Investigation on solution properties of surfactants in mixed solvent media: Landmark towards Surface Chemistry in Eastern Nepal

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Abstract

Surfactants are amphiphilic molecules having a hydrophilic or water soluble moiety (head group) and a hydrophobic, or water insoluble moiety (tail group). Surfactants are not only related to soaps and detergents, they are also in heavy demand for industrial processes requiring colloid stability, metal treatments, mineral flotation, pesticides, oil production, pharmaceutical formulation, emulsion polymerization, particle growth and many more. That is why surfactants have been and continue to be a very active area of scientific research and commercial growth for several decades. One interesting property of surfactants is that at low concentrations, they exist solely as monomers. The formation of micelles, begins at a specific surfactant concentration termed the critical micelle concentration (cmc), where the physical properties of the solution, such as interfacial tension, electrical conductivity, and light scattering behaviour, often changes abruptly due to the existence of micelles. The formation of micelles will be able to calculate various thermodynamic parameters. These parameters make surfactants not only an interesting and rich area for the exploration of novel phenomena but also an area of research which can lead to new applications in a variety of fields. However, most of the previous studies on surfactants are limited to aqueous media only. Studies in mixed solvent media are very natural one as one can modulate the conformations of surfactants and their interactions easily by simply varying the composition of the media. With this concept, the research team of Eastern Nepal has started to work the solution properties of surfactants in different mixed solvent media in presence and absence of salts and has also investigated cationic and anionic surfactant interaction in mixed solvent media.

Keywords: Surfactants; Mixed solvent media; Critical micelle concentration.

1. Introduction

Surfactants are amphiphilic materials containing both a polar long-chain hydrocarbon "tail" and polar, usually ionic, "head" groups. In polar solvents, for example water, this dual character of the amphiphile leads to self-association or micellization, the surfactant molecules arrange themselves into organized molecular assemblies known as micelles. In colloidal and surface chemistry, the critical micelle concentration (cmc) is defined as the concentration of surfactants above which micelles form and almost all additional surfactants added to the system go to micelles [1].

The properties of surfactants in mixed solvent media are an interesting subject. However, very less work has been done for solution properties of surfactants in mixed solvent media. The following popular methods were used in the eastern part of Nepal for scientific investigations on the solution properties of surfactants in mixed solvent media:

1.1. Electrical conductivity

In the case of ionic surfactants, the utilization of electrochemical measurement is much more convenient, especially the measurements of the electrical conductivity of their solutions with varying concentration. The conductometric method is based on the finding of a breaking point on the curves, which describe the concentration dependence of conductivity [2]. To investigate the solution properties of surfactants, the electrical conductivity method is very promising one as one can study the various thermodynamic parameters.

Shah et al. [3] measured 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 at 308.15 K. The specific conductivities of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate were increased with increment in concentration and decreased with increment in the volume fractions of methanol. Also, the critical micelle concentration (cmc) was increased with increment in volume fraction of methanol in case of both surfactants. The free energy of micellization ($\Delta G_o m$) was calculated.

Bhattarai [4] studied the solution behavior of a surfactant in methanol water mixed solvent media by electrical conductivity methods. Cetyltrimethylammonium bromide (CTAB) as the surfactant used in this investigation. The micelle behaviour of cetyltrimethylammonium bromide in methanol-water mixed solvent media containing 0.10 volume fractions of methanol at 308.15 K was observed by the value of critical micelle concentration (cmc) obtained from conductivity and found to be 1.13 mM which was higher than that of cmc of cetyltrimethylammonium bromide in water. In water, the cmc of CTAB was reported [5] to be 1.007 mM from conductometry.

Bhattarai et al. [6] measured the specific conductivity of cetylpyridinium chloride in pure water and ethanol-water mixed solvent media containing 0.10, 0.20, 0.30 and 0.40 volume fraction of ethanol at room temperature. It was found that the conductivity of cetylpyridinium chloride decreases with the increase in the volume fraction of ethanol. The critical micelle concentration of cetylpyridinium chloride was found to be increased with the increment in the volume fraction of ethanol.

