

Critical Intermolecular Forces: A New Physical Insight for the Formation of Wormlike Micelles

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Summary: Up to present date, no obvious and reasonable theoretical approach interpreting the formation of worm- or thread-like micelles together with the accompanying sharp change in the rheological properties. Consequently, systems of binary and ternary mixtures of 3 wt% anionic, cationic and nonionic surfactants have been investigated at different temperatures. The mixture of anionic [sodium dodecylsulfate (SDS)] and cationic [cetyltrimethylammonium bromide (CTAB)] surfactants exhibits a remarkable high viscosity peak at weight ratio of 80/20 CTAB/SDS. No wormlike micelles have been detected for binary mixtures of anionic- nonionic (Triton-X 100) nor for ternary mixtures of SDS/CTAB/Triton-X 100 surfactants. Approximate relations have been introduced for evaluating the thermodynamic change from spherical to one-dimensional supramolecular aggregate. Conductivity measurements have been performed for supporting the present investigation. The results reveal a new physical insight called Critical Intermolecular Forces (CIF), which is responsible for the transition phenomenon from three to one-dimensional shape of aggregate. It has been concluded that the suggested theory of CIF plays as a powerful tool in understanding not only the transition state towards wormlike micelles together with the associated significant increasing in solution viscosity, but also for helping researchers who are interested in exploring any kind of new wormlike systems.

Keywords: Wormlike micelles; Critical intermolecular forces; Sodium dodecylsulfate; Cetyltrimethylammonium bromide; Triton-X 100; Thermodynamic properties; Supramolecules.

Introduction

Indeed, the well-known common shape of micelles formed by surfactants in aqueous media at concentration over critical micelle concentration (cmc) is spherical. Such three-dimensional aggregates have employed in many applications. Among these: catalysis, analytical, solubility, and help in understanding biochemical process. Another class of such supramolecular aggregates, which can be formed in presence of cosolute is called wormlike or threadlike micelle. The rheological properties of the latter one-dimensional system in aqueous solution attracted the attention of researchers. The special characteristics of these self-assembled structures promise important industrial and commercial applications [1-3]. In addition, the dynamical structure of such supramolecular aggregates have great advantages to physicists who are interested in Toms effect, as an interesting model in contrast to flexible high molecular polymer whose chain length is fixed by covalent bond [4].

According to literature [5, 6], wormlike micelles could be obtained from mixed surfactants systems including ionic surfactant with cosurfactant, mixed nonionic surfactants, mixed cationic-anionic surfactants, and mixed of ionic surfactant with salt. Song *et al.*[7] found that the one-dimensional aggregate can be formed from anionic gemini

surfactants without addition of salts. Recently, Li *et al.*[3] stated that wormlike micelles also formed from surface active ionic liquid with organic salt in aqueous solution. In spite of the remarkable increasing in the number of investigations for reporting new systems of wormlike micelles [2, 5, 8]. So far, such investigations can be considered as guesswork, which there is no certain theory that could aid researchers for speculation a new wormlike system.

From the Cryo-transmission electron microscopy studies point of view [1, 3], the pronounced increases in magnitude of viscosity that gives sharp peak is attributed to the formation of wormlike micelles. In other words, the sudden change of surfactants solution to relatively high viscose due to change in its composite can be considered as a function for the transformation towards wormlike micelles. On the other hand, the publications show a significant lack not only of the driving force of the transition phenomenon from three to one dimensional aggregate, but also of the reasons for the accompanied substantial increase in viscosity of solution. For example, Cates model is only applicable for nonionic surfactants [9-11]. Moreover, investigations concerning the changes in thermodynamic properties for the transformation

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process towards wormlike micelles are quite rare [12-16]. In addition, they exhibit contradictory values of enthalpy change, which were achieved using isothermal titration microcalorimetry, ITC. Bijama *et al.*[12] and Liu *et al.*[13] found the enthalpy of transformation to one dimensional micelle change from exothermic to endothermic through the replacement of iodide and sodium tosylate by salicylate and sodium salicylate anions respectively. Šarac *et al.* [15] also found an endothermic enthalpy for the mixture of dodecyltrimethylammonium chloride with sodium salicylate. Indeed, such observation cannot reflect the high viscose behavior of gel-like state, which is not possible to be endothermic as the attractions of all kinds of intermolecular forces releasing heat. On the other hand, the relatively low magnitude of these having exothermic enthalpies [12-14], is also inconsistent with the significant increasing in solution viscosity. Therefore, the present article introduces approximate thermodynamic relations having physical meaning for treatment of the transition phenomenon towards wormlike micelles.

In this work, we have investigated the formation of wormlike micelles for mixtures of anionic SDS (sodium dodecylsulfate)-cationic CTAB (cetyltrimethylammonium bromide), anionic SDS-nonionic Triton X-100 surfactants, and their ternary system of anionic-cationic-nonionic surfactants at different temperatures. No such investigations have been observed in literature. The main objective of this study is for obtaining some useful information concerning the driving force of wormlike micelles, which could help in understanding such special type of aggregate, together with accompanying substantial changes in rheological properties. The present paper announces a new physical insight that could explain the formation of wormlike micelles, which is referred to as Critical Intermolecular Forces, *CIF*.

