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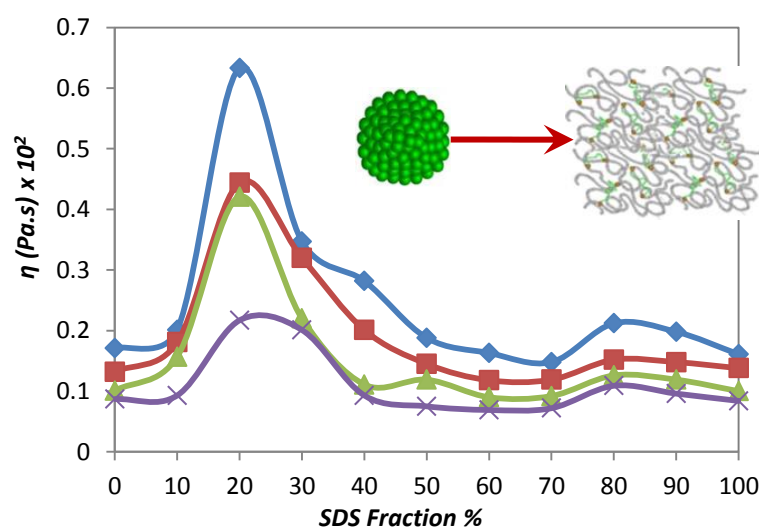
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Received 29 October 2014,
Accepted 29 November 2014

• Novelty and Highlights:

- 1 – The role of surfactant head group on the formation of wormlike micelle is still unclear.
- 2 – The head group plays a sensible part in the formation of wormlike micelles.
- 3 – The ionization potential of head group plays a significant role in enhancing or reducing the tendency of the formation of wormlike micelle.

• Graphical Abstract:



The role of surfactants head group in the formation of self-assembled supramolecular aggregate

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Abstract: Thermodynamically controlled supramolecular gel or aggregate is commonly resulted from the formation of one-dimensional micelles through specific self-assembling of amphiphilic molecules. Up to present date, the role of surfactant head group in the formation of such a condensed matter is still obscure. Consequently, this work presents a study of the effect of changing surfactant head group on the transformation phenomenon towards one dimensional shape of aggregate. Binary mixture of anionic sodium dodecylsulfate (*SDS*) and cationic cetylpyridinium chloride (*CPC*) has been examined for comparison with previously published *SDS* with cetyltrimethylammonium bromide (*CTAB*). The work has been extended through using ternary mixtures of *SDS*, *CPC* and *CTAB* at 1:1, 3:1 and 1:3 *CTAB:CPC* ratios. The thermodynamic properties have been determined for all of these mixtures. The results indicate that the presence of pyridinium cation in *CPC* surfactant causing a bad effect on the formation of wormlike micelle in contrast to that of trimethylammonium in *CTAB*. It has been suggested that the formation of supramolecular gel depends on ionization potential of the surfactant head group as needed for head to head electrostatic interaction through the construction of one dimensional shape of aggregate. It has been generally concluded that hydrophilic effect plays a sensible part in the formation of wormlike micelles in contrast to that of hydrophobic which plays the major role and hence supporting the critical intermolecular forces theory.

Keywords: wormlike micelles; critical intermolecular forces; surfactants thermodynamic properties; supra-molecular chemistry; soft matter.

Introduction

The unique characteristic of supra-molecular gel or aggregate as thermodynamically controlled living polymer makes special important applications in many fields [1-9]. Such composite is mainly produced from surfactants through transformation phenomenon from three to one dimensional shape of self-assembled aggregate [1-5, 10]. The latter type of aggregate is produced at relatively low concentration of surfactants which causing a significant increase in viscosity. This phenomenon is commonly referred to the formation of worm or thread like micelle which might be considered as a complicated process. For instance, it is quite tricky to do theoretical investigation using computational methods for the relationship between chemical structure and packing parameter of one dimensional aggregate in contrast to that of three dimensional (spherical) [11]. Recently, we have proposed a theory that called critical intermolecular forces (*CIF*) for interpreting the transformation process from three to one dimensional shape of aggregate [1]. According to this theory [1], the transformation process is resulted from the combination of three main intermolecular forces

