

# Speed of Sound Measurements on Zirconyl Soap Solutions in Xylene + Methanol

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The speed of sound in solutions of zirconyl soaps (caproate, caprylate, and caprate) in xylene + methanol (volume ratio of 4:1) increases with increasing concentration and chain length of the soap. The isentropic compressibility ( $k_s$ ), apparent molar compressibility ( $\phi_k$ ), and apparent molar volume ( $\phi_v$ ) were evaluated, and the results were explained in terms of solute–solvent interactions. It is concluded that the soap molecules do not aggregate appreciably below the critical micellar concentration.

## Introduction

A knowledge of the properties of metallic soap solutions is important for new technological developments. The industrial applications of soaps are mostly based on empirical knowledge, and the selection of the soap for a specific purpose is largely dependent on economic factors. The physicochemical characteristics and structure of soaps can be controlled to some extent by the method and conditions of their preparation, and so the studies of soaps in solutions are of much significance for their use in industry under different conditions. The molecular and ion–solvent interactions have been investigated by using various techniques (5, 11, 21). However, the micellization process in soap solutions in organic solvents is somewhat different from that in aqueous solutions as the association in organic solvents commences at very low concentrations. The determination of the critical micellar concentration in organic solvents cannot be carried out by the methods commonly used for aqueous solutions, and so speed of sound measurements have been used to study the solute–solvent interactions in soap solutions. The speed of sound measurements have been used to obtain useful information regarding various acoustic parameters and solute–solvent interactions in pure liquids, liquid mixtures, and electrolytic solutions (4, 15, 16, 18–20). The present work deals with the measurements of the density and speed of sound of the solutions of zirconyl soaps [caproate,  $\text{ZrO}(\text{C}_5\text{H}_{11}\text{COO})_2$ , caprylate,  $\text{ZrO}(\text{C}_7\text{H}_{15}\text{COO})_2$ , and caprate,  $\text{ZrO}(\text{C}_9\text{H}_{19}\text{COO})_2$ ] in xylene + methanol (volume ratio of 4:1) as these soaps possess maximum solubility in the solvent mixture of this composition.

## Experimental Section

All the chemicals used were of BDH/AR grade. The boiling points of purified methanol and *p*-xylene were 65 and 138 °C, respectively. Zirconyl soaps (caproate, caprylate, and caprate) were prepared by direct metathesis of the corresponding potassium soap with a slight excess of an aqueous solution of zirconium oxychloride. The soaps were washed with distilled water, methanol, and acetone to remove the excess metal ion, potassium soap, and unreacted fatty acid. The melting points of purified zirconyl caproate, caprylate, and caprate were 137, 146, and 158 °C, respectively. The purity of the soaps was checked by elemental analysis and by recording their IR spectra. The experimental results of elemental analysis were in agreement with the theoretical values, and the absence of coordinated water molecules was confirmed by the absence of the absorption peaks near 3500–3300  $\text{cm}^{-1}$ .

Solutions of different concentrations of soaps were prepared in xylene + methanol (volume ratio of 4:1) and were kept for 2 h in a thermostat. The densities were determined with a dilatometer calibrated with pure benzene. The volume of the dilatometer was 15  $\text{cm}^3$ , and the accuracy of the density results was  $\pm 0.0001 \text{ g cm}^{-3}$ . A multifrequency ultrasonic interferometer M-83 (Mittal Enterprises, New Delhi) was used to measure the speed of sound at  $(40 \pm 0.05) \text{ }^\circ\text{C}$  using a crystal of 1 MHz frequency. The relative mean error in the measurements of speed was  $\pm 0.2\%$ .

## Calculations

The isentropic compressibility ( $k_s$ ), apparent molar compressibility ( $\phi_k$ ), and apparent molar volume ( $\phi_v$ ) (17) were calculated by using the relationships

$$k_s = u^{-2} \rho^{-1} \quad (1)$$

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0 k_s - k_s^\circ \rho) + \frac{Mk_s^\circ}{\rho_0} \quad (2)$$

$$\phi_v = \frac{1000}{C\rho\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \quad (3)$$

where  $u$ ,  $u^\circ$ ,  $\rho_0$ ,  $\rho$ ; and  $k_s^\circ$ ,  $k_s$  are the speed of sound, density, and isentropic compressibility of the solvent and solutions, respectively, and  $M$  is the molar mass of the soap.

