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The role of organic additives in changing the sign of standard enthalpy of micellization

Rabah A.Khalil*, Alaa M.Hashim
Department of Chemistry, College of Science, University of Mosul, Mosul, (IRAQ)
E-mail: rakhalil64@yahoo.com
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ABSTRACT

The phenomenon of changing the sign of standard enthalpy of micellization (ΔH^{o}_{m}) from negative to positive for anionic surfactant [sodium dodecyl sulfate (SDS)]; due to presence of hydrocortisone acetate (HA) as an additive has been recently detected by Khalil and Hassan (J. Dispersion Science & Technology, 31:1195–1201, 2010). No such observation for cationic cetyltrimethylammonium bromide (CTAB) surfactant has been noticed by those authors. The reason for this phenomenon has been doubtfully attributed to the hydrogen bond between anionic polar head group of SDS with hydrogen of HA hydroxyl group. In order to investigate a certain reason for this problem, the effect of four organic additives (methyl salicylate (MS), benzene, toluene and cyclohexane) on the critical micelle concentration (*CMC*) of SDS and CTAB has been examined. The results exhibit that the effect of the presented additives on the sign of ΔH^{o}_{m} was in a similar manner to that of HA. It was concluded that the hydrophobic effect through iceberg formation which resulted from the presence of hydrophobic additives plays a major role in changing the sign of ΔH^{o}_{m} and increasing the *CMC* of both anionic and cationic surfactants. CTAB surfactant does not show such changes in the sign of ΔH^{o}_{m} which attributed to competitive between the hydrophobic effect with its high tendency towards forming micelle in contrast with that of SDS.

KEYWORDS

Critical micelle concentration;
Thermodynamic functions of micellization;
Standard enthalpy of micellization;
Sodium dodecyl sulfate;
Cetyltrimethylammonium bromide.

INTRODUCTION

It is well known that surfactants play an important role in industry and everyday life. Researchers pay considerable efforts in many aspects of these amphiphilic molecules. Among these, the effect of additives on self-assembly and critical micelle concentration (*CMC*) has been received significant attention[1-13]. Recently, we have studied the effect of hydrocortisone acetate (HA) as water insoluble on the *CMC*s of anionic [sodium dodecyl sulfate (SDS)] and cationic [cetyltrimethylammonium bromide (CTAB)] surfactants[14] The results interestingly show that the presence of HA in SDS changes the negative sign of standard enthalpy of micellization (ΔH^{o}_{m})

to positive. In other word, the micellization process of anionic SDS surfactant change from exothermic to endothermic due to presence of HA. While for cationic CTAB the latter process remains exothermic. The results also show that the *CMC* of both SDS and CTAB increase due to presence of HA[14]. Indeed, the latter phenomenon is opposite to that for polar amine additives[13] and also for alcohols[3] (1-propanol, 2-propanol, and allyl alcohol). No certain reason has been given for changing the sign of ΔH^{o}_{m} which has been attributed to the hydrogen bonding between H of HA hydroxyl group with the anionic polar head group of SDS surfactant[14].

In present work we have selected four related additives (methyl salicylate (MS), benzene, toluene and cyclohexane) in order to explain the reason for changing the micellization process of SDS from exothermic to endothermic. MS drug was selected as containing hydroxyl and ester groups mimic HA; noting that MS is not water insoluble as HA. Benzene additive will give the opportunity for the absence of OH in contrast to MS. In addition, benzene ring may inter the surface layer of cationic surfactant CTAB in contrast to that of SDS[15]. The presence of bulky methyl group in toluene may give some indication about the interance of benzene ring in the surface of CTAB. The non aromatic cyclohexane was selected for giving an indication for the effect of the presence of benzene ring within additive.

EXPERIMENTAL

MS was obtained in highly pure form from State Drug Industry (SDI), Samarra-Iraq. All other reagents were analytical grade commercial products. All solutions were prepared using conductivity water (4-5 $\mu S \cdot cm^{-1}$).

The electrolytic conductivity of the solutions (formerly as specific conductivity) was directly measured using WTW conductometer with accuracy $\pm 0.01\ \mu S \cdot cm^{-1}$. To control the temperature within $\pm 0.1^{o}C$, water thermostated Hakke NK22 was used.

The *CMC*s were determined from plots of electrolytic conductivity versus surfactant concentration[13-15] as illustrated in Figure 1. The measurements were carried out through addition of 0.05 and $0.005 mol \cdot l^{-1}$ of SDS and CTAB respectively, using burette to 40ml of conductivity water. The measurements were repeated to check the reproducibility of the data. Estimation of thermodynamic parameters was carried out using the following equations[14,17]

$$\Delta G^{O} = RT(2 - \alpha)\ln xCMC \quad (1)$$

$$\Delta H^{o} = -(2-\alpha)RT^{2}\left(\frac{\partial \ln xCMC}{\partial T}\right) \quad (2)$$

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

Where α is the ionization degree which calculated as the ratio of the slopes of the two intersecting lines, *xCMC* is the mole fraction of surfactant *CMC*.

