Molar Volume and Ultrasonic Studies of Europium Soaps in Mixed Organic Solvents

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ABSTRACT: The ultrasonic velocity and density measurements of europium soaps in a mixture of benzene and methanol (3:2, vol/vol) were used to evaluate various acoustic parameters and molar volume and to determine the critical micelle concentration. The results showed that the ultrasonic velocity, specific acoustic impedance, molar sound velocity, and molar compressibility increase, and intermolecular free length, adiabatic compressibility, and relative association decrease with increasing concentration and chainlength of the soap. The results were interpreted in terms of soap–solvent interaction.
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KEY WORDS: Acoustic parameters, critical micelle concentration, europium soaps, molar volume, soap–solvent interaction, ultrasonic velocity.

The complimentary use of ultrasonic measurements can provide interesting information on the specificities of ion–solvent interactions related to the structure of solute and the reciprocal effects that arise in the solvent. Many investigators (1–12) have used ultrasonic velocity measurements for studying ion–solvent interactions and solvation of salts in nonaqueous solvents. However, ultrasonic measurements of soap solutions have not drawn adequate attention, even though such a study is likely to provide important information on soap–solvent and soap–soap interactions, structural changes, and soap solutions that are not ideal.

Molecules of soap are characterized by the presence of both lyophilic and lyophobic moieties in the same molecule, and the micellization process in organic solvents is somewhat different from that in aqueous solutions. The main cause of micellization in organic solvents is the energy change due to dipole–dipole interactions between the polar head groups of soap molecules. The aggregation begins at low concentrations in organic solvents and results in the formation of much smaller aggregates than in aqueous solutions. The determination of critical micelle concentration (CMC) in organic solvents cannot be carried out by the methods commonly used for aqueous solutions because the association starts at very low concentrations. Although the micellar solutions are microheterogeneous, they are macroscopically homogeneous from a classical thermodynamic viewpoint; therefore, ultrasonic measurements can be used to obtain useful information regarding soap solutions in organic solvents.

The present work deals with the determination of molar volume and computation of various acoustic parameters from the ultrasonic velocity measurements of europium soaps (octanoate and dodecanoate) in a mixture of benzene and methanol (3:2, vol/vol) because these soaps possess maximum solubility in this solvent mixture. The results of ultrasonic measurements of samarium and neodynium soap solutions in other solvent mixtures have been reported in earlier communications (8–10).

Various acoustic parameters, such as adiabatic compressibility (β), specific acoustic impedance (13) (Z), intermolecular free length (14) (L_f), apparent molar compressibility (ϕ_k), molar sound velocity (R), relative association (15) (R_A), molar sound compressibility (W), solvation number (16,17) (S_n), molar volume ($\bar{V}$), and apparent molar volume (18) (ϕ_v), were evaluated by using the following relationships:

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

$$Z = v \cdot \rho \quad [2]$$

$$L_f = \left(\frac{\beta}{K}\right)^{1/2} \quad [3]$$

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

$$R = \frac{\bar{M}}{\rho \cdot v^{1/3}} \qquad \bar{M} = \frac{n_o M_o + nM}{n_o + n} \quad [5]$$

$$R_A = \left(\frac{\rho}{\rho_o}\right)\left(\frac{v_o}{v}\right)^{1/3} \quad [6]$$

$$W = \frac{\bar{M}}{\rho}\left(\beta^{-1/7}\right) \quad [7]$$

$$S_n = \frac{n_o}{n}\left[1 - \frac{\bar{V}\beta}{n_o\bar{V}_o\beta_o}\right] \quad [8]$$

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$$\bar{V} = \frac{M}{\rho} \quad [9]$$

$$\phi_v = \frac{1000}{C\rho\rho_o}(\rho_o - \rho) + \frac{M}{\rho_o} \quad [10]$$

where v_o, v; ρ_o, ρ; β_o, β; and $\bar{V}_o$, $\bar{V}$ are the ultrasonic velocity, density, compressibility, and molar volume of solvent and solution, respectively; n_o, n, and M_o, M are the number of moles and molecular weights of solvent and soap, respectively; C is molar concentration of the solution, and K is a temperature-dependent Jacobson's constant (14), which is related to the velocity and free length by Jacobson's empirical Equation 3 given on the basis of the concept of available volume. The values of K at 30, 40, and 50°C are 7.459, 7.820, and 8.181, respectively.

