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Critical micelle concentration of sodium dodecyl sulphate in pure water and in methanol-water mixed solvent media in presence and absence of KCl by surface tension and viscosity methods

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Abstract
Careful measurements of surface tension and viscosity of sodium dodecyl sulphate (SDS) in presence and absence of KCl in pure water and methanol-water mixed solvent media containing 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol at 308.15 K are reported. The concentration of KCl is 0.01M. The concentration of SDS varies from 4.86×10^{-3} to 29.56×10^{-3} mol.l^{-1}. The critical micelle concentration (cmc) increases with increase in percentage of methanol and decreases with addition of salt.

Key words: Critical micelle concentration; Sodium dodecyl sulphate; Surface tension; Viscosity; Methanol-water mixed solvent media.

1. Introduction

When an ionic surfactant dissolves in water or any other solvent, initially, the molecules or ions of the surfactant move freely in solution. As the concentration of the surfactant is increased, the ions or molecules start to associate, and finally organize into more complex unit, called micelle [1]. Generally micelles have spherical shape but sometime they also assume different shapes like cylindrical, conical, rod like etc. [2]. The particular concentration (actually an arbitrary concentration of a narrow range) value, where the aggregation process begins for the formation of micelle, is called critical micelle concentration (cmc). The cmc is one of the most useful physicochemical characteristics of surfactants. Chemically, surfactants are mostly low-molecular compounds. When they dissolve in solvent, they form true solutions in concentration ranges below the cmc. Micelles are collection of a larger number of simple molecules or ions of surfactants and the resulting size of such structures is in the colloidal range. The cmc of a solution can be determined by measuring different physical properties of the solution like conductance, surface tension, viscosity, UV-vis spectrum, fluorescence emission spectrum etc. [3]. In this paper, surface tension and viscosity methods are used for determination of cmc for sodium dodecyl sulphate.

The surface tension is an intensive thermodynamic quantity, which is very important for the determination of cmc of surfactant [4]. On addition of a surfactant, surface tension of solution decreases and at a particular concentration, the surface tension of the solution tends to remain constant. This concentration indicates critical micelle concentration (cmc) of the surfactant. The behaviour of the solution is thus different above and below the cmc.

Another property of surfactants which can be used for the measurement of cmc is viscosity. Viscosity can be defined as the internal resistance or friction of liquid or gas to flow. It is one of the most important properties of fluids and has a very important role in petroleum industry. When two or more than two liquids flow on a same surface, they move with different rates or they have different viscosities. Viscosity is generally represented by a Greek letter eta (η) [5]. The small change in viscosity causes an unexpected change in different properties of fluids [6].

The surface tension and the viscosity data have been measured with the help of simple instruments like Stalagmometer and Ostwald viscometer. These instruments consume more time and large amount of chemicals. Mansingh Survismeter helps to measure these properties in short time with small amount of chemicals. The surface tension and viscosity of hygroscopic as well as poisonous substances can be measured with the help of Mansingh Survismeter. It means it is cost effective and less hazardous [5].

The surface tension is generally represented by a Greek letter gamma (γ) [5], and it is determined by using the following relation:

$$\gamma_{soln} = \left(\frac{n_{solv}}{n_{soln}}\right)\left(\frac{d_{soln}}{d_{solv}}\right)\gamma_{solv} \qquad (1)$$

where,

γ_{soln} = surface tension of solution
γ_{solv} = surface tension of solvent
n_{soln} = number of drops of solution
n_{solv} = number of drops of solvent
d_{soln} = density of solution
d_{solv} = density of solvent

When surface tension of a solution is plotted against log[C], where C is the concentration of surfactant then it gives a curve. The two fitted lines meet in the curve at the particular point. That point of intersection is known as cmc of the solution.

Viscosity calculation can be worked out by the following mathematical relation:

$$\eta_1 = \left(\frac{d_1}{d_2}\right)\left(\frac{t_1}{t_2}\right)\eta_2 \qquad (2)$$

where, η_1 = coefficient of viscosity of the solution
η_2 = coefficient of viscosity of the solvent
t_1 = time flow of the solution
t_2 = time flow of the solvent
d_1 = density of the solution
d_2 = density of the solvent

When viscosity of a solution is plotted against log[C], where C is the concentration of surfactant then it gives a curve. The two fitted lines meet in the curve at the particular point. That point of intersection is known as cmc of the solution. The curve for surface tension is different from the curve of viscosity.

The aggregation of ionic surfactants in aqueous solution is influenced by the presence of electrolytes, temperature, pressure etc. Generally, the addition of an electrolyte tends to induce the formation of aggregates at concentration below the cmc of the pure surfactant [7,8] while with many electrolytes, specific interactions between the surfactant ion and electrolyte counter ion will lead to a reduction in solubility [9].

