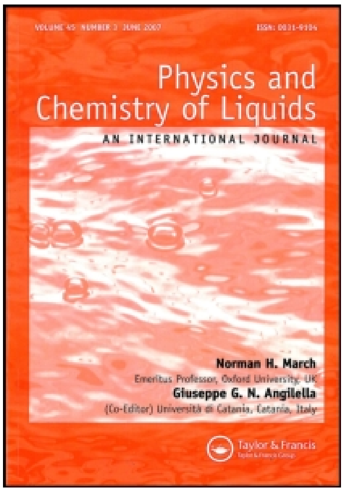

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ULTRASONIC STUDIES ON MICELLAR BEHAVIOUR OF YTTRIUM SOAPS IN MIXED ORGANIC SOLVENTS

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The ultrasonic measurements of yttrium soaps were made in a mixture of 50% benzene and 50% dimethylsulfoxide (V/V) to determine the critical micelle concentration, soap-solvent interaction and various acoustic and thermodynamic parameters. The values of the CMC decrease with increasing chain length of fatty acid constituent of the soap molecule and are in agreement with the values obtained from other micellar properties. The various acoustic parameters (inter-molecular free-length, adiabatic compressibility, apparent molar compressibility, specific acoustic impedance, apparent molar volume, molar velocity, solvation number, available volume and relative association) for yttrium soaps (myristate, laurate, caprate and linoleate) have been evaluated by ultrasonic velocity measurements.

KEY WORDS: Metallic soaps, ultrasonic velocity, solvation number.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technological and academic fields. It has been a subject of intense investigations in the recent past on account of its role in such diversified fields as detergents, softners, stabilizers, plasticizers, lubricants, cosmetics, medicines, emulsifiers, insecticides and water-proofing agents. The technological applications of these soaps are mostly based on empirical know-how, and the selection of the soap is dependent largely on economic factors.

The methods of preparation, properties and uses of metal soaps were reviewed by several researchers[1–3]. The study of molecular interactions has been a subject of extensive investigations by Raman[4], NMR[5,6], infrared[7,8] and ultrasonic absorption[9,10] measurements.

The present work deals with the ultrasonic velocity measurements of yttrium soaps (myristate, laurate, caprate and linoleate) in a mixture of 50% benzene and 50% dimethylsulfoxide (V/V) with a view to evaluate various allied parameters related to the acoustical properties of soap solutions.

EXPERIMENTAL

The chemicals used were of BDH/AR grade. Ytrrium soaps were prepared by direct methathesis of corresponding potassium soap with slight excess of aqueous solution of yttrium nitrate at 50–55°C. The precipitated soaps were washed with distilled water and acetone to remove the excess of metal ions and unreacted fatty acid. The purity of the soap was checked by elemental analysis and the results were found in agreement with theoretically calculated values. The reproducibility of the results was checked by preparing two samples of the soap under similar conditions.

The solutions of these soaps were prepared in a mixture of 50% benzene and 50% dimethylsulfoxide and were kept for 2 h in a thermostat at the desired temperature. The ultrasonic velocity measurements were recorded on a multi-frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40 ± 0.05°C using a crystal of 1 MHz frequency. The densities of the solvent and solutions were measured by a dilatometer calibrated with pure benzene.

The various acoustic parameters such as adiabatic compressibility, β, intermolecular freelength[11], L_f, specific acoustic impedance Z[12], apparent molar compressibility, ϕ_k, apparent molar volume, ϕ_v[13], available volume V_a[14], relative association, R_A[15] molar sound velocity, R, and solvation number, Sn[16], were calculated by using the following relationships

