Research Paper Chemistry

# Comparative Ultrasonic and Conductometric Studies of Solutions of Cadmium Soaps With Benzene-Methanol


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**ABSTRACT**

Densities (ρ), viscosities (η), ultrasonic velocities (u) and conductivities (κ) have been measured by using specific gravity bottle, Ostwald's viscometer, single frequency ultrasonic interferometer (1 MHz frequency) and conductivity meter respectively for soap concentration for solutions of cadmium soaps in benzene-methanol (50%-50% V/V). Various acoustical parameters viz. specific acoustic impedance, apparent molar compressibility, apparent molar volume and molar sound velocity of the solutions of Cd soaps at 40±0.05°C were calculated from these experimental data. The results are interpreted in terms of molecular interactions between components of solutions.

**KEYWORDS**

**Introduction**

At present the information on physico-chemical characteristics and structure of alkaline earth metal soap is of great importance due to their diversified applications in various fields. The popularity of metallic soaps is due to their importance in technology and in industry. The physico-chemical characteristics and structure of metal soaps can be controlled up to an extent by the method and conditions of their preparation and so the studies of soaps are of great significance for their uses in various industries under different conditions. While major developments have taken place in the study of alkali and transition metal soaps, the investigations on alkaline earth metal soaps remained almost untouched with the result that only few references are available in their relatively unexplored field. The present work deals with the physico-chemical properties of cadmium soaps in solid state as well as in solutions. Ultrasonic velocity of sound waves in a medium is essentially related to the binding forces between the molecules. Ultrasonic technique has been effectively employed to study the properties of any substance to understand the nature of molecular interactions in pure liquid[1], liquid mixtures[2-5] and ionic interactions in electrolytic solutions[6-7]. The conductivity was also measured at various concentrations. Dissolution of an electrolyte in water is accompanied by electrostriction of the solvent beneath the action of electrostatic fields of newly produced ions[8].

**Experimental**

The chemicals used in the present work were analytical reagent (AR). In all systems, the various concentrations of the mixtures were prepared in terms of % (V/V). Water used was prepared by distilling ordinary water thrice over alkaline KMnO4 in all glass apparatus. The specific conductance of water so obtained was 1.3x10-4 Ωcm-[1]

**Density measurement**

The density of aqueous solutions is measured using a 10 mL specific gravity bottle. The temperature is maintained constant by immersing the bottle in Juloba thermostat for 15 min.

**Viscosity measurement**

The viscosity of the aqueous solutions is measured using an Ostwald's viscometer calibrated with doubly distilled water. The Ostwald's Viscometer with the experimental liquid is immersed in a temperature controlled water bath. An electronic stop watch was employed to measure the time of flow. The viscosity can be calculated using the formula,

**Velocity measurement**

The ultrasonic velocity measurements of solutions of cadmium soaps were carried out with a Multifrequency Ultrasonic Interferometer (Mittal Enterprises, New Delhi) at frequency of 1 MHz at constant temperature (40±0.05°C). The uncertainity of velocity measurements was 0.2 per cent.

**Conductivity measurement**

Conductivity measurements are carried out using Conductivity meter. Before and after measurements, the instrument was calibrated with KCl solution. Each measurement was repeated three times and the average values were calculated.

**Theory**

From the observed values the adiabatic compressibility, β, intermolecular free length, $L_f$[9], specific acoustic impedance, Z[10], apparent molar compressibility, , apparent molar volume, [11], relative association, $R_A$[12] molar sound velocity, R, were calculated by using the following relationships :

1. $\beta_S = \frac{1}{V^2 \rho}$

2. $L_F = K\sqrt{\hat{a}_S}$

3. $Z = V \cdot \rho$

4. $\phi_K = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0}$

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

6. $R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{V_0}{V}\right)^{\frac{1}{3}}$

where, v, $v_0$; ρ, $\rho_0$ and β, $\beta_0$ are the ultrasonic velocity, density and adiabatic compressibility of the solute and solvent, respectively. M is molecular weight of solutes. K and C are the temperature dependent Jacobson's constant and concentration in mol l–1, respectively.

The conductivity measurements of the solutions of cadmium soaps in benzene-methanol (50%-50% V/V) were made with a Elico CM 183 using dipping type conductivity cell with plati-

nized electrodes.

