Ultrasonic Study of Molecular Interactions and Compressibility Behaviour of Potassium Carboxylates

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ABSTRACT

Ultrasonic measurements have been made on Potassium carboxylates (caproate, caprylate, caprate, laurate, myristate) in 70% chloroform-30% propylene glycol (v/v) with a review to determine the CMC (critical micelle concentration), carboxylate solvent interaction and various acoustic parameters of the system. The value of CMC increases with increase in the chain length of fatty acids. The results of ultrasonic velocity, adiabatic compressibility, intermolecular free length, specific acoustic impedance and apparent molar volume suggested that there is a significant interaction between carboxylate and solvent molecule.

Graphical Abstract
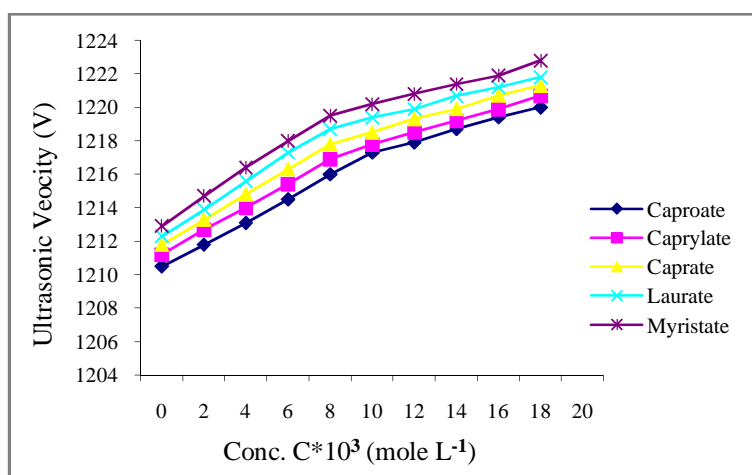
Ultrasonic Velocity Vs Concentration for Potassium carboxylates.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Potassium carboxylates, CMC values.
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INTRODUCTION

The complimentary use of ultrasonic measurement can provide interesting information on the specifications of the ion. Metallic carboxylates are widely used in industries as detergents, softeners, plasticizers, greases, lubricants, cosmetics and medicine. The physic-chemical characteristics and the structure of metallic carboxylates depend largely on the method and conditions of preparation, properties and used of metal carboxylates have been investigated by several workers [1-5]. Ultrasonic velocity techniques have been used for studying solute solvent interaction in a number of systems including organic liquid [6], dilute solutions in organic acids and complexes [7- 9]. The propagation of ultrasonic waves has been used to determine the nature of molecular interaction of the system. The present work has been initiated in a view to determine the (CMC), carboxylate- solvent interactions such as various acoustic parameters. The efforts were made to investigate the effect of concentration and chain length of carboxylates on aforesaid parameters.

MATERIALS AND METHODS

All chemicals used were AR/GR [E-Merck] grade. The Potassium carboxylates (caproate, caprylate, caprate, laurate, myristate) were prepared by direct metathesis of corresponding potassium carboxylates with the required amount of aqueous solution of Potassium Nitrate at 50-55°C under various stirring. The precipitated carboxylates were washed with water and acetone to remove the excess of metal ions and untreated fatty acid. The purity of the carboxylates 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 $40 \pm 0.05°C$ using a crystal of 1MHz frequency. The uncertainty of velocity measurements is 0.2% the densities of the solvent and solutions were measured with a dilatometer. The volume of dilatometer was 15 mL and the accuracy of the density results was ± 0.0001.

The various acoustic parameters namely adiabatic compressibility (β), intermolecular free length (L_f) [10], specific acoustic impedance (Z) [11], apparent molecular volume (Φv) have been evaluated using the following relationship

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

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

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

$$\Phi v = 1000/C\rho_0 \, (\rho_0 - \rho) + M/\rho^0 \quad .. (4)$$

Where ρ_0, ρ, β_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 carboxylate solvent interaction parameters for Potassium carboxylates (Caproate, Caprylate, Caprate, Laurate, Myristate) in 70% chloroform – 30% propylene glycol (v/v) are reported in table 1-5.

