



Design and Construction of Ion-Selective Electrode of Cetyl Pyridinium Chloride and Study on the Cetyl Pyridinium Chloride Micellization in Environmental Conditions

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The use of the ion-selective electrodes in the study of equilibrium properties of aqueous surfactant solutions has received much attention for their low equipment costs and the availability of construction materials. In this paper, a silver wire-coated selective electrode for cetyl pyridinium chloride which is more stable and sensitive than the previous ones was constructed and implemented for characterization of micelle solutions of cetyl pyridinium chloride in various experimental conditions. The values of critical micelle concentration (CMC) at various conditions with different temperatures and alcohol percentages have been interpreted and effective influencing factors on the structural stability of micelle were also investigated. The results revealed critical micelle concentration changes with respect to these factors. The critical micelle concentration changes at various temperatures indicated that the most important factors in micelle formation are entropy and enthalpy. This study marked the outstanding role of hydrophobic forces in the micelle formation process with respect to electrostatic interaction.

Key Words: Ion selective electrode, Cetyl pyridinium chloride, Silver wire-coated, Critical micelle concentration.

INTRODUCTION

A number of ion selective electrodes (ISEs) have been reported as sensor of cationic, anionic and neutral surfactants¹. Most of these sensors action based on an ion exchanger that does not have any special reaction with analyte and are based on formation of a charged complex with an inorganic cation about neutral analytes.

In order to design a suitable membrane, attempts started in early 20th century based on biochemical and electrochemical researches²⁻¹². In study on the surfactant system, using ion selective electrode of surfactants, they understood that inorganic ions inconvenience hardly in electrode reply to surfactant ions, indicates that electrode is very ion selective for surfactant ions with respect to inorganic salts. So study on the effects of added electrolyte on the surfactant system is easy and results show that the surfactant electrode is more sensitive to surfactant ions containing more carbon atoms. In ion selective electrodes in a galvanic cell, in which reference and ion selective electrodes are located in sample solution and link to potentiometer by connective wires.

Ion selective electrodes are special electrodes that are used to analyze a large number of compounds like shampoos, soaps and tooth pastes. These electrodes have been used to study the interaction of sodium alkyl sulfates and alkyl trimethyl ammonium bromides with proteins. These electrodes are usually

studied in an electrochemical cell which contains a reference electrode beside an ion selective electrode, sample solution and a potentiometer.

In this research, first the membranous ion selective electrode of surfactant is prepared, so an electrochemical cell is designed for attaining the potentiometry data of surfactant binding to CPC. Potentiometry reply is used to attain the binding isotherms of binding of surfactant to CPC. Surfactants as amphipatic materials aggregate in a specified concentration and produce micelle. Critical micelle concentration (CMC) depends on different structural and environmental parameters. Our purpose in this research is to investigate the effect of various concentration of alcohol on the CPC micellization at 25 and 37 °C in order to obtain comprehensive information about CMC of CPC in various conditions.

EXPERIMENTAL

Cetyl pyridinium chloride (CPC), carboxylated poly(vinyl chloride) (PVC) with high molecular mass and dioctyl phthalate (DOP) were obtained from Aldrich. Tetrahydro furan (THF) solvent, acetone, ethanol, propanol and sodium hydroxide were obtained from Merck and Sigma. Silver wire and reference electrode of sodium were obtained from Metrohm Company. For preparing all solutions we used double distilled water. All solutions were freshly prepared before using and experiments were carried out at 25 °C.

All potentiometry and pH-metry determinations were carried out on Ω Metrohm-744 potentiometer and pH-meter. Because of electrode sensitivity to temperature, all experiments were done under the temperature control of apparatus. We used accurate balance with accuracy of ± 0.0001 g for all measurements.

Methods: In this work, micellization process of cationic surfactant of CPC in methanol, ethanol and propanol in various concentrations of 10, 20 and 30 % at 25 °C were investigated and CMC was determined and related plots were constructed using Excel software.

Preparing the membrane and selective electrode of surfactant: In order to obtain a suitable membrane for making selective electrodes that act reversible for cationic surfactant ions of CPC, we used carboxylated poly(vinyl chloride) with high molecular mass which would be activated by surfactant cations. Poly(vinyl chloride) (0.5 g) was dissolved in THF (20 mL). This solution was added drop wise to the 50 mL of surfactant solution (3 mM) and was stirred slowly to attain a fibrous precipitate that was filtered and washed by double distilled water, then was put on a watch glass and transferred into a desiccators containing P_2O_5 , to be desiccated completely (complete desiccation took 4 h). In order to prepare plasticizer solution, 0.18 g of dioctyl phthalate was dissolved in 3-4 mL THF solvent. 0.12 g of desiccated membrane was added to dioctyl phthalate solution. It took 4-6 h to obtain a limpid and homogenized gel in effect of vaporizing the THF.