Results and discussion

Mixed Anionic-Cationic Surfactant System

The concentration used for all surfactants (3 wt %) is more than *cmc* in order to ensure the formation of wormlike micelles. Fig. 1 exhibits the variation of dynamic viscosity, η versus different compositions of CTAB/SDS at different temperatures. The relation indicates clearly the formation of wormlike micelles within the range of 90/10 to 70/30 CTAB/SDS. In other words, the composition of 80/20 CTAB/SDS is about two orders magnitude higher than the viscosities of the pure component of each surfactant solution. The relation also indicates that

the formation of wormlike micelles is temperature-independent in contrast to that of *cmc*. However, this temperature independency should be less than the amount of required heat for breaking the intermolecular forces. Hence, it is not possible to determine the thermodynamic functions of such type of aggregate in a similar manner for that of common spherical micelles [17, 18]. On the other hand, as the viscosity of these mixtures is temperature-depended, we have suggested approximate relations at this special case for evaluation of the thermodynamic properties for wormlike micelles with respect to change in viscosity. The standard Gibbs free energy (ΔG°), which might be considered as the excess free energy due to transformation to one dimensional shape could approximately be determined through replacing the concentration equilibrium constant by that of observed dynamic viscosity (η) divided by a factor $2 \times 10^{-3} Pa.s$ as presented in Eq. 1. The latter factor is the average viscosity of the initial state (before the transformation process).

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

where R is the gas constant, T is the absolute temperature. The approximate standard enthalpy (ΔH°) may also be estimated through modifying van't Hoff equation as following:

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

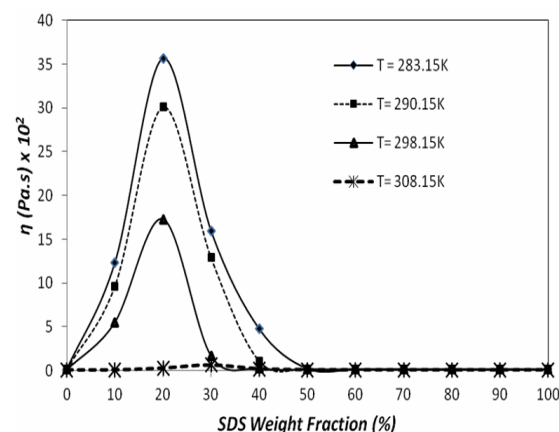


Fig. 1: Dynamic viscosity of CTAB/SDS mixed system as a function of SDS weight fraction in the mixture at different temperatures, the total surfactants concentration is 3wt%.

While the standard entropy (ΔS°) can be calculated using the following general thermodynamic relation:

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

The already well-known relation of activation energy of viscosity (E_a), which can give support to the above-suggested relations, as represented by following equation [19]:

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

Table 1 lists the viscosity (η) values with their related thermodynamic functions for *CTAB/SDS* mixtures at different temperatures. Interestingly, the results reflect the rheological change of the mixtures. In other words, these approximate values of thermodynamic functions give a physical meaning which may be able to help in understanding the driving force of wormlike micelles. The signs of ΔG° are quite parallel with the change in molecular self-assembly from spherical to one-dimensional aggregate. These indicate that the spontaneity of the transition to wormlike micelles at the same compositions range of that observed in Fig. 1 except that at 35°C. In spite of the approximation of these suggested thermodynamic functions, the values of ΔS° are also reflect the significant decrease in the order through forming the threadlike micelles, as the dynamic viscosity is increasingly proportional to the mobility of molecules. While the ordinary ΔS° of micellization (*cmc*) having positive sign that may be resulted from the presence of free gegenions and the increase in the degree of freedom. The magnitudes of ΔH° are also in parallel mode with the transition trend from three to one dimensional aggregate. The values of activation energy of viscosity (E_a) could give a direct support to those enthalpies, which indicate that the sign of ΔH° should be negative. The relatively high values of ΔH° that combined with the formation of threadlike micelles could reflect the significant amount of released heat at this transition, which is about 61 and 23 times for *cmc* of each *SDS* (-2.23 kJ.mol^{-1}) and *CTAB* (-5.88 kJ.mol^{-1}) respectively [18]. Indeed, this could suggest that such considerable amount of heat released due to transition phenomenon is over than that could be obtained from the intermolecular interactions of surfactants molecules. In other words, the electrostatic interactions between the opposite signs of head groups, the dispersion interactions between hydrophobic tail groups, and other types of attractions forces between surfactants and solvent molecules are not enough for releasing such amount

