Density and partial molar volume of cetyltrimethylammonium bromide in the presence and absence of Na_2SO_4 and $MgSO_4$

Ajaya Bhattarai, Chom Nath Adhikari, G.S. Shrivastav

***Abstract*— The density of cetyltrimethylammonium bromide in pure water and in the presence of Na_2SO_4 and $MgSO_4$ at room temperature is reported. The concentrations of cetyltrimethylammonium bromide are varied from (0.013 to 0.0002) mol/l^{-1}. Both the salts have a concentration of 0.01 M. On the basis of the obtained results of density measurements, the critical micelle concentration(cmc) and partial molar volume of cetyltrimethylammonium bromide in pure water and in the presence of Na_2SO_4 and $MgSO_4$ are determined. The obtained cmc values are also analyzed with those accounted on the basis of the conductivity data from the previous paper[1].**

***Index Terms*— Cetyltrimethylammonium bromide, Na_2SO_4, $MgSO_4$, density, partial molar volume.**

I. Introduction

When the surfactants are dissolved in water they distort the structure of water and thereby increase the free energy of the system. Therefore, they concentrate at the surface and are so orientated that their hydrophobic groups "turn away" from the solvent, and the free energy of the solution is minimized. On the other hand, the distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by aggregation of the surface-active molecules into micelles with their hydrophobic groups directed towards the interior of the micelle, and their hydrophilic groups directed towards the solvent. Micellization is, therefore, an alternative mechanism in relation to adsorption at interfaces for removing hydrophobic groups from their contact with water, reducing thereby the free energy of the system [2-4]. Since the properties of surfactant solutions change markedly when micelle formation occurs, many investigations have been focused on determining the values of the cmc in various systems and many studies have been carried out to elucidate the factors that determine the cmc value at which micelle formation becomes significant, especially in aqueous media.

The most important factor known to affect the cmc in aqueous solution is the structure of a surfactant [5].

Manuscript received November 04, 2014.

Ajaya Bhattarai, Department of Chemistry, M.M.A.M.C., Tribhuvan University, Biratnagar, Nepal, Mobile No.009779842077434
Chom Nath Adhikari, Department of Chemistry, M.M.A.M.C., Tribhuvan University, Biratnagar, Nepal, Mobile No.009779842084281.
G.S. Shrivastav, Department of Chemistry, M.M.A.M.C., Tribhuvan University, Biratnagar, Nepal, Mobile No.009779842022347

Volumetric, viscometric, and other thermodynamic data provide valuable information regarding solute-solvent, solute-solute, and solvent-solvent interactions [6,7]. We have found the explanation of the partial molar volume in a number of papers in details [8, 9, 10]. Hence, only basic relation will be used on our system to calculate the partial molar volume. The partial molar volume, $\overline{V}$, is defined by the following equation;

$$\overline{V} = (\partial V / \partial n)_{T,p} \quad (1)$$

Where, ∂V represent a change in total volume and n as the number of moles. The partial molar volume is often provided in units of partial molar volume (cm^3/mol). If there is concentration dependence, the partial molar volumes have to be extrapolated to concentration zero using one of the following two equations which calculate the apparent volume at the finite concentrations, c [10, 11]

$$v = \frac{1}{\rho_0} - \frac{1}{c}\left(\frac{\rho}{\rho_0} - 1\right) \quad (2)$$

With c in g cm^{-3} or

$$\overline{V} = \frac{M}{\rho_0} - \frac{10^3}{c}\left(\frac{\rho}{\rho_0} - 1\right) \quad (3)$$

where, M is the molecular weight of the cetyltrimethylammonium bromide, ρ_0 is the density of the solvent, ρ is the density of the solution and c is the equivalent concentration in mol.l^{-1}.

In order to calculate partial molar volumes, the solution densities are measured for cetyltrimethylammonium bromide in pure water and in the presence of Na_2SO_4 and $MgSO_4$ at room temperature.

In this work, the results are reported for density measurements on cetyltrimethylammonium bromide, a cationic surfactant, in the presence and absence of salts (Na_2SO_4 and $MgSO_4$) at room temperature. The aim of the present work is to analyze the influence of concentration and salts on cetyltrimethylammonium bromide in aqueous media for density and also see the influence of concentration and salts for partial molar volumes for cetyltrimethylammonium bromide.

