

# Ultrasonic Behaviour on Carboxylates of Vanadium in Mixed Organic Solvent

## Abstract

The ultrasonic measurements were made on Carboxylates of vanadium (Myristate and Palmitate) in mixture of Benzene and DMSO with a view to determine the Critical miceller concentration (CMC), soap solvent interaction and various acoustic parameters. The value of CMC decreases with the increase in the chain length of soap. The results of ultrasonic velocity and other interaction parameters suggested that there is a significant interaction between soap and solvent molecules.

**Keywords:** Carboxylates, Ultrasonic Velocity, Interaction Parameters.

## Introduction

Recently the study of metal soap is becoming increasingly important in technological and academic field. The metal soaps has been a subject intense investigation in the recent past on account of its role in such diversified fields as lubricant, Stabilizers, emulsifiers, water proofing agent, medicines, cosmetic, anti oxidant and germicides. The technological application of metal soaps are mostly based up on imperical know-how and the selection of the soap specific purpose mainly dependent largely on economic factors.

The methods of preparation and uses of metal soaps were reviewed by several workers<sup>1-7</sup>. The thermogravimetric analysis of yttrium soaps in solid state was studied by Khirwar<sup>8</sup>. The infrared absorption spectra, x-ray diffraction studies and thermal behavior of cerium and thorium laurate were studied by Gupta et al.<sup>9</sup>. The X-ray diffraction studies on Scandium soaps in solid state studies was studied by Khirwar<sup>10</sup>. The studies of ultrasonic velocity and allied properties of magnese, cobalt and copper soaps in non aqueous medium Rawat<sup>11</sup>. The present work deal with the ultrasonic measurements of Carboxylates of vanadium (Myristate and Palmitate) in Benzene and DMSO mixture with a view to evaluate various allied parameters related to the acoustical properties of soap solutions.

## Aim of the Study

The results of the survey of literature reveals that the ultrasonic behavior on carboxylates of Vanadium soaps have not been systematically investigated while they have many uses in industries and academic field. The aim of this research work is to study the ultrasonic behaviour on Carboxylates of vanadium (Myristate and Palmitate ) in mixture of Benzene and DMSO with a view to determine the Critical miceller concentration (CMC), soap solvent interaction and various acoustic parameters.

## Experimental

The Carboxylates of vanadium (Myristate and Palmitate) was synthesized by direct metathesis of corresponding potassium soaps with the required amount aqueous solution of Vanadium nitrate at 50-55<sup>o</sup> C under vigorous stirring. The precipited soap was washed with water and acetone and dried under reduced pressure. The soaps were purified by recrystallization with Benzene and DMSO mixture. The purity of the soap was checked by IR spectra and determination of their melting points. The densities of the solvent and soap solutions was measured by dilatometer. The ultrasonic velocity measurements was recorded on a multi frequency ultrasonic interferometer at 40 ± 0.05<sup>o</sup>C using a crystal of 1 MHz frequency. All the Chemicals used were of AR/BDH grade.

## Review of Literature

Present research work reviews the literature relevant with the aim of study. the ultrasonic behaviour on Carboxylates of transition metals have been studied by several workers. Some of them are listed below.

M.S.Khirwar (2017) was studied the X-ray diffraction studies on Scandium soaps in solid .



**M.S. Khirwar**

Assistant Professor,  
Deptt.of Chemistry,  
R.B.S College,  
Agra

Rajesh Dwivedi (2014) was studied the Physicochemical Studies on Erbium Soaps of Saturated Higher Fatty Acids in Solid State.

M. K. Rawat (2007) was studied the ultrasonic velocity and allied properties of magnese, cobalt and copper soaps in non aqueous medium.

### Result and Discussion

#### Density

The density,  $\rho$  of the solutions of Carboxylates of vanadium of Myristate and Palmitate in Benzene and DMSO mixture increases with increasing soap concentrations (Table-1). The plots of density,  $\rho$  vs C are characterized by an intersection of two straight at definite soap concentration which correspondence to the CMC of soap.

The value of critical micellar concentration decrease with increasing chain length of the soap molecules (Table-2). The plots of  $\rho$  vs c below the CMC have been extrapolated to zero concentration and extrapolated values of the density,  $\rho_0$  are in agreement with experimental values of the density of pure solvent mixture. It is, therefore concluded that the soap molecules do not show appreciable aggregation blow the CMC whereas there is a marked change in aggregation of the soap molecules at the definite soap concentration. The density results have also been explained in terms of Root's equation.

$$\rho = \rho_0 + AC - BC^{3/2}$$

where C is concentration (mol/L) and  $\rho$  and  $\rho_0$  are the density of soap solution and solvent, respectively. The constants A and B refer to the solute solvent and solute-solute interaction respectively.

