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A comparative study of Critical Micelle Concentration (CMC) and Free Energy of Micellization (ΔG^o_m) of cationic surfactant (Dodecyltrimethylammonium Bromide, DTAB) and anionic surfactant (Sodiumdodecyl Sulphate, SDS) in different composition of methanol-water mixed solvent media by conductometric method at 308.15 K

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Abstract

Precise measurements on the specific conductivity of cationic surfactant (Dodecyltrimethylammonium Bromide) and anionic surfactant (Sodiumdodecyl Sulphate) in methanol-water mixed solvent media containing 0.1, 0.2 and 0.3 volume fractions of methanol are reported at 308.15 K. Specific conductivities of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate increase with increase in concentration and decrease with increase in the volume fractions of methanol. Critical micelle concentration (cmc) increases with increase in volume fraction of methanol in case of both surfactants. Free energy of micellization (ΔG^o_m) has been calculated. Increase in cmc with increase in volume fractions of methanol has been explained in terms of breaking of structure of water due to co-solvent effect.

Keywords: Critical micelle concentration; methanol-water mixed solvent media; Specific conductivity; Dodecyltrimethylammonium Bromide; Sodiumdodecyl Sulphate

1. Introduction

Surfactants have various applications to different daily use products and in research fields [1]. Zana and coworkers [2-6] have reported extensive studies on the effect of the linear alcohols ethanol to hexanol on the critical micelle concentration (cmc), micelle molecular weight and degree of ionisation. The behaviour of Sodiumdodecyl Sulphate micelles in the presence of n-alcohols has been extensively investigated [7-14]. According to Rubio et al. [13] moderately hydrophobic alcohols in low concentration promote micellization probably by residing at the micellar surface and reducing unfavourable water hydrocarbon contacts. However, at higher concentrations these alcohols destabilize micelles by displacing water from the surface, therefore decreasing its effective dielectric constant, increasing head group repulsions, and disrupting surfactant packing. Since water-alcohol- surfactant systems are frequently used as media in the studies of chemical equilibria and reaction rates, it is essential to investigate the effect of the nature of the alkyl groups in the alcohol on the cmc of the surfactants. Addition of alcohols to aqueous solutions of surfactants has allowed the investigation of the effect of hydrophobic interactions on the micellar structure [15].

Almgren et al. [16] investigated on the effect of formamide and other solvents, including dimethylsulfoxide and dimethylacetamide on the micelle formation of Sodiumdodecyl Sulphate. They observed the reduction of both critical micelle concentration (cmc) and mean aggregation number of Sodiumdodecyl Sulphate micelles upon the addition of formamide. The gradual replacement of water with other organic polar solvent allows one to explore a wide bulk phase polarity range and its influence on micellization. Addition of small amount of an organic solvent has been known to produce marked changes, in the critical micelle concentration (cmc) of ionic surfactants due to tendency of added organic solvent either to break or make the water structure through solvation of hydrophobic tail of the surfactant by the hydrocarbon part of the organic solvent [17-18]. Akbas et al. [19] carried out an investigation on the effect of ethanol and ethylene glycol on the cmc of Cetyltrimethylammonium Bromide. They observed that cmc decreases upon the addition of ethanol and ethylene glycol.

The aim of the present work is to investigate the effect of methanol on the micellar behaviour of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate at 308.15 K by conductance measurement.

2. Experimental Section

Methanol (Merck, India) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.77723 ± 0.00004 g.cm^{-3} and a co-efficient of viscosity of 0.47424 ± 0.00005 mPa.s at 308.15 K; these values are in good agreement with the literature values [20]. Triply distilled water with a specific conductance less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents. The physical properties of methanol-water mixed solvents used in this study at 308.15 K are shown in Table 1 and those values are matched with the published works [21-23]. The relative permittivity of methanol-water mixtures at the experimental temperatures were obtained by regressing the relative permittivity data as function of solvent composition from the literature [24].

Dodecyltrimethylammonium Bromide (98% pure) and Sodiumdodecyl Sulphate (98% pure) were obtained from Loba Chemi, India and were dried in oven for one hour before use.

