Micellization of sodium lauryl sulphate in aqueous sodium malonate solution

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ABSTRACT

The micellization property of sodium lauryl sulphate (SLS) in water in presence of sodium malonate has been investigated conductometrically. The critical aggregation concentration (CAC) and critical saturation concentration (CSC) were determined. The molecular conductance value at infinite dilution for sodium malonate and sodium lauryl sulphate was calculated 225.5 Scm^2mol^{-1} and 81.88 Scm^2mol^{-1} at 298K respectively. The micellization of SLS in presence of sodium malonate in aqueous solution has shown that the formation of aggregates takes place between SLS and ions formed by sodium malonate. With increase in concentration of the surfactant at the saturation point beyond which ionization or dissociation of aggregates takes place justified by the binding capacity. The free energy of micellization has been reported for sodium lauryl sulphate in aqueous sodium malonate solution.

Keywords: Sodium Lauryl Sulphate, Sodium Malonate, Micellization, Critical Saturation Concentration, Binding capacity
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INTRODUCTION

The studies on aqueous miceller systems have received much attention in the literature due to their versatile and important use in all branches of science. The various systems have been investigated in order to obtain physical properties with thermodynamic parameters of micellization of surfactants in different solvents [1, 2, 3, 4, 5, 6, 7]. These studies are used to understand different kinds of associations, molecular packing, molecular motions, and various types of interactions influenced by the presence of solute present in solutions [8]. Micelles are one type of aggregation which is formed at a specific concentration range. Micellization is affected by various factors including the solvent, additives, temperature, ionic strength etc.

The micelles have specific importance in pharmacy is due to their ability to enhance the solubility of sparingly soluble substance in water [9, 10]. The importance of aggregation and their properties have now fully recognized as basic fundamental in all fields of solution and colloid science [11]. The process of micellization of surfactants in presence of electrolyte, polar or nonpolar organic compound and other surfactant has been reported during the past several years [12, 13, 14, 15]. The additive influences the micellization by their structure breaking or making character in water. There are reports on physicochemical properties of oxalic acid and its salt in aqueous solution in which they behave as structure maker in water [16, 17] but there is no any such study of malonic acid and its salt in micellar solution.

Present study describes the micellizatin of sodium lauryl sulphate in presence of sodium malonate in aqueous solution.

MATERIALS AND METHODS

Sodium malonate, CDH grade and sodium lauryl sulphate, pro analysi MERCK grade were used as such without further purification. All the solution were prepared in double distilled water having specific conductance of the order 2×10^{-6} $\Omega^{-1}cm^{-1}$.Conductance measurement of the solution were made using conductivity meter ,Systronics 306 with a dipping type conductivity cell having platinized electrode. The temperature of the solution was keptconstant with the help of thermostat (Tanco,Kanpur). The conductivity meter was calibrated with standard KCl solution. The accuracy of the conductivity meter was 0.01 mScm[1] during the study. The results were checked for constant readings.

RESULTS AND DISCUSSION

Keeping the malonate ion concentration constant in aqueous solution, the concentration of sodium lauryl sulphate is varied and the value of specific conductance obtained for each solution is given in Table 1.The variation of specific conductance with concentration was analyzed by plotting graph between specific conductance and concentration. The representative plots are presented in Figure 1A, Figure 1B and Figure 1C in different concentration range of SLS in which the plots are linear but have different gradients.

