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# ULTRASONIC VELOCITY AND OTHER ALLIED PARAMETERS OF IRON (III) SOAPS IN NON - AQUEOUS MEDIUM

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## ABSTRACT

The ultrasonic velocity of the solutions of iron (III) soaps (Caprate, Laurate and Myristate) were carried out in a mixture of benzene and methanol (50:50 v/v) at a constant temperature. The data obtained have been used to evaluate the critical micelle concentration (CMC) and to study the soap-soap and soap – solvent interactions. The various acoustic parameters, viz adiabatic compressibility, intermolecular free length, apparent molar compressibility, specific acoustic impedance, molar sound velocity and solvation number were evaluated. The results show that the values of CMC are in agreement with the values obtained from other micellization properties.

**Key words:** Ultrasonic velocity, allied parameters, aqueous medium and Iron (III).

## INTRODUCTION

In the recent years there has been considerable progress in the determination of thermodynamic, rheological and acoustical properties of metallic soaps from speed, density and viscosity measurements[1-4]. The physicochemical characteristics of metal soaps can be controlled up to an extent by the method and conditions of their preparation and so the studies of metal soaps are of importance for their uses in various industries[5-7]. The ultrasonic velocity techniques has been used for studying solute – solvent interactions in a number of system including organic liquid[8], dilute solutions in organic acids[9] and complexes[10-11]. The propagation of ultrasonic waves and the measurement of their velocity[12-14] and absorption[15-16] have been used to determine the nature of molecular interactions n the systems. The present work has been initiated in a view to determine the (CMC), soap – solvent interactions such as various acoustic parameters. The efforts have also been made to investigate the effect of concentration and chain length of soaps on aforesaid parameters.

## EXPERIMENTAL

### Preparation of soaps

All the chemicals used were of AR/BDH grade. The iron soaps (Caprate, Laurate and Myristate were prepared by direct metathesis of the corresponding potassium soap (Caprate, Laurate and Myristate) with slight excess of solution of iron nitrate at 50 – 60$^0$C under vigorous stirring. The metal soaps thus obtained were first dried in an air oven at 50 - 60$^0$C and the final drying of the soaps was carried out under reduced pressure. The purity of the soaps were confirmed by the determination of their melting points and IR.spectra. The melting points of the soaps were Caprate = 120$^0$C, Laurate = 130$^0$C and Myristate = 160$^0$C respectively.

### Preparation of soap solution

The calculated amount of metal soaps was weighed in a standard flask and the solution was made up by adding required amount of solvent mixture. In this way, a number of solutions containing different concentration of iron soaps (Caprate, Laurate and Myristate) in mixture of benzene and methanol (50:50 v/v) were prepared.

**Measurements**

The ultrasonic velocity measurements of the solutions of iron soaps (Caprate, Laurate and Myristate) were carried out with a "Multifrequency ultrasonic interferometer (F-81)" at a frequency of 1 MHz at 40 ± 0.05$^0$C.

A Pyrex glass dilatometer was used to measure the density of iron soap solutions at 40 ± 0.05$^0$C.

**Calculations**

The various acoustic parameters such as Adiabatic compressibility, $\beta$, Intermolecular free length. $L_f$, Specific acoustic impedance, Z, Apparent molar compressibility, $_k$, Molar sound velocity, R and Solvation number, $S_n$ were calculated by using following relationships.

Adiabatic compressibility,

$$\beta = V^{-2}\,\rho^{-1} \qquad (1)$$

Intermolecular free length,

$$L_f = (\beta/k)^{1/2} \qquad (2)$$

Specific acoustic impedance,

$$Z = V.\rho \qquad (3)$$

Apparent molar compressibility,

$$\phi_k = \frac{1000}{C.\rho_0}(\rho_0\beta - \beta_0) + \frac{M.\beta_0}{\rho_0} \qquad (4)$$

Molar sound velocity,

$$R = \frac{M}{\rho}.V^{1/3} \qquad (5)$$

where,

$$M = \frac{n_0M_0 + nM}{n_0 + n} \qquad (6)$$

Solvation number,

$$Sn = \frac{n_0}{n}\left(1 - \frac{\beta ad}{\beta^0 ad}\right) \qquad (7)$$

where V, $\rho$, $\rho_0$, $\beta$, $\beta_0$ are the ultrasonic velocity, density and adiabatic compressibility of the solutions and solvent respectively. N, $n_0$ and M, $M_0$ are the number of moles and molecular weight of solution and solvent respectively. K and C are the temperature dependent Jacobson's constant and concentration in moles per liter, respectively.