The apparent molar volume (ϕ_v) is related to the soap concentration (C) by Masson's equation (Ref. 19):

$$\phi_v = \phi_v^\circ + S_v C^{1/2} \quad [11]$$

The extrapolation of the plot of ϕ_v vs. $C^{1/2}$ to zero soap concentration gives the quantity ϕ_v° (limiting apparent molar volume or partial molar volume of solute), which is an additive property of ions. The magnitudes of ϕ_v° and S_v give an idea about the extent of solvation of the solute by solvent and change of ϕ_v with concentration, respectively.

The ultrasonic velocity (v) is related to the density (ρ) and compressibility (β) by Equation 1:

$$v = (\rho \cdot \beta)^{-1/2}$$

On differentiation of this equation with respect to concentration (C), one obtains:

$$\frac{dv}{dC} = -\frac{v}{2}\left(\frac{1}{\rho}\cdot\frac{\partial\rho}{\partial C} + \frac{1}{\beta}\frac{\partial\beta}{\partial C}\right) \quad [12]$$

The equation represents the variation of velocity (v) with concentration (C) in terms of variation of density (ρ) and compressibility (β) with soap concentration (C). The derivatives $\partial\rho/\partial C$ and $\partial\beta/\partial C$ are opposite in sign and, generally, the latter is negative and larger than the former. The velocity usually increases with increasing concentration of solute. The ultrasonic velocity (v) varies linearly with soap concentration (C) and follows this relationship:

$$v = v_o + GC \quad [13]$$

where v_o is the ultrasonic velocity of the solvent and G is Garnsey's constant (20). The values of Garnsey's constant can be determined from the slope of the plots of v vs. C for dilute solutions, and the magnitude of G represents the variation of velocity with soap concentration.

The adiabatic compressibility (β) of the solution can be expressed in terms of that of solvent (β_o) and molar concentration (C) by Bachem's empirical relationship (21):

$$\beta = \beta_o + AC + BC^{3/2} \quad [14]$$

The values of constants A and B can be determined from the intercept and slope of the plot of $[(\beta - \beta_o)/C]$ vs. $C^{1/2}$, and the magnitudes of constants A and B depend upon the nature of solute and solvent.

Gücker (22) observed that the plot of apparent molar compressibility (ϕ_k) vs. the square root of molar concentration ($C^{1/2}$) is linear up to the highest possible concentration and derived the limiting law by using Debye–Huckel's theory (23) of electrolytic solutions:

$$\phi_k = \phi_k^\circ + S_k C^{1/2} \quad [15]$$

The extrapolation of the plot of ϕ_k vs. $C^{1/2}$ to zero concentration (i.e., infinite dilution) gives the quantity ϕ_k° (limiting apparent molar compressibility), which is an additive property of ions. Generally, it is negative for strong electrolytes and is almost independent of temperature and pressure. The negative value of ϕ_k indicates that the interaction between solute and solvent is less due to breaking of the sheath of solvent surrounding the ions.

EXPERIMENTAL PROCEDURES

The europium soaps (octanoate and dodecanoate) were prepared by direct metathesis of corresponding potassium soap with the required amount of aqueous solution of europium acetate. The soaps were recrystallized, and the purity of the soaps was checked by elemental analysis and infrared spectra. The reproducibility of the results was checked by preparing two samples of the same soap under similar conditions. The melting points of purified octanoate and dodecanoate were 94.6 and 98.2°C, respectively.

The solutions of different concentrations of soaps were prepared in a mixture of benzene and methanol (3:2, vol/vol) and were kept for 2 h in a thermostat at the desired temperature, 313 ± 0.05 K. The ultrasonic velocity measurements were recorded on a multifrequency ultrasonic interferometer (M-83; Mittal Enterprises, New Delhi) at 313 ± 0.05 K by using a crystal of 1 MHz frequency. The uncertainty of velocity measurements was 0.2%. The densities of solvent and solutions were measured with a dilatometer, and the accuracy of density results was ±0.1 kg • m^{-3}.