Niraula et al. [7] studied the conductance of sodium dodecyl sulphate in presence and in absence of KCl and NaBr in methanol-water mixed solvent media containing 0.1, 0.2, 0.3, and 0.4 volume fractions of methanol at 308.15 K. The results showed a sharp increase in conductivity with increase in concentration of sodium dodecyl sulphate. Also, the conductivity of sodium dodecyl sulphate was increased with addition of salts. The conductivity of sodium dodecyl sulphate was decreased with increment in amount of methanol. The conductance of sodium dodecyl sulphate was found more in presence of KCl than NaBr in methanol-water mixed solvent media containing 0.1, 0.2, 0.3, and 0.4 volume fractions of methanol.

Bhattarai et al. [8] measured the specific conductivity of sodium deoxycholate in pure water and ethanol-water mixed solvent media containing 0.10 and 0.20 volume fraction of ethanol at 303.15 K.The conductivity of sodium deoxycholate was found to be decreased with the increase in the volume fraction of ethanol. The critical micelle concentration of sodium deoxycholate was found to be increase with increase in the volume fraction of ethanol.

Niraula et al. [9] studied conductivity of sodium dodecyl sulphate in presence and in absence of KBr and NaCl in methanol-water mixed solvent media containing 0.1, 0.2 and 0.4 volume fractions of methanol at 308.15K. The results showed a sharp increase in conductivity with increase in concentration of sodium

dodecyl sulphate. Also, the conductivity of sodium dodecyl sulphate was increased with addition of salts. The conductivity of sodium dodecyl sulphate was found to be decreased with increment in amount of methanol. The conductance of sodium dodecyl sulphate was found more in presence of KBr than NaCl in methanol-water mixed solvent media containing 0.1, 0.2 and 0.4 volume fractions of methanol.

Also, Niraula et al. [10] studied conductometric studies on the effect of NaBr on the micellization of sodium dodecyl sulphate in pure water and methanol water mixed solvent media at different temperatures containing 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol at 308.15 and 318.15 K.The conductance was decreased with addition of methanol. It was observed that the conductance of sodium dodecyl sulphate was found to be increased with increment in concentration as well as with addition of salt (NaBr). The result showed that critical micelle concentration increased with addition of methanol and with rise of temperature and decreased with addition of sodium bromide.

Shah et al. [11] measured the specific conductivity of solutions of cetyltrimethylammonium bromide in absence and in the presence of potassium chloride in methanol-water mixed solvent media containing 0.10, 0.20, 0.30 and 0.40 volume fractions of methanol at 308.15, 318.15 and 323.15 K. The conductance of cetyltrimethylammonium bromide decreased with addition of methanol. It was observed that the conductance of cetyltrimethylammonium bromide increased with increase in concentration as well as with addition of salt (KCl). The concentrations of KCl were taken 0.0001, 0.001 and 0.01 M during the experiments. The result showed that critical micelle concentration of cetyltrimethylammonium bromide increased with addition of methanol and with rise of temperature. Also, the critical micelle concentration of cetyltrimethylammonium bromide decreased with addition of potassium chloride.

Yadav et al. [12] investigated the comparative study of conductance of sodium dodecyl sulphate in different percentage of ethanol water mixed solvent media at 318. 15 K and found the conductance decreased with increase of ethanol.

Shah et al. [13] studied the effect of KCl on conductivity of dodecyltrimethylammouium bromide (DTAB) in presence and absence of methanol at 298.15 K and found the cmc increases with increase of methanol whereas decreases with the addition of KCl.

The above findings were supported by other works. For example, the effect of KCl and alcohol on the cmc of cetylpyridinium chloride (CPC) was studied by Chung et al.[14]. They observed the decrease in cmc with the addition of electrolyte and vice versa. Akbas and Kartal [15] carried out an investigation on the effect of ethanol and ethylene glycol on the critical micelle concentration (cmc) of CTAB. They observed that cmc decreases upon the addition of ethanol and ethylene glycol. The value of cmc increased with increase in temperature, such behavior was also observed by Dubey[16].