## Results and Discussion

The speed of sound ( $u$ ) of zirconyl soap solutions increases with increasing concentration and chain length of the soap (Table 1). The variation of the speed of sound ( $u$ ) with concentration ( $c$ ) depends on the concentration derivatives of density and isentropic compressibility and can be expressed as

$$\frac{du}{dc} = -\frac{u}{2} \left[ \frac{1}{\rho} \left( \frac{d\rho}{dc} \right) + \frac{1}{k_s} \left( \frac{dk_s}{dc} \right) \right] \quad (4)$$

The results indicate that the density increases while the isentropic compressibility decreases with increasing soap concentration. Thus, the quantity  $d\rho/dc$  is positive while  $dk_s/dc$  is negative. Since the values of  $dk_s/dc/k_s$  for soap solutions are larger than  $d\rho/dc/\rho$ , the concentration derivative of the speed of sound ( $du/dc$ ) is positive. The results are in agreement with the results that other researchers (9, 12, 14) have reported for electrolytic solutions. The

**Table 1. Concentration ( $c$ ), Density ( $\rho$ ), Speed of Sound ( $u$ ), Isentropic Compressibility ( $k_s$ ), Apparent Molar Volume ( $\phi_v$ ), and Apparent Molar Compressibility ( $\phi_k$ ) of Zirconyl Soaps in Xylene Methanol at  $(40 \pm 0.05)^\circ\text{C}$** 

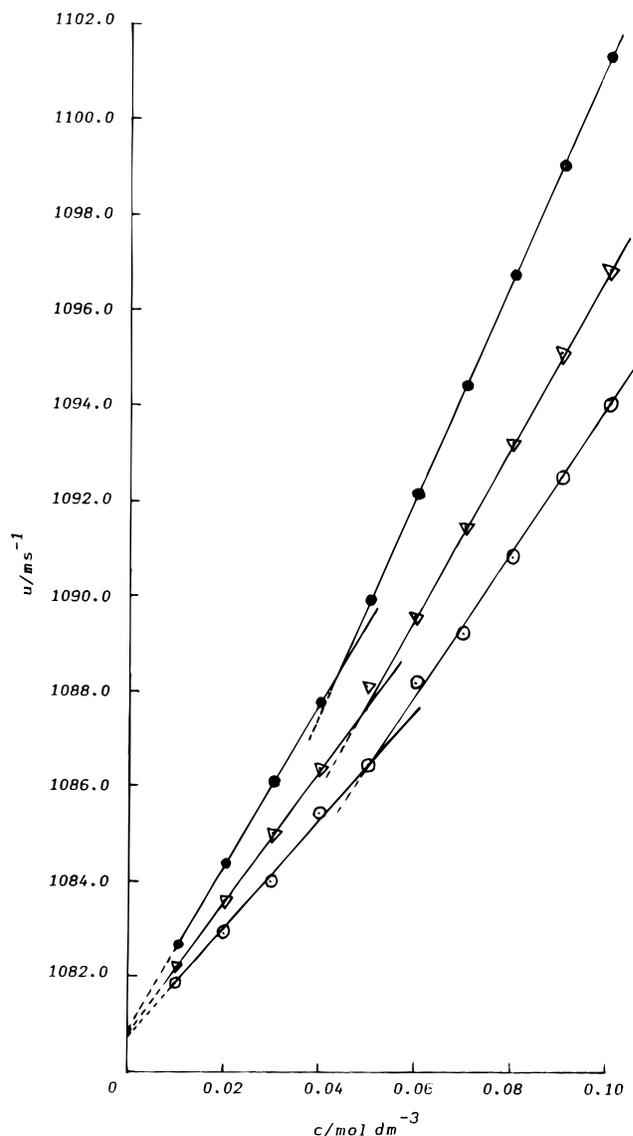
$c$ (mol dm <sup>-3</sup> )	$\rho$ (kg m <sup>-3</sup> )	$u$ /ms <sup>-1</sup>	$10^{10}k_s$ / (m <sup>2</sup> N <sup>-1</sup> )	$-10^3\phi_v$ / (m <sup>3</sup> mol <sup>-1</sup> )	$-10^7\phi_k$ / (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-1</sup> )
Caproate					
0.01	840.6	1081.8	10.165	127.10	4.088
0.02	841.4	1082.9	10.135	119.91	4.036
0.03	842.2	1084.0	10.105	117.43	4.008
0.04	842.9	1085.4	10.070	112.62	4.092
0.05	843.7	1086.4	10.042	112.52	4.027
0.06	844.8	1088.2	9.996	119.84	4.344
0.07	846.0	1089.1	9.965	126.22	4.374
0.08	847.5	1090.8	9.917	136.53	4.654
0.09	848.8	1092.5	9.871	141.38	4.823
0.10	850.1	1094.0	9.829	145.22	4.919
Caprylate					
0.01	840.8	1082.2	10.155	141.09	5.109
0.02	841.8	1083.6	10.117	148.08	5.170
0.03	842.8	1085.0	10.079	145.46	5.116
0.04	843.9	1086.4	10.040	151.13	5.200
0.05	845.1	1088.1	9.994	151.64	5.326
0.06	846.5	1089.5	9.952	158.89	5.421
0.07	847.8	1091.4	9.902	161.99	5.585
0.08	849.5	1093.2	9.850	171.22	5.795
0.09	851.1	1095.1	9.797	176.69	5.955
0.10	852.4	1096.8	9.752	176.89	5.967
Caprate					
0.01	841.0	1082.6	10.145	183.45	6.573
0.02	842.2	1084.3	10.099	176.12	6.312
0.03	843.4	1086.1	10.051	173.51	6.292
0.04	844.6	1087.7	10.008	172.09	6.157
0.05	846.1	1089.9	9.956	179.53	6.449
0.06	847.8	1092.1	9.890	189.01	6.717
0.07	849.5	1094.4	9.828	195.63	6.937
0.08	851.0	1096.7	9.770	197.04	7.022
0.09	852.7	1099.0	9.710	201.10	7.137
0.10	854.4	1101.3	9.650	204.23	7.229

