

Acoustic Behavior of Calcium Soap Solutions

K.N. Mehrotra and S.K. Upadhyaya

Department of Chemistry, Agra University, Agra - 282 004 India

The results of ultrasonic velocity for calcium soap solutions show that the adiabatic compressibility, intermolecular free length and solvation number decrease while the specific acoustic impedance, apparent molal compressibility, apparent molal volume and molar sound velocity increase with increasing soap concentration. The ultrasonic results are in agreement with the conductance measurements and confirm that calcium soaps behave as weak electrolytes in solutions.

Ion-solvent interaction (1-3) is always attractive because the solvent molecules can orient their dipoles in the direction which results in minimum potential energy. For many purposes, it is necessary to know the volumes and compressibilities of the solutions relative to their corresponding values at infinite dilution. The determination of such quantities requires the extrapolation of experimental data in very dilute solutions.

The present paper deals with the study of the solutions of calcium soaps in chloroform-propylene glycol mixtures with regards to their acoustical and physicochemical properties.

EXPERIMENTAL

Calcium soaps were prepared by the direct metathesis of the corresponding potassium soap with the required amount of aqueous solution of calcium acetate. The soap was recrystallized with a mixture of benzene and methanol and dried under reduced pressure. The absence of the hydroxyl groups and coordinated water molecules in the soaps was confirmed by studying their infrared spectra. The purity of the soaps was checked by elemental analysis and estimation of metal content, and the results (Table 1) were found in agreement with the theoretically calculated values.

The melting points of purified calcium stearate and palmitate were 160 and 151 C, respectively. The reproducibility of the results was checked by preparing two samples of the soap under similar conditions. The solutions were prepared by dissolving a known weight of the soap in a mixture of 50% chloroform and 50% propylene glycol (v/v), kept for two hr in a thermostat at 40 ± 0.05 C and then used for ultrasonic velocity and density measurements.

The measurements of ultrasonic velocity of the solutions of calcium soaps were carried out by an ultra-

sonic Interferometer (F 81, Mittal Enterprises, Delhi) at a frequency of 4 MHz at a constant temperature (40 ± 0.05 C).

The densities of the solvent and solutions of calcium soaps were determined by means of a pycnometer.

CALCULATIONS

The specific acoustic impedance, Z , i.e., unit area acoustic impedance of a sound medium on a given surface, can be expressed by the equation (4):

$$Z = \rho \cdot v \quad [1]$$

where v is the ultrasonic velocity and ρ is the density.

The intermolecular free length, L_f , i.e., the distance covered by a sound wave between the surfaces of the molecules, is given by the equation (5):

$$L_f = K \sqrt{\beta} \quad [2]$$

where K is the temperature dependent constant and β is the adiabatic compressibility which is given by the relationship:

$$\beta = v^2 \rho^{-1} \quad [3]$$

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

$$\Phi_k = \frac{1,000}{C} \frac{(\rho_0 \beta - \beta_0 \rho)}{\rho_0} + \frac{\beta_0 M_2}{\rho_0} \quad [4]$$

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

The apparent molal volume (6), Φ_v is calculated by the relationship:

$$\Phi_v = \frac{1,000}{C} \frac{(\rho_0 - \rho)}{\rho_0} + \frac{M_2}{\rho_0} \quad [5]$$

The molar sound velocity, R , is given by the equation:

$$R = \frac{\bar{M}}{\rho} v^{1/3} \quad [6]$$

$$\text{where } \bar{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

TABLE 1

Percentages of Elements in Calcium Soaps

Elements	Calcium stearate		Calcium palmitate	
	Found	Calculated	Found	Calculated
Carbon	71.1	71.2	69.4	69.5
Hydrogen	11.3	11.5	11.1	11.2
Calcium	6.4	6.6	7.0	7.2

ACOUSTIC BEHAVIOR OF CALCIUM SOAP SOLUTIONS

(M_1 and M_2 are the molecular weights and n_1 and n_2 are the number of moles of solvent and solute, respectively).