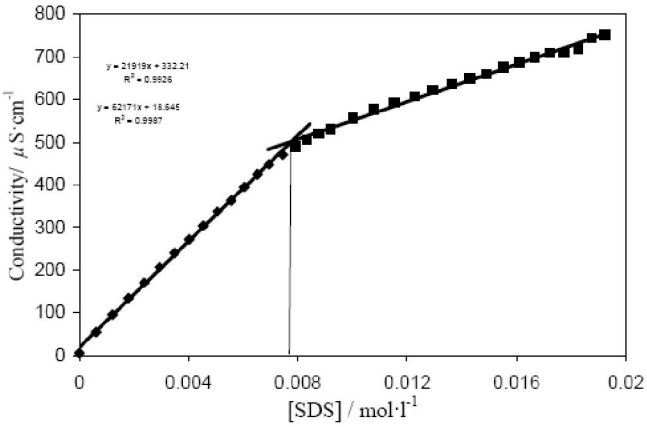

Figure 1 : Determination of CMC for SDS in the absence of additive at 20°C from the plot of electrical conductivity ($\mu S \cdot cm^{-1}$) vs. SDS molar concentration.

RESULTS AND DISCUSSIONS

TABLES 1, 2, 3 and 4 listed the effect of presence MS, benzene, toluene and cyclohexane on the *CMC* of SDS respectively at different temperatures. Interestingly, these also show change in the sequence of the relation between *CMC* and temperature in a similar manner to that of HA. In other word, such change in the sequence will definitely change the sign of ΔH^{o}_{m} from negative to positive due to presence of these additives. The latter phenomenon of changing ΔH^{o}_{m} sign is quite inconsistent with the earlier proposed reason of hydrogen bonding[14]. The results also exhibit an increase in the *CMC* of SDS due to presence of these additives as HA in the order MS<benzene<toluene ≈ cyclohexane.

The calculated values of ΔG^{o}_{m}, ΔH^{o}_{m} and ΔS^{o}_{m} for SDS at different concentrations of MS, benzene, toluene and cyclohexane are summarized in TABLES 5, 6, 7 and 8 respectively. All of these show that the presence of the presented additives change the sign of ΔH^{o}_{m} from nega-

TABLE 1 : Effect of MS on the *CMC* of SDS at different temperatures; in its natural pH (pH=6.0±0.1).

[MS]/ / mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	7.63	7.79	7.98	8.04
2×10^{-6}	8.21	7.93	7.91	7.85
6×10^{-6}	8.29	8.08	8.06	8.03
1×10^{-5}	8.29	8.11	8.09	8.08
3×10^{-5}	8.41	8.20	8.11	7.60
8×10^{-5}	8.43	8.26	8.13	7.98
2×10^{-4}	8.51	8.32	8.28	8.27
8×10^{-4}	8.51	8.48	8.43	8.29

TABLE 2 : Effect of benzene on the *CMC* of SDS at different temperatures; in its natural pH (pH=6.0±0.1).

[Benzene] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	7.63	7.79	7.98	8.04
2×10^{-6}	8.40	8.35	8.30	8.29
6×10^{-6}	8.59	8.38	8.32	8.17
1×10^{-5}	8.64	8.46	8.40	8.34
3×10^{-5}	8.81	8.71	8.58	8.52
8×10^{-5}	8.99	8.71	8.67	8.61
2×10^{-4}	9.02	8.72	8.69	8.67
8×10^{-4}	9.22	9.09	8.99	8.78

TABLE 3 : Effect of toluene on the *CMC* of SDS at different temperatures; in its natural pH (pH=6.0±0.1).

[Toluene] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	7.63	7.79	7.98	8.04
2×10^{-6}	8.43	8.23	8.17	8.11
6×10^{-6}	8.68	8.49	8.42	8.27
1×10^{-5}	8.89	8.67	8.67	8.60
3×10^{-5}	9.24	9.07	9.03	9.03
8×10^{-5}	9.36	9.27	9.06	9.02
2×10^{-4}	9.44	9.40	9.23	9.10
8×10^{-4}	9.59	9.52	9.48	9.34

TABLE 4 : Effect of cyclohexane on the *CMC* of SDS at different temperatures; in its natural pH (pH=6.0±0.1).