Table 1. Ultrasonic velocity and other various parameter of Potassium Caproate in 70% Chloroform-30% Propylene Glycol (v/v) at 40 $\pm$ 0.05 C

S. No.	Conc. C (mol L⁻¹)	Density ρ (g mol L⁻¹)	Ultrasonic Velocity v ms⁻¹	Adiabatic Compressibility B x 10¹⁰ (m² x N⁻¹)	Specific Acoustic Impedance Z	Apparent molar volume Φv x 10³ M⁵ N⁻¹ (Kmol)⁻¹
1	0.002	0.8867	1210.5	7.697	10.733	32.42
2	0.004	0.8873	1211.8	7.675	10.752	22.11
3	0.006	0.8880	1213.1	7.652	10.774	16.46
4	0.008	0.8885	1214.5	7.630	10.791	14.32
5	0.010	0.8891	1216.0	7.606	10.812	13.26
6	0.012	0.8897	1217.3	7.585	10.830	12.36
7	0.014	0.8900	1217.9	7.575	10.839	10.99
8	0.016	0.8902	1218.7	7.563	10.849	9.99
9	0.018	0.8904	1219.4	7.553	10.858	9.14
10	0.020	0.8906	1220.0	7.544	10.865	8.43

Table 2. Ultrasonic velocity and other various parameter of Potassium Caprylate in 70% Chloroform-30% Propylene Glycol (v/v) at 40 $\pm$ 0.05 C

S. No.	Conc. C (mol L⁻¹)	Density ρ (g mol L⁻¹)	Ultrasonic Velocity v ms⁻¹	Adiabatic Compressibility B x 10¹⁰ (m² x N⁻¹)	Specific Acoustic Impedance Z	Apparent molar volume Φv x 10³ M⁵ N⁻¹ (Kmol)⁻¹
1	0.002	0.8870	1211.2	7.685	10.743	37.37
2	0.004	0.8877	1212.7	7.660	10.765	23.35
3	0.006	0.8885	1214.0	7.637	10.786	18.54
4	0.008	0.8892	1215.4	7.613	10.807	16.09
5	0.010	0.8900	1216.9	7.588	10.830	14.84
6	0.012	0.8908	1217.8	7.569	10.848	13.522
7	0.014	0.8910	1218.5	7.559	10.857	11.86
8	0.016	0.8912	1219.2	7.549	10.866	10.62
9	0.018	0.8914	1219.9	7.538	10.874	9.78
10	0.020	0.8915	1220.7	7.528	10.883	8.87

Table 3. Ultrasonic velocity and other various parameter of Potassium Caprate in 70% Chloroform-30% Propylene Glycol (v/v) at 40 $\pm$ 0.05 C

S. No.	Conc. C (mol L⁻¹)	Density ρ (g mol L⁻¹)	Ultrasonic Velocity v ms⁻¹	Adiabatic Compressibility B x 10¹⁰ (m² x N⁻¹)	Specific Acoustic Impedance Z	Apparent molar volume Φv x 10³ M⁵ N⁻¹ (Kmol)⁻¹
1	0.002	0.8872	1211.8	7.676	10.758	41.14
2	0.004	0.8880	1213.3	7.649	10.774	25.31
3	0.006	0.8889	1214.8	7.623	10.798	20.23
4	0.008	0.8899	1216.3	7.596	10.824	17.85
5	0.010	0.8908	1217.8	7.569	10.848	16.28
6	0.012	0.8915	1218.5	7.555	10.862	14.37
7	0.014	0.8917	1219.3	7.543	10.873	12.59
8	0.016	0.8920	1219.9	7.533	10.882	11.21
9	0.018	0.8922	1220.7	7.522	10.891	10.18
10	0.020	0.8924	1221.3	7.513	10.899	9.26

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

$$(dv/dc) = - v / 2 \, [1/\rho \, (d\rho/dc) + 1/\rho \, (d\beta/dc)] \qquad .. (5)$$

The quantity dρ/dc is always positive while dβ/dc is negative since the values of l/β (dβ/dc) are higher than 1/β (dρ/dc) for these solutions, the quantity dv/dc is positive, i.e. ultrasonic velocity increases

with increase in carboxylate concentration. The variation in ultrasonic velocity with carboxylate concentration C follows the relationship –

$$v = v_0 + GC \quad ..(6)$$

where v_0 is the ultrasonic velocity in pure solvent and G is Garnsey's Constant [12] (Table 6). The value of G increases with the increase in chain length of the Carboxylate molecules.

