# Acoustic Studies of Zirconyl Soap in Mixed Organic Solvents

**M. ANIS**
**Department of Chemistry**
**School of Chemical Sciences**
**St. John's College, Agra – 282002, INDIA**
**Corresponding Author: anismohammad69@gmail.com**

## ABSTRACT

The critical micelle concentration and various acoustic parameters of zirconyl caprylate and caprate in benzene methanol mixture (4:1 v/v) have been determined by ultrasonic velocity measurements. The results show that ultrasonic velocity, specific acoustic impedance, apparent molar compressibility, solvation number, molar sound velocity and relative association increase while adiabatic compressibility, intermolecular free length and apparent molar volume decrease with increasing soap concentration.

## INTRODUCTION

The study of metallic soaps has attracted significant interest in biological, technological and academic fields in the recent years. The soaps have been a subject of intense investigations, because of their widespread applications in various industries as detergents, lubricants, softeners, plasticizers, stabilizers, cosmetics, medicines, emulsifiers, catalysts and water proofing agents. However, the technological applications of these soaps are mostly based on empirical knowledge and their selection is dependent largely on economic factors. Considering the range and relatively complex behaviour of these soaps, a knowledge of the fundamental physico-chemical properties of metallic soaps are required to understand their role in diversified fields [1-2]. The molecular and ion-solvent interactions have been investigated by using various techniques [3-7]. Critical micelle concentration in organic solvents can not be determined by the methods commonly used for aqueous solutions, therefore, ultrasonic measurements have been used to study the solute-solvent interactions in soap solutions. Several workers [8-13] used ultrasonic velocity measurements to obtain information regarding various

acoustic parameters and solute-solvent interactions in pure liquids, liquid mixtures and electrolytic solutions.

The present work deals with the density and ultrasonic measurements of the solutions of zirconyl soaps (caprylate and caprate) in benzene-methanol mixture (4:1 v/v). The results have been used to evaluate CMC and several allied parameters related to acoustic properties of soap solutions.

## EXPERIMENTAL

All the chemical used were of AR/BDH grade. Zirconyl soaps (caprylate and caprate) were prepared by direct metathesis of the corresponding potassium soaps with slight excess of the solution of zirconium oxychloride under vigorous stirring. The precipitated soaps were washed with water, methanol and acetone to remove excess of metal salt. The purity of the soaps was confirmed by m.p. (caprate, 137°C and caprate 146°C), elemental analysis and IR spectra. The solutions of different concentrations of zirconyl soaps were prepared in benzene-methanol mixture (4:1 v/v) and kept for one hour in a thermostat at constant temperature.

A Multi-frequency Ultrasonic Interferometer (M-83, Mittal Enterprises, New Delhi) at a frequency of 1 MHz was used to measure the ultrasonic velocity of the solutions of zirconyl soaps at a constant temperature (40±0.05)°C. The uncertainity of velocity measurements was ±0.2%.

### Calculations :

Various acoustic parameters such as adiabatic compressibility (β), specific acoustic impedance (Z) [14], Intermolecular free length ($L_f$), [15], apparent molar compressibility, ($\phi_k$), apparent molar volume, ($\phi_v$), molar sound velocity, (R), molar sound compressibility (W), [16], available volume ($V_a$), [17], relative association ($R_A$) [18], and solvation number (Sn), [19], were calculated using the relationships :

$$\beta = v^{-2} \rho^{-1} \quad (1)$$

$$Z = v \rho \quad (2)$$

$$L_f = (\beta/K)^{1/2} \quad (3)$$

$$\emptyset_k = \frac{1000}{C\,\rho_o}\ (\rho_o\beta - \beta_o\rho) + \frac{M\,\beta_o}{\rho_o} \quad (4)$$

$$\emptyset_v = \frac{1000}{C\,\rho_o}\ (\rho_o - \rho) + \frac{M}{\rho_o} \quad (5)$$

$$R = \frac{\bar{M}}{\rho}\ v^{1/3} \quad (6)$$

$$W = \frac{\bar{M}}{\rho}\ \beta^{-1/7} \quad \left[\bar{M} = \frac{n_o M_o + nM}{n_o + n}\right] \quad (7)$$