RESULTS AND DISCUSSION

Molar volume. The molar volume ($\bar{V}$) and apparent molar volume (ϕ_v) were evaluated from the density measurements by using Equations 9 and 10. The molar volume ($\bar{V}$) (m^3mol^{-1}) of the solutions of europium soaps (octanoate and dodecanoate) in benzene/methanol mixture (3:2, vol/vol) at 313 ± 0.05 K decreased with increasing soap concentration (C) (mol l^{-1}). The plots of molar volume ($\bar{V}$) vs. soap concentration (C) (Fig. 1) are characterized by a break at a definite soap concentration, which corresponds to the CMC of soaps (europium octanoate, 0.07 M; europium dodecanoate, 0.06 M). The CMC values are in agreement with those obtained from ultrasonic measurements (Table 1). The apparent

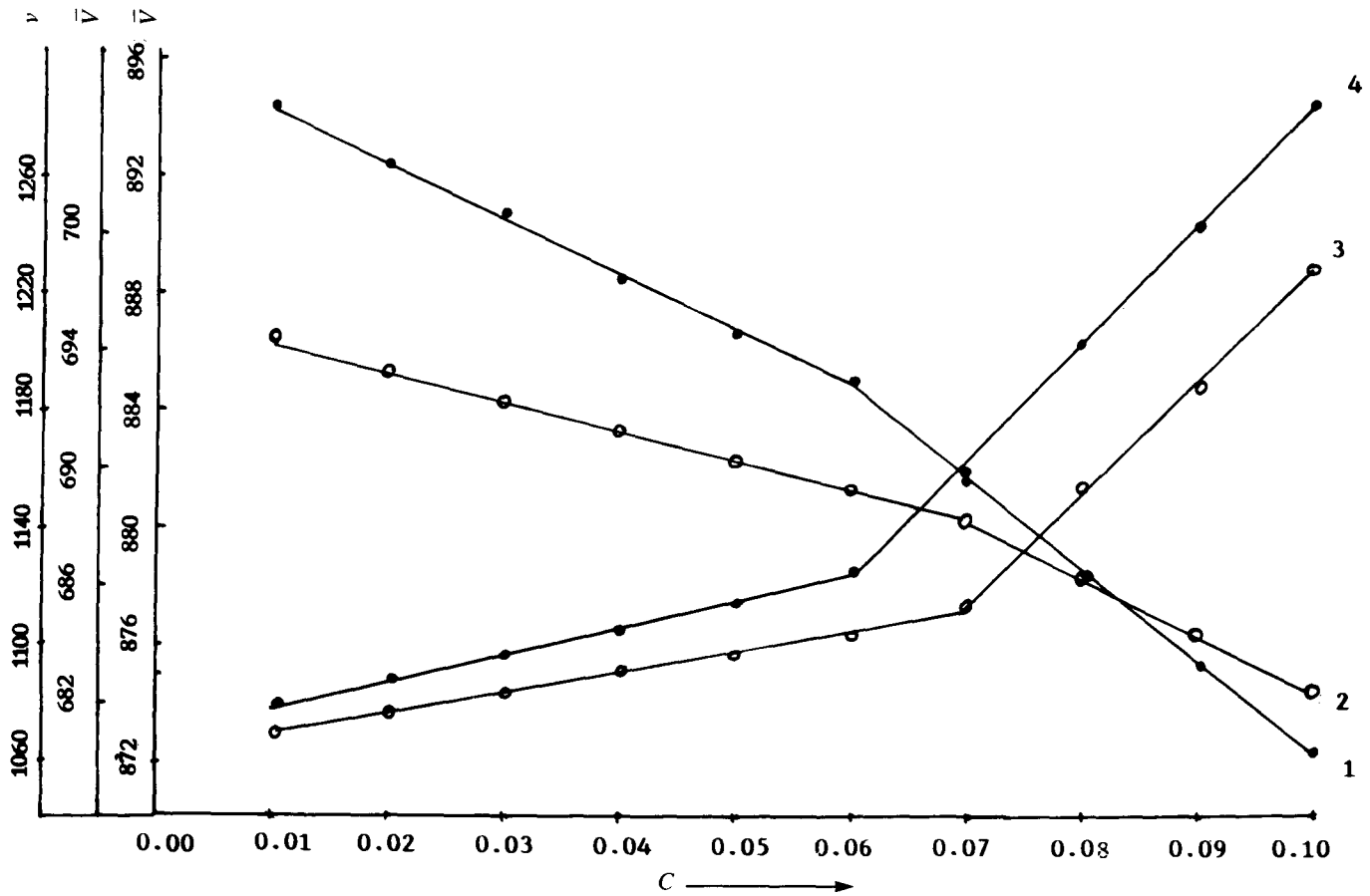

FIG. 1. Plots of molar volume vs. concentration (1 and 2) and ultrasonic velocity vs. concentration (3 and 4) for europium soaps in benzene/methanol mixture (3:2, vol/vol); ○, europium octanoate; ●, europium dodecanoate.

molar volume (ϕ_v) is related to the soap concentration (C) by Masson's equation (19) (our Eq. 11), and the values of constant S_v and limiting apparent molar volume ϕ_v° have been obtained from the slope and intercept of the plots of ϕ_v vs. $C^{1/2}$ (Fig. 2) for dilute soap solutions. The values of ϕ_v° decrease (octanoate, −180; dodecanoate, −210) while those of S_v increase (octanoate, 3.0×10^{-3}; dodecanoate, 3.3×10^{-3}) with increasing chainlength of the soap. The positive values of S_v suggested strong soap–soap interaction, and the decrease of ϕ_v° indicated increase in solvation.

