



CMC (Critical Micelle Concentration) Study of Some Detergents with or without Electrolyte and Calculation of Thermodynamic Parameters using Conductivity Method at Different Temperatures

ASHOKE HAZRA

A. K. P. C. Mahavidyalaya, Bengai, Hooghly Pin-712611, West Bengal, India.

*Corresponding author E-mail: hazra.ashoke@gmail.com

<http://dx.doi.org/10.13005/ojc/400407>

(Received: April 03, 2024; Accepted: July 13, 2024)

ABSTRACT

Present study determines the Critical Micelle Concentration (CMC) of some market available detergents at different temperatures in aqueous solutions. For this study we use Sunlight Surf and Safed Surf. Sodium Acetate Electrolyte was used. Conductance data was taken at different temperatures (15°C, 25°C, 35°C). From this study it was observed that with increase in temperature, cmc value decreases. Addition of electrolyte with surfactants (detergent), decrease cmc value which support our basic concept of surface chemistry. Different thermodynamic parameters like, ΔG , ΔH , ΔS were calculated and also supporting the formation of cmc.

Keyword: CMC, Electrolyte, Surfactant, Temperature, Thermodynamic parameters.

INTRODUCTION

In surface and colloidal chemistry, CMC is defined as the concentration of surfactants above which micelles form. All surfactants show a characteristic properties i.e, CMC (Critical Micelle Concentration). Surface tension changes strongly with concentration before CMC and after reaching the CMC point, surface tension mostly constant. The value of CMC depends of different parameters like, temperature, pressure, electrolyte etc.

Many researchers studied about the CMC of surfactants many years ago¹⁻⁵ and the effect of different parameters on CMC of surfactants⁶⁻⁹. Thermodynamic parameters studied on CMC of

surfactants have been done by many researchers¹⁰⁻¹².

Our aim to study on CMC of some daily usable detergents (surfactants) like, Sunlight, Safed (Market available in West Bengal) at different temperatures and effect of electrolyte for the determination of surfactants. Some thermodynamic parameters also studied. We used conductance method¹³⁻¹⁷ for the determination of CMC (Critical Micelle Concentration).

EXPERIMENTAL

Materials & Apparatus

Conductivity meter for cmc measurement of different detergents (Elico 183 EC-TDS Analyser),



Conductivity Electrode, Temperature Control Bath (CTT Instruments, Kolkata), Thermostat, Magnetic Stirrer etc.

Chemicals: Sodium Acetate (BDH Chemicals Ltd, England), KCl (EMerc, Mumbai), Sunlight and Safed Surf (West Bengal Market) and Deionized water.

Determination of Critical Micelle Concentration Conductivity measurement

Conductance of detergent solution was measured by a digital conductivity meter connected with a conductivity cell. The cell constant was determined by measuring the conductance of standard KCl solution using the relation:

Specific Conductance = Observed Conductance x Cell Constant

The value of cell constant was obtained from observed conductance and specific conductance of a standard solution of 0.1 M KCl solution. CMC value of detergents was obtained from the break point of the plot of specific conductance Vs Concentration of detergent concentration.

Equivalent conductance at infinite dilution

The equivalent conductance at infinite dilution was determined from the molar conductance of the studied detergent solution at 298 K to 308 K.

$$\Lambda = (1000 \times k)/C$$

Where, k = specific conductance (Scm^{-1}),
C = Normality of solution (g. Equiv. cm^{-1}).

Equivalent conductance at infinite dilution was measured by using Onsagar equation:

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B) C^{1/2}$$

Where A and B are constants.

RESULT AND DISCUSSIONS

Table 1 shows that the CMC (critical micelle concentration) of different detergent (surfactant) system at different temperatures from 288K to 308K. Here we have seen that for Sunlight + H_2O system, cmc decrease with increase in temperature.

With addition of Sodium Acetate (electrolyte) cmc also decreases with increase in temperature. This experiment was also carried out for (Safed + H_2O) system. Here also cmc decreases with increase in temperature. For (Sunlight + NaOAc) system, cmc changes for all temperatures. But for (Safed + NaOAc) system cmc shows only at 308K, at lower temperatures cmc does not arises, i.e, the curve is parallel to concentration axis.

