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Effect of Chain Length on Acoustic Behavior of Gadolinium Alkanoates in Mixed Organic Solvents, Mithlesh Shukla, Suman Kumari and R. K. Shukla, Acta Acustica **vol. 96** (Number 1), 2010, pp. 63-67

DOI
https://doi.org/10.3813/AAA.918256

Acta Acustica united with Acustica
Vol. 96 (2010) 63 – 67

DOI 10.3813/AAA.918256

Effect of Chain Length on Acoustic Behavior of Gadolinium Alkanoates in Mixed Organic Solvents

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Summary

Ultrasonic investigations on solution of gadolinium alkanoates in a mixture of benzene- methanol show that the value of the critical micellar concentration (CMC) decreases with increasing chain length of the fatty acid constituent of the alkanoate molecule. The values of the CMC agree with values obtained from other micellar properties. Various acoustic parameters (inter-molecular free length, adiabatic compressibility, apparent molal compressibility, specific acoustic impedance, apparent molal volume and solvation number) for these alkanoates have been evaluated from the ultrasonic velocity measurements.

PACS no. 43.58.-e

1. Introduction

Ultrasonic measurements can provide interesting information on the specificities of the ion-solvent interaction related to the structure of the solute and on the reciprocal effects which arise in the solvents. However, studies on ultrasonic measurements of alkanoate solutions have not drawn adequate attention, although such a study is likely to give more information on the solute- solvent interaction. Inspite of wide applications in many industries, the physico-chemical characteristics of lanthanide alkanoates have not been thoroughly investigated. Wu *et al.* [1] and Kanai [2] developed new technologies to synthesized metal alkanoates. Workers [3, 4, 5] studied spectroscopic and thermal behavior of metal alkanoates. The thermal properties and solution aggregation behavior of lanthanide alkanoates has been reviewed by Binnemans and Görller-Walrand [6]. A number of workers [7, 8, 9, 10, 11] studied the ultrasonic behavior of metal alkanoates. Ultrasonic velocity and conductivity of the solution of lanthanide and transition metal alkanoates have been determined [12, 13, 14] in different organic solvents.

In the present work, the investigations are focused on study of ultrasonic measurements of gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate) in a mixture of benzene and methanol. The results have been used to determine the effect of alkanoate concentrations and chain length on the critical micellar concentration (CMC), solute-solvent interaction and various acoustic parameters.

Received 23 April 2009,
accepted 8 September 2009.

2. Experimental

All chemicals used were of BDH/AR grade. Solvents benzene and methanol were purified by distillation under reduced pressure. Gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate) were synthesized by direct metathesis of corresponding potassium alkanoates with slight excess of the solution of gadolinium acetate at 50–55 °C under vigorous stirring. The precipitated alkanoates were washed several times with water and then acetone .The metal alkanoates thus obtained were first dried in an air oven at 50–60 °C and final drying of the alkanoates was carried out under reduced pressure. The alkanoates were purified by recrystallization with benzene–methanol mixture. The purity was checked by their melting points (decanoate −98 °C, dodecanoate −102 °C, tetradecanoate −112 °C and octadecanoate −118 °C). The values of melting points of gadolinium alkanoates were in close agreement with neodymium alkanoates14 (butanoate −95 °C, pentanoate −97 °C and hexanoate −101 °C) and absence of hydroxylic group was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same alkanoates under similar conditions.

The ultrasonic velocity of the solutions of gadolinium alkanoates was measured by a multi-frequency ultrasonic interferometer (Mittal Enterprises, New Delhi) at a frequency of 6 MHz at constant temperature (30 ± 0.05 °C).The maximum uncertainty in the velocity measurements was ±0.2%. The densities of the solvent and solutions were measured by a pyknometer at constant temperature (30 ± 0.05 °C). The pyknometer was calibrated with distilled water and buoyancy corrections were applied.

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Table I. Ultrasonic velocity v, density ρ, adiabatic compressibility β, inter-molecular free-length L_f, specific acoustic impedance Z and solvation number S_n of gadolinium alkanoates in benzene-methanol (7:3 v/v) at 30 °C±0.05 °C.