**RESULTS AND DISCUSSION**

The ultrasonic velocity, V of iron soap (Caprate, Laurate and Myristate) solutions increases with the increasing concentration and chainlength of the soap (Table - 1). The variation of velocity, V with concentration, C in solutions depends on the concentration derivatives of density, ($d\rho/dc$) and adiabatic compressibility, ($d\beta/dc$) according to the relationship.

$$\frac{dv}{dc} = \frac{-v}{2}\left[\frac{1}{\rho}.\frac{d\rho}{dc} + \frac{1}{\beta}.\frac{d\beta}{dc}\right]$$

The result shows that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Thus the quantity, $d\rho/dc$ is positive while $d\beta/dc$ is negative.

Since the values of [(1/$\beta$) . ($d\beta/dc$)] are larger than those [(1/$\rho$) . ($d\rho/dc$)] for the iron soap solutions. Hence the quantity dv/dc is positive. i.e. the ultrasonic velocity increases with increasing soap concentration. The results are in agreement with the results of other workers reported for electrolytic solutions[17] indicating that these soaps behaves as simple electrolyte in dilute solution in the benzene methanol mixture (50 : 50 v/v).

The plots of ultrasonic velocity, V v/s soap concentration, C (Fig. -1) for solutions of iron soaps (Caprate, Laurate and Myristate) in benzene – methanol mixture shows a break at a definite soap concentration which corresponds to the CMC of the metal soaps. The values of CMC decreases with increasing chain length of the soap are recorded in (Table - 2).

The plots of ultrasonic velocity, V v/s soap concentration, C have been extrapolated to zero soap concentration and the extrapolated value of velocity, $V_0$, for iron soaps (Caprate, Laurate and Myristate) are in close agreement with the experimental value in the solvent mixture (Table - 3) indicating that the soap molecules do not aggregate upto an appreciable extent below the CMC.

The variation of ultrasonic velocity, V with

**Table - 1: Ultrasonic Velocity and other Acoustic Parameters of Iron (III) soaps in a mixture of benzene & methanol (50 : 50 v/v) at 40 ± 0.05 $^0$C**

