Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Advances in Applied Science Research, 2015, 6(6):194-206

ISSN: 0976-8610
CODEN (USA): AASRFC

Effect of biologically active Oxoglutaric Acid on micellar properties of important anionic surfactant at different temperatures

Rehab Khaled Mahmoud[1*] and Rafat M. Amin[2]

[1]*Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt*
[2]*Department of Physics, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt*

ABSTRACT

In this study, interaction of 2-ketoglutaric acid (GL) with anion surfactant, sodium lauryl sulfate (SLS) in aqueous solution have been investigated using electric conductivity at different temperatures from 298.15-308.15 K. From the specific conductivity data, the critical micellar concentration, degree of counter ion association, degree of counterion dissociation, free energy of transfer of hydrophobic chain from the medium to interior of the micelle, and surface contribution, standard free energy of micellization, standard enthalpy of micellization, and standard entropy of micellization of sodium lauryl sulfate have been computed. The experimental data show that cmc values of SLS increase with increasing temperature. The thermodynamic parameters of micellization and the effect of additives on these parameters have been used to study the interactions between the 2-ketoglutaric acid and SLS in the micellar systems. Also, the dissociation constants (pK_a's) of 2-ketoglutatic acid were studied in aqueous and aqueous micellar solution of sodium lauryl sulfate–water mixtures (0.01 to 0.30 mol·dm^{-3}) at 298 ± 0.1 K, using a pH-metric technique. The protonation constants are calculated using computer program HYPERQUAD and the best fit chemical model is based on the statistical parameters. Based on the results obtained from the study, a charge of anionic surfactant leads to an electrostatic interaction between surfactant and the (GL) molecule. The electrostatic interactions can be attractive forces and influence of separation of protons and consequently decrease the acidity strength.

Keywords micellar media effect; conductivity measurement; potentiometry; dissociation constants; sodium lauryl sulfate.

Abbreviations
GL 2-Ketoglutaric acid
SLS sodium lauryl sulfate
Cmc critical micelles concentration

INTRODUCTION

Surfactants are composed of a polar hydrophilic group and a nonpolar hydrophobic chain. This unique structural feature makes them to establish interactions with both the hydrophilic as well as hydrophobic molecules [1, 2]. They form aggregates (micelles) in aqueous solutions over a narrow concentration range, known as the critical micelle concentration (cmc), below which the surfactant molecules are predominantly dispersed as monomers [3]. For many practical applications of detergent micelles play important roles. For instance, micelles in aqueous medium solubilize the organic compounds which are poorly soluble in water by incorporating them in the micellar phase; micelles are conveniently exploited to act as catalysts for many reactions due to their large surface area; they alter the reaction pathways, rates and equilibria [4,5]. Moreover, micelle systems are convenient to use because they are optically transparent, stable, and relatively non-toxic [4,5]. Surfactant solutions are often modified with additives in order to change and improve their characteristics [6-8]. The influence of additives on the physicochemical properties of micellar solutions and characteristics of micelle formation [9], as well as the binding of solutes by a micellar

pseudophase, has been intensively studied during recent years [10]. Sodium lauryl sulfate (SLS) is an anionic surfactant and profoundly influences the bulk properties of physiological systems. The structures suitable for solubility properties for surfactant activity vary with the nature of the solvent system to be employed and the conditions of use. In aqueous systems the standard surfactant, the hydrophilic group (the ‘‘head’’) will be ionic or highly polar, so that it can act as a solubilizing functionality. Moreover, an understanding of the electrostatic and hydrophobic interactions between surfactants and biomolecules can add to our existing knowledge because similar interactions prevail in biologically important processes [11-13]. The cmc in this narrow concentration range depends on the physical property observed and the precision of the measurement. It is essential to employ physical methodologies which are highly sensitive to structural changes for determining the cmc. The existence of cmc indicates aggregation of amphiphilic molecules in solutions. The knowledge of the cmc is important for the calculation of the thermodynamic parameters, which confirms the scientific interest of a precise determination of the cmc [14]. The cmc in aqueous solution is influenced by the degree of binding of counter ion to the micelles. For aqueous systems, the increased binding of the counter ion to the surfactant causes decreasing in the cmc and an increase in the aggregation number [15].

2-Ketoglutaric acid is one of two ketone derivatives of glutaric acid. The term "ketoglutaric acid" when not further qualified, almost always refers to the alpha variant. β-Ketoglutaric acid varies only by the position of the ketone functional group, and is much less common. α-Ketoglutarate is a key intermediate in the Krebs cycle, coming after isocitrate and before succinyl CoA. Anaplerotic reactions can replenish the cycle at this juncture by synthesizing α-ketoglutarate from transamination of glutamate, or through action of glutamate dehydrogenase on glutamate. pKa determination is considered an interesting topic in a wide range of research fields such as reaction rates, biological activity, biological uptake, biological transfer [16], and physico-chemical characteristics of a substance used as a drug consider its pKa value. pKa values can be used to determine the extent of drug absorption and applied in pharmacokinetic and bioavailability studies. The dissociation process of carboxylic acids belongs to the most important reactions in living organisms. The data obtained for such reactions in aqueous solutions or mixed water-organic solvents, usually do not reflect the peculiarities of the biological systems that are heterogeneous media [17-18]. This is due to the strong effect of the microaggregates, formed by amphiphilic compounds, on the acid–base and complexation equilibria in solutions [19-21]. The more reliable models of biological systems, called biomimetics, are self-organized solutions of surfactants [22-23], which provide the opportunities for electrostatic and hydrophobic interactions with compounds.

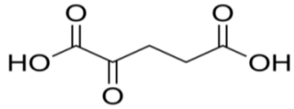
The literature survey indicates that (SLS) has been used as a dissolution aid [24-27], further, it was used in many pharmaceutical purposes [28-30]. Up to our knowledge, no work was related to the 2-ketoglutaric acid in the micellization of SLS surfactant, therefore, The study of physico-chemical properties of a GL-SLS interaction is significant from physical, chemical, biological and pharmaceutical outlook for their implication. Here, we show the interaction of GL with SLS at different temperatures by using an electric conductivity are rare. Such studies can provide better and valuable information towards understanding the behavior of these biomolecules in aqueous media of that surfactant. Lack of thermodynamic studies on SLS in aqueous 2-glutaric acid with two different concentrations lead us to investigate 2-ketoglutaric acid-SLS interactions through the determination of various electric conductivity at different temperatures. The effects of sodium lauryl sulfate (SLS) as an anionic surfactant was studied on the dissociation constants of 2-ketoglutaric acid by potentiometric technique.

