethylen(20) Sorbitanmono-stearate	C_nH_{2n+1}	17	20
Tween80	Polyoxyethylen(20) Sorbitanmonooleate	C_nH_{2n-1}	17	20

The fluorescence probe technique is becoming increasingly popular in the study of surfactant micellization due to its excellent sensitivity towards the environment surrounding the fluorophore which exhibits different fluorescence characteristics depending upon the properties of the solubilizing medium [18-22].

For example, fluorescence probes such as pyrene-3-carboxalaldehyde which are sensitive to the polarity of the solubilizing medium will exhibit different fluorescence behavior in micellar and nonmicellar solutions. Such changes of behavior as a function of surfactant concentration have been used to determine the critical micelle concentration (CMC) and other micelle characteristics of certain surfactants. However, from necessary in such applications to ensure the absence of any influence of the probe molecule itself on the specific property in question [23-25].

II. Experimental

a) Materials and Methods

Tween with 99% purity 20, 21, 40 and 60 were purchased from Sigma-Aldrich, while tween 80 was purchased from Merck Corporation, pyrene-3-carboxalaldehyde was purchased from Sigma-Aldrich and purified by two crystallization method from ethanol [22].

All fluorescence spectra were recorded on RF-1501 spectroflouro-photometer (Shimadzu) in a 1cm cell emission spectra of pyrene-3-carboxaldehyde were obtained by exciting the samples at 360 nm, the maximum λ emission has been shown to involved as indicator correlated with solvent polarity [22].

All surfactant stock solutions were prepared fresh in the range with deionized water and then allowed to equilibrate for 15 - 20 minutes [15-16].

Stock pyrene-3-carboxaldehyde solution was prepared by dissolving 5mg in 10 ml of distilled water. Working mixtures for fluorescence measurements ($\leq 10^{-6}$ kmol/m^3), a small aliquot (50μL) of the latter solution was transferred with an automatic pipette to a quartz fluorescence cell and mixed with the surfactant solution and appropriate volumes of distilled water to give a total final volume of 3ml, and to obtain the final surfactant concentrations range [(0.1-0.0001)mM]. The critical micelle concentration (CMC) values of the investigated surfactants were also determined from the measurements of the fluorescence emission spectrum of pyrene-3-carboxalaldehyde around of 435 nm as a function of the surfactant concentration [22, 26].

III. Results and Discussion

a) Determination of Critical micelle concentration

Fluorescence studies were carried out in the presence of tween series surfactants, with varying alkyl chain lengths, from C11 - C17 and varying of number of oxyethylene group (4, 20). In all cases, a similar enhancement in the emission intensity with a slight blue-shift in the emission maxima around of 435nm is observed. Figure (2) shown the fluorescence intensity as a function of wave length for tween 80.

The dependence of fluorescence of pyrene-3-carboxaldehyde on the concentration of tween series is illustrated in Figure (3). It is clear that an initial slowly decreased up to a certain surfactant concentration and decrease sharply above it. A lowering of the value of λ max is an indication of the solubilization of the probes in a more hydrophobic environment than water-in this case surfactant micelles. Therefore the concentration at which the first break occurs should correspond to the critical micelle concentration (CMC).

The CMCs of tween (20, 21, 40, 60 and 80) which determined by this procedure were (0.0499, 0.063, 0.0333, 0.0167 and 0.015) mM respectively. These values agree well with the CMCs report edinthe literature [4, 7, 10, 18].

b) Effect of length chain and oxy ethylene group

In the same homologous series, increase in the length of the hydrocarbon chain usually leads to a reduction in the CMC, because formation of micelle becomes easier with increase in hydrophobicity. Therefore, the CMCs of tween 20, 40 and 60 formation are expected. The lower CMC of tween 80 may be due to un-saturation in the aliphatic chain which restricts the conformation of the chain figure (4). However, decreased in the CMC with increasing the number of oxyethylene group as illustrated in figure (5), because increasing the hydration of the hydrophilic polyoxy-ethylene group, that not favor the micellization. In other words, they reflect that polyoxyethylene group acts as solvophilic group, while hydrocarbon chain acts as solvophobic group.

c) Effect of temperature

The system temperature increases, the CMC initially decreases and then slightly increases, as shown in Figure (6). Owing to the smaller probability of hydrogen bond formation at higher temperatures, the initial decrease of the CMC with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules. In other words, the increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favour micelle-zation. Consequently, as increase in temperature the micellization onset occurs at lower concentrations. On the other hand, dissolving the surfactant molecules in distilled water makes the hydrophobic group distorts the water structure. Additionally increase in temperature also causes an increase in the breakdown of the structured water surrounding the hydrophobic groups, which disfavors micellization. In addition to, the onset of micellization tends to occur at higher concentrations when increase the temperature. The longer fatty acid chain length, (tween60, tween 80) due to an increase of the rupture of hydrogen bonds, that give no significant change in CMC.

