

Studies on Ultrasonic Velocity and Electrical Conductivity of Samarium Soaps in Non-Aqueous Medium

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Summary. The ultrasonic velocity of solutions of samarium soaps in non-aqueous medium has been measured at a constant temperature and the results have been used to evaluate the various acoustic parameters. The pre-micellar association and the formation of micelles in samarium soap solutions have been determined by conductometric measurements. The molar conductance at infinite dilution, degree of ionisation and ionisation constant have been evaluated. The results show that samarium soaps behave as weak electrolyte in dilute solutions.

Keywords. Samarium soaps; Ultrasonic velocity; CMC.

Untersuchungen zur Ultraschallgeschwindigkeit und elektrischen Leitfähigkeit von Samarium-Seifen in nichtwäßrigem Medium

Zusammenfassung. Die Ultraschallgeschwindigkeit in Lösungen von Samarium-Seifen in nichtwäßrigem Medium wurde bei konstanter Temperatur gemessen, und die Ergebnisse wurden zur Auswertung verschiedener akustischer Parameter genutzt. Die vormicellare Assoziation und die Ausbildung von Micellen in Samarium-Seifen-Lösungen wurden mittels konduktometrischer Messungen bestimmt. Die molare Leitfähigkeit bei unendlicher Verdünnung, der Ionisierungsgrad und die Ionisationskonstante wurden ermittelt. Die Ergebnisse zeigen, daß sich Samarium-Seifen in verdünnten Lösungen als schwache Elektrolyte verhalten.

Introduction

The studies [1–14] on carboxylate chemistry of rare earth metals have not been carried out systematically so far although these metal carboxylates have found wide applications in various industries. Skellon et al. [1, 2] synthesized cerium soaps of unsaturated fatty acids by the process of double decomposition and metathesis. The methods of preparation and properties of lanthanide soaps have been reviewed by Mehrotra [3] and the uses of cerium soaps have been summarised by Chatfield [4]. The velocity of ultrasonic waves in aqueous solutions of electrolytes has been extensively studied by several workers but less attention has been paid to the solvation of salts in non-aqueous solvents.

The present work deals with the ultrasonic and conductivity measurements of the solutions of samarium soaps (valerate and caproate) in *DMF*. The work has been initiated with a view to study the micellar behaviour, solute-solvent interaction and acoustic parameters in pure *DMF*.

Experimental

All the chemicals used were of BDH/AR grade. Samarium soaps were synthesized by the process of direct metathesis as described in our earlier communications [13, 14]. The solutions were prepared by dissolving known weight of the soap in purified *DMF* and were kept for 2 h in a thermostat at $30 \pm 0.05^\circ\text{C}$ and then used for velocity and conductance measurements.

The ultrasonic velocity of the soap solutions was measured with a multi-frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at a frequency of 6 MHz at constant temperature. A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes were used for measuring the conductance of the solutions. All measurements were made at $30 \pm 0.05^\circ\text{C}$ in a thermostat.

Calculations

The adiabatic compressibility, β , specific acoustic impedance, Z , intermolecular frelength, L_f , apparent molal compressibility, ϕ_k , apparent molal volume, ϕ_v , molar sound velocity, R , and solvation number, Sn , were calculated by using the equations

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

$$Z = \rho v, \quad (2)$$

$$L_f = k \beta^{1/2}, \quad (3)$$

$$\phi_k = \frac{1000}{C \rho_0} [\beta \rho_0 - \beta_0 \rho] + \frac{\beta_0 M}{\rho_0}, \quad (4)$$

$$\phi_v = \frac{1000}{C \rho_0} [\rho_0 - \rho] + \frac{M}{\rho_0}, \quad (5)$$

$$R = \frac{\bar{M}}{\rho} v^{1/3}, \quad (6)$$

$$\bar{M} = \frac{n_0 M_0 + n M}{n_0 + n},$$

$$Sn = \frac{n_0}{n} \left[1 - \frac{\bar{V} \beta}{n_0 \bar{V}_0 \beta_0} \right], \quad (7)$$

where ρ_0 , ρ ; β_0 , β ; n_0 , n ; M_0 , M ; and \bar{V}_0 , \bar{V} are the density, adiabatic compressibility, number of moles, molecular weight and molar volume of the solvent and solution, respectively, k , C , and v are the temperature dependent Jacobson's constant, concentration (g mol l^{-1}) and ultrasonic velocity, respectively.