The primary solvation number, S_n , was calculated by the modified expression of Pasynskii (7,8):

$$S_n = \frac{n_1}{n_2} \left(1 - \frac{V\beta}{n_1 V_o \beta_o} \right) \quad [7]$$

where V is the volume of solution containing n_2 moles of solute and V_o is the molal volume of solvent.

RESULTS AND DISCUSSION

The ultrasonic velocity, v , in calcium soap solutions increases with increasing soap concentration (Tables 2 and 3). The variation of ultrasonic velocity, v , with concentration, C , in solutions depends on the concentration derivatives of density, ρ , and adiabatic compressibility, β .

$$\frac{dv}{dC} = -\frac{v}{2} \left(\frac{1}{\rho} \frac{d\rho}{dC} + \frac{1}{\beta} \frac{d\beta}{dC} \right) \quad [8]$$

The results show that the density increases while the adiabatic compressibility decreases with increasing soap concentrations. Thus, the quantity $(d\rho/dC)$ is positive while $(d\beta/dC)$ is negative.

Since the values of $(1/\beta \cdot d\beta/dC)$ are larger than $(1/\rho \cdot d\rho/dC)$ for soap solutions, the concentration derivative of velocity, dv/dC , is positive; this is in close agreement with the results reported by other workers (9-11) for electrolytic solutions.

The plots of ultrasonic velocity, v vs. soap concentration, C (Fig. 1) are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of calcium soaps (stearate, 0.0039 M, and Palmitate, 0.0058 M). The values of CMC are in agreement with the results of conductivity and viscosity measurements. The extrapolated values of the ultrasonic velocity (1.407×10^5 cm/sec) are in close agreement with the calculated value (1.402×10^5 cm/sec). The variation of ultrasonic velocity, v with the soap concentration, C below the CMC follows the relationship:

$$v = v_o + G C$$

where v_o is the ultrasonic velocity in the solvent and G is the Garnsey's constant. The values of Garnsey's

constant, G have been found from the slope of the plot of (v) vs. C below the CMC and the values for calcium stearate and palmitate are 9.6×10^5 and 7.3×10^5 , respectively.

The adiabatic compressibility, β of the dilute solutions of calcium soaps in the mixture of 50% chloroform and 50% propylene glycol (v/v) decreases with the increase in the soap concentration. The conductivity measurements (12) show that these soaps behave as weak electrolyte in chloroform-propylene glycol mixture and ionize into simple metal cations, Ca^{++} , and fatty acid anions, $RCOO^-$. The decrease in adiabatic compressibility may be due to the fact that the ions in solutions are surrounded by a layer of solvent molecules firmly bound and oriented toward the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of ions and thus the internal pressure increases, which lowers the compressibility of the solutions, i.e., the solution becomes harder to compress (13).

The plots of adiabatic compressibility and intermolecular free length, L_f , against soap concentration, C , show a break at a soap concentration which corresponds to the CMC of the soap (Figs. 2 and 3). The decrease in intermolecular free length, $L_f = (K \sqrt{\beta})$ is due to the decrease in the compressibility with increasing soap concentration (Tables 2 and 3). The decrease of intermolecular free length with increase in ultrasonic velocity indicates there is a significant interaction between soap and solvent molecules due to which the structural arrangement is considerably affected (14). The soap-solvent interaction in calcium soap solutions has also been confirmed by conductivity (12) and viscosity (15) measurements. The plots of β vs. C and L_f vs. C have been extrapolated to zero soap concentration, and the extrapolated values ($\beta_o = 4.765 \times 10^{-11}$ cm²/dyne, $L_{f_o} = 0.446$ Å) are in agreement with the calculated values ($\beta_o = 4.776 \times 10^{-11}$ cm²/dyne, $L_{f_o} = 0.444$ Å). The adiabatic compressibility, β , and intermolecular free length, L_f , also decrease with the increase in the chain length of the soap.

