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# Ultrasonic Velocity and other allied parameters of Dysprosium laurate and myristate

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## ABSTRACT

*Ultrasonic measurement of Dysprosium Laurate and Myristate in methanol have been used to determine the critical micelle concentration (CMC), soap-solvent interaction and various acoustic parameters of the system. The value of CMC increases with increase chain length of fatty acids. The results show that the soap molecules do not aggregate appreciably below CMC: there is a significant interaction between soap and solvent molecule in dilute solution. The results of ultrasonic measurements have also been explained in terms of well known equation.*

**Keywords:** Ultrasonic velocity, Dysprosium carboxylates, and CMC values.

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## INTRODUCTION

The metallic soaps are widely used in industries as detergents, softeners, plasticizers, greases, lubricants, cosmetics and medicine. The physico-chemical characteristics and the structure of Metallic soaps depend largely on the method and conditions of preparation, properties and used of metal soaps have been investigated by several workers[1-9]. Ultrasonic measurements[10-12] have been shown to be useful in the study of ion-solvent interactions since they take into account the important consequences of ion-solvent, viz. reduced volume and compressibility of the solvent molecule.

The present work deals with the measurements of the ultrasonic velocity of the solutions of Dysprosium laurate and Myristate in methanol and the results have been used to study the solute-solvent interaction and the evaluate the CMC and various acoustic and thermodynamic parameters.

## MATERIALS AND METHODS

All chemicals used were AR/GR [E-Merck] grade. The Dysprosium laurate and myristate were prepared by direct metathesis of corresponding potassium soap with the required amount of aqueous solution of Dysprosium nitrate at 50-55ºC under vigorous stirring. The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreacted fatty acid. The purity of the soaps was checked by elemental analysis and by their IR spectrum.

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 ($L_f$)[13], specific acoustic impedance (Z)[14], apparent molar volume ($\phi_v$) have been evaluated using the following relationship.

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

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

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

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

Where $\rho_0$, $\rho$, $\beta_0$, $\beta$, $\rho$, $v_0$ 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 Dysprosium laurate and myristate in methanol are recorded in table 1-2.

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

| **S.N.** | **Concen-tration C (mol $l^{-1}$)** | **Density $\rho$ (g mol $l^{-1}$)** | **Ultrasonic Velocity $v$ ms$^{-1}$** | **Adiabatic compressibility $\beta \times 10^{10}$ (m$^2$ × N$^{-1}$)** | **specific acoustic impedance Z** | **Apparent Molar volume $\phi_v \times 10^{-2}$ M$^5$N$^{-1}$ (Kmol)$^{-1}$** |
|---|---|---|---|---|---|---|
| 1. | 0.002 | 0.9219 | 1132.0 | 8.470 | 1043.59 | 46.72 |
| 2. | 0.004 | 0.9232 | 1133.0 | 8.438 | 1045.99 | 22.60 |
| 3. | 0.006 | 0.9246 | 1134.2 | 8.408 | 1048.68 | 14.72 |
| 4. | 0.008 | 0.9256 | 1135.3 | 8.382 | 1051.17 | 10.32 |
| 5. | 0.010 | 0.9268 | 1136.5 | 8.354 | 1053.31 | 7.86 |
| 6. | 0.012 | 0.9274 | 1137.1 | 8.339 | 1054.55 | 5.77 |
| 7. | 0.014 | 0.9281 | 1137.6 | 8.326 | 1055.81 | 4.34 |
| 8. | 0.016 | 0.9288 | 1138.1 | 8.312 | 1057.07 | 3.26 |
| 9. | 0.018 | 0.9394 | 1138.5 | 8.301 | 1058.12 | 2.38 |
| 10. | 0.020 | 0.9301 | 1139.0 | 8.288 | 1069.38 | 1.72 |

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.