1.2. Density

The density is very important parameter for the thermodynamic studies of surfactant [17]. The thermodynamic quantity known as the partial molar volume has proved to be very useful tool in elucidating the interactions occurring in solutions. Studies of partial molar volume of surfactants have been used to examine the behavior of surfactant solutions [18-23].

Shah et al. [24] measured the density of cetyltrimethylammonium bromide solutions in pure water and in methanol-water mixed solvent media containing 0.10, 0.20 and 0.30 volume fractions of methanol at 308.15, 318.15 and 323.15 K and then calculated the partial molar volumes. The results showed almost constant on the partial molar volumes with increasing surfactant concentration. Also, the partial molar

volumes were found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium and these values were found to decrease with increasing methanol content in the solvent composition.

Bhattarai et al. [25] measured the density of sodium lauryl sulfate in pure water and in methanol –water mixed solvent media containing (0.10, 0.20, 0.30, and 0.40) volume fractions of methanol at (298.15, 308.15, 318.15, and 323.15) K .The results were almost constant on the partial molar volumes with increasing surfactant concentration. Also, the partial molar volumes were found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium and were found to decrease with increasing methanol content in the solvent composition.

Bhattarai and Chatterjee [26] determined the densities of cetyltrimethylammonium bromide in methanol-water mixed solvent Media at 308.15, 318.15, and 323.15 K and found the densities increase with increase of concentration of surfactant. Also, the densities decreased with increment of temperature and also decreased with solvent composition.

Bhattarai et al. [27] measured the density of the binary mixtures of cetyltrimethylammonium bromide and sodium dodecyl sulphate in pure water and in methanol-water mixed solvent media containing (0.10, 0.20, and 0.30) volume fractions of methanol at 308.15, 318.15, and 323.15 K. The concentrations were varied from (0.03 to 0.12) mol.l^{-1} of sodium dodecyl sulphate in the presence of $\sim 5.0 \times 10^{-4}$ mol.l^{-1} cetyltrimethylammonium bromide. The results showed almost increase in the densities with increasing the concentration of surfactant mixture. Also, the densities were found to decrease with increasing temperature over the entire concentration range investigated in a given mixed solvent medium and these values were found to decrease with increasing methanol content in the solvent composition. The concentration dependence of the apparent molar volumes appeared to be negligible over the entire concentration range, investigated in a given mixed solvent medium and the apparent molar volumes increase with increasing temperature and were found to decrease with increasing methanol content in the solvent composition.

Shah et al. [13] measured the density of dodecyltrimethylammouium bromide (DTAB) in presence and absence of methanol at 298.15 K and found the partial molar volume. The results showed almost constant on the partial molar volumes with increasing surfactant concentration and the partial molar volumes were found to decrease with increasing methanol content in the solvent composition.

The above findings were supported by other works. For example, Iqbal and Siddiquah[28] measured the partial molar volume of the surfactant and found the partial molar volume increased significantly with temperature. With regard to the partial molar volume in a mixed solvent, Lee and Hyne[29] have been determined the partial molar volumes of tetraalkylammonium chlorides in ethanol-water mixtures. They found the partial molar volumes decreased with increasing ethanol content in the solvent composition.

1.3. Surface tension

Surfactants reduce the amount of work necessary to create unit surface area i .e. surface tension of a solution is lowered when surfactants are present [30]. The following are a few generalizations regarding surface tension and surfactants, followed by a discussion of surfactants and dynamic surface tension.

Higher concentrations of surfactants lower the surface tension in comparison to the pure solvent state. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration [31]. Bhattarai [4] measured the surface tension of cetyltrimethylammonium bromide in methanol water mixed solvent media by Ring method.