variation of the speed of sound  $u$  with the soap concentration  $c$  follows the relationship

$$u = u_0 + Gc \quad (5)$$

where  $u_0$  is the speed of sound of the solvent mixture and  $G$  is Garnsey's constant (3).

The plots of the speed of sound  $u$  against the soap concentration  $c$  (Figure 1) are characterized by an intersection of two straight lines at a definite soap concentration that corresponds to the critical micellar concentration (Table 2). The values of the critical micellar concentration were in close agreement with those obtained from viscosity and conductivity measurements. The value of the intercept of the plots (Figure 1) corresponds to the speed of sound of the solvent mixture  $u_0$ , which was found to be in close agreement with the experimental value of the speed of sound of the solvent mixture (Table 2). The values of the critical micellar concentration decrease while Garnsey's constant  $G$  increases with increasing chain length of the



**Figure 1.** Speed of sound ( $u$ ) against soap concentration ( $c$ ):  $\odot$ , caproate;  $\Delta$ , caprylate;  $\bullet$ , caprate.

fatty acid constituent of the soap (Table 2). The micellization is mainly caused by the energy change due to dipole-dipole interactions between the polar head groups of the soap molecules, and the micelles are held together by van der Waals forces acting between hydrocarbon chains of parallel layers and strong dipole-dipole interactions between polar heads.

The isentropic compressibility  $k_s$  of the solutions decreases with increasing soap concentration  $c$  (Table 1), which may be due to the fact that these soap molecules in dilute solutions are considerably ionized into zirconyl ions,  $\text{ZrO}^{2+}$ , and fatty acid anions,  $\text{RCOO}^-$  (where R is  $\text{C}_5\text{H}_{11}$ ,  $\text{C}_7\text{H}_{15}$ , and  $\text{C}_9\text{H}_{19}$  for caproate, caprylate, and caprate,

**Table 2. Critical Micellar Concentration (CMC), Garnsey's Constant ( $G$ ), Bachem's Constants ( $A$  and  $B$ ), Limiting Apparent Molar Volume ( $\phi_v^\infty$ ), Limiting Apparent Molar Compressibility ( $\phi_k^\infty$ ), Gucker's Limiting Law Slope ( $S_k$ ), Masson's Slope ( $S$ ), Extrapolated Value of the Speed of Sound ( $u_0$ ), and Extrapolated Value of Isentropic Compressibility ( $k_s^\infty$ ) of Zirconyl Soaps in Xylene + Methanol at  $(40 \pm 0.05)^\circ\text{C}$** 