[Cyclohexane] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	7.63	7.79	7.98	8.04
2×10^{-6}	8.54	8.36	8.16	8.14
6×10^{-6}	8.63	8.56	8.37	8.35
1×10^{-5}	8.74	8.59	8.48	8.44
3×10^{-5}	9.19	9.15	9.14	9.14
8×10^{-5}	9.42	9.21	9.18	9.17
2×10^{-4}	9.39	9.30	9.16	9.11
8×10^{-4}	9.75	9.39	9.38	9.15

tive to positive in a similar manner to that of HA[14]. The values of ΔG°_{m} were quite usual which always negative and slightly temperature dependent[18]. The positive sign of ΔS°_{m} is also quite normal and the temperature change of its values was related to that the micellization process is entropically driven[18]. However, the change of additive does not change significantly the values of ΔG°_{m}, ΔH°_{m} and ΔS°_{m} as shown clearly in the latter TABLES (5, 6, 7 and 8).

The effect of presence of the presented additives on *CMC* of cationic surfactant (CTAB) at different temperatures are listed in TABLES 9, 10, 11 and 12 for MS, benzene, toluene and cyclohexane respectively. As HA these show there is no change in the trend of *CMC* with temperature in contrast to that in anionic SDS. On the other hand, the results also display an increase in the *CMC* due to presence of these additives in a similar manner to that of SDS. The consequence of increasing the *CMC* due to presence of the presented additives is quite close to that for SDS.

The values of thermodynamic functions of micellization for cationic CTAB at different temperatures are illustrated in TABLES 13, 14, 15 and 16 in presence of MS, benzene, toluene and cyclohexane respectively. No change in the sign of ΔH°_{m} due to presence of the presented additives was observed in contrast to that of SDS. In general, the values of ΔG°_{m} and ΔH°_{m} of cationic CTAB as shown in the latter Tables are smaller than these of SDS which are reflect that CTAB have more tendency to form micelle in comparison with that of SDS. The spontaneity of micellization process (negative sign of ΔG°_{m}) for both SDS and CTAB can be attributed to the positive value of ΔS°_{m} which is resulted from the freedom of some gegin ions due to formation of micelle.

Finally, the above investigations suggest that the hydrophobic effect due to presence of the presented additives is the main factor for changing ΔH°_{m} sign of SDS. Such hydrophobic effect is created from iceberg formation (icebergs)[19] of water molecules around the addi-

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TABLE 5 : Effect of MS on the thermodynamic parameters of micellization for SDS at its natural pH (6.0±0.1) and different temperatures.

[MS] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol^{-1}·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-34.61	-2.351	113.93	-32.26
	T/ K =283.15	-35.57	-2.367	113.24	-33.20
	T/ K =283.15	-35.44	-2.298	111.16	-33.14
	T/ K =283.15	-36.57	-2.292	111.06	-34.22
2×10^{-6}	*T*/ K =283.15	-32.83	2.017	123.05	-34.84
	T/ K =283.15	-34.95	2.067	126.28	-37.02
	T/ K =283.15	-34.23	1.990	121.49	-36.22
	T/ K =283.15	-34.64	1.947	118.74	-36.59
6×10^{-6}	*T*/ K =283.15	-34.44	1.509	126.96	-35.95
	T/ K =283.15	-35.27	1.489	125.40	-36.76
	T/ K =283.15	-35.37	1.467	123.55	-36.84
	T/ K =283.15	-35.02	1.405	118.20	-36.43
1×10^{-5}	*T*/ K =283.15	-34.03	1.199	124.40	-35.23
	T/ K =283.15	-35.34	1.199	124.62	-36.54
	T/ K =283.15	-34.46	1.150	119.44	-35.61
	T/ K =283.15	-35.95	1.160	120.44	-37.12
3×10^{-5}	*T*/ K =283.15	-32.27	4.443	129.64	-36.71
	T/ K =283.15	-34.31	4.550	132.55	-38.86
	T/ K =283.15	-34.19	4.453	129.61	-38.65
	T/ K =283.15	-36.98	4.626	135.02	-41.61
8×10^{-5}	*T*/ K =283.15	-34.18	2.689	130.19	-36.86
	T/ K =283.15	-34.89	2.645	128.05	-37.54
	T/ K =283.15	-34.84	2.593	125.56	-37.44
	T/ K =283.15	-34.32	2.466	119.38	-36.79
2×10^{-4}	*T*/ K =283.15	-32.83	1.319	120.62	-34.15
	T/ K =283.15	-33.54	1.298	118.82	-34.83
	T/ K =283.15	-33.84	1.288	117.82	-35.13
	T/ K =283.15	-34.58	1.273	116.34	-35.85
8×10^{-4}	*T*/ K =283.15	-34.03	1.263	124.64	-35.29
	T/ K =283.15	-31.99	1.147	113.04	-33.14
	T/ K =283.15	-32.50	1.144	112.84	-33.64
	T/ K =283.15	-34.92	1.187	117.16	-36.10

TABLE 6 : Effect of benzene on the thermodynamic parameters of micellization for SDS at its natural pH (6.0±0.1) and different temperatures.