d) Determination of thermodynamic parameters

For nonionic surfactants, the standard free energy of micelle formation, ΔG°m, associated with the process that micelles are formed from monomeric surfactant molecules in aqueous solution, which related to the CMC by the following equation [27-31]:

$$\Delta G^\circ_m = R*T*\ln X_{cmc} \qquad (1)$$

Where:

R is the gas constant,

T is the temperature

$\mathbf{X_{cmc}}$ stands for the CMC in the mole fraction unit

From the temperature dependence of Δ G°m, the entropy of micelle formation, ΔS°m was estimate d on the basis of the following thermodynamic relation [32-341]:

$$\Delta S^\circ_m = -(\partial G^\circ_m/\partial T) \qquad (2)$$

Then, the enthalpy of micelle formation, ΔH°m , was calculated according to the relation as below :

$$\Delta H^\circ_m = \Delta G^\circ_m + T\,\Delta S^\circ_m \qquad (3)$$

Thus thermodynamic parameters obtained for micelle formation are illustrated in table (2) for tween series.

It is found that ΔG°m decreases monotonically as the temperature increases over the whole temperature range from (298 – 348)°K. ΔS°m appear to be increase monotonically with an increase in temperature, the negative value of ΔG°m of micellization is mainly due to the large positive value of entropy.

The increase in entropy of micellization in an aqueous medium can be explained from two aspects: First the iceberg formation of the water molecules surrounding the surfactant molecules would increase the system order, here the micellization process by removing the surfactant molecules from the aqueous medium to the micelle would certainly increase the entropy of the system simply due to the rupture of iceberg; second the degree of rotational freedom of the hydrophobic chain of surfactant molecules in the non-polar interior of the micelle is much larger than that in the aqueous medium; in other words, the configu-rationally entropy of hydrophobic chain of surfactant molecules is increased when the surfactant molecules are removed from the aqueous medium to the micelle.

The small enthalpy change means that in the micellization the attractive interaction among hydrophobic chains is opposed by the strong interaction of the oxyethylene chains of tween series with water molecules. Figure (7) shows the thermodynamic parameters as a function of temperature for tween 80.

The thermodynamic parameters for micelle formation as a function of chin length for tween series surfactant, as shown in figure (8) , it is found that ΔG°m ΔH°m, and ΔS°m are decreased with increasing the chain length , the enthalpy (ΔH°m) is converted from endothermic for shorter chain length to exothermic for longer chain length.

The thermodynamic parameters for micelle formation as a function of number of oxyethylene group for tween series surfactant, as shown in figure (9), it is found that ΔG°m is decreased with increasing the number of oxyethylene group, but ΔH°m , and ΔS°m are increased.

Table (2) : CMC values, mole fraction and thermodynamic parameters for tween series surfactant in the range temperatures 298 -348°K

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Tween	Temp.(°K)	CMC(mM)	X_{CMC}	ΔG(cal/mole)	ΔH(cal/mole)	ΔS(cal/mole)
20	298	0.0499	0.23	-870.2	4245.234	14.24575
	313	0.0342	0.17	-1102.1	4270.822	13.6448
	328	0.0149	0.082	-1630.1	4000.311	12.19607
	338	0.0161	0.088	-1632.2	4169.869	12.33689
	348	0.0171	0.093	-1640.6	4333.128	12.45152
21	298	0.063	0.274	-766.8	3567.271	11.97071
	313	0.0356	0.176	-1080.2	3472.028	11.09274
	328	0.025	0.13	-1330.7	3439.686	10.48685
	338	0.0232	0.122	-1410.2	3505.625	10.37167
	348	0.0219	0.116	-1492.2	3569.064	10.25593
40	298	0.0333	0.166	-1062.4	1950.399	6.544963
	313	0.0281	0.144	-1204.2	1960.25	6.262779
	328	0.0186	0.1002	-1499.3	1816.801	5.539027
	338	0.0196	0.1054	-1511.1	1906.101	5.639353
	348	0.021	0.111	-1520.3	1998.002	5.741385
60	298	0.0167	0.091	-1419.9	-26.2219	-0.08799
	313	0.0153	0.084	-1540.3	-76.4703	-0.24431
	328	0.0154	0.0845	-1610.8	-76.8187	-0.2342
	338	0.0161	0.088	-1630.6	-49.851	-0.14749
	348	0.0167	0.091	-1660	-32.4833	-0.09334
80	298	0.015	0.082	-1477.9	-410.966	-1.37908
	313	0.0139	0.077	-1593.2	-472.561	-1.50978
	328	0.0151	0.083	-1622.4	-448.056	-1.36603
	338	0.0161	0.088	-1633.7	-423.553	-1.25312
	348	0.0161	0.088	-1677.1	-431.15	-1.23894