In the next stage, glass tubes should be prepared, so we used glass tubes with diameter of 5 mL and length of 10 cm. In order to obtain a complete smoothness on the surface of glass tubes we used emery and then they were washed and dried for binding the membrane to them. To prevent the air current interference and smoothing the basic layer thickness of membrane, we closed the tube mouth by forefinger and then put it into the membrane gel. After emitting, we put them vertically exposed to the air for at least 12 h.

Coating the surface of silver wire: The surface of silver wire should be coated by precipitate of silver bromide. We used a saturated solution of sodium bromide and a dilute solution of nitric acid. At first stage the surface of silver wire was cleaned by emery and was washed with water and ethanol. The silver wire was immersed in the nitric acid solution. Surface of silver wire was oxidized in a short time (less than 1 min) and a thin layer of silver ions were formed on the wire surface that composed with bromide ions after transferring to the saturated solution of sodium bromide and precipitated again on the surface of the silver wire.

Conditioning solution: This solution is 1 mM related to the surfactant and 0.1 mM related to the NaBr. The prepared glass electrode in previous stage was put in solution from both inner and outer part. It took 24 h to prepare the membrane surface of electrode. After these stages we can use the surfactant electrode for basic determinations with entering a coated silver wire into the standard solution inside the tube.

Determination method: All potentiometry experiments were carried out using a 10 mL beaker as determination cell. Initial tests were done on electrode. 5 mL buffer solution of NaBr (10^{-4} M) was placed in the cell and ion selective electrode

of surfactant was placed in solution, next to a reference electrode of sodium. Wires of electrode were connected to the potentiometer. Using micropipette, equal volumes of 10 μ L of surfactant were added to test cells and potential was recorded. Finally we constructed the amounts of obtained potential difference *versus* $\log [s]_f$. Linearity of curves with Nernst slope indicates correctness of the electrode reply. After confidence of correct reply we repeated experiment in presence of methanol, ethanol and propanol in concentrations of 10, 20 and 30 %. This method is used just for determining the CMC of ionic surfactants. EMF change of aqueous solution of ionic surfactants at CMC point is in proportion to different degrees of surfactant ionization before and after the CMC point. Before CMC, surfactant monomers behave like a strong electrolyte and after CMC, micelles are ionized slightly.

For description the process of EMF changes with surfactant concentration we consider two stages, first stage is before CMC that micelle isn't formed. EMF of aqueous solution of CPC follows the equation stated as below:

$$EMF = E_o + m_1[CPC]$$

where m_1 is the slope of plot of EMF *versus* [CPC] changes. After CMC, in second stage we have m_2 :

$$EMF = E_o + m_2[CPC]$$

We can obtain CMC from refraction point of two curves.

RESULTS AND DISCUSSION

Determining the surfactant concentration: Designed electrochemical cell for determining the surfactant concentration contains reference electrode of sodium and an ion selective electrode of surfactant. A specified volume of buffer solution consist of NaBr (10^{-4} M) is used. After turning the potentiometer on, absolute volumes of surfactant are added gradually and potential difference is recorded. Obtained information is investigated using Excel software. The plot of potential difference *versus* logarithm of surfactant concentration is shown in Fig. 1.

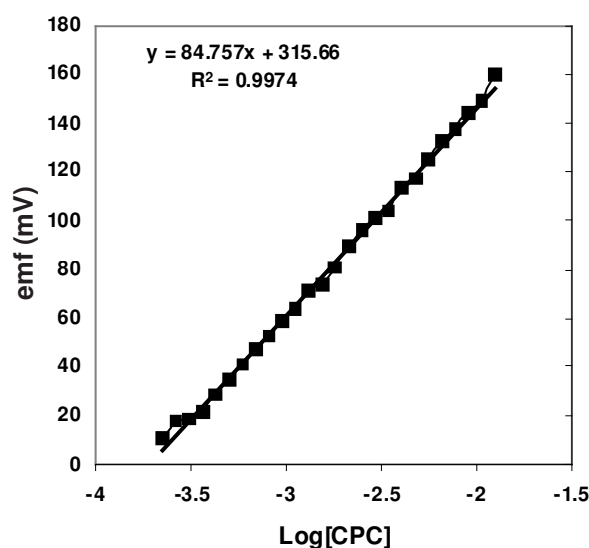


Fig. 1. EMF variations *versus* $\log [CPC]$ in ionic strength of 0.1 mM NaBr

Relation of potential with surfactant concentration is:

$$EMF = E_o + m \log [S]_f$$

where EMF is, obtained potential from potentiometer, E_0 is intercept of the plot and m is the slope, which has been obtained between 57-61 mV and is listed in Table-1. EMF amounts are presented in Table-2. Concentration of free surfactant in solution is calculated using equation mentioned as above.