Solutions were prepared of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate by weighing appropriate amount in an electronic balance, (Afcoset-ER120A) with a precision of 0.0001g. Conductivities were measured using digital conductivity meter (306) of Systronics which is a microcontroller based instrument for measuring specific conductivity of solutions. The accuracy in conductance measurements is ± 1%. The cell was calibrated by the method of Lind and co-workers [25] using aqueous potassium chloride solution. Measurements were carried out in a jacket containing conductivity cell of cell constant 1.002 cm^{-1}. Water was circulated in the jacket from thermostat and the temperature was maintained within ± 0.1ºC. The details of the experimental procedure have been described earlier [26-27]. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the electrolyte solutions.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed in three replicates.

3. Result and Discussion

Conductivity measurements are carried out in 0.1, 0.2 and 0.3 volume fractions of methanol in methanol-water mixed solvent media for Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate at 308.15 K in order to evaluate the cmc. The plots between specific conductance and concentration of surfactants solution in methanol-water mixed solvent media at 308.15 K is shown in fig. 1 to fig. 6. The critical micellar concentrations (cmc) of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate are found very easily from conductometry. These are obtained from the inflections in the plots of specific conductivity versus surfactant concentration. The data points above and below the inflection are fitted to two linear equations, and the cmcs are obtained from the common intersection. This method is found to be reliable and convenient for the present system because of the significant variations of specific conductivity with surfactant concentration in the pre- and postmicellar regions which allowed us to draw two unambiguous straight lines above and below the cmc. Temperature dependence values of cmc and α (degree of ionisation) can be used to obtain information about thermodynamics of micellization. Degree of ionisations are calculated by taking ratio of slope of line after micelle and the slope of line before micelle. The standard Gibbs free energy of micellization for ionic surfactant (ΔG^o_m) are calculated from the relation derived for the charged phase separation model of micellization[28-29]. This relation is given by

$$\Delta G^o_m = (2-\alpha)\, R\, T\, \ln(\chi_{cmc}) \tag{1}$$

χ_{cmc} represents cmc in mole fraction. The values of cmc and standard free energy of micellization of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate are listed in Table 2. With the increase in the volume fraction of methanol, values of cmc for both surfactants increases. This increase in values of cmc is also explained by the decrease in negative values of standard free energy change. Fig. 7 shows the effect of volume fraction of methanol on the free energy change for the micellization of Dodecyltrimethylammonium Bromide at 308.15 K. It can be observed that the volume fraction of methanol in water increases the negative values of free energy of micellization (ΔG^o_m) decreases thus making less favourable for the micelle to form. Similar behaviour can be seen in case of Sodiumdodecyl Sulphate (fig. 8).

It is well known that addition of solvents, which act as water structure breakers decrease the hydrophobic effect resulting into an increase in the cmc of ionic surfactants [30]. Breaking of water structure by methanol would facilitate interactions between the hydrophobic tail of the surfactant molecules and the hydrophobic part (methyl group) of the methanol and consequently, the local concentration of methanol molecules around the surfactant monomers becomes larger than the average of the bulk. Solvation of the surfactant molecules by the hydrophobic part of the organic solvent would, therefore, lead to delaying the aggregation of the surfactant monomers to form micelles and hence the increase in the cmc of the surfactant.

