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Acoustic behaviour of thorium soap solution

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ABSTRACT

The ultrasonic velocity of thorium soaps has been measured in benzene-methanol mixture (50-50%) at a constant temperature (40±0.05°C). The ultrasonic velocity and density data have been used to evaluate the adiabatic compressibility, intermolecular free length, molar sound velocity, specific acoustic impedance and other acoustic parameters. Thorium soap solutions obey Bachem's relation. The results confirm that thorium soaps act as weak electrolyte in dilute solution below the CMC. The values of CMC are in agreement with the values obtained from other properties.

Key words: Thorium, butyrate, valerate, caproate and caprylate.

INTRODUCTION

Metal soaps are used as stabilizers for nylon threads, PVC molding composition, polyester, as an adhesive for steel cord and rubber in radial tiers[1-4]. The structure and properties[5-7] of these soaps play and important role of their applications in different fields. Ultrasonic velocity have been found wide applications owing to their ability to characterise the physico-chemical behaviour of solutions. The velocity of ultrasonic waves in aqueous and non aqueous solution of electrolytes have been reported by several workers[8-10].

In the present communication attempts have been made to compute various acoustic parameters from ultrasonic velocity measurements of thorium soap (butyrate, valerate, cproate and caprylate) solutions.

EXPERIMENTAL

All the chemicals used for the preparation of thorium soaps were of BDH/AR grade and were purified by standard methods. Thorium soaps were prepared by direct metathesis of the corresponding soap with the required amount of aqueous solution of thorium nitrate with constant stirring, the precipitated soap was filtered off and wahsed first with distilled water and finally with alcohol. The soaps were first dried in an air-oven at 50-60°C and then under reduced pressure and further purified by recrystallisation. The solutions of thorium soaps were prepared by dissolving the weighed amount of soaps in the required volume of benzene-methanol mixture (50-50%). The solutions were kept at a constant temperature for two hours in a thermostat. The ultrasonic velocity measurements were recorded on an ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at a frequency of 1 MHz at a constant temperature (40±0.05°C).

The probable error in velocity results was 0.2%. The various acoustic parameters such as adiabatic compressibility, β, intermoluecular free length, L_f specific acoustic impedance, Z and molar sound vlocity, R have been calculated by using the following relationships.

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

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

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

$$R = \frac{\overline{M}}{\rho} v^{1/3} \quad ...(4)$$

$$\overline{M} = \frac{n_1 M_1 + n_2 - M_2}{n_1 + n_2} \quad ...(5)$$

where n_1, n_2 and M_1, M_2 are the number of moles and molecular weights of solvent and solutions respectively. K is Jacobson's constant[11].

RESULTS AND DISCUSSION

The ultrasonic velocity, v of thorium soap soltuions increases with the increasing concentration of soap in solution (Tables 1-4). The variations of velocity, v with concentration, C depends on concentration derivatives of ρ and β.

$$\frac{dv}{dC} = -\frac{v}{2}\left[\frac{1}{\rho}\cdot\frac{d\rho}{dC} + \frac{1}{\beta}\frac{d\beta}{dC}\right] \quad ...(5)$$

The results show that the density inreases while the adiabatic compressibility decreases with increasing soap concentration. Therefore, the quantity (dρ/dC) is positive while (dβ/dC) is negative. Since the values of [(1/β) (dβ/dC)] are larger than [(1/ρ) (dρ/dC)] for thorium soap solutions, thus the concentration derivative of velocity, dv/dC is positive, i.e. the ultrasonic velocity increases with increasing soap concentration.

The plots of ultrasonic velocity, v Vs soap concentration, C (Fig. 1) are characterized by an intersection of two straight lines corresponding to the CMC of the soap. The values of the CMC are 6.45×10^{-4}, 6.20×10^{-4},, 6.10×10^{-4} and 6.00×10^{-4} (g mol dm^{-3}) for butyrate, valerate, caporate and caprylate, respectively. The plots are extrapolated value of velocity, v0(1.102×10^{-5} cm/sec) is in agreement with the experimental value of velocity of the solvent whcih indicated that the aggregations of the soap molecules to an appreciable extent does not take place below the CMC.