Table 4. Ultrasonic velocity and other various parameter of Potassium Laurate in 70% Chloroform- 3 0% Propylene Glycol (v/v) at 40 $\pm$ 0.05 C

S. No.	Conc. C (mol L^{-1})	Density ρ (g mol L^{-1})	Ultrasonic Velocity v ms^{-1}	Adiabatic Compressibility B x 10^{10} (m^2 x N^{-1})	Specific Acoustic Impedance Z	Apparent molar volume Φv x 10^3 M^5 N^{-1} (Kmol)$^{-1}$
1	0.002	0.8874	1212.3	7.668	10.766	44.45
2	0.004	0.8883	1213.9	7.639	10.780	27.21
3	0.006	0.8894	1215.6	7.609	10.812	22.14
4	0.008	0.8905	1217.3	7.578	10.840	19.56
5	0.010	0.8915	1218.7	7.552	10.865	17.58
6	0.012	0.8922	1219.4	7.538	10.880	15.36
7	0.014	0.8924	1219.9	7.530	10.886	13.17
8	0.016	0.8927	1220.7	7.518	10.897	11.79
9	0.018	0.8929	1221.2	7.509	10.904	10.47
10	0.020	0.8933	1221.8	7.499	10.914	9.61

Table 5. Ultrasonic velocity and other various parameter of Potassium Myristate in 70% Chloroform- 30% Propylene Glycol (v/v) at 40 $\pm$ 0.05 C

S. No.	Conc. C (mol L^{-1})	Density ρ (g mol L^{-1})	Ultrasonic Velocity v ms^{-1}	Adiabatic Compressibility B x 10^{10} (m^2 x N^{-1})	Specific Acoustic Impedance Z	Apparent molar volume Φv x 10^3 M^5 N^{-1} (Kmol)$^{-1}$
1	0.002	0.8876	1212.9	7.658	10.765	48.22
2	0.004	0.8887	1214.7	7.626	10.795	30.06
3	0.006	0.8898	1216.4	7.596	10.824	23.82
4	0.008	0.8910	1218.0	7.565	10.852	20.74
5	0.010	0.8921	1219.5	7.537	10.879	18.65
6	0.012	0.8925	1220.2	7.525	10.890	15.84
7	0.014	0.8930	1220.8	7.514	10.902	13.86
8	0.016	0.8934	1221.4	7.503	10.912	12.28
9	0.018	0.8939	1221.9	7.493	10.923	11.28
10	0.020	0.8943	1222.8	7.482	10.936	10.11

Table 6. Values of CMC and various constants for Potassium carboxylates at 40 $\pm$ 0.05 C

	Caproate	Caprylate	Caprate	Laurate	Myristate
CMC	0.0118	0.0108	0.0102	0.0100	0.0096
G x 10^{-2}	1.50	2.00	2.25	2.50	3.25
-A	6.0	12.8	16.4	20.0	25.2
B x 10^{10}	2.40	3.00	4.00	5.00	6.00
Φ^0_v x 10^{-2}	37.20	38.40	39.80	41.60	47.0
S$_v$ x 10^{-5}	5.32	5.84	6.15	6.67	6.80

The plots of ultrasonic velocity versus concentration, C (Figure 1) are characterized by an intersection of two straight lines are a definite carboxylate concentration which corresponds to the CMC (Table 6) of these carboxylates. The CMC values of Potassium carboxylates 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 carboxylate molecules. The molecules of carboxylates are characterized by the presence of both lyophilic 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 in the solvent. The aggregation begins at a 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 [13, 14].

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 (v) Vs concentration (C) (Figure 1) are extrapolated to zero carboxylate 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 Potassium carboxylates (caproate, caprylate, caprate, laurate, myristate) do not aggregate upto an appreciable extent below the CMC.

The adiabatic compressibility (β) of these carboxylate solutions decreases with increasing the carboxylate concentration (Table 1-5). The decrease in adiabatic compressibility is attributed to the fact, that the molecule of Potassium carboxylates (caproate, caprylate, caprate, laurate, myristate) 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 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 [15].

