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RESEARCH ARTICLE

STUDY THE EFFECT OF ETHANOL ON THE FORMATION OF THE WORMLIKE MICELLES FOR A MIXTURE OF IONIC SURFACTANTS

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ABSTRACT

In this research, the anionic sodium Dodecyl Sulfate SDS surfactant had been blended with the cationic cetyltrimethylammonium bromide CATB surfactant using different concentrations (0.002-0.04M) of ethanol and at temperature ranges (293.15K, 298.15K, 303.15K and 308.15K). Through the viscosity measurements for a mixture of SDS / CTAB and at certain mixing ratios (10 / 90, 20 / 80, 30 / 70 and 40/60), it was found that the viscosity was increased in the presence of ethanol, leading to the growth of wormlike micelles. This increases could be attributed to the increases in the connections (Cross linking) caused by ethanol between the chains of the wormlike micelles, which in turn inevitably lead to an increase in viscosity as a result of cage effect. Also, the used alcohol didn't participate in the mechanism of wormlike micelle formation because there wasn't any clear effect on the ratio that gives greater viscosity. This confirmed the credibility of critical intermolecular forces theory (CIF). Moreover, thermodynamic functions as well as the activation energy for the process of micelles formation for the studied ratios were calculated.

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INTRODUCTION

Extensive investigations concern with study the rheological properties of the solutions are very important from the academic and industrial point of view. Surfactant plays a key role in many applications such as in the manufacturing of detergents, cosmetics and pharmaceutical industry (Khalil and Hammand, 2014) and others. The name of the surfactants refers to the molecules that are surfactative in aqueous solutions (Farn, 2006). It consists of two parts; the first part is the tail group or lyophobic part that has a weak affinity towards inorganic solvent. If the solvent is water, then it called hydrophobic (Yan and Caili, 2014; Mroginski *et al.*, 2015). Whereas, the second part is the head group or hydrophilic part that have a strong affinity towards inorganic solvents or water. The strong intermolecular forces of different surfactants lead to either supramolecular/aggregations or disintegration depending on the type of surfactant. Micelles are composing upon gathering about 100 molecules of surfactants so that it forms a hydrophobic hydrocarbon core. The increase in the concentration of surfactants in solution will increases the number or the size of the formed micelles (Khalil and Hammand, 2014). Surfactants are tending to self-assembly themselves in aqueous solution in different forms depending on their molecular structures. It could form spherical, cylindrical and wormlike micelles.

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The viscosity measurements give understanding about the molecular interactions between the (Ion - Ion) and (ion - solvent) of hydrophobic and hydrophilic molecules. Such interactions are hydrogen bonding, compatibility between the solvent and solute, wander vase forces and others. Theses interactions play a big role in changing the viscosity of the solution (Mahmood, 2011). There are a lot of studies (Lin *et al.*, 2004; Khalil and Saadoon, 2014) concerns with studying the effect of additives on the viscosity of the surfactants substances that give interpretations useful in understanding the driving force to form micelles.

Experimental part

Instruments

- **Viscometer:** viscosity for the solutions under study was measured through calculating the flow time by using Austold viscometer, which measures the flow time of the solution. Austold viscometer is a U-shaped glass tube with two cylinders where the big cylinder filled with solution and withdrawing it through the small cylinder by pressing and then the liquid leaves to flow back to big cylinder tube through a capillary tube. Then, flow time was calculated through two specific points on the capillary tube.
- **Sensitive balance:** Sartorius BL 210S device was used to weigh a certain amount of material in accordance with the requirements of the job.
- **Stopwatch** to calculate the time required for the solution under study to flow down to a hundred fraction of a second with $s \pm 0.15$ accuracy.

➤ **Water bath** type HAKKE Nk22 to control solution temperature during viscosity measurement.

Chemicals
Sodium Dodecyl Sulphonate SDS having the structural formula $(CH_3 (CH_2)_{10} CH_2 - OSO_3 Na^+)$

Table 1. Viscosity (η) values and other related thermodynamic functions for the CTAB/SDS mixed system in ethanol at different temperatures