including electrostatic interactions of the amphiphilic head groups, dispersion forces between hydrophobic groups, and the hydrophobic effect (icebergs) which resulted from the excess of formed hydrogen bonds between water molecules. It has been realized that the last effect is considered as the main factor for the formation of one dimensional micelle. In turns, this effect (hydrophobic) has not received a noticeable attention in previous publications. The *CIF* theory has been proposed throughout the exploration of some binary and ternary systems of mixed surfactants for the formation of wormlike micelles [1]. It has been found that the mixture of anionic sodium dodecylsulfate (*SDS*) and cationic cetyltrimethylammonium bromide (*CTAB*) surfactants forms supra-molecular gel at a weight ratio of 80/20 of 3 wt. % *CTAB/SDS*. Then, this theory was supported through studying the effect of presence of benzene ring in the hydrophobic chain on the transformation process using the mixture of anionic sodium dodecylbenzenesulphonate (*SDBS*) and *CTAB* surfactants [10]. Moreover, no wormlike micelles have been detected for binary mixtures of anionic-nonionic (*Triton-X 100*) nor for ternary mixtures of

SDS or SDBS/CTAB/Triton-X 100 surfactants [1, 10]. However, the role of surfactants head groups in the transformation phenomenon towards supra-molecular gel is still obscure.

Recently, Parker and Fieber [3] investigated the effects of ionic strength and small hydrophobic molecules on the viscoelasticity of anionic sodium lauryl ether sulphate wormlike micelles. They indicated that the viscosity increases with increasing the hydrophobic character of additive molecules which could give support to the CIF theory. Another study concerning the solution self-assembly of giant gemini surfactants based on polystyrene-hydrophilic polyhedral oligomeric silsesquioxane shape amphiphiles [4]. It was revealed that the morphological transition from vesicles to wormlike is proportional with the degree of ionization of the carboxylic acid groups on the amphiphilic heads. More recently, Wang et al. [12] studied the effect of a hydrophilic head group on Krafft temperature, surface behaviors and rheological properties of erucyl amidobetaines. They unexpectedly announced that the nature of head groups possesses little effect on the thickening ability and critical micelle concentration of these surfactants.

Hence, investigations concerning the effect of changing head group of surfactant on the transformation phenomenon from three to one dimensional shape of aggregate may be considered as essential. Such a job could provide a deeper insight for understanding the role of head group on the above transformation process. Therefore, the main task of the present work is to make a comparison with that of previously obtained results using different head group [1]. Thus, the present work introduces the effect of changing the head group of cationic surfactant from ammonium (CTAB) to pyridinium (cetylpyridinium chloride, CPC) group for the formation of worm like micelle with anionic SDS surfactant. No such study was mentioned in the literatures.

Experimental

The surfactants CPC ($\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}^+\text{C}_5\text{H}_5\text{Cl}^-$), SDS ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$) and Triton X-100 ($\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2-)_{10}\text{OH}$) were used as obtained in high purification form from Sigma-Aldrich company. Freshly distilled water was used for all preparations. 3 wt% aqueous solution of each surfactant was prepared at concentrations of 0.0909, 0.1072 and 0.0478M for CPC, SDS and Triton X-100 respectively.

Dynamic viscosity (η) measurements were done using modified Ostwald apparatus as detailed in Ref. 1. To

control the temperature within $\pm 0.1^\circ\text{C}$, water thermostated Hakke NK22 was used. All measurements are repeated for at least three times in order to check the reproducibility of the data. The approximate thermodynamic functions for the transition process towards one-dimensional shape including the change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were estimated using the following approximate relations [1, 10]:

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

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

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

where R is the gas constant, T is the absolute temperature and η is the observed dynamic viscosity.

