

# Ultrasonic Studies of Molecular Interactions in the Solution of Manganese Soaps

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Ultrasonic measurements were made on manganese soaps (caproate, caprylate, and caprate) in propan-1-ol with a view to determine the critical micellar concentration (cmc), soap-solvent interaction, and various acoustic and thermodynamic parameters. The values of cmc decrease with the increase in the chain length of the soap. The ultrasonic velocity, apparent molar compressibility, and apparent molar volume of the solution of manganese soaps increase while the adiabatic compressibility and solvation number decrease with increasing concentration of the soap. The results suggested that there is a significant interaction between the soap and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably above the cmc.

## Introduction

Metal soaps are widely used in different industries, and they play an important role in colloid phenomena. The physico-chemical characteristic and the structure of these soaps depend largely on the method and conditions of preparation. The method of preparation, properties, and uses of metal soaps have been reviewed by several researchers (1-5). The study of molecular interactions has been a subject of extensive investigations by IR (6, 7), NMR (8, 9), Raman (10), and ultrasonic absorption (11-13) measurements. The complementary use of ultrasonic measurements can provide interesting information on the specificities of ion-solvent interaction related to the structure of the solute and on the reciprocal effects which arise in the solvents. However, the studies on ultrasonic measurements of the soap solutions have not drawn adequate attention, although such a study is likely to give more information on the soap-solvent interaction.

The present work deals with the measurements of the ultrasonic velocity of the solutions of manganese soaps in propan-1-ol, and the results have been used to study the solute-solvent interaction and to evaluate the cmc and various acoustic and thermodynamic parameters.

## Experimental Section

Chemicals used were AR/GR (E. Merck) grade. The manganese soaps (caproate, caprylate, and caprate) were prepared by direct metathesis of the corresponding potassium soap with the required amount of aqueous solution of manganese acetate at 50-55 °C under vigorous stirring. The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreacted acid. The purity of the soaps was checked by elemental analysis, and the results were found to be in agreement with the theoretically calculated values. The absence of a hydroxyl group in the soaps was confirmed by their IR spectrum.

The ultrasonic velocity measurements were recorded on a multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40 ± 0.05 °C using a crystal of 1-MHz frequency. The uncertainty of velocity measurements is ±0.2%. The densities of the solvent and the solutions were measured with a dilatometer. The volume of the dilatometer

was 15 cm<sup>3</sup>, and the accuracy of the density results was ±0.0001.

The adiabatic compressibility,  $\beta$ , apparent molar compressibility,  $\phi_K$ , apparent molar volume,  $\phi_V$  (14), and solvation number,  $S_n$  (15) were calculated by using the following relationships:

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

$$\phi_K = (1000/c\rho_0)\chi\rho_0\beta - \beta_0\rho + M\beta_0/\rho_0 \quad (2)$$

$$\phi_V = (1000/c\rho_0)\chi\rho_0 - \rho + M/\rho_0 \quad (3)$$

$$S_n = (n_0/n)\chi(1 - \bar{V}\beta/n_0\bar{V}_0\beta_0) \quad (4)$$

where  $u$ ,  $u_0$ ;  $\rho$ ,  $\rho_0$ ;  $\beta$ ,  $\beta_0$ ; and  $\bar{V}$ ,  $\bar{V}_0$  are the ultrasonic velocity, density, adiabatic compressibility, and molar volume of the solution and solvent, respectively,  $n$  and  $n_0$  are the number of moles of the solute and solvent, respectively, and  $M$ ,  $K$ , and  $c$  are the molecular weight of the solute, temperature-dependent Jacobson's constant, and concentration (mol dm<sup>-3</sup>).

## Results and Discussion

The ultrasonic velocity,  $u$ , of the solutions of manganese soaps (caproate, caprylate, and caprate) in propan-1-ol increases with increasing concentration of soap and with the chain length of the soap (Table I). The variation of ultrasonic velocity with soap concentration depends on the concentration derivatives of density,  $\rho$ , and adiabatic compressibility,  $\beta$ :

$$\frac{du}{dc} = -\frac{u}{2} \left[ \frac{1}{\rho} \left( \frac{d\rho}{dc} \right) + \frac{1}{\beta} \left( \frac{d\beta}{dc} \right) \right] \quad (5)$$

The results show that the density increases while the adiabatic compressibility decreases with increasing soap concentration; i.e., the quantity  $d\rho/dc$  is positive, while  $d\beta/dc$  is negative. Since the values of  $[(1/\beta)(d\beta/dc)]$  are larger than the values of  $[(1/\rho)(d\rho/dc)]$  for these soap solutions, the concentration derivative of velocity  $du/dc$  is positive; i.e., the ultrasonic velocity rises with soap concentration.

