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THERMODYNAMIC AND KINETIC STUDIES ON THE MICELLIZATION OF SODIUM DODECYL SULPHATE IN AQUEOUS AND 1,4-DIOXANE SYSTEM

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ABSTRACT

The micellization behavior of anionic surfactant SDS in water and in mixed solvent media have been investigated by conductometric and kinetic method were monitored conductometrically using digital conductometer and The changes in absorbance of reaction mixture with time were monitored spectrophotometrically at 291 nm using cary 16 UV-visible spectrophotometer in the temperature range of 298.15 to 313.150K. The obtained results have been used to estimate the thermodynamic and kinetic parameters of micellization. Experimental data indicate that the CMC of surfactant increases with temperature, ΔG^0 is negative and remains practically constant indicating that the micellization process is exothermic in nature ΔH^0 is also negative and decrease with the temperature, indicating that the formation of micelles becomes increasingly exothermic as the temperature increased. The ΔS^0 was positive in all temperature range, decreases with increase in temperature, indicating that the micellization process is endothermic and The rate constant decreased with increasing in 1,4-dioxane concentrations The activation energy increases in concentration of solvent of the reaction medium.

Keywords: *micellization, conductometric, thermodynamic, activation energy.*

I.   INTRODUCTION

Anionic surfactants like sodium dodecyl sulphate, possess valuable characteristics like emulsification, wetting, water proofing, repellence, spreading, etc. which are relevant in several applications such as pharmaceuticals, enhanced oil recovery , metallurgical process for ore concentration, and solubilization of water insoluble dyes.[1-3] The formation of micelles is generally understood in terms of hydrophobic effect, which is the main driving force behind the formation of micelles in solution. [3,4] Besides the hydrophobicity of the surfactant molecule, hydrophobicity of the solvent media is also of importance in understanding the process of micellization. [1,5,6] Addition of small amount of organic solvent has been known to produce marked changes in the critical

micelle concentration (CMC) of ionic surfactants due to the tendency of the added organic solvent either to break or make the water structure through solvation of the hydrophobic tail of the surfactant by the hydrocarbon (hydrophobic) part of the organic solvent. [5,7] In view of this, there has been a renewed interest on the study of adsorption and aggregation of surfactants in solvent media containing a binary mixture of water and a polar non-aqueous solvent in recent year [8-9]. However some authors have reported that high cohesive energies, dielectric constants and considerable hydrogen bonding abilities between solvent molecules are prerequisite to aggregation of surfactants molecules in solution [10, 11]. The chemical literature contains a scattering of reports concerning reaction kinetics in aqueous and mixed solvent media containing ionic or nonionic surfactants. Over the last few years researcher have developed a research programme investigating the use of novel micellar media for the hydrolysis of dimethyl phthalate in highly alkaline medium. It has been proved that cationic surfactants accelerate the rate of hydrolysis. Surprisingly, mechanistic details of the hydrolysis of dimethyl phthalate and the effect of solvents in the presence of cationic surfactants have not yet been explored. Many features of the kinetics of reactions in micellar systems are related to those of reactions in monolayers and to those in the presence of polyelectrolytes. Excellent reviews of these topics are available.[12] The kinetics of organic reactions occurring in micellar systems are dominated by two factors: electrostatic interactions and hydrophobic interactions between the micellar phase and

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reactants, transition states, and products. In this paper we have reported the result of the conductometric and kinetic studies on the micellar behavior of anionic surfactant, sodium dodecyl sulphate(SDS) in aqueous and mixed aqueous-organic solvent media at **$298.15^0K, 303.15^0K, 308.15^0K$ and 313.15^0K**.

II.MATERIAL AND METHODS

Sodium dodecylsulphate (SDS), from BDH was recrystallized several times from hot ethanol and dried under vacuum. Dimethyl phthalate, and 1, 4-Dioxame (E.Merck, AR grade) were purified by standard procedures as described earlier [13]. The solvent 1,4-Dioxane were fractionally distilled prior to their use.

Conductometric measurement
The specific conductivity for the surfactant solutions were measured as a function of surfactant concentration with a Digital conductivity Analizer [ANALABS, model:μ con cal5] at 1 KHz. The pyrex conductivity cell of cell constant 0.985 cm-1 was used having bright platinum discs electrodes, containing about 200ml of solution. The conductivity cell with a sample was immersed in a thermostat both with the temperature fluctuation within ±0.010K. The conductivity cell was calibrated with standard decinormal aqueous KCl solution. The precision of the measurements was within ±0.003 m S cm-1.The cell was cleaned with chromic acid and finally washed with conductivity water before each run. A range of concentrations of the surfactants in each case was produced by adding well cooled stock solutions of appropriate concentration from a weight burette to a known quantity of the solvent mixture in the conductivity cell. In the present investigation the specific conductance data have been measured at different temperature (298.15, 303.15, 308.15 and 313.15 K).