Results and discussion

Indeed, the head group of cationic CPC surfactant that represented by aromatic pyridinium ion may be considered as significant choice for doing this job due to its obvious difference with that of aliphatic trimethylammonium of CTAB surfactant. No regard should be made in this study concerning the well discussed of some common features that already mentioned in our published papers [1,10]. Since one dealing with thermodynamically controlled living polymer, the presented work should be carried out at different temperatures in order to estimate ΔH° and ΔS° parameters.

Table 1 lists the viscosity (η) values and the related thermodynamic parameters for 3 wt.% CPC/SDS mixtures at different ratios and temperatures. Interestingly, the results show that the high dynamic viscosity peak is located at the ratio of 80/20 CPC/SDS (Figure 1) in a similar manner to that of CTAB/SDS [1] and CTAB/SDBS [10]. Indeed, this achievement could give a direct support to CIF theory as the hydrophobic effect plays the major role in the transformation process towards one dimensional shape of aggregate. In other words, both CPC and CTAB having longer hydrophobic chain which exceeds four - CH_2 - groups in contrast to that of SDS and SDBS [1,10]. In addition, the mixture of the anionic sodium oleate (NaOA) and cationic octyl trimethylammonium bromide (OTAB) gives the higher viscosity peak at 70/30 NaOA/OTAB 3 wt% ratio as NaOA tail have seven - CH_2 - groups more than that of OTAB [13]. In a

similar manner, Song et al. [14] have also detected this phenomenon for anionic gemini surfactants. Moreover, the salt-induced one dimensional micelle using N-alkyl-N-methylpyrrolidinium bromide (CnMPB, n= 12, 14 and 16) can only formed by n=16 in contrast to that of 12 and 14 [7].

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

Surfactant		η (Pa.s) $\times 10^2$				ΔH° kJ.mol ⁻¹
3 wt%		$(\Delta G^\circ$ kJ.mol ⁻¹)				$SE^{[a]}$ $r^{2[b]}$
		$(\Delta S^\circ$ J.mol ⁻¹ .K ⁻¹)				
SDS	CPC	10 °C	17 °C	25 °C	35 °C	
0	100	0.171	0.132	0.101	0.087	-19.88
		(0.36)	(1.02)	(1.76)	(2.28)	± 1.2
		{-71.50}	{-72.03}	{-72.60}	{-71.91}	{0.989}
10	90	0.201	0.181	0.157	0.093	-21.87
		(-0.01)	(0.24)	(0.60)	(1.96)	± 0.64
		{-77.19}	{-76.20}	{-75.36}	{-77.33}	{0.895}
20	80	0.633	0.444	0.421	0.217	-28.90
		(-2.71)	(-1.92)	(-1.84)	(-0.20)	± 0.75
		{-92.48}	{-92.97}	{-90.74}	{-93.10}	{0.914}
30	70	0.347	0.320	0.220	0.201	17.50
		(-4.08)	(-1.13)	(-0.23)	(-0.01)	± 0.45
		{-47.39}	{-56.41}	{-57.90}	{-56.74}	{-0.915}
40	60	0.282	0.201	0.111	0.093	-33.92
		(-0.80)	(-0.01)	(1.45)	(1.96)	± 0.68
		{-116.9}	{-116.9}	{-118.7}	{-116.4}	{0.987}
50	50	0.188	0.145	0.119	0.075	-26.02
		(0.14)	(0.77)	(1.28)	(2.51)	± 0.30
		{-92.40}	{-92.34}	{-91.58}	{-92.59}	{0.981}
60	40	0.163	0.118	0.090	0.069	-24.80
		(0.48)	(1.27)	(1.97)	(2.72)	± 0.21
		{-89.28}	{-89.85}	{-89.81}	{-89.32}	{0.989}
70	30	0.148	0.119	0.092	0.072	-21.10
		(0.70)	(1.25)	(1.92)	(2.61)	± 0.080
		{-77.01}	{-77.03}	{-77.22}	{-76.96}	{0.998}
80	20	0.212	0.152	0.126	0.109	-18.81
		(-0.13)	(0.66)	(1.14)	(1.55)	± 0.40
		{-65.94}	{-67.11}	{-66.92}	{-66.07}	{0.939}
90	10	0.198	0.148	0.119	0.096	-20.73
		(0.02)	(0.72)	(1.28)	(1.88)	± 0.23
		{-73.29}	{-73.94}	{-73.84}	{-73.37}	{0.983}
100	0	0.161	0.138	0.100	0.084	-19.82
		(0.51)	(0.89)	(1.71)	(2.22)	± 0.26
		{-71.79}	{-71.39}	{-72.23}	{-71.53}	{0.976}