**Table 2.** Ultrasonic Velocity and other various parameter of Dysprosium Myristate in methanol at 40 ± 0.05ºC

| **S.N.** | **Concen-tration** **C** **(mol $l^{-1}$)** | **Density** **ρ** **(g mol $l^{-1}$)** | **Ultrasonic Velocity** ***v*** **$ms^{-1}$** | **Adiabatic compressibility** **$\beta \times 10^{10}$** **($m^2 \times N^{-1}$)** | **specific acoustic impedance** **Z** | **Apparent Molar volume** **$\phi_v \times 10^{-2}$** **$M^5N^{-1}$ (Kmol)$^{-1}$** |
|---|---|---|---|---|---|---|
| 1. | 0.002 | 0.9224 | 1132.2 | 8.457 | 1044.34 | 48.07 |
| 2. | 0.004 | 0.9239 | 1133.5 | 8.424 | 1047.24 | 23.27 |
| 3. | 0.006 | 0.9254 | 1134.9 | 8.390 | 1050.24 | 15.01 |
| 4. | 0.008 | 0.9269 | 1136.1 | 8.359 | 1053.05 | 10.87 |
| 5. | 0.010 | 0.9280 | 1137.5 | 8.328 | 1055.60 | 8.03 |
| 6. | 0.012 | 0.9285 | 1138.0 | 8.316 | 1056.60 | 5.68 |
| 7. | 0.014 | 0.9291 | 1138.4 | 8.305 | 1057.69 | 5.28 |
| 8. | 0.016 | 0.9297 | 1138.9 | 8.293 | 1058.84 | 2.85 |
| 9. | 0.018 | 0.9302 | 1139.3 | 8.282 | 1059.78 | 1.86 |
| 10. | 0.020 | 0.9308 | 1139.7 | 8.271 | 1060.8 | 1.11 |

The variation in ultrasonic velocity with soap 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[15] (table 3). The values of G increases with the increase of chain length of the soap molecules.

The plots of ultrasonic velocity versus soap concentration, C (fig. 1) are characterized by an intersection of two straight lines at a definity soap concentration which corresponds to the CMC (table 3) of these soaps. The CMC values of Dysprosium 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 lypophilic and lyophobic 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 [16, 17]. 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.

**Table-3.** Values of CMC, and various constants for Dysprosium soaps at 40 ± 0.05ºC

| | **Laurate** | **Myristate** |
|---|---|---|
| CMC | 0.0094 | 0.0090 |

| | | |
|---|---|---|
| $G \times 10^{-3}$ | 2.50 | 3.00 |
| $-A$ | 17.40 | 21.60 |
| $B\times10^{10}$ | 3.33 | 5.38 |
| $\phi^{o}_{v}\times10^{-2}$ | 10.30 | 10.50 |
| $S_v\times10^{-2}$ | 75.20 | 65.15 |

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 Dysprosium laurate and myristate do not aggregate upto an appreciable extent below the CMC.

The adiabatic compressibility, $\beta$ of these soap solutions decreases with increasing the soap concentration (table 1-2). The decrease in adiabatic compressibility is attributed to the fact, that the molecule of Dysprosium 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 [18].

The plots of adiabatic compressibility $\beta$ versus soap concentration, C are also characterized by a break at a definite soap concentration which corresponds to the CMC of these soaps.

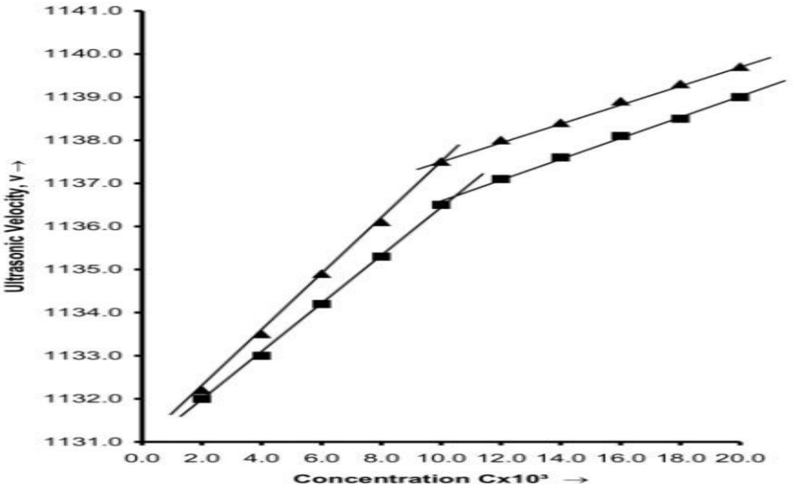

Fig.-1 Ultrasonic Velocity, v Vs. Concentration for Dysprosium Soaps ■ Laurate ▲ Myristate

The results of adiabatic compressibility have also been explained in the light of Bachem's relationship [19].