Kinetic measurement
In the present work all the kinetic runs were carried out with[NaOH]﹋24 to 1000 times that of [diester] at different temperature and at constant ionic strength (KCl). In a typical kinetic run, the solution containing all the reactants except dimethyl phthalate was equilibrated for 5 to 10 min and the reaction was initiated by adding a solution of dimethyl phthalate in acetonitrile to the reaction mixture. The concentration of acetonitrile in the reaction mixture, was thus only 1%. The changes in absorbance of reaction mixture with time were monitored spectrophotometrically at 291 nm using cary 16 UV-visible spectrophotometer and SDS with aqueous and water-1,4-dioxane have been made at different temperature (298.15, 303.15, 308.15 and 313.150K).

III.RESULT AND DISCUSSION

The CMC of SDS was determined using conventional conductivity measurement method. The CMC of the SDS were evaluated from the inflection point in the plots of conductance against concentration of SDS. Typical representative plots of the conductance against concentration of the surfactant in aqueous solution are shown in figure (**1.10, 1.11-1.14,**). We have measured the conductance of SDS in aqueous and 1,4-Dioxane media in order to bring out the influence of the added organic in the micellization process.
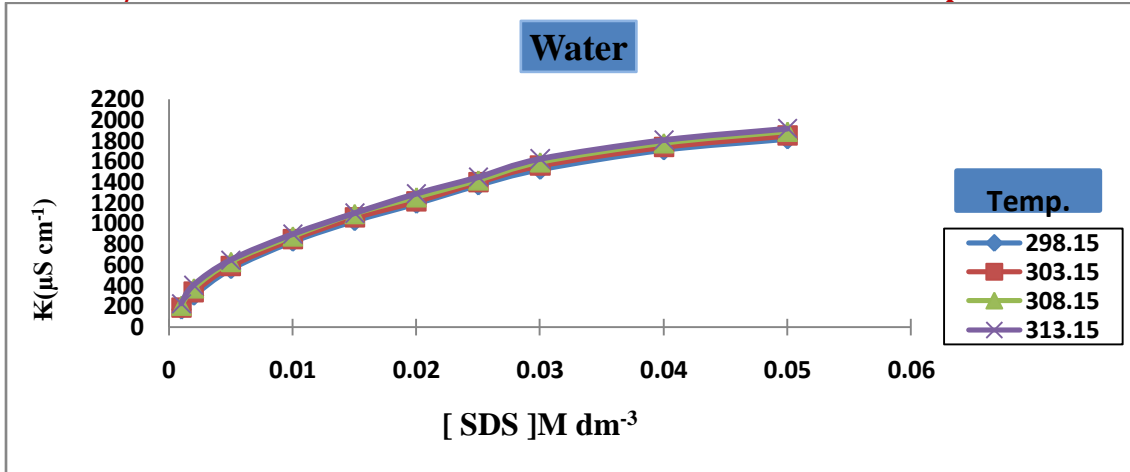
(C)Global Journal Of Engineering Science And Researches

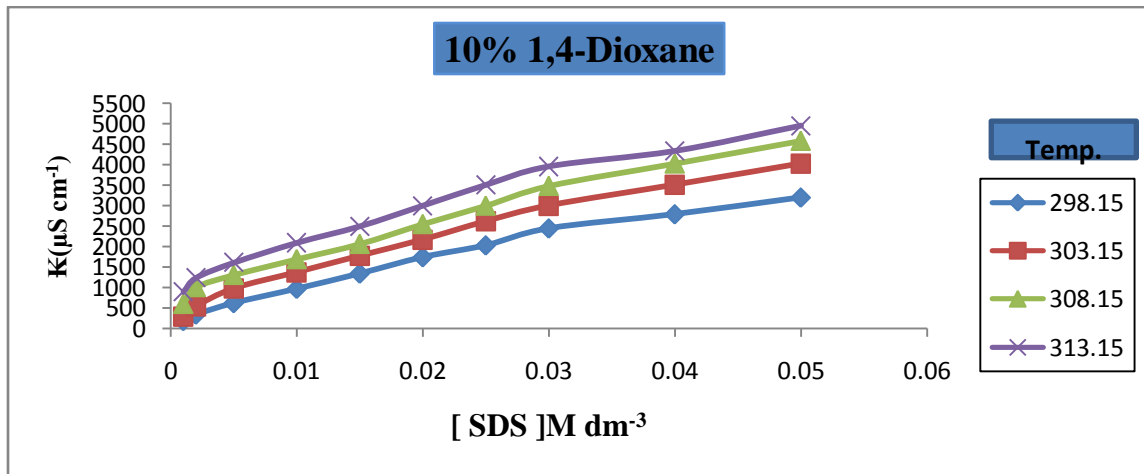*Fig :(1.10) Plots of K Vs M for SDS inWater at different temperatures.*