The adiabatic compressibility, β of thorium soap solutions in benzene-methanol (50-50%) mixture decreases with increases in the soap concentration and increases in the chain length of the soap. The soaps behave as weak electrolytes in solution and iozine into simple metal cations, Th^{4+}, and fatty acid anion, $RCOO^-$ where R is C_3H_7, C_4H_9, C_5H_{11} and C_7H_{15}. The decrease in adiabatic compressibility may be attributed to the fact that the ions in solution are surrounded by a layer of solvent molecules firmly bound and oriented toward the ions. The orienation of the solvent molecules around the ionsn due to the influence of the elctrostatic field of the ions, thus the internal pressure increases, which lowers the compressibility of solution i.e., the solution becomes more difficult to compress.

The plots of adabatic compressibility, β vs soap concentration, C and the specific acoustic impedance. Z vs concentration, C are also characterised by an intersection of two straight lines, which corresponds to the CMC of the soap. These plots have been extrapoated to zero soap concentration and the extrapolated values of adiabatic compressibility and specific acoustic impedance are in close agreement with the calculated values for the solvent.

The results of the adiabatic compressibility

Table 1: Ultrasonic velocity and acoustic parameters of thorium butyrate in benzene and methanol mixture (at 40±0.5°C)

S. No.	Concentration $C\times10^4$ (g mol dm^{-3})	Density ρ (g ml^{-1})	Ultrasonic Velocity $v\times10^{-5}$ (cm/sec)	Adiabatic Compressibility $\beta\times10^{11}$ (cm^2/dyne)	Intermo-lecular free length L_f (A°)	Specific acoustic Impedance $Z\times10^{-4}$ (CGS unit)	Molar sound velocity $R\times10^{-2}$ (cm/sec)
1.	1.0	0.8435	1.104	9.728	0.633	9.312	31.28
2.	2.0	0.8456	1.107	9.653	0.630	9.361	31.24
3.	3.0	0.8478	1.110	9.569	0.627	9.411	31.18
4.	4.0	0.8500	1.113	9.497	0.625	9.461	31.13
5.	5.0	0.8524	1.116	9.416	0.622	9.513	31.08
6.	6.0	0.8547	1.119	9.346	0.620	9.564	13.03
7.	7.0	0.8562	1.125	9.225	0.616	9.632	31.02
8.	8.0	0.8571	1.131	9.124	0.613	9.693	31.05
9.	9.0	0.8581	1.138	9.001	0.608	9.765	31.08
10.	10.0	0.8590	1.144	8.897	0.605	9.827	31.10

have bee explained in terms of Bachems's[12] equation

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

where A and B are the constants, C is the molar concentration of the soap and β and β_0 are the adiabatic compressibilities of the solution and solvent, respectively. The values of constants A and B have been obtained from the intercept and slope of the plots $(\beta-\beta_0)/C$ Vs $C^{½}$. The values of A are -14.52×10^{-9}, -11.72×10^{-9}, -10.44×10^{-9} and -9.20×10^{-9} for butyrate, valerate, caproate and caprylate, respectively while the values of B are -133×10^{-9}, -122×10^{-9}, -100×10^{-9} and -80×10^{-9} for butyrate, valerate, caproate and caprylate, respectively.

The intermolecular free length L_f for thorium soaps decreases with increasing soap concentration, which may be due to the decrease in adiabatic compressibility of the soap solution with increase in the soap concentration. The plots of L_f Vs sopa concentration are characterised by the CMC of the soaps. The extraploated values of L_f are in agreement with the calculated values of L_f for benzene-methanol mixture. The values of

Table 2: Ultrasonic velocity and acoustic parameters of Thorium valerate in Benzene and Methanol mixture (at 40±0.5°C)

S. No.	Concentration $C\times10^4$ (g mol dm^{-3})	Density ρ (g ml^{-1})	Ultrasonic Velocity $v\times10^{-5}$ (cm/sec)	Adiabatic Compressibility $\beta\times10^{11}$ (cm^2/dyne)	Intermolecular free length L_f (A°)	Specific acoustic Impedance $Z\times10^{-4}$ (CGS unit)	Molar sound velocity $R\times10^{-2}$ (cm/sec)
1.	1.0	0.8439	1.105	9.709	0.632	9.325	31.28
2.	2.0	0.8465	1.109	9.606	0.629	9.388	31.22
3.	3.0	0.8492	1.112	9.524	0.626	9.443	31.15
4.	4.0	0.8521	1.116	9.425	0.623	9.509	31.09
5.	5.0	0.8550	1.119	9.337	0.620	9.567	31.01
6.	6.0	0.8581	1.122	9.259	0.617	9.628	30.93
7.	7.0	0.8583	1.129	9.132	0.613	96.696	30.99
8.	8.0	0.8584	1.136	9.025	0.609	9.751	31.05
9.	9.0	0.8586	1.143	8.913	0.605	9.814	31.11
10.	10.0	0.8587	1.149	8.818	0.602	9.866	31.16