**Results and Discussion**

The ultrasonic velocity of the solutions of cadmium soaps (caproate, caprylate, caprate, laurate and myristate) in pure benzene increases with increasing concentration and chain length of the soap molecules. The results are in agreement with the results reported for electrolytic solutions[13-15] which shows that cadmium soaps behave as simple electrolyte in solutions. The plots of ultrasonic velocity, v Vs. soap concentration, C for solutions of cadmium soaps in benzene-methanol (50% - 50% V/V) show a break at a definite soap concentration which corresponds to the CMC of the soap increasing chain length of the soap molecules. 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 Vander Wall's forces acting between the hydrocarbons chains of parallel layers and strong dipole-dipole interaction between polar heads.

The adiabatic compressibility, β, of the solutions of Cd soaps decreases with increase in soap concentration and chainlength of the soap molecules. The decrease in adiabatic compressiblity is attributed to the fact that the soap molecules in dilute solutions are considerably ionised into metal cations ($Cd^{+2}$) and fatty acid anions, $RCOO^-$ (where R is $C_5H_{11}$, $C_7H_{15}$, $C_9H_{19}$, $C_{11}H_{23}$ and $C_{13}H_{27}$ or caproate, caprylate, caprate, laurate and myristate, respectively) and these ions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions.

The values of intermolecular free length, $L_f$, decreases while specific acoustic impedance, Z, increases with the increase in concentration and chain length of soap molecules which indicates that there is a significant interaction between the soap and solvent molecules.[16]

The negative values of apparent molar compressibility decrease linearly with concentration, but this decrease is sharp for pre-micellization region as compared to post micellization indicating poor compressibility at higher concentrations. The values of apparent molar volume are found to be negative for small soap concentration 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. The values of relative association, $R_A$ decreases with increasing soap concentration. The plots of relative association, $R_A$ Vs. soap concentration C are characterized by a break at a definite soap concentration which corresponds to the CMC of the soap. The decrease in the values of relative association with increasing soap concentration is attributed to the fact that the solvation of ions decreases with increasing soap concentration.

**Table 1 : Ultrasonic velocity vs Concentration (Cadmium soaps)**

| Concentration C mol $dm^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 1115 | 1120.0 | 1125.0 | 1128.0 | 1132.0 |
| 2 | 1126 | 1131.0 | 1136.0 | 1140.0 | 1145.0 |
| 3 | 1137 | 1142.0 | 1148.0 | 1154.0 | 1158.0 |
| 4 | 1147 | 1153.0 | 1159.0 | 1165.0 | 1170.0 |
| 5 | 1157 | 1162.0 | 1166.0 | 1170.0 | 1175.0 |
| 6 | 1163 | 1166.0 | 1169.0 | 1174.0 | 1177.0 |
| 7 | 1165 | 1168.0 | 1173.0 | 1177.0 | 1180.0 |
| 8 | 1168 | 1172.0 | 1176.0 | 1180.0 | 1183.0 |
| 9 | 1171 | 1176.0 | 1179.0 | 1183.0 | 1186.0 |
| 10 | 1174 | 1179.0 | 1183.0 | 1187.0 | 1190.0 |

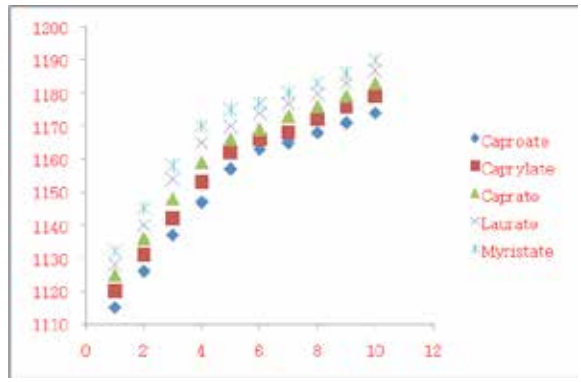



**Table 2 : Density Vs Concentration (Cadmium soaps)**

| Concentration C mol $dm^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 0.6759 | 0.6762 | 0.6764 | 0.6765 | 0.6767 |
| 2 | 0.6767 | 0.6769 | 0.6773 | 0.6775 | 0.6778 |
| 3 | 0.6774 | 0.6777 | 0.6780 | 0.6784 | 0.6789 |
| 4 | 0.6782 | 0.6785 | 0.6788 | 0.6793 | 0.6799 |
| 5 | 0.6789 | 0.6793 | 0.6795 | 0.6799 | 0.6802 |
| 6 | 0.6792 | 0.6795 | 0.6798 | 0.6802 | 0.6806 |
| 7 | 0.6794 | 0.6798 | 0.6801 | 0.6805 | 0.6808 |
| 8 | 0.6797 | 0.6800 | 0.6803 | 0.6807 | 0.6812 |
| 9 | 0.6798 | 0.6802 | 0.6806 | 0.6810 | 0.6815 |
| 10 | 0.6801 | 0.6805 | 0.6808 | 0.6813 | 0.6818 |