Table 1: CMC value at different temperatures of different detergents

Sl. No	System	CMC value		
		288K	298K	308K
1	Sunlight + H_2O	0.075	0.070	0.050
2	Sunlight + 0.1 M NaOAc	0.150	0.120	0.100
3	Safed + H_2O	0.120	0.100	0.070
4	Safed + 0.1 M NaOAc	0.100	-	-

Table 2 shows equivalent conductance at infinite dilution value (Λ_0) with different temperatures. We get the Λ_0 value from the plot of Λ Vs. \sqrt{C} of different detergent systems at different temperatures. With increase in temperature, Λ_0 value increases for all cases. Here we see that more Λ_0 value changes for (Safed + NaOAc) system at higher temperatures.

Table 2: Λ_0 value at different temperatures of different detergents

Sl No	System	Equivalent conductance at infinite dilution(Λ_0)		
		288K	298K	308K
1	Sunlight + H_2O	475.60	496.00	525.20
2	Sunlight + 0.1 M NaOAc	491.00	498.30	517.80
3	Safed + H_2O	484.70	485.90	495.70
4	Safed + 0.1 M NaOAc	493.20	497.80	556.20

Table 3 shows the data of InCMC at different temperatures of different detergent systems which helps us to calculate the thermodynamic parameters of micellization process.

Table 3: Data of InCMC values of different detergent systems at different temperatures

Sl No	System	InCMC		
		288K	298K	308K
1	Sunlight + H_2O	-2.59	-2.65	-2.99
2	Sunlight + 0.1 M NaOAc	-1.89	-2.12	-2.30
3	Safed + H_2O	-2.12	-2.30	-2.65
4	Safed + 0.1 M NaOAc	-2.30	-	-

Table 4 shows the thermodynamic data of the different detergent systems at different temperatures.

The positive value of ΔH for micellization increases from Sunlight water system to Safed water system.

We know that the positive value of ΔH means, the micellization process is endothermic in nature.

Table 4: Thermodynamic parameters of different detergent systems in different temperatures

SI No	System	Temperature	Thermodynamic parameters		
			ΔH (kJ/mole)	ΔG (kJ/mole)	ΔS (kJ/mole)
1	Sunlight + H ₂ O	288K	800	-15.89	2.83
		298K		-16.64	2.74
		308K		-17.95	2.65
2	Sunlight + 0.1 M NaOAc	288K	900	-14.16	3.17
		298K		-15.27	3.07
		308K		-16.18	2.97
3	Safed + H ₂ O	288K	1250	-14.76	4.39
		298K		-15.65	4.24
		308K		-17.22	4.11
4	Safed + 0.1M NaOAc		-	-	-

Negative value of ΔG for micellization means the formation of cmc of all these detergent systems are spontaneous in nature. For these detergent systems, ΔS value for micellization is higher at lower temperature, i.e, disorder ness decreases from lower to higher temperatures which indicate the cmc value decreases from lower to higher temperatures.