$$V_a = V\left(1 - \frac{v}{v_\alpha}\right) \quad (8)$$

$$R_A = \left(\frac{\rho}{\rho_o}\right)\left(\frac{v_o}{v}\right)^{1/3} \quad (9)$$

$$S_n = \frac{n_o}{n}\left(1 - \frac{\bar{V}\,\beta}{n_o\,\bar{V}_o\,\beta_o}\right) \quad (10)$$

where $v_o$ , v ; $\rho_o$ , $\rho$ ; $\beta_o$ , $\beta$ ; and $\bar{V}_o$ , $\bar{V}$ are the ultrasonic velocity, density, adiabatic compressibility and molar volume of the solvent and solution, respectively; $n_o$ , n and $M_o$ , M are the number of mole and molecular mass of solvent and solute respectively; K is the temperature dependent Jacobson's constant and concentration, $v_\alpha$ is the constant equal to 1600 $ms^{-1}$ and C is the molar concentration of solution in $dm^{-3}mol$.

## RESULT AND DISCUSSION

**Table-1 : Ultrasonic velocity and other acoustic parameters of zirconyl soap in benzene-methanol (4:1 v/v) mixture at (40±0.05)°C.**

| S. No. | Concentration $C \times 10^2$ (mol $dm^{-3}$) | Density $\rho$ (kg $m^{-3}$) | Ultrasonic velocity v (m $s^{-1}$) | Adiabatic Compressibility $\beta \times 10^{10}$ ($m^2$ $N^{-1}$) | Intermolecular free length $L_f$ (A°) | Specific acoustic impedance $Z \times 10^{-5}$ (kg $m^{-2}$ $s^{-1}$) | Solvation number $S_n$ (C.G.S. Unit) |
|---|---|---|---|---|---|---|---|
| **Caprylate** | | | | | | | |
| 1 | 1.0 | 845.8 | 1096.2 | 9.839 | 38.59 | 9.272 | 2.78 |
| 2 | 2.0 | 846.2 | 1096.7 | 9.825 | 38.56 | 9.280 | 52.36 |
| 3 | 3.0 | 846.7 | 1097.2 | 9.811 | 38.53 | 9.290 | 2.22 |
| 4 | 4.0 | 847.1 | 1097.8 | 9.795 | 38.50 | 9.299 | 2.22 |
| 5 | 5.0 | 847.8 | 1098.6 | 9.773 | 38.46 | 9.314 | 2.39 |
| 6 | 6.0 | 848.7 | 1099.7 | 9.743 | 38.40 | 9.333 | 2.68 |
| 7 | 7.0 | 849.5 | 1100.8 | 9.714 | 38.34 | 9.351 | 2.88 |
| 8 | 8.0 | 850.4 | 1101.9 | 9.685 | 38.29 | 9.371 | 3.02 |
| 9 | 9.0 | 851.2 | 1103.0 | 9.656 | 38.23 | 9.389 | 3.13 |
| 10 | 10.0 | 852.0 | 1103.9 | 9.632 | 38.18 | 9.405 | 3.15 |
| **Caprate** | | | | | | | |
| 1 | 1.0 | 846.0 | 1096.4 | 9.833 | 38.58 | 9.276 | 3.61 |
| 2 | 2.0 | 846.6 | 1097.1 | 9.814 | 38.54 | 9.288 | 3.12 |
| 3 | 3.0 | 847.2 | 1097.7 | 9.796 | 38.51 | 9.299 | 2.92 |
| 4 | 4.0 | 847.8 | 1098.5 | 9.775 | 38.46 | 9.313 | 2.92 |
| 5 | 5.0 | 848.9 | 1099.6 | 9.743 | 38.40 | 9.335 | 3.22 |
| 6 | 6.0 | 849.7 | 1100.9 | 9.710 | 38.34 | 9.354 | 3.45 |
| 7 | 7.0 | 850.6 | 1102.0 | 9.681 | 38.28 | 9.374 | 3.53 |
| 8 | 8.0 | 851.6 | 1103.2 | 9.648 | 38.21 | 9.395 | 3.66 |
| 9 | 9.0 | 852.6 | 1104.4 | 9.616 | 38.15 | 9.416 | 3.75 |
| 10 | 10.0 | 853.5 | 1105.7 | 9.583 | 38.09 | 9.437 | 3.83 |