of heat. It becomes clear that these types of intermolecular interactions also exist within spherical micelle of mixed anionic-cationic surfactants. For instance, the standard enthalpy of micellization (ΔH°_{cmc}) for mixed *SDS* and *CTAB* has value of -1.38 kJ.mol^{-1} at 25°C [20]. This suggests that the hydrophobic effect (icebergs) [21] is another factor, which plays an important role in releasing such excess amount of heat due to the transformation process. The last effect could also play a significant role in increasing the viscosity of the solution as well as in decreasing the entropy. Such contribution of hydrophobic effect could be supported through the fact that the formation of wormlike micelle here occurred at high fraction of the longer hydrophobic chain (*CTAB*), which exceeds four $-\text{CH}_2-$ groups than that of *SDS*. This already happened for the mixture of the anionic sodium oleate (*NaOA*) and cationic octyl trimethylammonium bromide (*OTAB*), which the formation of threadlike micelle took place at 70/30 *NaOA/OTAB* 3 wt% ratio (*NaOA* tail have 10 carbon atoms more than that of *OTAB*) [22]. Raghavan *et al.* [22] have experimentally found that the viscosity of mixed anionic-cationic surfactants increases with increasing the hydrophobic tail. A similar observation was also detected for anionic gemini surfactants [7]. Furthermore, Li *et al.* [3] studied the salt-induced wormlike micelle by N-alkyl-N-methylpyrrolidinium bromide ($C_n\text{MPB}$, $n=12, 14$ and 16). They found that only $C_{16}\text{MPB}$ could form wormlike micelle in contrast to others. Another observation could be realized through viewing the chemical structures of *SDS* and *CTAB*, which support the hydrophobic effect: the head part of *CTAB* has less ability for making hydrogen bonding with water molecules due to presence of bulky CH_3 groups. While the oxygen atoms of *SDS* head group could make hydrogen bonding with water, which then act against the icebergs in contrast to that of *CTAB*. In a similar way, the cationic surfactant *OTAB* has more tendencies towards hydrogen bonding through three hydrogen atoms, which are located at nitrogen than that of *NaOA* carboxylic group [22].

It should be noted that the electrostatic interactions have a considerable contribution for the transition to wormlike micelle in which the latter can be formed from systems of mixed ionic surfactant with salt [5]. Thus, the net potential energy (E_p) that belonging to intermolecular forces, having responsibility for the transition to one-dimensional shape may be presented as sum of three main components according to following equation:

$$E_p = E_{p(\text{Elec})} + E_{p(\text{Disp})} + E_{p(\text{Ice})} \quad (5)$$

where ($E_{p(Elec)}$) is the potential energy associated with intermolecular attraction forces between opposite charged polar groups, ($E_{p(Disp)}$) is the potential energy belonging to the dispersion force between the hydrophobic chains of surfactants, and ($E_{p(Ice)}$) is the heat released from the extra hydrogen bonds between water molecules due to hydrophobic effect (icebergs). The latter resulted through the contact between surfactant hydrophobic groups and water molecules. Hence, according to the above potential energy, one could represent the net enthalpy (ΔH^o) of wormlike micellization as follows:

$$\Delta H^o = \Delta H_{p(Elec)}^o + \Delta H_{p(Disp)}^o + \Delta H_{p(Ice)}^o \quad (6)$$

It is obvious from the above relations (5 and 6) that the transition from spherical to one-dimensional aggregate releasing heat, which depends mostly on three main intermolecular forces. In other words, if there is a lack in one of these forces there may be no formation of wormlike micelles, noting that, the icebergs contribution ($\Delta H_{p(Ice)}^o$) depends on the effective amount of hydrophobic groups in solution. While the magnitude of heat released due to electrostatic attractions between polar groups ($\Delta H_{p(Elec)}^o$) depends on the ionic strength of the opposite charged surfactants. On the other hand, the contribution regarded to dispersion forces ($\Delta H_{p(Disp)}^o$) may be the less significant in contrast to others ($\Delta H_{p(Ice)}^o$ and $\Delta H_{p(Elec)}^o$). This may be attributed to that the hydrocarbonic chains of one dimensional shape are not in parallel packing to each other as located in spherical micelle. However, as there is heat released due to the formation of wormlike micelles, this means that the solution of the latter aggregate is thermodynamically more stable than that of previous state. So, why such transformation cannot proceed spontaneously? Indeed, this could be due to the entropy factor, which the latter works against the transition process. This could be confirmed through the substantial loss in entropy as shown clearly in Table 1. Therefore, the transformation towards one-dimensional micelle commonly needs cosolute in order to overcome the entropy task. In other words, the entropy factor will not be that effective when solution molecules reach a specific state. It should be noted that the entropy factor works against simple spherical micellization, but cannot be the reason for transformation towards one-dimensional shape as the latter system is more organized.