The adiabatic compressibility, β , of the solutions of calcium soaps is found to obey Bachem's relationship (16)

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

where β_o is the compressibility of solvent, C is the molar concentration and A and B are constants. The

TABLE 2

Ultrasonic Velocity and Other Acoustic Parameters of Calcium Stearate in Chloroform/Propylene Glycol (50/50, v/v) at 40 ± 0.05 C

S.No.	Concentration $C \times 10^3$ (g mol l ⁻¹)	Density ρ (g ml ⁻¹)	Velocity $v \times 10^5$ (cm/sec)	Adiabatic compressibility $\beta \times 10^{11}$ (cm ² /dyne)	Intermolecular free length L_f (Å)	Specific acoustic impedence $Z \times 10^5$ (CGS)units	Apparent molal compressibility $\Phi_k \times 10^7$	Solvation number (S_n)	Apparent molal volume $\Phi_v \times 10^{-3}$	Molar sound velocity $R \times 10^{-1}$ (cm/sec)
1.	1.0	1.0680	1.412	4.696	0.440	1.508	-8.983	18.43	-2.059	474.1
2.	2.0	1.0704	1.422	4.620	0.436	1.522	-8.692	17.98	-1.871	476.4
3.	3.0	1.0722	1.430	4.561	0.434	1.533	-7.941	16.52	-1.621	477.9
4.	4.0	1.0739	1.441	4.484	0.430	1.547	-8.013	16.82	-1.472	481.5
5.	5.0	1.0742	1.443	4.471	0.429	1.550	-6.635	14.06	-1.120	483.8
6.	6.0	1.0750	1.447	4.443	0.428	1.556	-6.010	12.79	-0.963	486.2
7.	7.0	1.0752	1.452	4.411	0.426	1.561	-5.583	12.02	-0.771	488.8
8.	8.3	1.0768	1.456	4.381	0.425	1.568	-5.113	10.97	-0.742	491.5

TABLE 3

Ultrasonic Velocity and Other Acoustic Parameters of Calcium Palmitate in Chloroform/Propylene Glycol (50/50, v/v) at 40 ± 0.05 C

S.No.	Concentration $C \times 10^3$ (g mol l ⁻¹)	Density ρ (g ml ⁻¹)	Velocity $v \times 10^{-5}$ (cm/sec)	Adiabatic compressibility $\beta \times 10^{11}$ (cm ² /dyne)	Intermolecular free length Lf(A°)	Specific acoustic impedance $Z \times 10^{-5}$ (CGS)units	Apparent molal compressibility $\Phi_k \times 10^7$	Solvation number (Sn)	Apparent molal volume $\Phi_v \times 10^{-3}$	Molar sound velocity $R \times 10^{-1}$ (cm/sec)
1.	1.0	1.0678	1.411	4.704	0.440	1.507	-8.117	16.59	-1.922	473.8
2.	3.0	1.0709	1.425	4.599	0.435	1.526	-6.504	13.60	-1.265	478.1
3.	5.0	1.0740	1.440	4.490	0.430	1.547	-6.261	13.18	-1.133	482.4
4.	7.0	1.0750	1.449	4.431	0.427	1.558	-5.308	11.36	-0.795	486.9
5.	9.0	1.0756	1.458	4.374	0.425	1.568	-4.737	10.29	-0.566	491.7
6.	11.0	1.0768	1.465	4.327	0.422	1.578	-4.307	9.41	-0.471	495.7
7.	13.0	1.0778	1.476	4.259	0.419	1.591	-4.164	9.16	-0.391	500.9
8.	15.0	1.0785	1.480	4.233	0.418	1.596	-3.770	8.34	-0.313	504.7
9.	16.7	1.0798	1.487	4.188	0.415	1.606	-3.665	8.11	-0.302	508.3

plots of $[(\beta - \beta_0)/C]$ vs. \sqrt{C} are linear below the CMC. The values of A and B have been determined from the intercept and slope of the curves. The values of constant A for calcium stearate and palmitate are 11.1×10^{-10} and 8.1×10^{-10} and B are -75×10^{-10} and -40×10^{-10} , respectively.