[Benzene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-34.61	-2.351	113.93	-32.26
	T/ K =283.15	-35.56	-2.367	113.24	-33.20
	T/ K =283.15	-35.44	-2.298	111.16	-33.14
	T/ K =283.15	-36.52	-2.292	111.06	-34.22
2×10^{-6}	*T*/ K =283.15	-29.80	0.600	107.376	-30.40
	T/ K =283.15	-30.86	0.599	107.306	-31.46
	T/ K =283.15	-32.57	0.621	111.316	-33.19
	T/ K =283.15	-31.88	0.589	105.366	-32.47
6×10^{-6}	*T*/ K =283.15	-33.45	2.398	126.586	-35.847
	T/ K =283.15	-34.55	2.386	125.91	-36.937
	T/ K =283.15	-33.67	2.284	120.57	-35.95
	T/ K =283.15	-31.51	2.063	108.93	-33.57
1×10^{-5}	*T*/ K =283.15	-32.28	1.594	119.67	-33.87
	T/ K =283.15	-33.26	1.583	118.85	-34.847
	T/ K =283.15	-34.75	1.625	122.01	-36.38
	T/ K =283.15	-34.49	1.559	116.99	-36.06
3×10^{-5}	*T*/ K =283.15	-33.66	1.621	124.61	-35.28
	T/ K =283.15	-34.49	1.603	123.14	-36.10
	T/ K =283.15	-32.28	1.472	113.20	-33.75
	T/ K =283.15	-30.50	1.345	103.35	-31.85
8×10^{-5}	*T*/ K =283.15	-31.80	1.925	119.11	-33.73
	T/ K =283.15	-33.19	1.934	119.82	-35.13
	T/ K =283.15	-33.76	1.933	119.71	-35.69
	T/ K =283.15	-34.69	1.920	118.80	-36.61
2×10^{-4}	*T*/ K =283.15	-33.63	1.847	125.30	-35.48
	T/ K =283.15	-34.04	1.799	122.24	-35.84
	T/ K =283.15	-33.75	1.753	119.08	-35.50
	T/ K =283.15	-35.37	1.777	120.54	-37.15
8×10^{-4}	*T*/ K =283.15	-32.81	2.266	123.86	-35.07
	T/ K =283.15	-33.67	2.243	122.51	-35.91
	T/ K =283.15	-32.88	2.150	117.49	-35.035
	T/ K =283.15	-34.82	2.198	120.13	-37.02

tives molecules or even around their non polar groups. Therefore, the resulted crystalline character of water molecules could reduce the mobility of surfactant molecules toward micellization process. The latter reduction in the mobility is quite parallel with the enhancement of *CMC* for both SDS and CTAB due to presence of additives. On the other hand, the above consequence of additives molecules toward increasing the CMC is quite parallel to the predicted hydrophobic character of additives which is take the order cyclohexane>toluene> benzene>MS. Therefore, the micellization process could change from exothermic to endothermic. Furthermore, Jaing et. al.[13] concluded that polar additives decrease the *CMC* of ionic surfactants. The question now; why cationic surfactant does not change its sign of ΔH^{o}_{m} due to presence of the presented additives in contrast to that of

TABLE 7 : Effect of toluene on the thermodynamic parameters of micellization for SDS at its natural pH (6.0±0.1) and different temperatures.

