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# Ultrasonic Velocity and Other Allied Properties of Some Alkali Earth Metal Carboxylates in Mixed Organic Solvents

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## ABSTRACT

*The solutions of carboxylates of Strontium and barium (caprate laurate and myristate) have been used in a mixture of chloroform-propylene glycol (70%-30%v/v) at a constant temperature to determine the ultrasonic velocity. The data were used to evaluate the C.M.C. (critical micelle concentration) and to study the soap-soap and soap-solvent interaction. The various acoustic parameters viz: intermolecular free length, adiabatic compressibility, apparent molar compressibility and acoustic impedance have been evaluated. The results confirm that there is a significant interaction between the carboxylate and solvent molecules.*

**Keywords:** Alkaline earth metal carboxylates, ultrasonic velocity, molar volume and C.M.C.

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## INTRODUCTION

Metal soaps are salts of long chain fatty acid with alkaline earth metal or other metals. The physical properties of metal carboxylates vary considerably due to variation in the valency of metal cation and alkyl chain length of the fatty acid. The metal soaps are uses as optical polymer fiber [1], fungicide and pesticide [2], coating pigment in paper industry [3]. Physico-chemical studies on gadolinium soaps in solid state have been investigated by Meera et.al [4]. Ultrasonic studies [5-7] have been shown to be useful in the study of ion-solvent interactions since they take into account the importance of ion-solvent viz: reduced volume and compressibility of the solvent ion molecule. Spectroscopic studies on some metal soaps were studies by several workers [8-9]. The thermodynamics of dissociation and ultrasonic properties of carboxylates of Dysprosium in organic solvent have also been recorded in our previous paper [10-11].

In the present work, strontium and barium carboxylates of fatty acids (capric, lauric and myristic ) have been prepared and effects of chain length on spectroscopic and acoustic behavior have been discussed. Ultrasonic measurements of strontium and barium carboxylates in mixed organic solvent have been used to determine the CMC (critical micelle concentration), soap-solvent interaction and various acoustic parameters of the system. The results of ultrasonic measurements have also been explained in terms of well known equations.

## MATERIALS AND METHODS

**Preparation of carboxylates:** The chemical used for present research were of AR/GR grade. Strontium and barium carboxylates (caprate, laurate and myristate) have been prepared by direct metathesis of the Corresponding Potassium carboxylate with slight excess of solutions of metal Nitrate at 50 – 55ºC under vigorous stirring. The Precipitated carboxylates were filtered and washed with distilled water and acetone to remove the excess of metal ions and unreacted potassium carboxylates. The carboxylates were purified by re-crystallization with a mixture of chloroform-propylene glycol and dried under reduced pressure. The purity of these carboxylates was confirmed by determination of their melting point.

**Measurements:** The ultrasonic velocity measurements were recorded on a multi- frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40 ± 0.05ºC using a crystal of 1 MHz frequency. The uncertainty of velocity measurements is 0.2%. The densities of the solvent and the solutions were measured with a dilatometer. The volume of the dilatometer was 15 ml and the accuracy of the density results was ± 0.0001.

**Calculations:** The various acoustic parameters namely adiabatic compressibility (β), intermolecular free length ($L_f$)[12], specific acoustic impedance (Z)[13], apparent molar volume ($\phi_v$) have been evaluated using the following relationship.

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

$$L_f = k\sqrt{\beta} \quad \text{....(2)}$$

$$Z = \rho v \quad \text{....(3)}$$

$$\phi_v = \frac{1000}{c\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \quad \text{....(4)}$$

Where $\rho_0$, $\rho$, $\beta_0$, $\beta$, $v_0$ and $v$ are the density, adiabatic compressibility and ultrasonic velocity of solvent and solutions, respectively and M is Molecular weight of solute, and K and C are the temperature dependent Jacobson's constant and concentration in g mol $L^{-1}$.

## RESULTS AND DISCUSSION

The ultrasonic velocity and other acoustic and soap-solvent interaction parameters for Strontium and barium carboxylates in mixed organic solvents are recorded in tables 1-3. The variation in ultrasonic velocity with concentration (dv/dc) depends on the concentration derivatives of density and adiabatic compressibility.

$$(dv/dc) = -{}^{v}\!/_{2}\left(\frac{1}{\rho}(d\rho/dc) + \frac{1}{\rho}(d\beta/dc)\right)$$

The quantity dρ/dc is always positive while dβ/dc is negative since the values of 1/β (dβ/dc) are higher than 1/ρ (dρ/dc) for these solutions, the quantity dv/dc is positive, i.e. ultrasonic velocity increases with increase in soap concentration. The variation in ultrasonic velocity with carboxylate concentration C follows the relationship–

$$v = v_0 + GC$$

Where $v_0$ is the ultrasonic velocity in pure solvent and G is Garnsey's constant [14] (table-4). The value of G increases with the increase of chain length of the carboxylate molecules.