Thus, one could realize that the transition phenomenon of mixed surfactant systems over *cmc* to wormlike micelle could proceed when the solution

molecules reach a specific state, which could be termed as critical intermolecular forces, *CIF*. Such new termed effect (*CIF*) covers the intermolecular interactions, which are responsible for the formation of threadlike aggregate. The critical word introduced to this term could be interpreted as: at specific concentration of molecules, there are intermolecular interactions that could create a certain state which makes the transition towards wormlike micelle is energetically favorable. For example, the free regions at Gouy-Chapman layer of spherical micelle interact as ion-dipole with surrounding water molecules, which make decreasing in hydrogen bonding between water molecules, followed by depressing the icebergs. The later depressing makes an increase in the entropy leading to reduction in each of density and viscosity [21]. On the other hand, the presence of non-equivalent amount of opposite sign ionic surfactant may disturb the balance between free and combined counter ions. This could increase the electrostatic repulsion between the head groups of surfactants, which also makes the transition to one-dimensional energetically favorable. The latter could be supported by observing that, the tendency for one-dimensional growing has proportionality with the degree of counterion binding [12]. Therefore, the *CIF* could be considered as a balance of three main intermolecular forces, which the hydrophobic effect plays a major role in the formation of wormlike micelles. Since the formation of the crystalline structure of icebergs is due to the excess of hydrogen bonding between water molecules, the icebergs can be considered as the main factor for enhancing the solution viscosity. It should be mentioned that the crystalline characters of liquid water differ from that of ice of which the latter has lower density than that of ordinary liquid water [21].

It should be mentioned that the formation of wormlike micelles not only captured by ionic surfactants, but could also occur for some mixed nonionic surfactant systems [5, 6]. This may also give support to our proposition of *CIF*. This is because for such system the surfactants must relatively being in high concentration, as well as having relatively long hydrophobic chains in contrast to those of ionic surfactants. The dependency on relatively long hydrophobic chain indicates that the hydrophobic effect (icebergs) is the predominant factor for the transition towards one-dimensional shape. Furthermore, for nonionic surfactants system, there are no ion-ion and ion-dipole interactions as the dipole-dipole interaction between the head groups is more likely. Therefore, the factor of ($E_{p(Elec)}$) which is cited in equation 5 could cover all of these types of interactions.

The cosolute independency for the formation of wormlike micelle exhibited by anionic gemini surfactants [7] could also be elucidated in terms of *CIF* theory. The outcome of this: firstly, only surfactants that contain relatively long alkyl tails could form wormlike micelle, which corresponds to the factor of hydrophobic effect. Secondly, the presence of double tails in the structure may reduce the stability of three-dimensional aggregates due to steric hindrance, as the tails must locate within the micelle core in order to decrease their contact with water molecules. Therefore, any effect, which causes unsteadiness in three-dimensional aggregate (as the effect of cosolute) can be considered as a favorable factor for reaching the *CIF*. Indeed, the above mentioned aspects have no clear meaning through the pervious theory (end-cap theory) [16], which considered the temperature as the predominant factor for transformation process.

The electrical conductivity of the mixture has also been determined at different temperatures (Fig. 2). It is clearly shown that the electrical conductivity reach a minimum when the wormlike micelle is formed. Such a phenomenon reflects the hydrophobic effect ($E_{p(ice)}$) and the lack in free gegenions ($E_{p(Elec)}$) which both support the presented idea of *CIF*. No linear relationship has been found between the electrical conductivity and the viscosity of the presented mixture (i.e. square of correlation coefficient, $r^2=0.44$). This could be attributed to the change in surfactant ratio, as there is difference in conductivity between *SDS* and *CTAB*.

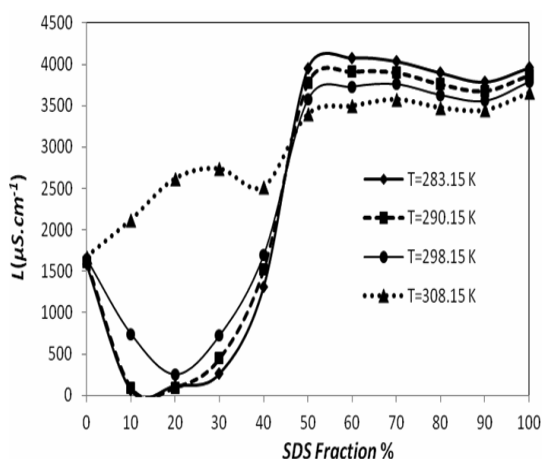
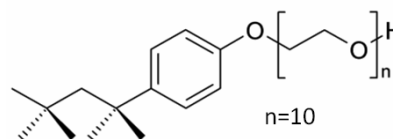


Fig. 2: Electrical conductivity L of *CTAB/SDS* mixed system as a function of *SDS* weight fraction in the mixture at different temperatures, the total surfactants concentration is 3wt%.

