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Acoustic Behaviour of Dysprosium Soaps in Methanol

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The studies of ultrasonic velocity in solutions of dysprosium butyrate and velerate soaps in methanol have been used to evaluate the various acoustic parameters. The result shows that ultarasonic velocity, molar sound velocity, density and specific acoustic impedence increases but adiabatic compressibility and intermolecular free length decreases with increasing soap concentration. The values of solvation number are almost constant for dilute solution but decreases rapidly above the critical micelle concentration (CMC) with increasing soap concentration. The apparent molal compressibility and apparent molal volume of dysprosium soap solution in methanol vary linearly below the CMC.

Key Words: Ultrasonic velocity, Adiabatic compressibility, Intermolecular free length, Specific acoustic impedence, Solvation number.

INTRODUCTION

The complimentary use of apparent molal compressibility and adiabatic compressibility data can provide interesting information an ion-solvent interaction and the structure of the solution. Several workers[1-9] have used ultrasonic velocity measurements for the determination of ion-solvent interaction and the solvation numbers obtained by this technique were found to be in agreement with those computed by other techniques.

EXPERIMENTAL

All chemicals used were of BDH/AR grade, Dysprosium soaps were prepared by direct metathesis as described earlier[10]. The solutions were prepared by dissolving known weight of the soap in methanol and were kept for 2 h in a thermostat at 40 ± 0.05ºC and then used for velocity measurements. The ultrasonic velocity of the soap solutions was measured with a multi-frequency ultrasonic interferometer (Mittal Enterprises, New Delhi) at a frequency of 1 MHz at constant temperature.

RESULTS AND DISCUSSION

The ultrasonic velocity of dysprosium solutions in methanol at different concentration are given in Fig. 1.

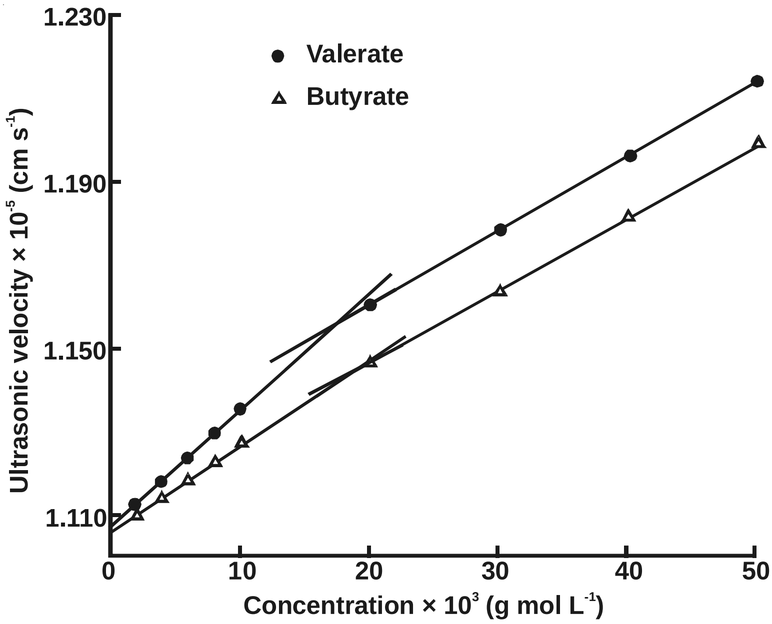

Fig. 1. Ultrasonic velocity *vs.* concentration of dysprosium soaps in methanol

For any homogeneous dissipative fluid system, the ultrasonic velocity (v) of a compressional acoustic wave is related to the density (ρ) and adiabatic compressibility (β) by the relationship

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

Adiabatic compressibility is calculated for solutions of dysprosium soap solutions of different concentrations from ultrasonic velocity values and presented in Tables 1 and 2.

The results indicate that the density increases but adiabatic compressibility decreases with soap concentration. These soaps behave as weak electrolytes and ionize. The ions in solution are surrounded by a layer of oriented solvent molecule firmly bound. The increase in internal pressure results in lowering of the compressibility of the soap solution. This explains the lowering of compressibility of the soap solution. This explains the decease in β with concentration.

The decrease in the intermolecular free length ($L_f = k\beta^{1/2}$) is due to the decrease in the compressibility with increasing soap concentration (Tables 1 and 2). The plots of intermolecular free length *vs.* soap concentration which corresponds to CMC of the soap (Fig. 2).