Therefore, the purpose of our article is to compare the cmc of cetyltrimethylammonium bromide in the presence of salts on the basis of our previous published work on conductivity measurements[1] with density methods.

II. EXPERIMENTAL

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 solution.

Cetyltrimethylammonium bromide was purchased from Loba Chemical Private Limited, India and it was recrystallised several times until no minimum in the surface tension-concentration plot was observed and its critical micellar concentration (cmc) agreed with the literature value[12].

To measure density the pycnometeric method was used. The stock solutions were freshly prepared for each concentration series to avoid problems of aging and microorganism contamination, which was found to occur with diluted surfactant solutions [13].The densities of solutions were determined by the use of Ostwald-Sprengel type pycnometer of about 10 cm^3 capacity. The sample solution was transfused into the pycnometer by using a medical syringe. The mass of the pycnometer was measured with electronic balance and the density was calculated. Density measurements are believed to be precise within ±0.00005, which is satisfactory for our purpose. In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

III. RESULTS AND DISCUSSION

The densities for the cetyltrimethylammonium bromide in the absence and presence of Na_2SO_4 and $MgSO_4$ in pure water at room temperature is depicted in Figure 1. Figure 1 shows the variation of densities of the investigated solutions as a function of the surfactant concentrations. From this figure it is evident that the densities exhibit almost increase with increasing concentration within the concentration range investigated here. Our density data of cetyltrimethylammonium bromide in the presence of salts(Na_2SO_4 and $MgSO_4$) in pure water is found to be higher than the density of cetyltrimethylammonium bromide in pure water. Moreover, the density of cetyltrimethylammonium bromide in pure water in the presence of Na_2SO_4 is higher than $MgSO_4$.

There are several methods to obtain cmc. We found very less literature[14] regarding the calculation of cmc from density measurement. So, we are using density methods to get the cmc.The intersection between two straight lines give the cmc (Table1).

From our previous paper[1] it appears that there are sharp break points on specific conductivity vs concentration of surfactant curves, which correspond to the critical micelle concentration(cmc) of the surfactant and the cmc values of cetyltrimethylammonium bromide in the absence and presence of Na_2SO_4 and $MgSO_4$ in pure water was 1.1 mM, 0.31 mM and 0.63 mM whereas from density measurements 1.2 mM, 0.40 mM and 0.71 mM respectively(Table1).

It is interesting that a higher value of cmc was obtained from density measurements in comparison with conductivity measurements. The differences between the cmc values determined by different methods for a given ionic surfactant probably result from the sensitivity of the given method to the decrease of the dissociation degree of the surfactant molecules and their activity with surfactant concentration increases, particularly in the range in which small aggregates of the surfactants can be formed. The cmc value determined on the basis of the conductivity (1.1 mM) and density (1.2 mM) measurements for cetyltrimethylammonium bromide was somehow similar to that presented in the literature[12] in which for water the cmcs of CTAB were reported to be 1.007 mM from conductometry, and 1.102 mM from tensiometry respectively at 308.15 K. Therefore, we can also state that the cmc values of the surfactants depend a little on the method by which it was determined.

Addition of electrolyte in the surfactant solution decreases the cmc value [15,16]. The addition of salt reduces the polarity of the surfactant molecules and therefore strongly reduces the cmc[17]. Salts decrease the cmc of surfactant in the order: $MgSO_4 < Na_2SO_4$ (Table1) which matched from our previous findings of conductivity works[1].

The partial molar volumes for the cetyltrimethylammonium bromide in the absence and presence of Na_2SO_4 and $MgSO_4$ in pure water at room temperature is depicted in Figure 2. Figure 2 shows the variation of partial molar volumes of the investigated solutions as a function of the surfactant concentrations. From this figure, it is evident that the partial molar volumes exhibit increase with increasing concentration of surfactant and then almost constant value is found to be observed with higher concentration of surfactant which was matched with our previous findings[18,19]. Actually, in lower concentration of cetyltrimethylammonium bromide in the absence and presence of Na_2SO_4 and $MgSO_4$ are concentration dependent. Such behaviour was also noticed by De Lisi et al. [20] while calculating apparent molar volumes of alkyltrimethylammonium bromide. At room temperature, the partial molar volume of CTAB is found to increase in the presence of $MgSO_4$ and further more higher values have been noted in the presence of Na_2SO_4 over the entire concentration range investigated (Figure 2).