Conc. Ethanol	$\eta (Pa.s) \times 10^3 \{ \Delta G^\circ kJ.mol^{-1} \} \{ \Delta S^\circ J.mol^{-1}.K^{-1} \}$				$\Delta H^\circ kJ.mol^{-1} SE[a]r^2[b]$	$E_a J.mol^{-1} SE[c]r^2[d]$
	293.15K	298.15K	303.15K	308.15K		
Ratio 10/90						
0	7.933 (-8.97) {-841.07}	5.520 (-8.22) {-829.47}	0.189 (+0.14) {-843.38}	0.083 (+2.25) {-83.55}	-255.53 ± 7.21 0.900	4344.89 ± 118.6 0.906
2×10^{-3} (0.1ml)	11.521 (-9.87) {-792.19}	7.089 (-8.84) {-782.38}	0.474 (-2.17) {-791.47}	0.130 (+1.10) {-782.11}	-242.11 ± 5.31 0.937	6146.54 ± 153.3 0.920
1×10^{-2} (0.5ml)	17.980 (-10.96) {-685.54}	8.013 (-9.14) {-680.14}	0.989 (-4.02) {-685.81}	0.326 (-1.25) {-683.69}	-211.93 ± 3.10 0.971	9053.94 ± 257.9 0.899
2×10^{-2} (1.0 ml)	20.885 (-11.32) {-672.04}	9.887 (-9.66) {-666.34}	1.011 (-4.08) {-673.78}	0.438 (-2.00) {-669.58}	-208.34 ± 3.83 0.955	10592.03 ± 294.9 0.903
3×10^{-2} (1.5 ml)	26.118 (-11.87) {-603.85}	11.894 (-10.12) {-599.58}	1.622 (-5.27) {-605.70}	0.767 (-3.44) {-601.82}	-188.89 ± 3.12 0.963	13028.03 ± 371.7 0.898
4×10^{-2} (2.0 ml)	39.104 (-12.85) {-606.593}	14.900 (-10.68) {-603.71}	3.727 (-7.37) {-604.68}	0.896 (-3.84) {-606.32}	-190.68 ± 1.63 0.989	18997.49 ± 589.2 0.882
Ratio 20/80						
0	22.034 (-11.46) {-710.28}	17.278 (-11.05) {-699.74}	3.111 (-6.91) {-701.84}	0.287 (-0.92) {-709.89}	-219.68 ± 6.48 0.892	11913.96 ± 264.0 0.936
2×10^{-3} (0.1ml)	34.119 (-12.52) {-632.51}	24.922 (-11.96) {-623.80}	3.811 (-7.42) {-628.46}	0.777 (-3.47) {-631.09}	-197.94 ± 4.55 0.931	18199.34 ± 412.1 0.933
1×10^{-2} (0.5ml)	51.541 (-13.53) {-661.19}	32.249 (-12.59) {-653.22}	5.707 (-8.44) {-656.12}	0.906 (-3.87) {-660.35}	-207.35 ± 4.43 0.940	26870.84 ± 530.0 0.949
2×10^{-2} (1.0 ml)	78.015 (-14.54) {-645.72}	48.730 (-13.62) {-637.97}	9.112 (-9.62) {-640.63}	1.456 (-5.08) {-644.97}	-203.83 ± 4.36 0.940	40547.37 ± 782.0 0.951
3×10^{-2} (1.5 ml)	116.303 (-15.51) {-548.44}	77.361 (-14.76) {-541.74}	15.633 (-10.98) {-545.29}	3.916 (-7.62) {-547.36}	-176.29 ± 5.37 0.948	60043.70 ± 1164 0.950
4×10^{-2} (2.0 ml)	702.282 (-19.89) {-807.74}	412.404 (-18.91) {-797.48}	27.001 (-12.36) {-805.94}	5.778 (-8.61) {-804.57}	-256.68 ± 3.50 0.942	373065.80 ± 9284 0.921
Ratio 30/70						
0	4.873 (-7.78) {-308.70}	1.685 (-5.28) {-311.91}	1.066 (-4.21) {-310.28}	0.642 (-2.98) {-309.23}	-98.27 ± 1.67 0.961	2009.49 ± 81.92 0.813
2×10^{-3} (0.1ml)	7.933 (-8.97) {-330.40}	2.277 (-6.02) {-334.72}	1.603 (-5.24) {-331.79}	0.857 (-3.72) {-331.33}	-105.82 ± 2.22 0.942	3313.96 ± 150.6 0.778
1×10^{-2} (0.5ml)	12.124 (-10.00) {-391.00}	3.141 (-6.82) {-395.10}	1.809 (-5.55) {-392.79}	0.923 (-3.91) {-391.71}	-124.62 ± 2.13 0.961	5286.87 ± 242.7 0.774
2×10^{-2} (1.0 ml)	15.050 (-10.53) {-421.87}	4.639 (-7.79) {-423.98}	2.112 (-5.94) {-423.10}	0.996 (-4.11) {-422.16}	-134.20 ± 1.87 0.990	6758.45 ± 269.8 0.819
3×10^{-2} (1.5 ml)	18.009 (-10.96) {-401.55}	5.900 (-8.38) {-403.47}	2.844 (-6.69) {-402.42}	1.326 (-4.84) {-401.87}	-128.68 ± 1.00 0.991	8028.82 ± 307.6 0.831
4×10^{-2} (2.0 ml)	31.225 (-12.30) {-427.61}	7.872 (-9.10) {-431.18}	3.009 (-7.49) {-429.39}	3.909 (-5.72) {-428.15}	-137.66 ± 1.89 0.974	13917.63 ± 633.8 0.777
Ratio 40/60						
0	1.011 (-3.94) {-247.47}	0.247 (-0.52) {-254.81}	0.209 (-0.11) {-251.97}	0.198 (+0.02) {-248.32}	-76.49 ± 4.02 0.723	379.118 ± 22.59 0.670
2×10^{-3} (0.1ml)	1.967 (-5.56) {-345.41}	0.503 (-2.28) {-350.62}	0.295 (-0.97) {-349.15}	0.222 (-0.267) {-345.80}	-106.82 ± 3.03 0.899	824.41 ± 41.24 0.743
1×10^{-2} (0.5ml)	2.370 (-5.81) {-327.64}	0.606 (-2.747) {-332.43}	0.366 (-1.52) {-330.99}	0.271 (-0.77) {-328.04}	-101.86 ± 2.75 0.908	990.19 ± 49.64 0.742

