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Ultrasonic Measurements and Other Allied Parameters of Yttrium Soaps in Mixed Organic Solvents

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Abstract. The ultrasonic measurements of yttrium soaps were made in a mixture of 70% benzene and 30% 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 chainlength of fatty acid constituent of the soap molecule and are in agreement with the values obtained from other micellar properties. The various acoustic parameters (intermolecular free-length, adiabatic compressibility, apparent molar compressibility, specific acoustic impedance, apparent molar volume, molar sound velocity, solvation number, available volume and relative association) for yttrium soaps (myristate, palmitate, stearate and oleate) have been evaluated by ultrasonic velocity measurements.

Keywords. Yttrium soaps; CMC; Acoustic parameters.

Ultraschallmessungen und damit verknüpfte Parameter von Yttrium-Seifen in gemischten organischen Lösungsmitteln

Zusammenfassung. Es wurden Ultraschallmessungen von Yttrium-Seifen in einer Mischung 70% Benzol und 30% Dimethylsulfoxid (*v*/*v*) durchgeführt, um die kritische Micellenkonzentration, Seifen-Solvens-Wechselwirkung und verschiedene akustische und thermodynamische Parameter zu bestimmen. Die CMC-Werte fallen mit steigender Kettenlänge der Fettsäurekomponente des Seifenmoleküls und sind damit in Übereinstimmung mit den aus anderen micellaren Eigenschaften bestimmten Werten. Verschiedene akustische Parameter (intermolekulare freie Länge, adiabatische Kompressibilität, effektive molare Kompressibilität, spezifische akkustische Impedanz, effektives molares Volumen, molare Schallgeschwindigkeit, Solvatationszahl, verfügbares Volumen und relative Assoziation) der Yttrium-Seifen (Myristat, Palmitat, Stearat und Oleat) wurden aus den Ultraschallmessungen ermittelt.

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, palmitate, oleate and stearate) in a mixture of 70% benzene and 30% 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. Yttrium soaps were prepared by direct metathesis 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 70% benzene and 30% 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, θ_k, apparent molar volume, θ_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:

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

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

$$Z = \rho v,$$

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

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

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

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{V_0}{V}\right)^{1/3},$$

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

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

and

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

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 ms^{-1}.

Results and Discussion

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

$$\frac{\mathrm{d}V}{\mathrm{d}C} = -\frac{V}{2}[1/\rho\,(\mathrm{d}\rho/\mathrm{d}C) + 1/\beta\,(\mathrm{d}\beta/\mathrm{d}C)].$$

The concentration derivative of density, ($\mathrm{d}\rho/\mathrm{d}C$), is positive while the quantity, ($\mathrm{d}\beta/\mathrm{d}C$), is negative and since the value of $1/\beta\cdot(\mathrm{d}\beta/\mathrm{d}C)$ is larger than $1/\rho\cdot(\mathrm{d}\rho/\mathrm{d}C)$ for soap solutions below the critical micelle concentration, the quantity ($\mathrm{d}V/\mathrm{d}C$) 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 electrolytes in a mixture of 70% benzene and 30% 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 concentrations. The initial concentration at which micelles first appear 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 from 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, (Fig. 1)

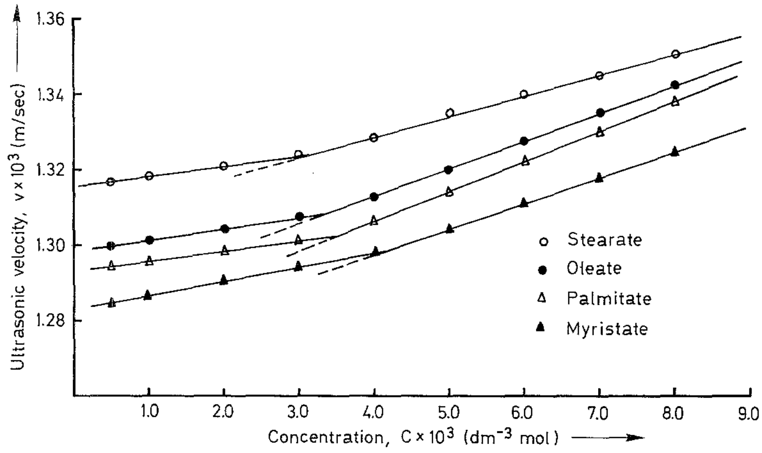

Fig. 1. Ultrasonic velocity, V, vs. concentration, C, of yttrium soaps in a mixture of 70% benzene and 30% dimethyl sulfoxide

