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ULTRASONIC STUDY OF MOLECULAR INTERACTIONS AND COMPRESSIBILITY BEHAVIOUR OF MAGNESIUM CARBOXYLATES

M. K. RAWAT*

Department of Chemistry, Agra College, AGRA – 282002 (U.P.) INDIA

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ABSTRACT

Ultrasonic measurements have been made on magnesium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) in 70% chloroform - 30% propylene glycol (v/v) with a view 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 chain length of fatty acids. The results of ultrasonic velocity, adiabatic compressibility, intermolecular free length, specific acoustic impedence and apparent molar volume suggested that there is a significant interaction between carboxylate and solvent molecule.

Key words: Ultrasonic velocity, Adiabatic compressibility, Magnesium carboxylates, CMC values.

INTRODUCTION

The complimentary use of ultrasonic measurement can provide interesting information on the specificities of the ion. Metallic carboxylates are widely used in industries as detergents, softeners, plasticizers, greases, lubricants, cosmetics and medicine. The physico-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 studing solute-solvent interaction in a number of system including organic liquid[6], dilute solutions in organic acids[7] and complexes[8,9]. 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 investigated the effect of concentration and chain length of carboxylates on aforesaid parameters.

EXPERIMENTAL

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

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*Author for correspondence; E-mail: rawatmk_chem@yahoo.com

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.

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

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

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

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

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

Where ρ_0, ρ, β_0, βρ, 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 magnesium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) in 70% chloroform -30% propylene glycol (v/v) are reported in Table 1-7.

Table 1: Ultrasonic velocity and other various parameter of magnesium caproate in 70% chloroform - 30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. C (mol L^{-1})	Density ρ (g mol L^{-1})	Ultrasonic velocity v ms^{-1}	Adiabatic compressibility β × 10^{10} ($m^2 \times N^{-1}$)	Specific acoustic impedance Z	Apparent molar volume $\phi_v \times 10^3$ M^5N^{-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 magnesium caprylate in 70% chloroform - 30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-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 magnesium caprate in 70% chloroform - 30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-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

Table 4: Ultrasonic velocity and other various parameter of magnesium laurate in 70%chloroform - 30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-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 magnesium myristate in 70% chloroform -30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-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: Ultrasonic velocity and other various parameter of magnesium palmitate in 70% chloroform -30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-1} $(Kmol)^{-1}$
1.	0.002	0.8879	1213.6	7.647	10.776	53.14
2.	0.004	0.8892	1215.4	7.613	10.802	32.94
3.	0.006	0.8905	1217.3	7.578	10.840	26.33
4.	0.008	0.8917	1219.2	7.545	10.872	22.85
5.	0.010	0.8926	1220.3	7.523	10.892	19.58
6.	0.012	0.8932	1220.9	7.511	10.905	16.67
7.	0.014	0.8938	1221.5	7.499	10.918	14.59
8.	0.016	0.8943	1222.1	7.487	10.929	12.95
9.	0.018	0.8948	1222.7	7.475	10.941	11.67
10.	0.020	0.8954	1223.3	7.463	10.953	10.71

Table 7: Ultrasonic velocity and other various parameter of magnesium stearate in 70%chloroform - 30% propylene glycol (v/v) at 40 ± 0.05ºC

S. No.	Conc. 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 $\phi_v \times 10^3$ M^5N^{-1} $(Kmol)^{-1}$
1.	0.002	0.8883	1214.4	7.633	10.786	59.36
2.	0.004	0.8897	1216.2	7.599	10.821	36.05
3.	0.006	0.8912	1218.3	7.600	10.858	28.99
4.	0.008	0.8925	1220.1	7.527	10.889	24.76
5.	0.010	0.8932	1221.0	7.509	10.905	20.55
6.	0.012	0.8937	1221.8	7.496	10.919	17.45
7.	0.014	0.8943	1222.4	7.483	10.932	15.19
8.	0.016	0.8948	1223.0	7.472	10.943	13.41
9.	0.018	0.8955	1223.6	7.458	10.957	12.17
10.	0.020	0.8962	1224.2	7.445	10.971	11.18

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

$$(dv/dc) = -v/2\left(\frac{1}{\rho}(d\rho/dc) + \frac{1}{\rho}(d\beta/dc)\right) \quad \ldots(5)$$

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

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

Where v_0 is the ultrasonic velocity in pure solvent and G is Garnsey's constant[12] (Table 8). The values of G increases with the increase in chain length of the carboxylate molecules.

Table 8: Values of CMC and various constants for magnesium carboxylates at 40 ± 0.05ºC

	Caproate	Caprylate	Caprate	Laurate	Myristate	Palmitate	Stearate
CMC	0.0118	0.0108	0.0102	0.0100	0.0096	0.0090	0.0084
$G \times 10^{-2}$	1.50	2.00	2.25	2.50	3.25	4.00	4.25
−A	6.0	12.8	16.4	20.0	25.2	28.4	34.2
$B \times 10^{10}$	2.40	3.00	4.00	5.00	6.00	8.00	8.50
$\phi^o_v \times 10^{-2}$	37.20	38.40	39.80	41.60	47.0	53.40	54.40
$S_v \times 10^{-5}$	5.32	5.84	6.15	6.67	6.80	7.00	7.68

The plots of ultrasonic velocity versus concentration, C (Fig. 1) are characterised by an intersection of two straight lines at a definity carboxylate concentration which corresponds to the CMC (Table 8) of these carboxylates. The CMC values of magnesium 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 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[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) (Fig. 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 magnesium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) 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 1-7). The decrease in adiabatic compressibility is attributed to the fact, that the molecule of magnesium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) 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 arround 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.

