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# Conductance And Miceliization Effect On CMC Of Surfactant (Zirconyl Soaps) In Mixed Non-Aqueous Solvent

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***Abstract:*** ***Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension, between two liquids or that between a liquid and a solid. The study of surfactants (zirconyl soaps) in a mixed non-aqueous solvent have been determined by conductometric measurements and scanning electron microscopic analysis. The results show that zirconyl soaps behave as moderate electrolyte in non-aqueous solvent. Micelles are formed at definite concentration these concentration are called critical micellar concentration of micelles. The value of cmc decreases with increasing numbers of carbon atoms in the soap molecules. The molar conductances at infinite dilute and, degree of ionization have been evaluated. Scanning electron microscopic results confirm the formation of reversed micelles and the shape and size of micelles formed in mixed non-aqueous solvent of zirconyl soaps.***

***Keywords: Zirconyl soaps, weak electrolyte, conductivity, CMC, micelle formation.***



## I. INTRODUCTION

Surfactants being surface-active agents have a number of industrial, emulsifiers and other academic fields. Metal soaps are termed as, surfactant because they have polar and non polar moieties in the same molecule, one part is lyophilic and other one is lyophobic. Which lends them unique characteristics and makes them useful for many industries. However applications of metal soaps are based on empirical knowledge and the selection of a soap for a specific purpose is mainly governed by economic factors. Kapoor & Mehrotra prepared tetracarboxylates of zirconium by the reaction of zirconium chloride with fatty acids in refluxing benzene. Hirosawa used zirconium soaps (palmitate & stearate) as waterproofing agents. Krystufek, et.al. reported that hydrophobization agents that contained zirconium oxysoaps facilitated hydrophobization of textile substrates. The present work deals with the determination of the cmc, degree of dissociation and dissociation constant of zirconyl soaps by conductometric measurement of the solution in xylene and methanol.

## II. EXPERIMENTAL

Zirconyl soaps were synthesized by metathesis of the corresponding sodium soaps with the required amount of aqueous solution of zirconium oxychlorid. Purity of soaps was checked by M.P, element of analysis and I.R.

The conductance of soap solution in xylene and methanol was measured with digital conductivity meter (Toshniwal CL 01.10A) and dipping type conductivity cell with platinised electrodes (cell constant 0.875) at $40 \pm 0.05^0$C in a thermostate and scanning electron microscopy (Leo430, Leo Electron Microscopy Ltd. Cambridge England) was performed to characterize the surface of the formed microspheres. Microspheres were mounted directly in to sample stub and coated with gold film (~200nm) under reduced pressure (0.133 Pa).

## III. RESULTS AND DISCUSSION

The specific conductance, (κ) of the solution of zirconyl soaps in xylene-methanol mixture, increases with increasing concentration and decreasing chain length of fatty acids constituent of soap (Fig -1). The increase in the specific conductance may be due to the fact zirconyl soaps behave as simple electrolytes in dilute solutions and are ionized into simple metal cations $Zr^{2+}$& fatty acid anions, $RCOO^-$ (where R is $C_5H_{11}$, $C_9H_{19}$, $C_{13}H_{27}$ and $C_{17}H_{35}$ for hexanoate, decanoate, tetradecanoate & octadecanoate. The decrease in specific conductance with increasing chain length of the soap may be due to increasing size & decreasing mobility of anions in the soap molecule. The plots of specific conductance vs soap concentration (Fig-1) are characterized by intersection of two straight lines at a definite soap concentration, which corresponds to the concentration of zirconyl soap at which aggregation begins.

It is suggested that the soap is considerably ionized in dilute solutions and anions begin to aggregate to form ionic micelles at CMC. The result shows that cmc decrease with increasing chain length of fatty acid constituent of the soap molecule.

