*International Journal of Theoretical & Applied Sciences,* **1**(1): 32-37(2009)

# Acoustic measurements and compressibility behaviour of terbium myristate in benzene-methanol mixture

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## ABSTRACT

**Ultrasonic velocity in the solutions of terbium myristate in 60/40 benzene-methanol mixture (v/v) have been measured at 25°C and 30°C in order to compute CMC, compressibility behaviour, Garnsey's constant and other acoustical constants (adiabatic and molar compressibility, molar sound velocity, solvation number, relative association, relaxation strength).These parameters are discussed in light of different theories of propagation of ultrasonic waves. The value of critical micellar concentration (CMC) for terbium myristate is in agreement with those obtained from other parameters. The results confirm that there is a significant interaction between soap and solvent molecules in dilute solutions and soap molecules do not aggregate appreciably below the CMC. The critical micellar concentration (CMC) increases with increase in temperature.**

**Keywords:** Terbium myristate, acoustical constants, ultrasonic velocity, compressibility, CMC

## INTRODUCTION

Salts of fatty acids with alkaline-earth metals or other polyvalent metals are water insoluble. Such "metallic soaps", are widely used in industries as detergents, softeners, plasticizers, greases, lubricants, cosmetics, medicines, emulsifiers and water proofing agents. The study and understanding of acoustical properties are necessary for their application in industries. Sound velocity is purely a thermodynamic function and with the help of this method [1], a number of other acoustical constants of electrolyte solutions can be determined. Ultrasonic methods have been used for investigating ion-solvent interactions in organic liquids [2] and in dilute solutions of inorganic acids [3]. Mehrotra et al [4,5,6] determined acoustical parameters of lanthanide soaps in mixed organic solvents. Suleman et al [7,8] studied ultrasonic behaviour of transition metal soap in liquor ammonia. Acoustical studies, compressibility behavior and Rao formalism of lanthanide soap solutions were carried out by Upadhyaya and Chaturvedi [9].

In the work reported here, ultrasonic velocity and density of terbium myristate in 60/40 benzene- methanol (v/v) of varying concentration and temperature have been measured in order to compute various acoustical constants. These constants give a clear insight into micellar aggregate formed by terbium myristate in non aqueous medium.

## MATERIAL AND METHODS

Anala R grade myristic acid, benzene, methanol, ethanol and terbium acetate (purity 99.9% received from Indian Rare Earth Limited, Kerala) were used for the present investigation. The terbium myristate was prepared by direct metathesis of corresponding potassium soap (myristate) by pouring a slight stoichiometric excess of aqueous terbium acetate solution into clear potassium myristate dispersion at raised temperature with vigorous stirring. The precipitate was filtered off and washed with hot distilled water and acetone. After initial drying in an air oven 50-60$^{0}$C, final drying was carried out under reduced pressure. The purity of soap was checked by the elemental analysis and results were found in agreement with theoretically calculated values. The purified soap has the melting point $106^0$C.

Solutions of terbium myristate were prepared by dissolving a known amount of soap in a mixture of 60/40 benzene-methanol and kept for 2 hrs. in a thermostat at desired temperature. Ultrasonic measurements were carried out on a multi frequency ultrasonic interferometer (MX-3, Mittal Enterprises, New Delhi) at 25°C and 30°C using a 1 MHz frequency. Water maintained at the desired temperature and controlled to ± 0.5°C by a thermostat passed through the jacket of cell before the measurement was actually made. The measured velocities have an uncertainty of ± 0.5 $ms^{-1}$. The densities of the solutions were determined at different temperatures with RD bottle calibrated with pure benzene.

**Calculations**

Acoustic parameters such as adiabatic compressibility$\beta$, molar compressibility W, apparent molar compressibility $\phi_k$ [11], intermolecular free length $L_f$ [10], specific acoustic impedance Z [11], available volume $V_a$ [12], molar sound velocity R [13], relative association $R_A$ [14], primary solvation number $S_n$ and relaxation strength r [15], were calculated using the following relationships.