**Caprate**

| S. No. | Conc. mol/ lt | Density ρ gms/ltr | Velocity V m/Sec. | Adiabatic Compr. $\beta x10^{10}$ $m^2$ $N^{-1}$ | Inter mole. free length $L_f$, $A^0$ | Specific Acoustic impedance Z x $10^{-5}$ $Kg.m^{-2}$ $s^{-1}$ | Molar sound velocity R x $10^3$ | Apparent molar compr. $\phi_k$ x $10^5$ | Solvation no.Sn. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.002 | 0.4113 | 1103.0 | 19.980 | 55.00 | 4.537 | 2.111 | 29.50 | 15.542 |
| 2 | 0.004 | 0.4115 | 1106.0 | 19.860 | 54.83 | 4.551 | 2.123 | 18.00 | 10.409 |
| 3 | 0.006 | 0.4118 | 1109.0 | 19.740 | 54.67 | 4.567 | 2.139 | 14.25 | 8.711 |
| 4 | 0.008 | 0.4120 | 1111.0 | 19.660 | 54.56 | 4.577 | 2.153 | 11.81 | 7.419 |
| 5 | 0.010 | 0.4126 | 1116.0 | 19.460 | 54.28 | 4.605 | 2.167 | 11.75 | 7.707 |
| 6 | 0.012 | 0.4131 | 1121.0 | 19.260 | 54.00 | 4.631 | 2.180 | 11.66 | 7.899 |
| 7 | 0.014 | 0.4145 | 1126.0 | 19.020 | 53.66 | 4.667 | 2.190 | 12.21 | 8.289 |
| 8 | 0.016 | 0.4152 | 1131.0 | 18.820 | 53.38 | 4.696 | 2.203 | 12.15 | 8.361 |
| 9 | 0.018 | 0.4159 | 1135.0 | 18.660 | 53.15 | 4.720 | 2.215 | 11.89 | 8.219 |
| 10 | 0.020 | 0.4170 | 1140.0 | 18.450 | 52.85 | 4.753 | 2.225 | 12.02 | 3.327 |
| **Laurate** | | | | | | | | | |
| 1 | 0.002 | 0.4116 | 1106.0 | 19.860 | 54.83 | 4.552 | 2.114 | 29.67 | 15.157 |
| 2 | 0.004 | 0.4128 | 1110.0 | 19.660 | 54.56 | 4.582 | 2.126 | 21.32 | 12.036 |
| 3 | 0.006 | 0.4132 | 1114.0 | 19.500 | 54.34 | 4.603 | 2.142 | 17.21 | 10.402 |
| 4 | 0.008 | 0.4140 | 1116.0 | 19.390 | 54.18 | 4.620 | 2.155 | 14.79 | 9.027 |
| 5 | 0.010 | 0.4148 | 1119.0 | 19.250 | 53.99 | 4.642 | 2.169 | 13.62 | 8.470 |
| 6 | 0.012 | 0.4156 | 1125.0 | 19.010 | 53.65 | 4.676 | 2.184 | 13.68 | 8.842 |
| 7 | 0.014 | 0.4166 | 1130.0 | 18.790 | 53.34 | 4.708 | 2.197 | 13.65 | 8.978 |
| 8 | 0.016 | 0.4176 | 1135.0 | 18.580 | 53.04 | 4.740 | 2.211 | 13.57 | 9.027 |
| 9 | 0.018 | 0.4184 | 1140.0 | 18.390 | 52.77 | 4.770 | 2.225 | 13.34 | 8.965 |
| **Myristate** | | | | | | | | | |
| 1 | 0.002 | 0.4124 | 1110.0 | 19.680 | 54.59 | 4.578 | 2.115 | 35.58 | 18.816 |
| 2 | 0.004 | 0.4134 | 1114.0 | 19.490 | 54.32 | 4.605 | 2.130 | 23.78 | 13.664 |
| 3 | 0.006 | 0.4145 | 1117.0 | 19.330 | 54.10 | 4.630 | 2.145 | 19.42 | 11.500 |
| 4 | 0.008 | 0.4154 | 1119.0 | 19.220 | 53.94 | 4.648 | 2.159 | 16.50 | 9.856 |
| 5 | 0.010 | 0.4166 | 1123.0 | 19.030 | 53.68 | 4.678 | 2.173 | 15.70 | 9.587 |
| 6 | 0.012 | 0.4174 | 1129.0 | 18.790 | 53.31 | 4.712 | 2.191 | 15.40 | 9.782 |
| 7 | 0.014 | 0.4182 | 1134.0 | 18.590 | 53.05 | 4.742 | 2.208 | 14.91 | 9.664 |
| 8 | 0.016 | 0.4194 | 1140.0 | 18.340 | 52.69 | 4.781 | 2.223 | 14.98 | 9.856 |
| 9 | 0.018 | 0.4212 | 1146.0 | 18.070 | 52.30 | 4.827 | 2.235 | 15.31 | 10.105 |
| 10 | 0.020 | 0.4228 | 1150.0 | 17.880 | 52.03 | 4.862 | 2.247 | 15.13 | 9.946 |

soap concentration, C follows the relationship.

$$V = V_0 + GC$$

Where $V_0$ is the ultrasonic velocity in pure solvent and G is the Garnsey's[18] constant. The values of Garnsey's constant for metal soaps have been calculated from the slope of the plots of V v/s C. The calculated values of Garnsey's constant increases with increasing the chain length of the soap. The values of Garnsey's constant, G are shown in (Table –2).