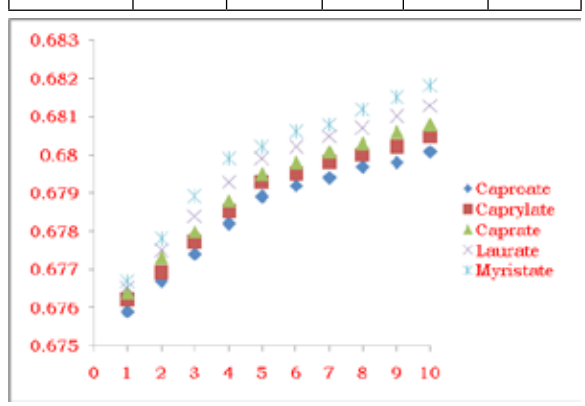



**Table 3 : Viscosity Vs Concentration (Cadmium soaps)**

| Concentration C mol $dm^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 0.444 | 0.446 | 0.448 | 0.450 | 0.454 |
| 2 | 0.452 | 0.456 | 0.460 | 0.464 | 0.469 |
| 3 | 0.462 | 0.467 | 0.471 | 0.476 | 0.483 |
| 4 | 0.471 | 0.477 | 0.482 | 0.487 | 0.496 |
| 5 | 0.479 | 0.485 | 0.490 | 0.496 | 0.503 |
| 6 | 0.485 | 0.491 | 0.497 | 0.502 | 0.509 |
| 7 | 0.490 | 0.495 | 0.501 | 0.507 | 0.514 |
| 8 | 0.494 | 0.499 | 0.507 | 0.513 | 0.520 |
| 9 | 0.498 | 0.504 | 0.510 | 0.517 | 0.526 |
| 10 | 0.503 | 0.509 | 0.515 | 0.523 | 0.531 |

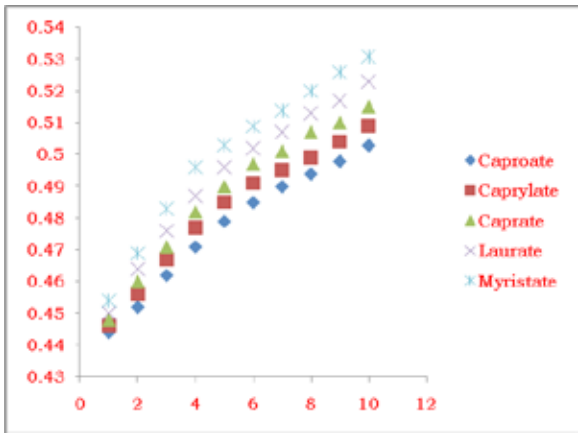



**Table 4 : Adiabatic compressibility Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myriswtate |
|---|---|---|---|---|---|
| 1 | 11.901 | 11.787 | 11.681 | 11.618 | 11.532 |
| 2 | 11.655 | 11.549 | 11.441 | 11.358 | 11.253 |
| 3 | 11.419 | 11.314 | 11.192 | 11.069 | 11.020 |
| 4 | 11.208 | 11.086 | 10.967 | 10.846 | 10.744 |
| 5 | 11.003 | 10.903 | 10.825 | 10.744 | 10.648 |
| 6 | 10.885 | 10.825 | 10.764 | 10.667 | 10.606 |
| 7 | 10.845 | 10.783 | 10.686 | 10.608 | 10.549 |
| 8 | 10.784 | 10.706 | 10.629 | 10.551 | 10.489 |
| 9 | 10.728 | 10.630 | 10.570 | 10.493 | 10.432 |
| 10 | 10.668 | 10.575 | 10.495 | 10.417 | 10.357 |

