International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Thermodynamic Study of Micellization of Sodium Dodecyl Sulphate Aqueous and Co-Solvent System

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Abstract: ***The critical micelle concentration (CMC) of Sodium Dodecyl Sulphate (SDS) in water and SDS+1-Propanol+water mixture of different composition has been determined in the temperature range 298.15^{0}K,303.15^{0}K,308.15^{0}K and 313.15^{0}K by means of conductance measurement. It has been observed that CMC is temperature dependent and it is found to increase with increase in amount of the co-solvent.the thermodynamic parameters of micellization have been computed and discussed.***

Keywords: Surfactant, micellization, hydrophilic, exothermic

1. Introduction

The role of co-solvents in the process of formation of micelles in surfactant solution is of considerable interest both from fundamental and applied view points since the interfacial phenomena and application of surfactants in many industrial processes largely depend on it [1-5].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 [5,6].

In addition to the counterrion of the solvents ability to from hydrogen bond, changes in the polarity or hydrophobicity of the solvent media are also expected to pay a critical role in determine the micellar behavior of ionic surfactants [7]. Studies on the micellar behavior of ionic surfactants in aqueous and aqueous – organic solvent media, therefore, assume significance in understanding the micellization process.

Anionic surfactants like sodium dodecyl sulphate (SDS) possess valuable characteristics like emulsification, wetting, water proofing, repellence, spreading etc. Which are relevant in several applications such as pharmaceuticals, enhanced oil recovery [8-10]. The importance of studying micellizatio of surfactants in water – organic mixed solvent systems is driven by both fundamental and practical considerations [11]. 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 [11-13].

2. Materials and Method

Sodium dodecylsulphate (SDS), from BDH was recrystallized several times from hot ethanol and dried under vacuum. 1-Propanol [14] by drying over calcium oxide for several days and then refluxing with fresh calcium oxide for four hours and distilled. The distilled 1-PrOH was then shaken with anhydrous calcium chloride and kept for 24 hours finally, the Propanol was redistilled after decantation and middle fraction of the alcohol was collected.

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 thermostate both with the temperature fluctuation within ±0.01^{0}k. 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 measurements have been made at different temperature for the following systems

3. Results and Discussion

The specific conductivity (**K**) of dilute solutions of [SDS] in water, 1-PrOH+H$_2$O, **(0.00,0.10,0.20,0.30, and 0.40)** mass fractions 1-PrOH have been measured as a function of concentration C, at **298.15, 303.15,308.15 and 313.15^{0}K** are present in **Table – IIIA: 1.1,** respectively. The values of specific conductance (**K**) versus [SDS] for the studied systems have been plotted.The SDS concentration at which micellization start is evident from the change in the slope of the plots and that particular concentration is the CMC under the experimental condition. The values of critical micelle concentration (CMC) obtained from these plots are given in **Table- IIIB: 1.1,** respectively for different co- solvent compositions and temperatures.

Table IIIA: (1.1) Specific Conductance,K (μS cm^{-1})as a function of Molar concentration, M (Mole dm^{-3}) of SDS in H_2O & 1-PrOH + H_2O mixture at different temperatures

M (Mole dm^{-3})	Specific Conductance K (μS cm^{-1})			
	Temperature (^{0}K)			
	298.15	303.15	308.15	313.15
H_2O				
0.001	168.4	399.4	406.3	509.3
0.002	302.8	533.8	540.8	643.6
0.003	537.1	769.3	775.3	878.3
0.004	687.4	919.2	925.1	1028.6
0.005	750.7	979.5	997.4	1078.2
0.01	1025.7	1184.7	1237.5	1353.4
0.015	1212.3	1317.3	1424.3	1533.4
0.025	1421.1	1526.6	1634.6	1742.3
0.035	1572.5	1736.3	1786.1	1893.1
0.045	1760.4	1864.4	1973.9	2081.5
0.05	1817.3	1922.5	2032.5	2138.4
10% 1-PrOH +H_2O				
0.001	346.1	431.5	526.8	630.1
0.002	471.6	556.1	649.3	754.4
0.003	825.8	910.6	1003.4	1108.3
0.004	1092.9	1177.4	1271.6	1376.1
0.005	1201.2	1285.3	1378.2	1481.6
0.01	1499.7	1583.2	1676.5	1778.2
0.015	1539.5	1623.7	1716.3	1819.5
0.025	1689.4	1776.3	1869.1	1968.4
0.035	1701.8	1789.1	1881.4	1980.2
0.045	1827.1	1915.4	2006.7	2106.7
0.05	1916.3	2004.6	2094.2	2195.3
20% 1-PrOH +H_2O				
0.001	571.5	656.7	754.2	865.4
0.002	691.7	776.2	874.6	985.3
0.003	996.2	1084.3	1179.4	1290.6
0.004	1093.4	1171.2	1266.1	1377.4
0.005	1191.3	1280.4	1373.5	1485.1
0.01	1601.1	1690.5	1785.7	1897.6
0.015	1730.7	1818.6	1913.4	2025.3
0.025	1805.6	1895.3	1992.1	2101.5
0.035	1849.3	1938.5	2036.2	2146.2
0.045	1995.4	2085.2	2183.5	2293.7
0.05	2016.2	2106.4	2205.2	2315.5
30% 1-PrOH +H_2O				
0.001	542.5	666.4	762.1	863.3
0.002	644.9	768.1	865.5	965.1
0.003	781.6	885.2	983.6	1099.5
0.004	901.2	1007.6	1106.2	1205.8
0.005	977.3	1084.7	1185.3	1271.2
0.01	1151.1	1260.5	1359.1	1455.7
0.015	1187.3	1296.1	1395.4	1491.3
0.025	1225.7	1334.6	1434.8	1528.1
0.035	1236.1	1345.4	1447.3	1541.6
0.045	1315.8	1424.5	1525.2	1621.4
0.05	1342.5	1452.3	1554.4	1650.5
40% 1-PrOH +H_2O				
0.001	568.1	665.4	747.6	849.3
0.002	661.9	759.6	846.2	948.1
0.003	821.4	919.2	1008	1108.4
0.004	902.3	1000.4	1088.6	1189.2
0.005	951.4	1087.1	1194.5	1266.8
0.01	1146.3	1245.6	1333.1	1435.1
0.015	1174.8	1273.5	1361.7	1463.5
0.025	1200.3	1298.4	1387.2	1490.4
0.035	1225.4	1323.2	1413.6	1516.2
0.045	1299.7	1398.1	1488.4	1591.3
0.05	1331.4	1433.7	1521.2	1623.5

