



MICELLIZATION AND CONDUCTOMETRIC INVESTIGATION OF ZIRCONYL SOAPS IN BENZENE-METHANOL SOLVENT

MEERA SHARMA, SAPNA AGARWAL AND AMRITA MISHRA
Department of Chemistry, Agra College, Agra 282002, INDIA

Abstract: The critical micelle concentration [CMC] of zirconyl soaps [butyrate, valerate, caproate and caprylate] were determined by using conductometric measurements. The molar conductance at infinite dilution, degree of ionization and ionization constant have been evaluated. The result shows that zirconyl soaps behave as simple electrolyte in dilute solutions and CMC was found to decrease with increasing chain length of the fatty acid constituent of the soap.

Keywords: Zirconyl soaps, critical micelle concentration, degree of ionization, ionization constant, molar conductance

I. Introduction

Metal soaps have been a subject of intense investigation on account of its role in diverse fields. Their vast importance in technological and academic fields are on account of their unique characteristics due to the presence of both lyophilic and lyophobic moieties in the same molecule. The use of zirconium soaps as water proofing agent was reported by Hirosawa [1] and Miyoshi [2]. They used mixture of transition metal soaps [including zirconium soaps] for coating the cosmetic pigments minute particles to improve the adhesive and water-repellent activities of the particles. Several workers reported the uses of metal soaps as binding[3] and molding material[4], adhesive[5,6], for steel cord, for making polish, lubricant, greases, soap blocks and molds, for copiers, fax machine, and printers. The utility of metal soaps as for rust prevention was studied by Nagakoti et. Al [7].

Several workers have also done conductometric studies on metallic soaps [8,9]. The present work has been initiated with a view to determine the CMC, molar conductance, degree of ionization, and ionization constant of zirconyl soaps.

II. Experimental

All chemicals used were of AR grade. Zirconyl soaps were prepared by direct metathesis of the corresponding sodium soaps with slight excess of the solution of zirconyl nitrate under vigorous stirring. The precipitated soaps were washed with water, methanol and acetone to remove excess of metal salt, sodium soaps and unreacted fatty acid. The soaps thus obtained were first dried in an air oven and the final drying of the soaps were carried out under reduced pressure. The purity of the soaps were confirmed by determination of their melting point. The melting point of zirconyl butyrate, valerate, caproate and caprylate were 90°C, 122°C, 138°C and 146°C respectively.

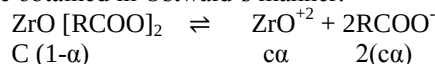
Solutions of zirconyl soaps were prepared by dissolving required amount of soap in a mixture of benzene and methanol [4:1 v/v]. The conductance were measured by Toshniwal Digital conductivity meter "Type CL 01.10 A" using dipping type conductivity cell with platinized electrode. The accuracy of the result was $\pm 0.5\%$.

III. Result and Discussions

The specific conductance k of the solutions of zirconyl soaps in a mixture of benzene and methanol [4:1 v/v] increase with increasing soap concentration and decreasing chain length of the fatty acid constituent of the soap molecule (Table I and II). The increase in specific conductance may be due to the ionization of zirconyl soaps into zirconyl cations ZrO^{+2} and fatty acid anions, $RCOO^-$ [where R is C_3H_7 , C_4H_9 , C_5H_{11} and C_7H_{15}] and due to the formation of micelle at higher soap concentration. The plots of specific conductance Vs. soap concentration for zirconyl soaps in benzene-methanol mixture [4:1 v/v] are characterized by an intersection of two straight lines at a definite soap concentration which correspond to the critical micelle concentration. The results show that the CMC decreases with increasing chain length of the soap molecule (Graph I).