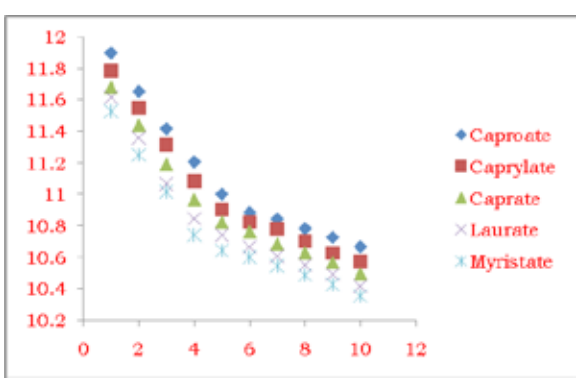



**Table 5 : Intra molecular free length Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 34.1579 | 33.9939 | 33.8408 | 33.7494 | 33.6242 |
| 2 | 33.8031 | 33.6489 | 33.4913 | 33.3696 | 33.2149 |
| 3 | 33.4591 | 33.3049 | 33.1248 | 32.9423 | 32.8693 |
| 4 | 33.1485 | 32.9676 | 32.7902 | 32.6088 | 32.4551 |
| 5 | 32.8439 | 32.6944 | 32.5772 | 32.4551 | 32.3098 |
| 6 | 32.6674 | 32.5772 | 32.4853 | 32.3386 | 32.2459 |
| 7 | 32.6073 | 32.5139 | 32.3674 | 32.2490 | 32.1592 |
| 8 | 32.5155 | 32.3976 | 32.2809 | 32.1623 | 32.0676 |
| 9 | 32.4309 | 32.2825 | 32.1912 | 32.0734 | 31.9803 |
| 10 | 32.3401 | 32.1988 | 32.0768 | 31.9574 | 31.8652 |

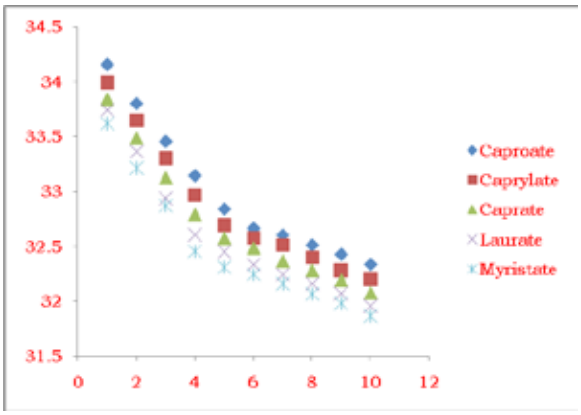



**Table 6 : Specific Acoustic Impedence Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 7.5363 | 7.5734 | 7.6095 | 7.6309 | 7.6602 |
| 2 | 7.6196 | 7.6557 | 7.6941 | 7.7235 | 7.7608 |
| 3 | 7.7020 | 7.7393 | 7.7834 | 7.8287 | 7.8617 |
| 4 | 7.7789 | 7.8231 | 7.8672 | 7.9138 | 7.9548 |
| 5 | 7.8548 | 7.8935 | 7.9229 | 7.9548 | 7.9924 |
| 6 | 7.8991 | 7.9229 | 7.9469 | 7.9856 | 8.0107 |
| 7 | 7.9150 | 7.9401 | 7.9776 | 8.0095 | 8.0334 |
| 8 | 7.9388 | 7.9696 | 8.0003 | 8.0323 | 8.0586 |
| 9 | 7.9604 | 7.991 | 8.0243 | 8.0562 | 8.0826 |
| 10 | 7.9844 | 8.0207 | 8.0479 | 8.0870 | 8.1134 |