It is well established that in general, in aqueous solution the plot between concentration and specific conductance consist a break point in the linear behavior which correspond to critical micelle concentration, cmc, value of the surfactant. In the present study, Figure1A, Figure 1B and Figure 1C, indicate the presence of two break points in the plot between concentration and specific conductance. In order to confirm the presence of two break points, the slope of the curve were calculated by plotting the graph in three different regions. The micellization studies in presence of polymer also have same nature as reported in literature [18]. In this study the second break point in the plot is defined as cmc of polymer surfactant complex or polymer saturation point in the aqueous solution. In our study the micellization of sodium lauryl sulphate (SLS) in presence of salt, sodium malonate in aqueous solution is somewhat similar to the reported behavior in presence of polymer.
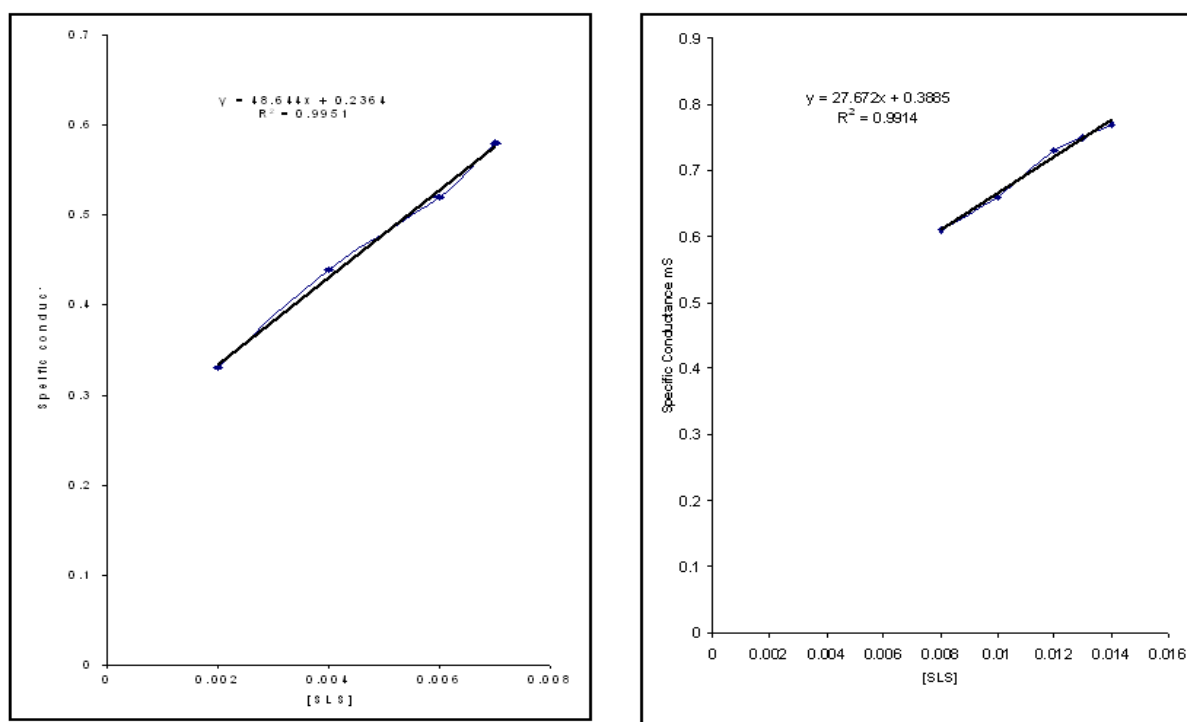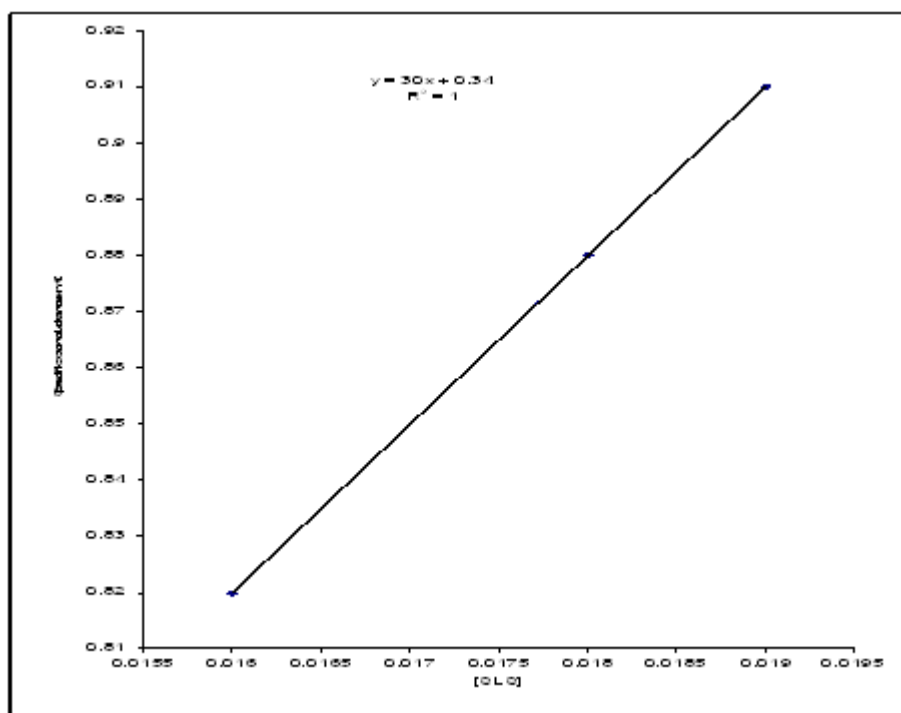
Figure: 1A and 1B