MATERIALS AND METHODS

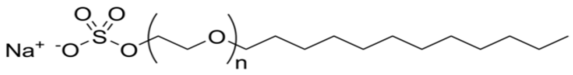
Materials

2-ketoglutaric acid was of analytical grade, and obtains from the ACRŌS ORGANICS, the ionic surfactant sodium lauryl sulfate (Fisher Scientific, high purity) (Scheme 1). All materials and reagents were used as provided by the chemical companies without further purification. The specification of the chemicals used are given in the Table 1. Carbonate-free sodium hydroxide (titrant, was prepared by dissolving the Analar pellets in 0.1 mol dm^{-3} $NaNO_3$ solution) was standardized potentiometrically with KH phthalate (Merck AG). A nitric acid solution (0.04 mol dm^{-3}) was prepared and used after standardization. Sodium hydroxide, nitric acid, and sodium nitrate were from Merck p.a. Analytical grade color-coded buffer solutions of pH= 4.0 (red) and 7.0 (green). All solutions used throughout the experiments were prepared freshly in ultra pure water with resistivity of 18.3 M Ω. cm^{-1}. We boil the resultant water for sufficient time to expel the carbon dioxide. All of the aqueous solution samples were prepared gravimetrically.

a



b



Scheme 1. Molecular structures of (a) 2-ketoglutaric acid; (b) sodium lauryl sulfate

Table 1. The specifications of the chemicals used

Name of Chemical	Molecular Formula	Grade	Purity	Company	Molecular Weight
2-ketoglutaric acid	$C_5H_6O_5$	Analytical	98%	Acros Organics	146.1
Sodium lauryl sulfate	$C_{12}H_{25}NaO_4S$	Analytical	99%	Fisher Scientific	188.173

Methods

Conductometric Study

We used conductivity measurements provide a consistent method to determine the cmc of an ionic surfactant-additive colloidal system [31], because of its high sensitivity (as any change in parameters, such as concentration of solution compounds, implies great changes of the system and high reproducibility). Electrical conductivity measurement of the GL solution was prepared in two different concentrations 0.005 mol kg^{-1} and 0.007 mol kg^{-1} in double distilled water. A Stock solution of GL used as solvent for preparing the SLS solutions with a concentration range from 0.001-0.18 Mol kg^{-1}. We used precisa X13-220A (Swiss-make) electric balance with a precision of ± 0.10 mg. All solutions are freshly prepared before measurement. The conductivity measured using digital conductivity meter model 4510 conductivity/TDS meter (Bibby Scientific Ltd). The conductivity meter was calibrated by measuring the electric conductivity of 0.01 and 0.10 N solutions of KCl (Merck, purity > 99%) at 298.15 K. Cell constants of the cell used was 1.00 cm^{-1}. The glass cell with two platinum electrodes was dipped in the sample solution and then immersed in an electronically controlled thermostated water bath (Julabo, Model MD Germany). The measurements were taken after allowing the system to attain equilibrium at the desired temperature for about 30 min and micellar systems were homogenized by stirring with magnatic stirrer. For each solution, 3-5 measurements were taken and the mean values independent measurements were reported. The accuracy of the conductivity measurement was ±1.50 %. Specific conductance of double distilled water is 1.82 μs/cm.

pH-potentiometric titrations

Equipment and procedure of dissociation constant determination

The protonation equilibria of GL were investigated by potentiometric titrations in aqueous and micellar solutions at desired temperature and I = 0.10 mol dm^{-3} $NaNO_3$ in aqueous solution but in SLS micellar solution the ionic strength were 0.1 mol dm^{-3} without added $NaNO_3$ under argon atmosphere, using an automatic titration set including a PC controlled Dosimat 665 Metrohma microburet delivery tube and a salt bridge connected with the reference cell filled with 1.00 mol dm^{-3} NH_4NO_3 (instead of KCl) was used solution in which a saturated calomel electrode was dipped. The Metrohm semimicro pH glass electrode (125 mm) was calibrated [32]. The glass electrode was calibrated before each titration with two Merck standard buffer solutions in nitrate medium: first with the pH 7.0 solutions (the same as in the bulb) and then with a pH 4.0 solution. The strong acid versus alkali titrations was analyzed using the computer program (GLEE, glass-electrode evaluation) [32]. For estimation of the protonation constants of 2-ketoglutaric acid (GL), the following aqueous solutions were prepared (total volume 50 ml) and then titrated potentiometrically against a standard Carbonate-free NaOH solution (0.10 mol dm^{-3}):

(a) 0.004 mol dm^{-3} HNO_3 + 0.10 mol dm^{-3} $NaNO_3$ or by adding the SLS solution
(b) Solution (a) + 0.001 mol dm^{-3} GL,

The pH titrations were carried out in an 80 ml commercial double walled glass vessel. Thermostated at desired temperature and left to stand for 15 minutes before titration, and the cell temperature was maintained at the required temperature by circulating thermostated water using an oil-bath setup. A magnetic stirrer was used during all titrations performed. Each titration was repeated at least 4 times. Typically, more than 40 pH reading (data points of potentiometric measurements) were collected into account for each titration. The protonation constants of the GL were obtained using computer program HYPERQUAD 2008 [33]. This software facilitates visual interpretation of refinements, which in turn helps greatly in obtaining the best fit.

RESULTS AND DISCUSSION

In the present work, two sets of experiments were carried out in order to describe the effect of 2-ketoglutaric acid on the thermodynamic properties of SLS micellization. For the first set of experiment, determined cmc values of SLS in aqueous solutions in the absence and presence of GL at 298.15, 303.15, 308.15 and 313.15 K (Table 2). The conductometric study of the present system is accomplished by the second set of experiment - potentiometric studies of GL in pure water and in the presence of the surfactants (SLS).

Table 2 Values of critical micelle concentration, cmc SLS in water and in aqueous 2-ketoglutaric acid at different temperatures

T(K)	cmc (mol kg^{-1})		
	Water	**Aqueous GL (5.10^{-3} mol.kg^{-1})**	**Aqueous GL (7.10^{-3}mol.kg^{-1})**
298.15	0.0080, 0.008[b], 0.0082[e]	0.0076	0.00745
303.15	0.0082, 0.00816[b], 0.0084[d], 0.0083[c], 0.00821[a]	0.0085	0.0084
308.15	0.0083,0.0085[c]	0.0088	0.0086
313.15	0.0087, 0.0089[c]	0.0092	0.00897

[a] *Reference [34].*
[b] *Reference [37].*
[c] *Reference [38].*
[d] *Reference [39].*

Conductometric study

The Electrical conductivity technique has been found to be highly important for studying the association behavior of various systems [3]. The experiments were carried out in order to know the effect of GL on the thermodynamic properties of SLS micellization (Fig. 1). The electric conductivity measurements for GL in aqueous SLS covering the pre-and post- micellar concentration ranges were made at different temperatures. Fig. 2a shows values of equivalent conductivity, Λ_m of (GL) in aqueous