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2×10^{-2} (1.0 ml)	3.172 (-6.73) {-350.39}	0.812 (-3.47) {-355.45}	0.409 (-1.80) {-355.10}	0.356 (-1.47) {-350.40}	-109.45 ± 3.35 0.885	1340.21 ± 67.38 0.741
3×10^{-2} (1.5 ml)	4.324 (-7.49) {-358.67}	0.934 (-3.82) {-364.97}	0.794 (-3.47) {-360.09}	0.378 (-1.63) {-360.24}	-112.63 ± 3.26 0.895	1813.28 ± 94.11 0.728
4×10^{-2} (2.0 ml)	7.466 (-8.820) {-409.36}	1.575 (-5.11) {-414.92}	0.917 (-3.83) {-412.29}	0.518 (-2.43) {-410.14}	-128.82 ± 2.96 0.931	3256.59 ± 165.4 0.737

[a] and [b] are the standard error ($kJ.mol^{-1}$) and square of correlation coefficient from the plot of $\ln\eta$ versus $1/T$ according to Eq.2. [c] and [d] are the standard error ($J.mol^{-1}$) and square of correlation coefficient from the plot of η versus $1/T$ according to Eq.4

and Cetyltrimethylammonium bromide (CTAB) having the structural formula $CH_3(CH_2)_{14}CH_2N(CH_3)_3Br$, and ethanol were supplied by sigma Aldrich and Fluka companies.

Preparation of solutions

SDS (100 ml) was prepared by dissolving (3 %wt) as a (Stock solution) of the SDS in a minimum amount of distilled water and then complete the size to (100 ml) using volumetric flask. From this solution, a series of solutions of different concentrations for SDS with ethanol were prepared. CTAB was prepared by following the same procedure for SDS (Khalil and Hammand, 2014).

Preparation of SDS and CTAB solutions in the presence of ethanol

Different solutions of a mixture of sodium Dodecyl sulphate and cetyl tri-ammonium bromide were prepared in the presence of ethanol (standard solution was prepared by weighting (4.60gm)) and concentrations ranging from ($2 \times 10^{-3}M$ to $4 \times 10^{-2}M$) and at temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K). The required sample weight at each concentration was transferred into volumetric flask (10 ml) in order to run the required measurements.

Measuring Rheological Properties

The Ostwald device for measuring the viscosity was used where the viscometer containing the sample to be measured (SDS / CTAB + Ethanol) was placed in a water bath so the viscometer almost covered with water then kept for 5 minutes with stirring from time to time. Then, the time required for the sample to move down from the start point to the end point identified on the viscosity measuring instrument had been measured.

RESULTS AND DISCUSSION

In spite of the development of critical intermolecular-forces theory⁽¹⁾, the formation of wormlike micelles still theoretically non-understandable. From this point and in order to support the theoretical basis of this theory in this study, the effect of adding aliphatic alcohol (ethanol) on the formation of wormlike micelles for a combination of cationic and anionic surfactant SDS and CTAB at temperatures (293.15, 298.15, 303.15, 308.15 K) had been studied. Results showing the effect of the presence of different concentrations of ethanol on four ratios for the process of blending (10/90, 20/80, 30/70, 40/60) for both SDS / CTAB are listed in Table (1). Figure 1 shows the relationship between viscosity and the percentage of the SDS at temperatures (293.15 and 303.15K).