Table 1. Ultrasonic velocity and other acoustic parameters of yttrium soaps in a mixture of 70% benzene and 30% dimethyl sulfoxide at 40 ± 0.05°C

Sl. No.	Concentration $C \cdot 10^3$ $dm^{-3}mol$	Density $\rho \cdot 10^{-3}$ $kg\,m^{-3}$	Ultrasonic velocity $V \cdot 10^{-3}$ ms^{-1}	Adiabatic compressibility $\beta \cdot 10^{10}$ m^2N^{-1}	Intermolecular freelength L_f A°	Specific acoustic impedance $Z \cdot 10^6$ $kg\,m^{-2}s^{-1}$	Solvation number Sn
Myristate							
1.	0.5	0.9602	1.284	6.317	0.3092	1.233	234
2.	1.0	0.9605	1.286	6.295	0.3087	1.235	159
3.	2.0	0.9612	1.290	6.252	0.3076	1.240	120
4.	3.0	0.9618	1.294	6.209	0.3066	1.245	119
5.	4.0	0.9625	1.299	6.157	0.3053	1.250	105
6.	5.0	0.9630	1.305	6.098	0.3038	1.257	106
7.	6.0	0.9633	1.310	6.049	0.3026	1.262	104
8.	7.0	0.9638	1.316	5.991	0.3011	1.268	105
9.	8.0	0.9640	1.323	5.927	0.2995	1.275	106
Palmitate							
1.	0.5	0.9651	1.292	6.207	0.3065	1.247	650
2.	1.0	0.9654	1.294	6.186	0.3060	1.249	364
3.	2.0	0.9659	1.298	6.145	0.3050	1.254	221
4.	3.0	0.9665	1.301	6.113	0.3040	1.257	168
5.	4.0	0.9670	1.306	6.063	0.3029	1.263	149
6.	5.0	0.9675	1.313	5.995	0.3012	1.270	145
7.	6.0	0.9680	1.322	5.991	0.3011	1.280	147
8.	7.0	0.9684	1.330	5.838	0.2970	1.288	146
9.	8.0	0.9689	1.337	5.774	0.2956	1.295	143
Oleate							
1.	0.5	0.9674	1.298	6.135	0.3047	1.256	922
2.	1.0	0.9680	1.300	6.113	0.3042	1.258	503
3.	2.0	0.9687	1.304	6.071	0.3031	1.263	291
4.	3.0	0.9693	1.307	6.039	0.3023	1.267	214
5.	4.0	0.9697	1.312	5.991	0.3011	1.272	183
6.	5.0	0.9704	1.318	5.932	0.2996	1.279	169
7.	6.0	0.9708	1.326	5.859	0.2978	1.287	164
8.	7.0	0.9714	1.335	5.776	0.2957	1.297	163
9.	8.0	0.9719	1.342	5.713	0.2941	1.304	157
Stearate							
1.	0.5	0.9681	1.316	5.964	0.3005	1.274	564
2.	1.0	0.9687	1.319	5.934	0.2997	1.278	841
3.	2.0	0.9693	1.321	5.912	0.2991	1.281	441
4.	3.0	0.9701	1.323	5.889	0.2986	1.288	309
5.	4.0	0.9701	1.328	5.843	0.2974	1.289	253
6.	5.0	0.9705	1.334	5.787	0.2960	1.295	224
7.	6.0	0.9710	1.340	5.733	0.2946	1.302	203
8.	7.0	0.9719	1.344	5.696	0.2936	1.306	184
9.	8.0	0.9723	1.349	5.652	0.2925	1.312	172

Table 2. Relative association and other allied parameters of yttrium soaps in a mixture of 70% benzene and 30% dimethylsulfoxide at 40 ± 0.05°C

