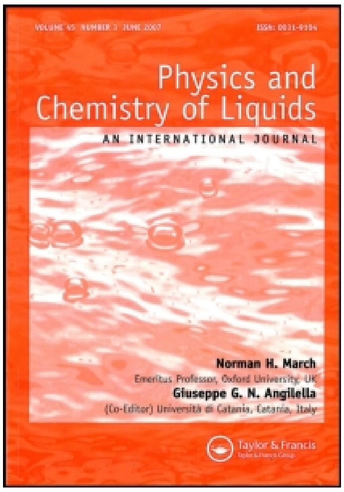

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K. N. Mehrotra[a]; Mithlesh Chauhan[a]; R. K. Shukla[a]
[a] Department of Chemistry, Institute of Basic Sciences, Agra, India

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MICELLAR AND ACOUSTIC BEHAVIOUR OF CERIUM SOAPS IN MIXED SOLVENTS

K. N. MEHROTRA, MITHLESH CHAUHAN and R. K. SHUKLA

Department of Chemistry, Institute of Basic Sciences,
Khandari Road, Agra 282-004, India.

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The studies of ultrasonic velocity in solution of cerium soaps (valerate and caprylate) in a mixture of 60% benzene and 40% methanol (V/V) have been used to evaluate various acoustic parameters. The conductometric measurements have been used to study the premicellar association, formation of micelles, molar conductance at infinite dilution, degree of ionisation and ionisation constant of cerium soaps. The results show that the critical micellar concentration (CMC) decreases with increasing chainlength of fatty acid constituent of the soap molecule and these soaps behave as weak electrolytes in dilute solutions.

KEY WORDS: Ionization, weak electrolytes.

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 diversified fields. The application of these metal soaps depend largely on their physical state, stability and chemical reactivity together with their volatility and solubility in common solvents.

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. Fogg[1] Nakamura[2] Prakash *et al.*[3,4] and Allam and Lee[5] have used the ultrasonic measurements for the determination of the ion solvent interaction and the solvation numbers obtained by this technique were found to be in close agreement with those computed by other methods. The present work deals with the ultrasonic and conductivity measurements of the solutions of cerium soaps (valerate and caprylate) in a mixture of benzene and methanol. The work has been initiated with a view to study the micellar behaviour, solute-solvent interaction and to calculate several allied parameters related to the acoustic properties of soap solutions.

EXPERIMENTAL

All the chemicals used were of BDH/AR grade. Cerium soaps (valerate and caprylate) were prepared by the direct metathesis of corresponding potassium soap with required amounts of aqueous solution of cerous chloride at 50–60°C with vigorous stirring. The soaps were purified by recrystallization with benzene-methanol mixture and the purity was checked by elemental analysis, infrared absorption spectra, and by the determination of melting points. The purified soaps have the melting points valerate: 128°C and caprylate: 138°C. The solutions were prepared by dissolving known weight of the soap in the mixture of 60% benzene and 40% methanol (V/V) and were kept for 2h in a thermostat at 40 ± 0.05°C and then used for velocity and conductivity measurements.

The ultrasonic velocity of the solutions of cerium soaps was measured by a multi frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at a frequency of 4 MHz at a constant temperature (40 ± 0.05)°C in a thermostat. The maximum uncertainty in the velocity measurements was ±0.20%.

CALCULATIONS

The adiabatic compressibility, β is given by the relationship:

$$\beta = V^{-2}\rho^{-1} \tag{1}$$

The apparent molal compressibility, ϕk in solution can be calculated from the compressibility and density data by the relationship:

$$\phi k = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M_2}{\rho_0}, \tag{2}$$

where β_0 and ρ_0 are the compressibility and the density of a solvent and β and ρ are the compressibility and density of a solution, respectively. M_2 and C are the molecular weight and the concentration (mol l^{-1}) of solute, respectively.