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Figure: 1C

Plot for 0.001 mol dm⁻³ Sodium malonate at 298 K

Table 1: Variation of Specific Conductance of SLS with concentration of sodium malonate
The values inside the bracket are the values of specific conductance at temperature 308K

S. No.	[SLS] moldm⁻³	Temp K	Specific conductance(mS) concentration of Na malonate		
			0.0005 mol dm-3	0.001 mol dm-3	0.002 mol dm-3
1.	0.002	298	0.24 (0.29)*	0.33 (0.45)*	0.53 (0.61)*
2.	0.004	298	0.34 (0.42)	0.44 (0.57)	0.66 (0.74)
3.	0.006	298	0.43 (0.53)	0.52 (0.67)	0.72 (0.84)
4.	0.007	298	0.49 (0.58)	0.58 (0.75)	0.76 (0.88)
5.	0.008	298	0.53 (0.63)	0.61 (0.82)	0.80 (0.92)
6.	0.010	298	0.60 (0.73)	0.66 (0.88)	0.83 (0.97)
7.	0.012	298	0.66 (0.79)	0.73 (0.96)	0.91 (1.07)
8.	0.013	298	0.68 (0.81)	0.75 (0.97)	0.92 (1.10)
9.	0.014	298	0.70 (0.85)	0.77 (1.03)	0.96 (1.14)
10.	0.016	298	0.79 (0.91)	0.82 (1.10)	1.02 (1.17)
11.	0.018	298	0.84 (0.99)	0.88 (1.15)	1.04 (1.26)
12.	0.019	298	0.87 (1.05)	0.91 (1.21)	1.07 (1.29)

In this study, the second break point can be taken as carboxylate ion saturation concentration, (csc). The values of csc obtained in the study are given in Table 2.

Table 2: Value of csc, cac and binding capacities of salt- SLS complex / aggregates

S. No.	[Sodium malonate] moldm⁻³	cac mmol	csc mmol	Binding Capacity mmol. SLS/mol. carboxylate	Degree of ionization (α)	
		298K	298K	298K	298K	308K
1.	0.0005	0.6	1.6	20.0	0.53	0.92
2.	0.001	0.7	1.6	16.0	0.61	0.60
3.	0.002	0.7	1.4	3.5	0.35	0.70

The critical micelle concentration, cmc of the surfactant in presence of salt in solution corresponds to the first break point in the plot between concentration and specific conductance. It has been found that the cmc of the SLS in presence of the salt is nearly equal to the cmc of SLS in water. As this salt is an electrolyte, hence in the study in place of the cmc the notation, cac, critical aggregation has been used. As seen from the experimental data, the value of cac remains constant. This indicates that the SLS and the salt can exist in ionic form below cac. To ascertain the nature of the salt and surfactant, the molecular conductance has been calculated for salt and SLS-separately in water. The plots between molecular conductance and √**c** for the salt and SLS have linear nature which indicates the