Results and Discussion

Ultrasonic Velocity

The ultrasonic velocity, v of the samarium soap solutions increases with the increase in concentration and chainlength of the soap (Tables 1 and 2). The variation of velocity, v with concentration C , in solutions depends on the concentration derivatives of ρ and β ,

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

Table 1. Ultrasonic velocity and other acoustic parameters of samarium valerate in DMF at $30 \pm 0.05^\circ\text{C}$

S. no.	Concentration C (g mol l ⁻¹)	Density ρ (g ml ⁻¹)	Velocity $v \cdot 10^{-5}$ (cm/s)	Adiabatic compressibility $\beta \cdot 10^{11}$ (cm ² /dyn)	Inter- molecular freelength $L_f \cdot 10^3$ cm	Specific acoustic impedance $Z \cdot 10^{-4}$ CGS unit	Apparent molal com- pressibility $-\phi_k \cdot 10^7$ (cm ² /dyn)	Apparent molal volume ϕ_v (ml/mol)	Solvation number S_n
1	0.01	0.9364	1.388	5.543	4.780	12.997	0.5017	228.9	14.37
2	0.02	0.9390	1.393	5.488	4.756	13.080	0.4677	218.2	13.46
3	0.03	0.9416	1.398	5.434	4.733	13.164	0.4530	214.6	13.08
4	0.04	0.9444	1.403	5.379	4.709	13.250	0.4512	207.5	12.95
5	0.05	0.9462	1.407	5.339	4.691	13.313	0.4081	224.6	12.18
6	0.06	0.9475	1.410	5.309	4.678	13.360	0.3786	244.9	11.29
7	0.07	0.9490	1.413	5.278	4.664	13.409	0.3248	256.4	10.69
8	0.08	0.9505	1.416	5.247	4.650	13.459	0.3002	265.0	10.24
9	0.09	0.9520	1.419	5.217	4.637	13.509	0.2799	271.7	9.86
10	0.10	0.9538	1.422	5.185	4.623	13.563	0.2675	273.9	9.61

Table 2. Ultrasonic velocity and other acoustic parameters of samarium caproate in DMF at $30 \pm 0.05^\circ\text{C}$

S. no.	Concentration C (g mol l^{-1})	Density ρ (g ml^{-1})	Velocity $v \cdot 10^{-5}$ (cm/s)	Adiabatic compressibility $\beta \cdot 10^{11}$ (cm^2/dyn)	Inter-molecular freelength $L_f \cdot 10^3$ cm	Specific acoustic impedance $Z \cdot 10^{-4}$ CGS unit	Apparent molal compressibility $-\phi_k \cdot 10^7$ (cm^2/dyn)	Apparent molal volume ϕ_v (ml/mol)	Solvation number S_n
1	0.01	0.9373	1.389	5.530	4.774	13.019	0.6604	177.6	17.34
2	0.02	0.9407	1.396	5.455	4.742	13.132	0.6585	172.2	17.23
3	0.03	0.9441	1.403	5.381	4.709	13.246	0.6544	170.4	17.11
4	0.04	0.9465	1.408	5.329	4.687	13.327	0.5824	196.3	15.80
5	0.05	0.9482	1.412	5.290	4.669	13.389	0.5048	226.8	14.42
6	0.06	0.9500	1.415	5.257	4.655	13.443	0.4441	245.4	13.27
7	0.07	0.9522	1.419	5.216	4.636	13.512	0.4156	252.5	12.71
8	0.08	0.9545	1.422	5.181	4.621	13.573	0.3874	256.5	12.12
9	0.09	0.9557	1.426	5.146	4.605	13.628	0.3582	272.8	11.66
10	0.10	0.9575	1.430	5.107	4.588	13.692	0.3424	279.3	11.38