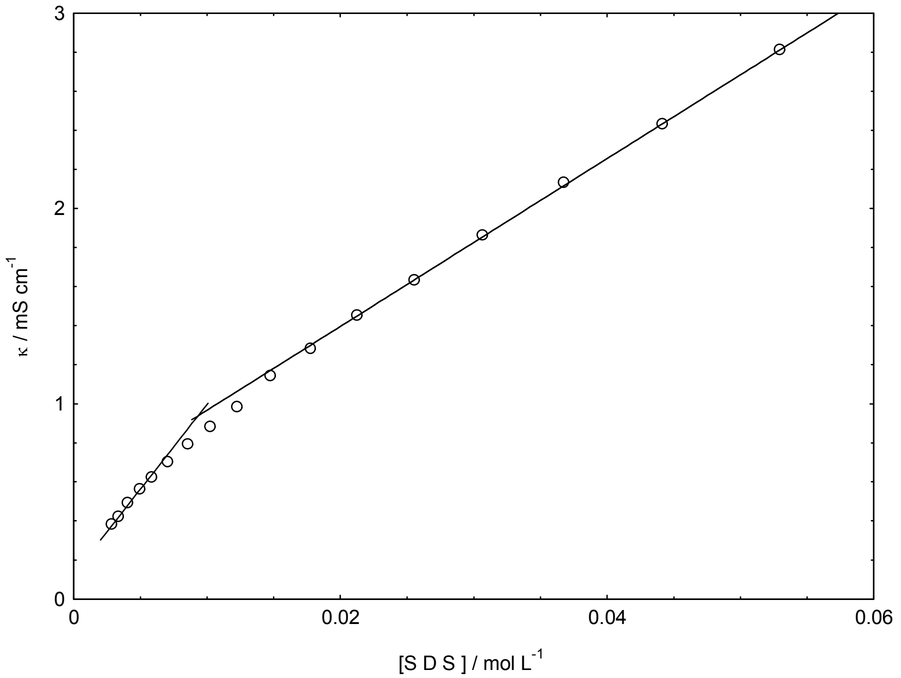

Fig. 1: Variation of specific conductance with molar concentration of Sodiumdodecyl Sulphate (SDS) in methanol water mixed solvent media containing 0.1 volume fraction of methanol at 308.15 K

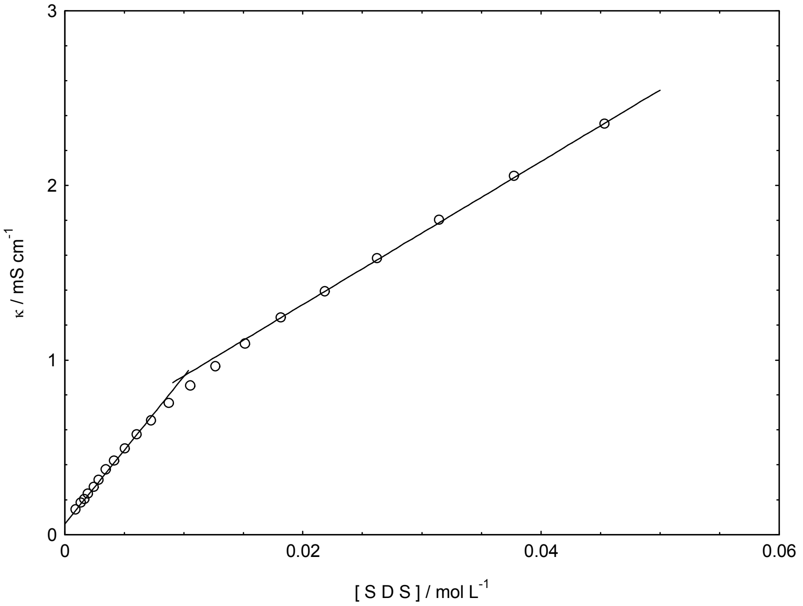

Fig. 2: Variation of specific conductance with molar concentration of Sodiumdodecyl Sulphate (SDS) in methanol water mixed solvent media containing 0.2 volume fraction of methanol at 308.15 K.

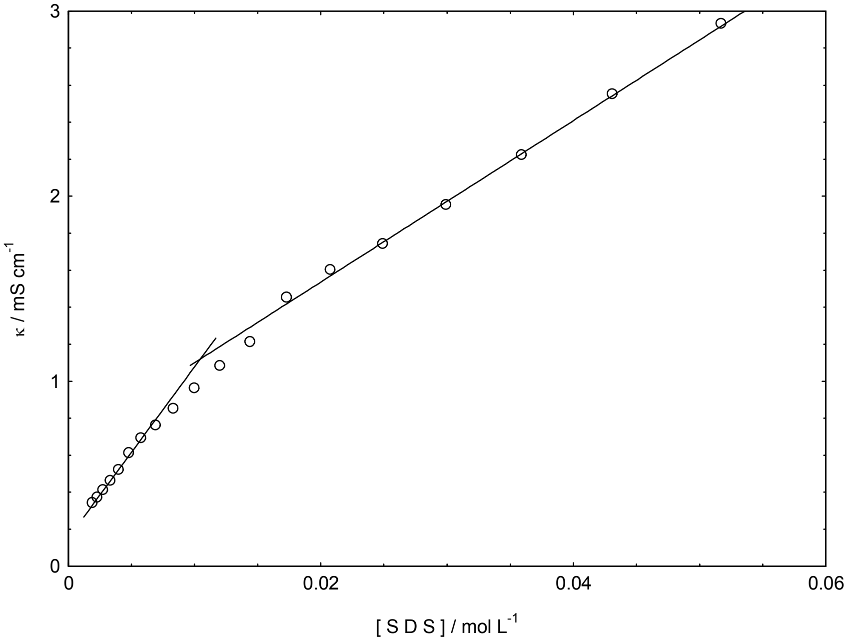

Fig. 3: Variation of specific conductance with molar concentration of Sodiumdodecyl Sulphate (SDS) in methanol water mixed solvent media containing 0.3 volume fraction of methanol at 308.15 K.