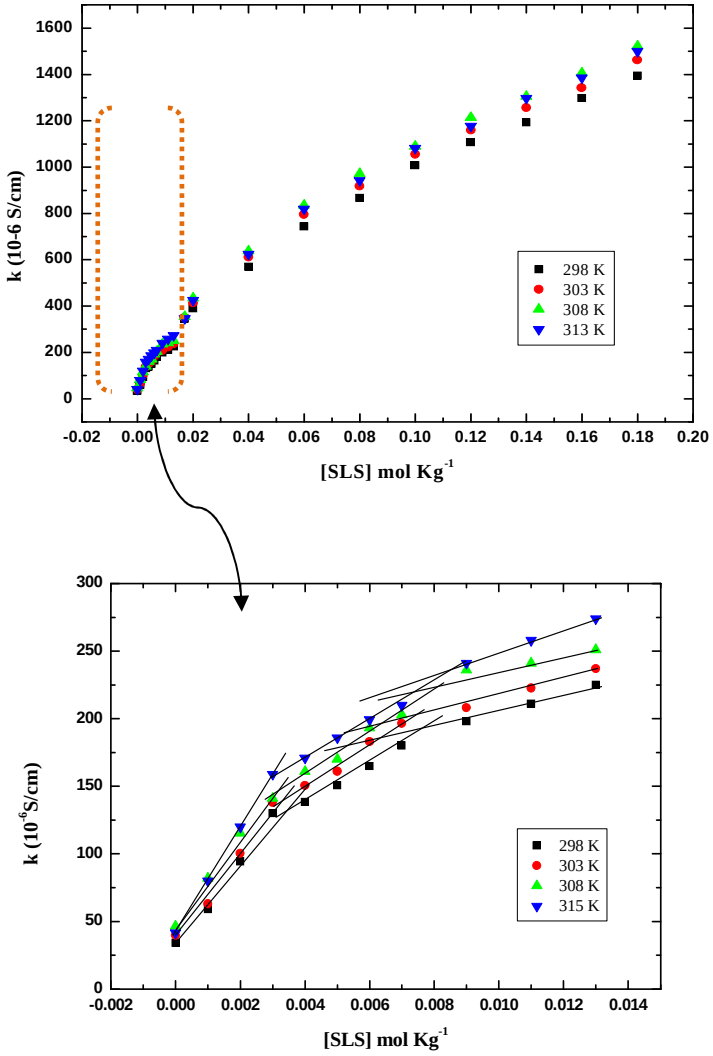


Fig 1. Variation of specific conductivity (k) with SLS in aqueous GL (0.007 mol kg^{-1}) at different temperatures

SLS at 25 C°, plotted in function of the square root of the concentration of SLS [Kohlousch's law: $\Lambda_m = \Lambda_m^{\circ} - k\sqrt{C}$]. We can see that the equivalent conductance is decrease sharply as (GL) was added, presumably because the SLS ones having been complexes were less effective as a charge carrier [30]. The straight line represents the linear

fits to experimental results for (GL) at the lowest concentration range available for our measurements. Extraplotation to zero concentration gives values of limiting equivalent conductivities uncorrected for activity (Fig. 2b), Λ_m° the values amounts to 78.66, 84.32, 89.40, and 94.83 mS m^2mol^{-1} at 25 C°, 30 C°, 35 C°, and 40 C° respectively.

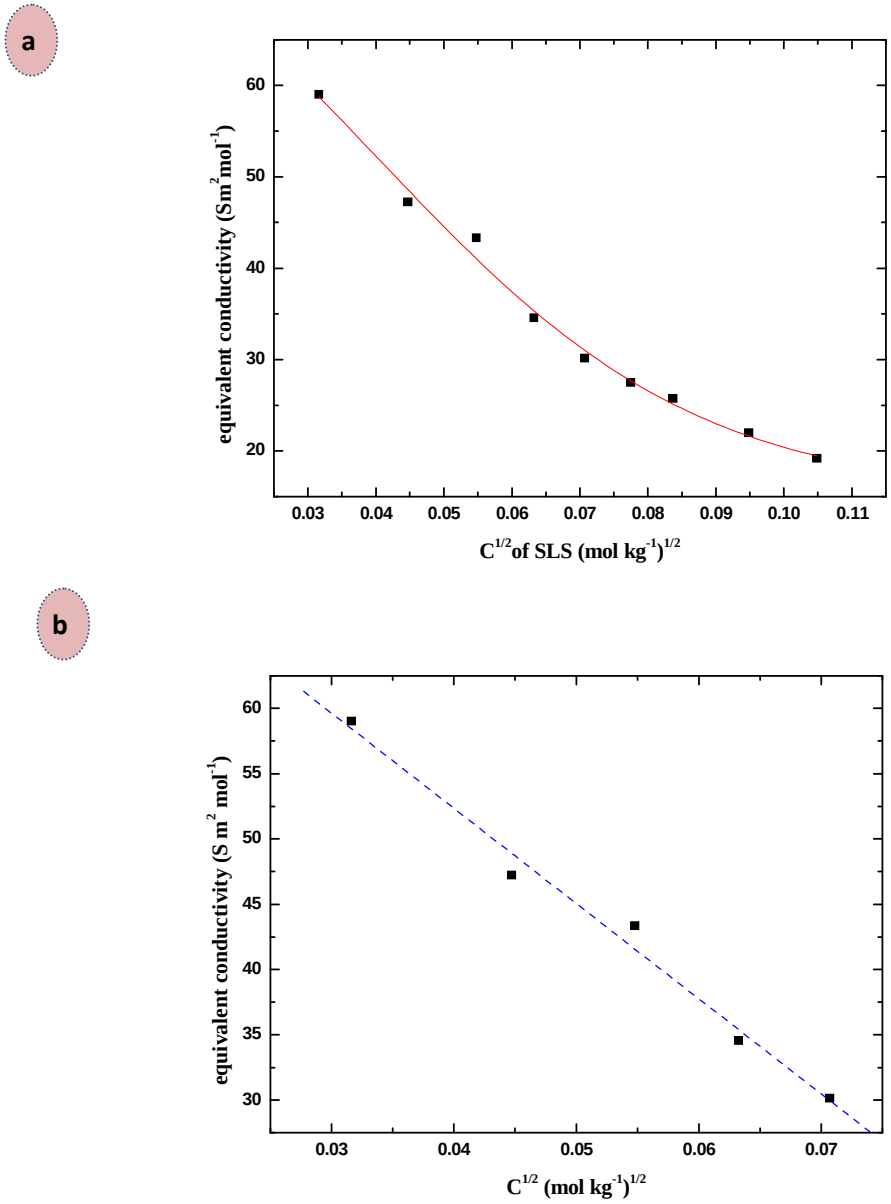


Fig. 2. Dependence of equivalent conductivity on $C^{1/2}$ of SLS in aqueous GL (0.007 mol kg^{-1}) at 298.15 K in (a) whole concentration range, and (b) low concentration range