Sl. No.	Concentration $C \cdot 10^3$ dm^{-3}mol	Relative association R_A	Available volume V_a	Molar sound velocity $R \cdot 10^2$	Apparent molar compressibility $-\theta_k \cdot 10^6$ m^5 N^{-1} (k mol)	Apparent volume θ_v m^3 mol^{-1}
Myristate						
1.	0.5	0.9989	16.38	90.04	12.93	1.675
2.	1.0	0.9987	16.28	90.16	8.87	1.566
3.	2.0	0.9983	16.07	90.30	6.82	1.566
4.	3.0	0.9979	15.87	90.40	6.11	1.529
5.	4.0	0.9974	15.61	90.52	6.00	1.538
6.	5.0	0.9964	15.30	90.68	6.05	1.499
7.	6.0	0.9954	15.05	90.83	5.89	1.438
8.	7.0	0.9944	14.74	90.99	5.92	1.425
9.	8.0	0.9929	14.38	91.19	5.99	1.374
Palmitate						
1.	0.5	1.0024	15.89	89.89	41.44	11.44
2.	1.0	1.0017	15.79	89.94	23.02	6.04
3.	2.0	1.0012	15.58	90.06	13.73	3.29
4.	3.0	1.0010	15.43	90.15	10.35	2.41
5.	4.0	1.0003	15.18	90.29	9.10	1.94
6.	5.0	0.9990	14.82	90.48	8.73	1.66
7.	6.0	0.9972	14.36	90.71	8.71	1.47
8.	7.0	0.9956	13.95	91.09	8.55	1.32
9.	8.0	0.9944	13.60	91.11	8.32	1.22
Oleate						
1.	0.5	1.0027	15.54	89.82	58.90	17.35
2.	1.0	1.0028	15.44	89.95	32.05	9.80
3.	2.0	1.0025	15.23	90.00	18.36	5.76
4.	3.0	1.0024	15.08	90.05	13.44	4.38
5.	4.0	1.0015	14.83	90.21	11.34	3.64
6.	5.0	1.0007	14.53	90.36	10.35	3.25
7.	6.0	0.9991	14.12	90.58	9.89	2.94
8.	7.0	0.9975	13.66	90.81	9.72	2.75
9.	8.0	0.9962	13.30	91.01	9.33	2.60
Stearate						
1.	0.5	0.9988	14.61	90.17	94.03	18.85
2.	1.0	0.9987	14.45	90.22	50.42	10.55
3.	2.0	0.9988	14.35	90.29	26.51	6.09
4.	3.0	0.9991	14.25	90.34	18.62	4.67
5.	4.0	0.9983	14.00	90.50	15.18	3.85
6.	5.0	0.9973	13.69	90.67	13.33	3.39
7.	6.0	0.9962	13.39	90.85	12.05	3.06
8.	7.0	0.9958	13.19	90.97	10.91	2.84
9.	8.0	0.9949	12.94	91.13	10.13	2.66

Table 3. Various acoustic parameters of yttrium soaps in a mixture of 70% benzene and 30% dimethylsulfoxide at 40 ± 0.05°C

Soap	$\mathrm{CMC} \cdot 10^3$ $\mathrm{dm^{-3}\,mol}$	$G \cdot 10^{-3}$	$-\mathrm{A} \cdot 10^9$	$B \cdot 10^9$	$-\theta_k^0 \cdot 10^7$ $\mathrm{m^5\,N^{-1}}$ (k mol)	$-S_k \cdot 10^6$	θ_v^0 $\mathrm{m^3\,mol^{-1}}$
Yttrium myristate	4.0	0.36	6.0	9.1	1.94	1.11	1.72
Yttrium palmitate	3.5	0.30	8.6	11.4	3.96	3.33	3.67
Yttrium oleate	3.3	0.25	12.8	43.5	5.60	8.00	6.50
Yttrium stearate	3.0	0.23	18.8	110.0	6.31	18.57	7.10

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) decreases with the increasing chainlength of fatty acid constituent of the soap molecule.

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 the electrostatic field of the 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 close 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 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 ($6.379 \cdot 10^{-10}\,\mathrm{m^2\,N^{-1}}$).

The results of adiabatic compressibility have also been explained in terms of Bachem's equation [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 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 constants A and B and are recorded in Table 3.

It follows from Debye-Hückel's theory that the apparent molar compressibility, θ_k is related to the molar concentration of soap, C, by the relationship

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

where θ_k^0 is the apparent molar compressibility of the solvent and S_k is a constant. The plots of apparent molar compressibility, θ_k, vs. the square root of concentration are linear below CMC. The values of limiting molar compressibility, θ_k^0, have been obtained by the extrapolation of the plots of θ_k vs. $C^{1/2}$ and are recorded in Table 3. The values of the 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 the 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 (Table 2) but increase with increasing chainlength of the soap molecule. The plots of apparent molar volume, θ_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 θ_v^0 have been obtained by the extrapolation of the plots of θ_v vs. $C^{1/2}$ (Table 3).

The values of available volume, V_a, and relative association, R_A, decrease with increasing soap concentration (Table 2). The plots of V_a and R_A vs. soap concentration are characterised by a break at the CMC. The decrease in the values of relative association, R_A, is attributed to the fact that the solvation of ions decreases with increasing soap concentration. The values of available volume, 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 increase with soap concentration (Table 2).

The results of ultrasonic velocity show that these soaps (myristate, palmitate, oleate and stearate) 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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