Sodium dodecyl sulphate is an ionic surfactant. It has different uses like as engine degreaser, floor cleaner etc. In recent studies it is considered as a novel microbicide against different viruses [10, 11]. Methanol - water mixtures have very special properties, which are different from that of the other alcohol - water mixtures. In Methanol- water mixture ions association has been found to be negligible up to methanol content of about 80% in the binary solvent. It may be due to the larger dielectric constant of the methanol-water mixture and the smaller size of ion.

Our interest is to see the effects of concentration and relative permittivity on the viscosity and surface tension of sodium dodecyl sulphate in pure water and methanol-water mixed solvent media in the presence and absence of KCl at 308.15 K., also to compare the calculated cmc of the surfactant solutions.

2. Experimental Methods

Methanol (Merck, India) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.77723 ± 0.00004g.cm^{-3} which was measured by the use of an Ostwald-Sprengel type pycnometer of about 25 cm^{3} capacity and a co-efficient of viscosity of 0.47424 ± 0.00005 mPa.s which was determined by the use of the viscometric measurements were performed at 308.15 K using a Schultz-Immergut-type viscometer [12] with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any and these values are in good agreement with the literature values [13]. 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.

Sodium dodecyl sulphate employed in these investigations was purchased from Merck Specialties Private Limited, Mumbai, India. Surface tension and Viscosity measurements were carried out by using Mansingh Survismeter. Potassium chloride employed in these investigations was purchased from Himedia laboratories limited, Mumbai, India**.** The measurements were made in a water bath maintained 308.15 K within ± 0.005 K.

For the measurement of surface tension and viscosity Mansingh Survismeter was washed with chromic acid after that it was washed with tap water, distilled water and then with doubly distilled water followed by triply distilled water and finally washed by acetone for drying and then kept to dry for 24 hours. In dry limb of Mansingh Survismeter, 30ml solvent was filled and number of drops formed by fixed volume of solution was counted by using a Counter machine. To measure the viscosity of surfactant's solution, the time flow for the given volume of solution was determined by using stop watch. 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. Results and Discussion

The experimental surface tension and viscosity of sodium dodecyl sulphate in pure water and four different methanol-water mixtures (containing 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol) in presence and in absence of KCl at 308.15K are represented in the figures 1 to 20. We have also calculated the critical micelle concentration (cmc) from figs. 1 to 20. Table 1 shows cmc of SDS with change in volume fraction of methanol in presence and in absence of 0.01M KCl. It was observed that the surface tension decreases with increase in concentration but viscosity increases with increase in concentration. After formation of cmc with addition of surfactant the ions or molecules associate with each other but not goes in solution hence viscosity or surface tension remains almost the same.

The cmc of SDS increases with increase in percentage of methanol and decreases with addition of KCl. The increase in cmc with increase in volume fraction of methanol is due to decrease in polarity of solvent molecule and decrease in hydrophobicity of solvent and surfactant hydrophobic part. The decrease in cmc with addition of KCl is due to inserts of counter ion between surfactant molecules or ions. We have observed the break in the curve of surface tension versus log[C] and viscosity versus log[C]. The breaking points indicate critical micelle concentration (cmc). The cmc of SDS calculated by using surface tension and viscosity are found almost same which are shown in Table 1. The value of cmc in distilled water is experimentally found to be 9.68 mM (Table1) which is almost same (9.4mM) which was obtained by Khan and Shah [14]. It was found from our experiments that the cmc of SDS solution decreases in the presence of KCl and our data matched with Baloch et.al [15].

The unit used here for surface tension is N/m and that for viscosity is Pa.s throughout the experiments.