The apparent molal volume, ϕv, is given by the relationship:

$$\phi v = \frac{1000}{C\rho_0}(\rho_0 - \rho) + \frac{M_2}{\rho_0} \tag{3}$$

specific acoustic impedance, Z and intermolecular freelength, Lf, can be calculated by using the equations:

$$Z = ve \tag{4}$$

$$Lf = K\beta^{1/2}. \tag{5}$$

Where K is the temperature dependent Jacobson's constant. The molar sound velocity, R is given by the equation

$$R = \frac{M}{\rho}\cdot V^{1/3}, \tag{6}$$

where $M = (n_1 m_1 + n_2 m_2)/(n_1 + n_2)$. ($M_1$ and M_2 are the molecular weight and n_1 and n_2 are the number of moles of solvent and solute, respectively.) The primary solvation number, Sn, is calculated by the modified expression of Passynskii[7],

$$\mathrm{Sn} = \frac{n_1}{n_2}\left(1 - \frac{\bar{V}\beta}{n_1 \bar{V}_0 \beta_0}\right),$$

where $\bar{V}$ is the volume of solution containing n_2 moles of solute and $\bar{V}_0$ is the molal volume of solvent.

RESULTS AND DISCUSSION

The ultrasonic velocity, V for the solutions of cerium soaps increases with increasing concentration and chainlength of the soaps (Tables 1 and 2). The variation of velocity, V, with concentration, C, in solution depends on the concentration derivatives of ρ and β

$$\frac{dv}{dc} = \frac{-V}{2}\left(\frac{1}{\rho}\cdot\frac{d\rho}{dc} + \frac{1}{\beta}\cdot\frac{d\beta}{dc}\right)$$

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 $(1/\beta \cdot d\beta/dc)$ are larger than $(1/\rho \cdot d\rho/dc)$ for soap solutions, the concentration derivative of velocity, dv/dc is positive which is in agreement with the results of other workers[8–10] reported for electrolytic solutions. The plots of ultrasonic velocity, V vs. concentration, C, of cerium soaps (Figure 1) are characterized by two breaks at a definite soap concentration which corresponds to the CMC(I) and CMC(II) of the soap (CMC(I): 0.040 M

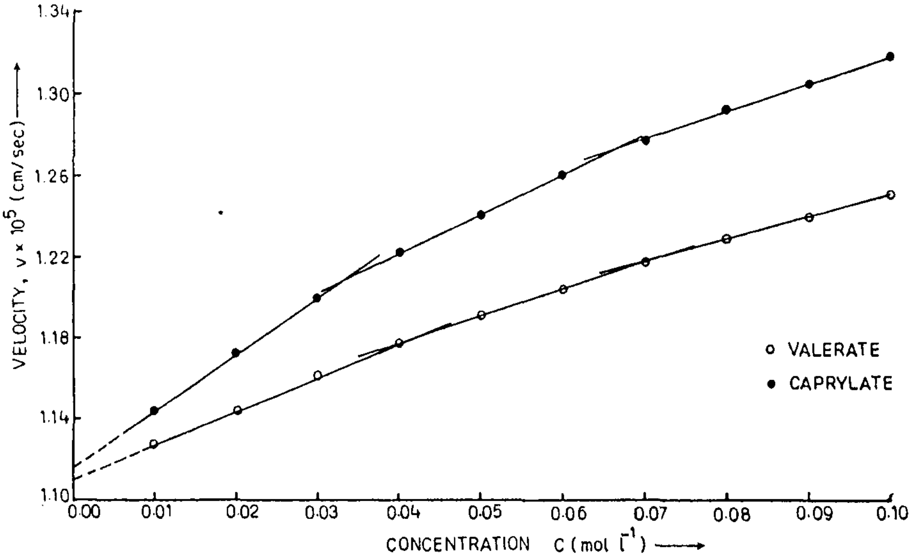

Figure 1 Ultrasonic velocity vs. concentration cerium soaps.

Table 1 Ultrasonic velocity and acoustic parameters of cerium valerate in benzene–methanol mixture at 40 ± 0.05°C.