The molar conductance, μ of the solutions of zirconyl soaps in benzene-methanol mixture decrease with increasing soap concentration. The plots of molar conductance, μ Vs. square root of concentration $C^{1/2}$ are not

linear indicating that the Debye-Huckel Onsager's equation is not applicable to these soap solutions and values of limiting molar conductance, μ cannot be obtained by usual extrapolation method. An expression for the dissociation of zirconyl soaps may be obtained in Ostwald's manner.



Where C is the concentration and α is the degree of dissociation of soap. The dissociation constant, K for the above dissociation may be expressed as-

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

$$k = \frac{(c\alpha)(2c\alpha)^2}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)}$$

Since the degree of ionization for dilute solutions of zirconyl soaps are small, the degree of ionization α may be taken as equal to the conductance ratio μ/μ_0 .

On substituting the value of α and rearranging equation (1)-

$$\mu^2 c^2 = \frac{K\mu_0^3}{4\mu} - \frac{K\mu_0^2}{4}$$

The values of μ_0 and K have been obtained from the slope, $(K\mu_0^3/4)$ and intercept, $(-K\mu_0^2/4)$ of linear portion of the plots of $\mu^2 c^2$ Vs. $1/\mu$ for dilute solutions and are recorded. The result shows that the value of limiting molar conductance μ_0 decrease while the dissociation constant, K increase with increasing number of carbon atoms in soap molecules (Table III). The values of the degree of dissociation, α at different concentrations have been calculated assuming it as equal to the conductance ratio, μ/μ_0 . From the plots of degree of dissociation, α Vs. soap concentration, C show that zirconyl soaps behave as simple electrolyte in these solutions.

Table-I: Conductivity measurement of zirconyl butyrate in a mixture of benzene-methanol (4:1 v/v) at (40±0.05)°C

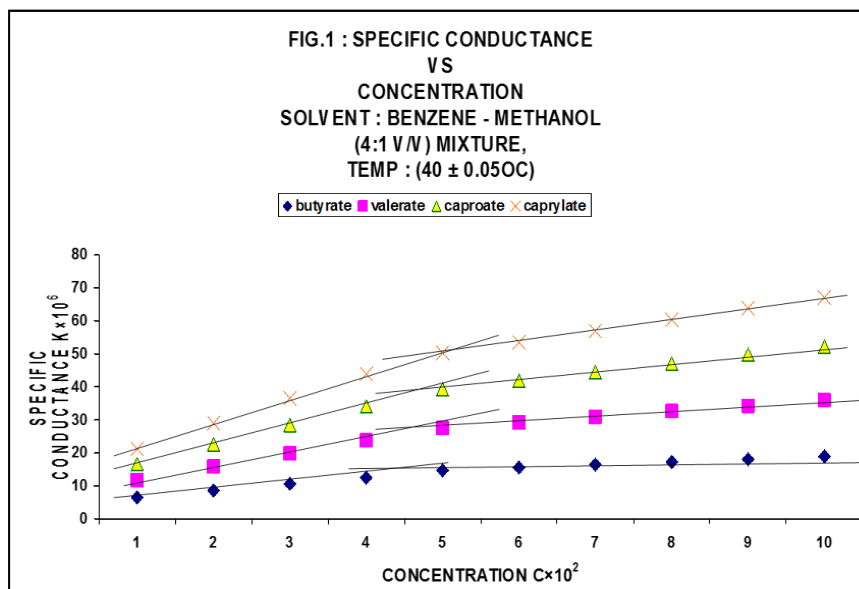
S.No.	Concentration $C \times 10^2 (\text{mol dm}^{-3})$	Specific Conductance $k \times 10^6 (\text{mhos cm}^{-1})$	Molar Conductance μ ($\text{mhos cm}^2 \text{mol}^{-1}$)	Degree of dissociation α	Dissociation constant $K \times 10^5$
1.	1.0	6.47	0.647	0.327	2.08
2.	2.0	8.58	0.429	0.217	2.09
3.	3.0	10.60	0.353	0.178	2.47
4.	4.0	12.49	0.312	0.156	2.88
5.	5.0	14.70	0.294	0.148	3.80
6.	6.0	15.55	0.259	0.131	3.72
7.	7.0	16.40	0.234	0.118	3.65
8.	8.0	17.21	0.215	0.109	3.72
9.	9.0	18.01	0.200	0.101	3.71
10.	10.0	18.90	0.189	0.095	3.79