**Table 1.** Ultrasonic Velocity and other various parameter of Strontium caprate in methanol at 40 ± 0.05ºC

| **S.N.** | **Concentration C (mol $dm^{-3}$)** | **Density $\rho$ (kg $m^{-3}$)** | **Ultrasonic Velocity $v$ $ms^{-1}$** | **Adiabatic compressibility $\beta \times 10^{10}$ ($m^2 N^{-1}$)** | **Specific acoustic impedance Z** | **Apparent Molar volume $-\phi_v \times 10^{-2}$ $dm^3mol^{-1}$** |
|---|---|---|---|---|---|---|
| 1. | 0.002 | 1.0752 | 1088.5 | 7.849 | 11.703 | 14.446 |
| 2. | 0.004 | 1.0773 | 1089.2 | 7.825 | 11.733 | 7.517 |
| 3. | 0.006 | 1.0794 | 1089.8 | 7.806 | 11.754 | 5.208 |
| 4. | 0.008 | 1.0811 | 1090.4 | 7.782 | 11.788 | 4.605 |
| 5. | 0.010 | 1.0829 | 1090.9 | 7.764 | 11.813 | 2.879 |
| 6. | 0.012 | 1.0854 | 1091.5 | 7.734 | 11.847 | 2.901 |
| 7. | 0.014 | 1.0871 | 1092.0 | 7.716 | 11.871 | 2.541 |
| 8. | 0.016 | 1.0876 | 1092.3 | 7.710 | 11.879 | 2.199 |
| 9. | 0.018 | 1.0886 | 1092.4 | 7.704 | 11.891 | 2.067 |
| 10. | 0.020 | 1.0899 | 1092.6 | 7.686 | 11.897 | 1.774 |

**Table 2.** Ultrasonic Velocity and other various parameter of Strontium laurate in benzene- methanol (50%v/v) at 40 ± 0.05ºC

| **S.N.** | **Concentration C (mol $dm^{-3}$)** | **Density $\rho$ (kg $m^{-3}$)** | **Ultrasonic Velocity $v$ $ms^{-1}$** | **Adiabatic compressibility $\beta \times 10^{10}$ ($m^2 N^{-1}$)** | **Specific acoustic impedance Z** | **Apparent Molar volume $-\phi_v \times 10^{-2}$ $dm^3mol^{-1}$** |
|---|---|---|---|---|---|---|
| 1. | 0.002 | 1.0780 | 1088.7 | 7.831 | 11.736 | 15.724 |
| 2. | 0.004 | 1.0808 | 1089.4 | 7.800 | 11.774 | 8.296 |
| 3. | 0.006 | 1.0827 | 1090.2 | 7.776 | 11.804 | 5.676 |
| 4. | 0.008 | 1.0850 | 1090.9 | 7.745 | 11.836 | 4.415 |
| 5. | 0.010 | 1.0870 | 1091.5 | 7.722 | 11.865 | 3.669 |
| 6. | 0.012 | 1.0895 | 1092.3 | 7.698 | 11.901 | 3.174 |
| 7. | 0.014 | 1.0916 | 1092.8 | 7.675 | 11.929 | 2.794 |
| 8. | 0.016 | 1.0930 | 1092.9 | 7.662 | 11.945 | 2.468 |
| 9. | 0.018 | 1.0936 | 1093.0 | 7.656 | 11.950 | 2.306 |
| 10. | 0.020 | 1.0944 | 1093.2 | 7.645 | 11.963 | 1.934 |