The values of specific acoustic impedance, Z, have been reported in Tables 2 and 3. The increase of specific acoustic impedance, Z, with increasing soap concentration, C, may be due to the interaction between soap and solvent molecules which increases the intermolecular distance making relatively wider gaps between the molecules and becoming the main cause of

impedient in the propagation of ultrasound waves. The plots of specific acoustic impedance Z, vs soap concentration, C (Fig. 4), show breaks at a definite soap concentration which corresponds to the CMC of these soaps. The linear increase in the values of Z also has been reported for the solutions of lithium salts by Ramabrahman and Suryanarayana (10).

The apparent molal compressibility, Φ_k , and apparent molal volume, Φ_v , of calcium soap solutions vary linearly below the CMC and the plots of Φ_k vs. \sqrt{C} and Φ_v vs. \sqrt{C} exhibit a break at a concentration which corresponds to the CMC of these soaps. The values of Φ_k and Φ_v are obtained by the extrapolation of plots of

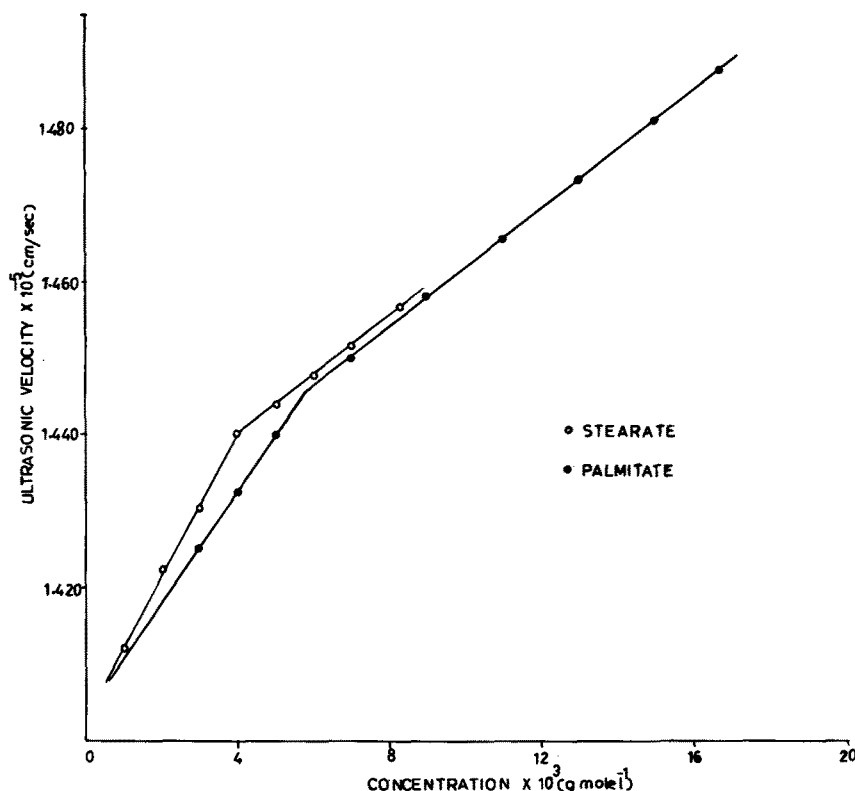


FIG. 1. Ultrasonic velocity vs. concentration.