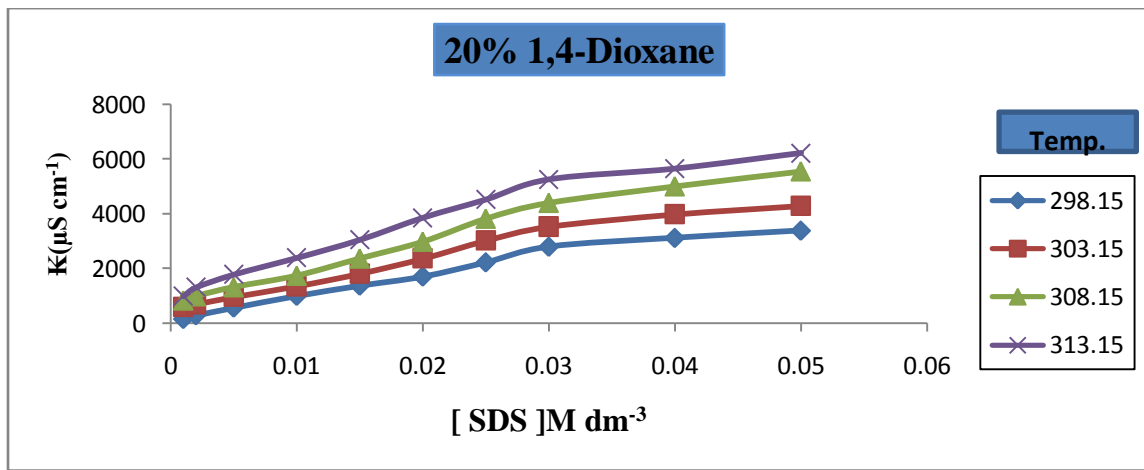*Fig :(1.11) Plots of K Vs M for SDS in 10% 1,4-Dioxane+Water at different temperatures.*

Fig :(1.12) Plots of K Vs M for SDS in 20% 1,4-Dioxane+Water at different temperatures.
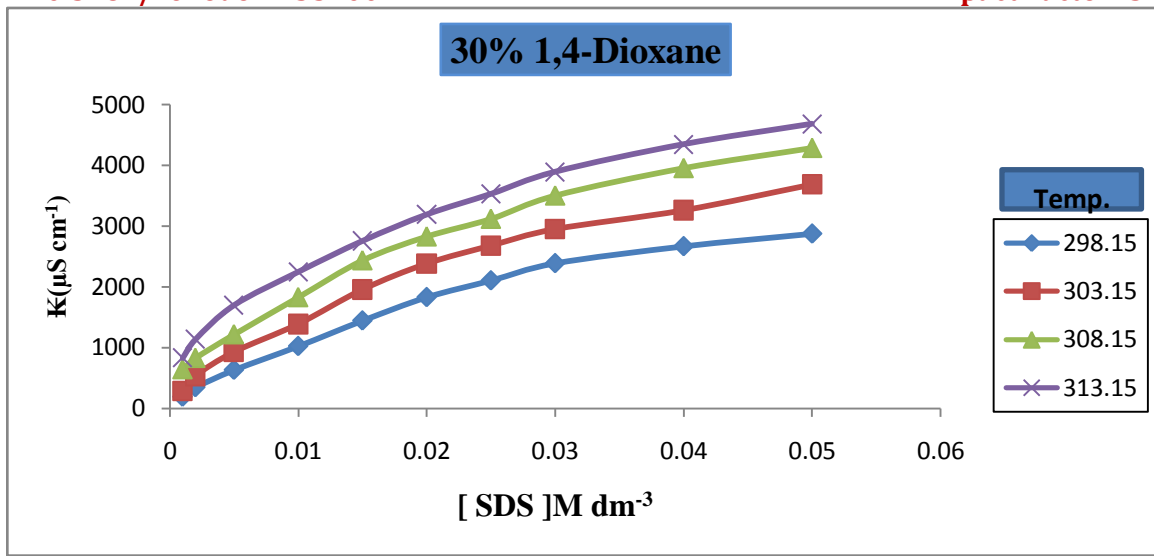
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Fig :(1.13) Plots of K Vs M for SDS in 30% 1,4-Dioxane+Water at different temperatures.
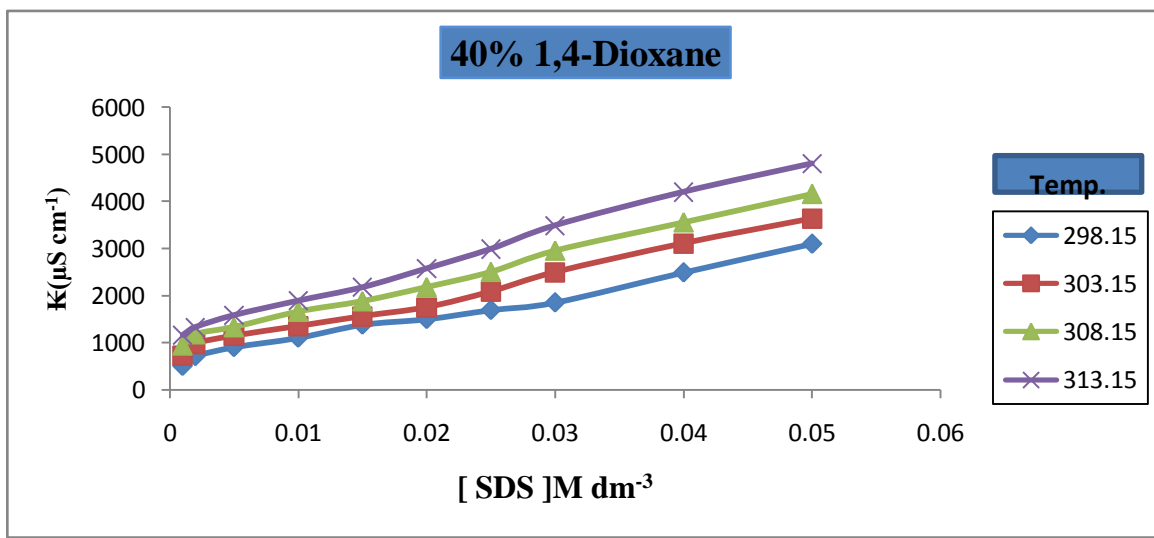