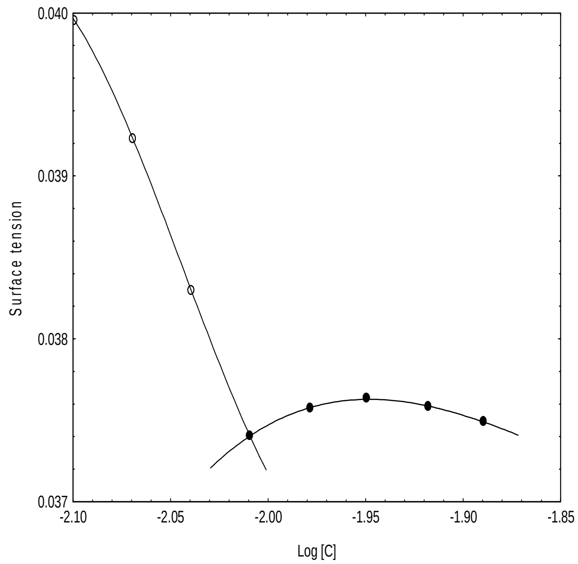

Fig. 1

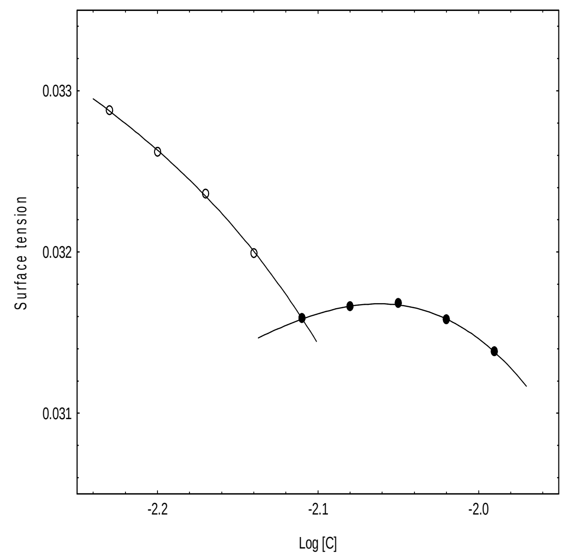

Fig. 2

Figure 1: Variation of Surface tension with Log[C] of SDS in pure water at 308.15 K (Indicating cmc).

Figure 2: Variation of Surface tension with Log[C] of SDS in pure water in presence of KCl at 308.15 K (Indicating cmc).

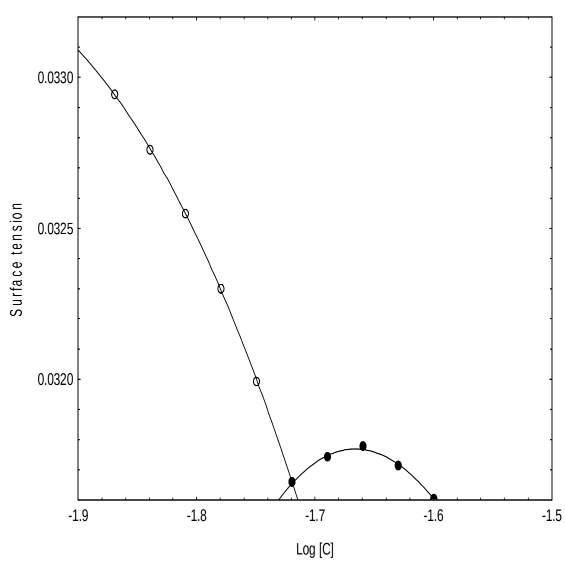

Fig. 3

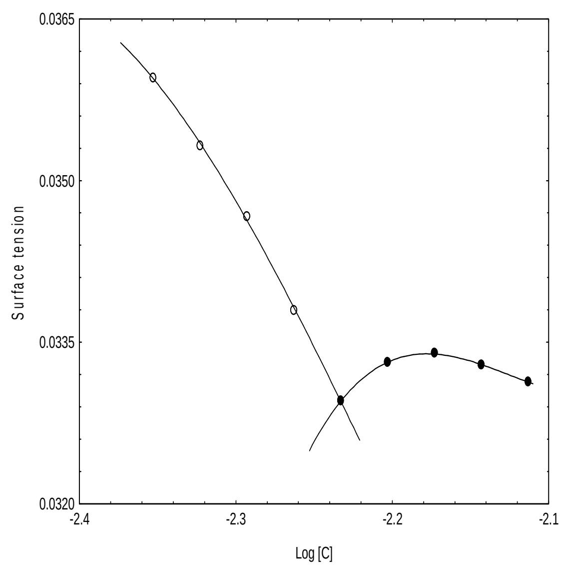

Fig. 4

Figure 3: Variation of Surface tension with Log[C] of SDS in 10% Methanol at 308.15 K (Indicating cmc).

Figure 4: Variation of Surface tension with Log[C] of SDS in 10% Methanol in presence of KCl at 308.15 K (Indicating cmc).