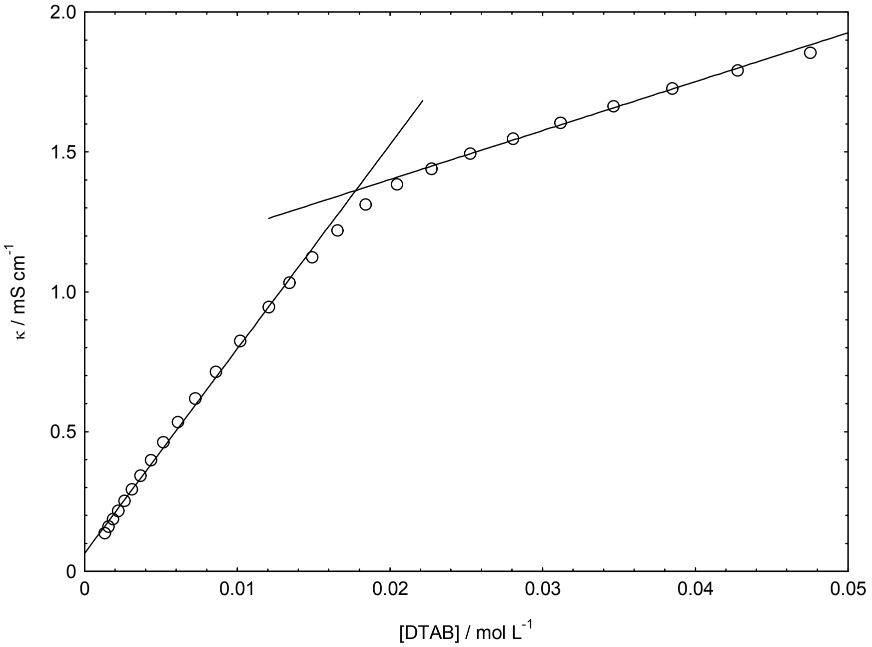

Fig. 4: Variation of specific conductance with molar concentration of Dodecyltrimethylammonium bromide (DTAB) in methanol water mixed solvent media containing 0.1 volume fraction of methanol at 308.15 K.

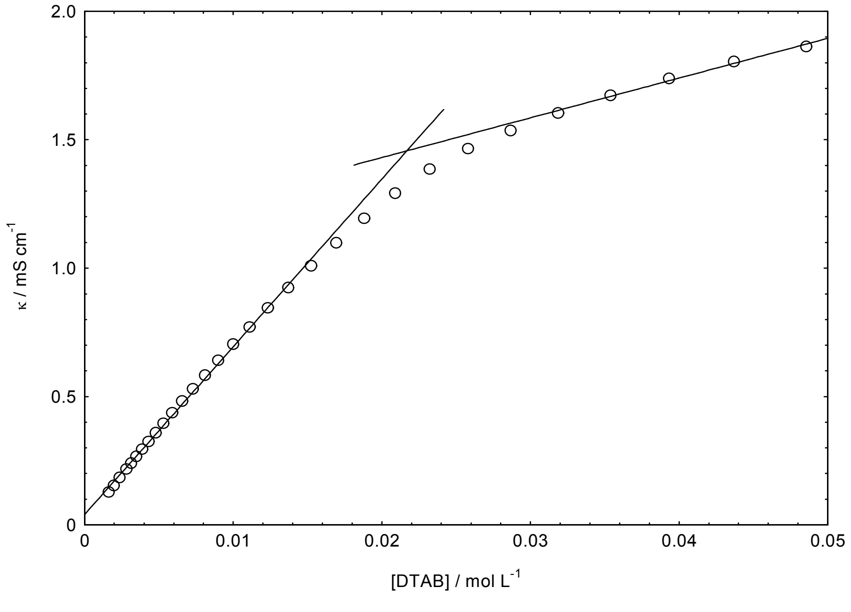

Fig. 5: Variation of specific conductance with molar concentration of Dodecyltrimethylammonium Bromide (DTAB) in methanol water mixed solvent media containing 0.2 volume fraction of methanol at 308.15 K.