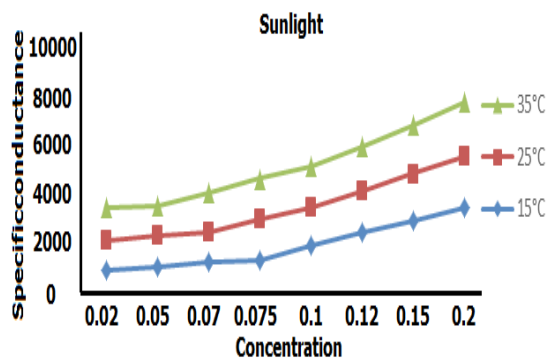


Fig. 1. Specific Conductance Vs. Concentration plot for Sunlight + H₂O

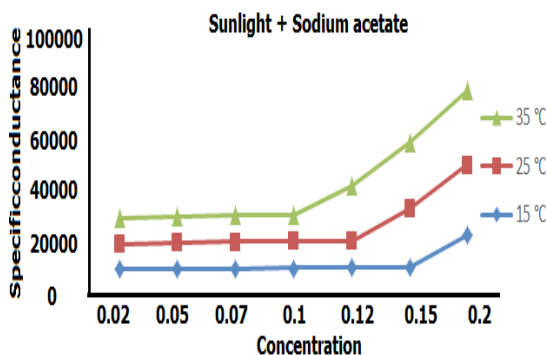


Fig. 2. Specific Conductance Vs. Concentration plot for Sunlight + NaOAc

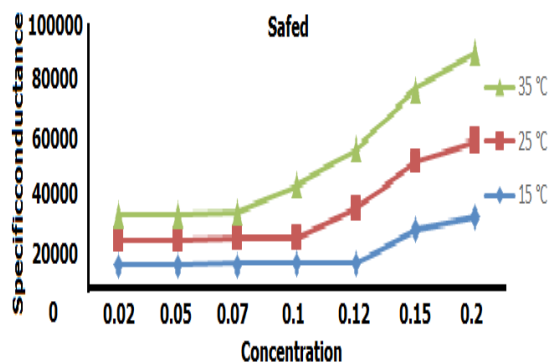


Fig. 3. Specific Conductance Vs. Concentration plot for Safed + H₂O

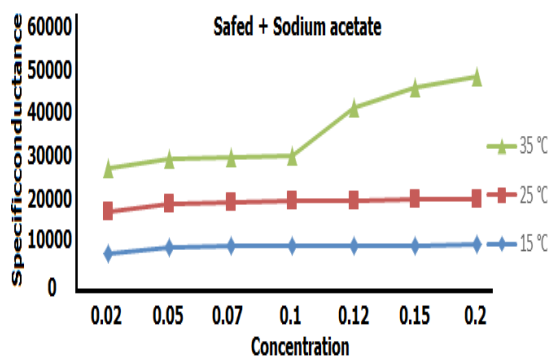


Fig. 4. Specific Conductance Vs. Concentration plot for Safed + NaOAc

Figure 1 to Fig. 4 shows the plot of specific conductance Vs. concentration value of different detergent systems. Break point of this curve indicates the cmc value of the system. With increase in temperature, cmc value decreases which support our basic concept of surface chemistry. This is due to the hydrophobicity and the dehydration of monomer occurs.

For the system (Safed + NaOAc) system, prominent cmc value found at 308K, but at 288K and 298K curve is parallel to concentration axis which shows that there was no break point, i.e, no cmc value.

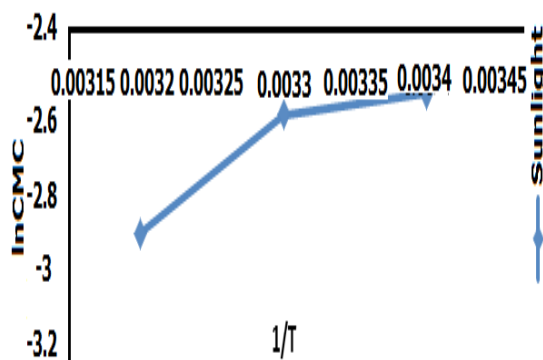


Fig. 5. Plot of lnCMC Vs. 1/T of Sunlight + H₂O

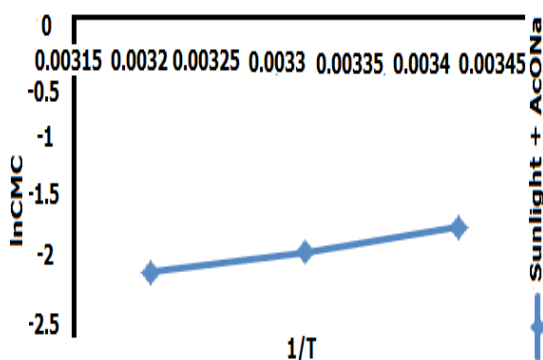


Fig. 6. Plot of lnCMC Vs. 1/T of Sunlight + NaOAc

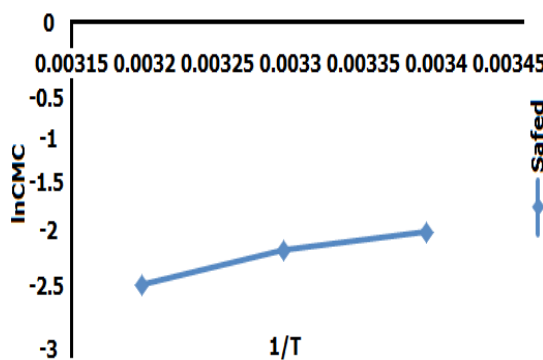


Fig. 7. Plot of lnCMC Vs. 1/T of Safed+ H₂O

Figure 5 to Fig. 7 shows the plot of lnCMC Vs. 1/T of the different detergent systems with different temperatures which helps to calculate thermodynamic parameters for micellization.