TABLE-1
ULTRASONIC VELOCITY AND OTHER ACOUSTIC PARAMETERS OF DYSPROSIUM BUTYRATE IN METHANOL AT 40 ± 0.05ºC

S. No.	Concentration $C \times 10^3$ (g mol L^{-1})	Denisity (g mL^{-1})	Ultrasonic velocity $V \times 10^{-5}$ (cm/s)	Adiabatic Compressibility $\beta \times 10^{11}$ (cm^2/dyne)	Intermolecular free length $L_f \times 10^3$ (cm)	Specific acoustic impedance $Z \times 10^{-4}$ (CGS unit)	Apparent molal compressibility (cm^2/dyne)	Apparent molal volume $\phi v \times 10^{-3}$ (mL/mol)	Molar sound velocity $R \times 10^{-3}$ (cm/s)	Solvation number Sn
1	2.0	0.7974	1.111	10.160	6.471	8.859	5.342	1.504	1.931	117.4
2	4.0	0.8014	1.115	10.037	6.432	8.936	7.270	1.756	1.925	133.1
3	6.0	0.8052	1.119	9.918	6.393	9.010	7.477	1.798	1.920	136.7
4	8.0	0.8086	1.123	9.806	6.358	9.081	7.426	1.756	1.916	136.4
5	10.0	0.8128	1.127	9.687	6.319	9.160	7.568	1.831	1.911	137.9
6	20.0	0.8312	1.145	9.177	6.150	9.517	7.260	1.819	1.887	130.7
7	30.0	0.8472	1.163	8.727	5.997	9.853	6.854	1.714	1.870	1.870
8	40.0	0.8638	1.181	8.300	5.849	10.201	5.613	1.680	1.852	118.4
9	50.0	0.8782	1.199	7.921	5.714	10.530	5.316	1.605	1.839	113.1

TABLE-2
ULTRASONIC VELOCITY AND OTHER ACOUSTIC PARAMETERS OF DYSPROSIUM VALERATE IN METHANOL AT 40 ± 0.05ºC

S. No.	Concentration $C \times 10^3$ (g mol L^{-1})	Density (g mL^{-1})	Ultrasonic velocity $V \times 10^{-5}$ (cm/s)	Adiabatic compressibility $\beta \times 10^{11}$ (cm^2/dyne)	Intermolecular free length $L_f \times 10^3$ (cm)	Specific acoustic impedance $Z \times 10^{-4}$ (CGS unit)	Apparent molal compressibility (cm^2/dyne)	Apparent molal volume $\phi v \times 10^{-3}$ (mL/mol)	Molar sound velocity $R \times 10^3$ (cm/s)	Solvation number Sn
1	2.0	0.7992	1.113	10.101	6.452	8.895	10.400	2.584	1.928	188.8
2	4.0	0.8042	1.118	9.948	6.403	8.991	10.350	2.584	1.921	186.9
3	6.0	0.8106	1.124	9.765	6.344	9.111	11.135	2.878	1.911	198.4
4	8.0	0.8152	1.130	9.607	6.293	9.212	10.924	2.742	1.906	196.6
5	10.0	0.8208	1.135	9.457	6.243	9.316	10.847	2.786	1.897	193.6
6	20.0	0.8452	1.161	8.777	6.015	9.813	10.110	2.647	1.866	179.7
7	30.0	0.8612	1.178	8.368	5.873	10.145	8.599	2.248	1.850	152.4
8	40.0	0.8772	1.196	7.970	5.731	10.491	7.816	2.049	1.835	138.4
9	50.0	0.8932	1.215	7.584	5.591	10.852	7.323	1.929	1.821	129.4

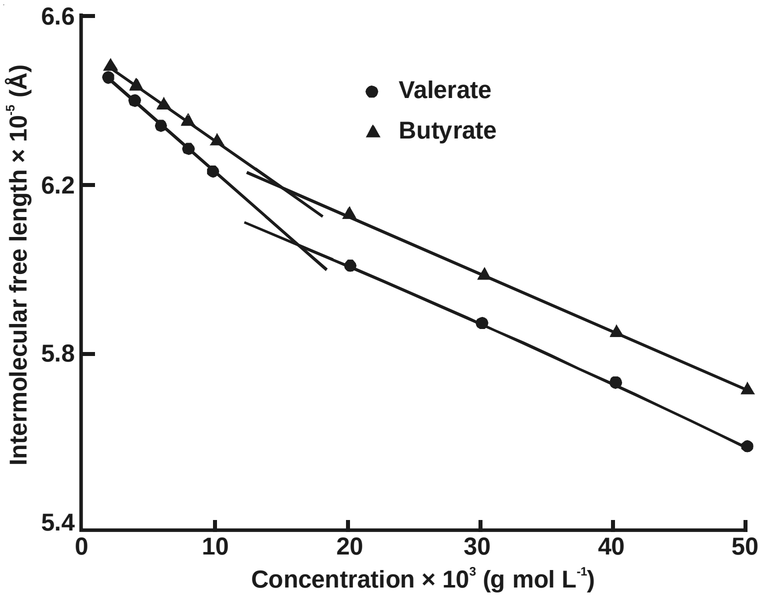

Fig.2 Intermolecular free length *vs.* concentration of dysprosium soaps in methanol

The plots of specific acoustic impedance *vs* soap concentration (Fig.3) show break at a definite soap concentration which corresponds to the CMC of the soap.