The Plots of  $\rho - \rho_0/C$  vs  $C^{1/2}$  indicate a break at a definite soap concentration which corresponds to the CMC of the soap. The values of constant A and B have been obtained from the intercept and slope of the plot of  $\rho - \rho_0/C$  vs  $C^{1/2}$  below the CMC and are recorded in (Table-2). The values of constant B are higher than constant A which shows that the solute-solute interactions is larger than the solute-solvents interaction in soaps solutions. It is therefore concluded that the soap molecules do not show appreciable aggregation below the CMC and there is marked increase in aggregation of the soap molecules at this definite soap concentration.

#### Ultrasonic Velocity

The ultrasonic velocity, v of the solutions of Carboxylates of vanadium (Myristate and Palmitate) in mixture of Benzene and DMSO increases with the increasing concentration chain length of the soaps (Table 1). The variation in ultrasonic velocity with concentration depends upon the concentration derivatives of density,  $\rho$  and adiabatic compressibility,  $\beta$ .

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

The results show that the density increases while the adiabatic compressibility decreases with increasing soap concentration and so the quantity

$\left( \frac{d\rho}{dC} \right)$  is positive while  $\left( \frac{d\beta}{dC} \right)$  is negative. Since

the value of  $\left[ \frac{1}{\beta} \left( \frac{d\beta}{dC} \right) \right]$  are larger than the value

of  $\left[ \frac{1}{\rho} \left( \frac{d\rho}{dC} \right) \right]$  for soap solutions, the concentration

derivatives of velocity  $\left( \frac{dv}{dC} \right)$  is positive, i.e.

ultrasonic velocity increases with increasing soap concentration. These results are in agreement with the results reported for electrolytic solutions which show that Carboxylates of vanadium behave as simple electrolyte in solutions.

The plot of ultrasonic velocity vs Soap concentration are characterized by an intersection of two straight line at a definite soap concentration which corresponds to the CMC of these soaps. The CMC of Carboxylates of vanadium decreases with increasing chain length of the soap molecules (Table 3). The plot of ultrasonic velocity vs soap concentration and extrapolated values of velocity,  $V_0$  are in close agreement with the experimental values of the solvent mixture (Table- 4) indicating that the soap molecules do not aggregate upto an appreciable extent below the CMC.

The variation of ultrasonic velocity, v with the soap concentration, c for the solutions below the CMC follows the relationship.

$$v = v_0 + GC$$

Where  $v_0$  is the ultrasonic velocity in pure solvents and G is Garnsey's constant<sup>12</sup>. The value of G (Table 3) has been calculated from the slopes of the plot of V vs C. The values of G increases with increasing chain length of the soap molecules.

The various acoustic parameter namely adiabatic compressibility ( $\beta$ )<sup>13</sup>, intermolecular free length ( $L_f$ )<sup>14</sup>, Specific acoustic impedance (Z)<sup>15</sup> and apparent molar compressibility $\Theta$ <sup>16</sup> were calculated using the following relationship.

$$\begin{aligned} \beta &= \rho^{-1} V^2 \\ L_f &= \sqrt{\frac{\beta}{K}} \\ z &= \rho V \\ \phi_K &= \frac{1000}{C\rho_0} (\rho_0 \beta - \beta_0 \rho) + \frac{\beta_0 M}{\rho_0} \end{aligned}$$

Where  $\rho_0$ ,  $\rho$ ,  $\beta_0$ ,  $\beta$  and  $v_0$ , v are the density, adiabatic compressibility and ultrasonic velocity of solvent and solutions respectively and M are the molecular weight of solute, and K and C are the temperature dependent Jacobson's constant and concentration respectively.

The adiabatic compressibility,  $\beta$  of these soaps solution decreases with the increasing of the soap concentration (Table-1). The decrease in adiabatic compressibility,  $\beta$  is attributed to the fact that the soap molecule in dilute solutions are considerably ionized into metal cations and fatty acid anions. These ions 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 field of the ion and the internal pressure increase which lowers the compressibility of the solutions, i.e. the solutions become harder to compress.