Fig : (1.14) Plots of K Vs M for SDS in 40% 1,4-Dioxane+Water at different temperatures.

The values of CMC and α for the studied systems are also given in Table 1 for SDS. 1,4-Dioxane. The thermodynamic parameters were calculated from the following relations.

$$\alpha = (1 - \beta) \qquad \text{……..………(1)}$$
$$\Delta G^0 mic = 2.303 \, RT \, (2-\alpha) \log CMC \qquad \text{……………. (2)}$$
$$\Delta S^0_{mic} = \left[-\frac{d \left(\Delta G^0_{mic} \right)}{dT} \right]_P \qquad \text{……………..(5)}$$
$$\Delta H^0_{mic} = -T^2 \left[\frac{\partial \, d \left(\Delta G^0_{mic} \right)}{\partial dT} \right]_P \qquad \text{…………….. (6)}$$

Further, the Gibbs energy of transfer values (ΔG⁰trans) which can be accounted for the effect of co-solvent on the micellization process was estimated through the relation [14,15].

ΔG⁰trans= ΔG⁰mic (w+cos) - ΔG⁰mic(w)   …..…… (7)

Where, $\Delta G^0mic(w)$ and $\Delta G0mic$ (w+cos) stands for standard Gibbs free energy of micellization in water and water+ cosolvent mixed media respectively. The change in the molar heat capacity for micelle formation ΔCp^0mic can be obtained from the slops of the plot of ΔH^0mic versus temperature

$$\Delta Cp^0_{mic} = [\frac{\partial d(\Delta H^0_{mic})}{d\partial T}]_p \quad ....(8)$$

TABLE- (1) : Values of Critical Micelle Concentration (CMC), Degree of Counter-ion Association (α) and Thermodynamic Parameters of Micellization for SDS in 1,4-Dioxane + H₂O Mixtures at Different Temperatures.

T (^{0}K)	CMC (mol dm^{-3})	α	- ΔG^0_{mic} (kJmol^{-1})	- ΔH^0_{mic} (kJmol^{-1})	ΔS^0_{mic} (kJmol^{-1})	ΔG^0_{trans} (kJmol^{-1})	$\Delta C_{p\ mic}^{0}$ (kJmol^{-1})
				H₂O			
298.15	0.027	0.767	10.98	3.96	32.87		
303.15	0.028	0.766	11.1	4.09	32.53		-16.18
308.15	0.029	0.765	11.14	4.23	31.39		
313.15	0.03	0.765	11.25	4.37	31.56		
			10% 1,4-Dioxane + H₂O				
298.15	0.028	0.62	12.21	4.47	36.49	-1.23	
303.15	0.03	0.6	12.44	4.63	36.41	-1.34	-18.58
308.15	0.031	0.53	13.11	4.78	37.77	-1.97	
313.15	0.032	0.52	13.23	4.94	37.31	-1.98	
			20% 1,4-Dioxane + H₂O				
298.15	0.029	0.58	12.41	4.49	37.14	-1.43	
303.15	0.03	0.57	12.62	4.64	36.99	-1.52	-18.14
308.15	0.032	0.55	12.75	4.79	36.59	-1.61	
313.15	0.033	0.53	13.14	4.95	37.02	-1.89	
			30% 1,4-Dioxane + H₂O				
298.15	0.031	0.46	13.28	4.8	39.75	-2.3	
303.15	0.032	0.45	13.42	4.96	39.31	-2.32	-19.21
308.15	0.035	0.42	13.53	5.13	38.78	-2.39	
313.15	0.035	0.4	13.93	5.29	39.2	-2.68	
			40% 1,4-Dioxane + H₂O				
298.15	0.033	0.42	13.44	4.84	40.24	-2.46	
303.15	0.035	0.39	13.65	5.01	40.02	-2.55	-20.12
308.15	0.036	0.38	13.77	5.17	39.52	-2.63	
313.15	0.038	0.32	14.31	5.34	40.36	-3.06	

It is found that CMC of SDS increases on increasing the temperature and the amount of cosolvents**.** In the present work the CMC value of SDS in pure aqueous solution appear to be in good agreement with the literature values [16, 17]. On mixing 1,4-Dioxane to be an aqueous surfactant solution, an increase in CMC irrespective of nature of the surfactant as reported in result. The decrease of dielectric constant of medium appears micellization by increasing mutual repulsion of ionic heads in the micelle, hence increasing the CMC [18]. In the case of 1, 4-Dioxane+H2O

partial micelle penetration is possible and it also lowers the dielectric constant of the medium. Hence, 1,4-Dioxane is a micellar structure breaker and due to lower dielectric constant than other system.