C [mol/dm^3]	$\rho \cdot 10^{-3}$ [Kg/m^3]	$v \cdot 10^{-3}$ [m/s]	$\beta \cdot 10^{10}$ [m^2/N]	L_f [A^0]	$Z \cdot 10^{-5}$ [Kg/(m^{2}s^1)]	S_n
Gadolinium Tetradecanoate						
0.0012	0.8527	1.122	9.315	56.89	9.496	176.23
0.0024	0.8531	1.126	9.245	56.68	9.533	135.54
0.0034	0.8534	1.130	9.176	56.47	9.578	128.68
0.0044	0.8537	1.133	9.125	56.31	9.599	118.28
0.0054	0.8541	1.136	9.072	56.15	9.626	112.34
0.0066	0.8547	1.142	8.971	55.83	9.671	116.80
0.0074	0.8554	1.149	8.855	55.47	9.726	129.66
0.0084	0.8562	1.155	8.755	55.16	9.800	133.59
0.0092	0.8567	1.160	8.674	54.90	9.854	136.29
0.0100	0.8573	1.166	8.579	54.60	9.901	140.83
Gadolinium Octadecanoate						
0.0012	0.8528	1.126	9.248	56.69	9.602	267.03
0.0024	0.8534	1.131	9.160	56.42	9.651	193.14
0.0034	0.8537	1.135	9.092	56.21	9.689	168.86
0.0044	0.8542	1.139	9.023	55.99	9.729	155.98
0.0054	0.8547	1.145	8.924	55.69	9.786	156.91
0.0066	0.8557	1.152	8.805	55.31	9.857	139.22
0.0074	0.8564	1.159	8.692	54.96	9.925	165.49
0.0084	0.8572	1.167	8.565	54.55	10.003	170.37
0.0092	0.8579	1.173	8.471	54.26	10.063	172.17
0.0100	0.8586	1.180	8.364	53.91	10.131	175.80

3. Calculations

The adiabatic compressibility β, specific acoustic impedance Z, inter-molecular free length L_f, apparent molal compressibility ϕ_k, apparent molal volume ϕ_v and solvation number S_n were calculated using the relationships

$$\beta = 1/(v^2\rho), \qquad Z = v\rho, \qquad L_f = \kappa\sqrt{\beta},$$
$$\phi_k = \frac{1000}{c\rho_0}\left[\beta\rho_0 - \beta_0\rho\right] + \frac{\beta_0 M}{\rho_0},$$
$$\phi_v = \frac{1000}{c\rho_0}\left[\rho_0 - \rho\right] + \frac{M}{\rho_0},$$
$$S_n = \frac{n_0}{n}\left[1 - \frac{\overline{V}\beta}{n_0\overline{V}_0\beta_0}\right],$$

where ρ_0, ρ; β_0, β; n_0, n; and $\overline{V}_0$, $\overline{V}$ are the density, adiabatic compressibility, number of moles, and molar volume of solvent and solution, respectively. M, K, C and v are the temperature-dependant molecular weight, Jacobson's constant, concentration (mol/dm^3) and ultrasonic velocity of gadolinium alkanoate solution.

4. Results and discussion

The ultrasonic velocity v, specific acoustic impedance, Z, apparent molal compressibility ϕ_k, apparent molal volume ϕ_v and solvation number S_n for solutions of gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate) in a mixture of benzene and methanol (7:3 v/v) increases, while adiabatic compressibility β and the inter-molecular free-length L_f, decrease with increasing solute concentration C (Table I). The variation of ultrasonic velocity with concentration (dv/dc), depends on the concentration derivative of density (dρ/dc), and the adiabatic compressibility (dβ/dc),

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

The results indicate that the density increases while the adiabatic compressibility decreases with increasing solute concentration. Thus the quantity (dρ/dc) is positive while (dβ/dc) is negative. Since the values of $1/\beta$ (dβ/dc) are larger than those of $1/\rho$ (dρ/dc), the concentration derivative of velocity (dv/dc) for the gadolinium alkanoate solutions is positive, and this is in close agreement with the results of other workers [7, 15, 16, 17] reported for solutions of electrolytic and metal alkanoate solutions.