The cmc (critical micelle concentration) obtained from the intersection of the fitting lines of the conductivity versus concentration plots above and below the break point, as a function of temperature are reported in Table 2. The dependence of specific conductance on SLS concentration in aqueous GL and temperature is graphically shown in Fig. 1. We can see that with added (GL) in the aqueous SLS unlike conventional conductivity profiles, there are two breakpoints corresponding to the cac and cmc. The first break called critical aggregation concentration (cac) occurs when the interaction of GL with surfactant aqueous solution starts [34]. presence of polar two (COOH) group. The addation of (GL) therefore enhances the hydrophbicity of SLS and makes the SLS micelles form more easily resulting in a decrease The cmc lowering values of SLS decrease in the presence of (GL) and as the GL concentration increase. The lowering of cmc may be attributed to the penetration of (GL) in micelles [35-36]. Also, it is worth to mention that GL is hydrophilic enough due to the of cmc. The cmc of SLS in the present of GL (Table 2) increases with increase in temperature. The effect of temperature on the cmc of surfactant in aqueous medium is complicated [40]. In general, the effect of temperature on the cmc of surfactants in aqueous medium is analyzed in

terms of two opposing effects [40-42]: (i) cmc first tends to decrease with increase in temperature, as temperature increase causes decrease in hydration of hydrophilic group, which favors micellization. (ii) However, at relatively higher temperature range disruption of the structured water surrounding the hydrophobic group occurs, this disfavors micellization [41,43], thereby, increasing the cmc of the surfactant. It is clear from the Table 2 that the second effect seems to be dominant over the first one for the present system, in the temperature range studied. Our finding is supported by the fact that for ionic surfactants, minimum in the cmc-temperature curve appears at 298 K [40], and then cmc tends to increase, as for SLS in this case. The solubility of hydrocarbon stabilizes the surfactant monomers increase with the temperature increase, hindering them to form micelles and, hence the increase in an the cmc values observed (Fig.3).

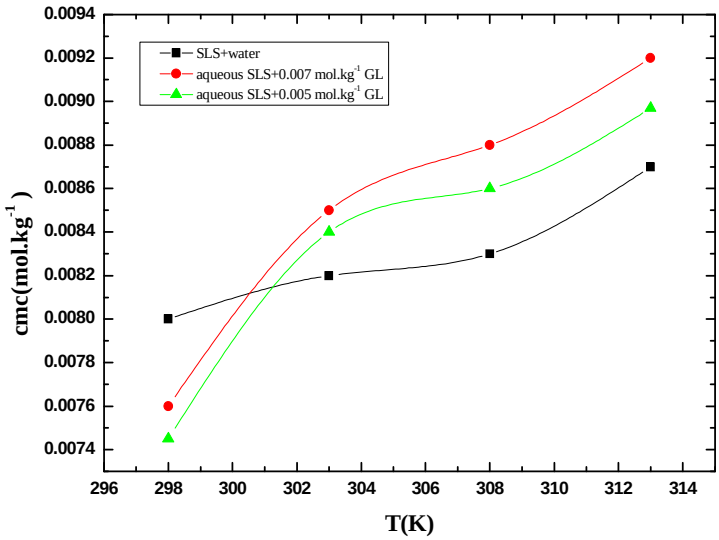


Fig. 3. Variation of cmc of SLS with temperatures in absence and present of 2-ketoglutaric acid

The degree of counterion dissociation (α) of the micelle near its cmc was obtained from the ratio (S_2/S_1) of the slopes of the post-micelle (S_2) to the pre-micelle (S_1) regions [3]. Table 3 shows that the degree of counterion dissociation increases regularly with temperature. The variations of α with T in the GL-SLS system are shown in Fig. 4. The increase in cmc and α with increase in temperature is in good agreement with the results reported for the ionic surfactants in aqueous medium [3]. The increase in α can be attributed to the combined effect due to the columbic and thermal forces [44]. The former force attracts the counterions toward the polar surfactant head groups while the latter one induces the dissociation of counterions from the surfactant head groups. It seems that the thermal forces predominate over the columbic forces, causing ionization of the surfactant (SLS) leading to the increased α value with temperature. It is to be observed that the values of α of SLS are higher in the presence of GL than in its absence. This may be due to the presence of the additive GL in the outer portion of the micelle and thus causing steric hindrance to the binding of counterions to the micelle, facilitating the dissociation of the counterions, which yields higher α values in the presence of GL than in its absence. The increase in the degree of counterion dissociation α of SLS in the presence of GL than in pure water (Table 3) is attributed to the solubilization of GL in the palisade layer of the micelle. This increases the surface area per ionic head group (or decreases the surface charge density), facilitating the ionization of the counterions, Na^+, from the micellar head groups of this surfactant, and, thereby, yielding higher α values in the presence of GL than in its absence. This is in accordance with the reported results [3, 45] for anumber of anionic surfactants, as in the present study. The degree of counterion association, is given as $\beta = 1 - \alpha$. However, in fact, like cmc [42-46], the degree of counterion dissociation α or, in turn, counterion association β is experimental technique dependent [47]. As a result, the values of a for Na^+ ions bound to SLS micelles are reported to lie in the range 0.46–0.86 [48] in aqueous medium, depending on the experimental technique employed (electromotive force, light scattering, massaction model, equilibrium dialysis, osmotic coefficient, electrophoresis, and zeta-potential). The values of α are included in Table 3 and its variation with temperature is shown in Fig. 4. It is evident from Tables 2, 3 that both cmc and α for the investigated systems increase with an increase in the temperature.

Table 3 Values of degree of ionization ∝ SLS in water and in aqueous 2-ketoglutaric acid at different temperatures

T (K)	∝		
	Water	**Aqueous GL (5.10^{-3} mol.kg^{-1})**	**Aqueous GL (7.10^{-3} mol.kg^{-1})**
298.15	0.33, 0.33[c]	0.51	0.57
303.15	0.37, 0.38[c]	0.55	0.58
308.15	0.40, 0.42[c]	0.59	0.62
313.15	0.43, 0.45[c]	0.68	0.76

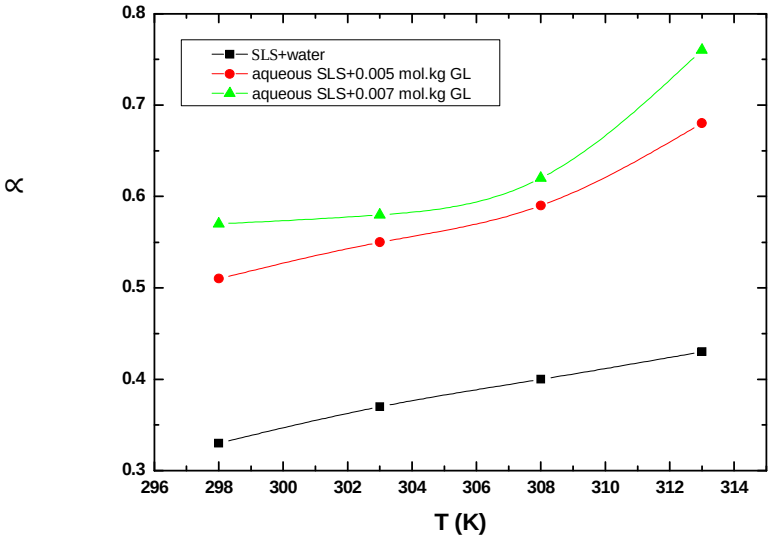


Fig. 4. Variation of degree of ionization (α) with temperatures (T) of SLS in absence and present of 2-ketoglutaric acid