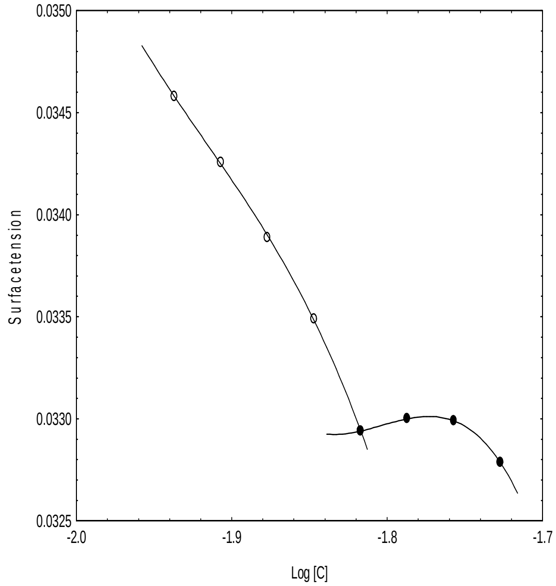

Fig. 5

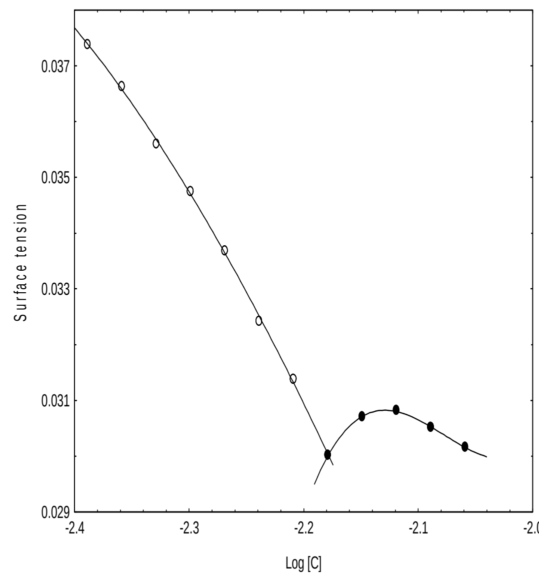

Fig. 6

Figure 5: Variation of Surface tension with Log[C] of SDS in 20% Methanol at 308.15 K (Indicating cmc).

Figure 6: Variation of Surface tension with Log[C] of SDS in 20% Methanol in presence of KCl at 308.15 K (Indicating cmc)

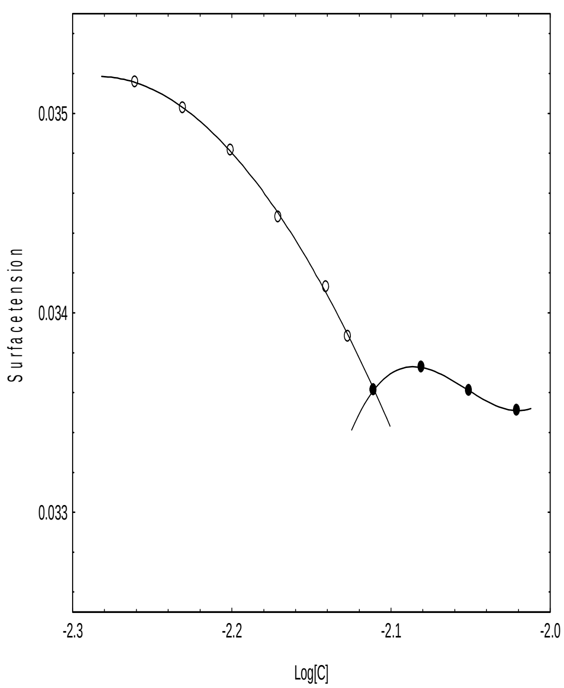

Fig. 7

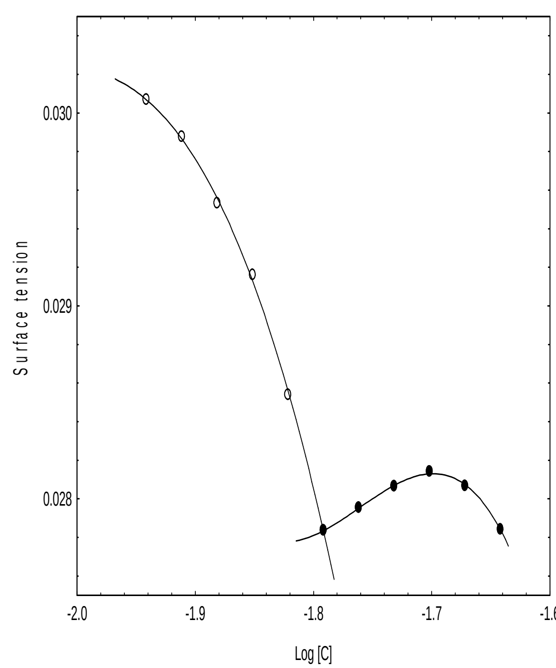

Fig. 8

Figure 7: Variation of Surface tension with Log[C] of SDS in 30% Methanol at 308.15 K (Indicating cmc).

Figure 8: Variation of Surface tension with Log[C] of SDS in 30% Methanol in presence of KCl at 308.15 K (Indicating cmc).