Ultrasonic waves are high frequency mechanical waves. Their velocities in medium depend inversely on compressibility of the medium reported by Hykes *et al.* [18]. The rapid decrease of adiabatic compressibility β with increase of solute concentration clearly indicates the formation of a large number of tightly bound systems. Since the velocity increases with concentration and the density does so, the compressibility must decrease with increase in concentration. Such reduction in compressibility has been found in the solution due to solute molecules. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length as observed in (Figure 3). At lower concentration of gadoli-

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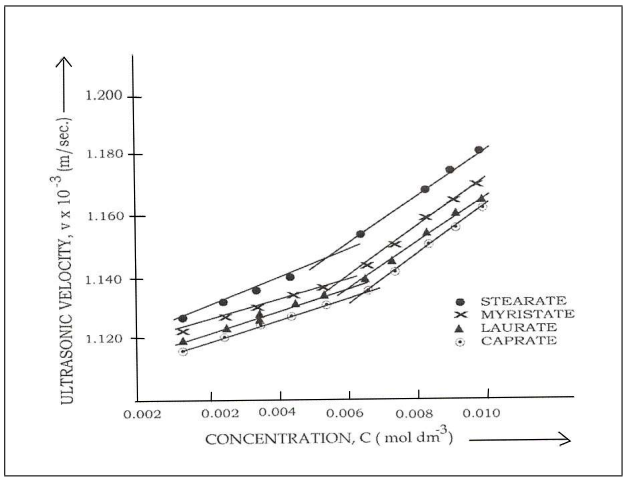

Figure 1. Ultrasonic velocity v vs. concentration C of gadolinium soaps.

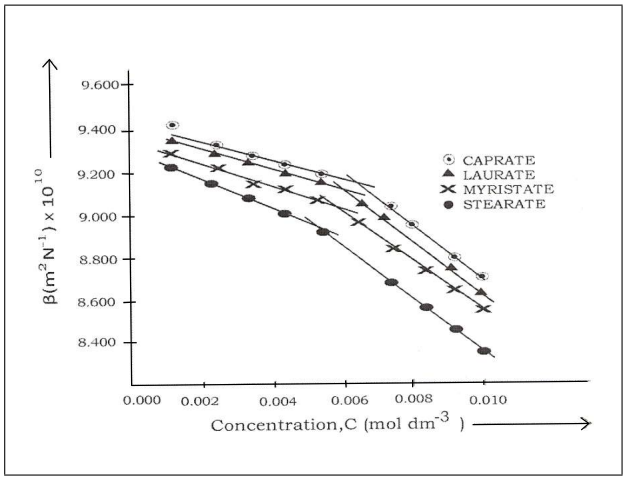

Figure 2. Adiabatic compressibility β vs. concentration C of gadolinium soaps.

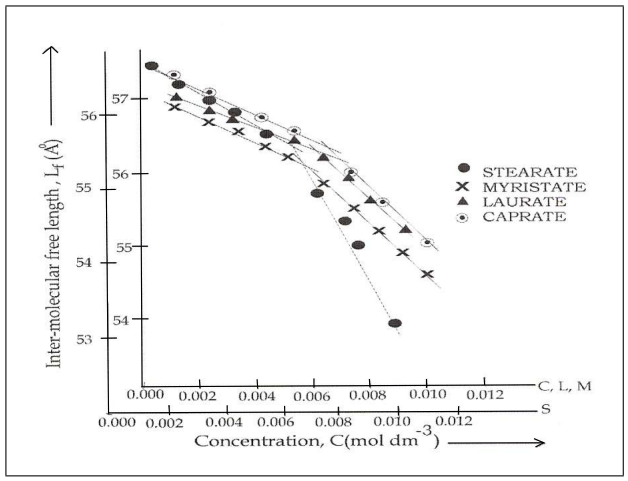

Figure 3. Inter-molecular free length $L : f$ vs. concentration C of gadolinium soaps.

