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Ultrasonic Studies of Zirconium(IV) Soaps in Mixed Solvents

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Several acoustic parameters *e.g.* the adiabatic compressibility, intermolecular free length, acoustic impedance, molar sound velocity, molar sound compressibility and solvation number of soaps in tetrachloromethane, toluene and xylene were calculated at 35 and 45°C in presence of 20% and 40% methanol. The results obtained provided important information about the structural change of the soaps.

INTRODUCTION

The characterisation and thermal decomposition of Zr(IV) soaps have been reported earlier[1] In the present work, ultrasonic studies of these soap solutions in tetrachloromethane, toluene and xylene in presence of methanol have been made at 35 and 45°C with a view to study the micellar aggregation and soap-solvent interaction.

EXPERIMENTAL

The chemicals were of AnalaR grade and the soaps were prepared by the method described elsewhere.[2] The ultrasonic velocity of soap solutions were measured by using a single crystal ultrasonic interferometer (Model No F-81, Mittal Enterprises, New Delhi, (India) at a fixed frequency of 2 MHz. Water was circulated through a thermostat maintained at the desired temperature and controlled up to ±0.05°C and was passed through the jacket of the cell before the measurements were made. The uncertainty in ultrasonic velocity in each measurement under different conditions was estimated to be $\pm$ 0.5 m s^{-1}. The densities were measured at constant temperature using dilatometer. The original data are available on request from the authors.

RESULTS AND DISCUSSION

The ultrasonic velocity, c (m s^{-1}) increases with increase in concentration of soap C (mol dm^{-3}) upto a definite concentration and then decreases with further increase in soap concentration. The plots of c *vs.* C (Fig. 1) show an intersection of straight lines at CMC *i.e.*, 0.015 M which is independent of percentage composition (v/v) of solvent mixture, nature of soap and temperature.

The variation in ultrasonic velocity c with soap concentration C follows the relationship

$$c = c_0 + GC \tag{1}$$

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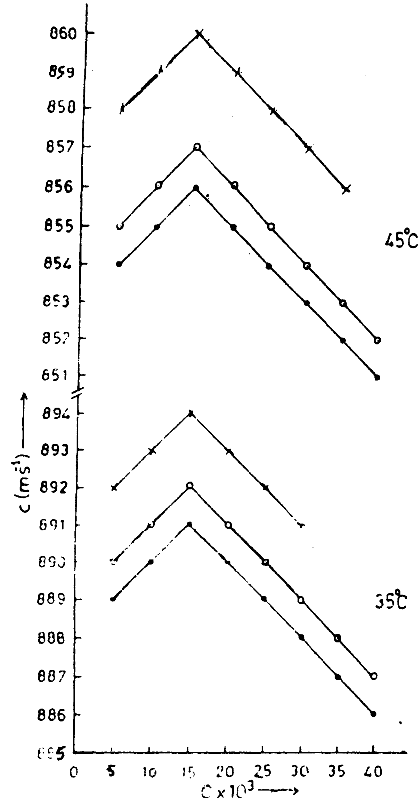

Fig. 1. Plots of ultrasonic velocity, c (m s^{-1}) *vs.* concentration C (mol dm^{-3}) of zirconium soaps in CCl_4 + methanol mixture (20 % v/v) at 35° and 45°C

● Butyrate; ○ Valerate; × Stearate

where c_0 is the ultrasonic velocity in pure solvent and G is the Garnsey's constant[3] given in Table-1.

The ratio of acoustic pressure in a medium to the associated particle velocity is defined as the acoustic impedance Z of the medium and given by the equation

$$Z = c\rho \tag{2}$$

for the particular type of wave motion present, where ρ is the density of the solution. The acoustic impedance shows similar variation with the change in concentration, temperature and with increase in chain length of soap, as in the case of ultrasonic velocity. The values of acoustic impedance (Z) decrease with increase in percentage ethanol in mixtures. The increase in the value of specific acoustic impedance Z with increase of concentration of soap can be explained on the basis of hydrophobic interaction between soap and solvent molecules.

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

$$\beta = \frac{1}{c^2\rho} \tag{3}$$

The plots of β *vs.* C (Fig. 2) show an intersection of two straight lines at CMC in different soaps. The values of β first decrease and then increase with increasing concentration of soap.