The plots of  $\beta$  vs C indicate a break at a definite soap concentration which corresponds to the CMC of the soap. The plots are extrapolated to zero soap concentration and the extrapolated values of  $\beta_0$  are in close agreement with the experimental values of the adiabatic compressibility of the solvent mixture (Table-5).

The results of adiabatic compressibility have been in term of Bachem's equations<sup>17</sup>.

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

Where A and B are constants, C is the molar concentration and  $\beta$  and  $\beta_0$  are the adiabatic compressibility of the solutions and solvents respectively. The values of A and B (Table-3) have been determined from the intercept and slope of the plots of  $(\beta - \beta_0)/C$  vs  $C^{1/2}$ .

The values of Inter molecular free length,  $L_f$  decreases with the increase in soap concentration and chain length. whereas specific acoustic impedance, Z increases with the increase in soap concentration but decrease with the chain length of soap (Table -1) which indicates that there is a significant interaction between the soap and solvent molecules<sup>18</sup> which considerably affect the structural agreement. The increase in the values of specific acoustic impedance, Z with increasing soap concentration, C can be explained on the basis of lyophobic interaction between soap and solvent molecules which increase with the intermolecular distance. The plot of Z vs C show a break at a definite soap concentration which corresponds to the CMC of this soaps.

The value of apparent molar compressibility,  $\phi_k$  decreases with increasing soap concentration (Table 1). The apparent molar compressibility  $\phi_k$  is related to the molar concentration, C by the relationship

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

Where  $\phi_k^0$  and  $S_k$  are the limiting apparent molar compressibility and a constant respectively. The value of  $\phi_k^0$  and constant  $S_k$  have been obtained from the intercept and slope of the plots  $\phi_k$  and  $C^{1/2}$  below the CMC and are recorded in (Table- 6).

**Table: 1**  
**Acoustic Parameters of Carboxylates of Vanadium in Benzene and DMSO Mixture at 40±0.05 °C**

S.No.	Concentration Cx10 <sup>3</sup> (mol l <sup>-1</sup> )	Density $\rho \times 10^{-3}$ (gm l <sup>-1</sup> )	Ultrasonic Velocity V x 10 <sup>-5</sup> (Cm sec <sup>-1</sup> )	Adiabatic Compressibility $\beta \times 10^{10}$ (Cm <sup>2</sup> dyne <sup>-1</sup> )	Intermolecular Free Length L <sub>f</sub> (A <sup>o</sup> )	Specific Acoustic Impedence Z x 10 <sup>-6</sup>	Apparent Moloar Compressibility - $\phi_k \times 10^7$ (Cm <sup>2</sup> dyne <sup>-1</sup> )
<b>Vanadium Myristate</b>							
1	0.3	0.9028	1.245	7.146	0.5293	1.1239	7.42
2	0.7	0.9032	1.248	7.108	0.5279	1.1271	7.28
3	1.0	0.9036	1.250	7.082	0.5269	1.1295	7.19
4	1.4	0.9039	1.252	7.057	0.5260	1.1316	7.00
5	2.1	0.9043	1.254	7.032	0.5251	1.1339	6.98
6	2.5	0.9047	1.256	7.006	0.5241	1.1363	6.96
7	2.9	0.9051	1.258	6.981	0.5232	1.1386	6.86
8	3.9	0.9058	1.264	6.909	0.5205	1.1449	6.84
<b>Vanadium Palmitate</b>							
1	0.3	0.9023	1.255	7.036	0.5252	1.1323	20.89
2	0.7	0.9025	1.257	7.012	0.5243	1.1344	15.00
3	1.0	0.9030	1.259	6.986	0.5234	1.1368	11.29
4	1.4	0.9033	1.261	6.962	0.5225	1.1390	11.20
5	2.1	0.9036	1.264	6.926	0.5211	1.1421	11.00
6	2.5	0.9039	1.266	6.902	0.5202	1.1443	10.92
7	2.9	0.9044	1.269	6.866	0.5188	1.1476	10.89
8	3.9	0.9048	1.274	6.809	0.5167	1.1527	10.85

Table: 2  
Values CMC and constants (A&B) of Carboxylates of Vanadium at 40±0.05 °C

S.no.	Carboxylates	CMC dm <sup>-3</sup> mol	A	B
1	Vanadium myristate	0.0036	1.39	3.85
2	Vanadium Palmitate	0.0025	1.63	4.23