Mixed Ionic-Nonionic Surfactant System

In order to achieve information that could support the above discussion about the effect of addition of an opposite charged ionic surfactant on the free counter ion. The investigation has extended for mixtures of nonionic *Triton-X 100* with each of *SDS* and *CTAB*. Table-2 lists the dynamic viscosity (η) values, approximate enthalpy and activation energy of viscosity (as there is no the special case for evaluating the thermodynamic functions as that in Table-1) for *Triton-X100/SDS* mixtures at different temperatures. The results show that there are no noticeable changes in viscosity, which indicate there is no formation of wormlike micelles. In other words, the solutions of this system cannot reach the critical intermolecular forces, *CIF*. This may be due to three main reasons, which have negative effects towards icebergs factor. The first comes from the hydrogen bonding between water and the polar groups of *Triton-X 100* (10 oxygen atoms and hydroxyl group), as shown clearly in Scheme 1. The second is due to that the latter nonionic surfactant has no ability upon changing positions of the free gegenions, which then no disturbing for the spherical structure of *SDS*, as the above-mentioned effect of *CTAB*. While the last reason arises from the involvement of both *Triton-X 100* and *SDS* within the spherical micelle, which enhances the stability of latter micelle through reducing the electrostatic repulsion between *SDS* polar groups. However, similar results have been found for mixed system of the nonionic *Triton-X 100* with the cationic *CTAB* [23], which give a direct support for that the icebergs factor plays a major role in the transformation phenomenon towards one-dimensional supramolecular aggregate.

The electrical conductivity measurements for the present mixed system (Fig. 3) show a clear inflection in conductivity at ratio 30/70 *Triton-X 100/SDS*, which may be resulted from the latter mentioned involvement of *Triton-X 100*, which leads to move some of Na free ions towards Stern layer. From the statistical point of view, the solutions of wormlike micelle were not fully complied with the van't Hoff equation, as clearly shown in Table-1 and 2 with respect to the values of square correlation coefficients (r^2).



Scheme-1: Chemical structure of *Triton-X 100*.

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

CTAB(3 wt%)	SDS(3 wt%)	η (Pa.s) $\times 10^2$ (ΔG° kJ.mol ⁻¹) { ΔS° J.mol ⁻¹ .K ⁻¹ }				ΔH° kJ.mol ⁻¹ SE ^[a] r ² [b]	E_a J.mol ⁻¹ SE ^[c] r ² [d]
		283.15K	290.15K	298.15K	308.15K		
100	0	0.171	0.145	0.110	0.087	-20.30	25.11
		(0.37)	(0.78)	(1.49)	(2.15)	± 0.13	± 0.24
		{-72.9}	{-72.6}	{-73.1}	{-72.9}	0.994	0.987
		12.342	9.637	5.520	0.083	-139.9	3589.6
90	10	(-9.71)	(-9.35)	(-8.22)	(2.25)	± 6.35	± 28.6
		{-460.2}	{-450.3}	{-441.9}	{-461.6}	0.779	0.991
		35.610	30.126	17.278	0.287	-135.3	10465.5
		(-12.20)	(-12.10)	(-11.05)	(-0.92)	± 6.30	± 145
80	20	{-434.7}	{-424.6}	{-416.7}	{-436.1}	0.769	0.974
		15.960	12.893	1.685	0.642	-102.2	4939.6
		(-10.31)	(-10.05)	(-5.28)	(-2.99)	± 2.35	± 150
		{-324.6}	{-317.7}	{-325.2}	{-322.1}	0.932	0.886
70	30	4.779	1.053	0.247	0.198	-94.26	1228.6
		(-7.47)	(-4.01)	(-0.53)	(0.02)	± 2.76	± 68.5
		{-306.5}	{-311.0}	{-314.4}	{-306.0}	0.894	0.699
		0.263	0.183	0.128	0.098	-28.73	47.28
50	50	(-0.64)	(0.22)	(1.10)	(1.82)	± 0.31	± 1.05
		{-99.2}	{-99.8}	{-100.1}	{-99.2}	0.985	0.935
		0.156	0.128	0.106	0.083	-17.98	20.72
		(0.59)	(1.08)	(1.58)	(2.24)	± 0.03	± 0.18
40	60	{-65.6}	{-65.7}	{-65.6}	{-65.6}	1.000	0.989
		0.154	0.126	0.107	0.098	-13.15	16.11
		(0.69)	(1.25)	(1.74)	(2.05)	± 0.25	± 0.39
		{-48.9}	{-49.6}	{-49.9}	{-49.3}	0.951	0.924
30	70	0.154	0.126	0.103	0.082	-18.01	20.48
		(0.62)	(1.11)	(1.64)	(2.27)	± 0.04	± 0.20
		{-65.8}	{-65.9}	{-65.9}	{-65.8}	0.999	0.987
		0.156	0.129	0.104	0.083	-18.27	21.02
20	80	(0.58)	(1.07)	(1.61)	(2.25)	± 0.03	± 0.02
		{-66.6}	{-66.6}	{-66.7}	{-66.6}	1.000	0.987
		0.166	0.136	0.109	0.087	-18.80	22.85
		(0.44)	(0.94)	(1.50)	(2.14)	± 0.05	± 0.24
0	100	{-67.9}	{-68.0}	{-68.0}	{-67.9}	0.999	0.985

[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.