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

$$W = (\overline{M}/\rho)\,(\beta)^{-1/7} \quad \text{--- (2)}$$

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0} \quad \text{--- (3)}$$

$$L_f = K\sqrt{\beta} \quad \text{--- (4)}$$

$$Z = \rho v \quad \text{--- (5)}$$

$$V_a = \overline{V}(1 - v/v_\alpha) \quad \text{--- (6)}$$

$$R = (\overline{M}/\rho)\,(v)^{1/3} \quad \text{--- (7)}$$

Where

$$\overline{M} = \frac{n_0 M_0 + nM}{n_0 + n}$$

$$R_A = (\rho/\rho_0)\,(v_0/v)^{1/3} \quad \text{--- (8)}$$

$$S_n = n_o/n\ [1 - \overline{V}\,\beta/n_o\beta_0\overline{V}_0] \quad \text{--- (9)}$$

and $$r = 1 - (v/v_\alpha)^2 \quad \text{--- (10)}$$

Here $\rho_o$, $\rho$, $\beta_o$, $\beta$, $v_o$, v, $\overline{V}_0$ and $\overline{V}$ are the density, adiabatic compressibility, ultrasonic velocity and molar volume of solvent and solutions, respectively and $n_o$, $M_o$, n and M are the number of moles and molecular weight of solvent and solute, respectively and K and $\overline{M}$ are the temperature dependent Jacobson's constant and effective molecular weight of solution. $v_\alpha$ is equivalent to 1600 m/sec. $\phi_k$ is apparent molar compressibility.

## RESULTS AND DISCUSSION

The various acoustical constants of terbium myristate were measured at 25 and 30°C in a mixture of 60/40 benzene-methanol (v/v) (Table1 and Table2). The results indicate that ultrasonic velocity and density increase with increasing soap concentration and decrease with increase in temperature. The variation of ultrasonic velocity v with soap concentration C depends upon the concentration derivative of density $\rho$ and adiabatic compressibility $\beta$ by the relationship.

$$\frac{dv}{dC} = -\frac{v}{2}\left[\frac{1}{\rho}\left(\frac{\partial\rho}{\partial C}\right) + \frac{1}{\beta}\left(\frac{\partial\beta}{\partial C}\right)\right] \quad \text{--- (11)}$$

The concentration derivative of density $(\frac{\partial\rho}{\partial C})$ is positive, while the quantity $(\frac{\partial\beta}{\partial C})$ is negative and since the value of $\frac{1}{\beta}(\frac{\partial\beta}{\partial C})$ predominates over $\frac{1}{\rho}(\frac{\partial\rho}{\partial C})$ for these soap solutions dV/dC will be positive, i.e. ultrasonic velocity increases with increasing soap concentration. The variation of ultrasonic velocity v with soap concentration C for dilute solution is given by following equation

$$v = v_0 + GC \qquad \ldots(12)$$

Where $v_0$ ultrasonic velocity of pure solvent and G is is Garnsey's constant [16].

The plots of ultrasonic velocity v versus soap concentration C are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of soap (Fig.1). The soap form micelles at a particular concentration of soap because of balance between the attractive hydrophobic interaction of the long chain hydrocarbon tails and repulsive forces between the ionic head groups. The variation in the CMC value with temperature is generally characterized in term of phase separation or equilibrium model for micelle formation. The micellization takes place where the energy resulting of association of hydrophobic chain of monomer is sufficient to overcome the repulsion between the ionic head groups and the decrease in entropy accompanying the aggregation. Therefore, the increase in the temperature of soap solutions results in the increase in critical micellar concentration (CMC).The value of Garnsey's constant G obtained from the plots of v versus C decrease with increasing temperature (Table3).

The nature of adiabatic compressibility β is reverse to that of ultrasonic velocity v. Increase in soap concentration causes decrease in the values of adiabatic compressibility (Fig.2).The decrease in adiabatic compressibility is attributed to the fact that soap molecules in dilute solutions are considerably ionized into metal cation and fatty acid anions. These ions are surrounded by a layer of solvent molecules firmly bounded and orient towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of the ions and thus the internal pressure increases, this lowers the compressibility of the soap solutions.

The results of adiabatic compressibility β have also been explained in term of Bachem's relationship [17].

$$\beta = \beta_0 + AC + BC^{3/2} \qquad \text{--- (13)}$$

Where A and B are constants, C is molar concentration of soap solutions. β and $\beta_0$ are the adiabatic compressibilities of solutions and solvent, respectively.

The values of constants have obtained from the intercept and slope of plots of $\beta$-$\beta_0$/C Vs $\sqrt{C}$. The plots of $\beta$-$\beta_0$/C Vs $\sqrt{C}$ show a break at CMC (Table 3).

The values of molar compressibility W, of terbium myristate in a mixture of 60/40 benzene-methanol (v/v) increase with increase in soap concentration. However, the rise in temperature results in decrease of molar compressibility.