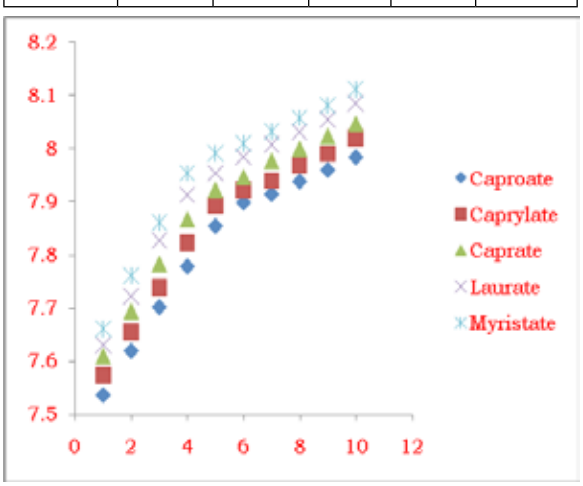



**Table 7: Apparent molar compressibility Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 1 | 5.088 | 10.431 | 15.329 | 18.186 | 22.169 |
| 2 | 8.175 | 10.571 | 13.100 | 14.975 | 17.390 |
| 3 | 9.025 | 10.601 | 12.439 | 14.318 | 15.096 |
| 4 | 9.185 | 10.537 | 11.855 | 13.238 | 14.421 |
| 5 | 9.210 | 10.087 | 10.731 | 11.436 | 12.259 |
| 6 | 8.511 | 8.908 | 9.312 | 10.005 | 10.421 |
| 7 | 7.492 | 7.841 | 8.410 | 8.865 | 9.183 |
| 8 | 6.858 | 7.233 | 7.603 | 7.989 | 8.291 |
| 9 | 6.321 | 6.753 | 6.994 | 7.321 | 7.574 |
| 10 | 5.926 | 6.267 | 6.572 | 6.870 | 7.082 |

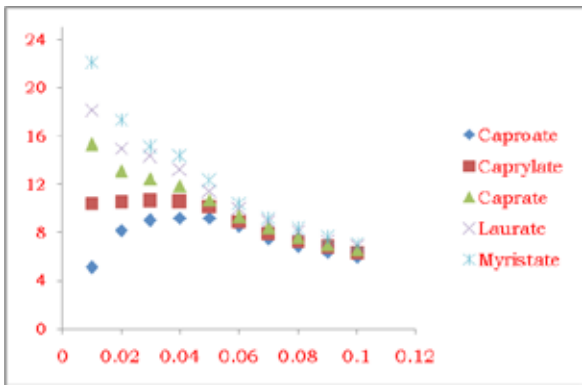



**Table 8 : Apparent molar Volume Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 0.01 | 7.40 | 11.84 | 14.80 | 16.28 | 19.24 |
| 0.02 | 9.62 | 11.10 | 14.06 | 15.54 | 17.76 |
| 0.03 | 9.87 | 11.35 | 12.83 | 14.80 | 17.27 |
| 0.04 | 10.36 | 11.46 | 11.10 | 14.43 | 16.64 |
| 0.05 | 10.36 | 11.54 | 12.13 | 13.32 | 14.21 |
| 0.06 | 9.37 | 10.11 | 10.85 | 11.84 | 12.82 |
| 0.07 | 8.46 | 9.30 | 9.93 | 10.78 | 11.41 |
| 0.08 | 7.95 | 8.51 | 9.06 | 9.81 | 10.73 |
| 0.09 | 7.23 | 7.89 | 8.55 | 9.21 | 10.03 |
| 0.10 | 6.95 | 7.25 | 7.99 | 8.73 | 9.47 |

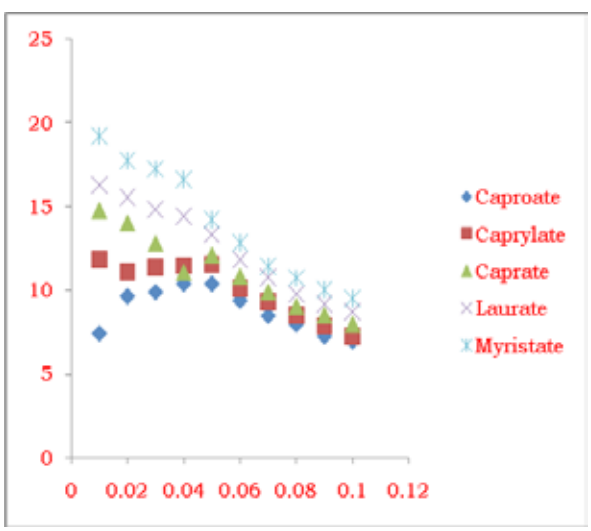
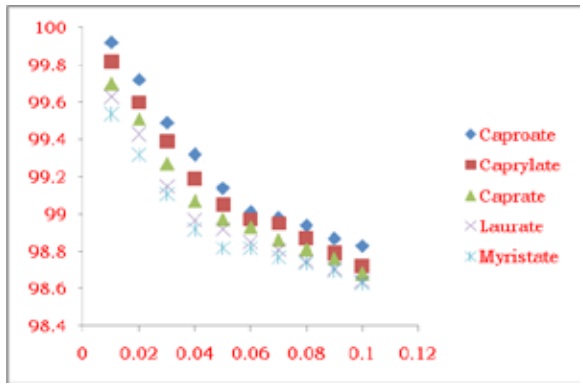