The adiabatic compressibility of iron soap solutions (Caprate, Laurate and Myristate) $\beta$ decrease with increase in the concentration, as well as with increase in the chain lenghth of the fatty acid constituent of the soap molecule. The use of adiabatic compressibility data provide interesting information on ion – solvent interaction and the structure of solute. The plots of $\beta$ v/s C also exhibit a break at a definite soap concentration, which corresponds to the CMC of the metal soaps. These plots are extrapolated to zero soap concentration and the extrapolated values of $\beta_0$ are in clear agreement with the experimental value (Table – 3)

The results of adiabatic compressibility have been explained in terms of Bachem's relation[19].

$$\beta = \beta_0 + AC + B/C^{3/2}$$

Where A and B are constant, C is the molar concentration and $\beta$, $\beta_0$ are the adiabatic compressibilities of the solution and solvent respectively. The plot of $\beta - \beta_0 / C$ v/s $C^{1/2}$ is linear. The intercept and slope of the plots have been used to explain values of constant A and B respectively (Table –4).

The intermolecular free length, $L_f$[20] decrease while the specific acoustic impedance, Z[21] increases with increasing soap concentration and with the chainlength of the soap molecule (Table – 1) indicating that there is a significant interaction between the soap and solvent[22] molecules which considerably affects the structural arrangement. The increase in the values of Z with increasing soap concentration can be explained on the bases of lyophobic interaction between soap & solvent molecules which increase the intermolecular distance making relatively wider gaps between the molecules and becoming the main cause of impedance in the propagation of ultrasound waves. The plots of $L_f$ v/s C and Z v/s C are characterized by the intersection of the two lines at definite soap concentrations which corresponds to the CMC of the soaps and the values are in agreement with the values obtained from other parameters.

**Table - 2: Values of CMC and Garnsey's constant, G.**

| S. No. | Metal Soaps | CMC x $10^3$ | G |
|---|---|---|---|
| 1. | Iron Caprate | 0.0144 | 1500.0 |
| 2. | Iron Laurate | 0.0140 | 2000.0 |
| 3. | Iron Myristate | 0.0132 | 2500.0 |

The molar sound velocity, R, increases with increase in concentration and chain length of soap. The solvation numbers, Sn, decreases with increase in concentration. The solvation number also increases with chain length of the soap. The higher values of solvation number suggests a significant interaction between soap - solvent molecules and the values are in agreement with the reported results for the solutions of cobalt

**Table - 3: Extrapolated and experimental values of ultrasonic velocity $V_0$ (m/sec) and adiabatic compressibility $\beta_0$ X $10^{10}$($m^2N^{-1}$) of metal soap at 40 ± 0.05°C**

| S. No. | Metal Soaps | Ultrasonic Velocity $V_0$ | | Adiabatic Compressibility $b_0$ | |
|---|---|---|---|---|---|
| | | Extrapolated | Experimental | Extrapolated | Experimental |
| 1. | Iron Caprate | 1100.0 | 1110.0 | 20.33 | 20.8 |
| 2. | Iron Laurate | 1103.0 | 1110.0 | 20.20 | 20.8 |
| 3. | Iron Myristate | 1107.0 | 1110.0 | 20.10 | 20.8 |