Table-II: Conductivity measurement of zirconyl caprylate in a mixture of benzene-methanol (4:1 v/v) at (40±0.05)°C

S.No.	Concentration $C \times 10^2 (\text{mol dm}^{-3})$	Specific Conductance $k \times 10^6 (\text{mhos cm}^{-1})$	Molar Conductance μ ($\text{mhos cm}^2 \text{mol}^{-1}$)	Degree of dissociation α	Dissociation constant $K \times 10^5$
1.	1.0	4.60	0.460	0.575	17.89
2.	2.0	6.40	0.320	0.400	17.67
3.	3.0	8.10	0.270	0.338	20.99
4.	4.0	9.81	0.245	0.306	26.42
5.	5.0	11.00	0.220	0.275	28.68
6.	6.0	11.70	0.195	0.244	27.67
7.	7.0	12.42	0.177	0.221	27.16
8.	8.0	13.30	0.166	0.208	29.09
9.	9.0	14.05	0.156	0.195	29.84
10.	10.0	14.85	0.148	0.185	31.08

Table- III: Values of CMC, limiting molar conductance μ_o and dissociation constant, K of zirconyl soaps in benzene-methanol (4:1 v/v) mixture at $(40 \pm 0.05)^\circ\text{C}$

Soaps	CMC $\times 10^2$ (mol dm ⁻³)	μ_o (mhos cm ² mol ⁻¹)	K $\times 10^5$
Butyrate	5.0	1.980	2.65
Valerate	4.7	1.030	10.61
Caproate	4.6	0.953	11.46
Caprylate	4.3	0.800	16.25



VI. References

- [1] S. Hirose, *Japan Patent*, (1974)7, 241, 048, *Chem. Abstr.* (1974), 80, 30208t.
- [2] Y.K.K Miyoshi, *Jpn. KokaiTokkyoKohApr.* 19. (1985) JP 6069, 011 (85 69, 011) (Cl. A 61K7100), Appl. 83/177. 807, Sep. 26 (1983), 4pp.
- [3] Hisida, Shingo, *Japan KokaiTokkyoKoho* June 15 (1999) J.P.11, 158, 292, Appl. 1997/324, 747, Nov. 26 (1997), 6pp.
- [4] Satio, Satoyuski, *Jpn KokaiTokkyoKoho* Sept. 12(2000) J.P. 248; Appl. 1999/53, 842, March 2 (1999).
- [5] Ogino, Yukio, Vymaguchi, Kazuyoshi, Usui, Testuo, *Jpn KokaiTokkyoKoho* Sept. 14 (1988) J.P. 63, 221, 131, Appl87/32, 861, March 10 (1987), 5pp.
- [6] Imori, Toru, Iida, Kazunori, *Jpn. KokaiTokkyoKoho* J.P.(2000), 219, 898, Appl. 199/23, 445, Feb (1999); Aug. 8 (2000), 5pp.
- [7] Nagakoti, B.S. Jain, Sait, M.F. *Addit. Pet Refin. Pet, Prod. Formulation Proc.*, (1997)125-127.
- [8] Sangeeta, M.K. Rawat *J.Curr. Chem. Pharm.* 2012, Sc. : 2(2), , 113-118
- [9] Kamal Kishore, S.K. Upadhyaya *Portugaliae Electrochemical Acta* 2012, 30(1), 45-51

IV. Acknowledgments

Authors are thankful to principal, Dr. M. K. Rawat and Dr. S.C. Goyal, Head of Department of Chemistry, Agra College, Agra for providing necessary facilities and also thankful for the grant given through major project by UGC.