[a] and [b] are the standard error (kJ mol⁻¹) and square of correlation coefficient from the plot of $\ln \eta$ versus $1/T$ [1,10].

Another interesting feature that can be realized from the significant decrease in the high viscosity peak due

to presence of *CPC* when compared with that of *CTAB* (Figure 1 and Table 1). For example, the higher viscosity peak of the mixtures of *CPC/SDS* at 25°C is reduced by 41 times in contrast to that of *CTAB/SDS* [1]. This could indicate that the head group also takes a sensible part in the transformation process. Indeed, this effect is resulted from the replacement of ammonium by pyridinium group and may also be resulted from changing chlorine by bromine counter ion. Consequently, in order to verify this effect, ternary mixture of three ionic surfactants (*CTAB+CPC/SDS*) at different ratios is suggested. In other words, ternary 3 wt% *CTAB+CPC/SDS* mixed system of 1:1, 3:1 and 1:3 *CTAB:CPC* ratios at different temperatures is investigated which might be considered as a helpful tool for understanding this phenomenon.

The results show there is an increase in the tendency of forming wormlike micelle at constant ratio of *SDS:CTAB+CPC* (20:40+40) for the 1:1 *CTAB:CPC* system in similar manner to that of *CTAB/SDS* and *CPC/SDS* as clearly shown in Table 2. Although, the higher viscosity value at 20:40+40 is increased only at relatively low temperatures of 17 and 20°C by about 3 and 2 folds respectively, but, it is not affected at 25 and 35°C. On the other hand, the viscosity at those of the last temperatures (25 and 35°C) is increased very slightly at ratio of 30:35+35 *SDS:CTAB+CPC*. This indicating there is a shift in the viscosity peak that is occurred at those temperatures when using 1:1 ratio of cationic *CTAB* and *CPC* surfactants. Table 3 records the viscosity values and other related thermodynamic functions for the ternary *CTAB+CPC/SDS* mixed system (3:1 *CTAB:CPC*) at different temperatures. Surprisingly, the results show there is a clear shift in the viscosity peak at 30:70 (52.5+17.5) *SDS:CTAB+CPC* instead of 20:80. This phenomenon may indicates there is an effect could be resulted from the combination of *CTAB* and *CPC* with *SDS* head groups which may somewhat perturb the hydrophobic control as considered as the main factor. Actually, this point needs further investigation which can be regarded as future work.

Whatever, the results (Table 3) exhibit a substantial increases in the viscosity at this ratio (3:1 *CTAB:CPC*) due to the increase in the proportion of *CTAB* to *CPC*. For example, the viscosity was increased by about 8, 9, 5 and 3 times in contrast to that of 20:80 *CPC:SDS* (Table 1) at 10, 17, 25 and 35°C respectively.

Although, the presence of *CPC* surfactant at relatively low ratio makes a bad effect on the formation of wormlike micelle in contrast to that of *CTAB/SDS* system [1].

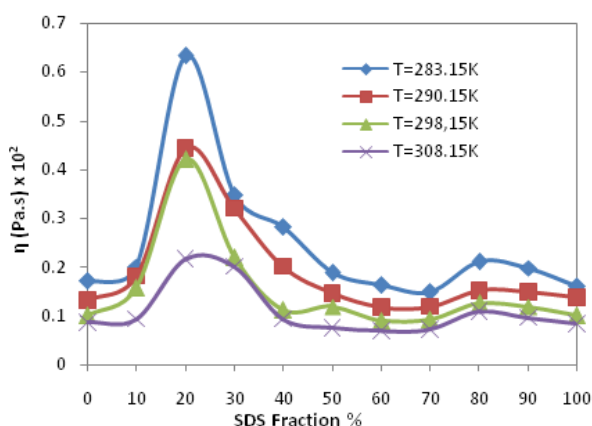


Figure 1 The relationship between the viscosity (η) for the binary system of *CPC/SDS* mixture versus *SDS* fraction% at different ratios and different temperatures.