The $\Delta G°$ value become more negative with increase in temperature and become less negative with the increase in the co-solvent content in the mixed media. At a fixed solvent composition. The negative value is like with reported by [19,20]. From the results presented in Table(1). The results also shows that the $\Delta H°$ values calculated for aqueous and all solvents medium are negative. The values of ΔH^0 was negative and decrease with the increase in temperature indicating that the micellisation process increasingly exothermic for SDS. As well as, on adding a cosolvent into surfactant solution, there is decrease in ΔH^0 irrespective of their chemical nature, again due to their intermolecular hydrogen bonding with water. The negative enthalpy value can be taken as evidence that London dispersion interaction represent the major attractive force for micellization. The overall micellization process was found to be exothermic. The $\Delta S°$values for surfactant solvent systems were positive indicating that the micellization process is entropy dominated. The standard entropy of micellization ΔS^0 was positive in all temperature range, decreases with increase in temperature, indicating that the micellizatin process is endothermic. The positive values of $\Delta S°$ clearly indicate that the micellization of the studied surfactant in aqueous as well as in various solvents is governed mainly by hydrophobic interaction between the surfactants anions resulting in the breakdown of the structured water surrounding the hydrophobic groups. The heat capacities at constant pressure ΔCp^0 was determined from the slopes of eq. (8). All the values of ΔCp^0 are negative and this favours the formation of micelles is an exothermic process. The positive values of ΔG^0trans indicates that it's responsible for the delay in the micellization of surfactants in the mixed media [21] and their value depends on the transfer Gibbs free energies from pure water and the cosolvents in addition to their mutual interaction.

Kinetic studies

The spontaneous hydrolysis of dimethyl phthalate was studied in water-1,4-Dioxane, ionic, micellar solutions, the surfactant being SDS. The dependence of the observed rate constant on surfactant concentration as well as on the percentage by weight of 1,4 Dioxane, varying from 0 to 40 wt %, was investigated. Information about changes in the critical micelle concentrations, in the micellar ionization degrees (for ionic surfactants), in the aggregation numbers, and in the polarity of the interfacial region of the micelles upon changing the weight percent of 1,4 Dioxane was obtained through spectrophotometric measurements. The absorbance at 291 nm increased with time attaining a maximum value in the initial phase of the reaction and then decreased to a minimum value in latter phase of the reaction. This indicates the involvement of a stable intermediate in the alkaline hydrolytic cleavage of dimethyl phthalate. All of the kinetic runs, the absorbance / time result fit very well to the first order rate equation,

$$\ln (A_\infty-At) = \ln(A_\infty- A_\circ)-kt$$

The first order rate constant can be determined by least square fits. The observed rate constant values increases upon increasing surfactant concentrations. This dependence can be explained by considering that an increases in the surfactant concentration results in further incorporation of dimethyl phthalate into the micelles. The observed rate constant decreases as the volume percent in the mixture increases. These variations in K_{obs} upon changing (w/v)% 1,4-Dioxane are a reflection of the thermodynamic and structural changes produced in the micellar solution by the presence of different amounts of the organic solvent. The observed rate constant profile is multiphase below the cmc for the surfactant, the rate constants are independent of surfactants concentration. Above the cmc, the rate constant rise rapidly with increasing concentration of this surfactants. The hydrolytic cleavage of dimethyl phthalate in 1,4-dioxane-water system and alkalie hydrolysis of dimethyl phthalate presumably involve a neutral and an ionic molecules and catiionic molecules respectively, in the rate determining steps. The rate of such reactions should increases with decreasing in the dielectric constant of the reaction medium. The unique dependence of rate constant on 1,4-dioxane content of the reaction medium has been observed. The rate constant decreased with increasing in 1,4-dioxane concentration. There was a good feet of observed data with Arrhenius equation.

$$k = A_e^{-Ea/RT}$$

and from this equation various activation parameters were calculated with linear and non linear least squares technique. The dependence of activation energy upon solvent composition reveals that the increase in concentration of solvent of the reaction medium increases the activation energy and increases the surfactant concentration ,decreasing activation energy.

Table 2- Observed Rate constant for the spontaneous hydrolysis of Dimethyl phthalate on benzalkonium chloride concentration in water and water-1,4-Dioxane micellar solution at different temperature.