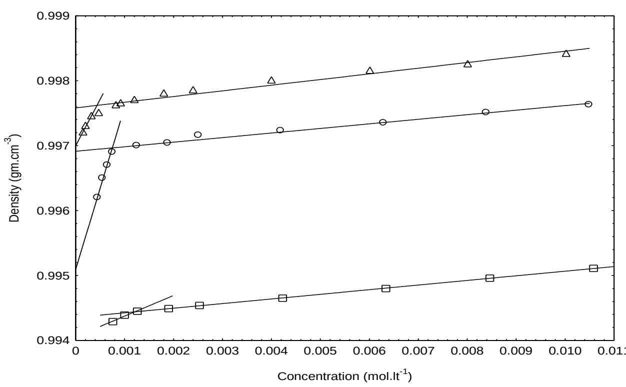

Figure 1. Density vs concentration of CTAB in pure water(square), $MgSO_4$(circle) and Na_2SO_4 (triangle) at room temperature: The intersection between two curves give critical micelle concentration(cmc)

Table 1. Critical micelle concentratiom (cmc) obtained from density methods of cetyltrimethylammonium bromide in pure water and in the presence of $MgSO_4$ and Na_2SO_4 at room temperature

T (K)	Water *cmc* (mM)	0.01 M $MgSO_4$ *cmc* (mM)	0.01 M Na_2SO_4 *cmc* (mM)
(Room temperature)	1.20	0.71	0.40

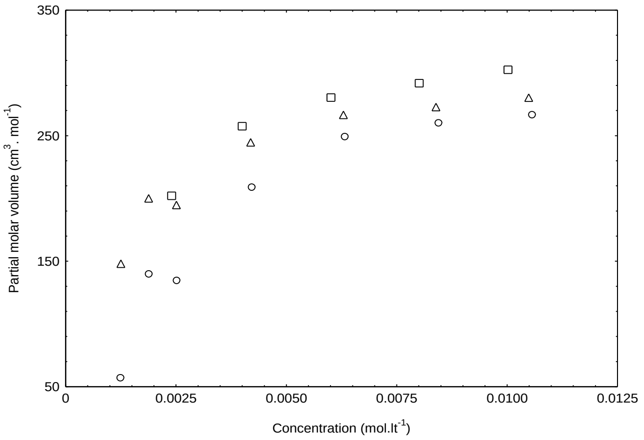

Figure 2. The Partial molar volume of CTAB in distilled water(circle), $MgSO_4$-Water(triangle) and Na_2SO_4-Water(square) solvent at room temperature

IV. CONCLUSION

The results showed that the density of cetyltrimethylammonium bromide increases with increase of concentrations. The density of cetyltrimethylammonium bromide in the presence of Na_2SO_4 found higher than $MgSO_4$. Similarly, the partial molar volume of cetyltrimethylammonium bromide in the presence of Na_2SO_4 found higher than $MgSO_4$.

It is found that the cmc of cetyltrimethylammonium bromide decreases with the addition of salts. The cmc of cetyltrimethylammonium bromide decreases more in the presence of Na_2SO_4 in comparison with the presence of $MgSO_4$.

REFERENCES

[1] A. Bhattarai, G. Shrivastav, C. N. Adhikari. (2014). Study of critical micelle concentration of cetyltrimethylammonium bromide (CTAB) in pure water in presence and absence of magnesium sulfate and sodium sulfate by measuring conductivity meter., *Bibechana*, 11. PP 123-127.

[2] J. M. Rosen. (1989). Surfactants and Interfacial Phenomena, Wiley–Interscience, NewYork, Chap. 6.

[3] K. Holmberg, B. Jonnson, B. Kronberg, B. Lindman. (2003). Surfactants and Polymers in Aqueous Solution, second ed., Wiley, England.