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

$$L_f = \left(\frac{\beta}{K}\right)^{1/2}$$

$$Z = v\rho$$

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0}$$

$$\phi_v = \frac{1000(\rho - \rho_0)}{C\rho_0\rho} + \frac{M}{\rho_0}$$

$$V_a = \bar{V}\left(1 - \frac{v}{v_a}\right)$$

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{v_0}{v}\right)^{1/3}$$

$$R = \frac{\bar{M}}{\rho} v^{1/3}$$

$$\left(\bar{M} = \frac{n_0 M_0 + nM}{n_0 + n}\right)$$

and

$$\mathrm{Sn} = \frac{n_0}{n}\left(1 - \frac{\bar{V}B}{n_0 \bar{V}_0 \beta_0}\right)$$

where v, v_0, ρ, ρ_0, β, β_0 and $\bar{V}$, $\bar{V}_0$ are the ultrasonic velocity, density, adiabatic compressibility and molar volume of the solution and solvent, respectively, n, n_0 and M, M_0 are the number of moles and molecular weight of solute and solvent, respectively and K and C are the temperature dependent Jacobson's constant and concentration in dm^{-3} mol, respectively. v_a is equivalent to $1600\ \mathrm{ms}^{-1}$.

RESULTS AND DISCUSSION

The variation of ultrasonic velocity with soap concentration (Table 1) depends on the concentration derivatives of density and compressibility

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

The concentration derivative of density, $(d\rho/dC)$ is positive while the quantity, $(d\beta/dC)$, is negative and since the value of $1/\beta(d\beta/dC)$ is larger than $1/\rho(d\rho/dC)$ for soap solutions below the critical micelle concentration, the quantity (dv/dC) is positive i.e. ultrasonic velocity increases with increasing soap concentration. These results are in agreement with the results reported for electrolytic solutions[17–19] which shows that these soaps behave as simple electrolyte in a mixture of 50% benzene and 50% dimethylsulfoxide and ionise into simple metal cation, Y^{3+} and fatty acid anion, $RCOO^-$. The anions begin to associate on increasing the soap concentration and form micelles which are in thermodynamic equilibrium with ions. Their formation occurs over a narrow range of concentration. The initial concentration at which micelles first appears is known as the critical micelle concentration. The physical properties of the soap solutions exhibit a discontinuity at the CMC.

The variation of ultrasonic velocity with the soap concentration follows the relationship

$$v = v_0 + GC$$

where v_0 is the ultrasonic velocity in pure solvent and G is Garnsey's constant[20]. The plots of ultrasonic velocity v, against soap concentration, C (Figure 1) are characterised by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of these soaps (Table 3). The values of the CMC decrease with increasing chainlength of the soap molecule and the results are in agreement with the values obtained from other micellar properties viz. conductivity, density and molar volume. It was found that the Garnsey's constant (Table 3) increase with the increasing chainlength of fatty acid constituent of the soap molecule.

Table 1 Ultrasonic velocity and other acoustic parameters of yttrium soaps in a mixture of 0% benzene and 50% dimethyl sulfoxide at 40 ± 0.05°C.