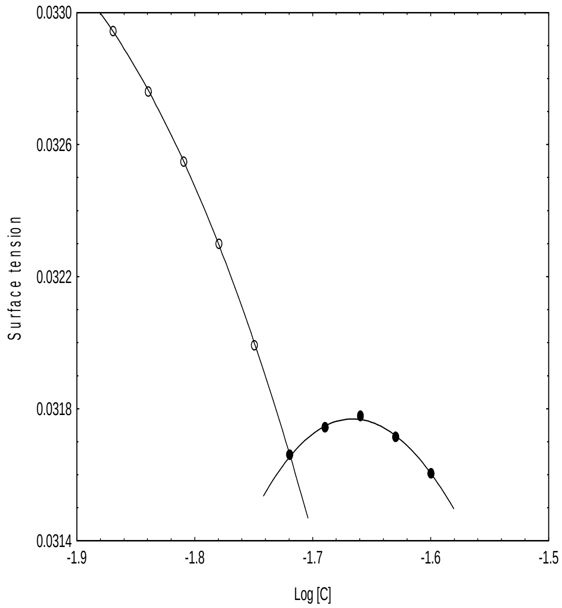

Fig. 9

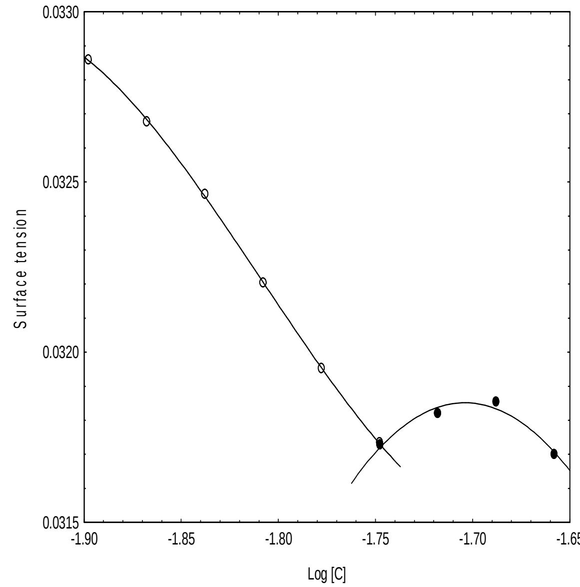

Fig. 10

Figure 9: Variation of Surface tension with Logarithm of concentration of SDS in 40% Methanol at 308.15 K (Indicating cmc).

Figure 10: Variation of Surface tension with Logarithm of concentration of SDS in 40% Methanol in presence of KCl at 308.15 K (Indicating cmc).

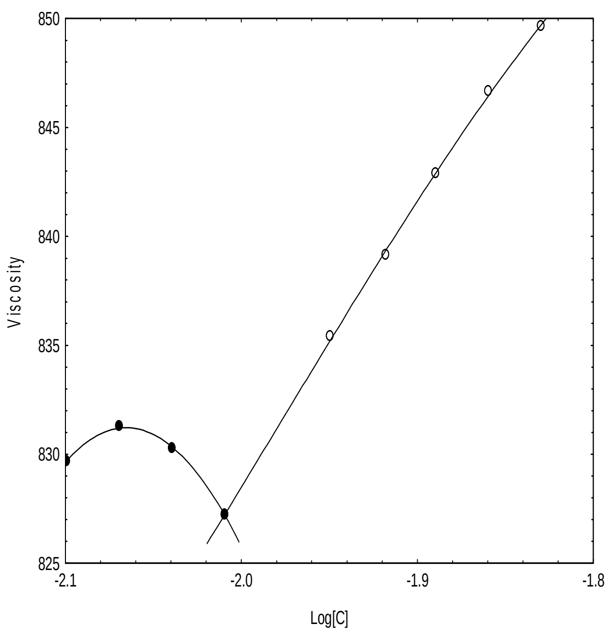

Fig. 11

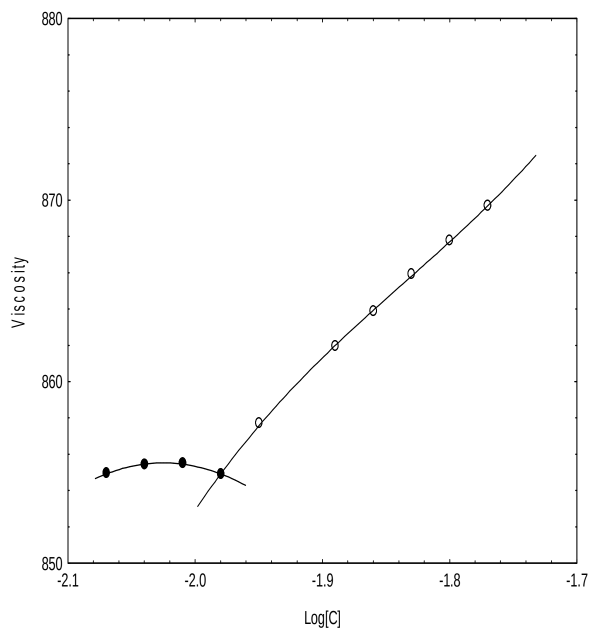

Fig. 12

Figure 11: Variation of Viscosity with Log[C] of SDS in pure water at 308.15K (Indicating cmc).