The results (Tables 1 and 2) indicate that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Thus the quantity, $d\rho/dC$, is positive while $d\beta/dC$ is negative. Since the values of $\left(\frac{1}{\beta} \cdot \frac{d\beta}{dC}\right)$ are larger than $\left(\frac{1}{\rho} \cdot \frac{d\rho}{dC}\right)$ for soap solutions, the concentration derivative of velocity, $d\nu/dC$

is positive which is in agreement with the results of other workers [15, 16] reported for electrolytic solutions. The plots of ultrasonic velocity, ν vs. concentration, C , of samarium soaps are characterized by an intersection of two straight lines at the concentration which corresponds to the CMC of the soaps (0.040 M for valerate and 0.035 M for caproate). The values of the intercept of the plots give the ultrasonic velocity of the solvent ($1.381 \cdot 10^5$ cm/s) which is in close agreement with the calculated value ($1.382 \cdot 10^5$ cm/s).

The decrease in adiabatic compressibility, β , with soap concentration may be due to the fact that these soaps behave as weak electrolytes in solutions and ionize into simple metal cations, Sm^{3+} and fatty acid anions, $\text{C}_4\text{H}_9\text{COO}^-$ and $\text{C}_5\text{H}_{11}\text{COO}^-$ for valeric and caproic acid, respectively. The ions in solutions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The increase in internal pressure results in the lowering of the compressibility of the soap solutions.

The adiabatic compressibility, β , of the dilute solutions of samarium soaps is found to obey Bachem's [17] relationship,

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

where A and B are constants and C is the concentration of soap solutions. The constant A and B have been determined from the intercept and slope of plots of $(\beta - \beta_0)/C$ vs. $C^{1/2}$. The values of A for valerate and caproate are $-6.6 \cdot 10^{-11}$ and $-7.8 \cdot 10^{-11}$ and of B are $-4.0 \cdot 10^{-11}$ and $2.0 \cdot 10^{-11}$, respectively.

The decrease in the intermolecular frelength, $L_f = k\sqrt{\beta}$, is due to the decrease in the compressibility with increasing soap concentration (Tables 1 and 2). The plots of intermolecular frelength, L_f , vs. concentration, C , (Fig. 1) indicate a break at a definite soap concentration which corresponds to the CMC of the soap. The extrapolated values of intermolecular frelength ($4.810 \cdot 10^{-3}$ cm) are in close agreement with the calculated values of the intermolecular frelength of the solvent ($4.807 \cdot 10^{-3}$ cm).

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

The values of apparent molal compressibility, ϕ_k are negative for samarium soap solutions. The plots of apparent molal compressibility, ϕ_k vs. $C^{1/2}$ and apparent molal volume ϕ_v vs. $C^{1/2}$ exhibit a break at a concentration which corresponds to the CMC of samarium soaps in *DMF*. The values of ϕ_k^0 and ϕ_v^0 have been obtained by extrapolation of these plots below the CMC to zero soap concentration and are found to be $-0.55 \cdot 10^{-7}$ and $-0.65 \cdot 10^{-7}$ and 252 and 187 for valerate and