soap	$10^2\text{CMC}$ / (mol dm <sup>-3</sup> )	$G$ /(ms <sup>-1</sup> dm <sup>3</sup> )	$-10^{10}A$ / (m <sup>2</sup> N <sup>-1</sup> mol <sup>-1</sup> dm <sup>3</sup> )	$10^{10}B$ / (m <sup>2</sup> N <sup>-1</sup> mol <sup>-3/2</sup> dm <sup>9/2</sup> )	$-10^3\phi_v^\infty$ / (m <sup>3</sup> mol <sup>-1</sup> )	$-10^7\phi_k^\infty$ / (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-1</sup> )	$10^7S_k$ / (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-3/2</sup> dm <sup>3/2</sup> )	$S$ / (m <sup>3</sup> mol <sup>-3/2</sup> dm <sup>3/2</sup> )	$u_0(\text{ex})$ / ms <sup>-1</sup>	$10^{10}k_s^\infty(\text{ex})$ / (m <sup>2</sup> N <sup>-1</sup> )
caproate	5.00	115	3.00	0.00	142.0	4.14	0.429	0.138	1080.7	10.200
caprylate	4.70	135	4.18	1.86	170.0	5.51	1.858	0.141	1080.8	10.196
caprate	4.30	175	5.32	3.14	200.5	6.98	4.142	0.142	1080.9	10.195
experimental value									1080.8	10.195

respectively). The ions in the solutions are surrounded by a layer of solvent molecules firmly bound and oriented toward the ions (10). The orientation of solvent molecules around the ions is attributed to the influence of the electrostatic field of the ions, and thus the internal pressure increases which lowers the compressibility of the solutions; i.e., the solutions become harder to compress (13). The decrease in isentropic compressibility at higher soap concentrations may be explained on the basis of close packing of the ionic head groups in the micelles, resulting in an increase in ionic repulsion and finally internal pressure.

The results of isentropic compressibility  $k_s$  have been explained in terms of Bachem's (1) equation

$$k_s = k_s^\circ + Ac + Bc^{3/2} \quad (6)$$

where  $A$  and  $B$  are constants,  $c$  is the concentration of the soap, and  $k_s^\circ$  is the isentropic compressibility of the solvent mixture. The values of  $A$  and  $B$  have been determined from the intercept and slope of the plots of  $(k_s - k_s^\circ)/c$  against  $c^{1/2}$ , and it was found that the values of  $A$  decrease while those of  $B$  increase with an increase in the chain length of the soap molecules (Table 2).

It follows from Debye-Huckel's theory that the apparent molar compressibility  $\phi_k$  is related to concentration  $c$  by the relationship

$$\phi_k = \phi_k^\circ + S_k c^{1/2} \quad (7)$$

where  $\phi_k^\circ$  is the limiting apparent molar compressibility and  $S_k$  is a constant. The plots of  $\phi_k$  against  $c^{1/2}$  are linear for dilute soap solutions. The values of  $\phi_k^\circ$  and  $S_k$  have been obtained from the intercept and the slope of the plots of  $\phi_k$  against  $c^{1/2}$ . The positive values of  $S_k$  (Table 2) signify a considerable soap-solvent interaction in dilute soap solutions (7, 8). The values of  $\phi_k^\circ$  become more negative at higher soap concentrations (Table 2), which suggests that the solvent becomes less compressible in dilute solutions. Hence, the solute-solvent interactions decrease with increasing soap concentration.

The densities of the solution  $\rho$  of zirconyl soaps in xylene + methanol were found to obey Root's equation

$$\rho = \rho_0 + Ac - Bc^{3/2} \quad (8)$$

where  $\rho_0$  is the density of the solvent mixture and the values of the constants  $A$  and  $B$  depend upon the nature of the solute and solvent. The validity of eq 8 justifies the use of Masson's equation (eq 9) for the estimation of

$$\phi_v = \phi_v^\circ + S_v c^{1/2} \quad (9)$$

apparent molar volume  $\phi_v$ , where  $\phi_v^\circ$  is the limiting apparent molar volume and  $S_v$  is a constant. The values of  $\phi_v^\circ$  and  $S_v$  have been evaluated from the intercept and slope of the plot of  $\phi_v$  against  $c^{1/2}$  (Table 2). The decrease in the values of  $\phi_v^\circ$  with increasing chain length of the soap suggests that the solute-solvent interaction decreases with increasing chain length of the soap. The values of  $S_v$  were found to be positive for zirconyl soaps, suggesting strong

ion-ion interactions (2). The results are in agreement with the results reported by Masson (6) for electrolytic solutions.

The results of speed of sound measurements confirm that there is a significant interaction between the soap and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably below the critical micellar concentration.

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