S. No.	*Concentration,* $C \times 10^2$ *(g mol l^{-1})*	*Density,* d *(g ml^{-1})*	*Velocity,* $V \times 10^{-5}$ *(cm/sec)*	*Adiabatic compressibility,* $\beta \times 10^{10}$ *(cm^2/dyne)*	*Intermolecular free-length,* $L_f \times 10^3$ *(cm)*	*Specific acoustic impedance,* $Z \times 10^4$ *(CGS Unit)*	*Apparent molal compressibility,* $-\phi_k \times 10^7$ *(cm^2/dyne)*	*Apparent molal volume,* ϕ_v *(ml/mol)*	*Molar sound velocity,* $R \times 10^{-3}$ *(cm/sec)*	*Solvation, number,* S_n
1	0.01	0.8306	1.127	9.479	6.251	9.361	0.985	462.10	2.960	24.3
2	0.02	0.8311	1.144	9.194	6.156	9.508	1.690	468.12	2.988	36.4
3	0.03	0.8315	1.162	8.907	6.059	9.662	1.927	474.15	3.016	40.6
4	0.04	0.8325	1.177	8.671	5.978	9.799	1.936	459.09	3.039	40.5
5	0.05	0.8342	1.191	8.451	5.902	9.935	1.925	433.19	3.058	39.9
6	0.06	0.8358	1.204	8.234	5.826	10.063	1.911	417.92	3.078	39.4
7	0.07	0.8376	1.217	8.061	5.764	10.194	1.842	403.58	3.097	38.0
8	0.08	0.8392	1.230	7.876	5.698	10.322	1.802	395.84	3.116	37.2
9	0.09	0.8408	1.240	7.735	5.646	10.426	1.722	389.81	3.132	35.7
10	0.10	0.8424	1.252	7.573	5.587	10.547	1.679	384.99	3.151	34.9

Table 2 Ultrasonic velocity and acoustic parameters of cerium caprylate in benzene–methanol mixture at 40 ± 0.05°C.

S. No.	*Concentration,* $C \times 10^2$ *(g mol l^{-1})*	*Density,* d *(g ml^{-1})*	*Velocity,* $V \times 10^{-5}$ *(cm/sec)*	*Adiabatic compressibility,* $\beta \times 10^{10}$ *(cm^2/dyne)*	*Intermolecular free-length,* $L_f \times 10^3$ *(cm)*	*Specific acoustic impedance,* $Z \times 10^4$ *(CGS Unit)*	*Apparent molal compressibility,* $-\phi_k \times 10^7$ *(cm^2/dyne)*	*Apparent molal volume,* ϕ_v *(ml/mol)*	*Molar sound velocity,* $R \times 10^{-3}$ *(cm/sec)*	*Solvation, number,* S_n
1	0.01	0.8320	1.144	9.183	6.152	9.518	3.858	449.10	2.975	74.7
2	0.02	0.8327	1.172	8.743	6.003	9.759	3.888	527.41	3.015	74.8
3	0.03	0.8337	1.199	8.343	5.864	9.996	3.742	541.47	3.053	72.6
4	0.04	0.8356	1.223	8.001	5.743	10.219	3.551	521.39	3.085	69.0
5	0.05	0.8377	1.242	7.739	5.648	10.404	3.281	535.44	3.112	64.1
6	0.06	0.8396	1.260	7.502	5.561	10.579	3.055	524.83	3.139	60.1
7	0.07	0.8418	1.277	7.285	5.480	10.750	2.870	512.35	3.164	56.8
8	0.08	0.8440	1.293	7.087	5.405	10.913	2.708	479.22	3.188	50.9
9	0.09	0.8458	1.306	6.932	5.345	11.046	2.528	478.55	3.211	50.9
10	0.10	0.8480	1.320	6.768	5.282	11.194	2.399	473.19	3.233	48.6

and 0.033; CMC(II) 0.070 M and 0.068 M, for valerate and caproate, respectively). The increase in ultrasonic velocity with concentration of soap can be represented by the Eq.

$$V = V_0 + GC$$

where G is the Garnsey's constant. The values of G have been calculated from the linear portion of the plots of V vs. C and found to be 2.00×20^{-5} and 3.60×10^{-5} for valerate and caprylate, respectively.

The adiabatic compressibility of dilute solutions of cerium soaps decreases with the increasing concentration and chainlength of the soap. The decrease in adiabatic compressibility may be due to the fact that these soaps behave as weak electrolytes in solutions and ionse into simple metal cations, Ce^{3+} and fatty acid anions, $RCOO^-$ (where $R = C_4H_9$ and C_7H_{15} for valerate and caprylate, respectively). The ions in solutions are surrounded by a layer of solvent molecule firmly bound and oriented towards the ions. The orientation of the solvent molecules around the ions may be due to the influence of electrostatic field of ions and result in the increase in internal pressure and in lowering of the compressibility of the solutions (the solutions become harder to compress[10]).