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applicability of Debye Huckel equation for strong electrolytes. The representative plot is given in Figure 2 and Figure 3.
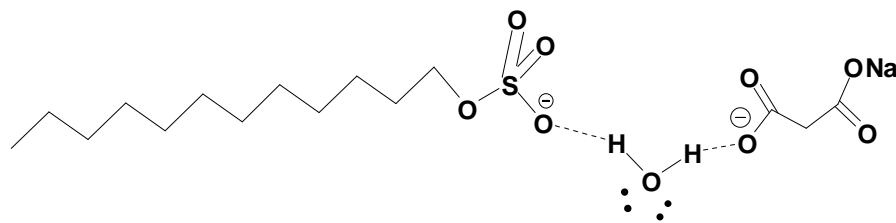
**Figure 2 Plot between sodium malonate vs √C at 298 K**
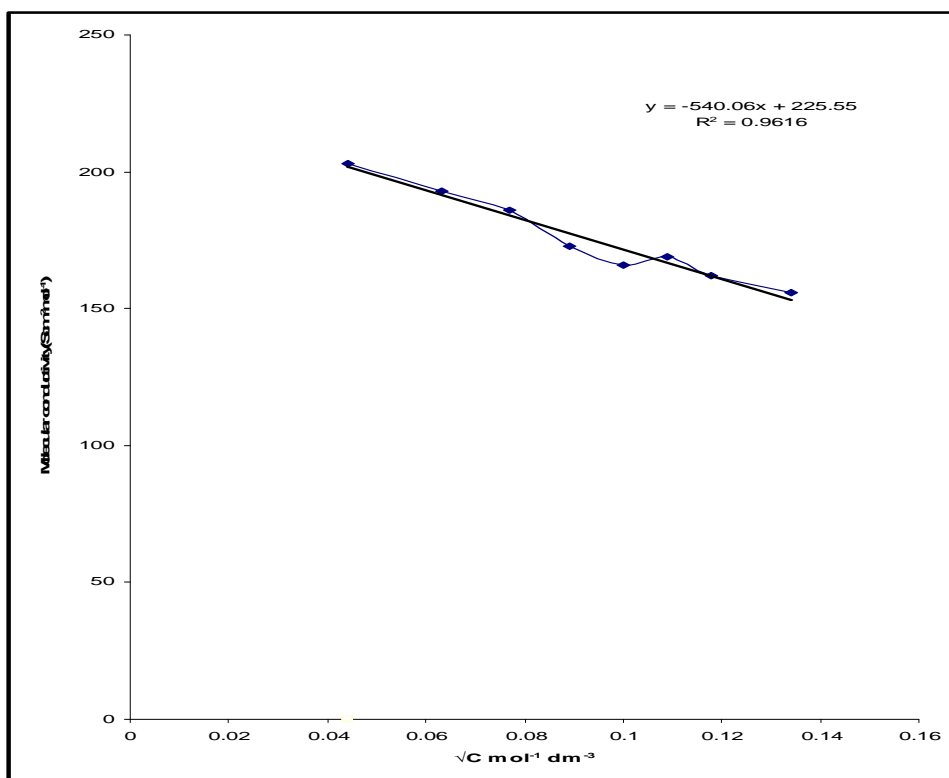
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In case of strong electrolytes the value of molecular conductivity at infinite dilution, λ^o_m can be obtained from the intercept is equal to λ^o_m at c=0 of Debye Huckel and Onsager plots. The molecular conductance values at infinite dilution of sodium malonate and sodium lauryl sulphate (SLS) at 298 K is 225.55 Scm^{2}mol^{-1} and 81.88 Scm^{2}mol^{-1} obtained respectively. The micellization of SLS in presence of sodium malonate under the experimental conditions used can be explained by the following considerations:

1. The sodium malonate behave as a strong electrolyte as shown by the molecular conductance in water. SLS also behaves like a strong electrolyte in water. The plot between molecular conductance and square root of concentration supports the fact experimentally.
2. At lower concentration of SLS below cmc of SLS in aqueous micellar solutions, all the sodium malonate form ions. It was expected that malonate ion at lower concentration do not interfere with monomeric form of SLS and the ionization constant of the acid is very low ($0.2 \times 10\text{-}5$) and more energy is required to separate the hydrogen ion from doubly charged anion then from the singly charged anion.
3. The λ^o_m has been regarded as a measure of solute-solvent interaction [19]. The large magnitude of λ^o_m shows the greater solute-solvent interaction. The λ^o_m values obtained in the study indicates the presence of solute-solvent interaction.
4. The solvation of mono sodium malonate ion in water can be supported by the fact that the malonate ion has both electrostatic as well as hydrophobic hydration due to the presence of –CH$_2$ group [20].
5. The hydrophobicity of mono sodium malonate ion facilitated it to incorporate with the SLS micelles. In addition, the carboxylate groups have negative charges which are expected to stay in the bulk and / on the surface of the SLS micelles.