[Toluene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-34.61	-2.351	113.93	-32.26
	T/ K =283.15	-35.57	-2.367	113.24	-33.20
	T/ K =283.15	-35.44	-2.298	111.16	-33.14
	T/ K =283.15	-36.52	-2.292	111.06	-34.22
2×10^{-6}	*T*/ K =283.15	-30.77	1.698	114.66	-32.47
	T/ K =283.15	-31.93	1.697	114.69	-33.62
	T/ K =283.15	-31.69	1.655	111.82	-33.34
	T/ K =283.15	-32.26	1.629	109.99	-33.89
6×10^{-6}	*T*/ K =283.15	-34.12	2.300	128.62	-36.42
	T/ K =283.15	-34.88	2.265	126.71	-37.15
	T/ K =283.15	-35.33	2.253	126.03	-37.58
	T/ K =283.15	-31.84	1.961	109.69	-33.80
1×10^{-5}	*T*/ K =283.15	-34.08	1.518	125.71	-35.60
	T/ K =283.15	-34.81	1.4933	123.83	-36.30
	T/ K =283.15	-34.65	1.4614	121.10	-36.11
	T/ K =283.15	-35.46	1.4460	119.77	-36.91
3×10^{-5}	*T*/ K =283.15	-29.11	0.9803	106.28	-30.09
	T/ K =283.15	-30.66	0.9950	107.99	-31.66
	T/ K =283.15	-31.73	1.012	109.80	-32.74
	T/ K =283.15	-31.74	0.979	106.18	-32.72
8×10^{-5}	*T*/ K =283.15	-29.37	1.665	109.61	-31.04
	T/ K =283.15	-29.72	1.625	106.93	-31.35
	T/ K =283.15	-30.88	1.656	109.11	-32.53
	T/ K =283.15	-33.66	1.746	114.90	-35.41
2×10^{-4}	*T*/ K =283.15	-30.33	1.689	113.07	-32.02
	T/ K =283.15	-29.91	1.608	107.52	-31.52
	T/ K =283.15	-31.63	1.668	111.69	-33.30
	T/ K =283.15	-32.86	1.675	112.08	-34.54
8×10^{-4}	*T*/ K =283.15	-32.72	1.2244	119.88	-33.95
	T/ K =283.15	-32.96	1.1903	116.49	-34.15
	T/ K =283.15	-32.48	1.153	112.79	-33.63
	T/ K =283.15	-33.28	1.141	111.71	-34.42

TABLE 8 : Effect of cyclohexane on the thermodynamic parameters of micellization for SDS at its natural pH (6.0±0.1) and different temperatures.

[Cyclohexane] / mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-34.61	-2.351	113.93	-32.26
	T/ K =283.15	-35.57	-2.367	113.24	-33.20
	T/ K =283.15	-35.44	-2.298	111.16	-33.14
	T/ K =283.15	-36.52	-2.292	111.06	-34.22
2×10^{-6}	*T*/ K =283.15	-33.99	2.429	128.61	-36.42
	T/ K =283.15	-34.73	2.392	126.64	-37.13
	T/ K =283.15	-33.82	2.284	121.10	-36.11
	T/ K =283.15	-35.77	2.336	123.65	-38.11
6×10^{-6}	*T*/ K =283.15	-32.29	1.625	119.78	-33.92
	T/ K =283.15	-33.04	1.605	118.19	-34.65
	T/ K =283.15	-33.66	1.603	118.26	-35.26
	T/ K =283.15	-33.35	1.537	113.23	-34.89
1×10^{-5}	*T*/ K =283.15	-33.93	1.712	125.85	-35.64
	T/ K =283.15	-34.57	1.682	123.67	-36.26
	T/ K =283.15	-34.82	1.663	122.37	-36.49
	T/ K =283.15	-36.24	1.674	123.04	-37.92
3×10^{-5}	*T*/ K =283.15	-29.83	0.271	106.31	-30.10
	T/ K =283.15	-32.29	0.284	111.10	-32.57
	T/ K =283.15	-32.53	0.281	110.05	-32.81
	T/ K =283.15	-32.84	0.274	107.46	-33.11
8×10^{-5}	*T*/ K =283.15	-30.68	1.206	112.61	-31.89
	T/ K =283.15	-30.16	1.142	106.77	-31.301
	T/ K =283.15	-30.45	1.133	105.92	-31.582
	T/ K =283.15	-28.93	1.041	97.25	-29.97
2×10^{-4}	*T*/ K =283.15	-30.86	1.424	114.01	-32.28
	T/ K =283.15	-32.07	1.427	114.25	-33.49
	T/ K =283.15	-31.96	1.396	111.89	-33.36
	T/ K =283.15	-32.49	1.373	109.89	-33.86
8×10^{-4}	*T*/ K =283.15	-29.43	2.559	112.97	-31.99
	T/ K =283.15	-31.34	2.620	115.84	-33.96
	T/ K =283.15	-31.38	2.579	113.88	-33.95
	T/ K =283.15	-32.12	2.548	112.50	-34.67

SDS? The reason for this could be attributed to that cationic CTAB had more tendencies towards forming micelles in contrast to that of SDS (*CMC* of SDS larger about 8 times than that of CTAB). The latter may be accused to the effect of hydrophobic chain length which CTAB have 16 carbons in comparison with 11 carbons in SDS[15]. Thus; we could suggest that there is a competitive between the hydrophobic effect due to presence of additive with the tendency of CTAB for micellization process which is lead to no change in its sign of ΔH^{o}_{m} in contrast to that of SDS. However, the presented investigations suggest hypothetically employing anionic and cationic surfactants with the same hydrophobic chain length as a future work. Noting that, SDS and CTAB are the most common anionic and cationic surfactants used in the literatures.

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TABLE 9 : Effect of MS on the *CMC* of CTAB at different temperatures; in its natural pH (pH=6.0±0.1).