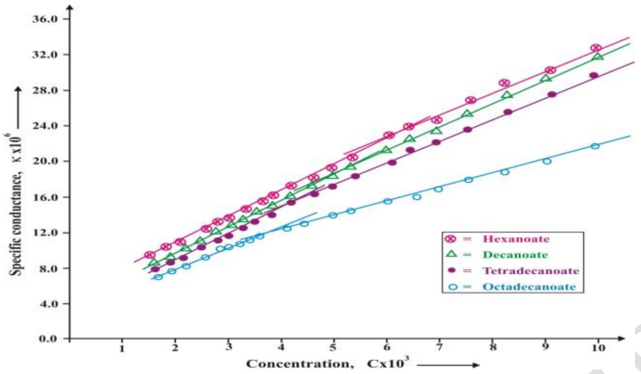


*Figure 1: Specific conductance Vs concentration zirconyl soaps*

The molar conductance (μ) of the solutions of zirconyl soaps in xylene-methanol decreases with increasing concentration and chain length of the soap. The decrease may be attributed to the combined effects of the ionic atmosphere, solvation of ions, decrease of mobility and formation of micelles. The plots of molar conductance vs square root at soap concentration, $(C^{1/2})$ (Fig.-2) are concave upwards, indicating that the soaps behave as weak electrolytes in dilute solutions.