The apparent molar compressibility $\phi_k$ is related to concentration C by Gucker's limiting law [18].

$$\phi_k = \phi_k^0 + S_k C^{1/2} \qquad \text{--- (14)}$$

Where $\phi_k^o$ is limiting apparent partial molar compressibility and $S_k$ is constant.

The $\phi_k$ Vs $\sqrt{C}$ plots are linear. $\phi_k^o$ and $S_k$ have obtained from intercept and slope of plots $\phi_k$ Vs $\sqrt{C}$ below the CMC. The positive value of $S_k$ signifies a considerable soap solvent interaction below CMC (Table3).

The intermolecular free length $L_f$ and specific acoustic impedance Z in a mixture of 60/40 benzene-methanol (v/v) at different temperatures suggest that the increase in specific acoustic impedance Z and decrease in the intermolecular free length $L_f$ with increase in soap concentration can be explained on the basis of lyophobic interactions between soap and solvent molecules. The $L_f$ increases with rising temperature. However Z has shown the reverse trend to that of intermolecular free length.

The solvation number $S_n$ decreases with increase in soap concentration and temperature. The value of $S_n$ corresponds to the number of solvent molecules in the primary solvation sheath of ions. The positive value of $S_n$ suggests appreciable solvation of ions. The Rao's number R increases with increasing soap concentration. However, there is decrease in values of R with rise in temperature. A rise in temperature increases the molar volume, probably due to decrease in the density of these solutions. The Rao's number is, however independent of temperature.

The relative association $R_A$ increases with rising temperature is due to decreasing in solvation. $R_A$ decreases with increasing concentration due to increasing solvation of ions. The values of available volume $V_a$ increases with rise in temperature and decreases with increasing soap concentration. The values relaxation strength r increase with the rise in temperature, however increase in soap concentration decreases the relaxation strength.

## CONCLUSION

The results confirm that there is a significant interaction between the soap-solvent molecules in dilute solutions. Data on ultrasonic velocity show that terbium myristate behave as weak electrolyte in 60/40 benzene-methanol mixture (v/v) and soap molecules do not aggregate appreciably below the CMC.

## ACKNOWLEDGEMENT

The authors are extremely grateful to Dr. A.K. Gangele, Principal S.S.L. Jain P.G. College, Vidisha for providing necessary lab facilities.

## REFERENCES

[1] S. J. Synder and J. R. Synder, *J. Chem. Eng. Data*, **19:** 270(1974).

[2] C. V. Chaturvedi and S. Prakash, *Acustica,* **27:** 248(1972).

[3] E. Kowalska, W. Kowalski, C. Mazanek and M. Bodzek, *Rocz. Chemii,* **40:** 469(1966).

[4] K. N. Mehrotra, M. Chauhan and R. K. Shukla, *Phys. Chem. Liq.,* **18**: 295(1988).

[5] K. N. Mehrotra and S. K. Upadhyaya, *Polish J. Chem.,* **65**: 1035(1991).

[6] K. N. Mehrotra and M. K. Rawat, *Tenside Surfactants Detergents*, **32**: 255(1995).

[7] Suleman, S. P. Verghese, F. M. Prasad and H. Kulshrestha, *J. Ind. Coun. Chem*., **24(2):** 21(2007).

[8] Suleman, S. P. Verghese, F. M. Prasad, *J. Indian Chem. Soc.,* **85:** 856(2008).

[9] S. K. Upadhyaya and P. K. Chaturvedi, *J. Ind. Coun. Chem,* **24**(4): 74(2007).

[10] B. Jacoboson, *Acta Chem. Scand.,* **6:** 1485(1952).

[11] I. E. E'lpiner, *Ultrasound Physical, Chemical and Biological Effects, Consultants Bureau, Moscow,* p.371 (1964).

[12] W. Schaafts, Z. *Phys. A,* **114:** 110(1939).

[13] M. R. Rao, *Indian J. Phys.* **14:** 109(1940); *J. Chem. Phys.,* **9:** 682(1941).

[14] A. Waissler, *J. Chem. Phys.,* **15:** 210(1947).

[15] S. K. Upadhyaya and R. Nagar, *Acoustics Letters,* **18**(1): 9(1994).

[16] R. Garnsey, R. J. Boe, R. Mohoney and T. A Litovitz, *J. Chem. Phys*., **50:** 5222(1969).

[17] C. Bachem, *Z Phys. A.,* **101:** 541(1936).