Conc. (Mole dm^{-3})	Rate Constant X 10^{-4}			
	Temperature			
	25°c	30°c	35°c	40°c
H2O				
0.001	0.01	0.01	0.011	0.012
0.002	0.012	0.014	0.015	0.016
0.005	0.014	0.017	0.018	0.019
0.01	0.017	0.02	0.021	0.022
0.015	0.018	0.024	0.025	0.027
0.02	0.02	0.025	0.026	0.028
0.025	0.022	0.026	0.027	0.029
0.03	0.025	0.032	0.033	0.034
0.04	0.028	0.034	0.036	0.037
0.05	0.032	0.04	0.042	0.044
10% 1,4-Dioxane				
0.001	0.012	0.013	0.014	0.015
0.002	0.014	0.017	0.018	0.019
0.005	0.016	0.02	0.022	0.023
0.01	0.019	0.024	0.025	0.026
0.015	0.022	0.027	0.028	0.029
0.02	0.023	0.027	0.029	0.03
0.025	0.025	0.03	0.031	0.033
0.03	0.027	0.036	0.037	0.038
0.04	0.031	0.039	0.04	0.041
0.05	0.036	0.042	0.044	0.046
20% 1,4-Dioxane				
0.001	0.0049	0.0045	0.0064	0.0071
0.002	0.0045	0.0055	0.0073	0.0089
0.005	0.0054	0.0066	0.0089	0.01
0.01	0.0063	0.0072	0.01	0.012
0.015	0.0076	0.0093	0.012	0.014
0.02	0.0098	0.0108	0.013	0.016

0.025	0.0114	0.0126	0.014	0.017
0.03	0.012	0.0139	0.016	0.019
0.04	0.0142	0.017	0.018	0.021
0.05	0.016	0.019	0.02	0.022
30% 1,4-Dioxane				
0.001	0.00236	0.00324	0.00485	0.00495
0.002	0.00324	0.00398	0.00475	0.00551
0.005	0.00396	0.00491	0.00545	0.00655
0.01	0.00464	0.00542	0.00645	0.00714
0.015	0.00451	0.00582	0.0074	0.00933
0.02	0.00541	0.00651	0.00913	0.012
0.025	0.00641	0.00734	0.011	0.014
0.03	0.00735	0.00915	0.013	0.015
0.04	0.00918	0.012	0.014	0.017
0.05	0.011	0.015	0.016	0.018
40% 1,4-Dioxane				
0.001	0.00104	0.00266	0.00346	0.00444
0.002	0.00161	0.00293	0.00393	0.00492
0.005	0.00261	0.00345	0.00444	0.00562
0.01	0.00321	0.00391	0.00492	0.00681
0.015	0.00388	0.00464	0.00562	0.00752
0.02	0.00454	0.00502	0.00681	0.00872
0.025	0.00451	0.00542	0.00752	0.00915
0.03	0.0053	0.00651	0.00872	0.00946
0.04	0.0066	0.00772	0.00915	0.01
0.05	0.00782	0.00862	0.00946	0.012

Table 3 - Activation Parameters for Alkaline Hydrolysis of Dimethyl Phthalate with banzalkonium chloride in water and 1,4-Dioxane(DIO).

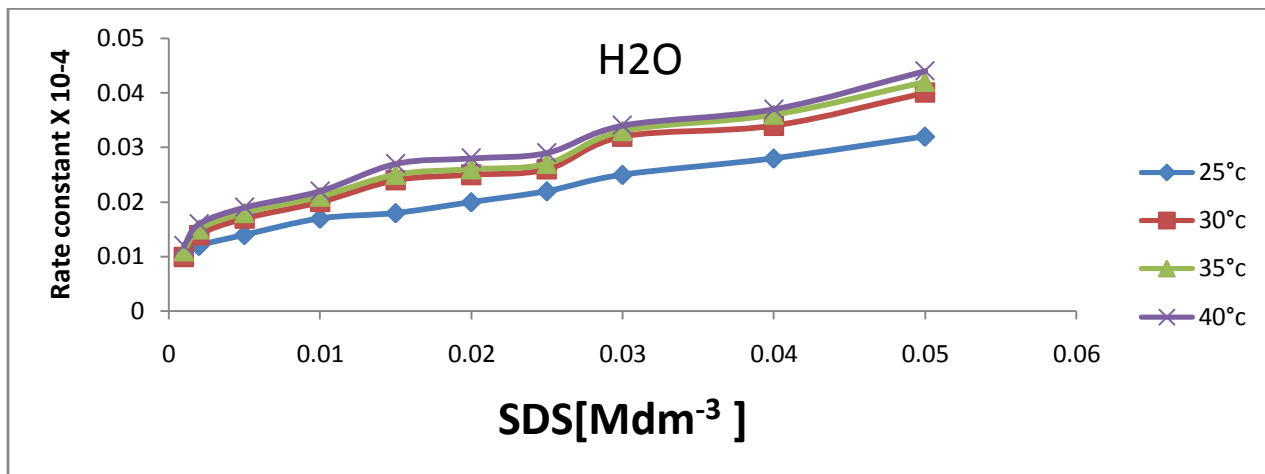| Molar Conc.	Ea KJ/mol				
	H2O				
		10% DIO	**20% DIO**	**30% DIO**	**40% DIO**
0.001	20.53	15.05	46.65	61.2	69.5
0.002	19.59	21.94	63.22	72.5	79.3
0.005	16.22	17.3	59.2	62.4	68.2
0.01	13.41	12.65	48.3	52.1	59.3
0.015	12.22	11.5	34.1	45.2	50.3
0.02	11.6	10.2	28.1	36.5	46.2
0.025	10.1	9.35	20.2	32.1	39.1
0.03	9.4	8.36	15.6	21.2	30.5
0.04	8.31	725	10.6	15.3	21.3
0.05	7.2	6.66	9.5	10.3	13.6