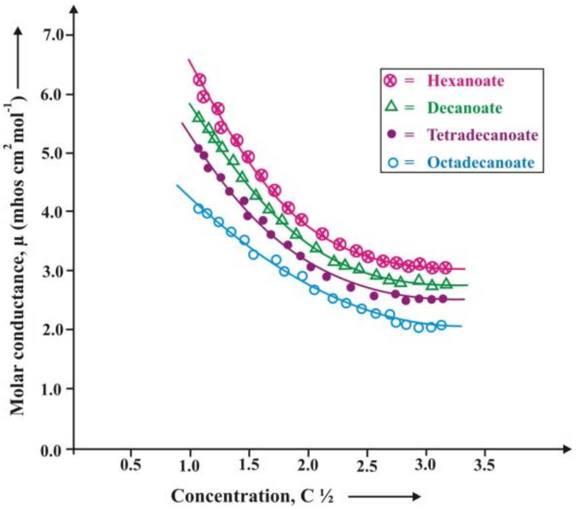


*Figure 2: Molar conductance Vs square root of concentration zirconyl soaps*

| CONDUCTOMETRIC MEASUREMENTS OF ZIRCONYL SOAP IN XYLENE-MEHANOL (7:3 V/V) 40+0.05°C | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Zirconyl Hexanoate | | | Zirconyl decanoate | | | Zirconyl tetradecanoate | | | Zirconyl octadecanoate | | |
| $Cx10^3$ (gmol $l^{-1}$) | $κx10^6$ (mhos $cm^{-1}$) | μ | α | $κx10^6$ (mhos $cm^{-1}$) | μ | α | $κx10^6$ (mhos $cm^{-1}$) | μ | α | $κx10^6$ (mhos $cm^{-1}$) | μ | α |
| 10.0 | 32.8 | 3.28 | 0.364 | 32.1 | 3.21 | 0.360 | 29.9 | 2.99 | 0.342 | 21.2 | 2.12 | 0.247 |
| 9.2 | 30.8 | 3.34 | 0.371 | 29.8 | 3.24 | 0.364 | 28.7 | 3.11 | 0.356 | 19.5 | 2.12 | 0.247 |
| 8.4 | 28.8 | 3.42 | 0.380 | 28.0 | 3.33 | 0.374 | 26.2 | 3.11 | 0.356 | 18.2 | 2.16 | 0.251 |
| 7.6 | 26.5 | 3.48 | 0.386 | 25.6 | 3.36 | 0.378 | 23.8 | 3.13 | 0.358 | 17.6 | 2.31 | 0.269 |
| 7.0 | 26.1 | 3.72 | 0.413 | 23.8 | 3.40 | 0.382 | 22.0 | 3.14 | 0.360 | 16.8 | 2.40 | 0.279 |
| 6.5 | 24.3 | 3.73 | 0.414 | 22.4 | 3.45 | 0.387 | 20.9 | 3.21 | 0.368 | 16.0 | 2.46 | 0.286 |
| 6.1 | 22.9 | 4.73 | 0.414 | 21.4 | 3.50 | 0.393 | 20.3 | 3.32 | 0.380 | 15.5 | 2.54 | 0.295 |
| 5.4 | 21.6 | 4.00 | 0.444 | 19.6 | 3.62 | 0.407 | 18.6 | 3.44 | 0.394 | 14.8 | 2.74 | 0.318 |
| 5.0 | 20.8 | 4.16 | 0.462 | 18.8 | 3.76 | 0.422 | 17.7 | 3.54 | 0.405 | 14.0 | 2.80 | 0.325 |
| 4.4 | 19.0 | 4.32 | 0.480 | 17.6 | 4.00 | 0.449 | 16.1 | 3.66 | 0.420 | 13.0 | 2.95 | 0.343 |
| 4.1 | 18.3 | 4.46 | 0.495 | 16.9 | 4.12 | 0.462 | 15.4 | 3.75 | 0.430 | 12.6 | 3.07 | 0.356 |
| 3.7 | 17.0 | 4.59 | 0.510 | 16.0 | 4.32 | 0.485 | 14.3 | 3.86 | 0.442 | 11.5 | 3.10 | 0.360 |
| 3.5 | 16.4 | 4.68 | 0.520 | 15.4 | 4.40 | 0.494 | 13.8 | 3.93 | 0.450 | 11.4 | 3.25 | 0.378 |
| 3.3 | 15.9 | 4.81 | 0.534 | 14.8 | 4.48 | 0.503 | 13.0 | 3.93 | 0.450 | 11.0 | 3.33 | 0.387 |
| 3.0 | 14.8 | 4.93 | 0.547 | 13.8 | 4.60 | 0.517 | 12.5 | 4.16 | 0.477 | 10.1 | 3.37 | 0.392 |
| 2.6 | 13.6 | 5.23 | 0.581 | 12.9 | 4.96 | 0.557 | 11.2 | 4.30 | 0.493 | 9.3 | 3.57 | 0.415 |
| 2.4 | 12.8 | 5.33 | 0.592 | 12.0 | 5.00 | 0.561 | 10.6 | 4.41 | 0.505 | 8.7 | 3.62 | 0.420 |
| 2.1 | 11.9 | 5.66 | 0.629 | 10.9 | 5.19 | 0.583 | 9.7 | 4.61 | 0.528 | 8.1 | 3.82 | 0.448 |
| 1.8 | 10.8 | 6.00 | 0.666 | 9.8 | 5.44 | 0.611 | 9.0 | 5.00 | 0.573 | 7.2 | 4.00 | 0.465 |
| 1.6 | 9.8 | 6.13 | 0.681 | 9.0 | 5.62 | 0.631 | 8.0 | 5.00 | 0.573 | 6.6 | 4.12 | 0.479 |

*Table 1*

The limiting molar conductance ($μ_o$) of these soap solutions cannot be obtained by the usual extrapolation method and the Debye-Huckel-Onsager equation is not applicable to these soap solutions behave as weak electrolytes and so an expression for the ionization of zirconyl soaps can be developed using the Ostwald model. It C, is the concentration in mol/L and α is the degree of ionization of the soaps, the equivalent concentratidn of different species can be represented as -

$$\underset{C\,(1-\alpha)}{ZrO(RCOO)_2} \rightleftharpoons \underset{C\alpha}{ZrO^{2+}} + \underset{2(C\alpha)}{2RCOO^-}$$

Where, R is $C_5H_{11}$, $C_9H_{19}$, $C_{13}H_{27}$ and $C_{17}H_{35}$ for hexanoate, decanoate, tetradecanoate and octadecahoate, respectively. The ionization constant K can be expressed as:

$$K = \frac{[ZrO^{2+}][RCOO^-]^2}{[ZrO(RCOO)_2]}$$

$$K = \frac{(C\alpha)(2C\alpha)^2}{C(1-\alpha)}$$

$$K = \frac{4C^2\alpha^3}{1-\alpha} \quad \text{-----(1)}$$

Since the ionic concentrations are low and the interionic effects are almost negligible in these solutions by assuming α is, equal to the conductance ratio $(μ/μ_0)$, after rearranging, equation (1) can be expressed as:

$$\mu^2C^2 = \frac{K\mu_0^3}{4\mu} - \frac{K\mu_0^2}{4} \quad \text{-----(2)}$$

The values of K and $μ_0$ have been obtained from the slope and intercept of the linear plots of $μ^2C^2$ Vs 1/μ below the cmc and are recorded in (Table-2).