The adiabatic compressibility, β, is found to obey Bachem's relationship[12].

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

where A and B are constants and C is the concentration of soap solutions. The constants A and B have been determined from the intercept and slope of the plots of $(\beta - \beta_0)/C$ vs. $C^{1/2}$ and found to be -11.6×10^{-11}, -28.6×10^{-11}, and -44.0×10^{-11} and -97.5×10^{-11} for valerate and caprylate, respectively.

The apparent molal compressibility, ϕk for dilute solutions of soap varies linearly with the square root of the concentration (Tables 1 and 2). From the Debye–Huckel theory, it follows that the apparent molal compressibility, ϕk is related to the molar concentration of soap C by the relationship:

$$\phi k = \phi k^0 + Sk\ C^{1/2}.$$

The values of limiting apparent molal compressibility, ϕk^0 and constant Sk have been evaluated from the intercept and slope of the linear part of the plots of ϕk vs. $C^{1/2}$ at lower concentration.

The positive values of Sk (valerate: 133.33×10^{-7} and caprylate: 100.00×10^{-7}) signifies a considerable soap-solvent interaction in dilute soap solutions. The values of ϕk^0 are found to be increased with the increase in chainlength of soap molecule and are found to be -1.10×10^{-7} and -4.00×10^{-7} cm^2/dyn for valerate and caprylate, respectively.

The apparent molal-volume, ϕv of cerium soap solutions varies linearly (Tables 1 and 2) with the square root of the soap concentration. The values of ϕv^0 can be obtained by extrapolation and found to be 445 and 514 ml/mol for valerate and caproate, respectively. The values of ϕk and ϕv for the solutions of cerium soaps increase for dilute solutions but decrease linearly above 0.03 M soap concentration. The decrease in the values at higher soap concentrations may be explained on the basic of close packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and, finally internal pressure.

The decrease in the values of intermolecular freelength, Lf and increase in the values of specific acoustic impedance, Z with increase in soap concentration as well as with the chainlength of the soap (Tables 1 and 2) can be explained on the basis of hydrophobic interaction between soap and solvent molecules, which increases the intermolecular distance, leaving relatively wider gaps between the molecules and thus becoming the main cause of impediment to the propagation of ultrasound waves. All the plots show breaks, indicate the CMC which are in accordance with the values obtained from other parameters.

The values of molar sound velocity show a regular increase with increase in the concentration and chainlength of soap. The solvation number, Sn of dilute solutions of cerium soap solutions varies linearly with the concentration of soap. The higher values of solvation number are in good agreement with other hydration numbers in the literature[6,13,14].

SPECIFIC CONDUCTANCE, *k*

The specific conductance, k of the solutions of cerium soaps (valerate and caprylate) in a mixture of 60% benzene and 40% methanol (V/V) increases with increasing soap concentration and decreasing chainlength of the fattyacid constituent of the soap (Tables 3 and 4). The increase in the specific conductance with the increase in soap concentration may be due to the ionisation of cerium soaps into simple metal cation, Ce^{3+} and fatty acid anions, $RCOO^-$ (where R is C_4H_9 and C_7H_{15} for valerate and caprylate, respectively) in dilute solutions and due to the formation of micelles at higher soap concentrations. The decrease in specific conductance with increasing chainlength of the soap may be due to the increasing size and decreasing mobility of anions with increasing chainlength of soap. The plots of k–C (Figure 2) are characterized by two breaks corresponding to the CMC(I) and CMC(II) of cerium soaps. The appearance of the two breaks corresponding to CMC(I) and CMC(II) can be explained on the basis of formation of ionic and neutral micelles in these soap solutions. It is suggested that the soap is considerably ionised in dilute solutions and the anions begin to aggregate to form ionic micelles at the CMC(I). The soaps are largely present in the form of ionic micelles at moderate concentrations (between CMC I and CMC II) and there is an increasing formation of neutral micelles at the CMC(II). The increase of specific conductance with increasing soap concentration above the CMC(II) may be mainly due to the liberation of ions from neutral micelles. The results show that the values of the CMC decrease with the increase in the number of carbon atoms in the soap molecules (Valerate: CMC I (0.039 M), CMC II (0.071 M), caprylate: CMC I (0.034 M), CMC II (0.064 M)).