Ultrasonic measurements. The ultrasonic velocity v of europium soap solutions increases with increasing concentration and chainlength of the soap (Table 2). The variation in velocity v with soap concentration C depends on the concentration derivatives of density and compressibility according to Equation 12. The experimental results (Table 2) indicate that the density ρ increases, and the adiabatic compressibility β decreases with increasing soap concentration. Thus, the quantity $(d\rho/dC)$ is positive, and $(d\beta/dC)$ is negative. Because the values of $[(1/\beta)(d\beta/dC)]$ are larger than those of $[(1/\rho)(d\rho/dC)]$ for soap solutions, the concentration derivative of velocity (dv/dC) is positive, which is in agreement with the results of other workers (4,6), reported for electrolyte 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 that corresponds to the CMC of the soap (Table 1). The variation of ultrasonic velocity v with soap concentration C for dilute solutions below the CMC follows Equation 13. Values of the intercept of the plots of v vs. C give the ultrasonic velocity of the solvent mixture v_o

TABLE 1
Values of Critical Micelle Concentration (CMC) and Various Acoustic Parameters of Europium Soaps in Benzene/Methanol Mixture at 313 ± 0.05 K

Soaps	CMC (mol l^{-1})	Garnsey constant	Bachem's equation		Limiting apparent molar compressibility	
			$-A \times 10^{10}$	$B \times 10^{10}$	$(-\phi_k^\circ \times 10^7)$	$S_k \times 10^7$
Octanoate	0.07	727.30	31.60	55.56	4.15	11.70
Dodecanoate	0.06	923.10	45.40	84.21	4.90	12.50