S.No.	[pr] (mg/mL)	pH	[NaBr] $\times 10^5$ (M)	[Urea] (M)	Slope	R^2
1	1	6.5	1	0	58.9	1
2	2	6.5	1	0	60.4	0.998
3	3	6.5	1	0	58.3	0.998
4	1	9.5	1	0	58.2	0.999
5	1	6.5	1	1	60.4	0.996
6	1	6.5	1	3	60.3	0.997
7	1	6.5	1	5	58.3	0.996
8	1	6.5	1	7	59.4	0.997
9	1	6.5	1	9	58.3	0.994
10	1	6.5	1	0	58.3	0.999
11	1	6.5	10	0	58.3	0.998
12	1	6.5	100	0	57.3	0.999
13	1	6.5	1000	0	57.8	0.996

Emf [Br ⁻] (mV)	Emf [Na ⁺] (mV)	[CPC] (mM)
22	31	1.15
35	51	1.16
47	60	1.17
55	68	1.21
73	77	1.27
89	84	1.29
105	92	1.31
122	109	1.33
131	115	1.35
145	124	1.36
150	130	1.37

Analysis of experimental results of micelle: Analysis of CMC changes with kind and percentage of different alcohols and its molecular interpretation and also trend of m_1 and m_2 changes in each plot, before and after the CMC and trend of EMF changes *versus* [CPC] before and after the CMC are shown in Figs. 1-5.