The information of the thermodynamic parameters of micellar formation is found to be highly important for a clear understanding of the micellization process. In turn to investigate and calculate the thermodynamic parameters that are related to the micellization process, ΔG_m°, ΔH_m°, and ΔS_m° can be evaluated using the equilibrium model [49-50]. The total free energy per surfactant molecule associated with forming the micelle is given by eq. 1:

$$\Delta G_m^\circ = (2-\alpha)\mathrm{RT}\ln X_{cmc} \quad (1)$$

In presence of an additive, the free energy, ΔG_m°, consists of the SLS–SLS, additive-SLS, and additive–additive interactions. The energies associated with these interactions can be divided into three types of contributions (eq. 2) [49,51-53]:

$$\Delta G_m^\circ = \Delta G_{HP}^\circ + \Delta G_{el}^\circ + \Delta G_{all\ other}^\circ \quad (2)$$

where $\Delta G_{HP}^\circ$is the hydrophobic free energy associated with transferring the surfactant hydrocarbon chain from the medium to the interior of the micelle, this derives micellization ΔG_{el}° is associated with the electrostatic interactions between the head groups and counterions, this opposes micellization. $\Delta G_{all\ other}^\circ$ are all other contributions arising from specific interactions. The last two interaction energies ΔG_{el}° *and* $\Delta G_{all\ other}^\circ$ can be combined [49, 51] to give the energy associated with the surface contributions, $\Delta G_s^\circ = \Delta G_{el}^\circ + \Delta G_{all\ other}^\circ$. The values of ΔG_{HP}° and ΔG_s° can be estimated by considering the equilibrium model [53-54] which relates the degree of counterion binding to the electrostatic interactions between surfactant head groups and counterions. Moreover, this provides an estimation of the free energy of transferring the surfactant hydrocarbon chain from water into the interior of the micelle. The equilibrium between counterions, surfactant monomers and monodisperse micelles for an anionic surfactant can be represented by the following:

$$(n\text{-}p)C^+ + nS^- \Longleftrightarrow M^{p-} \quad (3)$$

Where C^+, S^- and M^{p-} represent the counterions, surfactant monomers and the aggregate of n monomers with an effective charge p, respectively. The equilibrium constant for Eq. (1) can be related to the standard free energy of micelle formation per monomer as:

$$\frac{\Delta G_m^\circ}{RT} = -\left(\frac{1}{n}\right) lnC_{Mp-} + lnC_{S-} + (1\text{-}p/n)lnC_{C+} \quad (4)$$

In case of typical micelles in aqueous medium, as those of SLS, they normally contain from 50-100 surfactant molecules. The term C_{Mp-} is small and insensitive to large errors [33], and can be therefore neglected. Both C_{C+} and C_{S-} can be replaced by the cmc in second and third terms [37] in Eq. (4) to give:

$$\Delta G_{HP}^\circ = RTlnX_{cmc} + RT\left(1 - {}^{P}/_{N}\right)lnX_{cmc} \quad (5)$$

where P/N (=∝) is the degree of ionization of counterions from the micelles and X_{cmc} is the cmc value expressed in the mole fraction. Combining Eq. 5 with Eq. 2, the equilibrium model yields.

T (K)	ΔG_{HP}° (kJ.mol^{-1})	ΔG_S°(kJ.mol^{-1})	$\Delta G_{HP,tr}^\circ$(kJ.mol^{-1})	$\Delta G_{S,tr}^\circ$(kJ.mol^{-1})
SLS in water				
298.15	-36.60	14.68	-	-
303.15	-36.22	14.00	-	-
308.15	-36.09	13.53	-	-
313.15	-35.80	13.00	-	-
SLS in 0.005 mol kg^{-1} aqueous GL				
298.15	-32.84	10.80	3.76	-3.88
303.15	-32.09	10.09	4.13	-4.04
308.15	-31.60	9.19	4.50	-4.35
313.15	-29.90	7.25	5.89	-5.75
SLS in 0.007 mol kg^{-1} aqueous GL				
298.15	-31.59	9.50	5.00	-5.18
303.15	-31.47	9.31	4.75	-4.69
308.15	-31.00	8.54	5.09	-5.00
313.15	-28.18	5.45	7.62	-7.54

$$\Delta G_S^\circ = -\beta RTlnX_{cmc} \quad (6)$$

From the computed values of ΔG_{HP}° and ΔG_S°, using Eqs. 5 and 6, the corresponding transfer values, $\Delta G_{HP,tr}^\circ$ and $\Delta G_{S,tr}^\circ$ of micelles from water to aqueous GL solutions can be evaluated by the relation

$$\Delta Y_{HP/(s,tr)}^\circ = \Delta Y_{HP/s(in\ aqueous\ GL)}^\circ - \Delta Y_{HP/S(in\ water)}^\circ \quad (7)$$

Where $\Delta Y_{HP/S}^\circ$ stand for $\Delta G_{HP\ or}^\circ \Delta G_S^\circ$, the values of $\Delta G_{HP,tr}^\circ$ and $\Delta G_{s,tr}^\circ$ thus obtained, together with the values of $\Delta G_{HP\ and}^\circ \Delta G_s^\circ$ at investigated temperatures are presented in Table 4. It is clear from Table 4 that the values of ΔG_S° for SLS in aqueous GL are lower than that of SLS in pure water and as the concentration of GL increase the values of surface free energy will decrease more. The values of ΔG_{HP}° are less negative in the presence of additives than in pure water at all studied temperatures.

The values of ΔG_s° decrease while those of ΔG_{HP}° increase with increase in temperature. From the thermodynamic point of view, the decrease in ΔG_s° can be ascribed to the energy associated with the non-availability of Na^+ counterions, as a **Table 4** Values of ΔG_{HP}°, ΔG_S°, $\Delta G_{HP,tr}^\circ$, and $\Delta G_{S,tr}^\circ$ of SLS in water and in 2-ketoglutaric acid at different temperatures Aresult of increased temperature, for electrostatic interactions with the head groups on the surface of the micelle due to interactions between dipolar GL molecules with the counterions. The electrostatic repulsion between the head groups is increased due to removal of counterions from the micellar surface. This, in turn, increases the electrostatic repulsions between the head groups, which consequently destabilizes the micelles, thus, ΔG_{HP}° becomes less negative. At a given temperature, ΔG_{HP}° becomes less negative as we move from lower concentration to higher concentration one of aqueous GL (Table 4). This may be attributed to the solubilization of some portions of the GL in the palisade layer of the micelle, and the solubilization becomes more significant.