In view of the above, it is suggested that the malonate ions NaCH$_2$(COO)$_2^{2-}$ interact on the micellar surface as shown below:

Figure 3: Plot between SLS Vs √C at 298 K
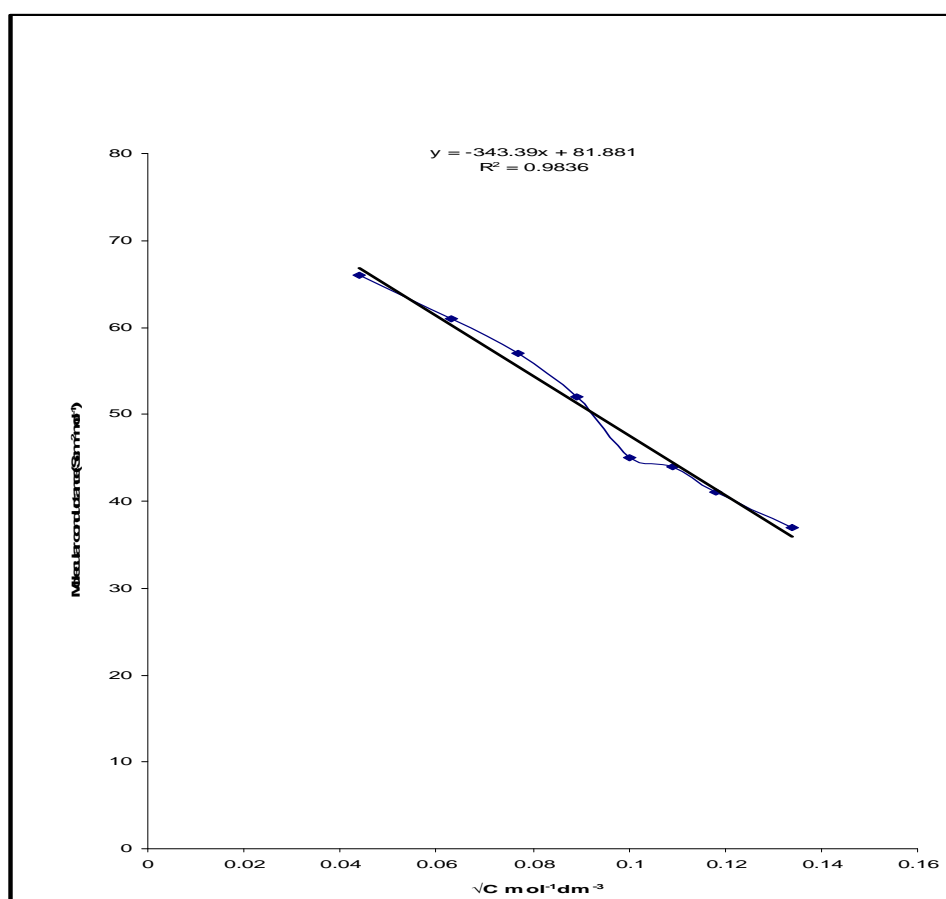
The above situation is responsible for critical aggregation of surfactant monomer. The close packing of surfactant molecule in the aggregates attains saturation in the presence of mono sodium malonate ions but the micellar / aggregate loosened in the higher concentration of ions above critical saturation concentration due to the mutual repulsion between higher charges in aqueous solution. A pictorial representation of micellar aggregates in aqueous solution can be shown as below :