Table III B (1.1): Values of Critical Micelle Concentration (CMC), Degree of Counter-ion Association (α) and Thermodynamic Parameters of Micellization for SDS in Water and 1-PrOH + H_2O Mixtures at Different Temperatures

T (^{0}K)	CMC * 10^3 (mol dm^{-3})	α	$-\Delta G^0_{mic}$ (kJmol^{-1})	$-\Delta H^0_{mic}$ (kJmol^{-1})	ΔS^0_{mic} (kJmol^{-1})	ΔG^0_{trans} (kJmol^{-1})	$\Delta C_p{}^0{}_{mic}$ (kJmol^{-1})
H_2O							
298.15	8.14	0.36	28.92	7.34	72.38		-63.345
303.15	8.38	0.34	29.64	7.68	72.44		
308.15	8.62	0.33	30.18	7.98	72.06		
313.15	8.92	0.32	30.71	8.29	71.59		
10% 1-PrOH +H_2O							
298.15	7.82	0.36	29.08	5.92	77.67	-0.163	-30.37
303.15	7.96	0.37	29.32	6.08	76.63	0.324	
308.15	8.2	0.38	29.49	6.25	75.42	0.696	
313.15	8.4	0.4	29.5	6.37	73.85	1.212	
20% 1-PrOH +H_2O							
298.15	8.67	0.32	29.36	6.57	76.45	-0.442	-31.36
303.15	9	0.33	29.52	6.75	75.11	0.122	
308.15	9.2	0.34	29.73	6.93	73.98	0.457	
313.15	9.4	0.37	29.58	7.03	72	1.136	
30% 1-PrOH +H_2O							
298.15	8.42	0.29	30.01	10.89	64.12	-1.091	-56.63
303.15	8.65	0.3	30.22	11.19	62.76	-0.578	
308.15	8.98	0.31	30.37	11.49	61.25	-0.184	
313.15	9.6	0.33	30.21	11.73	59.01	0.502	
40% 1-PrOH +H_2O							
298.15	7.66	0.278	30.62	15.14	51.93	-1.705	-78.56
303.15	8.24	0.305	30.34	15.4	49.25	-0.696	
308.15	8.85	0.31	30.44	15.87	47.27	-0.247	
313.15	9.12	0.32	30.62	16.29	45.74	0.096	

The critical micellar concentrations (CMC) were determined from the inflections in the plots of conductivity as a function of the SDS concentration (C). The data points above and below the inflection are fitted to two linear equations and the CMC was obtained from the intersection. This method is found to be reliable and convenient for the present systems because of the significant variations of conductivity with surfactant concentration in the pre and post micellar regions according to William's method [15]. Which allow us to draw two unambiguous straight lines above and below the CMC.

It is found that CMC value increases on increasing the temperature for a given solvent system. In the case of aquo-organic additive system CMC gradually increases with the increasing the amount of co-solvents and temperature of the organic substances chosen for this study **(Table-IIIA).** In the present study the CMC value of SDS in pure water appear to be in good agreement with the literature values [16-17]. On mixing 1-PrOH, to be an aqueous surfactant solution, an increase in CMC irrespective of the nature of the surfactant as reported in **Table-IIIB.** The decrease of dielectric constant of medium appears micellization by increasing mutual repulsion of ionic heads in the micelle, hence increasing the CMC [18].

