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Comparative Studies of Cerium and Thorium Soap Solution

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ABSTRACT

The Ultrasonic velocity of cerium and thorium soaps has been measured in benzene-methanol mixture (50-50%) at a constant temperature (40 ± 0.05^{0}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 cerium and Thorium soap solutions obey Bachem's relation. The result Confirm that cerium and 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: Cerium Thorium Laurate, Myrestate.

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 in owing to their ability to characterise the physico–chemical behaviour of solution .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 cerium thorium soap (laurate myrestate) Solutions .

EXPERIMENTAL

All the chemicals used for the preparation of cerium and thorium soaps were of BDH/AR grade and were purified by standard methods. Cerium and Thorium soaps was prepared by direct metathesis of the corresponding soap with the required amount of aqueous solution of cerium nitrate and thorium nitrate with constant stirring. The precipitated soap was filtered off and washes first with distilled water and finally with alcohol. The soaps were first dried in an air-oven at 50-60^{0}C and then under reduced pressure and further purified by recrystallisation. The solution of cerium and thorium soaps were preapared 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 result was 0.2%.The various acoustic parameters such as adiabatic compressibility. β, intermoluecular free length, L, specific acoustic impedance, Z and molar sound viocity, R have been calculated by using the following relationships.

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

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

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

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

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

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]

RESULT AND DISCUSSION

The ultrasonic velocity, v of Cerium and thorium soap solutions 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.

$$\frac{dv}{dC} = -\frac{v}{2}\left[\frac{1}{\rho}.\frac{d\rho}{dC} + \frac{1}{\beta}\frac{d\beta}{dC}\right] \quad ...(6)$$

The results show that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Therefore, the quantity $(\frac{d\rho}{dC})$ is positive while $\left[\left(\frac{1}{\beta}\right)(d\beta/dC)\right]$ is negative. Since the values of $\left[\left(\frac{1}{\beta}\right)(d\beta/dC)\right]$ are larger than $\left[\left(\frac{1}{\rho}\right)(d\rho/dC)\right]$ for cerium and 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} (gmol dm^{-3})for Cerium laurate cerium myrestate and thorium laurate, thorium myrestate, respectively. The plot are extrapolated value of velocity, V0(1.102 $\times 10^{-5}$ cm/Scc) in agreement with the experimental value of velocity of the solvent which indicated the aggregations of the soap molecules to an appreciable extent does not take place below the CMC.

The adiabatic compressibility, β of cerium and 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, Ce^{3+} ,Th^{4+}, and fatty acid anion, RCOO where R is $C_{11}H_{23}$, $C_{13}H_{27}$ 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 orientation of the solvent molecules around the ionsn due to the influence of the electrostatic 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 adiabatic compressibility, β Vs soap concentration. C and the specific acoustic impedance. Z vs concentration, C are also characterized by an intersection of two straight lines which corresponds to the CMC of the soap. These plots have been extrapolated to zero soap concentration and the extrapolated value of adiabatic compressibility and specific acoustic impedance are in close agreement with the

Table 1: Ultrasonic Velocity and Acoustic Parameters of Cerium Laurate in 50% benzene and 50% methanol at 40 ± 0.05ºC

S. No	Concentration C (g mole l^{-1})	Density, p (g ml^{-1})	Ultrasonic velocity v × 10^{-5} (cm/sec)	Adiabatic compressibility y, β × 10^{11} (cm^2/dyne)	Intermolecular free length, L_f (Aº)	Specific acoustic amredance z × 10^{-6} (CGS Unit)	Apparent molal compressibility ϕk × 10^{7} (cm^2/dyne)	Apparent molal volume, ϕ_v × 10^{-3} (ml/mole)	Molar sound velocity R × 10^{-1} (cm/sec)	Solvation number S_n
1	0.0012	0.8281	1.122	9.59	0.628	9.29	-23.71	-1.227	272.55	40.52
2	0.0014	0.8292	1.125	9.53	0.626	9.32	-25.35	-1.804	272.87	42.47
3	0.0016	0.8305	1.127	9.48	0.625	9.35	-25.955	-2.236	273.11	42.81
4	0.0019	0.8314	1.131	9.4	0.622	9.39	-26.572	-2.395	273.69	43.65
5	0.0022	0.833	1.135	9.31	0.619	9.45	-28.018	-3.061	273.93	45.09
6	0.0026	0.8346	1.139	9.24	0.617	9.49	-26.739	-2.934	274.74	43.01
7	0.003	0.8393	1.143	9.12	0.613	9.58	-29.06	-4.455	274.23	44.5
8	0.0036	0.8456	1.149	8.96	0.607	9.7	-30.32	-5.499	273.91	45.11
9	0.0044	0.857	1.158	8.7	0.598	9.92	-33.994	-7.739	272.31	47.58
10	0.0049	0.8643	1.163	8.55	0.593	10.04	-35.215	-8.598	271.46	48.25
11	0.0055	0.8712	1.169	8.4	0.588	10.18	-35.532	-9.115	270.86	47.91
12	0.0062	0.8832	1.176	8.18	0.58	10.38	-37.292	-10.339	269.04	48.91