Fig.(1.20) :- Plot of the observed rate constant for the spontaneous hydrolysis of dimethyl phthalate on SDS concentration in water.
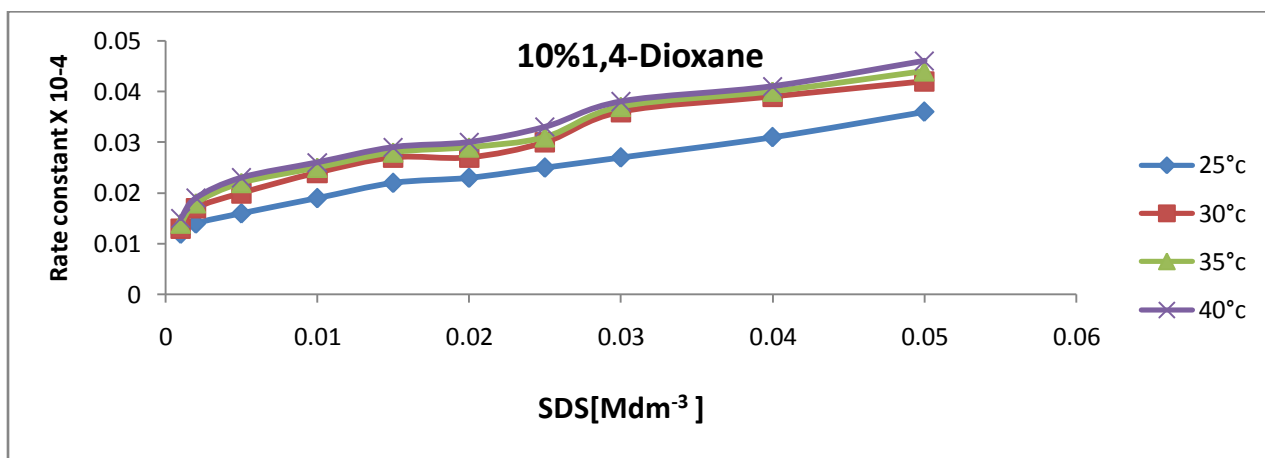

Fig.(1.21) :- Plot of the observed rate constant for the spontaneous hydrolysis of dimethyl phthalate on SDS concentration in 10%-1,4-Dioxane.
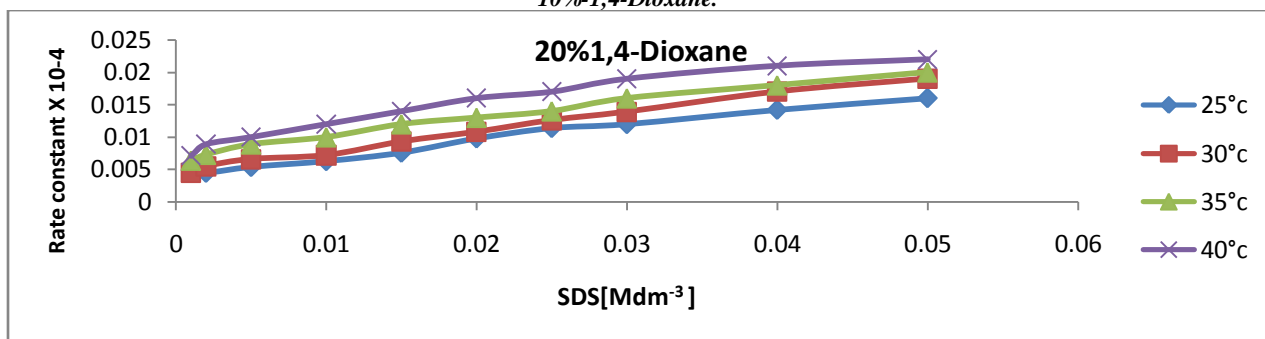