The plots of ultrasonic velocity vs soap concentration for solutions of manganese soaps in propan-1-ol show a break at a definite soap concentration which corresponds to the cmc of the soap. The cmc decreases with increasing chain length of the soap (Table II). The micellization process is due to the energy change arising from the polar head groups of the soap molecules. The micelles are held together by van der Waals forces acting between the hydrocarbon chains of parallel layers and strong dipole-dipole interactions between polar heads.

The variation of ultrasonic velocity,  $u$ , with soap concentration,  $c$ , follows the relationship

$$u = u_0 + Gc \quad (6)$$

where  $u_0$  is the ultrasonic velocity in pure solvent and  $G$  is Garnsey's constant (16). The calculated values of Garnsey's constant increase with increasing chain length of the soap molecule. The plots were extrapolated to zero soap concentration, and the extrapolated values of velocity,  $u_0$ , are in close agreement with the experimental velocity (1124.6 m/s) in solvent, indicating that the soap molecules do not aggregate up

**Table I. Ultrasonic Velocity  $u$ , Density  $\rho$ , Adiabatic Compressibility  $\beta$ , Apparent Molar Compressibility  $\phi_K$ , Apparent Molar Volume  $\phi_v$ , and Solvation Number  $S_n$  for Manganese Soaps (Caproate, Caprylate, and Caprate) in Propan-1-ol at  $40 \pm 0.05$  °C**

$c/$ (mol dm <sup>-3</sup> )	$\rho \times 10^{-3}/$ (kg m <sup>-3</sup> )	$u/$ (m s <sup>-1</sup> )	$\beta \times 10^{10}/$ (m <sup>2</sup> N <sup>-1</sup> )	$-\phi_K \times 10^7/$ (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-1</sup> )	$-\phi_v \times 10^2/$ (dm <sup>3</sup> mol <sup>-1</sup> )	$S_n$
Manganese Caproate						
0.001	0.7934	1125.2	9.955	21.03	63.54	21.47
0.002	0.7935	1126.1	9.938	19.64	39.69	22.14
0.003	0.7936	1126.8	9.924	18.18	31.74	21.02
0.004	0.7937	1127.6	9.910	17.45	27.77	20.46
0.005	0.7938	1128.3	9.896	17.01	25.38	20.13
0.006	0.7939	1129.0	9.882	16.72	23.79	19.90
0.007	0.7941	1129.4	9.873	15.98	24.92	18.78
0.008	0.7945	1129.5	9.866	15.48	29.72	17.61
0.009	0.7948	1129.8	9.857	15.18	31.70	17.00
0.010	0.7952	1130.1	9.847	15.12	34.85	16.64
Manganese Caprylate						
0.001	0.7934	1126.3	9.936	40.03	63.53	46.97
0.002	0.7936	1127.4	9.914	32.27	47.63	38.24
0.003	0.7937	1128.4	9.895	28.27	37.03	34.00
0.004	0.7938	1129.5	9.874	26.76	31.73	32.54
0.005	0.7939	1130.5	9.856	25.26	28.55	30.86
0.006	0.7941	1131.1	9.843	23.64	29.07	28.62
0.007	0.7945	1131.4	9.833	22.41	33.97	26.45
0.008	0.7949	1131.6	9.824	21.36	37.63	24.66
0.009	0.7952	1132.0	9.814	20.46	38.72	23.41
0.010	0.7956	1132.4	9.802	20.17	41.16	22.68
Manganese Caprate						
0.001	0.7935	1127.2	9.919	58.29	79.41	69.78
0.002	0.7936	1128.6	9.893	42.74	47.62	52.33
0.003	0.7938	1130.0	9.866	38.35	42.31	46.97
0.004	0.7939	1131.6	9.837	36.33	35.69	44.95
0.005	0.7941	1132.8	9.813	34.37	34.89	42.40
0.006	0.7944	1133.1	9.804	30.77	36.99	37.36
0.007	0.7948	1133.4	9.794	28.52	40.75	33.93
0.008	0.7953	1133.6	9.785	26.86	45.54	31.20
0.009	0.7956	1133.8	9.778	25.08	45.74	28.77
0.010	0.7960	1134.1	9.768	24.07	47.48	27.48