**Table-2 : Apparent molar volume and other allied parameters of zirconyl soap in benzene-methanol (4:1 v/v) mixture at (40±0.05)°C.**

| S. No. | Concentration $C\times10^2$ (mol $dm^{-3}$) | Apparent molar volume $\phi_v\times10^6$ ($m^3mol^{-1}$) | Apparent molar compressibility $-\phi_k\times10^7$ ($m^5N^{-1}kg^{-1}$ $mol^{-1}$) | Molar sound velocity $R\times10^4$ {$m^3mol^{-1}(ms^{-1})^{1/3}$} | Molar sound compressibility $W\times10^4$ {$m^3mol^{-1}(N/m^2)^{1/7}$} | Available volume $V_a\times10^6$ ($m^3$) | Relative association $R_A\times10^2$ |
|---|---|---|---|---|---|---|---|
| **Caprylate** | | | | | | | |
| 1 | 1.0 | 394.25 | 2.698 | 7.558 | 14.186 | 23.098 | 100.01 |
| 2 | 2.0 | 406.08 | 2.282 | 7.585 | 14.236 | 23.137 | 100.05 |
| 3 | 3.0 | 406.08 | 2.183 | 7.611 | 14.286 | 23.189 | 100.09 |
| 4 | 4.0 | 409.04 | 2.154 | 7.639 | 14.340 | 23.243 | 100.12 |
| 5 | 5.0 | 403.72 | 2.327 | 7.664 | 14.387 | 23.276 | 100.18 |
| 6 | 6.0 | 396.22 | 2.614 | 7.688 | 14.433 | 23.289 | 100.25 |
| 7 | 7.0 | 392.56 | 2.786 | 7.711 | 14.478 | 23.300 | 100.31 |
| 8 | 8.0 | 388.33 | 2.933 | 7.736 | 14.526 | 23.315 | 100.39 |
| 9 | 9.0 | 386.36 | 3.033 | 7.759 | 14.571 | 23.326 | 100.44 |
| 10 | 10.0 | 384.78 | 3.063 | 7.783 | 14.617 | 23.349 | 100.51 |
| **Caprate** | | | | | | | |
| 1 | 1.0 | 436.84 | 3.533 | 7.562 | 14.192 | 23.082 | 100.07 |
| 2 | 2.0 | 448.67 | 3.067 | 7.593 | 14.253 | 23.141 | 100.12 |
| 3 | 3.0 | 452.62 | 2.878 | 7.623 | 14.310 | 23.201 | 100.17 |
| 4 | 4.0 | 454.59 | 2.858 | 7.654 | 14.369 | 23.251 | 100.22 |
| 5 | 5.0 | 443.94 | 3.180 | 7.681 | 14.421 | 23.279 | 100.31 |
| 6 | 6.0 | 442.76 | 3.358 | 7.710 | 14.478 | 23.293 | 100.37 |
| 7 | 7.0 | 440.22 | 3.443 | 7.739 | 14.533 | 23.320 | 100.44 |
| 8 | 8.0 | 438.84 | 3.571 | 7.767 | 14.586 | 23.339 | 100.52 |
| 9 | 9.0 | 434.21 | 3.659 | 7.794 | 14.640 | 23.357 | 100.60 |
| 10 | 10.0 | 433.29 | 3.728 | 7.823 | 14.695 | 23.372 | 100.63 |