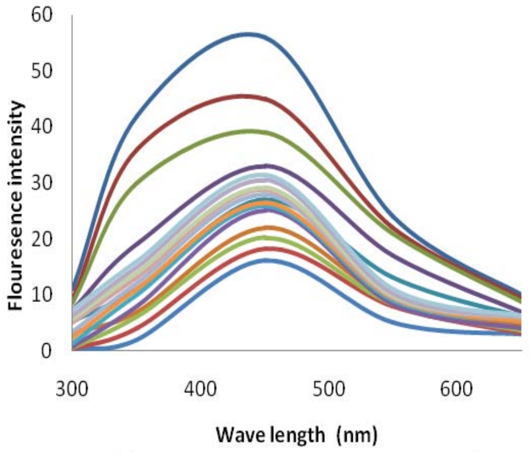


Figure (2) : Effect of Tween 80 concentration (in range 0.1-0.0001mM) on flouresence of pyrenecarboxylaldehyde in water

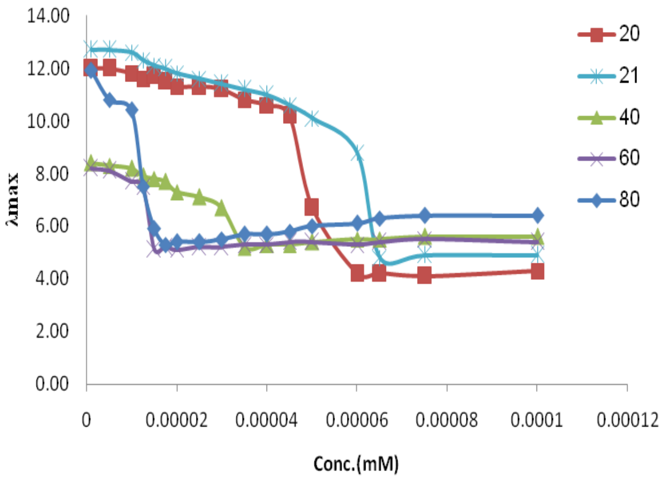
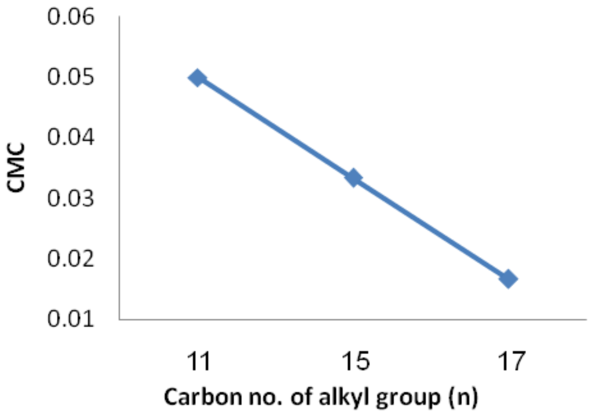


Figure (3) : Variation of flouresence λmax of pyrenecarboxylaldehyde as a function of Tween series concentration.



Figure(4) :Dependance of CMC on the carbon number of alkyl chain for Tween series at 298°K

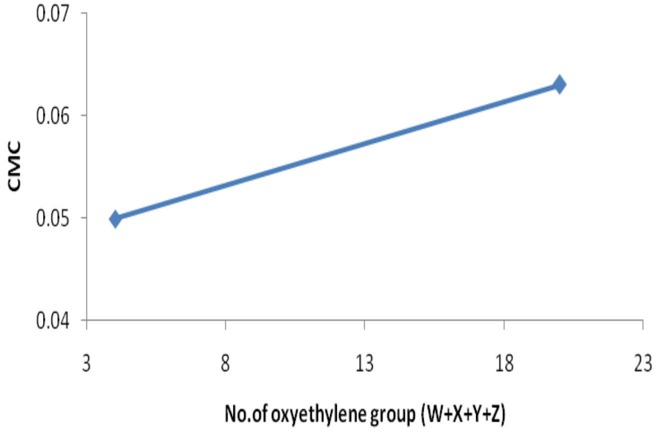


Figure (5) : Dependance of the CMC on the number of oxyethylene group for Tween series at 298°K