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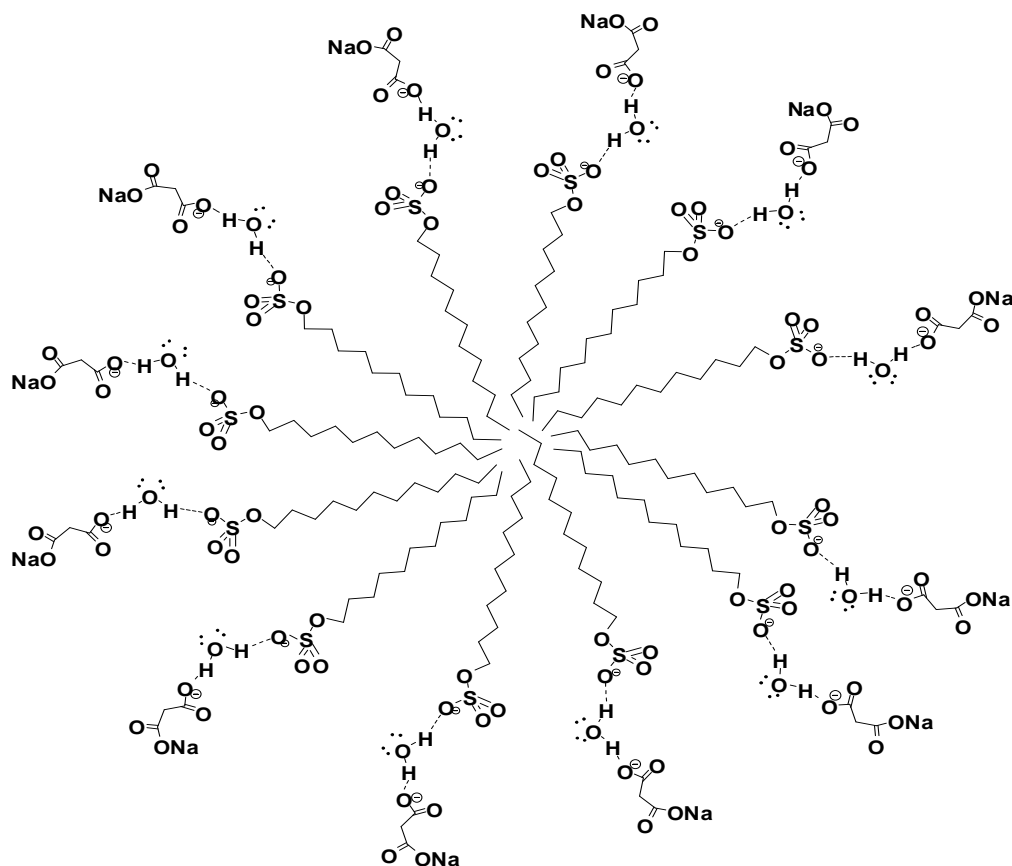
Thermodynamic quantities of micellization

In the study it has been concluded on the basis of cac and csc, micelles / micellar aggregations are formed between malonate ion and monomers of SLS. Thermodynamic quantity provides more information about the interaction between surfactant and malonate ion. At cac, the degree of ionization (α) value of malonate-SLS complex / aggregate, from the slope of conductance –concentration plots below cac and above csc. The values are given in Table2. For ionic surfactant, the free energy of micellization, ΔG^0_{mic} at csc

$$\Delta G^0_{mic} \ = \ (2 - \alpha) \ RT \ln csc \tag{1}$$

Where csc is in mol fraction scale.

The ΔG^0_{mic} at, csc is expressed in per molar unit by conceptual approximation. At csc, the monomer concentration remains non variant with increase in surfactant concentration; above csc micelles are only formed. The above concept has been used in calculation of free energy of micellization [21]. Standard entropy of micellization ΔS^0_{mic}, were calculated using equation 2, as used in case of mixed surfactant.

$$\Delta S^0_{mic} \ = \ \delta \ (\Delta G^0_{mic)} \ / \ \delta T \tag{2}$$

The thermodynamic quantities calculated on the basis of above equation 1 and equation 2 is recorded in Table 3.

It is clear from the data obtained, for all concentration of malonate has negative value of ΔG^0_{mic}. This confirms that the strong interaction between SLS monomer and malonate ion which results in the formation of micelles / aggregation in aqueous solutions. These interactions have less magnitude at higher temperature due to the increase in thermal energy. The ΔS^0_{mic} values also support the interaction between surfactant and mono sodium malonate ion.

Table 3: Thermodynamic parameters of malonate – SLS system at csc

S. No.	[Sodium malonate] mol dm^{-3}	$-\Delta G^0_{mic}$ K J mol^{-1}		ΔS^0_{mic} K J K^{-1} mol^{-1}
		298 K	**308 K**	
1.	0.0005	29.66	22.52	- 0.714
2.	0.001	28.04	29.19	+ 0.115
3.	0.002	33.82	27.54	- 0.628

CONCLUSION

In this study, it has been observed that the formation of malonate-SLS aggregation/ micelle takes place, which was justified by the value obtained for binding capacities at different concentration. At higher concentration of SLS, the interaction with malonate ion decreased beyond the critical saturation concentration of sodium malonate in aqueous solutions.

The study may be useful for micellization studies in the field of polymer and solution chemistry having industrial importance. Such type of finding may give useful information regarding the micellar catalysis.

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