[18] F. T. Gucker, *Chem. Re.,* **13:** 111(1933).

Table 1.Ultrasonic velocity, compressibility & other acoustical parameters of terbium myristate in 60/40 benzene-methanol(v/v)mixture at $25^0C\pm0.5^0C$

| S. No. | $C \times 10^3$ (g mol $l^{-1}$) | ρ ($g.ml^{-1)}$) | $v \times 10^{-5}$ (cm/sec) | $\beta \times 10^{11}$ ($cm^2dyne^{-1)}$) | $W \times 10^{-2}$ | $-\phi_{k \times 10}{}^6$ ($cm^2dyne^{-1}$) | $L_f$ (Å) | $Z \times 10^{-5}$ | $S_n$ | R | $V_a$ | $R_A$ | r |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 1.0 | 0.8490 | 1.168 | 8.63 | 16.37 | 7.37 | 0.5965 | 0.992 | 174.43 | 2920 | 16.13 | 0.995 | 0.467 |
| 2. | 1.5 | 0.8500 | 1.189 | 8.32 | 16.44 | 7.04 | 0.5856 | 1.011 | 138.67 | 2935 | 15.33 | 0.990 | 0.448 |
| 3. | 2.0 | 0.8510 | 1.210 | 8.03 | 16.51 | 6.79 | 0.5751 | 1.030 | 119.83 | 2950 | 14.54 | 0.986 | 0.428 |
| 4. | 2.5 | 0.8518 | 1.230 | 7.76 | 16.58 | 6.51 | 0.5655 | 1.048 | 107.27 | 2965 | 13.79 | 0.981 | 0.409 |
| 5. | 3.0 | 0.8526 | 1.245 | 7.57 | 16.64 | 6.08 | 0.5585 | 1.061 | 96.30 | 2976 | 13.22 | 0.978 | 0.394 |
| 6. | 3.5 | 0.8530 | 1.251 | 7.49 | 16.66 | 5.43 | 0.5556 | 1.067 | 84.87 | 2981 | 13.00 | 0.977 | 0.389 |
| 7. | 4.0 | 0.8534 | 1.256 | 7.43 | 16.68 | 4.91 | 0.5533 | 1.072 | 75.95 | 2985 | 12.81 | 0.976 | 0.384 |
| 8. | 4.5 | 0.8540 | 1.263 | 7.34 | 16.70 | 4.56 | 0.5501 | 1.079 | 69.59 | 2989 | 12.55 | 0.975 | 0.377 |
| 9. | 5.0 | 0.8544 | 1.269 | 7.27 | 16.73 | 4.25 | 0.5473 | 1.084 | 64.19 | 2994 | 12.33 | 0.974 | 0.371 |

Table 2.Ultrasonic velocity, compressibility & other acoustical parameters of terbium myristate in 60/40 benzene-methanol(v/v)mixture at $30^0C\pm0.5^0C$.

| S. No. | $C \times 10^3$ (g mol $l^{-1}$) | ρ ($g.ml^{-1)}$) | $v \times 10^{-5}$ (cm/sec) | $\beta \times 10^{11}$ ($cm^2dyne^{-1)}$) | $W \times 10^{-2}$ | $-\phi_{k \times 10}{}^6$ ($cm^2dyne^{-1}$) | $L_f$ (Å) | $Z \times 10^{-5}$ | $S_n$ | R | $V_a$ | $R_A$ | r |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.0 | 0.8488 | 1.160 | 8.75 | 16.34 | 6.52 | 0.6007 | 0.985 | 164.19 | 2914 | 16.43 | 0.997 | 0.474 |
| 2 | 1.5 | 0.8496 | 1.180 | 8.45 | 16.41 | 6.39 | 0.5902 | 1.002 | 130.99 | 2929 | 15.68 | 0.992 | 0.456 |
| 3 | 2.0 | 0.8506 | 1.202 | 8.14 | 16.49 | 6.40 | 0.5791 | 1.022 | 115.14 | 2945 | 14.84 | 0.987 | 0.436 |
| 4 | 2.5 | 0.8514 | 1.222 | 7.86 | 16.56 | 6.22 | 0.5693 | 1.040 | 103.75 | 2960 | 14.08 | 0.983 | 0.417 |
| 5 | 3.0 | 0.8522 | 1.240 | 7.63 | 16.62 | 5.98 | 0.5609 | 1.057 | 94.77 | 2973 | 13.41 | 0.979 | 0.399 |
| 6 | 3.5 | 0.8526 | 1.247 | 7.54 | 16.65 | 5.38 | 0.5576 | 1.063 | 83.95 | 2979 | 13.16 | 0.977 | 0.393 |
| 7 | 4.0 | 0.8532 | 1.252 | 7.48 | 16.67 | 4.88 | 0.5551 | 1.068 | 75.22 | 2982 | 12.96 | 0.977 | 0.388 |
| 8 | 4.5 | 0.8534 | 1.259 | 7.39 | 16.70 | 4.52 | 0.5520 | 1.074 | 68.86 | 2988 | 12.71 | 0.975 | 0.381 |
| 9 | 5.0 | 0.8538 | 1.265 | 7.32 | 16.73 | 4.21 | 0.5492 | 1.080 | 63.56 | 2993 | 12.48 | 0.974 | 0.375 |