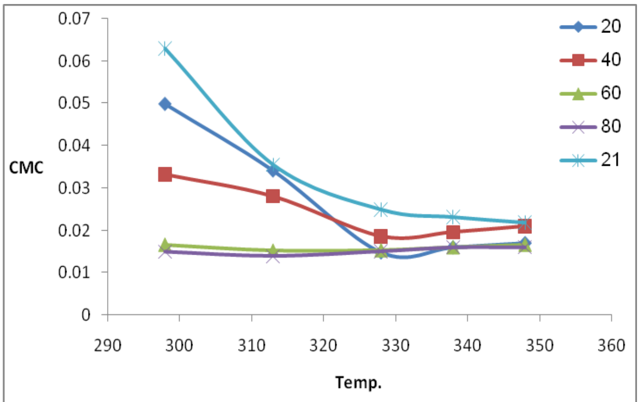


Figure (6) : The variation of CMC as a function of temprature Tween series surfactants .

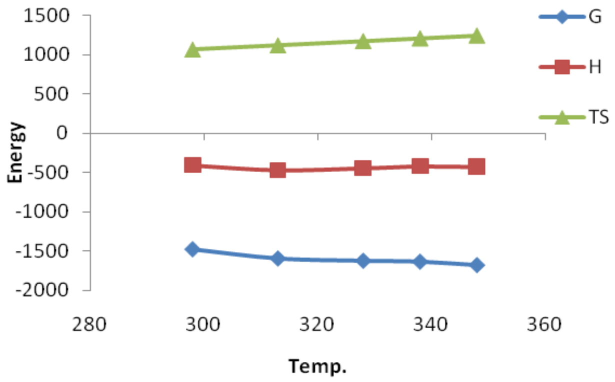


Figure (7) : Thermodynamic parameters for micelle formation of Tween 80 solution as a function of temprature .

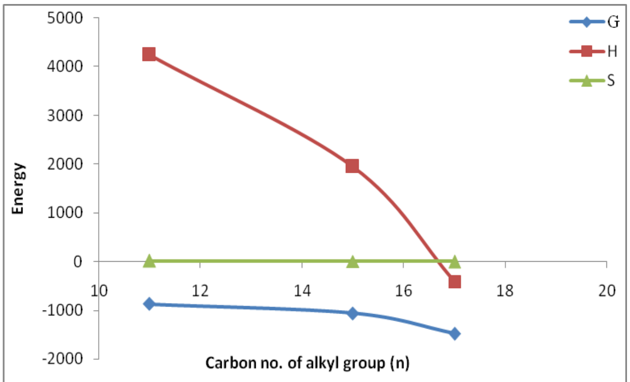
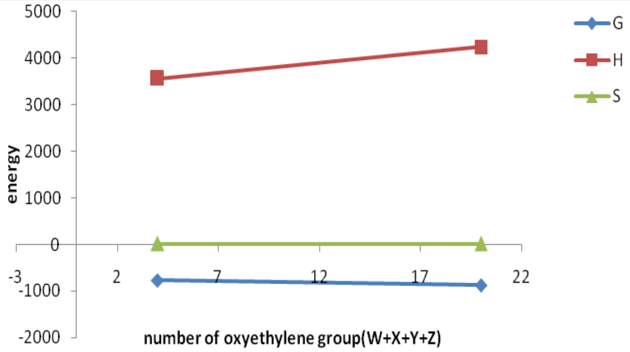


Figure (8) : Thermodynamic parameters for micelle formation as a function of carbon atom number for Tween series at 298 °k .



Figure(9) : Thermodynamic parameters for micelle formation as a function of the number of oxyethylene group for Tween series at 298 °k .

IV. CONCLUSION

The fluorescence technique is very good and easy for determination the critical micelle concentration for nonionic surfactant, the incensement in fluorescence intensity is accompanied by a concomitant blue-shift in the emission maximum, and often by the evolution of a shoulder in the blue region.

The changes in the nature of the surfactant (such as changes in chain length and polar head group) have a severe effect on the subsequent self-assembly in aqueous medium. The increase in hydrophobic character of the surfactant decreases the CMC, induces sphere-to-rod transition at lower concentration and increases the solubilizing, but the increase in hydrophilic character of the surfactant increase the CMC.

The temperature is affected on the tween series surfactant that shorter chain than longer one, which shows no significant change in CMC. The increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favors micellezation, which has a severe effect on the CMC.

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