Table 2: Ultrasonic Velocity and Acoustic Parameters of Cerium Myrestate in 50% benzene and 50% methanol at 40 ± 0.05ºC

S. No	Concentration C (g mole l^{-1})	Density, p (g ml^{-1})	Ultrasonic velocity v × 10^{-5} (cm/sec)	Adiabatic compressibility y, β × 10^{11} (cm^2/dyne)	Intermolecular free length, L_f (Aº)	Specific acoustic amredance z × 10^{-6} (CGS Unit)	Apparent molal compressibility ϕk × 10^{7} (cm^2/dyne)	Apparent molal volume, ϕ_v × 10^{-3} (ml/mole)	Molar sound velocity R × 10^{-1} (cm/sec)	Solvation number S_n
1	0.001	0.829	1.125	9.53	0.626	9.32	-35.701	-2.841	272.46	59.46
2	0.0012	0.8302	1.128	9.46	0.624	9.36	-36.432	-3.245	272.78	60.09
3	0.0014	0.8311	1.132	9.39	0.622	9.4	-36.955	-3.533	273.19	60.53
4	0.0016	0.8324	1.135	9.33	0.62	9.44	-36.721	-3.749	273.56	59.74
5	0.0018	0.8353	1.137	9.26	0.617	9.49	-38.422	-5.263	273.15	59.28
6	0.002	0.838	1.14	9.18	0.615	9.55	-40.282	-6.473	272.87	61.33
7	0.0022	0.8415	1.143	9.1	0.612	9.61	-41.804	-7.464	272.6	62.32
8	0.0025	0.8456	1.147	8.99	0.608	9.69	-42.992	-8.41	272.26	62.79
9	0.0028	0.8502	1.152	8.86	0.604	9.79	-45.866	-9.586	271.73	64.45
10	0.0032	0.8551	1.158	8.72	0.599	9.9	-45.563	-10.181	271.49	64.29
11	0.0037	0.8633	1.165	8.53	0.592	10.05	-47.003	-11.316	270.62	64.88
12	0.0043	0.8712	1.173	8.34	0.586	10.21	-49.961	-11.879	270.04	63.8

Table 3: Ultrasonic Velocity and Acoustic Parameters of Thorium Laurate in 50% benzene and 50% methanol at 40 ± 0.05ºC

S. No	Concentration C (g mole l^{-1})	Density, p (g ml^{-1})	Ultrasonic velocity v × 10^{-5} (cm/sec)	Adiabatic compressibility y, β × 10^{11} (cm^2/dyne)	Intermolecular free length, L_f (Aº)	Specific acoustic amredance z × 10^{-6} (CGS Unit)	Apparent molal compressibility ϕk × 10^{7} (cm^2/dyne)	Apparent molal volume, ϕ_v × 10^{-3} (ml/mole)	Molar sound velocity R × 10^{-1} (cm/sec)	Solvation number S_n
1	0.0012	0.8311	1.125	9.5	0.625	9.34	-33.879	-3.934	272.97	54.02
2	0.0014	0.8323	1.128	9.44	0.623	9.38	-34.021	-4.078	273.35	54.04
3	0.0018	0.8344	1.133	9.34	0.62	9.44	-33.099	-4.27	274.26	52.07
4	0.0022	0.8362	1.139	9.22	0.616	9.52	-33.422	-4.392	275.18	52.45
5	0.0026	0.839	1.146	9.07	0.611	9.61	-35.258	-4.942	275.92	54.8
6	0.0033	0.8442	1.155	8.86	0.604	9.74	-35.719	-5.493	276.96	54.67
7	0.004	0.8536	1.16	8.71	0.599	9.9	-35.712	-7.061	276.38	51.87
8	0.0049	0.8657	1.166	8.5	0.591	10.08	-36.161	-8.525	275.5	50.08
9	0.0062	0.8812	1.175	8.22	0.582	10.38	-35.946	-9.729	274.69	47.74
10	0.0083	0.9073	1.19	7.78	0.566	10.79	-35.614	-10.704	273.48	45.23
11	0.01	0.9289	1.203	7.44	0.553	11.16	-35.281	-11.238	272.62	43.68