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

Where A and B are constants, C is the concentration and $\beta$ 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 $\beta\text{-}\beta_0/C$ against $C^{1/2}$.

The intermolecular free length $L_f$, decreases while specific acoustic impedance, Z increases with the increase in soap concentration,(table 1-2) which indicate that there is a significant interaction between the soap and solvent molecules which considerably affects the structural arrangement. The increase in the values of specific acoustic impedance, Z with increase in soap concentration, C can be explained on the basis of lyophobic interaction between soap and solvent molecules which increases the intermolecular distance, making relatively wider gap between the molecules and becoming the main cause of impedance in the progation of ultrasonic waves.

The plots of intermolecular free length, $L_f$ and specific acoustic impedance, Z against the soap concentration, C (fig-2) show a break at a definite soap concentration which corresponds to the CMC of these soaps.

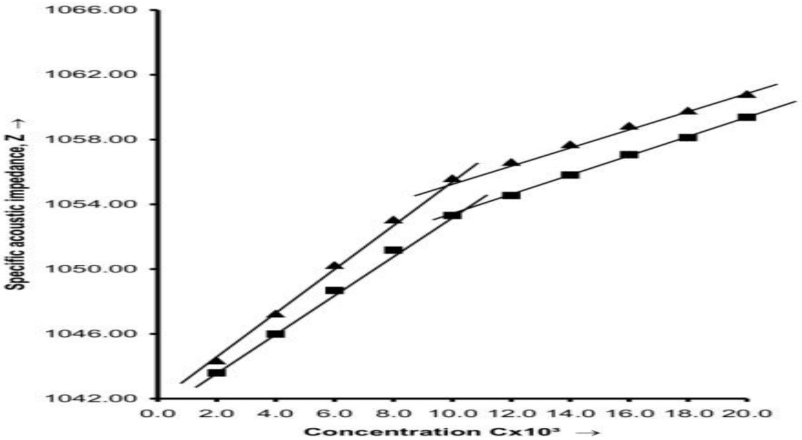

Fig.-2 Specific acoustic impedance, Z Vs. Concentration for Dysprosium Soaps ■ Laurate ▲ Myristate

The values of apparent molar volume decreases with increase in soap concentration (table 1-2). The values of apparent molar volume of Dysprosium 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-3) below the CMC and are recorded in(table-3).

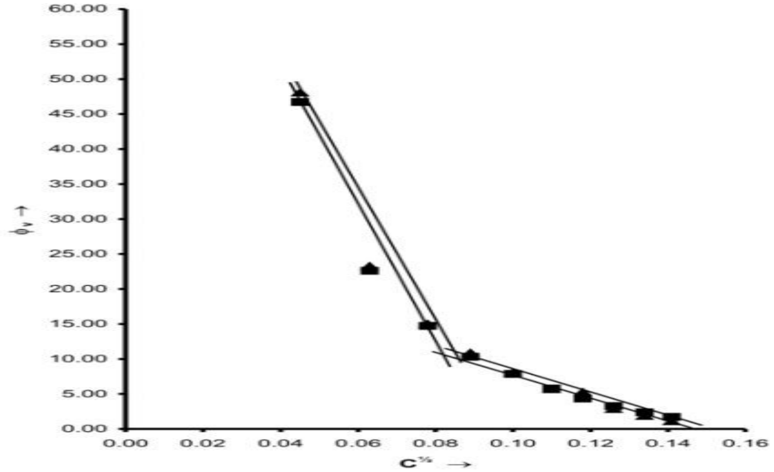

Fig.-3 Apparent Molar Volume, $\phi_v$ Vs. $C^{½}$ for Dysprosium Soaps ■ Laurate ▲ Myristate

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