ACOUSTIC BEHAVIOR OF CALCIUM SOAP SOLUTIONS

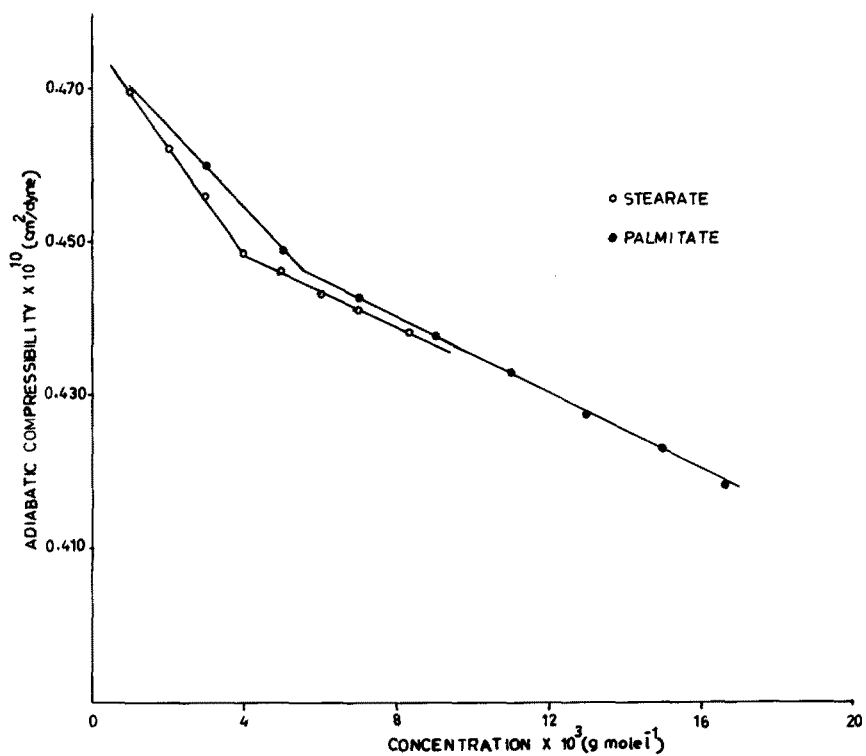


FIG. 2. Adiabatic compressibility vs. concentration.

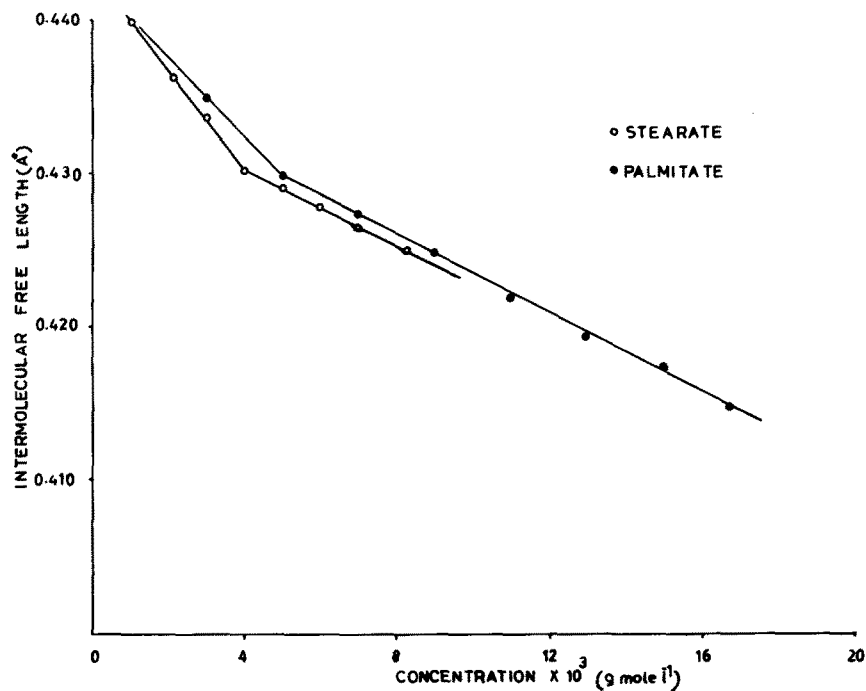


FIG. 3. Intermolecular free length vs. concentration.