From the plo of logX cmc Vs. 1/T plot, we get the value of ΔH for different detergent systems with different temperatures.

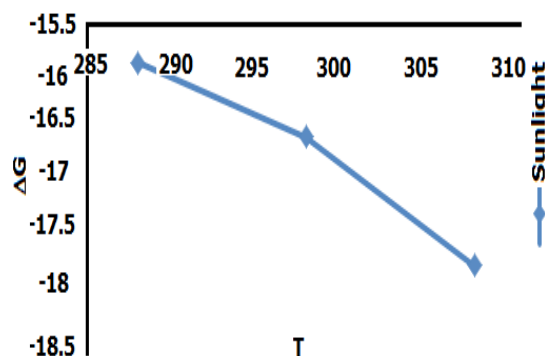


Fig. 8. Plot of Free Energy Change Vs. Temperature of Sunlight detergent

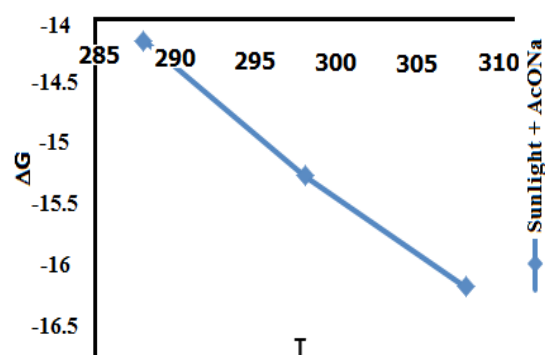


Fig. 9. Plot of Free Energy Change Vs. Temperature of Sunlight + NaOAc detergent

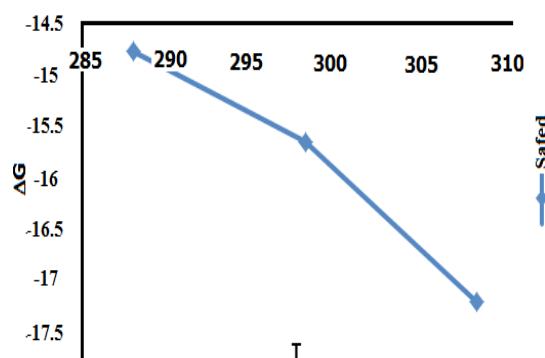


Fig. 10. Plot of Free Energy Change Vs. Temperature of Safed detergent

Figure 8 to Fig. 10 shows the plot of Free energy changes in micellization Vs. temperatures of different detergent systems. This plot helps us to understand the stabilization of cmc at different temperatures.

Figure 11 to Fig. 13 shows the plot of Entropy change in micellization process Vs. Temperatures of different detergent systems. Change of entropy increase at lower temperature and decreases at higher temperatures i.e, cmc value decreases.