The standard enthalpy of micellization, ΔH_m° and standard entropy of micellization, ΔS_m° of SLS in aqueous solutions of GL have been calculated using the equations [55-56]:

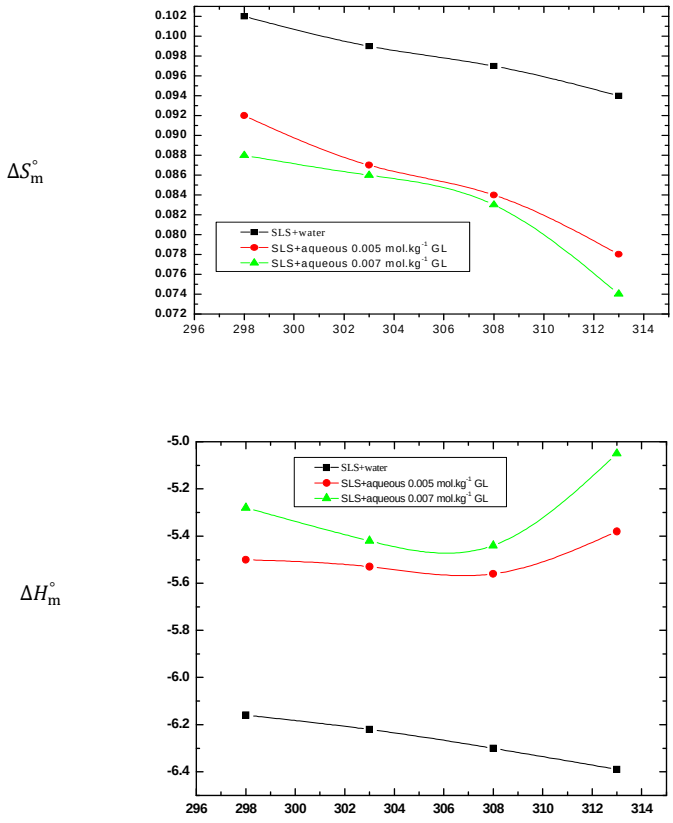
$$\Delta H_m^\circ = -(2-\alpha)RT^2\left[\frac{\partial lnX_{cmc}}{\partial T}\right] \quad (8)$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T} \quad (9)$$

Table 5 Values of ΔG_m°, ΔH_m°, ΔS_m°, and $T\Delta S_m^\circ$ Of SLS in water and in 2-ketoglutaric acid at different temperatures

T (K)	ΔG_m° (kJ.mol^{-1})	ΔH_m°(kJ.mol^{-1})	ΔS_m°kJ.mol^{-1})	$T\Delta S_m^\circ$(kJ.mol^{-1})
SLS in water				
298.15	-36.60	-6.16	0.102	30.43
303.15	-36.22	-6.22	0.099	30.00
308.15	-36.09	-6.30	0.097	29.57
313.15	-35.80	-6.39	0.094	29.42
SLS in 0.005 mol kg^{-1} aqueous GL				
298.15	-32.84	-5.50	0.092	27.34
303.15	-32.09	-5.53	0.087	26.56
308.15	-31.60	-5.56	0.084	26.03
313.15	-29.91	-5.38	0.078	24.53
SLS in 0.007 mol kg^{-1} aqueous GL				
298.15	-31.59	-5.28	0.088	26.31
303.15	-31.47	-5.42	0.086	26.05
308.15	-31.00	-5.44	0.083	25.56
313.15	-28.18	-5.05	0.074	23.12

The values of the ΔG_m°, ΔH_m° *and* ΔS_m° are listed in Table 5. It shows that the negative ΔG_m° Values are indicating that the process of the micelle s formation process was spontaneous as shown in Fig. 5. The spontaneity for micelle formation process decreased with increase temperature, which may be attributed to the trend of α values increase with increase temperature. However, the overall process is spontaneous. ΔH_m° values are negative and become less negative with rise in temperature for our system, suggesting that the process of micellization of SLS in present of (GL) is favorable which becomes relatively less favorable as the temperature of system increase. It is important to investigate the enthalpic and entropic componants of ΔG_m°, for the SLS larger values of -TΔS_m°, than those of H_m°, indicate that the process of micellization is governed mainly by entropy gain and that the driving force for the micellization is the tendency of hydrophobic group of the surfactant in transferring from the bulk solvent to the interior of the micelle [3,41]. This may be attributed to the breaking up of the structured water molecules surrounding the hydrophobic alkyl groups of SLS when it is transferred from the solvent environment to the interior of the micelle and also due to the increased freedom of these hydrophobic group in the non polar interior of the micelle than in the aqueous environment [3].



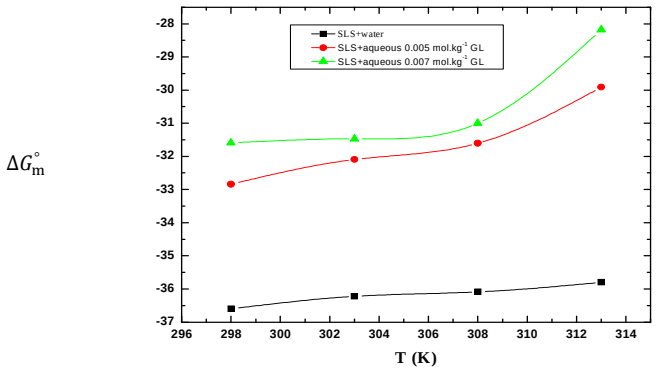


Fig. 5. Variation of ΔG_m°, ΔH_m°, and ΔS_m° with temperatures (T) of SLS in aqueous GL system

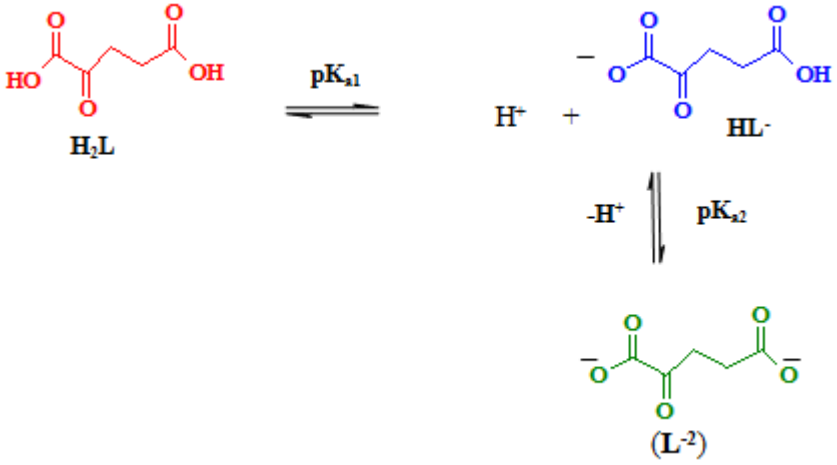
Potentiometric study

In this work, by fitting the experimental data of the pH potentiometric titrations of GL using the HYPERQUAD 2008 program, two protonation constants as overall equilibrium constants (log β_1 and log β_2) for GL acid were determined and evaluated (Table 6).