Table: 3  
Values of Various Constants Obtained from Ultrasonic Measurements Carboxylates of Vanadium at 40±0.05 °C

S.No.	Carboxylates	CMC (dm <sup>-3</sup> mol)	G	-Ax10 <sup>10</sup>	B x 10 <sup>10</sup>
1.	Vanadium Myristate	0.0036	7791	7.3	12.8
2.	Vanadium Palmitate	0.0025	8106	8.0	15.9

Table: 4  
Extrapolated and Experimental Values of Ultrasonic Velocity v<sub>o</sub> (cm/sec) of Carboxylates of Vanadium at 40±0.05 °C

S.No	Carboxylates	Extrapolated V x 10 <sup>-5</sup>	Experimental V x 10 <sup>-5</sup>
1	Vanadium Myristate	2.653	2.62
2	Vanadium Palmitate	2.371	2.40

Table:5  
Extrapolated and Experimental Values of Adiabatic Compressibility  $\beta_o \times 10^{10}$  (cm<sup>dyne</sup><sup>-1</sup>) of Carboxylates of Vanadium at 40±0.05 °C

S.No	Carboxylates	Extrapolated( $\beta_o \times 10^{10}$ )	Experimental ( $\beta_o \times 10^{10}$ )
1	Vanadium myristate	7.693	7.723
2	Vanadium Palmitate	7.541	7.953

Table: 6  
Values of  $\Phi_k^o$  and S<sub>k</sub> of Carboxylates of Vanadium at 40±0.05 °C

S.No.	Carboxylates	$\Phi_k^o \times 10^7$	S <sub>k</sub> x 10 <sup>5</sup>
1	Vanadium myristate	39.12	25.66
2	Vanadium Palmitate	45.75	38.63

## Conclusion

It is concluded that the ultrasonic velocity on Carboxylates of vanadium (Myristate and Palmitate) behave as a simple electrolytes in solutions and the CMC value are in agreement with the values obtained from other parameters. The results confirm that there is a significant interaction between the soap and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably below the CMC.

## Reference

1. S. Nakamura, *J.Amer.Chem.Soc.*, 89, 1765 (1967)
2. Rain, Hubert, Steffens; Klaus-Juengon (*Euro-Celtique*) S.A. Huxembourg Fur, Pat. App. Ex 1, 479. 380 (Cl A6/kg/20) 24 Nov. 2004 April 2003 / 11, 028, 19 May. 20 App (Eng.) (2003)
3. M.K Rawat and Geeta sharma *J.Ind.chem.Soc.*84, 46-49 (2007).
4. R.K Shukla and U. Mishra, *Asian J. Chemistry*, 15 (3&4), 1703-1708 (2003).
5. Meera Sharma, Amrita Mishra and Suman Kumari *J. Chemtracks*, 11(1), 315-320, 2009.
6. M.K Rawat and Sangeeta, *Ind, J. Pure & applied physics*, 46, 187-192 (2008)
7. W. Mao-Yin and L. Da-Guang, *Guangdong Gongge Daxue Xuebao*, 16 (3), (1999), 109-113.
8. Khirwar, M.S., *Acta Ciencia Indica*, XLII C, No. 1 (2016).
9. Gupta, Anushri, Upadhyaya, S.K., and Kishore, Kamal, *Int. J. of Theoretical and Applied Science* 4(1), 1-5 (2012).
10. Khirwar, M.S., *J. Innovation*, Vol. 2, Issue 11, 2017.
11. Rawat, M.K. and Sharma, Geeta, *J. Ind. Chem. Soc.*, 84, 46-49 (2007).
12. G.Garnsey, R.J Boe, R. Mahoney and T.A Litovitz, *J.Chem,phys.*, 50, 5222, (1969)
13. B. Jacobson, *Acta Chem. Scand.*, 6, 1485 (1952)
14. I.E. E, piner, "Ultrasound Physical, Chemical and Biological effects", New York consultants Bureau, P.370, 1964.
15. P. Renand, *chim. Ana (Paris)*, 46(5), 227, 1964.
16. K.Nakanishi, "Infrared absorptions spectroscopy", Holden day, San. Francisco; P-14 (1977).
17. C. Bachem, *Z. Physk*, 101, 541, (1936)
18. H. Eyring and J.F Kincaid, *J.chem., Phys.*, 6,620, (1938)