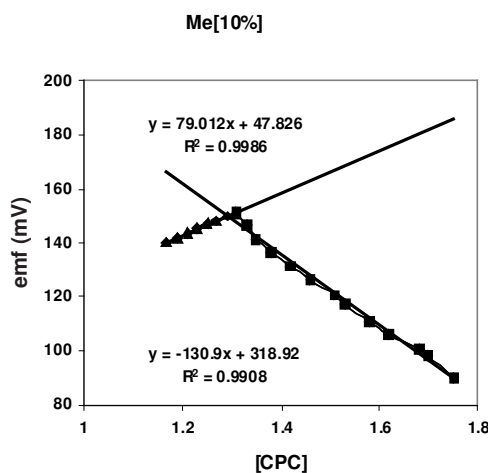


Fig. 2. EMF variations *versus* log [CPC] in methanol (10 %) at 25 °C

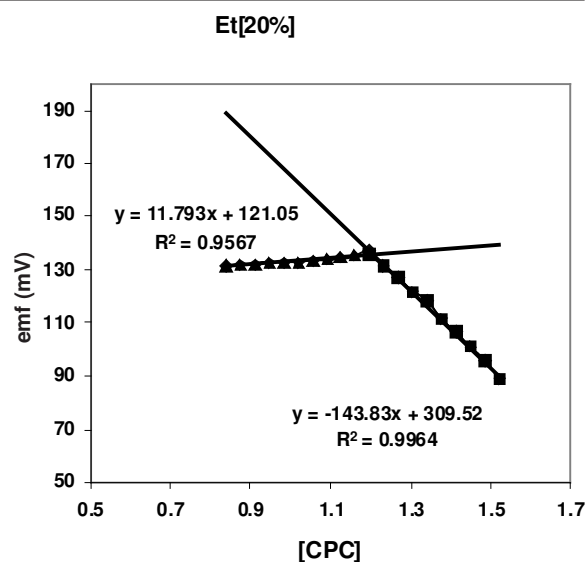


Fig. 3. EMF variations *versus* log [CPC] in ethanol (20 %) at 25 °C

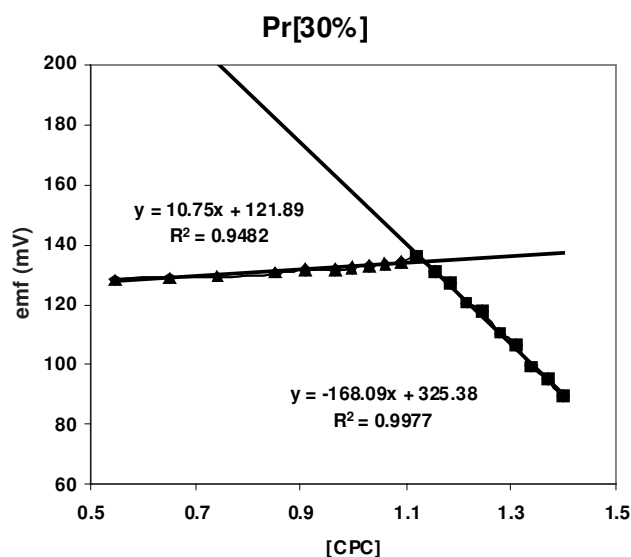


Fig. 4. EMF variations *versus* log [CPC] in propanol (30 %) at 25 °C

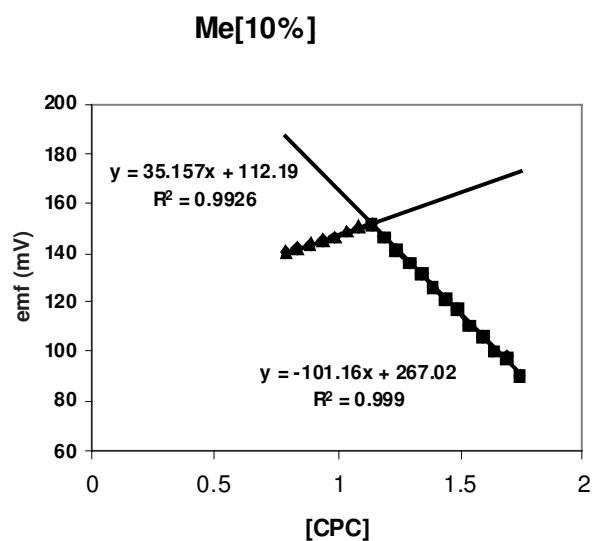


Fig. 5. EMF variations *versus* log [CPC] in methanol (10 %), at 37 °C

In all cases the slope is positive and small before CMC and negative and large after CMC. Figs. 2-5 show EMF variations *versus* CPC concentration in solutions with various concentrations of methanol, ethanol and propanol at 25 and 37 °C. We considered all plots with two slopes of m_1 and m_2 before and after the CMC. All plots contain two linear parts before and after a refraction point, which is CMC. The linear equations of all plots have been extracted.

The slope of plots represents amount of ionic dissociation of surfactant molecules and formed micelle. In all plots the slope before CMC is positive and after the CMC is negative and its amount before CMC is less than that after the CMC. This issue is more obvious with increasing the alcohol percentage and increasing the number of alcohol hydrocarbon groups. This issue is due to the vast aggregation of opposite ions around the micelle, which seems, formed micelle is neutralized excessively. Increasing the alcohol percentage causes to decrease the amount of polarity and dielectric coefficient, this issue increase the attraction forces between opposite ions and causes to create ionic aggregations around the micelle.

In other word ionic charge of micelle is neutralized a lot. Fig. 6, shows CMC changes of CPC *versus* different percentages of alcohol at 25 °C. Based on this figure CMC at first, show an intense decrease upon increasing the methanol percentage and then shows a light decrease. This is true for ethanol but about propanol CMC is nearly constant. CMC variations with increasing of alcohol percentage follow a specified trend and variations are intense about methanol. We can justify this issue based on different effective factors on the micelle stability. Various factors effect on stability of micelle, such as micelle size, amount of charge neutralization on the micelle surface, solvent solution inside the micelle and *etc.* If charge on the micelle surface be neutralized more, micelle becomes more stable because of decreasing the electrostatic repellent forces.

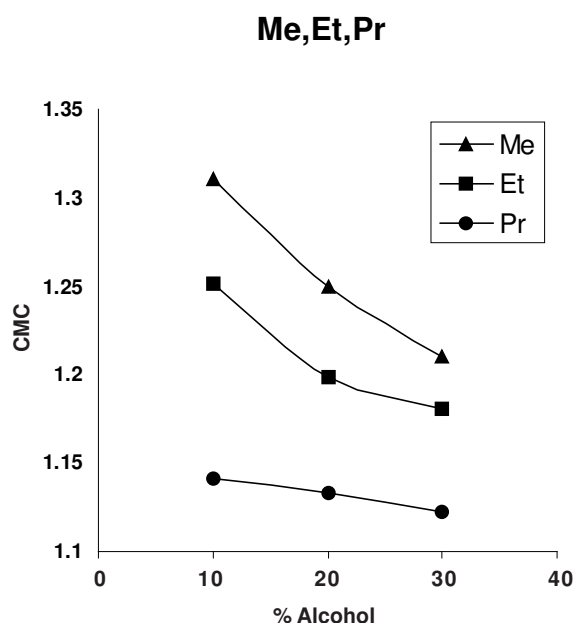


Fig. 6. Curve of CMC and CPC variations *versus* alcohol percentage at 25 °C

With increasing the alcohol percentage, amount of charge neutralization on the surface increase and micelle becomes more stable, so CMC decreases because dielectric coefficient and concentration of solution decrease. Second factor is amount of hydrophobic interactions between hydrophobic tails of surfactant. Increasing the alcohol percentage destroys structure of water and decreases amount of water hydrophobic, so hydrophobic interactions between surfactant tails decrease and formation of micelle decreases.