Table 3 Conductivity of cerium valerate in mixture of 60% benzene and 40% methanol at 40 ± 0.05°C.

S. No.	*Concentration, $C \times 10^2$*	*Specific conductance, $k \times 10^6$ (mhos)*	*Molar conductance, μ*	*$1/\mu$*	*$\mu^3 C^3 \times 10^6$*	*Degree of ionisation, α*	*Ionisation constant, $K \times 10^5$*
1	1.00	14.2	1.42	0.70	2.86	0.696	2.08
2	1.18	15.4	1.31	0.77	3.65	0.642	2.11
3	1.43	16.6	1.16	0.86	4.57	0.569	1.92
4	1.54	17.4	1.13	0.89	5.27	0.554	2.08
5	1.65	18.1	1.10	0.92	5.93	0.538	2.22
6	1.91	19.6	1.03	0.97	7.53	0.505	2.47
7	2.07	20.7	1.00	1.00	8.87	0.490	2.71
8	2.26	22.0	0.97	1.03	10.65	0.475	3.02
9	2.49	23.4	0.94	1.06	12.81	0.461	3.49
10	2.77	25.2	0.91	1.10	16.00	0.446	4.10
11	3.12	27.3	0.88	1.14	20.35	0.431	4.97
12	3.57	30.3	0.85	1.18	27.82	0.417	6.26
13	4.16	33.1	0.80	1.26	36.26	0.392	7.55
14	4.54	35.1	0.77	1.29	43.24	0.377	8.06
15	4.99	37.5	0.75	1.33	52.73	0.368	9.74
16	5.55	40.2	0.72	1.38	64.96	0.353	11.08
17	6.24	43.6	0.70	1.43	82.88	0.343	11.99
18	7.14	47.7	0.67	1.50	108.53	0.328	16.93
19	8.33	52.8	0.63	1.58	147.20	0.309	20.59
20	10.00	58.8	0.59	1.70	203.30	0.289	26.49

Table 4 Conductivity of cerium caprylate in mixture of 60% benzene and 40% methanol at 40 ± 0.05°C.

S. No.	*Concentration,* $C \times 10^2$	*Specific conductance,* $k \times 10^6$ *(mhos)*	*Molar conductance,* μ	$1/\mu$	$\mu^3 C^3 \times 10^6$	*Degree of ionisation,* α	*Ionisation constant,* $K \times 10^5$
1	1.00	11.5	1.15	0.87	1.52	0.590	7.98
2	1.18	12.6	1.07	0.94	2.00	0.549	8.94
3	1.43	13.8	0.97	1.04	2.63	0.497	9.58
4	1.54	14.4	0.94	1.07	2.99	0.482	10.28
5	1.65	15.1	0.92	1.09	3.44	0.472	11.40
6	1.91	16.6	0.87	1.15	4.57	0.446	13.44
7	2.07	17.7	0.86	1.17	5.55	0.441	16.20
8	2.26	18.9	0.84	1.20	6.75	0.431	18.90
9	2.49	20.0	0.80	1.25	8.00	0.410	19.96
10	2.77	21.7	0.78	1.28	10.22	0.400	24.48
11	3.12	23.4	0.75	1.33	12.81	0.385	29.30
12	4.16	29.0	0.73	1.37	17.58	0.374	38.40
13	4.54	30.3	0.70	1.43	24.39	0.359	50.37
14	4.99	32.5	0.67	1.40	27.82	0.345	54.65
15	5.55	35.0	0.65	1.54	33.70	0.333	61.85
16	6.24	37.9	0.63	1.59	42.88	0.323	74.21
17	6.24	37.9	0.61	1.65	54.44	0.313	91.65
18	7.14	41.2	0.58	1.73	69.93	0.297	108.77
19	8.33	46.1	0.55	1.81	97.97	0.282	137.46
20	10.00	51.3	0.52	1.95	135.01	0.267	187.20