Table 3. Values of various constants for terbium myristate in a mixture of 60/40 benzene - methanol (v/v) at different temperatures.

| S.No. | Temperature ($^0C$) | $CMC \times 10^3$ (g mol $l^{-1}$) | Garnsey's constant(G $\times 10^{-6}$) | $-A \times 10^9$ | $B \times 10^9$ | $-\phi_k^0 \times 10^6$ | $S_k \times 10^6$ |
|---|---|---|---|---|---|---|---|
| 1. | 25 | 2.77 | 4.25 | 7.12 | 20.02 | 7.48 | 25.74 |
| 2. | 30 | 2.90 | 4.18 | 5.70 | 21.62 | 6.90 | 26.07 |

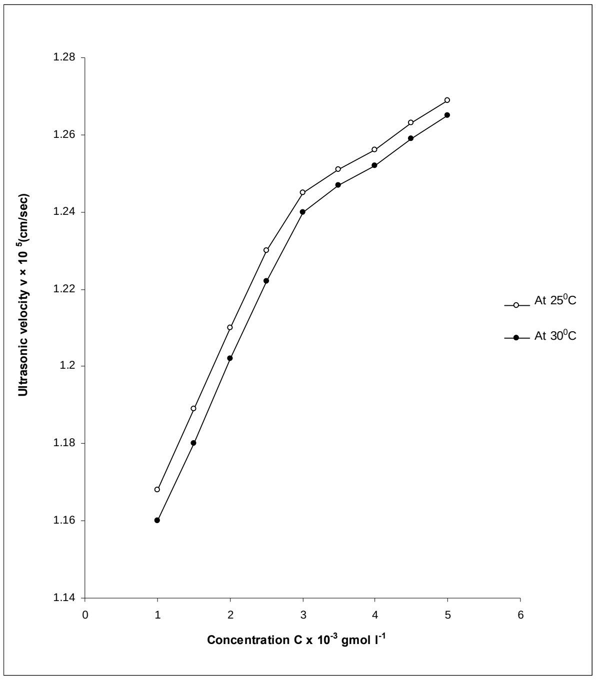

Fig. 1. Ultrasonic velocity Vs Concentration of terbium myristate in a mixture of 60/40 benzene – methanol (V/V)

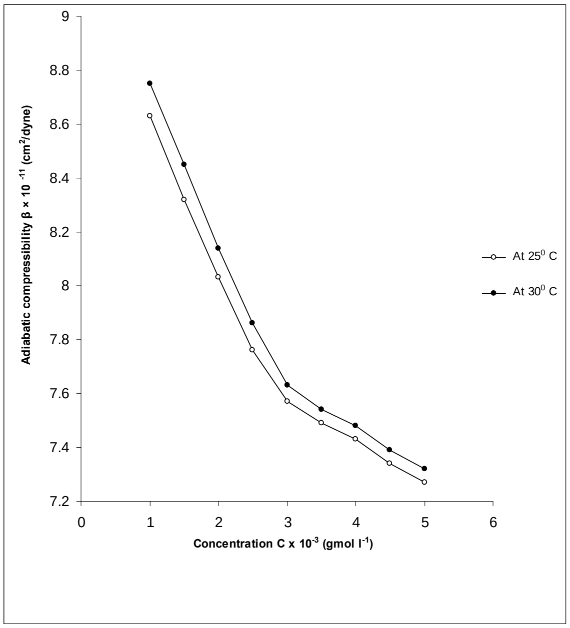

Fig. 2. Adiabatic compressibility Vs Concentration of terbium myristate in a mixture of 60/40 benzene – methanol (V/V)