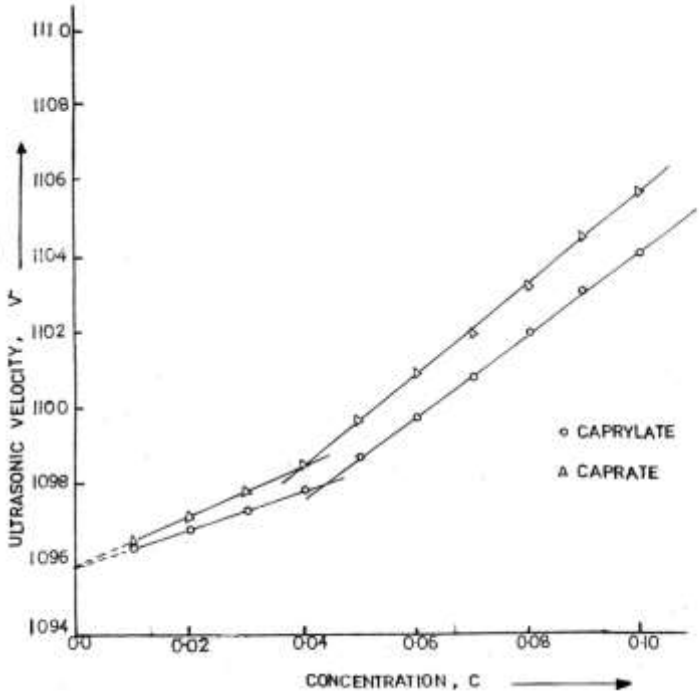


**Fig.-1 : Ultrasonic velocity Vs concentration of zirconyl soaps in benzene-methanol mixture (4:1 v/v)**

**Ultrasonic Measurements:**

The ultrasonic velocity, v of zirconyl soap (caprylate and caprate) solutions in benzene-methanol mixture (4:1 v/v) increases with increasing concentration and chain length of the soap (Table 1). The variation of velocity, v with soap concentration, C depends on the concentration derivatives of density and adiabatic compressibility and can be expressed as :

$$\frac{dv}{dC} = -\frac{v}{2}\left[\frac{1}{\rho}\left(\frac{d\rho}{dC}\right) + \frac{1}{\beta}\left(\frac{d\beta}{dC}\right)\right] \qquad (1)$$

The results indicate that density, ρ increases while adiabatic compressibility, β decreases with increasing soap concentration. Thus, the quantity (dρ/dC) is positive, while (dβ/dC) is negative. Since the values of 1/β (dβ/dC) for these soap solutions are larger than 1/ρ (dρ/dC), the concentration derivative of velocity (dv/dC) is positive. The results are in agreement with the results of other workers {20-21} reported for electrolytic solutions.

The variation of ultrasonic velocity, v with soap concentration, C follows the relationship :

$$v = v_o + GC \qquad (2)$$

where $v_o$ is the ultrasonic velocity in the solvent and G is Garnsey's constant [22] which is a measure of variation of velocity of solution with soap concentration.

The plots of ultrasonic velocity, v Vs soap concentration, C (Fig.- 1) are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of these soaps (0.043 M for caprylate and 0.039 M for caprate). The values of the CMC decrease with increasing chain length of the soap molecule and the results are in agreement with the values obtained from other micellar properties viz. conductivity, density and molar volume. It was found that Garnsey's constant (50 for caprylate and 65 for caprate) increase with increasing chain length of fatty acid constituent of the soap molecule.

The adiabatic compressibility, β of soap solutions decreases with increase in soap concentration (Table-1). The decrease in adiabatic compressibility may be due to the ionization of zirconyl soaps into zirconyl ions, $ZrO^{2+}$ and fatty acid anions, $RCOO^-$ (where R is $C_7H_{15}$ and $C_9H_{19}$ for caprylate and caprate, respectively) in dilute solutions. The ions in the solutions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic fields of the ions and thus the internal pressure increases which lower the compressibility of the solutions i.e. the solutions become harder to compress [23]. The decrease in adiabatic compressibility at higher soap concentrations may be explained on the basis of closed packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and finding of Internal Pressure.