Table 2 Viscosity (η) values and other related thermodynamic functions for the ternary *CTAB+CPC/SDS* mixed system (*1:1 CTAB:CPC*) at different temperatures.

Surfactant 3 wt%			η (Pa.s) $\times 10^2$			ΔH° kJ.mol^{-1} $SE^{[a]}, [2]^{[b]}$	
SDS	CTAB	CPC	10 °C	17 °C	25 °C		35 °C
0	50	50	0.128 (1.05) [-51.15]	0.101 (1.64) [-51.98]	0.091 (1.95) [-51.60]	0.079 (2.37) [-51.31]	-13.43 ± 0.25 {0.955}
10	45	45	1.102 (-4.01) [-184.1]	0.951 (-3.76) [-180.5]	0.289 (-0.91) [-185.2]	0.192 (0.10) [-182.5]	-56.13 ± 1.41 {0.919}
20	40	40	1.817 (-5.19) [-214.5]	0.999 (-3.88) [-213.9]	0.301 (-1.01) [-217.7]	0.214 (-0.17) [-213.4]	-65.93 ± 1.36 {0.944}
30	35	35	1.447 (-4.65) [-188.9]	0.932 (-3.71) [-187.6]	0.318 (-1.14) [-191.1]	0.222 (-0.26) [-187.8]	-58.13 ± 1.13 {0.950}
40	30	30	0.295 (-0.91) [-99.49]	0.191 (3.78) [-113.3]	0.139 (0.90) [-100.6]	0.107 (1.60) [-99.59]	-29.08 ± 0.43 {0.972}
50	25	25	0.178 (0.27) [-57.83]	0.138 (0.89) [-58.57]	0.122 (1.22) [-58.11]	0.100 (1.77) [-58.01]	-16.10 ± 0.22 {0.976}
60	20	20	0.138 (0.87) [-37.82]	0.125 (1.13) [-37.80]	0.118 (1.30) [-37.37]	0.097 (1.85) [-37.93]	-9.84 ± 0.17 {0.961}
70	15	15	0.138 (0.87) [-38.54]	0.124 (1.15) [-38.58]	0.118 (1.30) [-38.06]	0.096 (1.88) [-38.68]	-10.04 ± 0.190 {0.953}
80	10	10	0.186 (0.17) [-68.90]	0.163 (0.49) [-68.35]	0.122 (1.22) [-68.97]	0.098 (1.82) [-68.69]	-19.34 ± 0.193 {0.986}
90	5	5	0.145 (0.75) [-43.41]	0.132 (1.00) [-43.21]	0.119 (1.28) [-43.00]	0.097 (1.85) [-43.45]	-11.53 ± 0.14 {0.980}
100	0	0	0.161 (0.51) [-71.72]	0.138 (0.89) [-71.31]	0.100 (1.71) [-72.16]	0.084 (2.22) [-71.46]	-19.79 ± 0.26 {0.977}

[a] and [b] are the standard error (kJ mol^{-1}) and square of correlation coefficient from the plot of $\ln \eta$ versus $1/T$ [1,10].

The viscosity values and other related thermodynamic parameters of *1:3 CTAB:CPC* ternary mixed system of *SDS:CTAB+CPC* are illustrated in Table 4. No shifting in the high viscosity peak was detected which is remained at ratio of 20:20+60 *SDS:CTAB+CPC*. The observed dynamic viscosity is higher than that of

CPC/SDS indicating the positive effect of the presence of *CTAB* towards the transition to one dimensional shape of aggregate. Hence, the viscosity (η) increases in the following sequence:

$$CPC/SDS < 1:3CTAB + CPC/SDS < 1:1CTAB + CPC/SDS < 3:1CTAB + CPC/SDS < CTAB/SDS$$

Table 3 Viscosity (η) values and other related thermodynamic functions for the ternary *CTAB+CPC/SDS* mixed system (*3:1 CTAB:CPC*) at different temperatures.

