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Ultrasonic Velocity and Density Measurements of Zr (VI) Soaps in Benzene

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Ultrasonic velocity and density of Zr (IV) soaps *viz* caproate, caprate and laurate have been measured in benzene at 35°C. Using these data the adiabatic compressibility, inter-molecular free length apparent molar compressibility, molar sound velocity, molar sound compressibility, solvation number and apparent molar volume have been evaluated.

INTRODUCTION

Although there has been considerable research interest in the studies of alkali[1], alkaline earth[2–5] and transition metals[6,7], but only a few solid compounds examplifying the +4 state were prepared. Cerium (IV) has sufficiently long half life with respect to reduction in aqueous solution[8]. Although Zr (IV) soaps were prepared[9–11] by treating an aqueous zirconium salt solution with aqueous alkaline soap of fatty acid but the studies on their physical properties are rare. In this comunication the study of ultrasonic velocity and density of soap solutions at 35°C has been undertaken in order to calculate adiabatic compressibilities, molar sound velocities, solvation number and apparent molal volume from these data, which may give a clear insight into the micellar aggregation of Zr (IV) soaps in benzene.

EXPERIMENTAL

AnalaR (BDH) $Zr(NO_3)_4$, caproic, capric, lauric acids and benzene were used. The fatty acids were purified by distillation under reduced pressure and their purity was confirmed by determination of melting and boiling points.

Soaps were prepared by the interaction of the metal salt solution in a small quantity of distilled water with a hot solution of sodium soap, the latter being added dropwise while stirring at 50°–55°C. The precipitate was filtered off and washed with hot water. After initial drying in an air oven (100°–105°C) final drying was carried out under reduced pressure.

The densities were measured at constant temperature (± 0.05°C) with a dilatometer constructed of pyrex glass having a reservoir volume of 15 cm^3. The measuring section was constructed of precisely bored graduated capillary. The uncertainity in density measurement is $\pm 10^{-4}$ g cm^{-3}.

Ultrasonic velocity of samples was measured with the help of a single crystal ultrasonic interferometer working at a fixed frequency of 2MHz. Water maintained at the desired temperature and controlled upto ± 0.05°C by a thermostat was passed through the jacket of the cell before the measurement was actually made. The measured velocities have an uncertainty of $\pm 0.5 \text{ ms}^{-1}$.

RESULTS AND DISCUSSION

Ultrasonic velocity

The variation of ultrasonic velocity $u(\text{ms}^{-1})$ with soap concentration (mol dm^{-3}) is plotted. The value of u (Table 1) decreases upto CMC and then increases with further increase in soap concentration. All the soaps show the same CMC, *i.e.* 0.015 M which is independent of temperature. This is possible that the first CMC range becomes small due to high solubility of soaps in benzene. However, the ultrasonic velocity decreases with increase in chain length.

The adiabatic compressibility, β of a solution is determined using the relation

$$\beta = \frac{1}{u^2 d} \tag{1}$$

where d is the density of the solution. The adiabatic compressibility increases upto CMC and then decreases. The variation of ultrasonic velocity with concentration is obtained by differentiation of equation (1).

$$\frac{du}{dc} = -\frac{u}{2}\frac{1}{d}\frac{d(d)}{dc} - \frac{1}{\beta}\frac{d\beta}{dc} \tag{2}$$

The velocity increases or decreases with concentration as the term $\frac{d(d)}{dc}$ and $\frac{d\beta}{dc}$ have opposite signes.

The apparent molal compressibility ϕ_k of the solution is calculated by using the relation:

$$\phi_k = \frac{1000(\beta d_o - \beta_o d)}{d d_o} + \beta M \tag{3}$$

Where M is the molecular weight of solute, d_o and β_o are density and compressibility of solvent, respectively. The ϕ_k values at different concentrations are best fitted to the equation for dilute solutions.

$$\phi_k = \phi_k^o + S_k C \tag{4}$$

Where ϕ_k^o is the apparent molal compressibility at infinite dilution and S_k is the experimental slope. The polts of ϕ_k against soap concentration C are characterised by the intersection of two straight lines at the CMC. The results

TABLE 1
ULTRASONIC VELOCITY AND OTHER RELATED PARAMETERS FOR Zr (IV) SOAPS SOLUTIONS IN BENZENE AT 35°C.