Figure 12: Variation of Viscosity with Log[C] of SDS in pure water in presence of 0.01M KCl at 308.15 K (Indicating cmc).

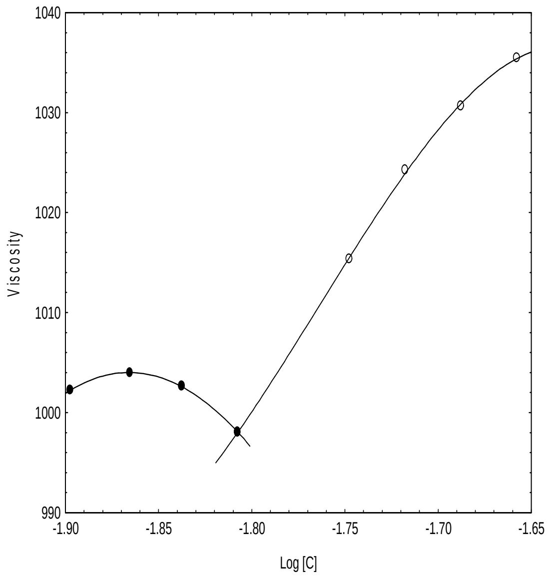

Fig. 13

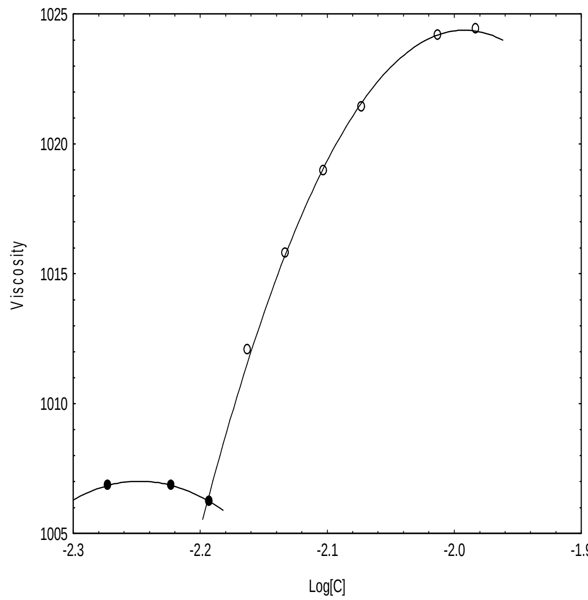

Fig. 14

Figure 13: Variation of Viscosity with Log[C] of SDS in 10% Methanol at 308.15 K (Indicating cmc) .

Figure 14: Variation of Viscosity with Log[C] of SDS in 10% Methanol in presence of 0.01M KCl at 308.15 K (Indicating cmc).

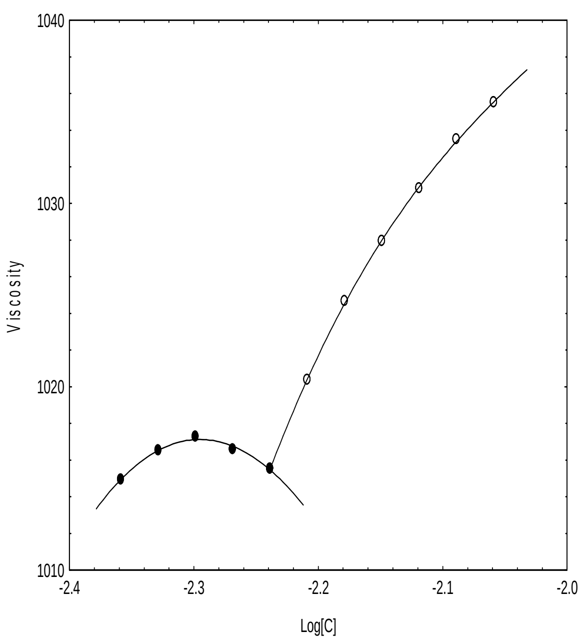

Fig. 15

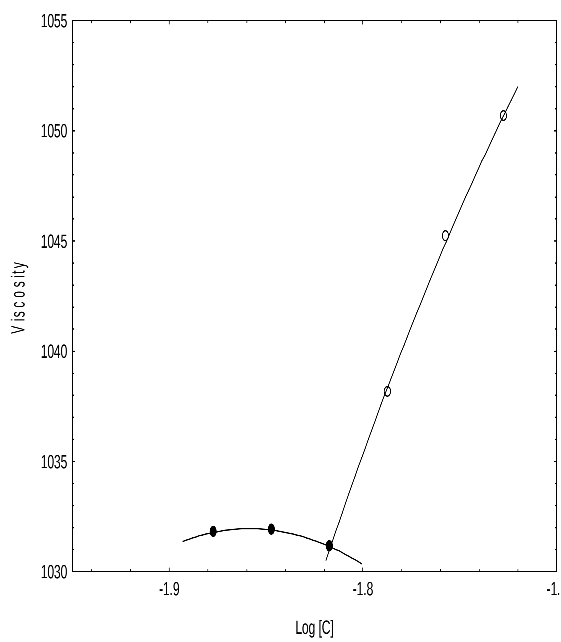

Fig. 16

Figure 15: Variation of Viscosity with Log[C] of SDS in 20% Methanol at 308.15 K (Indicating cmc).