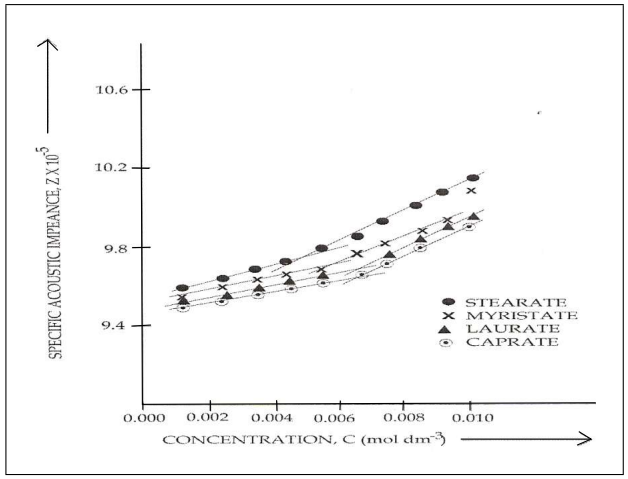

Figure 4. Specific acoustic impedance Z vs. concentration C of gadolinium soaps.

nium alkanoates in the mixture of benzene and methanol the molecules are not closer and thus L_f is high. In the more concentrated solution the molecules come closer and segment–segment interaction will exist, thereby decreasing the L_f and hence internal pressure decreases. A continuous decrease in β or L_f is a clear evidence for the existence of strong interactions. Such strong interaction may be due to dipole-dipole, dipole-induced dipole, H-bonding, etc.

Plots of ultrasonic velocity v, adiabatic compressibility β, intermolecular free length L_f and specific acoustic impedance Z vs. alkanoate concentration C (mol/dm^{-3}) are characterized by an intersection of two straight lines at definite alkanoate concentration, which corresponds to the CMC of the alkanoates (Figures 1–4).

The concentration at which micelle formation starts, known as critical micellar concentration. Around this concentration the bulk properties of the surfactant, such as osmotic pressure, turbidity, solublization, surface tension, viscosity, ultrasonic velocity and conductivity changes abruptly. If the micelles are formed in a non-aqueous medium the aggregates are called "reversed micelles", as in this case the polar head groups of the surfactant are concentrated in the interior and the lyophilic groups extend towards and into the non-polar solvent. The driving force for formation of reverse micelle is the dipole-dipole interactions of the surfactant. The values of CMC found to decrease with an increasing chain length of the gadolinium alkanoate molecules, and results are in agreement with the values obtained from other micellar [14] properties, viz. viscosity, density and conductometric [19] investigations (Table II).

Adiabatic compressibility β is a measure of intermolecular association or dissociation. It also determines the orientation of the solvent molecules around the solute molecules. The decrease in β may be due to the ionization of gadolinium alkanoate in to simple metal ion, Gd^{+3} and fatty acid anions, $RCOO^-$ in dilute solutions and due to the formation of micelles at higher alkanoate concentration. The intermolecular free length, L_f is the distance between the surfaces of the neighboring molecules. The decrease in intermolecular free length indicates the interac-

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Table II. CMC, Garnsey's constant G and other acoustic parameters of gadolinium alkanoates in benzene-methanol (7:3 v/v) at 30 ± 0.05 °C. CMC_v: CMC from ultrasonic velocity, CMC_C: CMC from Conductivity CMC_V: CMC from Viscosity.

	$G \cdot 10^{-3}$	$A \cdot 10^{10}$	$B \cdot 10^{8}$	$\phi_k^0 \cdot 10^{7}$	$\phi_v^0 \cdot 10^{2}$	CMC_v	CMC_C	CMC_V
Decanoate	3.28	-0.40	1.05	21.0	2.20	0.0064	0.0064	0.0064
Dodecanoate	3.44	-44.0	4.66	69.0	2.40	0.0061	0.0061	0.0061
Tetradecanoate	3.68	-115.0	6.10	140.0	2.77	0.0057	0.0057	0.0057
Octadecanoate	3.88	-182.5	12.90	216.0	2.83	0.0054	0.0054	0.0054

tion between the solute and solvent molecule due to which the structural arrangement in the neighborhood of constituent ions or molecules get affected considerably. Specific acoustic impedance Z indicates interaction between the solute and solvent molecules.