TABLE-1
VALUES OF GARNSEY CONSTANTS FOR ZIRCONIUM(IV) SOAPS IN 20% AND 40% METHANOL AT 35° AND 45°C

Volume % of methanol	Temp. (°C)	Butyrate		Valerate		Stearate	
		c_0	G	c_0	G	c_0	G
		Tetrachloromethane					
20	35	887.9	200	888.9	200	890.9	200
	45	852.8	200	853.9	200	856.9	200
40	35	913.0	200	914.0	200	916.9	200
	45	882.9	205	884.0	200	886.9	200
		Toluene + methanol					
20	35	1202.0	200	1203.0	200	1207.0	200
	45	1164.0	200	1165.0	200	1167.0	200
40	35	1166.0	200	1167.0	200	1168.0	200
	45	1122.0	200	1123.0	200	1124.0	200
		Xylene + methanol					
20	35	1122.0	200	1223.0	200	1225.0	200
	45	1180.0	200	1180.9	200	1183.0	200
40	35	1180.0	200	1181.0	200	1183.0	200
	45	1135.9	200	1137.0	200	1140.0	200

The variation of ultrasonic velocity with concentration dc/dC depends on the concentration derivatives of density and adiabatic compressibility and can be explained by differentiating the equation

$$\frac{dc}{dC} = \frac{-c}{2}\left[\frac{1}{\rho}\frac{d\rho}{dC} \cdot \frac{1}{\beta}\frac{d\beta}{dC}\right] \tag{4}$$

The ultrasonic velocity increases or decreases with concentration according to the signs of $d\rho/dC$ and $d\beta/dC$. If $(1/\rho)(d\rho/dC)$ and $(1/\beta)(d\beta/dC)$ both are positive the ultrasonic velocity decreases whereas if $(1/\rho)(d\rho/dC)$ is positive and $(1/\beta)(d\beta/dC)$ is negative the ultrasonic velocity increases.

The apparent molar compressibility ϕ_k of the solution has been calculated by using the relation:

$$\phi_k = \frac{1000(\beta\rho_0 - \beta_0\rho)}{\rho\rho_0} + \frac{\beta M}{\rho} \tag{5}$$

where M is the molecular weight of the solute, β and β_0 are adiabatic com-

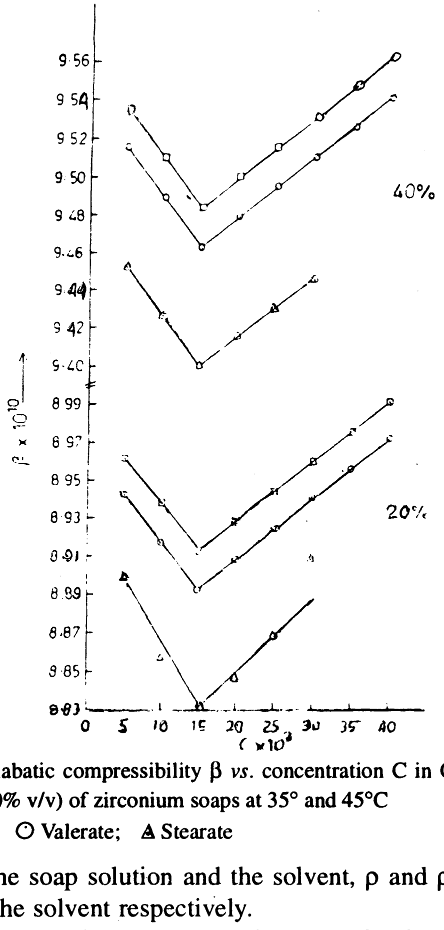

Fig. 2. Plots of adiabatic compressibility β *vs*. concentration C in CCl_4 + methanol mixture (20% and 40% v/v) of zirconium soaps at 35° and 45°C

● Butyrate; ○ Valerate; ▲ Stearate

pressibilities of the soap solution and the solvent, ρ and ρ_0 are the densities of the solution and the solvent respectively.

The ϕ_k *vs*. C plots (Fig. 3) show a change at CMC. It is observed that the values of ϕ_k of soaps show sharp change upto CMC and then increase gradually with increase in concentration. However, ϕ_k of soaps increase with increase in temperature of mixtures.

The value of ϕ_k is related to the concentration of soap by the realtionship

$$\phi_k = \phi_k^0 + S_k C \qquad (6)$$

where ϕ_k^0 is the apparent molar compressibility at infinite dilution and S_k is the experimental slope. The values of S_k (Table 2) below CMC decrease with rise in temperature. It is observed that the S_k values below CMC are lower than the values above CMC. Therefore the difference in these values show the point of inflection at CMC. The value of ϕ_k^0 increases with increase in temperature and chain length of soaps and percentage of methanol in the respective solvent mixtures.

Intermolecular free length L_f has been calculated as per following relation:[4]

$$L_f = (\beta/k)^{1/2} \qquad (7)$$

where k is a temperature-dependent constant.