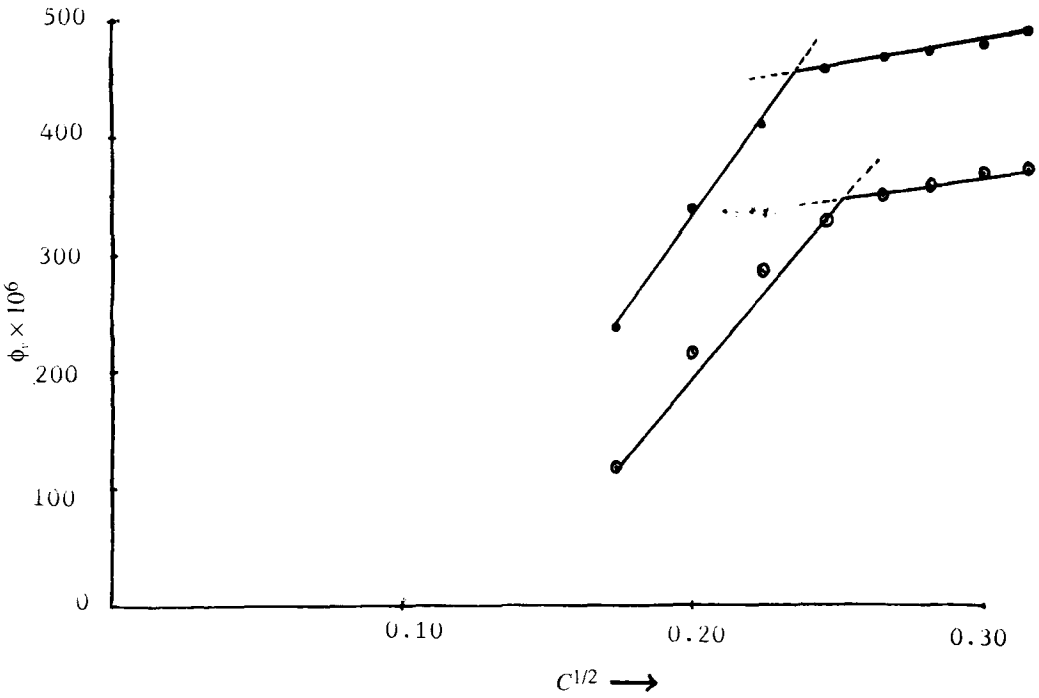

FIG. 2. Plots of apparent molar volume vs. square root of concentration for europium soaps in benzene/methanol mixture (3:2, vol/vol); ○, europium octanoate; ●, europium dodecanoate.

(octanoate, 1060.5; dodecanoate, 1061.5 ms^{-1}), which were in close agreement with the experimental value of ultrasonic velocity of the solvent mixture (1057.5 ms^{-1}). The values of the CMC decrease while Garnsey's constant increases with increasing chainlength of the fatty acid constituent of the soap molecule (Table 1).

TABLE 2
Ultrasonic Measurements of Europium Soaps in Benzene/Methanol Mixture at 313 ± 0.05 K

Concentration, C (mol L^{-1})	Density (kg • m^{-3})	Ultrasonic velocity, v ($m\ s^{-1}$)	Adiabatic compressibility $\beta \times 10^{10}$ ($m^2\ N^{-1}$)	Intermolecular free length, L_f ($A°$)	Specific acoustic impedance, $Z \times 10^5$ (ky $m^{-2}s^{-1}$)	Apparent molar compressibility, $-\phi_k \times 10^7$ (m^2N^{-1})	Molar sound velocity, $R \times 10^6$ ($m\ s^{-1}$)	Molar sound compressibility $W \times 10^2$ ($m^2\ N^{-1}$)	Relative association, $R_A \times 10^2$	Solvation number, S_n
Octanoate										
0.01	836.8	1068	10.477	12.60	8.93	44.85	27.66	14.239	101.070	57
0.02	838.0	1074	10.348	12.51	9.00	26.34	27.66	15.365	101.060	38
0.03	839.1	1081	10.198	12.42	9.07	20.58	27.67	16.502	100.990	33
0.04	840.7	1088	10.048	12.33	9.15	17.80	27.68	17.631	100.970	30
0.05	841.9	1094	9.924	12.25	9.21	15.50	27.69	18.763	100.930	28
0.06	843.1	1100	9.802	12.18	9.27	13.94	27.70	19.893	100.890	26
0.07	845.0	1112	9.570	12.03	9.40	16.22	27.74	21.041	100.760	28
0.08	847.3	1152	8.893	11.60	9.76	20.59	28.00	22.335	99.847	37
0.09	849.5	1186	8.369	11.25	10.01	23.60	28.18	23.608	99.140	42
0.10	851.9	1226	7.810	10.44	10.44	26.38	28.41	24.917	98.327	46
Dodecanoate										
0.01	837.6	1077	10.293	12.48	9.02	63.35	27.69	14.619	101.580	84
0.02	839.5	1085	10.118	12.37	9.11	36.75	27.69	16.044	100.920	55
0.03	841.1	1094	9.934	12.26	9.20	28.05	27.72	17.511	100.840	46
0.04	843.3	1102	9.765	12.16	9.29	23.52	27.31	18.964	100.860	41
0.05	845.0	1112	9.570	12.03	9.40	21.19	27.74	20.434	100.760	38
0.06	846.6	1122	9.383	11.92	9.50	19.48	27.77	23.908	100.640	37
0.07	849.7	1156	8.807	11.54	9.82	24.10	27.94	23.486	100.010	44
0.08	853.0	1199	8.155	11.11	10.23	28.55	28.17	25.124	99.188	51
0.09	856.1	1240	7.597	10.72	10.61	30.95	28.38	26.764	98.439	54
0.10	858.8	1232	7.085	10.35	11.01	32.33	28.60	28.433	97.659	57

