



Study of Conductance and Micellar behaviour of anionic surfactant (KDeS) in (alcohol+ water) Systems at a temperature range of 30⁰C-45⁰C

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Abstract

Surface active agents find applications in food and agriculture, lubricants, ore beneficiation, detergents, textile, rubber and plastics, pharmaceuticals, biological modeling, building materials and soil sciences etc. Micelles are not formed in very dilute solutions. On increasing the concentration above CMC nearly all additional solute forms micelles. The variation in CMC of surfactants depends upon the number and chain length of monomers and properties of counter ions. As an approximation, higher the CMC value, broader is the concentration range for this transition. Above all CMC parameters vary according to whether the solute is monomer or aggregation. Since above the CMC, the activity of monomers rises very slowly, so it is also a measure of the concentration at which the thermodynamic activity of the monomers and therefore, its net surface activity and absorbability to various substrates, level off to a nearly constant value. In order to understand the colloidal behaviour of anionic surfactants in mixed solvents, a systematic study on the conductance of Potassium decyl sulfate in aqueous and alkanols have been made with a view to determine whether or not the micellar aggregates are formed for such systems. CMC are determined, if any by the graphs and investigate the validity of various equations in these systems.

Key Words: Potassium decyl sulfate, CMC, Micelles, conductivity, anionic surfactants, alcohol-water system.

Introduction

CMC is probably the simplest method of characterizing the micellar behaviour of surface active agents (solutes). The micellar behaviour determines the industrial application and biological activity of surface active agents. Not only is that, it is also a measure of the structurally interesting solute-solvent and solute-solute interaction. The usefulness of CMC values in various qualitative and quantitative investigations involving surface active agents can be gauged from the fact that the surface and interfacial activity of the amphipathic (polar and non-polar) monomers is closely reflected in CMC values. Diversified uses of surface active agents depend on their tendency to aggregate in a particular solvent. The aggregation of monomers of surface active agents in some solvents forms particles of colloidal dimensions, called micelles. The concentration at which the micelle formation takes place is called critical micelle concentration (CMC)

Influence of alcohols on the micellar behaviour of surfactant solution has received considerable attention in recent years. The effect of organic additives on micellar behaviour of ionic and nonionic surfactants in water has been well studied by some authors (1-2), with the effects that aliphatic alcohols have been being of particular interest, for the addition of aliphatic alcohols to aqueous surfactant solutions. Shinoda (3) has described a linear relationship between their critical micelle concentration,

decreasing power, and the number of carbon atoms in the alcohol molecules. Studies on Potassium dodecylbenzene sulphonate has been reported by Bahadur and Chand (4).

Several reviews exist on micellization of surfactants in aqueous (5-8) and non aqueous (9-13) media. However, among the limited studies on non aqueous systems, which in common practice refer to surfactant solution in solvents of low dielectric constants, studies on surfactant behaviour in solvents of media and high dielectric constants have also been made (14-15). Moshe and Magdassi (16) studied the surface activity and micellar properties of anionic surfactants and found that surface activity of gemini surfactant was higher as compared to mono alkyl analogues. Micelle formation in aqueous solution is well known to be affected by a number of environmental factors such as pH, ionic strength, temperature and the presence of inorganic and organic additives.

The micelle formation in an aqueous solution is known to be affected by organic additives and there have been many investigations concerning the effects of organic additives on the CMC of anionic surfactants (17-18). Mesa (19) observed the dependence of CMC on temperature and reported the existence of minimum CMC value at a temperature which is peculiar to the system.

From the detailed literature survey on the effect of additives, particularly alcohols and other related substances, which markedly influence the hydrophobic effect and the micelle formation; it seems that there exist two different views regarding the effect of additives on micelle formation. The first deals with the solubilization of alcohols in micelle and the second view are that additives have direct effect on the water structures. The effect of terbium chloride on the micellization properties of Potassium decylsulfate and Potassium dodecylsulfate solutions was studied by Valente and coworkers (20). Recently Gebicka and Banasiak (21) reported interaction of anionic surfactant with methemoglobin.

Materials and Methods

The surface active agents were procured from various organizations. Potassium decyl sulfate (Anionic) surfactant KDeS used was of high degree of purity (checked by observing no minima in γ vs. $\log C$ plots). The CMC of these surfactants in water were found closer to the literature value (1). Most of the chemicals used in the study were A.R grade, except a few which were laboratory chemicals of high grade purity. These were used after proper purification. The purity of organic liquids was checked by measuring physical constants like boiling point, density, refractive index and viscosity. Triple distilled water and pyrex glass assembly were used throughout the experiment. Fresh solutions of surfactants were employed for all measurements.

A digital conductivity meter model CM-180 (Elico private limited) and a dipping type conductivity cell with plantinized electrodes were used for measuring the conductance of the surfactant solutions. The experiments were carried out in a thermostat at constant temperature $\pm 0.05^\circ\text{C}$. The cell constant (1.01) for the cell was determined by using standard solutions of KCl of A.R grade. All data were obtained by concentration runs i.e. solutions were diluted by adding the solvent into the clean dry cell and the conductance was measured. Several measurements were made to ascertain the reproducibility of results and the conductivity data were reproducible to 0.5%.