[MS] / Mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	8.47	8.65	8.85	9.01
2×10^{-6}	8.52	8.97	8.97	9.09
6×10^{-6}	8.56	8.97	8.99	9.25
1×10^{-5}	8.76	8.93	9.11	9.22
3×10^{-5}	8.88	9.01	9.18	9.30
8×10^{-5}	8.92	9.08	9.18	9.41
2×10^{-4}	9.22	9.41	9.44	9.55
8×10^{-4}	9.23	9.46	9.55	9.60

TABLE 10 : Effect of benzene on the *CMC* of CTAB at different temperatures; in its natural pH (pH=6.0±0.1).

[Benzene] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	8.47	8.65	8.85	9.01
2×10^{-6}	8.70	8.88	9.07	9.15
6×10^{-6}	8.88	8.97	9.12	9.22
1×10^{-5}	9.02	9.18	9.29	9.32
3×10^{-5}	9.14	9.20	9.35	9.54
8×10^{-5}	8.83	9.13	9.31	9.47
2×10^{-4}	9.27	9.40	9.40	9.48
8×10^{-4}	9.27	9.53	9.57	9.99

TABLE 11 : Effect of toluene on the *CMC* of CTAB at different temperatures; in its natural pH (pH=6.0±0.1).

[Toluene] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	8.47	8.65	8.85	9.01
2×10^{-6}	8.56	8.66	8.88	9.18
6×10^{-6}	8.64	8.88	8.90	9.28
1×10^{-5}	8.66	8.98	9.02	9.34
3×10^{-5}	9.22	9.40	9.45	9.59
8×10^{-5}	9.26	9.57	9.69	9.75
2×10^{-4}	9.34	9.65	9.75	9.82
8×10^{-4}	9.45	9.74	9.76	9.99

TABLE 12 : Effect of cyclohexane on the *CMC* of CTAB at different temperatures; in its natural pH (pH=6.0±0.1).

[Cyclohexane] /mol·l^{-1}	*CMC* /mol·l^{-1} x10^3 ±0.02			
	T/ K =308.15	*T*/ K =298.15	*T*/ K =293.15	*T*/ K =283.15
0	8.47	8.65	8.85	9.01
2×10^{-6}	8.56	8.78	8.96	9.05
6×10^{-6}	8.71	8.81	9.20	9.21
1×10^{-5}	8.88	9.00	9.30	9.31
3×10^{-5}	9.13	9.36	9.52	9.65
8×10^{-5}	9.19	9.41	9.43	9.67
2×10^{-4}	9.20	9.511	9.56	9.72
8×10^{-4}	9.32	9.70	9.80	9.83

TABLE 13 : Effect of MS on the thermodynamic parameters of micellization for CTAB at its natural pH (6.0±0.1) and different temperatures.

[MS] / mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-45.60	-3.209	149.72	-42.40
	T/ K =283.15	-45.01	-3.064	143.07	-41.94
	T/ K =283.15	-45.15	-3.029	141.26	-42.12
	T/ K =283.15	-45.04	-2.928	136.64	-42.11
2×10^{-6}	*T*/ K =283.15	-39.09	-2.753	128.34	-36.34
	T/ K =283.15	-41.81	-2.857	132.87	-38.95
	T/ K =283.15	-38.55	-2.590	120.61	-35.96
	T/ K =283.15	-39.70	-2.584	120.43	-37.11
6×10^{-6}	*T*/ K =283.15	-36.87	-3.112	119.23	-33.76
	T/ K =283.15	-40.38	-3.306	126.47	-37.07
	T/ K =283.15	-40.53	-3.263	124.98	-37.27
	T/ K =283.15	-38.47	-3.004	115.08	-35.46
1×10^{-5}	*T*/ K =283.15	-37.71	-2.227	125.33	-35.49
	T/ K =283.15	-38.76	-2.214	124.65	-36.54
	T/ K =283.15	-36.46	-2.052	115.40	-34.41
	T/ K =283.15	-39.73	-2.166	121.89	-37.56

TABLE 14 : Effect of benzene on the thermodynamic parameters of micellization for CTAB at its natural pH (6.0±0.1) and different temperatures.

