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Research Article

Effect of chain length on spectroscopic and acoustic behavior of Europium Carboxylates

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Abstract

In this manuscript, Europium carboxylates of fatty acids (lauric, myristic and palmitic) have been prepared and effect of chain length on spectroscopic and acoustic behavior have been discussed. Ultrasonic measurements of europium 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.

Keywords: Europium carboxylates, IR Spectra Ultrasonic velocity and CMC Values

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Introduction

Europium carboxylates are materials which have wide range of applications as lubricant stabilizer, water proofing agent, plasticizer, emulsifier, textile, paper and textile industries etc. The uses of metal carboxylates largely depend on their physical state, stability, chemical reactivity and solubility in polar or non polar solvents.

Many metal carboxylates have been prepared by fusion and metathesis methods and their x-ray and acoustic studies have also been discussed by several workers [1-7]. Ultrasonic measurements [8-10] have been shown to be useful in the study of ion- solvent interaction since they take into account the importance consequence of ion-solvent, viz compressibility and reduced volume of the solvent molecule.

In this manuscript, we report on effect of chain length on spectral and acoustic studies of europium carboxylates, the results of acoustic studies have been used to study the solute-solvent interaction and to evaluate the CMC and various parameters.

Experimental

Preparation of carboxylates

The chemical used for present research were of AR/GR grade. Europium carboxylates (Laurate, Myristate and Palmitate) have been prepared by direct metathesis of the Corresponding Potassium carboxylate with slight excess of solutions of Europium 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 recrystallisation with a mixture of benzene and methanol and dried under reduced pressure. The purity of these carboxylates was confirmed by determination of their melting point.

Measurements

The IR spectra were obtained with Perkin Elmer "577 Model" Grating spectrophotometer in the region of 4000 – 200 cm^{-1} using potassium bromide disc method.

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) [11], specific acoustic impedance (Z) [12], apparent molar volume (ϕ_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 ρ_0, ρ, β_0, β, 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 spectra of Europium carboxylates (Laurate, Myristate and Palmitate) have been recorded and compared with the results of the corresponding fatty acids (**Table 1**).

The absorption bands observed near 2656, 1541 – 1545, 1412-1417, 930-950, 690 and 430 cm^{-1} in the spectra of fatty acids were associated with the localised COOH (carboxyl group) of the acid molecules in the dimeric state and confirmed the existance of hydrogen bonding between two molecules of carboxylic acids.

Table 1 Infrared Absorption frequencies (cm^{-1}) together with their assignments

S.No.	Absorption	Europium		
		Laurate	Myristate	Palmitate
1.	CH_3, C-H asymmetrical stretching	2950	2950	2956
2.	CH_2, C–H asymmetrical stretching	2918	2919	2916
3.	CH_2, C–H symmetrical stretching	2845	2850	2856
4.	OH, stretching	—	—	—
5.	C=O stretching	—	—	—
6.	COO^-, C–O asymmetrical stretching	1545	1547	1541
7.	CH_2 deformation	1466	1465	1466
8.	COO^-, C–O symmetrical stretching	1412	1411	1417
9.	CH_2, (adjacent to COOH group) deformation	—	—	—
10.	CH_3, asymmetrical deformation	1342	1339	1351
11.	Progressive bonds (CH_2 twisting and wagging)	1316 -1195	1315-1192	1316-1198
12.	CH_3, rocking	1115	1114	1108
13.	OH, out of plane deformation	—	—	—
14.	CH_2, rocking	718	720	722
15.	COOH bending Mode	—	—	—
16.	COOH wagging Mode	—	—	—
17.	Eu—O bond	410	428	430

The result confirms that the fatty acid exist with dimeric structure through intermolecular hydrogen bonding between carboxyl groups of two acid molecules, whereas potassium, europium carboxylates are ionic in nature and the metal – to –oxygen bond the carboxylate has an ionic character. The IR spectra of europium carboxylates donot show any absorption maxima in the region of 3500-3300 cm-1 which confirms the absence of any co-ordinated water molecule in these carboxylates.

The ultrasonic velocity and other acoustic and soap-solvent interaction parameters for Europium carboxylates in methanol are recorded in **Tables 2-4**.