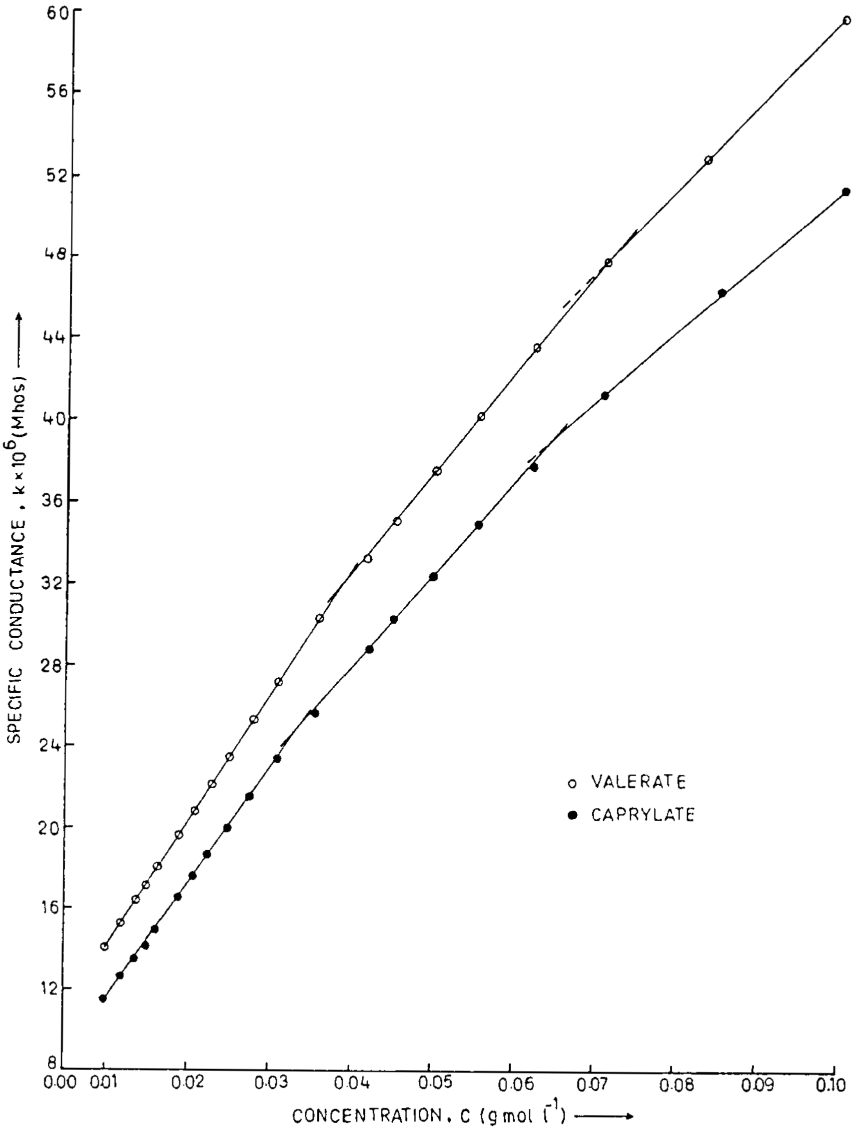

Figure 2 Specific conductance vs. concentration cerium soaps.

MOLAR CONDUCTANCE, μ AND IONISATION CONSTANT, K

The molar conductance, μ of the solutions of cerium soaps decreases with increasing soap concentration and increasing chainlength of the soap molecules (Tables 3 and 4). The decrease in molar conductance is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionisation with the formation of micelles. The molar conductance of the solutions of cerium soap does not vary linearly with the square root of the soap concentration, $C^{1/2}$ (Figure 3) indicating that the Debye–Huckel onsager's equation is not applicable to these soap solutions. The plots of μ against $C^{1/2}$ are concave upwards below 0.22 M for cerium soap solutions and this concavity decreases with increase in the number of carbon atoms in the soap molecules. The molar conductance results show that the dilute solutions of cerium soaps behave as weak electrolyte. The number of ions for 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 concentration 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 dilution 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:

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \tag{1}$$

The values of K and μ_0 can be obtained from the slope and intercept of the linear part of the plots of $\mu^3 C^3$ vs. $1/\mu$ for dilute soap solutions. The values of limiting molar conductance, μ_0 are 2.04 and 1.95 whereas for ionisation constant are 4.13×10^{-5} and 1.82×10^{-5} for cerium valerate and caprylate, respectively.