[Benzene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-45.60	-3.209	149.72	-42.40
	T/ K =283.15	-45.01	-3.064	143.07	-41.94
	T/ K =283.15	-45.15	-3.029	141.26	-42.12
	T/ K =283.15	-45.04	-2.928	136.64	-42.11
2×10^{-6}	*T*/ K =283.15	-44.59	-2.660	148.07	-41.93
	T/ K =283.15	-45.42	-2.622	146.00	-42.80
	T/ K =283.15	-45.39	-2.582	143.59	-42.81
	T/ K =283.15	-43.50	-2.395	133.38	-41.10
6×10^{-6}	*T*/ K =283.15	-43.63	-1.918	147.32	-41.72
	T/ K =283.15	-43.73	-1.858	142.83	-41.87
	T/ K =283.15	-42.92	-1.796	137.93	-41.13
	T/ K =283.15	-38.02	-1.541	118.37	-36.48
1×10^{-5}	*T*/ K =283.15	-42.25	-3.549	136.67	-38.70
	T/ K =283.15	-43.57	-3.513	136.64	-40.06
	T/ K =283.15	-41.73	-3.338	128.78	-38.40
	T/ K =283.15	-40.22	-3.126	120.38	-37.10

[MS] / mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
3×10^{-5}	*T*/ K =283.15	-42.73	-2.280	142.85	-40.45
	T/ K =283.15	-43.24	-2.231	139.89	-41.01
	T/ K =283.15	-41.89	-2.129	133.37	-39.76
	T/ K =283.15	-40.83	-2.010	125.98	-38.82
8×10^{-5}	*T*/ K =283.15	-39.76	-2.409	131.91	-37.35
	T/ K =283.15	-45.31	-2.656	145.50	-42.65
	T/ K =283.15	-45.02	-2.597	142.27	-42.42
	T/ K =283.15	-45.36	-2.538	138.95	-42.82
2×10^{-4}	*T*/ K =283.15	-41.83	-1.642	141.92	-40.19
	T/ K =283.15	-41.68	-1.583	136.78	-40.10
	T/ K =283.15	-41.92	-1.566	135.34	-40.35
	T/ K =283.15	-41.86	-1.515	130.92	-40.34
8×10^{-4}	*T*/ K =283.15	-39.65	-1.781	133.72	-37.87
	T/ K =283.15	-39.95	-1.737	130.35	-38.21
	T/ K =283.15	-40.32	-1.713	128.52	-38.32
	T/ K =283.15	-42.81	-1.773	133.18	-41.04

[Benzene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
3×10^{-5}	*T*/ K =283.15	-36.98	-1.818	124.19	-35.17
	T/ K =283.15	-36.68	-1.731	119.20	-34.95
	T/ K =283.15	-36.52	-1.708	116.75	-34.81
	T/ K =283.15	-38.57	-1.749	119.50	-36.82
8×10^{-5}	*T*/ K =283.15	-39.90	-3.163	129.74	-36.74
	T/ K =283.15	-41.95	-3.221	132.11	-38.73
	T/ K =283.15	-42.39	-3.206	131.42	-39.18
	T/ K =283.15	-43.46	-3.185	130.70	-40.28
2×10^{-4}	*T*/ K =283.15	-40.43	-1.013	139.21	-39.42
	T/ K =283.15	-41.59	-1.008	138.45	-40.59
	T/ K =283.15	-43.34	-1.032	141.89	-42.31
	T/ K =283.15	-45.12	-1.041	143.04	-40.78
8×10^{-4}	*T*/ K =283.15	-43.93	-3.606	142.41	-40.33
	T/ K =283.15	-44.37	-3.527	139.34	-40.85
	T/ K =283.15	-45.60	-3.565	140.98	-42.04
	T/ K =283.15	-45.55	-3.459	136.59	-42.09

TABLE 15 : Effect of toluene on the thermodynamic parameters of micellization for CTAB at its natural pH (6.0±0.1) and different temperatures.

[Toluene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-45.6038	-3.2088	149.72	-42.40
	T/ K =283.15	-45.0056	-3.0644	143.07	-41.94
	T/ K =283.15	-45.1479	-3.0289	141.26	-42.12
	T/ K =283.15	-45.0360	-2.9279	136.64	-42.11
2×10^{-6}	*T*/ K =283.15	-44.9111	-3.6004	145.89	-41.31
	T/ K =283.15	-40.3488	-3.1278	126.97	-37.22
	T/ K =283.15	-45.2299	-3.4551	140.11	-41.78
	T/ K =283.15	-45.5611	-3.3777	136.89	-42.18
6×10^{-6}	*T*/ K =283.15	-43.9285	-3.3741	143.22	-40.55
	T/ K =283.15	-45.2497	-3.3655	142.87	-41.88
	T/ K =283.15	-45.5281	-3.3298	141.53	-42.20
	T/ K =283.15	-45.8399	-3.2564	138.19	-42.58
1×10^{-5}	*T*/ K =283.15	-44.2553	-3.6026	143.57	-40.65
	T/ K =283.15	-45.1025	-3.5578	141.71	-41.55
	T/ K =283.15	-43.6677	-3.3881	135.09	-40.28
	T/ K =283.15	-44.6639	-3.3638	134.02	-41.30
3×10^{-5}	*T*/ K =283.15	-34.9061	-1.5477	117.81	-33.36
	T/ K =283.15	-36.2827	-1.5566	118.45	-34.73
	T/ K =283.15	-36.0324	-1.5207	115.75	-34.51
	T/ K =283.15	-35.7002	-1.4598	111.11	-34.24
8×10^{-5}	*T*/ K =283.15	-39.0333	-2.2849	129.78	-36.75
	T/ K =283.15	-42.2236	-2.3945	135.86	-39.83
	T/ K =283.15	-43.1204	-2.4071	136.55	-40.71
	T/ K =283.15	-43.5689	-2.3545	133.74	-41.21