The values of L_f decrease up to CMC and then increase with futher increase

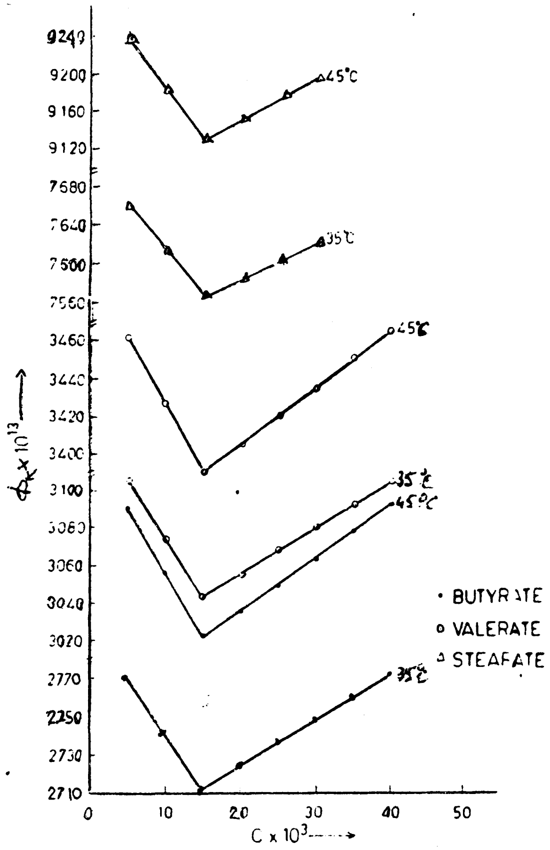

Fig. 3. Plots of molar compressibility, ϕ_k *vs.* concentration C of zirconium soaps in CCl_4 + methanol mixture (20% v/v) at 35° and 45°C.

in soap concentration. The values also increase with increase in temperature, as well as with increase of percentage of methanol in mixtures.

The molar sound velocity R and molar adiabatic compressibility W are calculated from the following expressions

$$R = \frac{M}{\rho} C^{1/3} \tag{8}$$

$$W = \frac{M}{\rho} \beta^{-1/7} \tag{9}$$

where M is the average molecular weight of the solution calculated from the relation $M = X_1M_1 + X_2M_2$, X_1 and X_2 being the mole fractions of the solute and solvent and M_1 and M_2 their respective molecular weights.

The values of R and W increase with increase in soap concentration and chain length of soaps and show a point of inflection at CMC. These values decrease with the increase in percentage of methanol in mixtures and are almost independent of temperature.

The adiabatic compressibility data have been used to calculate the solvation number n_s of soap by using Passynsky's relation.[5]

TABLE-2

VALUES OF $S_k \times 10^{10}$ ($m^5 N^{-1} kg^{-1} mol^{-2}$) FOR ZIRCONIUM(IV) SOAPS IN 20% AND 40% METHANOL AT 35° AND 45°C

Volume % of Methanol	Temp. °C	Butyrate		Valerate		Stearate	
		Below CMC	Above CMC	Below CMC	Above CMC	Below CMC	Above CMC
Tetrachloromethane							
20	35	-5.90	2.35	-6.16	2.43	- 9.39	3.63
	45	-6.78	2.81	-7.11	2.94	-10.78	4.45
40	35	-7.19	2.55	-7.50	2.61	-11.48	3.86
	45	-8.07	2.89	-8.48	3.00	-13.01	4.61
Toluene + methanol							
20	35	-12.92	2.76	-18.04	1.86	-20.79	3.01
	45	-15.51	2.80	-16.49	3.03	-26.81	5.15
40	35	-13.26	1.71	-14.05	1.75	-22.16	2.17
	45	-14.32	1.60	-15.04	1.71	-23.93	1.78
Xylene + methanol							
20	35	-12.66	3.11	-13.35	3.21	-21.41	5.68
	45	-14.47	5.22	-14.95	3.26	-23.88	7.97
40	35	-14.13	3.25	-15.24	3.53	-24.34	8.12
	45	-16.27	3.51	-17.15	3.56	-27.36	8.88

$$n_s = \frac{n_1}{n_2}\left(1 - \frac{V\beta}{n_1 V_1^0 \beta o}\right) \qquad (10)$$

where V is the molar volume of the solution containing n_2 moles of the solute and V_1^0 is the molar volume of the solvent.

The value of n_s has a general trend of nonlinear decrease with the increase in concentration of soap solution while increase with the increase in temperature and percentage of methanol in different mixtures. There is no appreciable change of n_s values in different soaps. In dilute range, solute-solvent interaction is expected which decreases with increase in soap concentration. Solvation is overcome by micellar aggregation of soaps; thereby a small change in n_s values occurs above CMC.

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