[4] J. Eastoe, J. S. Dalton. (2000). Dynamic Surface Tension And Adsorption Mechanisms Of Surfactants At The Air–Water Interface., *Adv. Colloid Interface Sci*. 85. Pp 103-144.

[5] J. Harkot, B. Janczuk. (2009). Surface and volume properties of dodecylethyldimethylammonium bromide and benzyldimethyldodecylammonium bromide., *J. Colloid & Interface Sci.* 330. PP 467-473.

[6] M. R. J. Dack, K. J. Bird, A. J. Parker. (1975). Solvation of ions. XXV. Partial molal volumes of single ions in protic and dipolar aprotic solvents ., *Aust. J. Chem.* 28. PP 955-963.

[7] J. M. Mc Dowali, C. A. Vincent. (1974).Viscosity behaviour of some simple electrolytes in formamide solution., *J. Chem. Soc. Faraday Trans*. PP 1862-1868.

[8] H. Eisenberg. (1976). In Biological Macromolecules and polyelectrolytes in Solution; Clarendron, Oxford .

[9] H. Durchschlag. (1986). In Thermodynamic Data for Biochemistry and Biotechnology (ed. Hinz, H.-J.) Springer, Berlin. PP. 45.

[10] C. Wandrey, A. Bartkowiak, D. Hunkeler. (1999). Partial Molar and Specific Volumes of Polyelectrolytes: Comparison of Experimental and Predicted Values in Salt-free Solutions., *Langmuir*,. Vol. 15(12). PP. 4062-4068.

[11] C. Tondre, R. Zana. (1972). Apparent molal volumes of polyelectrolytes in aqueous solution., *Journal of Physical Chemistry*, Vol. 76(23). PP. 3451 - 3459.

[12] T. Chakraborty, I. Chakraborty, S. Ghosh. (2006). Sodium carboxymethylcellulose-CTAB interaction: A detailed thermodynamic study of polymer-surfactant interaction with opposite charges., *Langmuir* 22.PP 9905-9913.

[13] A. Domard, M. Rinaudo. (1983). Preparation and Characterization of fully deacetylated Chitosan., *Int. J. Biol. Macromol*, 5. PP 49-52.

[14] M. Usman, A. Khan, M. Siddiq. (2009). Thermodyanmic and Solution properties of Amphiphilic Anti-Allergic Drug Cetirizine HCl., *J. Chem. Soc. Pak*., 31. PP 221-227.

[15] K. Manna, A. Panda. (2011). Physicochemical Studies on the Interfacial and Micellization behaviour of CTAB in Aqueous Polyethylene Glycol Media., *J. of Surfact. Detergent*, 14. PP 563-576.

[16] S. K. Shah, S. K. Chatterjee, A. Bhattarai. (2014). Micellization behaviour of cetyltrimethylammonium bromide in methanol-water mixed solvent media in the absence and in the presence of a salt at (308.15, 318.15 and 323.15) K by conductometry., *Advance Journal of Physical Sciences*, 2(1). PP 10-13.

[17] C. Oelschlaeger, N. Willenbacher. (2012). Mixed wormlike micelles of cationic surfactants: Effect of the cosurfactant chain length on the bending elasticity and rheological properties., *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 406. PP 31– 37.

[18] S. K. Shah, G. S. Shrivastav, A. Bhattarai, S.K. Chatterjee. (2009). The Effects of Concentration, Temperature and Solvent Composition on the Partial Molar Volumes of Cetyltrimethylammonium Bromide in Methanol – Water Solvent Media., *J. Nepal Chem.Soc.*, Vol. 24. PP 24-30.

[19] S.K. Shah, A. Bhattarai, S. K. Chatterjee . (2014). Densities and partial molar volumes of dodecyltrimethylammonium bromide in binary systems (methanol+water) at T=(298.15 to 323.15) K., *Am. J. Chem. Eng.*, 2(6): PP 76-85.

[20] R. De Lisi, S. Milioto, R. E. Verrall. (1990). Partial molar volumes and compressibilities of aikyltrimethylammonium bromides., *J. Solution Chem.* 196. PP 65- 692.