**Table 9 : Relative association Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 0.01 | 99.92 | 99.82 | 99.70 | 99.63 | 99.54 |
| 0.02 | 99.72 | 99.60 | 99.51 | 99.43 | 99.32 |
| 0.03 | 99.49 | 99.39 | 99.27 | 99.15 | 99.11 |
| 0.04 | 99.32 | 99.19 | 99.07 | 98.97 | 98.92 |
| 0.05 | 99.14 | 99.05 | 98.97 | 98.92 | 98.82 |
| 0.06 | 99.01 | 98.97 | 98.93 | 98.85 | 98.82 |
| 0.07 | 98.98 | 98.95 | 98.86 | 98.81 | 98.77 |
| 0.08 | 98.94 | 98.87 | 98.81 | 98.75 | 98.74 |
| 0.09 | 98.87 | 98.79 | 98.76 | 98.71 | 98.70 |
| 0.10 | 98.83 | 98.72 | 98.68 | 98.64 | 98.63 |




The increase in specific conductance with the increase in soap concentration may be due to the ionisation of cadmium soaps into simple metal cations $Cd^{2+}$ and fatty acid anions $RCOO^-$ (where, R is $C_5H_{11}$, $C_7H_{15}$, $C_9H_{19}$, $C_{11}H_{23}$ and $C_{13}H_{27}$ for caproate, caprylate, caprate, laurate and myristate) in solutions and due to the formation of micelles at higher soap concentrations. The plots of specific conductance, k Vs. soap concentration, C are characterised by an intersection of two straight lines at a definite soap concentration which corresponds to the critical micelle concentration (CMC) of the soap, indicating the formation of ionic micelles at this soap concentration. The results show that the values of CMC decreases with increasing chain length of fatty acid constituent of the soap. The molar conductance, μ of the cadmium soap solutions decreases with the increasing soap concentration. The decrease in molar conductance may be attributed to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionisation with the formation of micelles. The plots of molar conductance, μ Vs. square root of soap concentration, $C^{1/2}$ are not linear which indicates that these soaps behave as a simple electrolytes in these solutions.

**Table 10 : Conductance Vs Concentration (Cadmium soaps)**

| Concentration C mol dm$^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 10.0 | 5.42 | 6.03 | 6.53 | 6.78 | 7.02 |
| 9.4 | 5.27 | 5.78 | 6.25 | 6.55 | 6.82 |
| 8.8 | 5.08 | 5.62 | 6.05 | 6.30 | 6.50 |
| 8.3 | 5.02 | 5.45 | 5.95 | 6.25 | 6.48 |
| 7.7 | 4.87 | 5.32 | 5.74 | 5.95 | 6.30 |
| 7.2 | 4.66 | 5.12 | 5.63 | 5.84 | 6.08 |
| 6.8 | 4.58 | 4.86 | 5.42 | 5.72 | 5.87 |
| 6.1 | 4.48 | 4.83 | 5.25 | 5.53 | 5.73 |
| 5.7 | 4.35 | 4.56 | 5.03 | 5.35 | 5.65 |
| 5.1 | 3.95 | 4.35 | 4.86 | 5.23 | 5.40 |
| 4.7 | 3.67 | 4.20 | 4.75 | 5.04 | 5.26 |
| 4.2 | 3.41 | 3.78 | 4.44 | 4.84 | 5.05 |
| 3.8 | 3.18 | 3.52 | 4.13 | 4.43 | 4.86 |
| 2.4 | 2.89 | 3.25 | 3.75 | 4.12 | 4.75 |
| 3.1 | 2.65 | 3.01 | 3.53 | 3.95 | 4.53 |
| 2.8 | 2.44 | 2.74 | 3.26 | 3.62 | 4.24 |
| 2.4 | 2.32 | 2.61 | 2.85 | 3.45 | 3.85 |
| 2.1 | 2.04 | 2.32 | 2.74 | 3.13 | 3.62 |
| 1.9 | 1.86 | 2.23 | 2.51 | 2.94 | 3.40 |
| 1.7 | 1.67 | 2.02 | 2.28 | 2.65 | 3.15 |