Table 6. The dissociation constants of GL in water and micellar solution of of SLS at 298.15 K with standard deviations in parentheses

Media	$pK_{a1}(\log\beta_1)$	ΔpK^a_{a1}	pK_{a2} $(\log\beta_2 - \log\beta_1)$	ΔpK_{a2}
0.10 mol dm^{-3} $NaNO_3$	2.49 (0.01)	0.00	4.60(0.01)	0.00
0.09 mol dm^{-3} $NaNO_3$+ 0.01 mol dm^{-3} SLS	2.52(0.02)	0.03	4.59(0.01)	-0.01
0.07 mol dm^{-3} $NaNO_3$+ 0.03 mol dm^{-3} SLS	2.57(0.02)	0.08	4.61(0.02)	0.01
0.05 mol dm^{-3} $NaNO_3$+ 0.05 mol dm^{-3} SLS	2.58(0.03)	0.09	4.60(0.03)	0.00
0.03 mol dm^{-3} $NaNO_3$+ 0.07 mol dm^{-3} SLS	2.62(0.01)	0.13	4.63(0.01)	0.03
0.10 mol dm^{-3} SLS	2.65(0.02)	0.16	4.61(0.02)	0.01
0.15 mol dm^{-3} SLS	2.66(0.06)	0.17	4.59(0.05)	-0.01
0.20 mol dm^{-3} SLS	2.68(0.05)	0.19	4.58(0.02)	-0.02
0.25 mol dm^{-3} SLS	2.72(0.03)	0.23	4.63(0.05)	0.03
0.30 mol dm^{-3} SLS	2.75(0.03)	0.26	4.61(0.01)	0.01

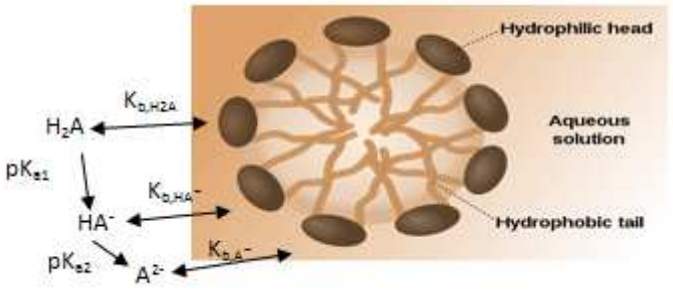
These constants were then presented as the minus logarithm of a stepwise acid dissociation constant (pKa). The dissociation constants are related to the protons loss at two carboxylic groups (Scheme 2). The obtained values for determination of pKa's of GL in pure water are in good accordance with previously published [56-58].The small differences between our values and the literature values are due to the random error, systematic errors arise in instrumental measurement and the dissociation constants are obtained with limited precision and accuracy.



Scheme 2. Show the chemical structure of the 2-Ketoglutaric acid and its protonation equilibria

We analysis the effect of anionic surfactant media on the protolytic properties of GL, the dynamic self-organized surfactant aggregates in solution were formed in psedophase that cannot be mechanically separated from the bulk

aqueous phase, the acid-base equilibria in the presence of micelles are complexesd by the secondary eqilibria of each protolytic form with surfactant micelles (Scheme 3).



Scheme 3. The acid-base equilibria of 2-Ketoglutaric acid in micellar solution

The calculation of the binding constants of each protolytic form is difficult [59-61]. Thus the description of the acid-base equilibria in micellar solutions of SLS is the appearent dissociation constants [21], which can be expressed as follows:

$$pK_a^{app} = pH_W + log\left\{\frac{[H_iA]_{tot}}{[H_{i-1}A]_{tot}}\right\}$$
$$= pH_W + log\left\{\frac{[H_iA]_w + [H_iA]_m}{[H_{i-1}A]_w + [H_{i-1}A]_m}\right\} \quad (9)$$

Where pH_W is the value measured in the bulk phase, and $[H_iA]_{tot}$ and $[H_{i-1}A]_{tot}$ are the total concentrations of protonated and deprotonated forms of GL, which are the sum of concentrations of corresponding protolytic forms in the bulk aqueous phase and micellar psedophase.

The binding of H_iA and $H_{i-1}A$ by micelles can be treated as are reaction of GL with SLS micelle:

$$H_iA + Mic \rightleftharpoons H_iAMic$$
$$K_{bHiA} = \frac{[H_iA]_m}{[H_iA]_w(C_s - cmc)} \quad (10)$$

K_{bHiA} is the binding constant of GL by the micellar psedophase, *i* for GL equal 2

Cs is the total concentration of SLS. After apply Eq. (10) into Eq. (9) the following relation between dissociation constants of the acid in aqueous and micellar solution can be obtained:

$$\Delta pK_a = pK_a^{app} - pK_a = log\left\{\frac{1+K_{bHiA}(C_s - cmc)}{1+K_{bHi-1A}(C_s - cmc)}\right\} \quad (11)$$

As we see from Eq. (11) the effect of micellar media on the dissociation constants of GL is related to binding of each protolytic form by micellar media. The pK_{a1} value is significantly affected by the micellar media of anionic surfactant (SLS) and that agree with Hartely's rule [23] (which related changes in the equilibrium constant to molecular charge), and the value of ΔpK_a are positive (Table 4). The micellar media effect increases when the concentration of SLS increases (Fig. 6).

CONCLUSION

The increase in the cmc values of SLS in aqueous GL in the studied temperature range is attributed to the breaking up of the structured water surrounding the hydrophobic groups of the SLS. A marked decrease in the cmc of SLS in aqueous GL than those of SLS in water, which is attributed to the solubilization of the additive GL molecule in the palisade layer of the micelle, resulting in decreased mutual repulsion of the ionic groups in the micelle which requires less work for the formation of the micelles. The determined values of free energy were negative, suggesting that the formation of micelles in presence of GL is favorable. The observed enthalpy change values found negative, indicating that micellization is by exothermic nature. The micellar media of anionic SLS surfactants have a pronounced effect on the protolytic properties of aliphatic carboxylic acids with 3 to 6 carbon atoms. The acidity decreases with increasing surfactant concentration. The adequate selection of the micellar media for investigation of the fundamental properties of active compounds could be essential for the reliable description of the reactions in

vivo. The present work emphasizes on the importance of both conductivity and potentiometric measurements of GL-SLS system which would be of great value in understanding the mechanisms of the chemical equilibria.