Solution of solvent inside the micelle, especially solution of alcohols, causes that micelle becomes more voluminous and average aggregation number increases. Existence of these opposite forces causes that predominant changes don't occur in CMC with changing the kind and percentage of alcohol. So larger alcohols show more decrease in the CMC, indicates that electrical charge neutralization of micelle temperature has more role with respect to hydrophobicity decrease.

Figs. 2 and 5 are CMC amount at 25 and 37 °C that indicate slight change of CMC with temperature and indicates slight amount of micellization enthalpy. In other word we can claim that the process of micelle aggregation is an entropy process and this issue indicates more roles of hydrophobic interactions with respect to electrostatic interactions in micelle formation process.

Conclusion

Critical micelle concentration (CMC) of cetyl pyridinium chloride (CPC) is 0.951 mM at 25 °C and $I = 0.1$ mM NaBr in distilled water. With replacing the alcoholic solvents instead of distilled water, the CMC increases. Results are shown in Figs. 2-5 and Tables 3 and 4 increasing of CMC can be due to the hydrogen bond of alcohols with water that causes to destroy the water structure and decrease hydrophobicity of surfactants, so surfactant monomers become more stable in alcoholic environment and micelle is formed in higher concentrations. In other hand dielectric constant of alcohols are much less than water so repellent forces between cationic heads of surfactants increase that help to increase the CMC.

Sample	CMC	CMC	CMC
CPC (water)	0.951	0.951	0.951
CPC (propanol)	1.141	1.133	0.122
CPC (ethanol)	1.251	1.199	0.181
CPC (methanol)	1.311	1.250	1.210
	10 % alcohol	20 % alcohol	30 % alcohol

Increasing of CMC in alcohols indicates that increase of CMC in methanol is more than ethanol and propanol. We can justify this behaviour based on hydrophobic interactions between ethyl and propyl groups of ethanol and propanol to hydrocarbon tail. Hydrocarbon tail of alcohols increases trend of participation of alcohol in micelle structure and these hydrophobic interactions slightly cause to decrease CMC.

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TABLE-4
SLOPE AMOUNTS IN DIFFERENT ALCOHOLS WITH VARIOUS PERCENTAGES

Total percentage (%)	Methanol		Ethanol		Propanol	
	Slope -	Slope +	Slope -	Slope +	Slope -	Slope +
10	-130.90	79.012	-137.69	14.914	-141.13	12.494
20	-134.44	26.264	-143.83	11.793	-142.46	11.788
30	-192.29	18.937	-193.92	9.989	-168.09	10.750

REFERENCES

1. E. Bakker, P. Buhlmann and E. Pretsch, *Chem. Rev.*, **98**, 1593 (1998).
2. B.J. Birch and D.E. Clarke, *Anal. Chim. Acta*, **61**, 159 (1972).
3. F. Haber and Z. Klemensiewicz, *Z. Phys. Chem.*, **67**, 385 (1909).
4. G. Eisenman, D.O. Rudin and J.U. Casby, *Science*, **126**, 831 (1957).
5. H.J.C. Tendeloo, *J. Biol. Chem.*, **113**, 333 (1936).
6. I.M. Kolthoff and H.L. Sanders, *J. Am. Chem. Soc.*, **59**, 416 (1937).
7. E. Pungor and E. Hallos, *Acta Chim. Acad. Sci. Hung.*, **27**, 63 (1961).
8. J.W. Ross, *Science*, **156**, 1378 (1967).
9. M. Cremer, *Z. Biol.*, **47**, 562 (1906).
10. K. Shirahama and T. Kashiwabara, *J. Colloid Interf. Sci.*, **36**, 65 (1971).
11. A.G. Fogg, A.S. Pathan and D.T. Burns, *Anal. Chim. Acta*, **69**, 238 (1974).
12. S.G. Cutler, D.G. Hall and P.J. Meares, *Electroanal. Chem.*, **85**, 145 (1997).