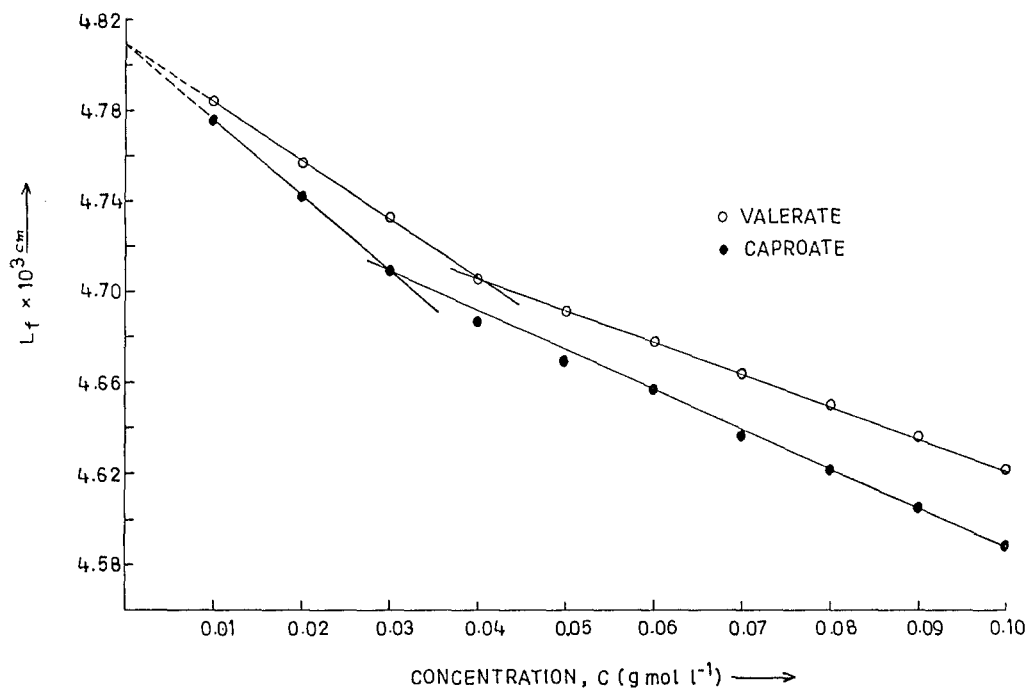


Fig. 1. Intermolecular frelength L_f vs. concentration C of samarium soaps

caproate, respectively. The values of solvation number, Sn , decreases linearly with increasing concentration and decrease in the chainlength of the soap.

The ultrasonic velocity results show that the adiabatic compressibility, intermolecular frelength, apparent molal compressibility and solvation number decrease while specific acoustic impedance increases with the increase in soap concentration.

Specific Conductance

The specific conductance, k , of the solutions of samarium soaps (valerate and caproate) in *DMF* increases with increasing soap concentration and decreasing chainlength of fatty acid constituent of the soap molecule (Tables 3 and 4). The increase in the specific conductance may be due to the ionisation of samarium soaps into simple metal cations, Sm^{3+} and fatty acid anions ($C_4H_9COO^-$ and $C_5H_{11}COO^-$ for valerate and caproate, respectively) in dilute solutions and due to the formation of micelles at higher soap concentrations. The decrease in specific conductance with increasing chainlength of soap may be due to the increasing size and decreasing mobility of anions with increasing chainlength of soap. The plots of specific conductance vs. soap concentration (Fig. 2) are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of samarium soaps (valerate: 0.041 *M* and caproate: 0.035 *M*, respectively). It is suggested that these soaps are considerably ionized in dilute solutions and the anions begin to aggregate to form ionic micelles at CMC.

Molar Conductance and Ionisation Constant

The molar conductance, μ , of the solutions of samarium soaps in *DMF* decreases with increasing soap concentration as well as chainlength of the soap. The decrease