**Table 3.**Ultrasonic Velocity and other various parameter of Strontium myristate in benzene- methanol (50%v/v) at 40 ± 0.05ºC

| **S.N.** | **Concentration C (mol $dm^{-3}$)** | **Density $\rho$ (kg $m^{-3}$)** | **Ultrasonic Velocity $v$ $ms^{-1}$** | **Adiabatic compressibility $\beta \times 10^{10}$ ($m^2 N^{-1}$)** | **Specific acoustic impedance Z** | **Apparent Molar volume $-\phi_v \times 10^{-2}$ $dm^3mol^{-1}$** |
|---|---|---|---|---|---|---|
| 1. | 0.002 | 1.0794 | 1089.0 | 7.813 | 11.755 | 16.338 |
| 2. | 0.004 | 1.0825 | 1090.0 | 7.776 | 11.799 | 8.648 |
| 3. | 0.006 | 1.0846 | 1090.6 | 7.751 | 11.828 | 5.926 |
| 4. | 0.008 | 1.0876 | 1091.5 | 7.716 | 11.871 | 4.673 |
| 5. | 0.010 | 1.0899 | 1092.2 | 7.692 | 11.904 | 3.895 |
| 6. | 0.012 | 1.0920 | 1093.1 | 7.668 | 11.937 | 3.321 |
| 7. | 0.014 | 1.0948 | 1093.5 | 7.639 | 11.972 | 2.961 |
| 8. | 0.016 | 1.0950 | 1093.6 | 7.639 | 11.975 | 2.535 |
| 9. | 0.018 | 1.0979 | 1093.7 | 7.616 | 12.008 | 2.476 |
| 10. | 0.020 | 1.0993 | 1093.8 | 7.605 | 12.024 | 2.115 |

(Fig. 1), the plots of ultrasonic velocity Vs soap concentration, C are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC (Table-4) of these soaps. The CMC values of strontium and barium soaps decreases with the increase of chain length of fatty acid. The main cause of micellization in organic solvent mixture is the energy change due to dipole-dipole interaction between the polar head groups of soap molecules. The molecules of soaps are characterized by the presence of both lipophilic and lyphobic moieties in the same molecules and the micelles in organic solvents can be visualized as Hartley's Inverted micelles in which polar head groups are present in the centre of the micelles with the hydrocarbon chains extending outwards into the solvent. The aggregation begins at very low concentration in organic solvent and results in the formation for smaller aggregates. The association in organic solvent can be described in terms of a stepwise association model [15, 16].

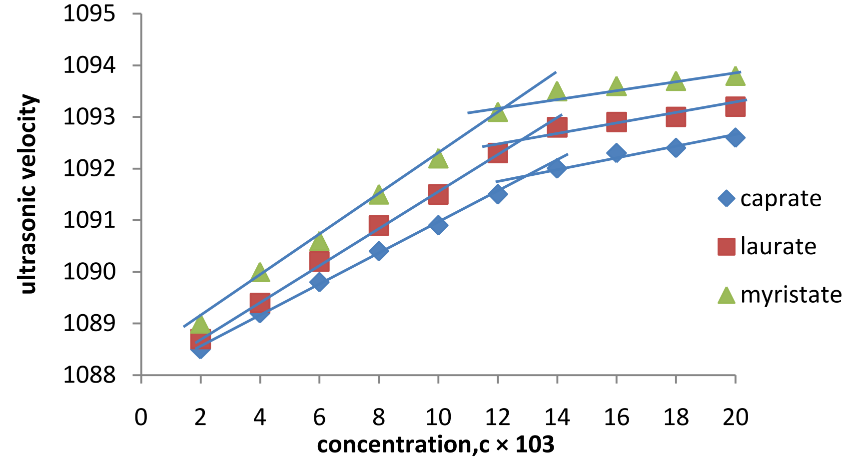

**fig-1 Ultrasonic velocity Vs Concentration**

The determination of CMC in organic solvent cannot be carried out by the methods commonly used for aqueous solutions as the association starts at very low concentration. Therefore, the ultrasonic velocity and density measurements were used to determine the CMC value and various other acoustical parameters.

The plots of ultrasonic velocity Vs concentration, C (Fig.1) are extrapolated to zero soap concentration and the extrapolated values of velocity, $v_0$ are in good agreement with the experimental velocity in mixed solvent, indicating that the molecules of Strontium and barium carboxylates (caprate, laurate and myristate) do not aggregate upto an appreciable extent below the CMC.