The conductance behaviour of all these surfactants in solutions has been studied (6) by applying the general equation for their conductance behaviour in solution:

$$\log \Lambda_M = A + B \log_{10} C$$

Where A and B are constants and C is the concentration of the surfactants in mole litre⁻¹ and Λ_M is the molar conductivity in ohm⁻¹mole⁻¹cm². The value of $\log \Lambda_M$ for zero values of $\log C$ (i.e. C=1) have been calculated by extrapolation of $\log \Lambda_M$ vs. $\log C$ curves which signify for the constant A as $\log \Lambda_{(C=1)}$.

Results and Discussion

The conductivity (κ) in $\text{ohm}^{-1}\text{cm}^{-1}$ of surfactant Potassium decyl sulfate (KDeS) has been measured for different concentration of methanol, propanol-1, butanol-1 and t-butanol in presence of water at 30°C . The conductivity of KDeS (Table-1) has also been determined for 0.5M alkanol+water systems within the temperature range 30°C to 45°C . The conductivity values for all the alkanol+water systems increase with increase in KDeS surfactants concentration and the temperature as well. For a given KDeS concentration an increase in conductivity values with increasing concentration of methanol and propanol-1 has been observed whereas a decrease in conductivity has been noticed with increasing concentration of butanol in water. In methanol+water and propanol-1+water systems the increase in conductivity values has been explained in term of release of counter ions and partly due to liberation of surfactants ions whereas in case of butanol-1 and t-butanol a decrease has been assigned due to relative solubility of butanol in water.. The CMC values of KDeS in 0.5M butanol+water systems at different temperature have also been shown in Fig.1 The CMC values of KDeS in different alkanol+water systems at 30°C are reported in Table-2.

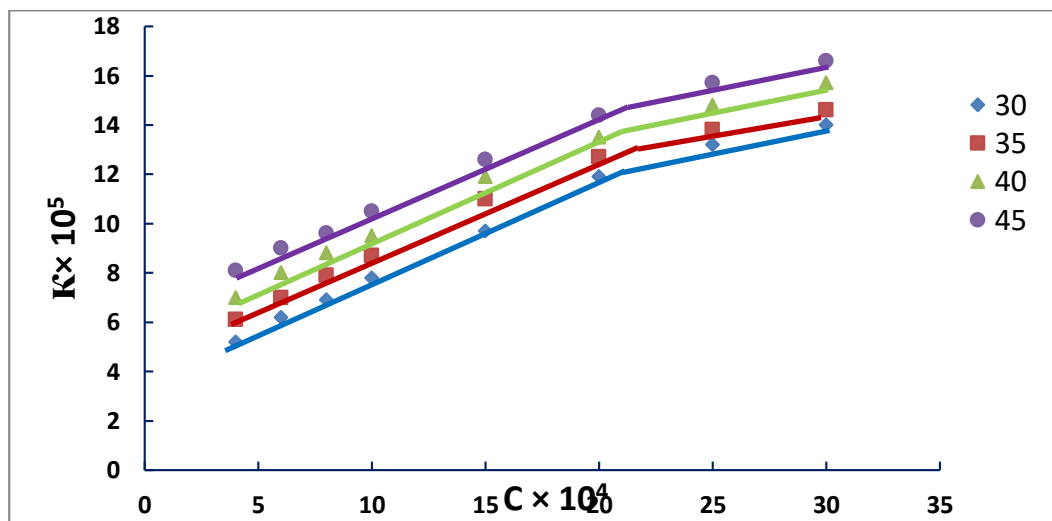


Fig.1: Plots of conductivity (κ) vs. molar concentration (C) of KDeS in 0.5M butanol-1+water systems at different temperature.

The plots of CMC for different alkanol+water systems for the surfactant KDeS (Fig.2) show an increase in CMC values with increasing methanol and propanol-1 concentration in water and a decrease in CMC for butanol+water systems. Furthermore, for propanol-1+water system CMC at first decreases and after passing through a minimum it increases on increasing propanol-1 concentration. The driving force of micellization is the hydrophobic effect and opposing micelle formation is the electrostatic repulsion between similar charged polar head groups of the surfactants.