Table 3. Conductivity of samarium valerate in DMF at 30 ± 0.05 °C

S. no.	Concentration $C \cdot 10^2$ (g mol l ⁻¹)	Specific conductance $k \cdot 10^6$	Molar conductance μ	$1/\mu$	$\mu^3 C^3 \cdot 10^4$	Degree of dissociation α	Dissociation constant $K \cdot 10^5$
1	1.25	21.8	1.744	0.57	0.10	0.610	1.87
2	1.32	22.7	1.720	0.58	0.12	0.601	2.03
3	1.39	23.6	1.698	0.59	0.13	0.594	2.22
4	1.47	24.6	1.673	0.60	0.15	0.585	2.42
5	1.56	25.8	1.654	0.61	0.17	0.578	2.71
6	1.66	27.0	1.627	0.62	0.20	0.569	3.00
7	1.79	28.5	1.592	0.63	0.23	0.557	3.36
8	1.92	30.1	1.568	0.64	0.27	0.548	3.81
9	2.08	32.1	1.543	0.65	0.33	0.540	4.49
10	2.27	34.4	1.515	0.66	0.41	0.530	5.30
11	2.63	38.5	1.464	0.68	0.57	0.512	6.92
12	2.94	41.9	1.425	0.70	0.74	0.498	8.41
13	3.33	46.0	1.381	0.72	0.97	0.483	10.50
14	3.85	51.2	1.330	0.75	1.34	0.465	13.46
15	4.17	54.7	1.312	0.76	1.64	0.459	16.06
16	5.00	62.1	1.242	0.81	2.40	0.434	21.16
17	5.56	66.9	1.203	0.83	2.99	0.421	25.18
18	7.14	80.6	1.129	0.89	5.24	0.395	39.54
19	8.33	86.9	1.043	0.96	6.56	0.365	37.69
20	10.00	98.5	0.985	1.02	9.56	0.344	57.81

Table 4. Conductivity of samarium caproate in DMF at $30 \pm 0.05^\circ\text{C}$

S. no.	Concentration $C \cdot 10^2$ (g mol l^{-1})	Specific conductance $k \cdot 10^6$	Molar conductance μ	$1/\mu$	$\mu^3 C^3 \cdot 10^4$	Degree of dissociation α	Dissociation constant $K \cdot 10^5$
1	1.25	16.2	1.296	0.77	0.04	0.561	1.19
2	1.32	16.9	1.280	0.78	0.05	0.554	1.31
3	1.39	17.6	1.266	0.79	0.06	0.540	1.45
4	1.47	18.5	1.259	0.80	0.06	0.545	1.67
5	1.56	19.2	1.231	0.81	0.07	0.533	1.77
6	1.66	20.1	1.211	0.83	0.08	0.524	1.96
7	1.79	21.2	1.184	0.84	0.10	0.513	2.20
8	1.92	22.2	1.156	0.87	0.11	0.500	2.39
9	2.08	23.5	1.130	0.89	0.13	0.489	2.72
10	2.27	25.5	1.109	0.90	0.17	0.480	3.22
11	2.63	28.7	1.091	0.92	0.24	0.472	4.22
12	2.94	31.1	1.058	0.95	0.30	0.458	5.57
13	3.33	34.4	1.042	0.96	0.41	0.451	7.51
14	3.85	38.1	1.003	1.00	0.55	0.434	9.66
15	4.17	40.6	0.990	1.01	0.67	0.429	11.61
16	5.00	46.3	0.926	1.08	0.99	0.401	14.57
17	5.56	49.8	0.905	1.11	1.24	0.392	18.02
18	7.14	59.3	0.835	1.20	2.09	0.361	26.12
19	8.33	65.2	0.783	1.28	2.77	0.339	31.18
20	10.00	77.0	0.770	1.30	4.57	0.333	49.78