Fig.(1.22) :- Plot of the observed rate constant for the spontaneous hydrolysis of dimethyl phthalate on SDS concentration in 20%-1,4-Dioxane.
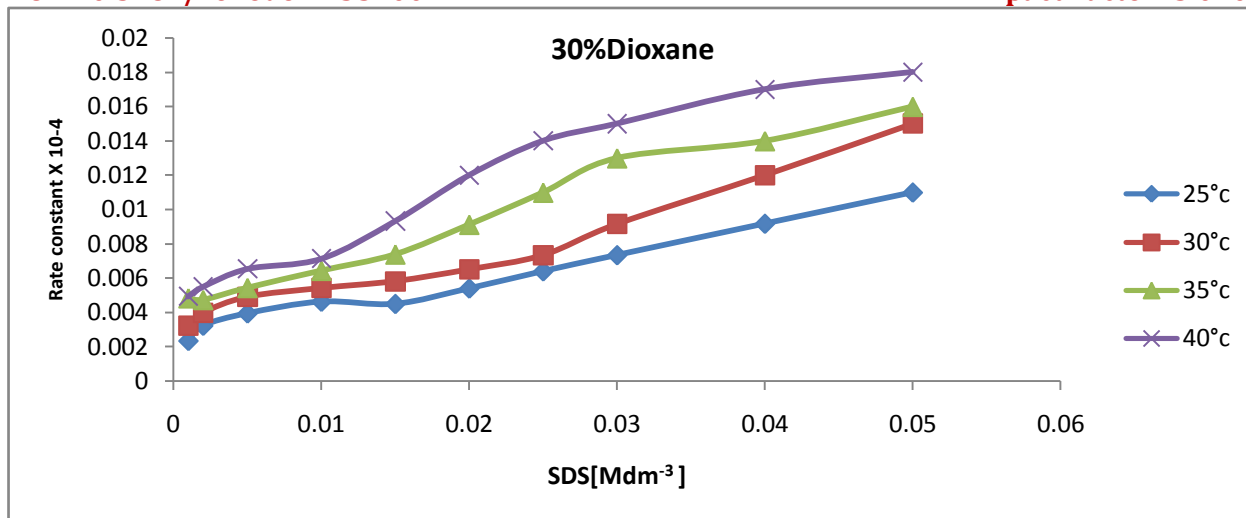
Fig.(1.23) :- Plot of the observed rate constant for the spontaneous hydrolysis of dimethyl phthalate on SDS concentration in 30%-1,4-Dioxane.
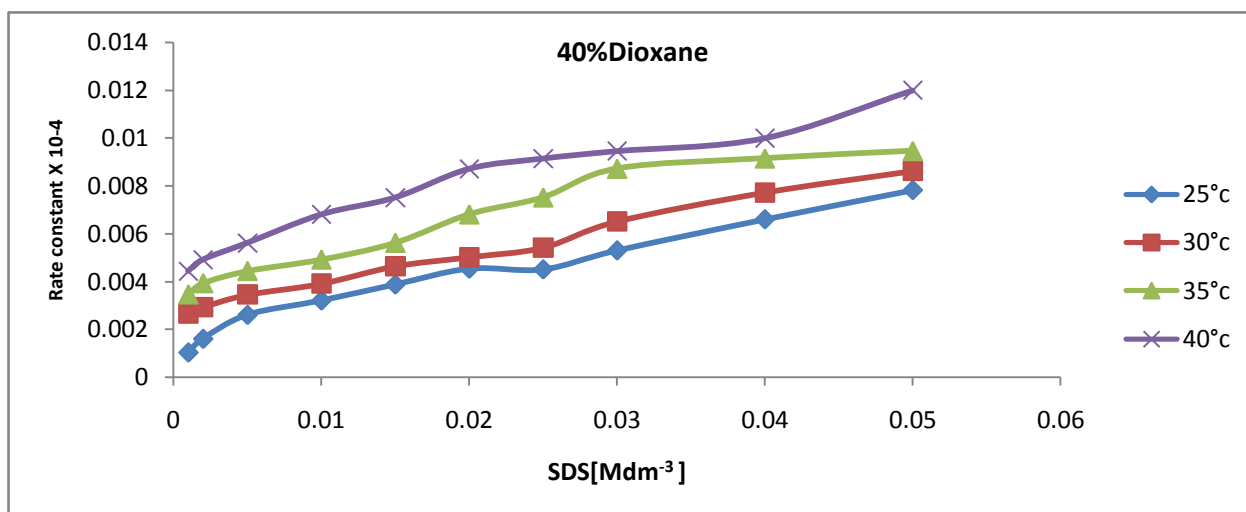

Fig.(1.24) :- Plot of the observed rate constant for the spontaneous hydrolysis of dimethyl phthalate on SDS concentration in 40%-1,4-Dioxane

IV.CONCLUSION

The conductivity is a best technique for the determination of the thermodynamic parameters of micellization of surfactants, and in probing the effect on their structure on the properties of the aggregated formed. The temperature dependence of the CMC and the micellization process has been determined for SDS by measuring the concentration dependence of the conductivity at different temperatures. The obtained results have been used to estimate the thermodynamic parameters of micellization. Experimental data indicate that the CMC of surfactant increases with temperature, ΔG^0 is negative and remains practically constant indicating that the micellizatin process is exothermic in nature ΔH^0 is also negative and decrease with the temperature, indicating that the formation of micelles becomes increasingly exothermic as the temperature increased. The ΔS^0 was positive in all temperature range, decreases with increase in temperature, indicating that the micellizatin process is endothermic. The reaction is accelerated by these surfactants, as compared to the bulk phase in any of water-1,4-dioxane micellar solutions. But the observed rate constant decreases as the volume percentage of solvent increases and observed rate constant increases as the

concentration of surfactant and temperature increases the observed activation energy increases as the volume percentage of solvent increases and decreases as the concentration of surfactant increases.

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