The degree of counter – ion dissociation constant (β) of surfactant, SDS, was calculated from the ratio of slopes of the plots at post micellar and pre micellar regions. The degree of counter – ion association constant (α) is given by.

$$\alpha = (1 - \beta) \quad \text{----------} \ (1)$$

The values of α for the studied systems are also given in **Table – IIIB** The values of α roughly decreases with the increase of temperature in SDS+ H_2O system. As is observed in the case of 1-PrOH+H_2O decrease in α with respect to the solvent composition is expected due to decrease in the polarity of the bulk phase caused by the addition of cosolvents [19-20].

4. Thermodynamic Properties of Micellization

Phase- separation and mass-action approaches present two models which have got wide acceptance for the interpretation of energetic of micellization. For the ionic surfactants, however, the mass-action approach is usually preferred [21] and various thermodynamic parameters may be deducted from the temperature dependence of the CMC values. According to mass action model, the standard Gibbs free energy of micellization (ΔG^0_{mic}) for ionic surfactant solutions were calculated using following equation [22, 23].

$$\Delta G^0_{mic} = RT\ (1+\beta)\ \text{In CMC} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

$$\Delta G^0_{mic} = 2.303\ RT\ (2-\alpha)\ \log \text{CMC}$$

$$\Delta G^0_{mic} = 2.303\ RT\ (2-\alpha)\ \log X_{CMC} \ \ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Where α is counter-ion association constant X_{CMC} is the surfactant mole fraction at CMC. R is gas constant (8.314JK^{-1} mol^{-1}) and T is the absolute temperature .The mole fraction X_{CMC} was calculated the equation

$$Xcmc = \left[\frac{Xcmc/cmc}{(CMC + \text{Number of moles of solvent})}\right] \ldots\ldots(4)$$

The corresponding entropy and enthalpy of micellization were calculated from the following expression respectively.

$$\Delta S^0_{mic} = \left[\frac{-d\,(\Delta G^0_{mic})}{dT}\right]_p \ldots\ldots\ldots \ (5)$$

$$\Delta H^0_{mic} = -T^2\left[\frac{\partial(\Delta G^0_{mic})}{\partial T}\right]_p \ldots\ldots\ldots\ldots \ (6)$$

Further, the Gibbs energy of transfer values (ΔG^0_{trans}) which can be accounted for the effect of co solvent on the micellization process was estimated through the relation [24-25].

$$\Delta G^0_{trans} = \Delta G^0_{MIC}\ (w+cos) - \Delta G^0_{MIC}(w) \ldots\ldots\ldots\ldots\ldots(7)$$

Where, $\Delta G^0_{MIC}(w)$ and ΔG^0_{MIC} (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^0_{MIC} can be obtained from the slops of the plot of ΔH^0_{MIC} versus temperature.

$$\Delta C^0 p_{mic} = \left[\frac{\partial(\Delta H^0_{mic})}{\partial T}\right]_p \ldots\ldots\ldots\ldots\ldots\ldots \ (8)$$

The values of thermodynamic parameters, of micellization ΔG^0_{MIC} , ΔH^0_{MIC} , ΔS^0_{MIC} and ΔG^0_{trans} and ΔCp^0_{MIC} calculated using equations (2) to (7) for the studied surfactants (SDS) are presented in **Table IIIB (1.1).** The ΔG^0_{MIC} values in all the cases except 1-PrOH+H_2O system are negative and become less negative with the increase in the cosolvent constant in the mixed media. At a fixed solvent composition, the values become slightly more negative with the rise in temperature, and remain practically constant in the temperature range. The negative value is like with reported by [26-27]. From the results presented in **Table IIIB (1.1)** it can be generalized that the micellization is exothermic and spontaneous for SDS surfactant in the all temperature range studied.

The standard entropy of micellization (ΔS^0_{MIC}) though positive in all temperature range, decreases with increase in temperature, indicating that the micellizatin process is endothermic.

The values of ΔH^0_{MIC} were negative and decrease with the increase in temperature indicating that the micellisation process increasingly exothermic for ionic surfactant, SDS. The positive value of ΔG^0_{trans} indicates that, it is responsible for the delay in the micellization of surfactants in the mixed media [28]

5. Conclusion

The micellization behavior of anionic SDS in water and mixed media have been investigated by conductometric method in the temperature range of 298.15 to 313.15^{0}K. The conductivity is a useful technique for the determination of the thermodynamics parameters of micellization of surfactants, and in probing the effect of 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 result has been used to estimate the thermodynamic parameters of micellization. Experimental data indicate that the CMC of surfactant increases with temperature, ΔG^0_{mic} is negative and remains practically constant indicating that the micellizatin process is exotherming in nature

ΔH^0_{mic} is also negative and decrease with the temperature, indicating that the formation of micelles becomes increasingly exothermic as the temperature increased.

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