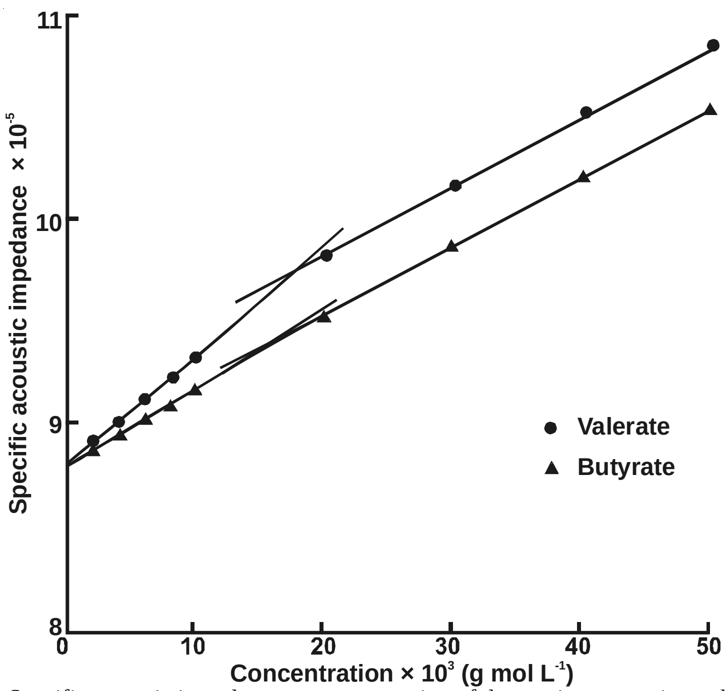

Fig.3 Specific acoustic impedance *vs.* concentration of dysprosium soaps in methanol

The increase in the values of specific acoustic impedance, z, with the soap concentration, c, may be due to interaction between the soap and solvent molecules which increases with intermolecular distance making relatively wider gaps between the molecules and becoming the main cause of impediment in propagation of ultrasonic waves.

The apparent molal properties are found to be dependent on the concentration of the solutions. The apparent molal compressibility ϕ_k can be expressed as:

$$\phi_k = 1000/c\rho\ (\rho_0\beta-\beta_0\rho) + \mu\beta_0/\rho_0$$

where M is the molecular weight of the soap. The value of ϕ_k increase with increasing soap concentration and also the molecular weight of the soap molecule.

The adiabatic compressibility data have been used to determine the solvation number of the soap by assuming that the ions and the solvent molecules in immediate contact are compressible. This is because the ions add some electrosatatic stiffing on the adjacent solvent molecules which is considered to be equivalent to a large internal pressure on these molecules. Pasynkic[11] defined the solvent number S_n and the number of solvent molecules present in the primary solvent sheath and is given by the relationship.

$$S_n = (n_1/n_2)\ (1-V\beta/n_1V_0\beta_0)$$

where V is the volume of solution containing n_2 moles of solute and V_0 is the molar volume of the solvent. The results show that the solvation number decreases with increasing concentration and increases with the molecular weight of the soap. The higher values of the solvation number are in agreement with the results reported by Padmini and Rao[12] for cobalt acetate.

The plots of ultrasonic velocity *vs* concentration (Fig. 1) shows that it consists of two straight lines intersecting at a point. The slope of this is positive, in agreement with the behaviour reported for electrolytic compounds[13,14].

The values of molar sound velocity, R increase linearly with increasing soap concentration and chain length of soap molecules (Tables 1 and 2).

The linear part in lower concentration range represents normal solution of the soap; the point of intersection represents CMC. The value of CMC decreases with the molecular weight of the soaps (Table-3). The linear increase in V with C can be represented by the equation[15].

$$(V-V_0) = GC$$

where G is the Garney's constant. The value of G has been calculated from the slope of the linear graph (Fig. 1) and found to increase with the molecular weight of the soap (Table-3).

TABLE-3
CMC AND VARIOUS OTHER ACOUSTIC CONSTANT OF DYSPROSIUM SOAPS IN METHANOL AT 40 ± 0.05ºC

S. No.	Name of the Soap	CMC (g mol L^{-1})	Garnsey's constant G x 10^{-5}	Constant A × 10^{11}	Constant B × 10^{11}	$-\phi k^o \times 10^{-1}$	$-\phi^0 V \times 10^{-3}$
1	Butyrate	0.021	1.95	40	+ 175	6.5	1.22
2	Valerate	0.018	2.77	72	+ 125	9.4	2.42

The adiabatic compressibility, β, of the dilute solution of dysprosium soaps is found to obey Bachem's[16] relationship.

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

where A and B are constants and C is the concentration of soap solution. The values of A for dysprosium soaps increase while B decrease with the increase in atomic mass of metal ion in the soap (Table-3)

The values of limiting apparent molar compressibility ϕ_k have been obtained by extrapolating the linear portion of the plots of ϕ_k *vs.* $C^{1/2}$ and found to increase with molecular weight if the dysprosium soap (Table-3). The values of ϕ_k are negative for all the solutions.

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