The adiabatic compressibility, β of these solutions decreases with increasing the concentration (Table 1-3). The decrease in adiabatic compressibility is attributed to the fact, that the molecule of Strontium and barium carboxylates (caprate, laurate and myristate) in dilute solutions are considerably ionised into metal cation and fatty acid anions. These ions are surrounded by a layer of solvent molecules firmly bounded and oriented towards the ions. The orientation of solvent molecules around the ion is attributed to the influences of their electrostatic field and the internal pressure increases lowering the compressibility of the solutions [17]. The plots of adiabatic compressibility β versus soap concentration, C are also characterized by a break at a definite soap concentration which corresponds to the CMC of these carboxylates. The results of adiabatic compressibility have also been explained in the light of Bachem's relationship [18].

$$\beta = \beta_0 + AC - BC^{3/2}$$

Where A and B are constants, C is the concentration and β and $\beta_0$ are the adiabatic compressibility of solution and solvent respectively, and the values of A and B have been obtained from the intercept and slope of the plots of $\beta-\beta_0/C$ against $C^{1/2}$. The intermolecular free length $L_f$, decreases while specific acoustic impedance, Z increases with the increase in soap concentration, (Table 1-3) which indicate that there is a significant interaction between the soap and solvent molecules which considerably affects the structural arrangement. The plots of intermolecular free length, $L_f$ and specific acoustic impedance, Z against the soap concentration, C show a break at a definite soap concentration which corresponds to the CMC of these soaps.

The value of apparent molar volume decreases with increase in soap concentration (Table 1-3). The values of apparent molar volume of Strontium and barium carboxylates (caprate, laurate and myristate) are negative which indicate that this restrict molecular motion within the solutions. The negative values of apparent molar compressibility decrease linearly with concentration but this decrease is sharp for the pre-micellization region as compared to post micellization indicating poor compressibility at higher concentration. However, this negative value of apparent molar compressibility is probably due to the decrease in internal pressure. The apparent molar compressibility, $\phi_k$ and apparent molar volume, $\phi_v$ are related to the molar concentration of the soap, C by the relationships.

$$\phi_k = \phi^o{}_k + S_k C^{1/2}$$
$$\phi_v = \phi^o{}_v + S_v C^{1/2}$$

Where $\phi^o{}_k$ and $\phi^o{}_v$ are limiting apparent molar compressibility and limiting apparent molar volume respectively, $S_k$ and $S_v$ are constant. The values of $\phi^o{}_k$ and $\phi^o{}_v$ and constant $S_k$ and $S_v$ have been obtained from the intercept and slope of the plots of $\phi_k$ vs $C^{1/2}$ and $\phi_v$ vs $C^{1/2}$(fig-2) below the CMC and are recorded in(Table-4).

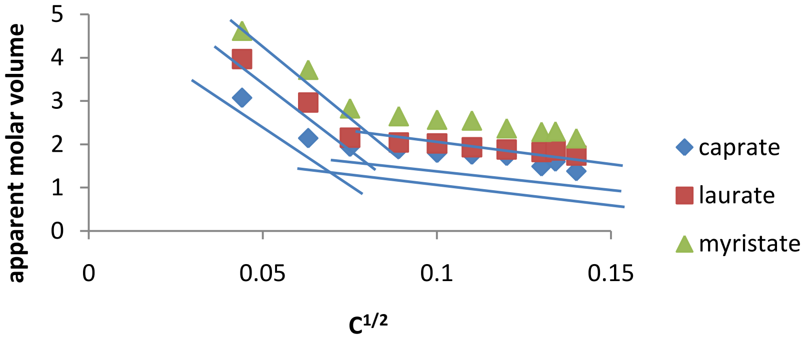

**fig-2 Apparent molar volume Vs Square root of...**

**Table 4.** Values of CMC and various constant for strontium and barium carboxylates at 40±0.05ºC

| Name of the metal soaps | CMC | $G \times 10^{-3}$ | $-A\times10^{10}$ | $B\times10^{8}$ | $-\phi^o{}_v$ | $S_v$ |
|---|---|---|---|---|---|---|
| Strontium Caprate | 0.0140 | 0.277 | 108.0 | 11.10 | 16.80 | 50.00 |
| Strontium Laurate | 0.0136 | 0.333 | 116.0 | 14.80 | 17.20 | 53.00 |
| Strontium Myristate | 0.0128 | 0.500 | 124.0 | 14.80 | 18.60 | 54.55 |
| Barium Caprate | 0.0134 | .357 | 38.0 | 1.90 | 5.30 | 15.00 |
| Barium Laurate | 0.0130 | .450 | 45.0 | 3.70 | 5.60 | 37.50 |
| Barium Myristate | 0.0122 | .500 | 54.0 | 7.40 | 6.90 | 37.50 |

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