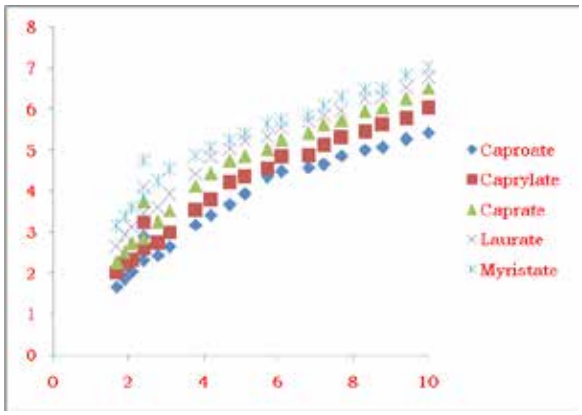
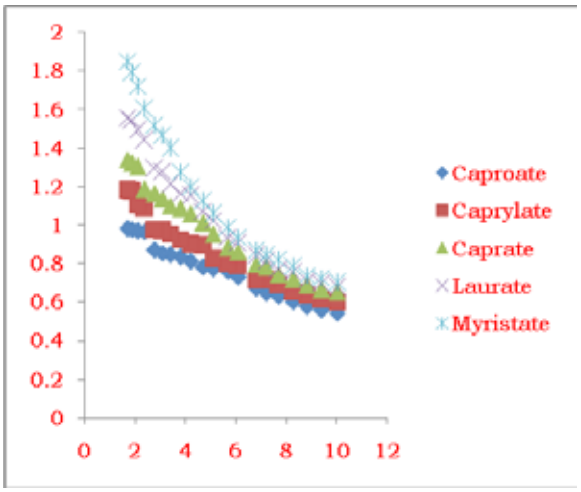



**Table 11 : Molar conductance Vs Concentration (Cadmium soaps)**

| Concentration C mol $dm^{-3}$ | Caproate | Caprylate | Caprate | Laurate | Myristate |
|---|---|---|---|---|---|
| 10.0 | 0.542 | 0.603 | 0.653 | 0.678 | 0.702 |
| 9.4 | 0.560 | 0.615 | 0.665 | 0.696 | 0.726 |
| 8.8 | 0.577 | 0.638 | 0.688 | 0.716 | 0.739 |
| 8.3 | 0.605 | 0.656 | 0.717 | 0.753 | 0.781 |
| 7.7 | 0.633 | 0.691 | 0.745 | 0.773 | 0.818 |
| 7.2 | 0.647 | 0.711 | 0.782 | 0.811 | 0.840 |
| 6.8 | 0.673 | 0.715 | 0.797 | 0.841 | 0.863 |
| 6.1 | 0.734 | 0.791 | 0.861 | 0.907 | 0.939 |
| 5.7 | 0.763 | 0.800 | 0.883 | 0.939 | 0.991 |
| 5.1 | 0.775 | 0.823 | 0.953 | 1.025 | 1.058 |
| 4.7 | 0.781 | 0.894 | 1.011 | 1.072 | 1.121 |
| 4.2 | 0.812 | 0.900 | 1.057 | 1.152 | 1.202 |
| 3.8 | 0.836 | 0.926 | 1.087 | 1.166 | 1.278 |
| 2.4 | 0.847 | 0.956 | 1.103 | 1.212 | 1.397 |
| 3.1 | 0.855 | 0.971 | 1.138 | 1.274 | 1.461 |
| 2.8 | 0.871 | 0.978 | 1.164 | 1.293 | 1.514 |
| 2.4 | 0.967 | 1.088 | 1.188 | 1.438 | 1.604 |
| 2.1 | 0.971 | 1.105 | 1.305 | 1.490 | 1.724 |
| 1.9 | 0.979 | 1.174 | 1.321 | 1.547 | 1.789 |
| 1.7 | 0.982 | 1.182 | 1.341 | 1.559 | 1.853 |




**Conclusion**

The results suggested that there is a significant interaction between the soap and solvent moelcules in dilute solutions and the soap molecules do not aggregate appreciably below the CMC. The results of ultrasonic measurements were found in close agreement with the conductivity results.

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