S. no.	*Concentration* $c \times 10^3$ *(mol l^{-1})*	*Density, ρ (g ml^{-1})*	*Ultrasonic velocity* $v \times 10^{-5}$ *(cm/sec)*	*Adiabatic compressibility* $\beta \times 10^{11}$ *(cm^2 $dyne^{-1}$)*	*Intermolecular free length* L_f *(Å)*	*Specific acoustic impedance* $Z \times 10^{-5}$ *(C.G.S)*	*Solvation number Sn*
Caprate							
1.	1.0	0.9513	1.3252	6.036	0.09519	1.261	81
2.	2.0	0.9515	1.3261	5.986	0.09511	1.262	49
3.	3.0	0.9517	1.3270	5.976	0.09503	1.263	37
4.	4.0	0.9520	1.3274	5.967	0.09500	1.264	30
5.	5.0	0.9522	1.3280	5.962	0.09494	1.265	26
6.	6.0	0.9525	1.3288	5.946	0.09487	1.266	24
7.	7.0	0.9530	1.3300	5.932	0.09476	1.268	24
8.	8.0	0.9533	1.3320	5.912	0.09460	1.270	25
9.	9.0	0.9542	1.3328	5.900	0.09450	1.272	25
10.	10.0	0.9545	1.3348	5.880	0.09434	1.274	25
Laurate							
1.	1.0	0.9525	1.3262	5.969	0.09505	1.263	109
2.	2.0	0.9527	1.3272	5.959	0.09497	1.264	63
3.	3.0	0.9531	1.3280	5.949	0.09489	1.266	47
4.	4.0	0.9534	1.3286	5.942	0.09483	1.267	38
5.	5.0	0.9540	1.3396	5.929	0.09473	1.268	35
6.	6.0	0.9544	1.3308	5.916	0.09463	1.270	33
7.	7.0	0.9554	1.3330	5.891	0.09443	1.274	34
8.	8.0	0.9564	1.3343	5.873	0.09428	1.276	33
9.	9.0	0.9569	1.3360	5.855	0.09414	1.278	33
10.	10.0	0.9582	1.3384	5.826	0.09390	1.283	34
Myristate							
1.	1.0	0.9535	1.3288	5.939	0.09481	1.267	158
2.	2.0	0.9537	1.3297	5.930	0.09474	1.268	86
3.	3.0	0.9543	1.3310	5.915	0.09462	1.270	66
4.	4.0	0.9548	1.3316	5.907	0.09456	1.271	52
5.	5.0	0.9551	1.3326	5.896	0.09447	1.273	46
6.	6.0	0.9559	1.3340	5.879	0.09433	1.275	43
7.	7.0	0.9569	1.3365	5.851	0.09411	1.279	43
8.	8.0	0.9576	1.3375	5.838	0.09400	1.281	40
9.	9.0	0.9580	1.3393	5.819	0.09385	1.283	39
10.	10.0	0.9588	1.3416	5.795	0.09365	1.286	39
Linoleate							
1.	1.0	0.9564	1.3337	5.878	0.09432	1.276	257
2.	2.0	0.9568	1.3344	5.870	0.09426	1.277	135
3.	3.0	0.9575	1.3356	5.855	0.09414	1.279	98
4.	4.0	0.9581	1.3367	5.842	0.09403	1.281	79
5.	5.0	0.9585	1.3386	5.823	0.09388	1.283	69
6.	6.0	0.9590	1.3404	5.804	0.09373	1.285	63
7.	7.0	0.9595	1.3440	5.770	0.09345	1.290	62
8.	8.0	0.9597	1.3460	5.751	0.09330	1.292	58
9.	9.0	0.9603	1.3493	5.720	0.09305	1.296	57
10.	10.0	0.9607	1.3546	5.698	0.09287	1.299	55

The adiabatic compressibility, β of these soap solutions decreases with increasing soap concentration (Table 1). The decrease in adiabatic compressibility is attributed to the fact that the soap molecules in dilute solutions are considerably ionised into metal cations and fatty acid anions. These ions 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 the

Table 2 Relative association and other allied parameters of yttrium soaps in a mixture of 50% benzene and 50% dimethylsulfoxide