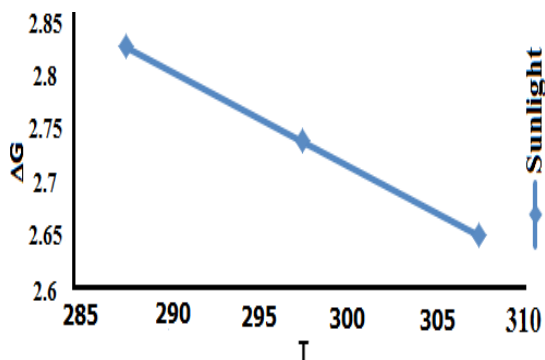


Fig. 11. Plot of Entropy Change Vs. Temperature of Sunlight detergent

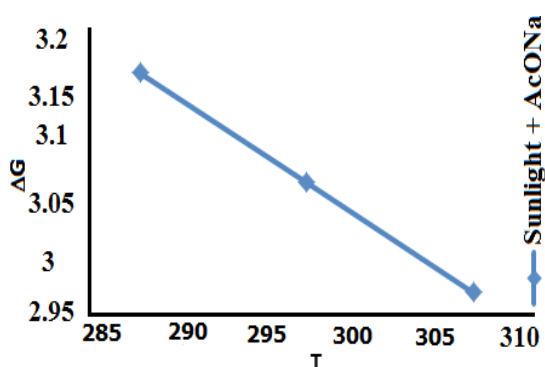


Fig. 12. Plot of Free Energy Change Vs. Temperature of Sunlight + NaOAc detergent

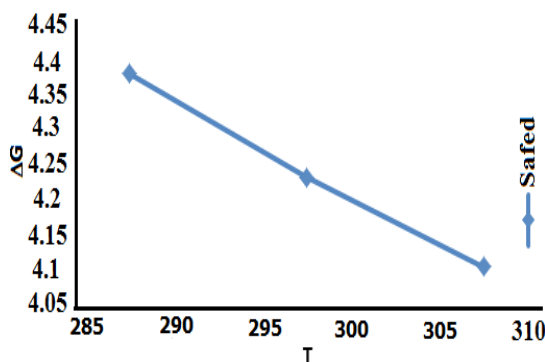


Fig. 13. Plot of Entropy Change Vs. Temperature of Safed detergent

Sodium acetate can influence the solubility of detergents in water at different temperatures. At lower temperatures, the solubility of both sodium acetate and detergents may decrease. However, as temperature increases, the solubility of both compounds tends to increase. This increased solubility can affect the overall concentration of detergent molecules available for micelle formation. Sodium acetate, being a salt, can increase the ionic strength of the solution. This increase in ionic

strength can have an effect on the electrostatic interactions between detergent molecules, affecting their tendency to aggregate and form micelles. Generally, an increase in ionic strength can lead to a decrease in CMC, as higher ionic strength screens the electrostatic repulsions between charged detergent molecules, promoting micelle formation.

Sodium acetate can also affect the hydrophobic interactions between detergent molecules. As temperature increases, the thermal energy of the system increases, leading to greater molecular motion and disruption of hydrophobic interactions. This disruption may lead to a decrease in CMC at higher temperatures, as detergent molecules become more prone to forming micelles to minimize exposure of their hydrophobic tails to water.

Overall, the effects of sodium acetate on detergents and their CMC at different temperatures can be complex and depend on factors such as solubility, ionic strength, hydrophobic interactions, and pH. Experimental investigation would be necessary to fully understand the specific effects in a given detergent system.

Sodium acetate can affect the formation of critical micelle concentration (CMC) in detergents due to its influence on the solution properties, including temperature-dependent effects. Let's explore how sodium acetate may impact the CMC of detergents over the temperature range of 15 to 35 degrees Celsius:

Sodium acetate is a salt, and salts like sodium acetate can influence the solubility of surfactants and the formation of micelles in solution. At low concentrations, sodium acetate may have a salting-out effect, which decreases the solubility of the detergent molecules.

The salting-out effect can lead to an increase in the CMC of detergents, meaning that higher concentrations of surfactants are required to form micelles in the presence of sodium acetate.

Temperature plays a crucial role in the behavior of surfactants and the formation of micelles. Generally, as temperature increases, the kinetic energy of molecules increases, promoting micelle formation.

At lower temperatures (15-25 degrees Celsius), the kinetic energy of molecules is lower, which may hinder micelle formation. In this temperature range, the presence of sodium acetate could exacerbate the salting-out effect, further increasing the CMC of detergents.

Conversely, at higher temperatures (25-35 degrees Celsius), the kinetic energy is higher, which facilitates micelle formation. In this range, the impact of sodium acetate on the CMC may be less pronounced due to the increased kinetic energy overcoming the salting-out effect to some extent.

The combined effect of sodium acetate and temperature on the CMC of detergents will depend on their relative influences.

At lower temperatures (e.g., 15°C), the influence of sodium acetate on the ionic strength may dominate, leading to a decrease in the CMC of detergents due to increased ionic strength.