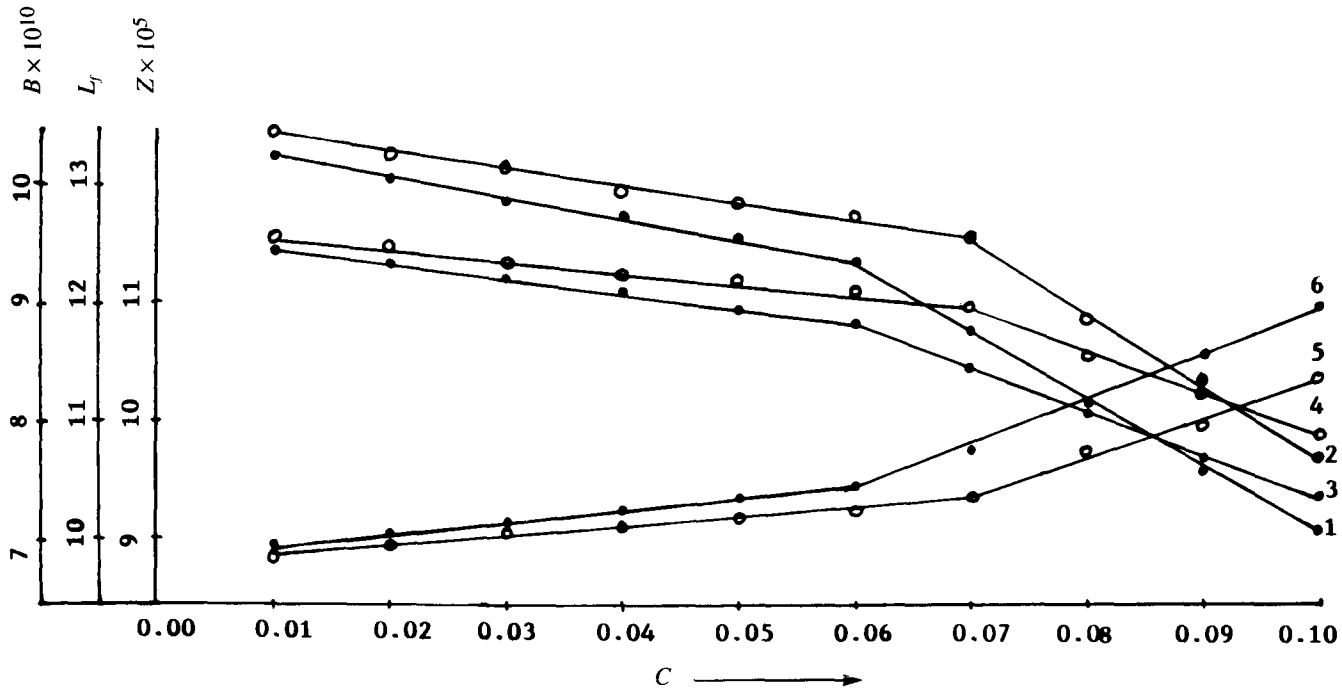

FIG. 3. Plots of adiabatic compressibility vs. concentration (1 and 2), intermolecular free length vs. concentration (3 and 4), and specific acoustic impedance vs. concentration (5 and 6) for europium soaps in benzene/methanol mixture (3:2, vol/vol); ○, europium octanoate; ●, europium dodecanoate.