Sr. no.	*Concentration* $C \times 10^3$ *mol* l^{-1}	*Relative association* R_A	*Molar sound velocity* $R \times 10^{-3}$	*Apparent molar compressibility* $-\phi_k \times 10^7$	*Available volume* V_a
Caprate					
1.	1.0	1.0023	3.862	6.524	13.01
2.	2.0	1.0023	3.865	3.633	12.97
3.	3.0	1.0023	3.868	4.147	12.93
4.	4.0	1.0025	3.870	2.053	12.90
5.	5.0	1.0026	3.872	1.731	12.87
6.	6.0	1.0027	3.875	1.560	12.82
7.	7.0	1.0029	3.877	1.528	12.73
8.	8.0	1.0027	3.881	1.562	12.73
9.	9.0	1.0035	3.881	1.543	12.69
10.	10.0	1.0033	3.884	1.569	12.60
Laurate					
1.	1.0	1.0033	3.858	5.934	12.95
2.	2.0	1.0033	3.862	5.311	12.91
3.	3.0	1.0035	3.864	3.713	12.88
4.	4.0	1.0037	3.867	3.143	12.86
5.	5.0	1.0040	3.869	2.737	12.81
6.	6.0	1.0042	3.849	2.731	12.76
7.	7.0	1.0047	3.873	2.278	12.57
8.	8.0	1.0054	3.874	2.243	12.59
9.	9.0	1.0055	3.877	2.802	12.51
10.	10.0	1.0063	3.877	2.291	12.39
Myristate					
1.	1.0	1.0037	3.857	12.520	12.81
2.	2.0	1.0037	3.861	6.530	12.78
3.	3.0	1.0040	3.864	4.814	12.72
4.	4.0	1.0044	3.860	3.767	12.13
5.	5.0	1.0044	3.870	3.173	12.66
6.	6.0	1.0049	3.872	2.930	12.60
7.	7.0	1.0054	3.874	2.932	12.48
8.	8.0	1.0058	3.876	2.722	12.43
9.	9.0	1.0058	3.880	2.600	12.36
10.	10.0	1.0061	3.883	2.586	12.25
Linoleate					
1.	1.0	1.0055	3.851	20.364	12.55
2.	2.0	1.0058	3.855	10.413	12.52
3.	3.0	1.0062	3.858	7.393	12.47
4.	4.0	1.0066	3.861	5.817	12.42
5.	5.0	1.0065	3.866	4.967	12.35
6.	6.0	1.0066	3.870	4.410	12.27
7.	7.0	1.0062	3.877	4.226	12.11
8.	8.0	1.0059	3.882	3.877	12.03
9.	9.0	1.0057	3.888	3.768	11.88
10.	10.0	1.0056	3.893	3.577	11.78

ions and thus the internal pressure increases, which lowers the compressibility of the soap solutions, i.e. solutions become harder to compress[21]. The decrease in adiabatic compressibility at higher soap concentrations may be explained on the basis of closed packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and finally of internal pressure.

The plots of adiabatic compressibility, β, Vs soap concentration, C, indicate a break

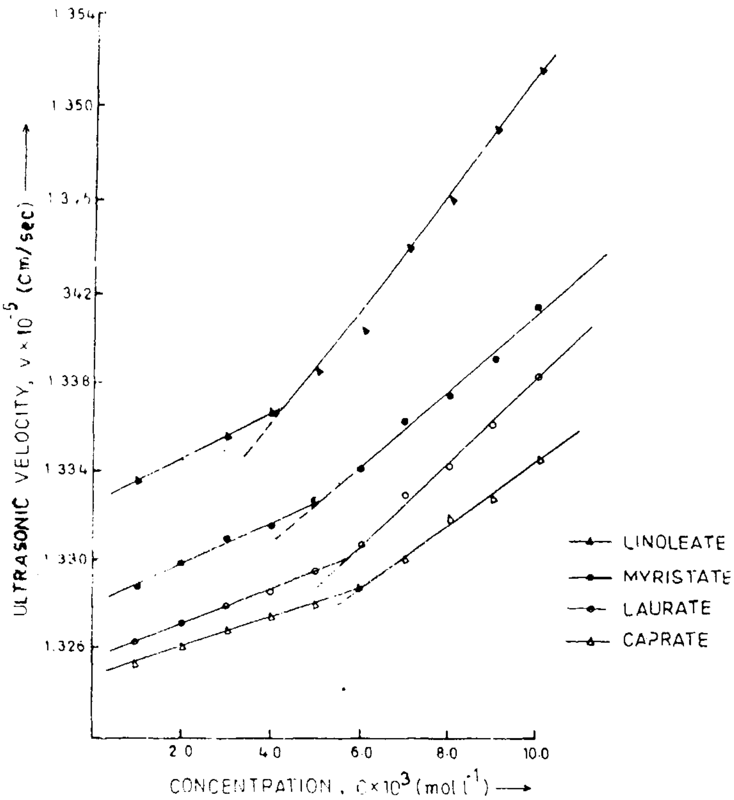

Figure 1 Ultrasonic velocity vs concentration of yttrium soaps in a mixture of 50% benzene and 50% dimethylfulfoxide.

at a definite soap concentration which corresponds to the CMC of these soaps and these plots are extrapolated to zero soap concentration and the extrapolated value of adiabatic compressibility, β_0 is in agreement with the experimental value of adiabatic compressibility of the solvent, (6.379 m^2 N^{-1}).