Table-2: Viscosity (η) values, approximate enthalpy and activation energy of viscosity for the Triton-X 100/SDS mixed system at different temperatures.

Triton-X 100 (3 wt%)	SDS(3 wt%)	η (Pa.s) $\times 10^2$				ΔH° kJ.mol ⁻¹ SE ^[a] r ² [b]	E_a J.mol ⁻¹ SE ^[c] r ² [d]
		283.15K	290.15K	298.15K	308.15K		
100	0	0.159	0.131	0.107	0.087	-17.58	20.87
		± 0.05				± 0.05	± 0.23
		0.999				-18.73	22.67
						± 0.05	± 0.23
90	10	0.165	0.135	0.109	0.087	-18.82	23.31
		± 0.05				± 0.04	± 0.24
		0.999				-18.90	23.45
						± 0.05	± 0.25
80	20	0.169	0.138	0.112	0.089	-18.65	23.13
		± 0.04				± 0.04	± 0.24
		0.999				-18.79	23.33
						± 0.04	± 0.23
70	30	0.170	0.138	0.112	0.089	-18.71	22.97
		± 0.05				± 0.04	± 0.23
		0.999				-18.65	23.13
						± 0.05	± 0.25
60	40	0.169	0.138	0.112	0.089	-18.97	23.52
		± 0.04				± 0.04	± 0.24
		0.999				-18.79	23.33
						± 0.04	± 0.23
50	50	0.169	0.139	0.112	0.088	-18.71	22.97
		± 0.02				± 0.04	± 0.23
		1.000				-18.65	23.13
						± 0.04	± 0.24
40	60	0.167	0.137	0.111	0.088	-18.71	22.97
		± 0.04				± 0.04	± 0.23
		1.000				-18.79	23.33
						± 0.04	± 0.23
30	70	0.169	0.138	0.112	0.088	-18.84	23.35
		± 0.04				± 0.04	± 0.24
		0.999				-18.84	23.35
						± 0.04	± 0.23
20	80	0.169	0.138	0.112	0.088	-18.84	23.35
		± 0.03				± 0.03	± 0.23
		1.000				-19.04	23.58
						± 0.04	± 0.24
10	90	0.170	0.138	0.113	0.088	-18.80	22.56
		± 0.04				± 0.04	± 0.24
		0.999				-18.80	22.56
						± 0.05	± 0.22
0	100	0.166	0.136	0.109	0.087	-18.80	22.56
		± 0.05				± 0.05	± 0.22
		0.999				-18.80	22.56
						± 0.05	± 0.22

[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.

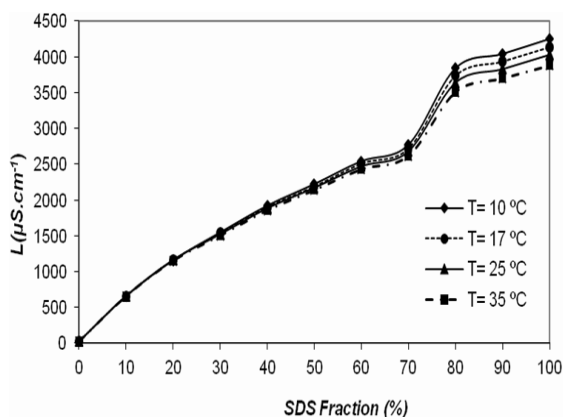


Fig. 3: Electrical conductivity L of Triton-X 100/SDS mixed system as a function of SDS weight fraction in the mixture at different temperatures, the total surfactants concentration is 3wt%.

Ternary system of mixed anionic-cationic and nonionic surfactants

The use of ternary system of three different classes of surfactants could provide an opportunity for distinguishing between the effect of surfactants concentration (solute) and the proposed *CIF* for the transition to wormlike micelle. Therefore, investigation concerning the effect of addition of nonionic surfactant (Triton-X 100) on the higher viscosity mixture 80/20 CTAB/SDS has been suggested. Empirically, due to the pronounced viscosity of the latter mixture, there was a problem in solubility. For that reason, the exploration was carried out at 35°C. It should be noted that the last solubility problem was not resulted from the high concentrations of solute, since saturation at low concentrations has been considered as a unique characteristic of surfactant solutions [24]. Fig. 4 shows the effect of the presence of Triton-X 100 on the dynamical viscosity of the mixture 80/20 CTAB/SDS at 3 wt% total concentration. It is clearly shown from this Figure that the presence of small amount of Triton-X 100 (2.6×10^{-3} mol. dm^{-3}) decreases sharply the viscosity of this mixture. This indicates that any contamination of wormlike shape solution by Triton-X 100 will disturb the *CIF* through breaking the icebergs structure due to hydrogen bonding, as illustrated in the preceding section. This could also give the reason for introducing the critical word in our proposed term. Furthermore, the nonionic surfactant works as anti-wormlike micelle which makes reverse transition from one to three dimensional micelles due to relatively higher hydrophilic character of Triton-X 100. This could

also give a direct evidence for influencing the suggested *CIF* by hydrophobic effect through the formation of icebergs structure by water molecules.