REFERENCES

[1] P.C. Hiemenz, in: J.J. Lagowski (Ed.), Principles of Colloid and Surface Chemistry, second ed., Marcel Dekker, New York, **1986**.
[2] O. Cudina, K. Karljikovic-Rajic, I. Ruvarac-Bugarcic, I. Jankovic, *Colloids Surf.*; **2005**, A 256, 225.
[3] M. J. Rosen, Surfactants and Interfacial Phenomena, third ed. Wiley-Interscience, New York, **2004**.
[4] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, **1975**.
[5] M.E.D. Garcia, A. Sanz-Medel, *Talanta* **1986**, 33, 255–264
[6] K.Holmberg, D.O. Shah, M.J. Schwuger. Handbook of Applied Surface and Colloid Chemistry. Wiley, Chichester, **2002.**
[7] M.J. Rosen, M. Dahanayake. Industrial Utilization of Surfactants. Principles and Practice. AOCS Press, Urbana, **2000**.
[8] R. Zana, *Adv. Colloid Interface Sci.* **1995**, 57, 1–64.
[9] L.P Loginova, E.Yu Yakovleva, M.N. Galat, A.P. Boichenko, *J. Mol. Liq.* **2009**, 145, 177–181.
[10] S.D. Christian, J.F. Scamehorn, Solubilization in Surfactant Aggregates. Marcel Dekker, New York, Basel, Hong Kong, **1995**.
[11] B. Gohain, P.M. Saikia, S. Sarma, S.N. Bhat, R.K. Dutta, *Phys. Chem. Chem. Phys.* **2002**, 4, 2617–2620.
[12] Sarmiento, G. Prieto, M.N. Jones, *J. Chem. Soc. Faraday Trans.* **1992**, 88, 1003–1007.
[13] C. Tanford, The Hydrophobic Effect: Formation of Micelles and Biological Membranes, Wiley-Interscience, New York, **1980**.
[14] M. S. Chauhan, G. Kumar, A. Kumar, S. Chauhan, *Coll. Surfaces A*, **2000**, 166, 51-57.
[15] S. Pandey, R. P. Bagwe, D. O. Shah, *J. Colloid Interface Sci*., **2003**, 267, 160-166.
[16] D. Kara, M. Alkan, *Spectrochim. Acta A* **2000**, 5, 2753–2761.
[17] M. Enache, E. Volanschi, *J. of Pharmacy and Pharmacology* **2012**, 64, 688-696.
[18] O. Čudina, J. Brborić, I. Janković, K. Karljiković-Rajić, S. Vladimirov, *Coll. Surfaces B*: *Biointerfaces* **2008**, 65 80-84.
[19] N.O. Mchedlov-Petrossyan, *Pure and Applied Chemistry* **2008**, 80, 1459-1510.
[20] A.P. Boichenko, O.S. Chernyshova, A.Y. Kulikov, L.P. Loginova, *Russian J. of Applied Chemistry* **2011**, 84, 957-963.
[21] A.P. Boichenko, L.T.K. Dung, L.P. Loginova, Journal of Solution Chemistry **2011**, 40, 968-979.
[22] C. Treiner, J. of Colloid and Interface Science **1983**, 93, 33-42.
[23] H. Le Cong, A.P. Boichenko, I.V. Levin, A.G. Matveeva, L.P. Loginova, *Journal of Molecular Liquids* **2010**, 154, 76-81.
[24] B.B. Madhavi, B. Kusum, R. Ramalingam, G. Arjun, K. Shekar, *Asian Journal of Chemistry* **2011**, 23(12) , 5481-5485.
[25] M.K. Rawat, A. Jain, A. Mishra, M.S. Muthu, S. Singh, *Curr. Drg. Deliv*. **2010**, 7, 44-5.
[26] L. Bajerski, R.C. Rossi, C.L. Dias, A.M. Bergold, P.E Fröehlich., *Pharm. Sci. tech*. **2010**, 11, 637-644.
[27] F. Zhao, V. Malayev, M. Hussain, *Pharm. Res*.**2004**, 21: 144-148.
[28] C. Huang, L. Chen, *Guang. Pu. Xue. Yu. Guang. Pu. Fen. Xi.*, **1998**,18, 420-424.
[29] A.M. Al-Mohizea, F.I. Al-Jenoobi, M.A. Alam, *Pak. J. Pharm. Sci.*, **2015**, 28(2): 617-622.
[30] H. Beiginejad, A. Bagheri, L.S. Yekta, Z.B. Nojini, *J. Incl Phenom Macrocyclic Chem.* **2010**, 67, 247-252.
[31] L. García-garcia-Río, J.R. Leis, J.C. Mejuto, V. Mosquera, P. Rodríguez-Dafonte, *Colloids and Surfaces A* **2007**, 309, 216–223.
[32] P. Gans, O'Sullivan, B. Glee, *Talanta* **2000**, 51, 33-37.
[33] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, 43, 1739-1753.
[34] M. Prasad., R. Palepu., S. P. Moulik, *Colloid Polym Sci* **2006**, 284, 871–878.
[35] U. Dash, J. Meher, P.K. Mirsa, *J Mol Liq* **2013**,177, 317– 324.
[36] L.R. Harutyunyan, M.L. Lachinyan, R.S. Harutyunyan, *J Chem Eng Data* **2013**, 58, 2998–3008.
[37] K. Chari, W.C. Lenhart, *J Colloid Interface Sci* **1990**, 137, 204-216.
[38] R. Sadeghi, S. Shahabi, *J Chem Thermodyn* **2011**, 43, 1361–1370.
[39] A. Ali., N. H. Aneari, *J. Surfact Deterg.* **2010**, 13, 441-449.
[40] M.J. Rosen, Surfactants and interfacial phenomena, 2nd edn. Wiley, New York, **1989**.
[41] S.K. Mehta, S. Chaudhary, K.K. Bhasin, R. Kumar, M. Aratono, *Colloids Surf A* **2007**, 304, 88–95
[42] G.B. Ray, S. Ghosh, S.P. Moulik, *J Surfact. Deterg* **2009**, 12, 131–143
[43] A.K. Rakshit, B. Sharma, *Colloid Polym Sci* **2003**, 281, 45–51.
[44] J. James, A. B. Mandal, *Colloids Surf.* **2011**, B84, 172-180.

[45] R. Zana, *J. Colloid Interface Sci.* **1980**, 78, 330–337.
[46] R.C. Bazito, O.A. El Seoud, *Langmuir* **2002**, 18, 4362–4366
[47] Y. Moroi, Micelles: theoretical and applied aspects. Plenium Press, New York, **1992**.
[48] T. Sasaki, M. Hottori, J. Sasaki, K. Nukina , *Bull Chem Soc Jpn* **1975**, 48,1397–1403.
[49] M.S. Bakshi, *Bull. Chem.. Soc. Jpn.* **1996**, 69, 2723-2729.
[50] R.D. Lisi, S. Milioto, *Chem.. Soc. Rev.* **1994**, 23, 67-73.
[51] M.S. Bakshi, P. Kohli, *Indian J Chem* **1997**, 36A, 1075–1077.
[52] D.F. Evans, B.W. Ninham, *J Phys Chem* **1983**, 87, 5025–5032.
[53] M. Uneo, Y.H. Tsao, J.B. Evans, D.F. Evans, *J Solution Chem* **1992**, 21,445–457.
[54] P. Mukerjee, K.J. Mysels, P. Kapauan, *J. Phys. Chem.* **1967**, 71, 4166–4175.
[55] S. Chauhan, K. Sharma, D.S. Rana, G. Kumar, A. Umar, *J Mol Liq* **2012**, 175, 103–110.
[56] F. Jalali, A.S. Rad, *J Iran Chem Soc* **2008**, 5, 309–315.
[57] Robert C. Kerber, Marian S. Fernando. *Journal of chemical education*. **2010**, 87, 1079-1084.
[58] J. Kozlowski, P. Zuman, *Bioelectrochem. Bioenerg.* **1992**, 28, 43–70.
[59] J. Jen, W. Knoche, *Phys. Chem.* **1969**, 73, 539–541.
[60] K.V. Kunchev, Y.A. Tur'yan, K.A. Dinkov, *J. Gen. Chem. USSR* **1992**, 62, 311–315.
[61 M.L. Fonda, *Biochemistry* **1972**, 11, 1304–1306