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The results show that the values of limiting molar conductance, $\mu_0$ and ionization constant, K decrease with the increase in number of carbon atoms in fatty acid moiety of soap molecules.

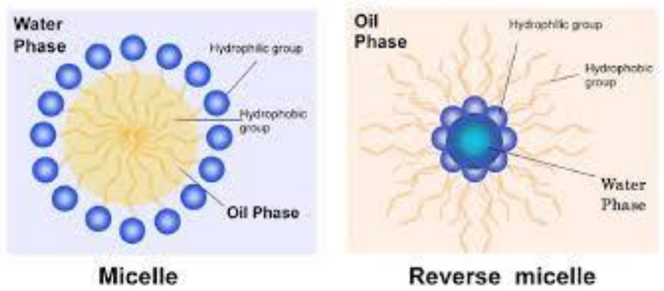
| Name of Zirconyl Soaps | CMC | $\mu_0$ | K |
|---|---|---|---|
| Hexanoate | 0.0061 | 9.00 | 7.41 |
| Decanoate | 0.0054 | 8.90 | 6.00 |
| Tetradecanoate | 0.0041 | 8.72 | 4.41 |
| Octadecanoate | 0.0037 | 8.60 | 2.42 |

*Table 2: CMC and values of various constants for zirconyl soaps at $40\pm0.05^0C$*

The values of degree of dissociation (α) and dissociation constant (K) have been calculated at different concentrations by using the values of $\mu_0$ and equation (1). The values of dissociation constant remain almost constant in dilute solutions but show drift at higher concentration which may be due to the failure of Debye-Huckel's activity equation at higher soap concentration.

## IV. MICELLES ("AGGREGATION COLLOIDS")

The *micellar behaviour* shape and the size of micelles formed in metal soaps solutions were in mixture of xy!ene and methanol were determined by scanning electron microscopy. Micelles are aggregates of surfactants (metal soaps) in a liquid medium which are formed when the surfactant concentration exceeds the critical micellar concentration (CMC). In the normal micelle the surfactant is orientated in such a way that the hydrophobic hydrocarbon chains are towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous, medium. If the micelles are formed in non-aqueous medium. The aggregates are called "reversed micelles" as in this case the hydrophilic head groups are now towards the core of the micelle while leaving the hydrophobic groups out side of the micelles. The driving force for formation of reversed micelles is the dipole-diplole interactions of the surfactant.



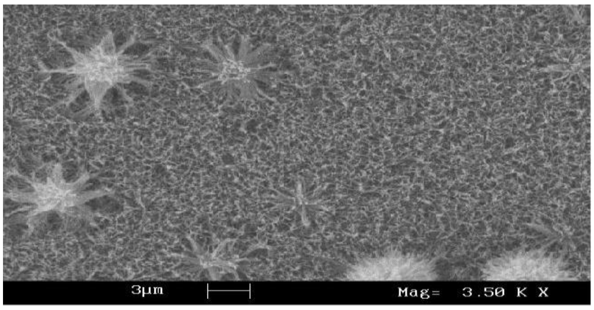




*Figure 3: SEM of zirconyl soap*

The SEM analysis above CMC indicates that the reversed micelles formed in non-aqueous solvent are spherical in shape having 6-8 monomers joined together to form one micelle. The size of micelles obtained in range of micrometer. The average diameter of micelles found to be independent of chain length of metal soap.

- ✓ Micelles are formed at the cmc.
- ✓ Micelle formation is therefore a spontaneous process.
- ✓ Micelles are dynamic structure and are continually formed and broken down in solution-they should not be thought of as solid spheres.
- ✓ There is an equilibrium between micelles and free surfactant molecules in solution.
- ✓ When the surfactant concentration is increased above the cmc, the number of micelles increases but the free surfactant concentration stays constant at the cmc value.

## V. CONCLUSION

The critical micellar concentration (CMC) of zirconyl soaps (hexanoate, decanoate, tetradecanoate and octadecanoate) in xylene and methanol mixture decrease with increasing chain length of fatty acids constituent of soap molecules and determine the nature of micelles formed in soap solutions.



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