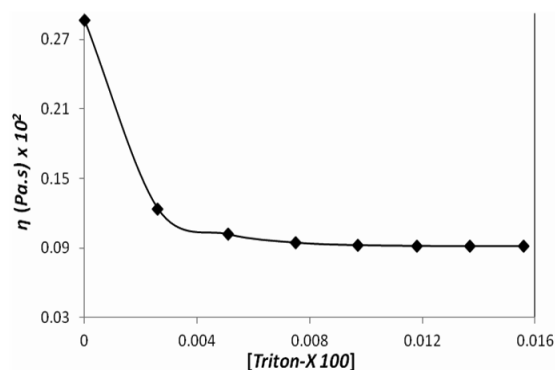


Fig. 4: Effect of addition Triton-X 100 (mol. dm^{-3}) on the dynamic viscosity of 80/20 CTAB/SDS mixture (3wt %) at 35°C.

Table-3 records the dynamic viscosity of the ternary system that contains three different types of surfactants (Triton-X 100/CTAB/SDS), at different composition ratios and temperatures. Again, no wormlike micelle has been formed, as the viscosity dropped due to presence of the nonionic surfactants. Indeed, this also supports our proposed term of *CIF* with the same reasons mentioned above for the addition of Triton-X 100 to 80/20 CTAB/SDS mixtures. Again, no need to evaluate the thermodynamic parameters for this system, due to the apparent closeness in viscosity trend with that of nonionic-anionic mixed system (Table-2).

Table-3: Viscosity (η) values for the ternary mixed system of SDS, CTAB and Triton-X 100 surfactants at different temperatures, the total surfactants concentration is 3wt%.

SDS (3wt%)	CTAB (3wt%)	Triton X 100 (3 wt%)	η (Pa.s) $\times 10^2$			
			283.15 K	290.15 K	298.15 K	308.15 K
0	0	100	0.159	0.131	0.107	0.087
5	5	90	0.173	0.138	0.113	0.095
10	10	80	0.166	0.137	0.112	0.095
15	15	70	0.170	0.139	0.115	0.097
20	20	60	0.183	0.147	0.118	0.095
25	25	50	0.206	0.166	0.138	0.111
30	30	40	0.169	0.137	0.113	0.094
35	35	30	0.186	0.149	0.121	0.095
40	40	20	0.161	0.130	0.104	0.083
45	45	10	0.160	0.129	0.104	0.091
50	50	0	0.263	0.183	0.128	0.098

Hence, the *CIF* could also be considered as a powerful tool for aiding researchers who are interested in preparing new wormlike solutions through considering the following four points:

- If there are gegenions due to presence of ionic surfactant, an addition of opposite sign surfactant or electrolyte will increase the tendency towards reaching the *CIF*.
- The longer hydrocarbon chain is more favorable by *CIF* due to increases in hydrophobic effect.
- The presence of any secondary group at the head of surfactant having the tendency for making hydrogen bonding with water molecules leads to a negative effect on *CIF*.
- Any replacement of hydrogen atom, which belongs to the alkyl chain by other atoms or groups, will act against *CIF*.

We should bear in mind that the origin of rheological behavior of wormlike solution differs merely from that of fixed polymers. It is clear that the dynamical aggregate of wormlike micelles can be related to the flexible intermolecular forces. While the viscosity of polymers solutions depend on concentration, degree of polymerization, degree of cross-linking, and degree of interactions with solvent molecules, noting that, we have found within this manuscript that the last factor works importantly against the formation of wormlike micelles. Finally, it should be noted that, the determination of *CIF* could be observed experimentally by following the sudden sharp increasing in solution viscosity.

Experimental

The surfactants SDS ($(\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na})$), CTAB ($(\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Br}^-)$) 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 obtained in high purification form from Aldrich and Fluka companies. Conductivity water was used for preparation of all solutions with specific conductance of 3-5 $\mu\text{S}\cdot\text{cm}^{-1}$ which prepared through redistilling distilled water with addition of little amounts of KMnO_4 and KOH .

3 wt% solution of each surfactant is made to give concentrations of 0.1072, 0.08486 and 0.0478M for SDS, CTAB and Triton-x respectively.

The dynamic viscosity (η) measurements were carried out using modified Ostwald tool as detailed in general previously [25, 26], noting that, when the viscosity become very high (gel-like state), a 10ml pipette was used for measuring the dynamic viscosity due to impossibility of using Ostwald tool at this special case of very high solution viscosity. The viscosity (η) of the solution was calculated from the following relation [25]:

$$\eta_s = \eta_w \frac{t_s \rho_s}{t_w \rho_w} \quad (7)$$

where ρ is the density ($\text{kg}\cdot\text{m}^{-3}$), t is the time (s) and the subscripts s and w represent solution and water respectively.