Table 3: Ultrasonic velocity and acoustic parameters of Thorium caproate in benzene and methanol mixture (at 40±0.5°C)

S. No.	Concentration $C\times10^4$ (g mol dm^{-3})	Density ρ (g ml^{-1})	Ultrasonic Velocity $v\times10^{-5}$ (cm/sec)	Adiabatic Compressibility $\beta\times10^{11}$ (cm^2/dyne)	Intermolecular free length L_f (A°)	Specific acoustic Impedance $Z\times10^{-4}$ (CGS unit)	Molar sound velocity $R\times10^{-2}$ (cm/sec)
1.	1.0	0.8441	1.105	9.699	0.632	9.327	31.27
2.	2.0	0.8468	1.110	9.588	0.628	9.399	31.22
3.	3.0	0.8500	1.113	9.497	0.625	9.461	31.13
4.	4.0	0.8532	1.117	9.390	0.621	9.530	31.06
5.	5.0	0.8563	1.120	9.311	0.619	9.591	30.97
6.	6.0	0.8591	1.124	9.217	0.615	9.656	30.91
7.	7.0	0.8607	1.130	9.099	0.612	9.726	30.91
8.	8.0	0.8620	1.138	8.961	0.607	9.810	30.94
9.	9.0	0.8625	1.144	8.857	0.604	9.867	30.98
10.	10.0	0.8633	1.152	8.726	0.599	9.945	31.02

Table 4: Ultrasonic velocity and acoustic parameters of thorium caprylate in benzene and methanol mixture (at 40±0.5°C)

S. No.	Concentration $C\times10^4$ (g mol dm^{-3})	Density ρ (g ml^{-1})	Ultrasonic Velocity $v\times10^{-5}$ (cm/sec)	Adiabatic Compressibility $\beta\times10^{11}$ (cm^2/dyne)	Intermolecular free length L_f (A°)	Specific acoustic Impedance $Z\times10^{-4}$ (CGS unit)	Molar sound velocity $R\times10^{-2}$ (cm/sec)
1.	1.0	0.8442	1.107	9.662	0.630	9.345	31.29
2.	2.0	0.8470	1.111	9.569	0.627	9.410	31.22
3.	3.0	0.8501	1.116	9.452	0.623	9.487	31.16
4.	4.0	0.8533	1.121	9.328	0.619	9.565	31.13
5.	5.0	0.8566	1.125	9.225	0.616	9.637	31.01
6.	6.0	0.8598	1.130	9.107	0.612	9.716	30.94
7.	7.0	0.8608	1.136	9.009	0.608	9.779	30.96
8.	8.0	0.8612	1.144	8.873	0.604	9.852	31.02
9.	9.0	0.8611	1.153	8.734	0.599	9.928	31.11
10.	10.0	0.8612	1.156	8.688	0.598	9.955	31.14

intermolecular free length, L_f decrease with increasing ultrasonic velocity according to Erying and Kincoid[13], which indicates a significant interaction between solute and solvent molecules, which affects the structural arrangement of the soap molecules.

The variation in the values of molar sound velocity, R with soap concentration are recorded (Tables 1-4). The molar sound velocity decreases upto the CMC and then increases above the CMC.

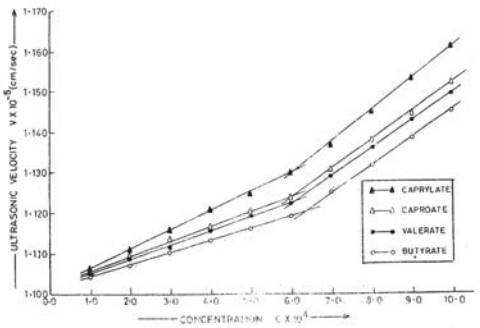

Fig. 1: Ultrasonic velocity Vs concentration

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