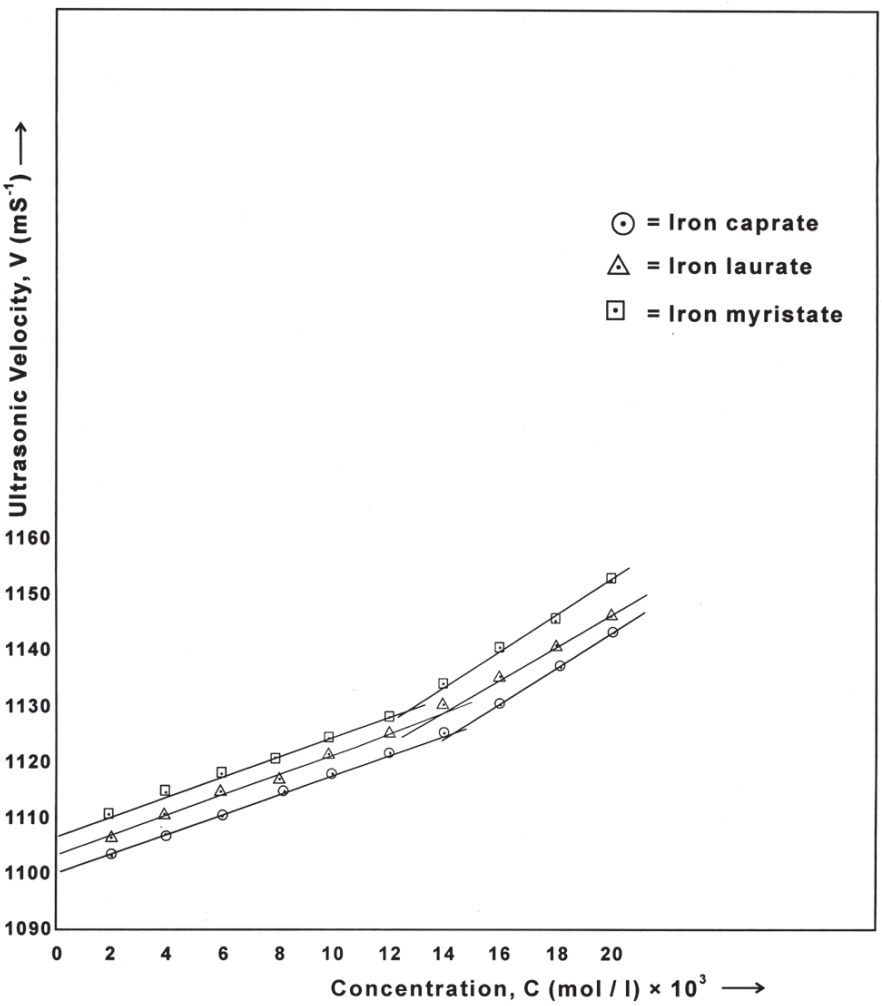


**Fig. - 1: Ultrasonic velocity, V Vs Concentration, C**

**Table - 4: Values of constant A and B as obtained from the plots of $\beta - \beta_0/C$ Vs $\sqrt{C}$ and values of constants $\phi_k^0$ and $S_k$ obtained from plots of $\phi_k$ Vs $\sqrt{C}$ of metal soaps at 40 ± 0.05°C**

| S. No. | Metal Soaps | -A x $10^{10}$ | B x $10^8$ | $f_k^0$ x $10^5$ | $S_k$ x $10^3$ |
|---|---|---|---|---|---|
| 1. | Iron Caprate | 17.5 | 1.85 | 52.0 | 6.0 |
| 2. | Iron Laurate | 19.0 | 2.50 | 54.0 | 10.5 |
| 3. | Iron Myristate | 21.0 | 3.00 | 58.0 | 16.0 |

soaps[23]. The plots of solvation number, Sn v/s soap concentration, C shows a break at definite soap concentration which corresponds to the CMC of the soaps and the values are in agreement with those obtained from $\beta$ v/s C (Fig. - 2).