Table 3 Various acoustic parameters of yttrium soaps in a mixture of 50% benzene 50% dimethylsulfoxide at 40 ± 0.05°C.

Soap	*CMC* × 10^3 *mol* l^{-1}	$G \times 10^{-5}$	$-A \times 10^{10}$	$B \times 10^9$	$\phi_k^0 \times 10^7$	$-s_k \times 10^6$	$-\phi_v^0$
Yttrium caprate	6.2	0.75	1.32	0.95	7.0	8.5	189.0
Yttrium laurate	5.7	0.80	3.60	2.50	10.0	11.5	278.0
Yttrium myristrate	5.0	0.89	5.58	4.17	12.7	14.3	292.0
Yttrium linoleate	4.2	0.92	7.20	4.40	15.4	20.0	325.0

The results of adiabatic compressibility have also been explained in terms of Bachem's Eq. (22)

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

where A and B are constants, C is the molar soap concentration and β and β_0 are the adiabatic compressibility of the solution and solvent, respectively. The plots of $(\beta - \beta_0)/C$ against the square root of soap concentration, $C^{1/2}$, are linear below CMC. The intercept and slope of the plots have been used to obtain the values of constant A and B and are recorded in Table 3.

It follows from Debye–Huckel's theory that the apparent molar compressibility, ϕ_k is related to the molar concentration of soap, C by the relationship

$$\phi_k = \phi_k^0 + S_k C^{1/2}$$

where ϕ_k^0 is apparent molar compressibility of the solvent and S_k is a constant. The plots of apparent molar compressibility, ϕ_k Vs square root of concentration are linear below CMC. The values of limiting molar compressibility, ϕ_k^0 have been obtained by the extrapolation of the plots of ϕ_k Vs $C^{1/2}$ and are recorded in Table 3. The values of constant, S_k for these soaps have been obtained from the slope of the plots. The results are in agreement with the results reported by Masson[23] for electrolytic solutions.

The intermolecular freelength, L_f decreases while specific acoustic impedance, Z increases with the increase in soap concentration (Table 1) which indicates that there is a significant interaction[24] between the soap and solvent molecules which considerably affects the structural arrangement. The increase in the values of specific acoustic impedance, Z with increasing soap concentration, C can be explained on the basis of lyophobic interaction between soap 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 ultrasound waves. The plots of intermolecular freelength, L_f and specific acoustic impedance, Z against the soap concentration, C show a break at a definite soap concentration, which corresponds to the CMC of these soaps.

The values of apparent molar volume decrease with increasing soap concentration but increase with increasing chainlength of the soap molecule. The plots of apparent molar volume, ϕ_v Vs square root of concentration, $C^{1/2}$ exhibit a break at a concentration which corresponds to the CMC of these soaps. The values of ϕ_v^0 have been obtained by the extrapolation of the plots of ϕ_v Vs $C^{1/2}$ (Table 3).

The values of available volume, V_a decrease while the values of relative association, R_A increase with increasing soap concentration (Table 2). The increase in the values of R_A has been attributed either to the increased association between soap and solvent molecules at higher concentration or increasing solvation of ions,[25] but the former seems to be predominant because the solvation number, S_n decreases with increase in soap concentration. The values of available V_A decrease with the increase in the chainlength of fatty acid constituent of the soap molecule.

The plots of solvation number, Sn Vs soap concentration, C are characterised by a break at the CMC. The values of solvation number exhibit a marked change above the CMC which may be attributed to more intake of solvent molecules above the CMC to reduce the repulsive forces acting between heads of ionic micelles. The molar sound velocity, R shows a regular almost linear decrease with soap concentration (Table 2).

The results of ultrasonic velocity show that these soaps (myristate, laurate, caprate and linoleate) behave as simple electrolytes in solutions. These results confirm that there is a significant interaction between the soap and solvent molecules in dilute solutions. The values of various acoustic parameters are in close agreement with the results of other workers[21–26].

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