Surfactant 3 wt%			η (Pa.s) $\times 10^2$			ΔH° kJ.mol^{-1} $SE^{[a]}, [2]^{[b]}$	
SDS	CTAB	CPC	10 °C	17 °C	25 °C		35 °C
0	75	25	0.153 (0.63) [-48.75]	0.126 (1.11) [-49.25]	0.112 (1.43) [-49.00]	0.096 (1.88) [-48.85]	-13.17 ± 0.14 {0.983}
10	67.5	22.5	3.721 (-6.88) [-135.2]	2.301 (-5.89) [-135.4]	1.362 (-4.75) [-135.5]	0.789 (-3.51) [-135.2]	-45.16 ± 0.11 {0.999}
20	60	20	4.932 (-7.54) [-173.4]	2.790 (-6.36) [-173.4]	1.800 (-5.44) [-171.8]	0.666 (-3.08) [-173.9]	-56.66 ± 0.63 {0.983}
30	52.5	17.5	5.102 (-7.62) [-180.5]	4.007 (-7.23) [-177.5]	2.101 (-5.82) [-177.4]	0.693 (-3.18) [-180.2]	-58.72 ± 1.17 {0.948}
40	45	15	2.835 (-6.24) [-110.7]	1.779 (-5.27) [-111.3]	1.013 (-4.02) [-112.5]	0.803 (-3.56) [-110.4]	-37.57 ± 0.66 {0.959}
50	37.5	12.5	0.211 (-0.12) [-82.19]	0.179 (0.26) [-81.6]	0.122 (1.22) [-82.59]	0.098 (1.82) [-81.86]	-23.39 ± 0.30 {0.977}
60	30	10	0.152 (0.64) [-46.85]	0.123 (1.17) [-47.5]	0.119 (1.28) [-46.64]	0.095 (1.90) [-47.14]	-12.62 ± 0.26 {0.942}
70	22.5	7.5	0.149 (0.69) [-50.39]	0.138 (0.89) [-49.87]	0.119 (1.28) [-49.84]	0.092 (1.98) [-50.51]	-13.57 ± 0.27 {0.948}
80	15	5	0.146 (0.74) [-59.55]	0.136 (0.93) [-58.77]	0.121 (1.24) [-58.25]	0.083 (2.25) [-59.63]	-16.12 ± 0.46 {0.900}
90	7.5	2.5	0.138 (0.87) [-59.46]	0.120 (1.23) [-59.26]	0.095 (1.84) [-59.73]	0.081 (2.31) [-59.31]	-15.96 ± 0.14 {0.989}
100	0	0	0.161 (0.51) [-71.72]	0.138 (0.89) [-71.32]	0.100 (1.71) [-72.16]	0.084 (2.22) [-71.46]	-19.79 ± 0.26 {0.977}

[a] and [b] are the standard error (kJ mol^{-1}) and square of correlation coefficient from the plot of $\ln \eta$ versus $1/T$ [1,10].

Thus, it is apparent that the presence of the cationic surfactant *CPC* causing two effects with respect to the transformation process towards one dimensional aggregate. The first one was observed through the significant reduction in the ability of forming wormlike micelle as detected from remarkable decrease in solution viscosity. While the second was aroused from the shifting of the high viscosity peak through using the ternary system which only occurred when the ratio of *CPC* was less or equal to that of