**Table II. Values of Cmc and Constants of Equations 7-9 for Manganese Soaps in Propan-1-ol at  $40 \pm 0.05$  °C**

soap	$cmc \times 10^3/$ (dm <sup>-3</sup> mol)	$G \times 10/$ (mol <sup>-1</sup> s <sup>-1</sup> dm <sup>4</sup> )	$A \times 10^{10}$	$B \times 10^8$	$-\phi_K^0 \times 10^7/$ (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-1</sup> )	$-\phi_v^0/$ (dm <sup>3</sup> mol <sup>-1</sup> )	$S_K \times 10^6/$ (mol <sup>-3/2</sup> dm <sup>13/2</sup> N <sup>-1</sup> kg <sup>-1</sup> )	$S_v/$ (mol <sup>-3/2</sup> dm <sup>9/2</sup> )
caproate	6.1	812.5	-19.5	0.8	23.5	0.68	0.9	6.2
caprylate	5.6	1000.0	-34.5	1.6	43.5	0.96	1.8	10.4
caprate	5.1	1400.0	-52.0	2.8	54.5	1.10	3.1	12.2

to an appreciable extent above the cmc.

The adiabatic compressibility of the solution of manganese soaps decreases with the increase in soap concentration as well as with the chain length of the soap (Table I). The decrease in adiabatic compressibility is attributed to the fact that the soap molecules in dilute solutions are considerably ionized into metal cation Mn<sup>2+</sup> and fatty acid anions RCOO<sup>-</sup> (where R is C<sub>6</sub>H<sub>11</sub>, C<sub>7</sub>H<sub>15</sub>, and C<sub>9</sub>H<sub>19</sub> for caproate, caprylate, and caprate, respectively) and these ions 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 the electrostatic field of the ions, and thus, the internal pressure increases, which lowers the compressibility of the soap solutions; i.e., the solutions become harder to compress (17).

The plots of adiabatic compressibility,  $\beta$ , vs soap concentration,  $c$ , indicate a break at a definite soap concentration which corresponds to the cmc of these soaps. The  $\beta$ - $c$  plots are extrapolated to zero soap concentration, and the extrapolated values of adiabatic compressibility,  $\beta_0$ , are in close agreement with the experimental value of adiabatic compressibility of propan-1-ol ( $9.971 \times 10^{-10}$  m<sup>2</sup> N<sup>-1</sup>).

The results of adiabatic compressibility have been explained in terms of Bachem's equation (18)

$$\beta[(m^2 N^{-1}) = \beta_0/(m^2 N^{-1}) + A(c/(dm^3 mol^{-1})) + B(c/(dm^3 mol^{-1}))^{3/2} \quad (7)$$

where  $A$  and  $B$  are constants,  $c$  is the molar concentration of soap, and  $\beta$  and  $\beta_0$  are the adiabatic compressibilities of the solution and solvent, respectively. The constants  $A$  and  $B$  have been determined from the intercept and slope of the plots of  $(\beta - \beta_0)/c$  vs  $c^{1/2}$  and are recorded in Table II. The values of  $A$  decrease while those of  $B$  increase with increasing chain length of the soap molecule.

The values of apparent molar compressibility,  $\phi_K$ , and apparent molar volume,  $\phi_v$ , increase with increasing soap concentration (Table I). The values of apparent molar volume are found to be negative for small soap concentrations which suggests that when a small amount of soap is added to the solvent, there is an initial decrease in the molar volume of the solution. This may be due to the phenomenon of electrostriction in which the cations Mn<sup>2+</sup> with a strong electric field pack solvent molecules around themselves in a smaller volume than in the bulk of the solvent.