The values of apparent molar compressibility, $\phi_k$, decreases with increase in soap concentration and increases with the increase in chain length of the soap. It follows from Debye – Huckel theory that the following relationship exist

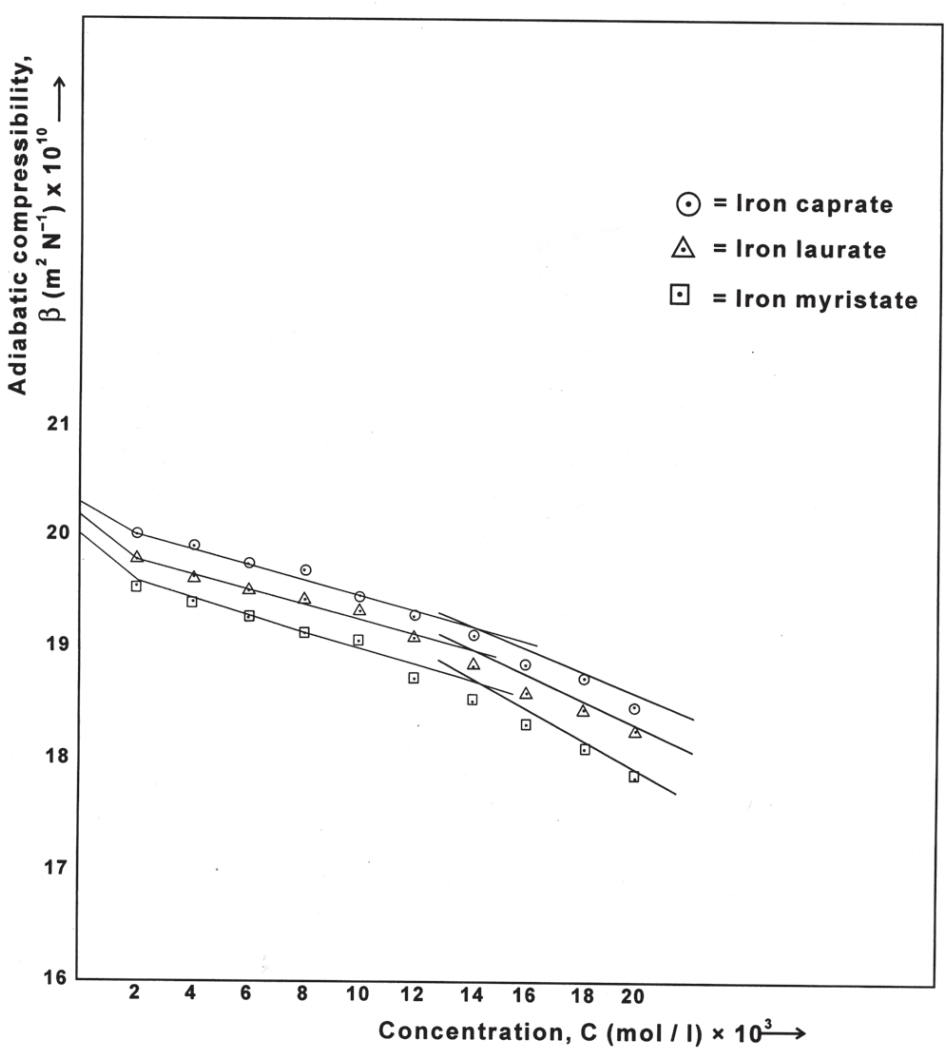


**Fig. - 2: Adiabatic Compressibility, β Vs Concentration, C**

between the apparent molar compressibility, $\phi_k$ and molar concentration of the soap, C

$$\phi_k = \phi_k^0 + S_k C^{1/2}$$

Where $\phi_k^0$ and $S_k$ are the limiting apparent molar compressibility and a constant. The plot of apparent molar compressibility, $\phi_k$ v/s $C^{1/2}$ exhibit a break at a concentration corresponding to the CMC of metal soaps. The intercept and slope of the plot have been used to obtain value of $\phi_k^0$ and constant $S_k$ respectively for Caprate, Laurate and Myristate of iron soap solutions shown in (Table - 4) The results are in agreement with the results reported by Masson[24] for electrolytic solutions.

**Significance**

Ultrasonic measurements are the excellent tools to determine solute – solute and solute – solvent interactions. It also enables to determine CMC, the critical micelle concentration at which the soap molecules aggregates and to calculate the different acoustic parameters. The ultrasonic velocity results show that iron soaps behaves as a simple electrolyte in the solutions and that there is significant interaction between the soap and solvent molecules in dilute solutions.

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