Table 2 Ultrasonic Velocity and other various parameter of Europium Laurate in methanol at 40 ± 0.05ºC

S.No.	**Concentration 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	0.9216	1131.8	8.571	1043.06	54.81
2.	0.004	0.9227	1132.8	8.446	1045.23	26.28
3.	0.006	0.9238	1134.0	8.418	1047.59	16.76
4.	0.008	0.9250	1135.1	8.391	1049.96	12.14
5.	0.010	0.9259	1136.2	8.366	1052.00	9.05
6.	0.012	0.9268	1136.5	8.354	1053.31	6.98
7.	0.014	0.9274	1137.0	8.341	1054.45	5.27
8.	0.016	0.9280	1137.4	8.329	1055.51	3.99
9.	0.018	0.9287	1137.8	8.317	1056.67	3.10
10.	0.020	0.9293	1138.2	8.306	1057.73	2.25

Table 3 Ultrasonic Velocity and other various parameter of Europium Myristate in methanol at 40 ± 0.05ºC

S.No.	**Concentration 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	0.9221	1132.1	8.462	1043.91	56.60
2.	0.004	0.9234	1133.4	8.430	1046.58	27.25
3.	0.006	0.9249	1134.6	8.399	1049.39	17.83
4.	0.008	0.9264	1135.8	8.368	1052.21	13.12
5.	0.010	0.9276	1137.0	8.339	1054.68	9.97
6.	0.012	0.9282	1137.5	8.326	1055.83	7.33
7.	0.014	0.9288	1138.0	8.314	1056.97	5.44
8.	0.016	0.9294	1138.5	8.301	1058.12	4.02
9.	0.018	0.9300	1138.9	8.289	1059.18	2.92
10.	0.020	0.9305	1139.4	8.278	1060.21	1.98

Table 4 Ultrasonic Velocity and other various parameter of Europium palmitate in methanol at 40 ± 0.05ºC

S.No.	**Concentration 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	0.9228	1132.5	8.449	1045.07	59.48
2.	0.004	0.9244	1134.0	8.412	1048.37	29.05
3.	0.006	0.9261	1135.4	8.376	1051.49	19.08
4.	0.008	0.9278	1136.8	8.340	1054.72	14.11
5.	0.010	0.9290	1138.0	8.312	1057.20	10.57
6.	0.012	0.9295	1138.5	8.300	1058.23	7.58
7.	0.014	0.9299	1139.0	8.289	1059.16	5.37
8.	0.016	0.9304	1139.4	8.279	1060.01	3.78
9.	0.018	0.9308	1139.8	8.269	1060.92	2.48
10.	0.020	0.9313	1140.3	8.258	1061.96	1.49

The variation in ultrasonic velocity with concentration (dv/dc) depends on the concentration derivatives of density and adiabatic compressibility.

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

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 inccreases with increase in soap concentration. 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 [13] (**Table 5**). The values of G increases with the increase of chain length of the soap molecules.

Table 5 Values of CMC and various constant for Europium carboxylates at 40±0.05°C

	Laurate	**Myristate**	**Palmitate**
CMC	10.2×10^{3}	9.8×10^{3}	9.4×10^{3}
$G \times 10^{-3}$	1.33	2.50	3.25
−A	52.20	56.50	59.00
$B \times 10^{10}$	2.68	4.50	5.55
$\phi^{o}_{v} \times 10^{-2}$	34.30	36.40	37.50
$S_v \times 10^{-2}$	45.20	50.50	52.22

The plots of ultrasonic velocity versus soap concentration, C (**Figure 1**) are characterised by an intersection of two straight lines at a definity soap concentration which corresponds to the CMC (table-5) of these soaps. The CMC values of Europium 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 characterised by the presence of both lyophilic and lyophobic moieties in the same molecules and the micelles in organic solvents can be visualised 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 [14, 15].

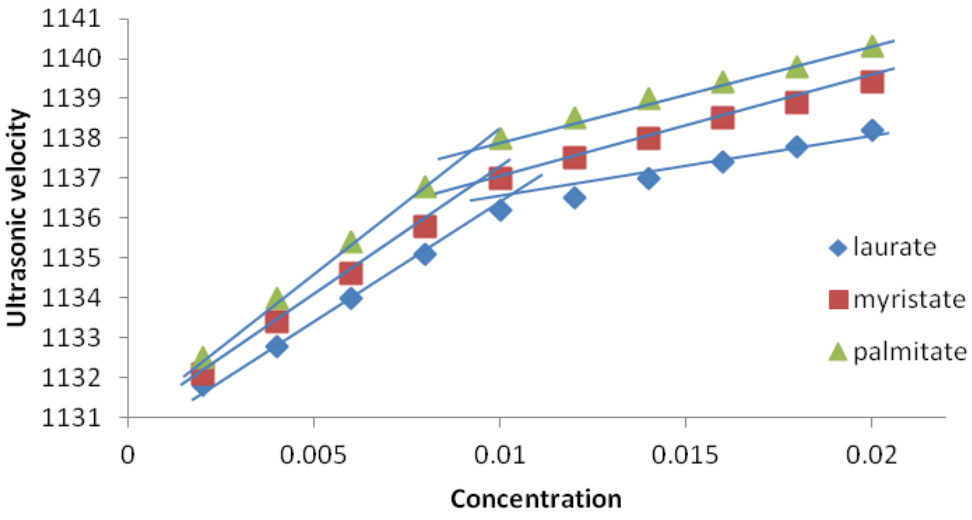

Figure 1 Ultrasonic velocity Vs concentration

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 (Figure 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 Europium laurate, myristate and palmitate do not aggregate upto an appreciable extent below the CMC.