The results revealed that the highest value for the viscosity was at the temperature 293.15 K and ratio of 20/80. Results in Table (1) indicated a significant increase in the viscosity values for the SDS / CTAB in the presence of ethanol particularly when the temperature (293.15K) and ($4 \times 10^{-2} M$) concentration.

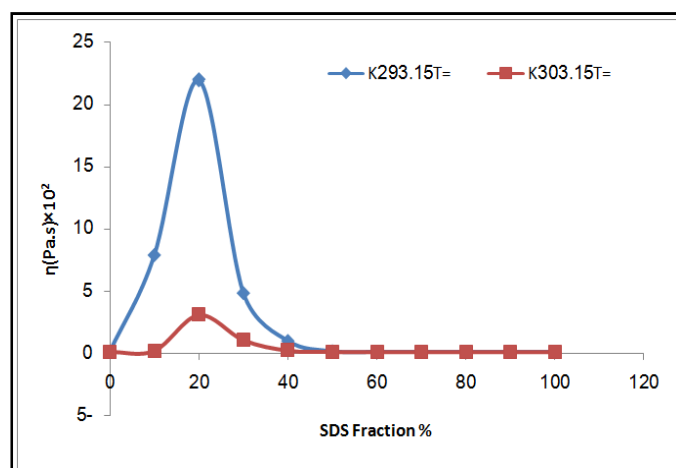


Fig. 1. Relationship between the viscosity of 20/80 SDS/CTAB mixture versus SDS fraction % at temp.(293.15K and 303.15K)

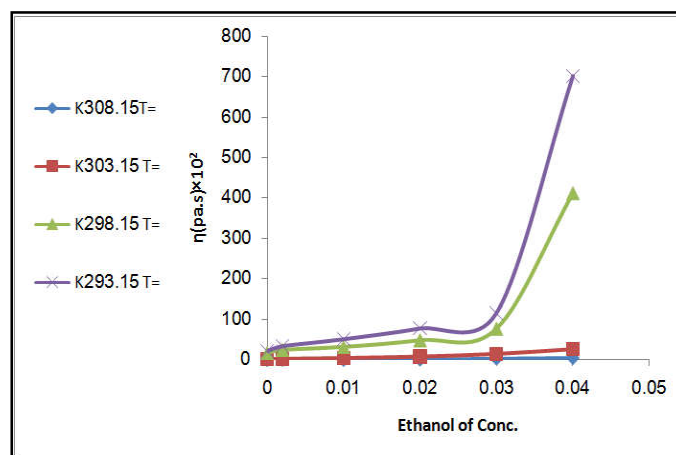


Fig. 2. Effect of addition alcohol on the dynamic viscosity of 80/20CTAB/SDS mixture (3wt %) at different temp

The reason for which, is that the low temperature facilitated the process of micelles formation by providing kinetic energy which increased the possibility of overlapping between oppositely charged surfactant because of the presence of strong electrostatic attractive forces as well as the presence of hydrophobic effect. At a temperature above (308.15 K) or more, increasing in the kinetic energy of the surfactant molecules will cause difficulty in gathering it and by the result affect micelles formation.

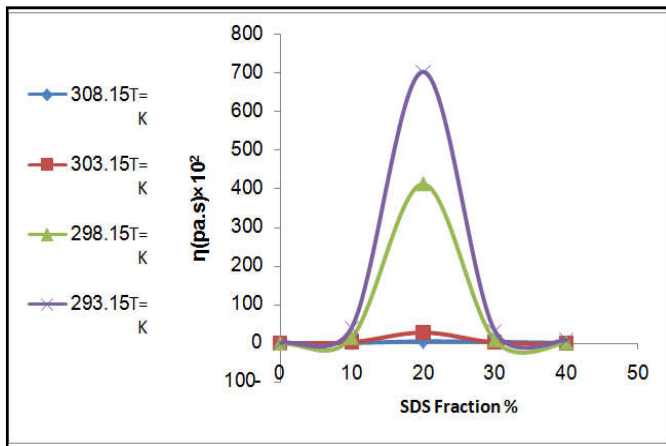


Fig. 3. Relationship between the viscosity of 20/80 SDS/CTAB mixture versus SDS fraction % at temp. different in ethanol (0.04M)

Moreover, the increasing in the kinetic energy will also cause a decrease in viscosity values and this is identical to what was found in the case of the SDS and the literature (Khalil and Saadoon, 2014).