The values of the degree of ionisation, α at different soap concentrations have been calculated by assuming it as equal to conductance ratio, μ/μ_0 and show that the degree of ionisation of cerium soaps decreases rapidly with the soap concentration

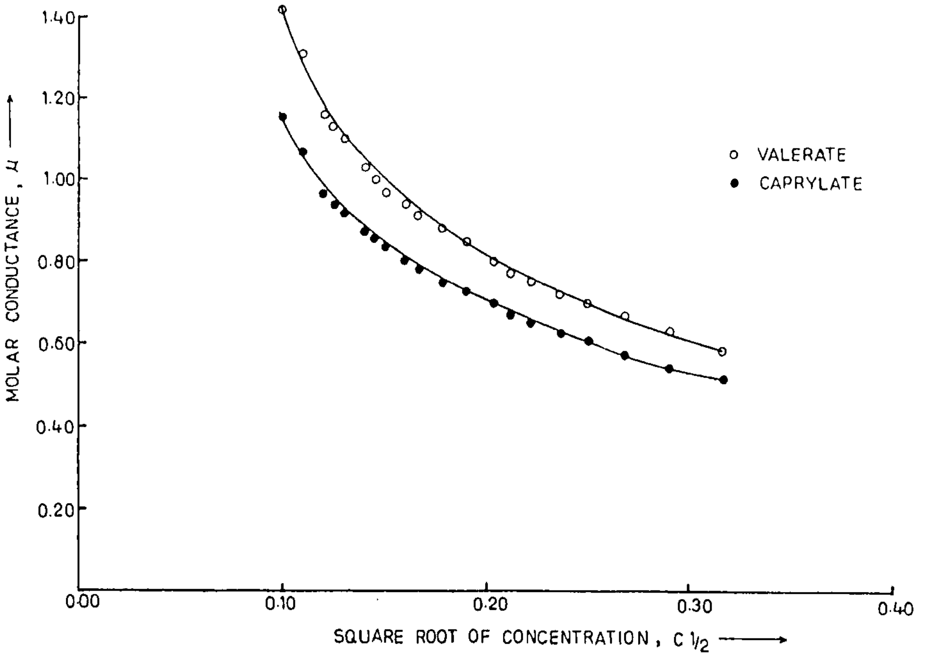

Figure 3 Molar conductance vs. square root of concentration cerium soaps.

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 dilute solutions. The values of K 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 co-efficients of ions are not exactly equal to unity and due to the failure of simple Debye–Huckel's activity equation under these conditions.

The results show that these soaps behave as weak electrolyte in dilute solutions below the CMC and there is a significant interaction between the soap solvent molecules in dilute solutions and the soap molecules do not aggregate in dilute solutions.

References

1. P. G. I. Fogg, *J. Chem. Soc.*, 4111 (1948).
2. S. Nokamura, *J. Am. Chem. Soc.*, **89**, 1765 (1967).
3. S. Prakash and O. Prakash, *Acoustica*, **32**, 279 (1975).
4. S. Prakash, N. Prasad and O. Prakash, *J. Chem. Engg. Data*, **22**, 51 (1977).
5. D. S. Allam and W. Lee, *J. Chem. Soc.*, **2**, 6049 (1964).
6. B. Jacobson, *Acta Chem. Sand*, **6**, 1485 (1952).
7. A. Passynskii, *Acta Physico-Chim. URSS*, **8**, 385 (1938).
8. I. G. Mikhailov, M. V. Rozina, and V. A. Shutilov, *Akust. Zh.*, **10**, 213 (1964).
9. S. Prakash and C. V. Chaturvedi, *Indian J. Chem.*, **10**, 669 (1972).
10. S. Prakash, F. M. Icihaporia and J. D. Panday, *J. Phys. Chem.*, **58**, 3078 (1964).
11. R. Garnsey, R. J. Boe, R. Mahoney and T. A. Litovitz, *J. Chem., Phys.*, **50**, 5222 (1969).
12. C. Bachem. *Z. Physik.*, **101**, 541 (1936).
13. K. N. Mehrotra, A. S. Gahlaut and M. Sharma, *J. Colloid Interface Sci.*, **120**, 110 (1987).
14. P. Padmini and B. Rao, *Indian J. Phys.*, **34**, 565 (1960).