Since molecules or atom of a liquid are bound elastically to one another, the excess pressure results in a wave propagation through the liquid [20].The plots of v vs. C have been extrapolated to zero alkanoate concentration; extrapolated value of ultrasonic velocity v_0 is in agreement with the calculated values of the ultrasonic velocity for solvent mixture. The variation of the ultrasonic velocity v with alkanoate concentration, C follows the relationship

$$v = v_0 + GC,$$

where G is *Garnsey's constant* [21].

The values of Garnsey's constant G have been obtained from the slope of the plots of ultrasonic velocity v vs. alkanoate concentration C below CMC. The values of Garnsey's constant G increase with increasing number of carbon atoms in the fatty acid chain of gadolinium alkanoate (Table II).

All the micellar measurements show that these alkanoates behave as simple electrolytes in solutions of benzene–methanol mixture and ionize into simple metal cations, Gd^{+3} and fatty acid anions, $RCOO^-$. So, adiabatic compressibility, β of the dilute solutions of gadolinium alkanoates decreases with the increase in alkanoate concentration as well as chain length of alkanoate molecules (Table I) due to the fact that the ions in solutions 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 ions, and thus the internal pressure increases which lowers the compressibility of the solutions; i.e. the solution becomes harder to compress. The adiabatic compressibility β of the solution of gadolinium alkanoates was found to obey *Bachem's relationship* [22]

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

where β_0 is the compressibility of mixture of benzene–methanol (7:3 v/v), C is the alkanoate concentration and A and B are constants. Values of A and B have been determined from the intercept and slope of the linear plots of $(\beta - \beta_0)/C$ vs. $C^{1/2}$ are recorded in Table II. The values of A decrease, while B increases with the increase in the chain length of the alkanoate molecule.

The values of intermolecular free length L_f , decreases while specific acoustic impedance Z increase with increasing alkanoate concentration as well as chain length of alkanoate molecules (Table I) are in agreement with the results of Mehrotra [11, 23], which indicates that there is a significant interaction between solute and solvent molecules which considerably affect the structural arrangement. The increase in the values of specific acoustic impedance Z with increasing alkanoate concentration C can be explained on the basis of hydrophobic interaction between the solute and solvent molecules, which increases the intermolecular distance, making relatively wider gaps between the molecules and becoming the main cause of impedance in the propagation of ultrasonic waves. The plots of apparent molal compressibility ϕ_k and apparent molal volume, ϕ_v against $C^{1/2}$ exhibit breaks at a concentration; corresponds to the CMC, the values of limiting apparent molal compressibility ϕ_k^0 and limiting apparent molal volume ϕ_v^0 were found by the extrapolation of the plots of ϕ_k vs. $C^{1/2}$ and ϕ_v vs. $C^{1/2}$, respectively below the CMC to zero solute concentration. The values of ϕ_k^0 and ϕ_v^0 (Table II) are found to increase with increase in fatty acid chain length of alkanoate molecule. These results are in agreement with other workers [7, 11, 24] results for metal alkanoates solutions. Solvation number S_n is the number of solvent molecule present in the primary solvation sheath. The values of Sn decrease with increasing solute concentration below the CMC, but above the CMC it becomes almost constant with slight increase which may be attributed to more intakes of solvent molecules to reduce the repulsive forces acting between heads of ionic inverse micelles. The values of solvation number S_n also increase with increase in carbon chain length. This variation is in agreement with the other workers [7, 11, 25] results of metal alkanoate solutions.

5. Conclusion

The critical micellar concentration (CMC) of gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate) in benzene and methanol mixture (7:3 v/v) decrease with increasing chain length of fatty acids constituent of alkanoate molecules. Various acoustic parameters; viz. specific acoustic impedance Z, apparent molal compressibility ϕ_k and solvation number S_n increase while adiabatic compressibility β, inter-molecular free-length L_f and apparent molal volume ϕ_v decrease with increase in chain length of the alkanoate molecule.

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