Table 4: Ultrasonic Velocity and Acoustic Parameters of Cerium Myrestate in 50% benzene and 50% methanol at 40 ± 0.05ºC

S. No	Concentration C (g mole l^{-1})	Density, p (g ml^{-1})	Ultrasonic velocity v × 10^{-5} (cm/sec)	Adiabatic compressibility y, β × 10^{11} (cm^2/dyne)	Intermolecular free length, L_f (Aº)	Specific acoustic amredance z × 10^{-6} (CGS Unit)	Apparent molal compressibility ϕk × 10^{7} (cm^2/dyne)	Apparent molal volume, ϕ_v × 10^{-3} (ml/mole)	Molar sound velocity R × 10^{-1} (cm/sec)	Solvation number S_n
1	0.001	0.8322	1.126	9.47	0.624	9.36	-44.933	6.017	272.45	70.25
2	0.0012	0.8341	1.129	9.4	0.622	9.41	-45.062	-6.824	272.68	69.07
3	0.0014	0.8365	1.133	9.31	0.619	9.47	-46.583	-7.401	272.68	70.81
4	0.0016	0.8374	1.137	9.24	0.617	9.51	-45.728	-7.077	273.62	69.86
5	0.0018	0.8382	1.14	9.18	0.615	9.55	-44.507	-6.824	274.17	68.12
6	0.002	0.8413	1.143	9.1	0.612	9.61	-45.724	-7.833	274.06	68.53
7	0.0022	0.8459	1.146	9.01	0.609	9.68	-44.716	-9.219	273.61	69.69
8	0.0025	0.8501	1.15	8.89	0.605	9.77	-49.03	-10.376	273.24	69.99
9	0.0028	0.8564	1.154	8.77	0.601	9.87	-50.489	-11.725	272.6	70.23
10	0.0032	0.8648	1.159	8.61	0.595	9.01	-52.009	-13.13	271.71	70.48
11	0.0037	0.873	1.166	8.42	0.589	10.17	-52.853	-14.132	270.96	73.23
12	0.0043	0.8552	1.175	8.18	0.58	10.39	-54.219	-15.365	269.8	70.52

calculated values for the solvent

The results of the adiabatic compressibility have been 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 $\beta = \beta_0$ are the adiabatic compressibility 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 $C^{1/2}$. The values of A are -14.52×10^{-9}, -11.72×10^{-9}, -10.44×10^{-9} and 9.20×10^{-9} for, Cerium laurate cerium myrestate and thorium laurate, thorium myrestate, respectively while the values of B are 133×10^{-9}, -122×10^{-9}, -100×10^{-9} and -80×10^{-9} for Cerium laurate cerium myrestate and thorium laurate, thorium myrestate respectively.

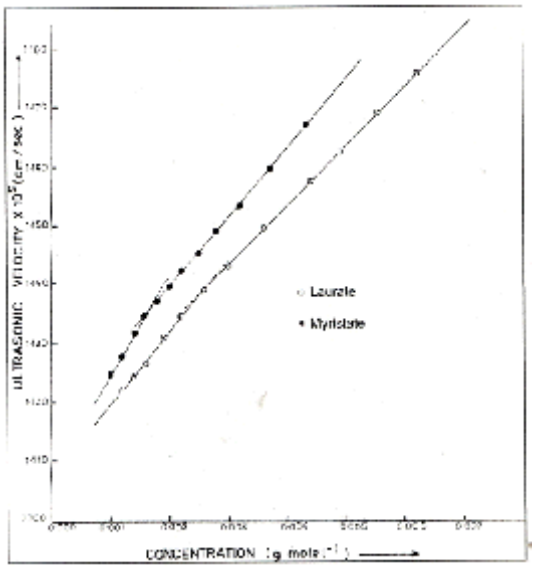

Fig. 1: Ultrasonic Velocigy vs Concentration

The intermolecular free length L_f for cerium and 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 soap concentration are characterized by the CMC of the soaps. The extrapolated values of L_f are in agreement with the calculated values L_f for benzene-methanol mixture. The values of 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 (Table 1-4) The molar sound velocity decreases up to the CMC and then increases above the CMC.

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