The plots of adiabatic compressibility, β Vs soap concentration, C indicate a break at a definite soap concentration which corresponds to the CMC of the soaps

and these plots are extrapolated to zero soap concentration and the extrapolated values of adiabatic compressibility, $\beta_0$ ($9.854\times10^{10}m^2N^{-1}$) are in close agreement with the experimental values of adiabatic compressibility for solvent mixture ($9.8559\times10^{10}m^2N^{-1}$).

The results of adiabatic compressibility, β of the solutions of zirconyl soaps have also been explained in terms of Bachem's equation [24]

$$\beta = \beta_o + AC + BC^{3/2} \quad (3)$$

where A and B are constants, C is the molar concentration (mol $dm^{-3}$) of soap in solution and $\beta_o$ is the adiabatic compressibility of the solvent mixture. The values of A and B have been determined from the intercept and the slope of the plots of $(\beta - \beta_o/C)$ Vs $C^{1/2}$ for the soap solution. The values of A for caprylate and caprate are $-2.28\times10^{10}$ and $-3.25\times10^{10}$ and the values of B are $3.84\times10^{10}$ and $6.85\times10^{10}$, respectively. The values of constant A decrease while of B increase with an increase in the chain length of the soap molecules.

It follows from Debye-Huckel's theory [25], that the apparent molar compressibility, $\phi_k$ is related to molar concentration of the soap, C by the relationship

$$\phi_k = \phi_\kappa^o + S_k C^{1/2} \quad (4)$$

where $\phi_\kappa^o$ is the limiting apparent molar compressibility ($m^5N^{-1}kg^{-1}mol^{-1}$) and $S_k$ is constant. The plots of $\phi_k$ Vs $C^{1/2}$ are linear for dilute soap solutions. The values of $\phi_\kappa^o$ ($-3.26\times10^7$ and $-4.42\times10^7$) and $S_k$ ($6.14\times10^7$ and $8.97\times10^7$) for the solutions of caprylate and caprate respectively, have been obtained from the intercept and slope of the plots

of $\phi_k$ Vs $C^{1/2}$. The positive values of $S_k$ signify a considerable soap-solvent interaction in dilute soap solutions [26-27].

The values of apparent molar volume, $\phi_v$ first increases then decreases with increasing soap concentration and increase with increasing chain length of soap which suggests that there is an increase in solvation with increasing size of anion in the soap molecules.

The plots of apparent molar volume, $\phi_v$ Vs square root of concentration, $C^{1/2}$ exhibit a break at a concentration which corresponds to the CMC of these soaps. The values of $\phi_v^o$ can be obtained by extrapolation and found to be $378\times10^6$ and $415\times10^6$ $m^3mol^{-1}$ for caprylate and caprate, respectively. The results were found to be in agreement with the results reported by Masson [28].

The intermolecular free length, $L_f$ decreases while specific acoustic impedance, Z increases with the increase in concentration and chain length of soap (Table 1) which indicates that there is a significant interaction between the solute and solvent molecules due to which the structural arrangement is considerably affected [29]. The results can be explained on the basis of hydrophobic interaction between the soap and solvent molecules and thus becoming the main cause of impediment to the propagation of ultrasound waves.

The plots of intermolecular free length, $L_f$ Vs soap concentration, C and specific acoustic impedance, Z Vs soap concentration, C show a break at a definite soap concentration whcih corresponds to the CMC of these soaps.

The values of available volume $V_a$ and relative association, $R_A$ increase with increasing soap concentration (Table-2). The increase in the values of $R_A$ has been attributed to the increased association of soap molecules at higher soap concentration.

The plots of solvation number, $S_n$ Vs soap concentration, C are characterised by a break at the CMC. The values of solvation number decreases with increase in

soap concentration in dilute solutions but exhibit a marked change above the CMC which may be attributed to more intake of solvent molecules above the CMC to reduce the repulsive forces acting between head to ionic micelles. The molar sound velocity, R and molar sound compressibility, W increase with increase in concentration and chain length of soap.

The results of ultrasound velocity measurements confirm that there is a significant interaction between the soap-solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably in dilute solutions. The values of critical micellization concentration for zirconyl soaps are in agreement with the values obtained from other parameters.

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