Conc. (mol dm^{-3})	Density × 10^{-3} (kg m^{-3})	u (ms^{-1})	($\beta \times 10^{10}$) (m^{2}N^{-1})	L_f (Å)	Z × 10^{-3} (Kg m^{-2}s^{-1})	R × 10^{-3} $\frac{m^3}{mol}\left(\frac{m}{s}\right)^{1/3}$	W × 10^{-3} $\frac{m^3}{mol}\left(\frac{N}{m^2}\right)^{1/7}$	η_s
				Caproate				
0.005	0.8640	1249	7.41	40.287	1078.1	974.82	1823.82	2011
0.010	0.8651	1246	7.44	40.355	1077.9	975.4	1825.4	1003
0.015	0.8664	1244	7.45	40.675	1077.8	976.2	1827.4	667
0.020	0.8676	1246	7.42	40.304	1080.9	978.2	1830.3	499
0.025	0.8687	1248	7.39	40.214	1084.1	980.2	1835.4	398
0.030	0.8701	1250	7.35	40.124	1087.5	982.2	1839.3	331
				Caprate				
0.005	0.8643	1246	7.45	40.379	1076.9	975.0	1824.4	2008
0.010	0.8651	1244	7.468	40.420	1076.2	977.3	1829.2	1000
0.015	0.8663	1242	7.48	40.461	1076.0	979.6	1833.9	663
0.020	0.8675	1244	7.44	40.369	1079.2	982.8	1840.2	496
0.025	0.8683	1246	7.41	40.277	1081.9	986.0	1846.3	395
0.030	0.8698	1248	7.38	40.185	1085.3	989.2	1852.7	328

Conc. (mol dm^{-3})	Density × 10^{-3} (kg m^{-3})	u (ms^{-1})	$(\beta \times 10^{10})$ $(\text{m}^2\text{N}^{-1})$	L_f (Å)	Z × 10^{-3} $(\text{Kg m}^{-2}\text{s}^{-1})$	R × 10^{-3} $\frac{\text{m}^3}{\text{mol}}\left(\frac{\text{m}}{\text{s}}\right)^{1/3}$	W × 10^{-3} $\frac{\text{m}^3}{\text{mol}}\left(\frac{\text{N}}{\text{m}^2}\right)^{1/7}$	η_s
				Laurate				
0.005	0.8651	1244	7.469	40.423	1076.2	974.21	1823.3	2008
0.010	0.8662	1242	7.48	40.464	1075.8	977.0	1829.1	999
0.015	0.8673	1240	7.49	40.502	1075.5	979.8	1834.8	663
0.020	0.8678	1242	7.47	40.425	1077.8	984.4	1843.5	494
0.025	0.8682	1244	7.44	40.350	1080.0	989.2	1852.3	393
0.030	0.8695	1246	7.41	40.274	1083.9	993.9	1861.1	326

show that the values of ϕ_k increase sharply upto CMC and then increases. It is due to the fact that the soap molecules in dilute solutions are considerably ionised into metal cation, *i.e.* Zr^{4+} and fatty acid anions. These ions are surrounded by a thin film 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 ions and the internal pressure thus increases, reducing the solution compressibility[12].

The values of ϕ_k^o and S_k have been evaluated (Table 2) from the intercept and slopes of the linear plots of ϕ_k vs C below and above CMC. The values of S_k below CMC are positive which signifies a considerable soap-solvent interaction. The values of ϕ_k^o and below CMC, S_k increases with increase in chain length of the soap.

TABLE 2
VALUES OF ϕ_k^o AND S_k OF Zr (IV) SOAPS SOLUTIONS IN BENZENE AT TEMPERATURE 35°C.