The adiabatic compressibility, β of these solutions decreases with increasing the concentration (Tables 2-4). The decrease in adiabatic compressibility is attributed to the fact, that the molecule of Europium laurate, myristate and palmitate 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 [16].

The plots of adiabatic compressibility β versus soap concentration, C are also characterised 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 [17].

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

Where A and B are constants, C is the concentration and β and β_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 impedence, Z increases with the increase in soap concentration, (table 2-4) 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 impedence, 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 impedence in the progation of ultrasonic waves.

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

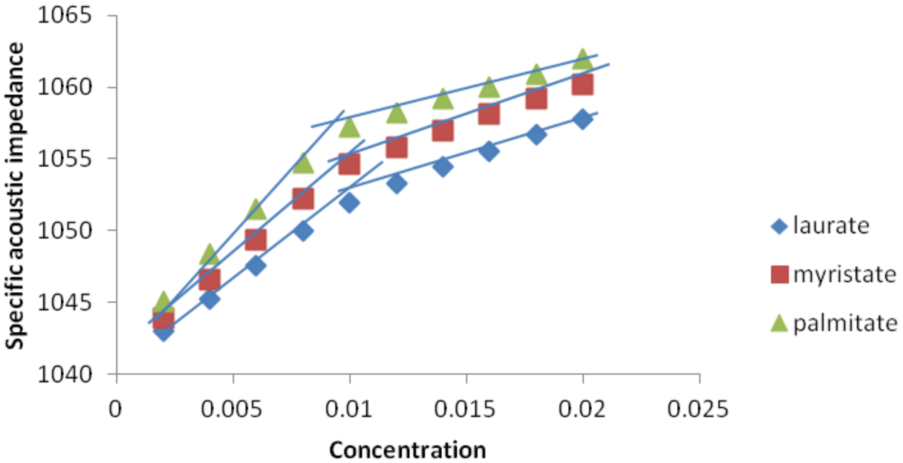

Figure 2 Specific acoustic impedance Vs concentration

The values of apparent molar volume decreases with increase in soap concentration (Tables 2-4). The values of apparent molar volume of Europium laurate, myristate and palmitate 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, ϕ_k and apparent molar volume, ϕv 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 ϕ°k and ϕ°v are limiting apparent molar compressibility and limiting apparent molar volume respectively, Sk and Sv are constant. The values of ϕ°k and ϕ°v and constant Sk and Sv have been obtained from the intercept and slope of the plots of ϕk vs c1/2 and ϕv vs c1/2 (**Figure 3**) below the CMC and are recorded in Table 5.

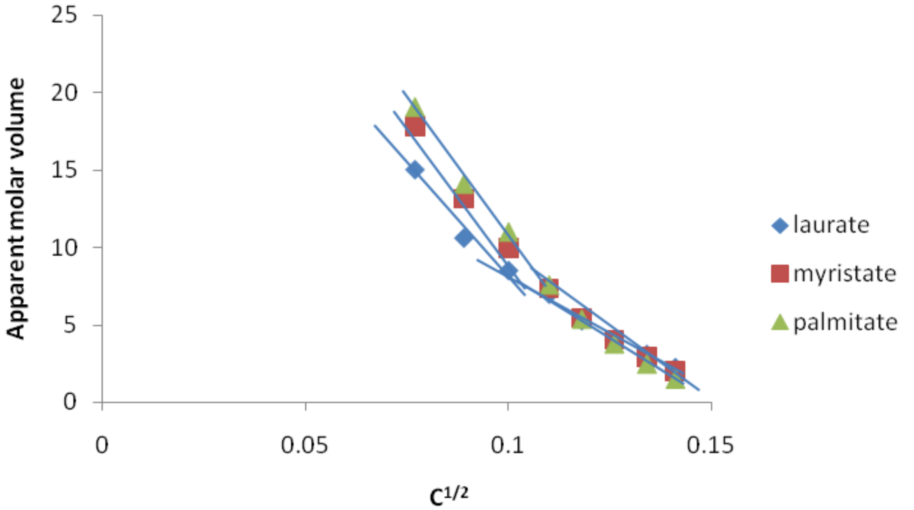

Fig 3-apparent molar volume Vs square root of concentration

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