CTAB. The first effect may be attributed to the electrostatic interactions between the opposed charges of cationic and anionic head groups through the formation of wormlike micelle (one dimensional chain of electrostatic head to head and hydrophobic tail to tail interactions). In other words, the alkalinity of trimethylammonium group ($pK_a= 9.8$) is stronger than that pyridinium cation ($pK_a= 5.2$) as the effect of aromatic ring through resonance plays the major role in reducing the alkalinity of the last group. Hence, the ionization potential of head groups might be added to the factors that affecting the formation of wormlike micelle. The second effect of shifting phenomenon may be related to the presence of chlorine counter ion of *CPC*. Such proposition can be explained by the formation of *NaCl* due to presence of *CPC* and *SDS* through trans ionization process as *Na* has more tendency for binding with *Cl* in comparison with *Br* ion. For example, the association constant of *NaCl* is quite higher than that of *NaBr* [15]. This means when both *CPC* and *CTAB* existing with *SDS* in solution all *Cl* ions of *CPC* will bind with *Na* and then perturbing the interactions between *CTAB* and *SDS* head groups. Moreover, the produced *NaCl* could act as a co-solvent which therefore disturbing the transformation process towards one dimensional shape of aggregate. Indeed, the relatively high association constant of sodium chloride which could reduce the hydrophobic effect as working against the icebergs structure and therefore reduce the tendency of forming wormlike micelle [16].

Thermodynamic investigations including the evaluation of ΔG° , ΔH° and ΔS° for all mixtures have been completed as displayed in Tables 1-4. In general, the results demonstrate excellent agreement with the rheological changes of all of these mixtures. In other expression, the amounts and signs of all of these thermodynamic parameters are reflecting the transformation phenomenon from three to one dimensional shape of aggregate. In consequence, the sign and values of ΔG° are reflecting the formation of worm like micelle as the sign of ΔG° turns to negative at high viscosity peak. The amounts of ΔH° exhibit an equivalent mode with the trend of transformation from three to one dimensional micelle which express the relatively high amount of heat released due to the hydrophobic effect. The large decrease in ΔS° values at the high viscosity peak also reveals the construction of iceberg structure through the excess of hydrogen bonding between water molecules. More detailed discussions about the thermodynamical behavior of the formation of wormlike micelle can be found in our related previous researches [1, 10]. However, the

presence of *CPC* displays a systematic effect on the values of these parameters due to the following observations (Tables 1-4). For instance, The heat released due to transformation process (ΔH°) at the higher viscosity peak decreasing from *CTAB/SDS* to *CPC/SDS* as having values -135.3 [1] to $-28.9 \text{ kJ.mol}^{-1}$ respectively. While for standard entropy (ΔS°) for inversion process increased from *CTAB/SDS* to *CPC/SDS* as having values -416.7 [1] to $-90.74 \text{ J.mol}^{-1} \cdot \text{K}^{-1}$ respectively.

Table 4 Viscosity (η) values and other related thermodynamic functions for the ternary *CTAB+CPC/SDS* mixed system (1:3 *CTAB:CPC*) at different temperatures.