Soap	$\phi_k^o \times 10^{10}$	$S_k \times 10^{10}$	
		Below CMC	Above CMC
Caproate	4.55	3.4	–15.0
Caprate	6.55	2.6	–18.1
Laurate	7.54	2.8	–13.9

Inter molecular free length L_f has been calculated by using semi empirical relation given by Jacobson[13] and specific acoustic impedance, Z as equal to d.u. (Table 1). The values of L_f increases upto CMC but decreases with further increase in concentration. Specific acoustic impedance, Z does not change much below CMC but increases with further increase in soap concentration. These values decrease with increase in chain length of soaps.

Molar sound velocity, R and molar sound compressibility W have been calculated as

$$R = \frac{Mu^{1/3}}{d} \tag{5}$$

and

$$W = \frac{M}{d}\beta^{-1/7} \tag{6}$$

Where M is the average molecular weight of solution calculated from the relation: $M = X_1M_1 + X_2M_2$, X_1 and X_2 are the mole fractions of the solute and solvent and M_1 and M_2 are their respective molecular weights. The values of R and W increase with increase in soap concentration but show a point of inflection at CMC.

The adiabatic compressibility data have been used to calculate the solvation number, n_s by using Passynsky's relation[14]. The values of n_s show (Table 1) a decrease with increase in soap concentration. The decrease is rapid at lower concentration but is very small above CMC. There is no appreciable change in n_s values in different soaps. The values of n_s correspond to the solvent molecule in the primary solvation sheaths of the ions. On account of electrostriction molecules in the solvation sheaths will be highly compressed so that the molecules will be less compressible than those in the bulk of solvation. When an external pressure is applied, the compressibility of solvent molecules near but not in the primary solvation sheaths is the same as that of pure solvent. The solvation number is an indication of more of electrostriction effects of the ions on surrounding solvent molecules than of the actual primary solvation numbers. The higher values of solvation number suggest a considerable dissociation of the molecule. Thus, the results confirm that there is a significant interaction between soap solvent molecules in dilute solutions and soap forms micelles at higher concentrations.

Density: The d–c plots show a change at CMC which are in accordance with the values observed in ultrasonic velocity measurements.

The density results have been explained in terms of Root's equation[15].

$$d = d_o + AC - BC^{3/2} \tag{7}$$

The breaks in the plots of $(d - d_o)/C$ vs $C^{1/2}$ agree with the CMC values. Constants A below CMC and the slopes B_1, B_2 respectively below and above CMC have been calculated (Table 3). These constants increase with increase in chain length of the soaps.

TABLE 3
VALUES OF A, B_1, B_2 AND ϕ_V^o AND S_v OF ZR (IV) SOAPS SOLUTIONS IN BENZENE

Soap	A	B_1	B_2	ϕ_V^o	$S_v \times 10^{-2}$ Below CMC	$S_v \times 10^{-2}$ Above CMC
Caproate	0.569	2.272	0.550	130	26.00	–6.75
Caprate	0.622	2.733	0.600	154	33.50	4.25
Laurate	0.972	5.000	2.150	200	63.25	23.00

The apparent molar volume ϕ_v of soaps has been calculated from the measured density data using the following equation:

$$\phi_v = \frac{M_2}{d_o} - \frac{(d - d_o) \times 10^3}{cd_o} \tag{8}$$

Where M is the molecular weight of the soap.

The apparent molar volume increases rapidly upto CMC and then increases slowly above this concentration. Various factors such as solvation of amphilic solutes, electrostriction of solvent molecules by charged moieties, nature of ionic head group and length of non polar portion of amphilic molecules contribute to apparent molar volume and affect the volume differently and to a different extent.

The limiting apparent molar volume (ϕ_v^o) have been obtained by extrapolating the linear plots of ϕ_v vs $C^{1/2}$ for dilute soap solutions according to Masson's equation[16].

$$\phi_v = \phi_v^0 + s_v C^{1/2} \qquad (9)$$

Where S_v is the experimental limiting slope. The values of ϕ_v and S_v are recorded in Table 3 which are measures of solute-solvent and solute-solute interactions respectively. These values increase with increasing chain length of the soaps. The values of S_v below and above CMC differ much showing micellar aggregation.

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