TABLE 16 : Effect of cyclohexane on the thermodynamic parameters of micellization for CTAB at its natural pH (6.0±0.1) and different temperatures.

[Cyclohexane] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
0	*T*/ K =283.15	-45.60	-3.209	149.72	-42.40
	T/ K =283.15	-45.01	-3.064	143.07	-41.94
	T/ K =283.15	-45.15	-3.029	141.26	-42.12
	T/ K =283.15	-45.04	-2.928	136.64	-42.11
2×10^{-6}	*T*/ K =283.15	-44.44	-2.947	146.54	-41.49
	T/ K =283.15	-45.54	-2.814	145.73	-42.72
	T/ K =283.15	-45.84	-2.782	144.40	-43.06
	T/ K =283.15	-42.12	-2.689	127.95	-39.43
6×10^{-6}	*T*/ K =283.15	-43.91	-3.001	144.45	-40.90
	T/ K =283.15	-45.17	-2.985	143.88	-42.18
	T/ K =283.15	-45.68	-2.980	143.22	-42.70
	T/ K =283.15	-40.82	-2.577	124.11	-38.25
1×10^{-5}	*T*/ K =283.15	-41.87	-2.457	139.17	-39.41
	T/ K =283.15	-44.32	-2.516	142.59	-41.80
	T/ K =283.15	-43.91	-2.458	139.03	-41.45
	T/ K =283.15	-42.43	-2.298	130.23	-40.13
3×10^{-5}	*T*/ K =283.15	-35.72	-2.275	118.12	-33.45
	T/ K =283.15	-34.52	-2.128	110.50	-32.39
	T/ K =283.15	-38.39	-2.330	120.94	-36.06
	T/ K =283.15	-34.76	-2.044	106.16	-32.71
8×10^{-5}	*T*/ K =283.15	-42.80	-2.397	142.69	-40.41
	T/ K =283.15	-42.78	-2.319	138.03	-40.46
	T/ K =283.15	-43.61	-2.324	138.47	-41.29
	T/ K =283.15	-43.96	-2.273	135.28	-41.69

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[Toluene] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
2×10^{-4}	*T*/ K =283.15	-42.0070	-2.4176	139.81	-39.59
	T/ K =283.15	-42.0333	-2.3436	135.39	-39.69
	T/ K =283.15	-42.3415	-2.3235	134.22	-40.02
	T/ K =283.15	-44.8292	-2.3817	137.75	-42.45
8×10^{-4}	*T*/ K =283.15	-42.7819	-2.5760	141.99	-40.21
	T/ K =283.15	-42.9436	-2.5044	137.94	-40.44
	T/ K =283.15	-44.1532	-2.5322	139.59	-41.62
	T/ K =283.15	-45.5327	-2.5319	139.54	-43.01

[Cyclohexane] /mol·l^{-1}	Temperature	ΔG^{o}_{m} / kJ·mol^{-1}	ΔH^{o}_{m} / kJ·mol^{-1}	ΔS^{o}_{m} / J·mol.$^{-1}$·K^{-1}	$-T\Delta S^{o}_{m}$ / kJ·mol^{-1}
2×10^{-4}	*T*/ K =283.15	-41.72	-2.523	138.43	-39.20
	T/ K =283.15	-42.95	-2.516	137.93	-40.44
	T/ K =283.15	-43.92	-2.531	138.80	-41.39
	T/ K =283.15	-43.36	-2.477	132.67	-40.88
8×10^{-4}	*T*/ K =283.15	-41.00	-2.463	136.11	-38.54
	T/ K =283.15	-41.46	-2.414	133.20	-39.05
	T/ K =283.15	-40.44	-2.440	127.43	-37.99
	T/ K =283.15	-44.69	-2.478	136.97	-42.21

CONCLUSIONS

On the basis of our results we could conclude that the hydrophobic effect due to presence of additives (MS, benzene, toluene and cyclohexane) play a major role in changing the sign of ΔH^{o}_{m} for anionic SDS from negative to positive. In addition, the latter hydrophobic effect also causes an increase in the *CMC* of both anionic and cationic surfactants.

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