Results also revealed that the viscosity values of CTAB in the presence of SDS irregularly increase with increasing the concentration of ethanol. The reason for which (Abdul-gau and Mahmood, 2009), is that the ethanol is a polar material so it will be close to the surface of the micelles which will separate polar material so it will be close to the surface of the micelles which will separate the oppositely charged polar heads causing disruption the electrostatic attractive forces by steric effect as well as the ability to form hydrogen bond between hydrogen atom belongs to the hydroxyl of ethanol and polar head group (-OSO₃ in the case of the SDS), which again disturb the process of attraction between oppositely charged polar heads and lead to an increase in viscosity values.

The results in Table (1) also indicated a slight decrease in the viscosity values for the CTAB in the presence of SDS with temperature increase and in the presence or absence of ethanol with reporting a slight increase in viscosity at temperature value (308.15 K) without ethanol. In general, we notice that the viscosity decreased with temperature increasing (Atkins, 2001). Figure 2 shows the relationship of ethanol concentration and viscosity at different temperatures. Figure 3 shows the relationship between viscosity and the percentage of the mixture SDS / CTAB at different temperatures and the concentration of ethanol 0.04M. The following equations (Khalil and Hammand, 2014; Atkins, 2001) had been used to calculate the thermodynamic parameters for the process of wormlike micelles formation type CTAB in the presence of SDS using different concentrations of ethanol and different temperatures.

$$\Delta G^{\circ} \approx -RT \ln(\eta / 2 \times 10^{-3}) \quad \text{-----(1)}$$

ΔG° was calculated from equation (2), where R is the gas constant, T absolute temperature. Enthalpy of formation was calculated from the following equation:

$$d(\ln \eta / 2 \times 10^{-3}) / d(1/T) \approx -\Delta H^{\circ} / R \quad \text{-----(2)}$$

where ΔS° from equation below:

$$\Delta S^{\circ} = \Delta H^{\circ} - \Delta G^{\circ} / T \quad \text{-----(3)}$$

Activation energy for the wormlike micelles was calculated from equation (4):

$$\eta \propto e^{E_a/RT} \quad \text{-----(4)}$$

The results in table (1) showed that the values of the free energy ΔG° for the process of micelles formation for combination of SDS / CTAB in the presence of different concentrations of ethanol were between positive and negative. ΔG° for the process of micelles formation was positive when the viscosity decreases by temperature increase. Ethanol considered a simple alcohol with short-chain hydrocarbon, as when added to a combination of surfactants working to form clusters (Day, 2002; Bernold *et al.*, 1996; Ezrahi *et al.*, 2006) known as Supramolecular and thus give us the so-called wormlike micelles.

The enthalpy value for the process of micelles formation for SDS / CTAB mixture in the presence of ethanol had been calculated. The negative signal for ΔH° means that the process was exothermic (Sharma, 1983). The pronounce increase in viscosity was predominantly belongs to the hydrogen bonding which diminished surfactants role in the formation micelles due to the presence of ethanol.

The values of entropy for the process of micelles formation for combination of SDS / CTAB showed that the spontaneous formation of micelles mainly due to increases in randomization ($T\Delta S^{\circ}$). Activation energy for the process of micelles formation was also calculated as shown in Table (1). The presence of ethanol in the mixture of SDS / CTAB will interfere with the process of micelles formation through forming hydrogen bonding with polar groups the surfactants reducing the charge on the surface micelles. This confirm the validity of the CIF theory proposed through previous studies (Khalil and Saadoon, 2014; Khalil and Hammand, 2014) for some binary and tertiary systems for a combination surfactants used for the formation of micelles.

Conclusion

The results indicated that the cationic CTAB and anionic SDS surfactants revealed a big tendency towards formation of wormlike micelles in ethanol. The reason for which the viscosity of the surfactants SDS / CTAB had increased was due to the intermolecular interactions and ability to form hydrogen bonding.

This had proved that the rheological properties for the supramolecular dynamic were differ from that for high molecular weight polymers which composed of carbon based backbones covalently bonded. And that these alcohol were interacted with process of wormlike micelles formation and formed hydrogen bonding with the polar groups of the surfactants and by result reduce the charge on the micelles surface. Moreover, this alcohol had no role in the mechanism of micelles formation because there was no effect on the ratio that gave the highest viscosity and this was a good support for the CIF theory.

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