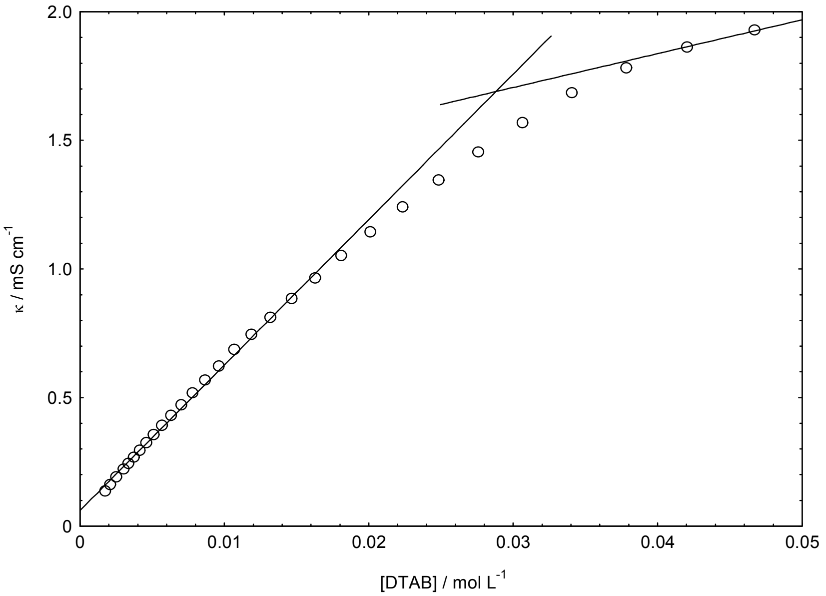

Fig. 6: Variation of specific conductance with molar concentration of Dodecyltrimethylammonium Bromide (DTAB) in methanol water mixed solvent media containing 0.3 volume fraction of methanol at 308.15 K.

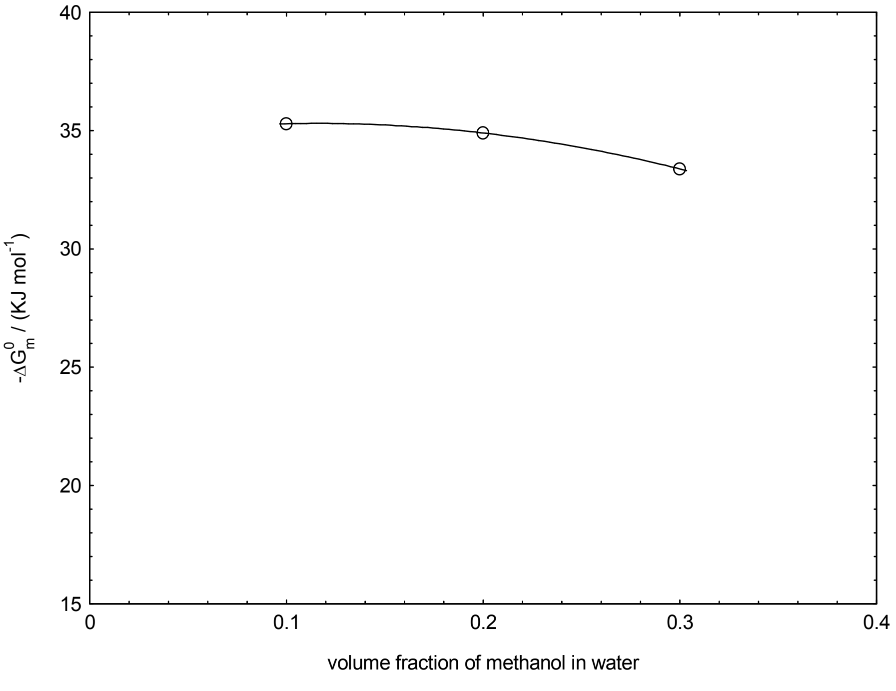

Fig. 7: Variation of standard free energy change of micellization of Dodecyltrimethylammonium Bromide (DTAB) with volume fractions of methanol in water.