The critical micelle concentration of cetyltrimethylammonium bromide in methanol-water mixed solvent media containing 0.10 volume fractions of methanol at 308.15 K was obtained 1.11mM but in water, the cmc of CTAB was reported [5] to be 1.102 mM from tensiometry at 308.15 K which was less than the cmc of cetyltrimethylammonium bromide in methanol water mixed solvent media.

Jha et al. [32] measured surface tension of cetyltrimethylammonium bromide in presence and in the absence of KCl and NaCl in aqueous media. The results showed a sharp decrease in surface tension with increase in concentration of cetyltrimethylammonium bromide and then almost constant value of surface tension was observed. Also, the surface tension was found to decrease with addition of salts. In presence of monovalent salts, the critical micelle concentration of surfactant was found to decrease.

Shah et al. [13] measured the surface tension of dodecyltrimethylammouium bromide (DTAB) in presence and absence of KCl in methanol-water mixed solvent medai at 298.15 K and found the critical micelle concentration increasing with solvent composition and decreasing with presence of salt.

The above findings were supported by other works. For example, Bhattarai [33] measured the surface tension of cetyltrimethylammonium bromide and found the increase in the value of cmc with increasing methanol and temperature. With the addition of inorganic salts, the reduced electrostatic repulsion among the surfactant head groups is a key factor to influence the morphology of aggregates in ionic surfactant solutions. For conventional single-chain cationic surfactants, micelles may change from global to rod like or wormlike with the addition of inorganic salts. Hence the cmc of surfactant found to decrease with addition of inorganic salts [34, 35].

1.4. Viscosity
Like all other surfactants, cetyltrimethylammonium bromide also shows a rapid change in viscosity when the physical and chemical compositions of the solution are changed. This rise in viscosity has been mainly attributed to the change in the structure of the cetyltrimethylammonium bromide micelles depending upon the ambient condition to which it has been subjected. A similar phenomenon happens on dodecyltrimethylammonium bromide. Viscosities of solutions increase with increase in the concentrations. The increase in the concentration of the surfactants, make the micelles larger. There is slightly breakage at certain concentration, called cmc.

 It is also observed that there is increase in the viscosity with the addition of salt. By adding salt to a surfactant, the solution becomes thicker. The electrolyte increases the size of the micelles in the surfactants. Hence the addition of electrolyte to the surfactant solution induces the growth of micelle or change in morphology of micelle due to which viscosity is increased and hence cmc of the surfactant decreases [36]. In the presence of 0.1 mol.l^{-1}KBr salt, the relative viscosity of 0.01 mol.l^{-1} CTAB systems increases with increasing amount of benzyl alcohol to a value of approximate 1.9 for a benzyl alcohol content of 0.6% (v/v). If more benzyl alcohol is added, the viscosity is decreased. In the absence of KBr salt, the viscosity of 0.01 mol.l^{-1}CTAB solution increases slightly with addition of alcohol due to the increase of volume fraction of mixed micelles [37].

The above findings of other works were supported by the work of research team of Eastern Nepal. For example, Shah et al. [13] studied the effect of KCl on viscosity of Dodecyltrimethylammouium bromide (DTAB) in the presence and absence of methanol at 298.15 K and found the cmc increases with increase of methanol whereas decreases with the addition of KCl.

References

[1] A. D. McNaught, A. Wilkinson, Compendium of Chemical Terminology, Second Edition, Blackwell Scientific Publications, Oxford, IUPAC, 1997.

[2] A. Bhattarai, S.K. Shah, A. K. Yadav, Nepal J. Sci. and Tech., 13 (2012) 89.

[3] S. K. Shah, T. P. Niraula, A. Bhattarai, S.K. Chatterjee, BIBECHANA, 8 (2012) 37.

[4] A. Bhattarai, Sonsik Journal, 4 (2012) 52.

[5] T. Chakraborty, I. Chakraborty and S. Ghosh, Langmuir, 22(2006)9905.

[6] A. Bhattarai, S. K. Shah, A. K. Yadav, Nepal J. Sci. & Tech., 13 (2012) 89.