It follows from Debye-Huckel's theory and Masson's equation (19) that the apparent molar compressibility,  $\phi_K$ , and apparent molar volume,  $\phi_v$ , are related to the molar concentration of the soap by the relationships

$$\phi_K = \phi_K^0 + S_K c^{1/2} \quad (8)$$

and

$$\phi_v = \phi_v^0 + S_v c^{1/2} \quad (9)$$

where  $\phi_K^\circ$  and  $\phi_V^\circ$  are limiting apparent molar compressibility and limiting apparent molar volume, respectively.  $S_K$  and  $S_V$  are constants. The values of  $\phi_K^\circ$  and  $\phi_V^\circ$  and constants  $S_K$  and  $S_V$  have been obtained from the intercept and slope of the plots of  $\phi_K$  vs  $c^{1/2}$  and  $\phi_V$  vs  $c^{1/2}$  below the cmc and are recorded in Table II. The comparison of the data with that of electrolytes (20) shows that these soaps behave as simple electrolytes in dilute solutions.

The values of solvation number,  $S_n$ , of the solutions of manganese soaps in propan-1-ol decrease with increasing soap concentration (Table I). The plots of  $S_n$  vs  $c$  are characterized by a break at the cmc. The values of the solvation number exhibit a marked change above the cmc which may be attributed to more intake of solvent molecules above the cmc to reduce the repulsive forces acting between polar heads of ionic micelles.

Data on ultrasonic velocity show that the manganese soaps behave as simple electrolytes in solutions. The results confirm that there is a significant interaction between the soap-solvent molecules in dilute solutions, and the soap molecules do not aggregate appreciably above the cmc.

**Registry No.** Manganese caproate, 16571-42-9; manganese caprylate, 6819-13-2; manganese caprate, 7436-86-4; 1-propanol, 71-23-8.

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# Excess Volumes of 1,2-Dibromoethane + 1-Propanol, + 1-Butanol, or + 1-Pentanol from 293.15 to 333.15 K

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**Excess molar volumes  $V^E$  of 1,2-dibromoethane with 1-propanol, 1-butanol, and 1-pentanol have been measured at five temperatures, from 293.15 to 333.15 K. NMR shifts have also been reported for the mixtures of 1,2-dibromoethane with 1-butanol at 303.15 K.  $V^E$  is positive in all the mixtures studied over the whole range of compositions at all temperatures and increases in the order 1-pentanol > 1-butanol > 1-propanol. The temperature coefficient of  $V^E$  is positive. The positive excess molar volumes have been ascribed to deassociation of self-associated alcohol aggregates.**

## Introduction

We report new data on excess molar volumes,  $V^E$ , for three binary mixtures of 1,2-dibromoethane with 1-propanol, 1-butanol, and 1-pentanol as a function of temperature from 293.15 to 333.15 K. We also report NMR chemical shifts for the mixtures of 1,2-dibromoethane in 1-butanol at 303.15 K. The experimental results have been used to examine the effect of hydrogen bonding between like and unlike molecules of  $V^E$ . The results have also been used to study the effect of temperature on  $V^E$ .

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**Table I. Normal Boiling Points,  $T_b$ , and Densities,  $\rho$ , of Pure Components**

component	$T_b$ /K		$\rho$ (303.15 K)/ (kg m <sup>-3</sup> )	
	this work	lit. (2)	this work	lit. (3)
1,2-dibromoethane	404.15	404.51	2158.9	
1-propanol	370.10	370.301	795.36	795.61
1-butanol	390.65	390.875	802.51	801.91
1-pentanol	410.65	411.133	806.94	807.12

## Experimental Section

**Apparatus and Procedure.** The batch dilatometers used for measuring  $V^E$  were similar to that described by Choudary and Naidu (1). The mixing cell contained two bulbs of different capacities that were connected through a U-tube with mercury separating the two compartments. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a Teflon stopper. Twelve dilatometers of this type were used to cover the whole range of compositions. The composition of each mixture was determined directly by weighing. After the experiment a few mixtures were analyzed on GC (Schimadzu GC, R1A, dual column gas chromatograph with flame ionization detector) to confirm the correctness of the compositions of mixtures. The measurements were made using a thermostatic bath controlled to