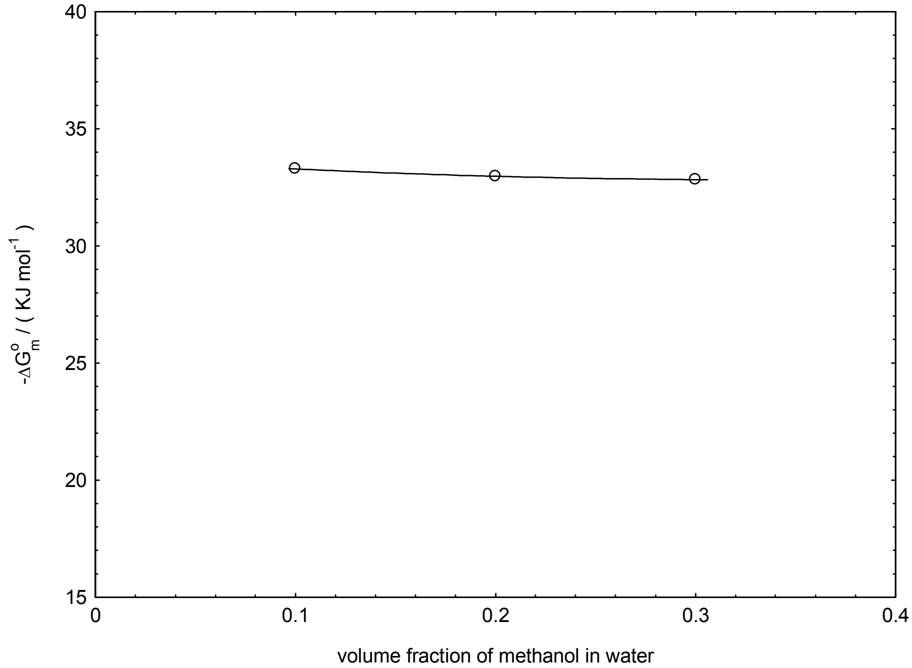

Fig. 8: Variation of standard free energy change of micellization of Sodiumdodecyl Sulphate (SDS) with volume fraction of methanol in water.

Table 1: Properties of Methanol-Water Mixtures Containing 0.1, 0.2, and 0.3 volume fractions of Methanol at 308.15 K.

T/*K*	ρ_0 /g.cm^{-3}	η_0 / mPa.s	*D*
0.1 volume fraction of methanol			
308.15	0.9797	0.8665	71.57
0.2 volume fraction of methanol			
308.15	0.9663	1.0217	68.14
0.3 volume fraction of methanol			
308.15	0.9516	1.1418	64.25

Table 2: Values of cmc and free energy of micellization of Sodiumdodecyl Sulphate (SDS) and Dodecyltrimethylammonium Bromide (DTAB) in methanol water mixed solvent media containing 0.1, 0.2 and 0.3 volume fractions of methanol at 308.15 K

Volume fractions of Methanol	cmc (mM)	Degree of ionisation (α)	-ΔG°m (KJ mol^{-1})
SDS			
0.0	8.7*		
0.1	9.31	0.493	33.28
0.2	10.04	0.473	32.97
0.3	10.75	0.466	32.83
DTAB			
0.0	15.6**		
0.1	18.75	0.263	35.29
0.2	21.62	0.237	34.90
0.3	28.86	0.233	33.38

Ref. No. [31] *, [32] **

4. Conclusion

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Effects of concentration and solvent composition on Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate in methanol–water mixed solvent media have been studied by measuring specific conductance through conductometric method. The following conclusions have been drawn from the above results and discussion. The conductance decreases with increase of alcohol content for the studied methanol-water mixed solvent system. The presence of methanol reduces the dielectric constant of the solvent phase and makes easier for the formation of ion-pairs in the solution phase. The cmc increases with the increase of methanol for Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate but Dodecyltrimethylammonium Bromide has higher cmc values in comparison with Sodiumdodecyl Sulphate in the measured ranges of methanol-water mixed solvent media. Furthermore, the negative value of free energy of micellization decreases with the increase of methanol for Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate but Dodecyltrimethylammonium Bromide has higher values in comparison with Sodiumdodecyl Sulphate in the measured ranges of methanol-water mixed solvent media.

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