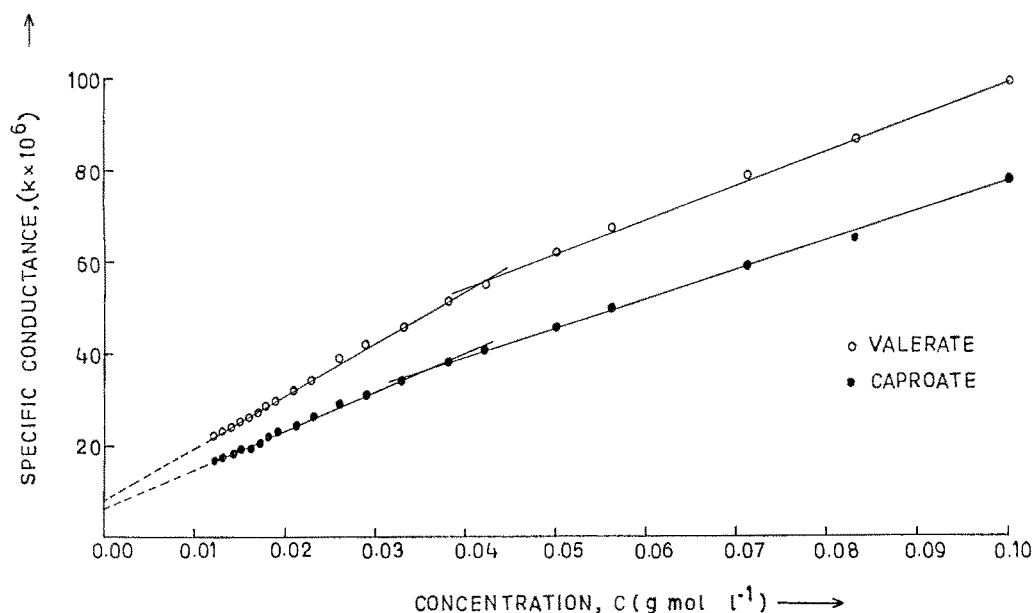


Fig. 2. Specific conductance vs. concentration of samarium soaps

is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and the formation of micelles. The plots of molar conductance μ vs. the square root of soap concentration, $C^{1/2}$, are not linear which indicate that the soaps behave as weak electrolyte in dilute solutions. The limiting molar conductance, μ_0 , of these soap solutions cannot be obtained by usual extrapolation method and the Debye-Hückel-Onsager's equation is not applicable to these soap solutions.

The molar conductance results show that the dilute solutions of samarium soaps behave as weak electrolyte. Since the number of ions for a weak electrolyte is relatively small in dilute solutions and the interionic effects are negligible and so the activities of ions may be taken as almost equal to the concentrations and conductance ratio, μ/μ_0 is a reasonably good measure for the degree of ionisation, α , where μ is the molar conductance at finite concentration and μ_0 is the molar conductance at infinite dilution. On substituting the value of α in the equation of ionisation constant for 1 : 3 electrolyte one gets

$$\mu^3 C^3 = \frac{K \mu_0^4}{27 \mu} - \frac{K \mu_0^3}{27} \quad (8)$$

The values of the ionisation constant K and μ_0 can be obtained from the slope and intercept of the linear plots of $\mu^3 C^3$ vs. $1/\mu$ for dilute soap solutions. The values of limiting molar conductance, μ_0 , are 2.86 and 2.31 whereas the ionisation constants are $0.372 \cdot 10^{-3}$ and $0.260 \cdot 10^{-3}$ for samarium valerate and caproate, respectively.

The values of degree of ionisation, α , at different concentrations have been calculated by assuming that they are equal to the conductance ratio, μ/μ_0 (Tables 3 and 4). The values of degree of ionisation, α , show that the solutions of samarium soaps behave as weak electrolyte. The plots of the degree of ionisation vs. soap concentration show that the degree of ionisation of samarium soaps decreases

rapidly with the soap concentration in dilute solutions whereas it decreases slowly in concentrated solutions.

The values of ionisation constant, K (Tables 3 and 4) again confirm that these soaps behave as a weak electrolyte in solutions. The ionisation constant exhibits a drift with increasing soap concentration which may be due to the fact that the conductance ratio, μ/μ_0 is not exactly equal to the degree of ionisation α and the activity coefficients of ions are not exactly equal to unity and the failure of the simple Debye-Hückel activity equation under these conditions.

The results show that the soap behaves as a weak electrolyte in dilute solutions below the CMC.

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