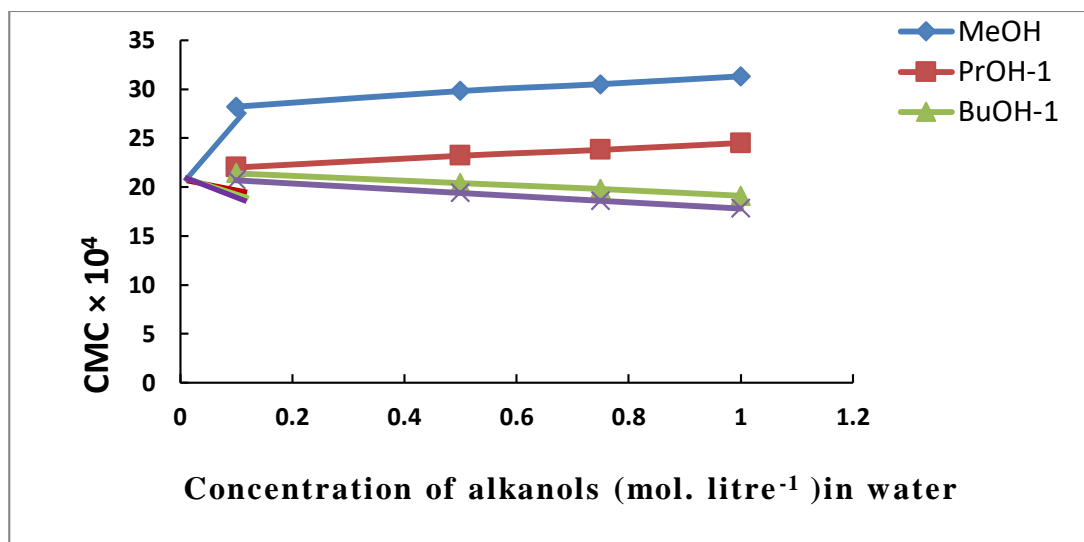
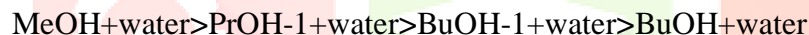


Fig.2: Effect of concentration of added alkanols on CMC of KDeS at 30°C.

The decrease in CMC is thus due to incorporation of the alkanol into the micelle whereas an increase may be assigned due to the fact that alkanol disrupts the water structure. Initial decrease in CMC on addition of propanol-1 may result from the penetration of propanol-1 molecules into the micelle. At the minimum CMC, micelles become saturated with propanol-1, additional propanol-1 molecule moves into solvent resulting it to be more hydrophobic. This causes an increase in CMC on further addition of propanol-1.

However in butanol increasing hydrophobic character in alkanol chain prevents them to get solubilized in water and thus only decreasing effect has been observed. For a given conc. of alkanol, the CMC values of KDeS exhibit the order:



The CMC values however increase with increasing temperature of each system studied and can be satisfactorily explained in terms of the dominating behaviour of increased kinetic energy of monomer over the aggregation of the hydrocarbon chain. The similar trend has also been observed in KDeS for all the system as well as at different temperatures. This might be due to same number of carbon atoms in hydrocarbon chain (C=10) of both the surfactants i.e. KDeS and KDeS. However CMC values for KDeS are relatively lower than KDeS under similar conditions. The values of $\log \Lambda_M$ and $\log C$ for KDeS and KDeS in all the alkanol+water systems and at different temperatures confirm the validity of equation.

TABLE-1

Conductivity (κ) for potassium decylsulfate (KDeS) in 0.5M alkanol+water systems at different temperatures.

Alkanol + water system	Conc. of KDeS in mol.litre ⁻¹	$\kappa \times 10^5 (\text{ohm}^{-1} \text{cm}^{-1})$			
		30°C	35°C	40°C	45°C
5M PrOH-1 + water	0.0004	12.7	13.8	14.1	14.8
	0.0006	14.5	14.9	15.7	16.5
	0.0008	15.3	15.8	16.6	17.2
	0.0010	15.9	16.5	17.2	18.1
	0.0015	17.8	18.5	19.3	19.9
	0.0020	19.9	20.6	21.1	22.0
	0.0025	20.8	21.4	22.5	23.3
	0.0030	21.6	22.3	23.4	24.2
0.5M BuOH-1+ water	0.0004	5.2	6.1	7.0	8.1
	0.0006	6.2	7.0	8.0	9.0
	0.0008	6.9	7.9	8.8	9.6
	0.0010	7.8	8.7	9.5	10.5
	0.0015	9.7	11.0	11.9	12.6
	0.0020	11.9	12.7	13.5	14.4
	0.0025	13.2	13.8	14.8	15.7
	0.0030	14.0	14.6	15.7	16.6
0.5M t-BuOH + water	0.0004	3.1	4.5	5.7	7.7
	0.0006	4.8	5.7	7.2	8.1
	0.0008	5.6	6.7	7.4	8.9
	0.0010	6.3	7.2	8.1	9.4
	0.0015	8.2	9.3	10.4	11.2
	0.0020	10.5	11.2	12.3	13.1
	0.0025	11.2	12.4	13.1	14.4
	0.0030	12.4	13.6	14.6	15.7

TABLE-2

Values of CMC for potassium decylsulfate (KDeS) in different alkanol+water systems at 30°C obtained by κ vs. C plots.

Concentration of alkanol in mol.litre ⁻¹	CMC $\times 10^3$ (mol.litre ⁻¹)			
	MeOH	PrOH-1	BuOH-1	t-BuOH
0.10 M	2.82	2.20	2.14	2.07
0.50 M	2.98	2.32	2.04	1.94
0.75 M	3.05	2.38	1.98	1.86
1.00 M	3.13	2.45	1.91	1.78

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