[7] T.P. Niraula, S. K. Chatterjee, A. Bhattarai, J. Nepal Chem. Soc., 29 (2012) 5.

[8] A. Bhattarai, S. K. Shah, A. K. Yadav, J. Adhikari, BIBECHANA, 9 (2013) 63.

[9] T.P. Niraula, S. K. Chatterjee, A. Bhattarai, BIBECHANA, 9 (2013) 159.

[10] T.P. Niraula, A. Bhattarai, S. K. Chatterjee, Proc. Modern Trends in Sci.& Tech., (2013) 62.

[11] S. K. Shah, A. Bhattarai, S.K. Chatterjee, Advance J. Physical Sci., 2 (2014) 10.

[12] C.D.K. Yadav, S.K. Shah, T.P. Niraula, A. Bhattarai, TUTA Journal, 6 (2013) 60.

[13]S. K. Shah, A. Bhattarai, S.K. Chatterjee, J. Nepal University Grants Commission (In Press).

[14] J. J. Chung, S.W. Lee, J. H. Choi, Bull. Korean Chem. Soc., 12(1991) 411.

[15] H. Akbas, C. Kartal, Colloid J., 68(2006)125.

[16] N. Dubey, J. Surface Sci. Technol., 24(2008) 139.

[17] M. Singh, Surface & Interface analysis, 40 (2008)1344.

[18] K. Shinoda,T. Soda, J. Phys. Chem., 67(1963) 2072.

[19] J. M. Corkill, J. F. Goodman, T. Walker, Trans. Faraday Soc., 63(1967) 768.

[20] J. E. Desnoyers, M. Arel, Can. J. Chem., 45(1967) 359.

[21] G. M. Brown, P. Dubreuil, F. M. Ichhaporia, J. E. Desnoyers, Can. J. Chem.,48(1970)2525.

[22] G. M. Musbally, G. Person, J. E. Desnoyers, J. Colloid Interface Sci., 48 (1974)494.

[23] P. A. Leduc, J. L Fortier, J. E. Desnoyers, J. Phys. Chem., 78(1974)1217.

[24] S. K. Shah, G. Srivastav, A. Bhattarai, S. K. Chatterjee, J. Nepal Chem. Soc., 24 (2009) 24.

[25] A. Bhattarai, S. K. Chatterjee, T. K. Deo, T. P. Niraula. J. Chem. & Eng. Data, 56 (2011) 3400.

[26] A. Bhattarai, S. K. Chatterjee, J. Nepal University Grants Commission, 1 (2012) 50.

[27] A. Bhattarai, S. K. Chatterjee, T.P. Niraula, Springer Plus J., 2 (2013) 280.

[28] M. J. Iqbal, M. Siddiquah, J.Braz. Chem. Soc., 17(2006)851.

[29] I. Lee, J.B. Hyne, Can. J. Chem., 46 (1968)2333.

[30] M. Austin, B .B. Bright and E .A. Simpson , J. Colloid and Interface Sci, 23(1967) 108.

[31] J .A. Caskey and W.B. Jr. Barlage, J . Colloid and Interface Sci., 35 (1971) 46.

[32] K. Jha, S. K. Chatterjee, A. Bhattarai,   BIBECHANA, 10 (2014) 52.

[33] A. Bhattarai, Polyelectrolyte-Surfactant Interactions in Mixed Solvent Media, Ph.D. Dissertation, University of North Bengal, India, 2010.

[34] J.H. Mu, G.Z. Li, X. L. Jia, H.X. Wang, G.Y. Zhang, J. Phys. Chem. B, 106 (2002) 11685.

[35] A. Khatory, F. Lequeux., F. Kern, S. J. Candau, Langmuir, 9 (1993) 1456.

[36] V. K. Aswal, P. S. Goyal, Phys. Rev., E61 (2000) 2947.

[37] W. Zhang, G. Li, J. Mu, L. Zheng, J. Disp. Sci. & Tech., 21 (2000)605.