The plots of adiabatic compressibility (β) Vs concentration (C) are also characterized by a break at a definite carboxylate concentration which corresponds to the CMC of these carboxylates.
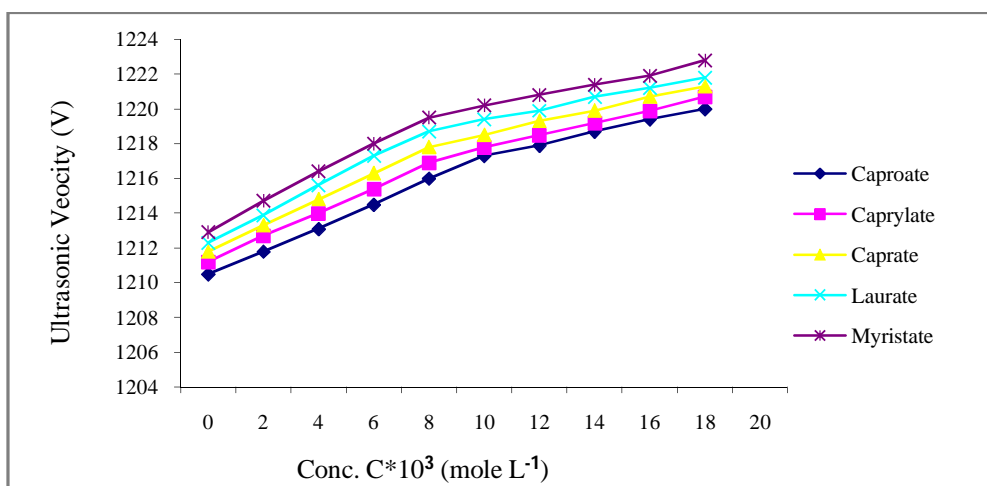

Figure 1. Ultrasonic Velocity Vs Concentration for Potassium carboxylates.

The results of adiabatic compressibility have also been explained in the light of Bachem's relationship [16-18].

$$\beta = \beta_0 + AC - BC^{3/2} \qquad ..(7)$$

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 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 carboxylate concentration, (Table 1-5). This may be due to the increase in density and velocity with increasing concentration of carboxylate (Eq. 1, 2 and 3). The change in the values of L_f and Z can also be explained on the basis of a lyophobic interaction which reduces the intermolecular distance between the molecules and thus becomes the main cause of impedence to the propagation of ultrasonic waves. The values of apparent molar volume decreases with increase in carboxylate concentration (Table 1-5). The values of apparent molar volume of Potassium carboxylates (caproate, caprylate, caprate, laurate, myristate) are negative, which indicates that this restrict molecular motion within the solutions.

The apparent molar volume, Φ_v is related to the molar concentration of the carboxylate by the relationships.

$$\Phi_v = \Phi^0_v + S_v\, C^{1/2} \quad ..(8)$$

where Φ^0_v is limiting apparent molar volume and S_v is constant. The values of Φ^0_v and constant S_v have been obtained from the intercept and slope of the plots of Φv Vs $C^{-1/2}$ (Figure 2) below the CMC and the recorded in (Table 6).

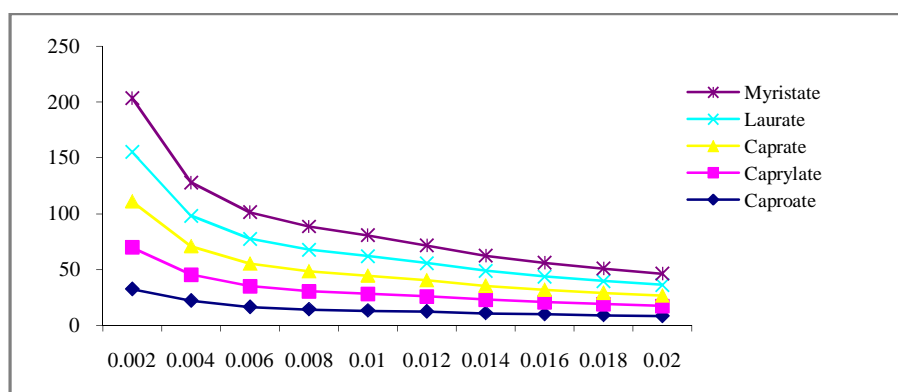**Figure 2.** ϕ_v Vs $C^{-1/2}$ for Potassium carboxylates.

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