At higher temperatures (e.g., 35°C), the effect of temperature on micelle formation may be more significant, potentially outweighing the influence of sodium acetate on the ionic strength. In this case, the CMC of detergents may decrease primarily due to the increase in temperature, with less pronounced effects from sodium acetate.

CONCLUSION

From this study it was observed that with increase in temperature, cmc value decreases. Addition of electrolyte with surfactants (detergent), decrease cmc value which support our basic concept of surface chemistry. Different thermodynamic parameters like, ΔG , ΔH , ΔS were calculated and also supporting the formation of cmc. From this study the stability of the CMC formation (Sunlight+H₂O) < (Sunlight+NaOAc) < (Safed+H₂O). All the thermodynamic parameters i.e, ΔH , ΔG , ΔS increased in case of (Safed+H₂O) system. At lower temperatures (e.g., 15°C), the influence of sodium acetate on the ionic strength may dominate, leading to a decrease in the CMC of detergents due to increased ionic strength. At higher temperatures (e.g., 35°C), the effect of temperature on micelle formation may be more significant, potentially outweighing the influence of sodium acetate on the ionic strength. In this case, the CMC of detergents may decrease primarily due to the increase in temperature, with less pronounced effects from sodium acetate.

ACKNOWLEDGEMENT

Author is thankful to the Department of Chemistry, A. K. P. C. Mahavidyalaya for all necessary supports and also thankful to Arnab Hazra, 1st Year Mechanical Engineering student of NIT Durgapur, West Bengal for drawing necessary plots.

REFERENCES

- Chen, L. J.; Lin, S. Y.; Chern, C. S.; Wu, S. C., *Physicochemical and Engineering Aspects.*, **1997**, 122(1-3), 161–168.
- Hunter, R. J.; *Foundations of Colloid Science* Oxford University Press., **1987**, 1.
- Hutin, A.; –LinkedIn–Researchgate Application Notes–Method: Measurement of Critical Micelle Concentration (CMC) DOI: 10.5281/zenodo.6639700, **2021**.
- Shinoda, K.; Nakagawa, T. and Tamamushi, B. I., Academic Press., **1963**.
- Holmberg, K.; Jonsson, B.; Kronberg, B. and Lindman, B., "Surfactant Micellization", 2002.
- Perez-Rodríguez, M.; Prieto, G.; Rega, C.; Varela, L. M.; Sarmiento, F. and Mosquera, V., *Langmuir*, **1998**, 14(16), 4422–4426.
- Niraula, T. P.; Chatterjee, S.K. and Bhattarai, A., *J. of Molec. Liquids.*, **2018**, 250, 287–294.
- Koya, P. A.; -ud-Din, K., and Ismail, K., *J. of Solution Chem.*, **2012**, 41(8), 1271–1281.
- Shah, S. K.; Chatterjee, S. K., and Bhattarai, A., *Journal of Surfactants and Detergents.*, **2016**, 19(1), 201–207.
- Inoue, T.; H. Yamakawa, H., *Journal of Colloid and Interface Science.*, **2011**, 356, 798–802.
- Batigoc, C. D.; H. Akbas, H.; M. Boz, M., *J. Chem. Thermodynamics.*, **2012**, 43, 1349–1354.
- N. Dubey, N., *Journal of Molecular Liquids.*, **2013**, 184, 60–67.
- Chakraborty, T.; Chakraborty, I. ; Ghosh, S., *Langmuir*, **2006**, 22(24), 9905–9913.
- Patel, R.; Khan, A. B.; Dohare, N.; Maroof Ali, M.; Rajor, H. K., *Journal of Surfactants and Detergents.*, **2015**, 18(5), 719–728.
- Mohajeri, E.; Noudeh, G. D., *E-Journal of Chemistry.*, **2012**, 9(4), 2268- 2274.
- Cirin, D. M.; Poša, M. M.; Krstonoši, V. S.; Milanovi, M. L., *Hem. Ind.*, **2012**, 66(1), 21–28.
- Fainerman, V. B.; Miller, R., *Studies in Interface Science.*, **2001**, 13(C), 99–188.