Figure 16: Variation of Viscosity with Log[C] of SDS in 20% Methanol in presence of 0.01M KCl at 308.15 K (Indicating cmc) .

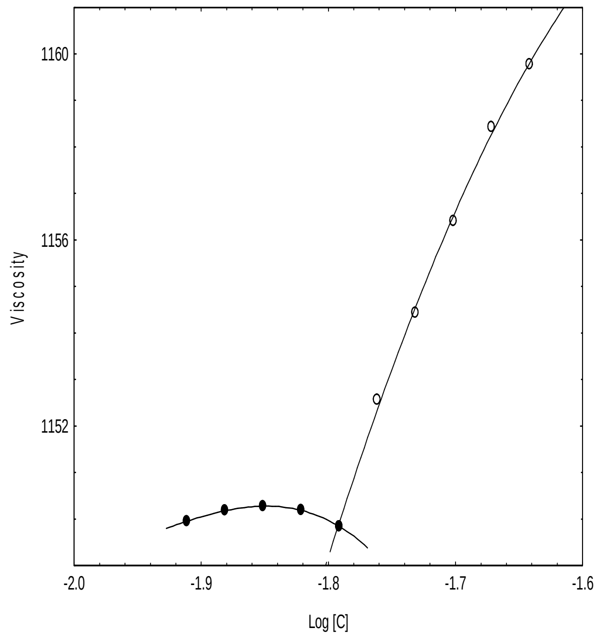

Fig. 17

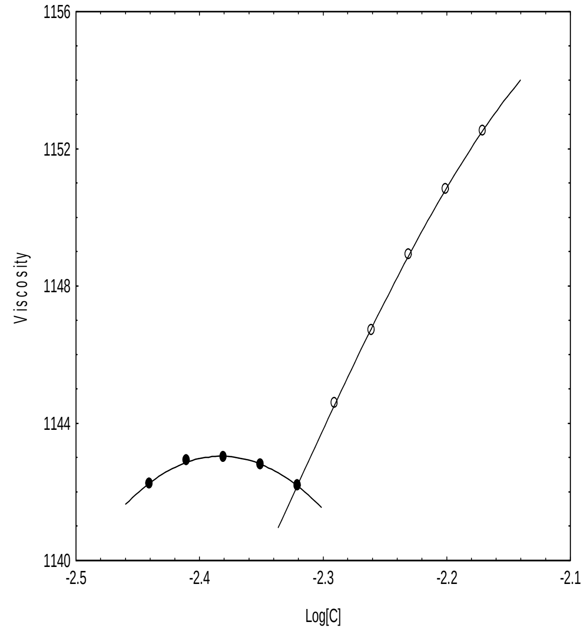

Fig. 18

Figure 17: Variation of Viscosity with Log[C] of SDS in 30% Methanol at 308.15 K (Indicating cmc).
Figure 18: Variation of Viscosity with Log[C] of SDS in 30% Methanol in presence of 0.01M KCl at 308.15 K (Indicating cmc).