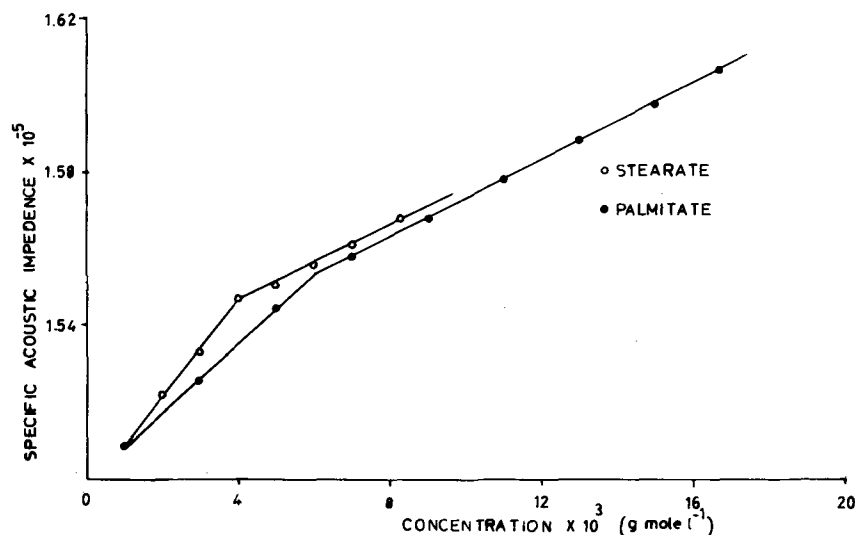


FIG. 4. Specific acoustic impedance vs. concentration.

Φ_k vs. \sqrt{C} and Φ_v vs. \sqrt{C} . The limiting values of apparent molal compressibility, Φ_v , are found to be -10.6×10^{-7} , -10.3×10^{-7} and -2.35×10^3 , -2.86×10^3 for calcium stearate and palmitate, respectively. The results are in agreement with the results reported by Masson (17) for electrolytic solutions.

The values of molar sound velocity, R , increase linearly with increasing soap concentration. The solvation number, S_n , of calcium soap solutions in a mixture of 50% chloroform and 50% propylene glycol decreases with the increase in the soap concentration.

The results show that the ultrasonic velocity, specific acoustic impedance, apparent molal compressibility, apparent molal volume and molar sound velocity increase while the adiabatic compressibility, intermolecular free length and solvation number decrease with increasing soap concentration in the solutions of calcium soaps in a mixture of chloroform-propylene glycol (50%, v/v). The results confirm that these soaps behave as weak electrolytes in dilute solutions below the CMC and ionize into simple metal cations, Ca^{++} , and anions, $RCOO^-$. The anions begin to aggregate to form ionic micelles at a definite soap concentration which corresponds to the CMC of these soaps.

ACKNOWLEDGMENT

The authors thank S. K. Agrawal, vice chancellor of Agra University, for providing necessary facilities and encouragement throughout the present investigations.

REFERENCES

1. Parkar, A.J., and J. Miller, *J. Am. Chem. Soc.* 83:117 (1961).
2. Prakash, S., and O. Prakash, *Acoustica* 32:279 (1975).
3. Fogg, P.G.T., *J. Chem. Soc.* 4111 (1958).
4. E'lpimer, L.E., *Ultrasound Physicochemical and Biological Effects*, Consultant Bureau (1964).
5. Jacobson, B., *Acta Chem. Scand.* 6:1485 (1952).
6. Renaud, P., *Chim. Anal. (Paris)* 46(5):227 (1964).
7. Pasynskii, A., *Acta Physicochem. (U.S.S.R.)* 8:385 (1938).
8. Pasynskii, A., *J. Phys. Chem. (U.S.S.R.)* 11:608 (1938).
9. Mikhailov, I.G., M.V. Rozina and Shutilov, *Akust. Zh.* 10:213 (1964).
10. Ramabrahman, K., and M. Suryanaryana, *Ind. J. Pure and Appl. Phys.* 6:422 (1968).
11. Prakash, S., and C.V. Chaturvedi, *Indian J. Chem.* 10:669 (1972).
12. Mehrotra, K.N., and S.K. Upadhyaya, *Bulletin of Electrochemistry* 2(3), May-June, pp. 309-311 (1986).
13. Prakash, S., F.M. Ichiaporia and J.D. Pandey, *J. Phys. Chem.* 58:3078 (1964).
14. Eyring, H., and J.F. Kincaid, *J. Chem. Phys.* 6:620 (1938).
15. Mehrotra, K.N., and S.K. Upadhyaya, *Tenside Detergents*, (In press).
16. Bachem, C., *Z. Physik* 101:541 (1936).
17. Masson, D.O., *Phil. Mag.* 8:218 (1929).

[Received January 9, 1987;
accepted October 15, 1987]