The conductivity measurements were determined [27], using WTW conductometer with accuracy $\pm 0.01 \mu\text{S}\cdot\text{cm}^{-1}$. To control the temperature of the above determined physical properties within $\pm 0.1^\circ\text{C}$, water thermostated Hakke NK22 is used. All measurements are repeated for at least three times in order to check the reproducibility of the data.

Conclusions

It is well clear that the amphiphilic molecules tend to form spherical micelles when their concentrations reach the cmc in aqueous solution. This self-assembly occurs in order to decrease the free energy through keeping the hydrophobic tails at the core of micelle. The transformation from sphere to one-dimensional aggregate expresses that there is a substantial increasing in the contact area between water and hydrocarbonic chains. Therefore is still obscure in spite of the considerable efforts that based on theoretical considerations which have been made in order to obtain a suitable model for the transformation process [3, 6, 9-11, 28-30]. On the other hand, thermodynamic investigations concerning the transformation process are quite rare [12-15]. Moreover, they only captured through evaluating the enthalpy change using ITC technique. At the same time, there are problems that noticed by means of the signs [12, 13, 15] and magnitudes of the evaluated enthalpies [12-14], which they can not reflect the change in rheological behavior of wormlike solution. This may indicates that the ITC measurements are not sufficient for such purpose. Therefore, systems of binary and ternary mixtures of different classes of surfactants at low concentrations have been investigated. A new approach for evaluating the approximate thermodynamic properties for the formation of wormlike micelles from the dependency of viscosity on temperature has been introduced. The results show that the magnitudes of thermodynamic parameters are in good agreement with rheological change of solution. For instance, the relatively high change in enthalpy (*less than* $-100\text{kJ}\cdot\text{mol}^{-1}$), which reflects the significant amount of heat released due to the formation of gel-like state, in contrast to those reported using ITC technique [12-15]. The latter showed that the enthalpies for such process just change in few kilojoules [12-15], in addition to the appearance of a positive sign as the transformation to gel-like state is an endothermic process [12, 13]. This

suggests there may be a serious technical problem in measuring the enthalpy of wormlike micelle using ITC apparatus.

The obtained values of entropy change suggest there is a substantial loss in entropy (*less than* $-400\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), due to the transition to one-dimensional shape of aggregate. Indeed, this could reflect that the change from spherical to wormlike micelle is accompanied with the solution translation from two phases (the spherical micelle is considered as pseudophase [4]) to one phase. This means there is no interface within the solution of wormlike micelles. In fact, such conversion to one phase may be considered as one of the main reasons for the absence of optimal theoretical model that could cover all classes of wormlike systems [3, 6, 9-11, 28-30]. While, the values of free energy change are clearly show that the wormlike solution is more stable than that of spherical, but the main task that works against the transformation process is the entropy factor, as the latter decreased substantially. Therefore, the addition of cosolute could aid for overcoming this task. Thus, our presented values of approximate thermodynamic properties in this special case could be considered as a significant approach for understanding the transformation phenomenon towards one-dimensional aggregate.

In general, the results suggest there is a new physical insight referred to as critical intermolecular forces (*CIF*), which could logically clarify the formation of wormlike micelles. The formation of any system of one-dimensional micelles is due to sum of three main intermolecular forces. One is belonging to the electrostatic interactions between polar head groups ($E_{p(Elec)}$). The second is resulted from dispersion forces between hydrophobic chains of surfactants ($E_{p(Disp)}$). The last one has been achieved from the excess of hydrogen bonds between water molecules (icebergs) due to the hydrophobic effect ($E_{p(Ice)}$), which plays a major role in the transformation process. Indeed, this contradicts with the early view about that the head groups effect is the main driving force for transition to worm like micelle [6, 12, 30]. Lin *et al.* [28] illustrated the formation of wormlike micelle in terms of effective areas of both the hydrophilic head group and the hydrophobic chain of surfactant. They concluded that the increase in the effective area of hydrocarbon chain is an important factor for transition mechanism. A very interesting feature which realized from the presented *CIF* theory is that the significant enhancement in solution viscosity can be interpreted in terms of the hydrophobic effect. In other words, the substantial increases in the viscosity is resulted from the

crystalline structure of water or solvent molecules (icebergs), not as previous which was attributed to the length of one-dimensional micelle in a similar manner to that of fixed polymers [2,8,29,30]. Thus, the mechanism of changing the rheological properties by these living or equilibrium polymers differs merely from these of high molecular polymers, which chain length fixed by covalent bond. Hence, the *CIF* theory could aid in understanding the transition phenomenon towards wormlike micelles, together with the accompanying sharp change in rheological solution properties. A unique characteristic of the presented theory, is its ability for illustrating all systems of wormlike micelles in contrast to that of previous models [3, 6, 9-11, 28-30]. This could reflect the correctness of the postulated physical factors in the *CIF* theory. Finally, the presented theory (according to the listed comments in the preceding section) can be considered as a powerful tool for helping researchers who are interested in exploring any kind of new wormlike systems, hoping for no more guesswork in the near future.

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