Surfactant 3 wt%			η (Pa.s) $\times 10^2$			ΔH° kJ.mol^{-1} $SE^{[a]} r^{2[b]}$	
SDS	CTAB	CPC	$(\Delta G^\circ \text{ kJ.mol}^{-1})$ $(\Delta S^\circ \text{ J.mol}^{-1} \cdot \text{K}^{-1})$				
			10°C	17°C	25°C	35°C	
0	25	75	0.120	0.100	0.091	0.076	-12.77
			(1.20)	(1.67)	(1.95)	(2.48)	± 0.13
			{-49.34}	{-49.77}	{-49.38}	{-49.49}	{0.985}
10	22.5	67.5	0.289	0.121	0.101	0.097	-29.26
			(-0.87)	(1.21)	(1.69)	(1.85)	± 1.56
			{-100.3}	{-105.1}	{-103.8}	{-101.0}	{0.717}
20	20	60	1.163	0.893	0.299	0.203	-55.12
			(-4.14)	(-3.61)	(-0.99)	(0.04)	± 1.19
			{-180.1}	{-177.6}	{-181.6}	{-179.0}	{0.939}
30	17.5	52.5	1.092	0.871	0.293	0.185	-55.98
			(-3.99)	(-3.55)	(-0.95)	(0.19)	± 1.17
			{-183.6}	{-180.7}	{-184.6}	{-182.3}	{0.943}
40	15	45	0.281	0.181	0.127	0.112	-26.77
			(-0.80)	(0.24)	(1.12)	(1.48)	± 0.65
			{-91.7}	{-93.10}	{-93.57}	{-91.70}	{0.923}
50	12.5	37.5	0.193	0.167	0.103	0.092	-23.46
			(0.08)	(0.43)	(1.64)	(1.18)	± 0.57
			{-83.17}	{-82.37}	{-84.22}	{-79.98}	{0.924}
60	10	30	0.137	0.122	0.111	0.089	-12.21
			(0.89)	(1.20)	(1.46)	(2.07)	± 0.15
			{-46.29}	{-46.26}	{-45.87}	{-46.38}	{0.979}
70	7.5	22.5	0.141	0.128	0.115	0.093	-11.94
			(0.82)	(1.08)	(1.37)	(1.96)	± 0.14
			{-45.07}	{-44.86}	{-44.65}	{-45.11}	{0.979}
80	5	15	0.133	0.119	0.097	0.087	-12.85
			(0.96)	(1.25)	(1.79)	(2.13)	± 0.16
			{-48.78}	{-48.61}	{-49.12}	{-48.63}	{0.978}
90	2.5	7.5	0.127	0.113	0.086	0.071	-17.63
			(1.07)	(1.38)	(2.09)	(2.65)	± 0.19
			{-66.03}	{-65.50}	{-66.14}	{-65.82}	{0.983}
100	0	0	0.161	0.138	0.100	0.084	-19.79
			(0.51)	(0.89)	(1.71)	(2.22)	± 0.26
			{-71.72}	{-71.32}	{-72.16}	{-71.46}	{0.977}

[a] and [b] are the standard error (kJ mol^{-1}) and square of correlation coefficient from the plot of $\ln \eta$ versus $1/T$ [1,10].

No formation of wormlike micelles by the binary mixture of *CPC* with nonionic surfactant *TritonX-100* in a similar manner to that with cationic *CTAB*, anionic *SDS* and *SDBS* [1,10]. Also, no transition towards wormlike micelles by the ternary system of anionic, cationic, nonionic surfactants *SDS/CPC/TritonX-100* in a parallel mode to that of *SDS/CTAB/TritonX-100* and *SDBS/CTAB/TritonX-100* [1,10].

Indeed, such observations could give a direct support to the *CIF* theory as the hydrophobic effect plays the major role in the transformation towards wormlike aggregates [1].

Furthermore, Rodriguez et al. [17] studied the effect of nonionic head group size on the transformation towards one dimensional micelle in mixed nonionic/cationic surfactant. They found that the ethylene oxide group is working against the formation of worm like micelle.

Conclusions

In general, one could conclude that the presence of pyridinium cation in *CPC* head group causing a bad effect on the formation of wormlike micelle in contrast to that of trimethylammonium in *CTAB*. In addition, the results show there is no changing in the ratio of higher viscosity peak due to the replacement of *CTAB* by *CPC* which confirming that the hydrophobic effect plays the major role in the transformation process towards one dimensional shape of aggregate. Indeed, the presented suggestion of using ternary system of ionic surfactants (*SDS*, *CPC* and *CTAB*) could provide more details about the role of head group on the transformation process. Interestingly, the results show there is a clear shift in the higher viscosity peak (From 20 to 30% *SDS*) which only occurred when the ratio of *CPC* is less or equal to that of *CTAB*. Hence, the hydrophilic effect plays a sensible part in the formation of wormlike micelles. The ionization potential and type of counter ion of the head group are suggested as the reasons for the two effects including the reduction and shifting of the higher viscosity peak respectively. Finally, the outlined results of this research could give direct support to the previously proposed *CIF* theory [1] for interpreting the formation of one dimensional supra-molecular gel.

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