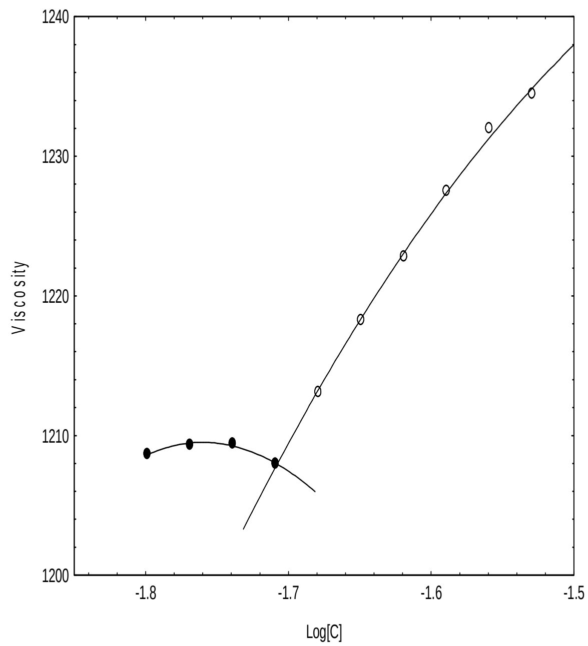

Fig. 19

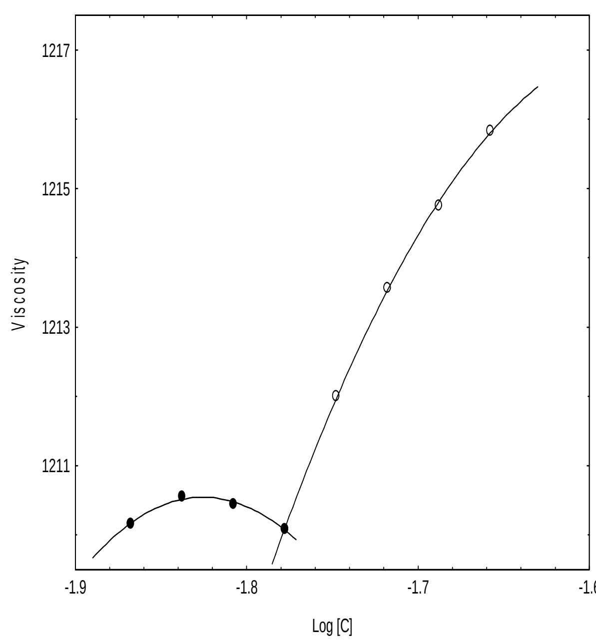

Fig. 20

Figure 19: Variation of Viscosity with Log[C] of SDS in 40% Methanol at 308.15 K (Indicating cmc).
Figure 20: Variation of Viscosity with Log[C] of SDS in 40% Methanol in presence of 0.01M KCl at 308.15 K (Indicating cmc).

Table 1: Critical micelle concentration values of SDS in presence and in absence of 0.01M KCl calculated from surface tension and viscosity in pure water and methanol-water mixed solvent media at 308.15 K.

S.N.	Volume fraction of methanol	Cmc /mM			
		From Surface tension		From Viscosity	
		308.15 K		308.15 K	
		In absence of KCl	In Presence of KCl	In absence of KCl	In Presence of KCl
1	zero	9.68	6.03	8.85	6.08
2	0.1	14.13	6.24	15.09	6.40
3	0.2	15.16	6.64	15.24	7.01
4	0.3	16.48	8.18	16.21	8.15
5	0.4	18.19	17.78	18.36	17.60

Conclusion

Effects of concentration and solvent composition on the surface tension and viscosity of sodium dodecyl sulphate in absence and presence of KCl in pure water and methanol-water mixed solvent media have been studied by measuring number of drops and time flow for fixed volume of solution through two different limbs of Mansingh Survismeter. The following conclusions have been drawn from the above results and discussion. The critical micelle concentration increases with increase in volume fractions of methanol and decreases with addition of KCl in methanol-water mixed solvent media.

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References

[1] Y. Bayrak, Turk. J. Chem., 27 (2003) 487.
[2] B. Halle, M. Landgren, B. Jönsson, J. Phys. France, 49 (1988) 1235.
[3] A. Domínguez, A. Fernández, N. González, E. Iglesias, L. Montenegro, J. Chem. Education, 74 (1997) 1227.
[4] K. Lunkenheimer, A. Lind , M. Jost, J. Phys. Chem. B, 107 (2003) 7527.
[5] A. Singh, V.K. Mishra, S.K. Patel, S. Sheikh, K. Sahu, N.K. Courey. Int. J. Pharm & Life Sci., 1 (2010) 182.

[6] L. M. Kushner, B. C. Duncan, J. I. Hoffman, J. Rese, Nati. Bue. Std., 49 (1952) 2346.
[7] T. P. Niraula, S. K. Chatterjee, A. Bhattarai, J. Nepal Chem. Soc., 29 (2012) 5.
[8] A. J. M. Valente, H. D. Burrows, R. F. Pereira, A. C. F. Ribeiro, J. L. G. Costa Pereira, V. M. M. Lobo, Langmuir, 22 (2006) 5625.
[9] J. Mata, J. Patel, N. Jain, G. Ghosh, P. Bahadur, J. Colloid & Interface. Sci., 297 (2006) 797.
[10] F. C. Krebs, S. R. Miller, B. J. Catalone, P. A. Welsh, D. Malamud, M. K. Howett, B. Wigdahl, J. Am. Soc. for Micro, 7 (1954) 44.
[11] Nutan Gupta, S. K. Gupta, Ind. J. Med. Res., 134 (2011) 939.
[12] J. Schulz, E. H. Immergut, J. Polym. Sci., 9 (1952) 279.
[13] H. Doe, T. Kitagawa, K.Sasabe, J. Phys. Chem., 88 (1984) 3341.
[14] A.M. Khan, S.S. Shah, J. Chem. Soc. Pak., 30 (2008) 186.
[15] M.K. Baloch, G. Hameed, A. Bano, J. Chem. Soc. Pak., 24 (2002) 77.