The adiabatic compressibility (β) of soap solutions decreases with increasing soap concentration (C) (Table 2). The conductivity measurements of the solutions show that these soaps behave as simple electrolytes in solution and are considerably ionized into simple metal cations, Eu^{3+} and fatty acid anions. The ions in solution are surrounded by a layer of solvent molecules, which results in increasing the internal pressure and lowering of the compressibilty of solutions.

The plots of compressibility (β) vs. soap concentration (C) (Fig. 3) indicate a break at a definite soap concentration, which corresponds to the CMC of soaps (octanoate, 0.07 M; dodecanoate, 0.06 M). The values are in agreement with those obtained from the plots of v vs. C (Table 1). The plots of β vs. C are extrapolated to zero soap concentration, and the extrapolated values (octanoate, 1.065×10^{-9}; dodecanoate, 1.050×10^{-9} m^2N^{-1}) are in agreement with the experimental value ($\beta_o = 1.085 \times 10^{-9}$ m^2N^{-1}) for the solvent mixture. The results of adiabatic compressibility β also have been explained in terms of Bachem's empirical Equation 14. The values of constants A and B of Bachem's equation were obtained from the intercept and slope of the plots of $[(\beta - \beta_o)/C]$ vs. $C^{1/2}$ and are recorded in Table 1. The value of constant A decreases, and that of B increases with increasing chainlength of the fatty acid constituent of the soap molecules.

According to Gücker's limiting law (22), the relation between the apparent molar compressibility (ϕ_k) and soap concentration (C) can be expressed by Equation 15. The plots of ϕ_k vs. $C^{1/2}$ are linear for dilute soap solutions, and the values of constant S_k and limiting molar compressibility ϕ_k° have been obtained from the slope and intercept of the plots of ϕ_k vs. $C^{1/2}$. The positive values of S_k (Table 1) signify a considerable soap–solvent interaction in dilute soap solutions. The values of ϕ_k° decrease, and those of S_k increase with an increase in chainlength of the soap molecules. The decrease in the values of ϕ_k at higher soap concentrations may be explained on the basis of the close packing of ionic head groups in the ionic micelles, resulting in an increase in ionic repulsion and finally of internal pressure.

The decrease of intermolecular free length L_f and increase of specific acoustic impedance Z with increase in concentration and chainlength of the soap (Table 2) indicate that there is a significant interaction between the solute and solvent molecules, due to which the structural arrangement is considerably affected. This can be explained on the basis of hydrophobic interaction between the soap and solvent molecules, which increases with the intermolecular distance, leaving relatively wider gaps between the molecules and thus becoming the main cause of impediment to the propagation of ultrasound waves. Both plots (L_f vs. C and Z vs. C) (Fig. 3) show a break at a definite soap concentration, which corresponds to the CMC of the soap (octanoate, 0.07 M; dodecanoate, 0.06 M), and the values are in agreement with those obtained from the plots of β vs. C.

The values of relative association R_A decrease with increasing concentration and chainlength of the fatty acid constituent of the soap molecule (Table 2). The decrease in the values of relative association R_A is attributed to the fact that solvation of ions decreases with increasing soap concentra-

tion. The values of molar sound velocity R and molar sound compressibility W increase with increasing concentration and chainlength of the soaps. The values of solvation number of europium soaps decrease with an increase in soap concentration in dilute solutions (<0.06 M) and then show an increase with increasing soap concentration (Table 2). The solvation number increases with the increasing chainlength of the fatty acid constituent of the soap molecule.

The results confirm that there is significant interaction between the soap and solvent molecules in dilute solutions. The values of the CMC, obtained from different plots, are in agreement and decrease with increasing chainlength of the fatty acid moiety of the soap molecule.

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