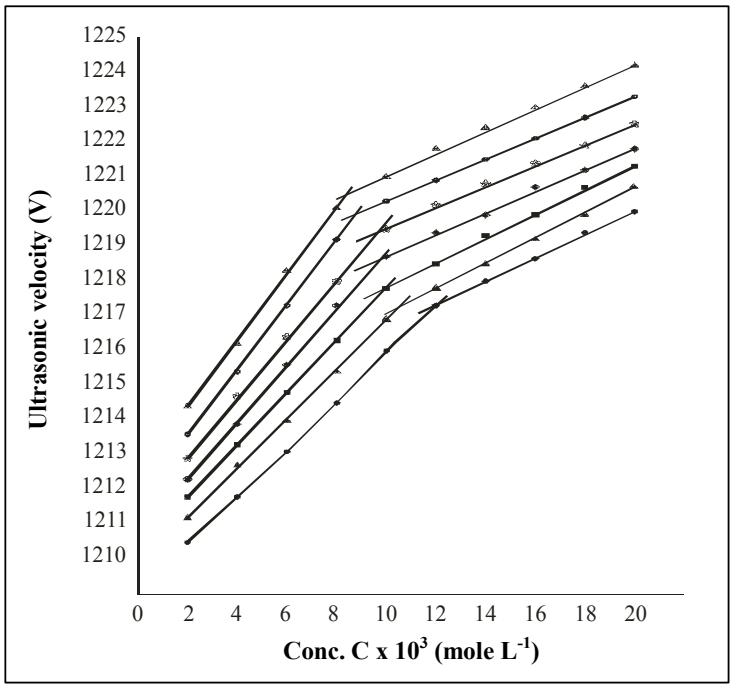

Fig. 1: Ultrasonic velocity vs concentration for magnesium carboxylates (●) Caproate, (▲) Caprylate, (■) Caprate, (♦) Laurate, (✡) Myristate, (○) Palmitate, (Δ) Stearate

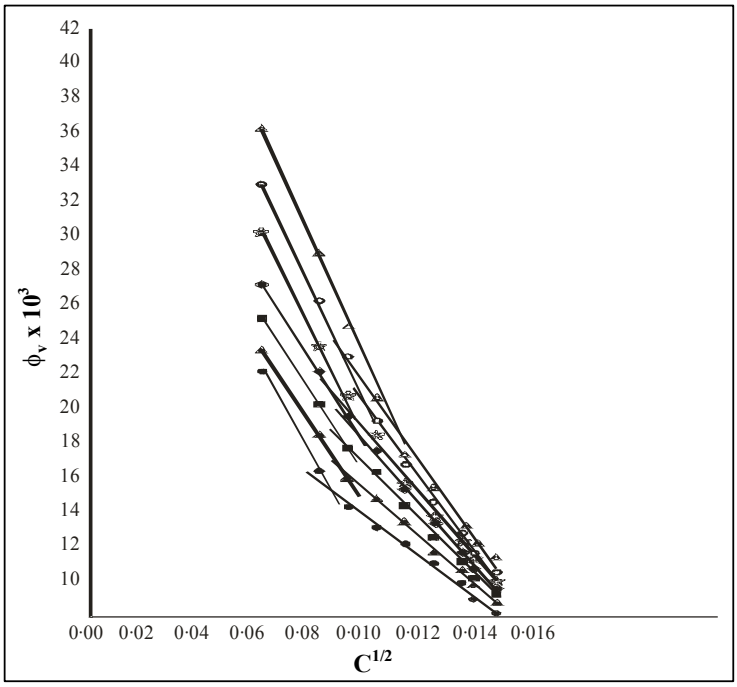

Fig. 2: ϕ_v vs $C^{1/2}$ for magnesium carboxylates (●) Caproate, (▲) Caprylate, (■) Caprate, (♦) Laurate, (✡) Myristate, (○) Palmitate, (Δ) Stearate

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

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

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 the plots of $\beta-\beta_0/C$ against $C^{1/2}$.

The intermolecular free length L_f, decreases while specific acoustic impedence, Z increases with the increase in carboxylate concentration, (Table 1-7). 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 reduce 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 1-7). The values of apparent molar volume of magnesium carboxylates (caproate, caprylate, caprate, laurate, myristate, palmitate and stearate) 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, C by the relationships.

$$\phi_v = \phi^o_v + S_v C^{1/2} \quad \ldots(8)$$

Where ϕ^o_v is limiting apparent molar volume and S_v is constant. The values of ϕ^o_v and constant S_v have been obtained from the intercept and slope of the plots of ϕ_v vs $C^{1/2}$ (Fig. 2) below the CMC and are recorded in (Table 8).

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