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# Micellar Behaviour and Various Acoustic Properties of Manganese Soaps

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**Abstract**

The studies of ultrasonic velocity in solution of manganese myristate and stearate soap in a mixture of benzene and methanol (7:3 v/v) have been used to evaluate various acoustic parameter and micellar behaviour. The result shows that critical micelle concentration decrease with chain length of fatty acid constituent of soap molecule. The results also confirms that soap molecules do not aggregate appreciably below the CMC and there is significant interaction between soap and solute molecules.

**Keywords:** Ultrasonic Measurements, Micellar, Acoustic,CMC,Ultrasonic Velocity, Manganese Myristate, Manganese Stearate

**Introduction**

The study of metallic soaps is becoming increasingly important in technological and academic fields. The application of these metal soaps depends largely on their physical state, stability and chemical reactivity together with their volatility and solubility in common solvents. The velocity of ultrasonic waves in aqueous solution of electrolytes has been extensively studied by several workers but less work has been paid to the solvation of salts in non aqueous solvents. several workers[1– 7] have been used the ultrasonic measurements to determine the ion solvent interaction and various acoustic parameter.

**Aim of the Study**

The present work deals with ultrasonic measurements of the solutions of manganese myristate and stearate in a mixture of benzene-methanol (7:3 v/v).The work has been initiated with a view to study the micellar behaviour, solute and solvent interaction and to calculate several allied parameters related to the acoustic properties of the soap solutions.

**Experimental**

All the chemical used were of BDH/AR grade. Manganese soaps (myristate and stearate) were prepared by the direct metathesis of corresponding potassium soaps with a slight excess of aqueous solution of manganese chloride. The soaps were dried and purified by recrystallization with a mixture of benzene and methanol and purity was checked by elemental analysis, IR absorption spectra and by determination of melting points. The soap solutions were prepared by dissolving known amount (weight) of soap in the mixture of benzene-methanol (7:3 v/v) and were kept 2 hour in thermostate at 40±0.05°C and then used for velocity measurements.

The ultrasonic velocity of soap solutions was measured by multifrequency ultrasonic pulse ECO interferometer type SDUI-003 at constant temperature 40±0.05°C at 1MHz frequency.

**Calculations**

The adiabatic compressibility, β, specific acoustic impedence, Z, intermolecular free length, L molal compressibility apparent molal volume and solvation number were calculated using the following equations.

$\beta = V^{-2}d^{-1}$

$Z = dV,$

$$L_f = \sqrt{\beta} \times K$$

$$\phi_k = \frac{1000}{Cd_0}[d_0\beta - \beta_0 d] + \frac{\beta_0 M}{d_0}$$

$$\phi_v = \frac{1000}{Cd_0}\left[d - d_0\right] + \frac{M}{d_0}$$

$$Sn = \frac{n_0}{n}\left(1 - \frac{\bar{v}\beta}{n_0 \bar{v}_0 \beta_0}\right)$$

Where K,C and V are temperature dependent Jacobson's constant,concentration and ultrasonic velocity respectively.

**Result and Discussion**

The ultrasonic velocity, v, with the increase in soap concentration, C. The variation of ultrasonic velocity, v, with the soap concentration, C depends on the concentration derivatives of density, d and adiabatic compressibility, β according to the relationship :

$$\frac{\partial v}{\partial c} = -\frac{v}{2}\left[\frac{1}{d}\frac{\partial d}{\partial c} + \frac{1}{\beta}\frac{\partial \beta}{\partial c}\right]$$

The results fromtables-1,2 show that the density, d increases while the adiabatic compressibility, β decreases with increasing soap concentration.

**Table 1**

**Ultrasonic Velocity And Other Acoustic Parameters Of Manganese Myristate In A Mixture Of Benzene And Methanol (7 : 3 V/V) AT 40 ± 0.05$^{O}$C.**

| S. No. | Conc, C g mol $l^{-1}$ | Density, d g $ml^{-1}$ | Velocity v × $10^{-4}$ cm $sec^{-1}$ | Adiabatic compressibility β × $10^{11}$ $cm^2$ $dyne^{-1}$ | Inter molecular free length, $L_f$ × $10^3$ cm | $\sqrt{C}$ × $10^2$ | Specific acoustic impedance, z × $10^{-4}$ gm $cm^{-2}$ $s^{-1}$ | β - $\beta_0$/C | Apparent molar compressibility - $\varphi_k$ × $10^{-6}$ $cm^2$ $dyne^{-1}$ | Apparent molar volume -$\varphi_v$ × $10^{-2}$ ml $mol^{-1}$ | Solvation number Sn × $10^{-4}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.001 | 0.834 | 11.1 | 9.60 | 6.29 | 3.2 | 9.324 | 10.0 | 1.02 | 2.29 | 21.42 |
| 2 | 0.002 | 0.835 | 11.2 | 9.52 | 6.26 | 4.5 | 9.367 | 9.0 | 0.93 | 3.48 | 11.08 |
| 3 | 0.003 | 0.836 | 11.2 | 9.46 | 6.24 | 5.5 | 9.401 | 8.0 | 0.83 | 3.47 | 7.49 |
| 4 | 0.004 | 0.837 | 11.2 | 9.40 | 6.22 | 6.3 | 9.437 | 7.5 | 0.78 | 4.06 | 5.82 |
| 5 | 0.005 | 0.838 | 11.3 | 9.27 | 6.18 | 7.1 | 9.506 | 8.6 | 0.89 | 4.17 | 4.89 |
| 6 | 0.006 | 0.841 | 11.4 | 9.10 | 6.12 | 7.7 | 9.612 | 10.6 | 1.07 | 7.83 | 4.33 |
| 7 | 0.007 | 0.843 | 11.5 | 8.94 | 6.07 | 8.4 | 9.711 | 10.8 | 1.17 | 9.29 | 3.94 |
| 8 | 0.008 | 0.844 | 11.6 | 8.78 | 6.01 | 8.9 | 9.808 | 11.5 | 1.24 | 9.99 | 3.62 |
| 9 | 0.009 | 0.846 | 11.7 | 8.63 | 5.96 | 9.5 | 9.907 | 11.8 | 1.29 | 10.92 | 3.37 |
| 10 | 0.010 | 0.848 | 11.8 | 8.46 | 5.90 | 10.0 | 10.013 | 12.4 | 1.34 | 14.27 | 3.18 |

**Table 2**

**Ultrasonic Velocity And Other Acoustic Parameters Of Manganese Stearate In A Mixture Of Benzene And Methanol (7 : 3 v/v) AT 40 ± 0.05$^{O}$C.**

| S. No. | Conc. C g mol $l^{-1}$ | Density, d g $ml^{-1}$ | Velocity v × $10^{-4}$ cm $sec^{-1}$ | Adiabatic compressibility β × $10^{11}$ $cm^2$ $dyne^{-1}$ | Inter molecular free length, $L_f$ × $10^3$ cm | $\sqrt{C}$ × $10^2$ | Specific acoustic impedance, z × $10^{-4}$ gm $cm^{-2}$ $s^{-1}$ | β - $\beta_0$/C | Apparent molar compressibility -$\varphi_k$ × $10^6$ $cm^2$ $dyne^{-1}$ | Apparent molar volume -$\varphi_v$ × $10^{-2}$ ml $mol^{-1}$ | Solvation number Sn × $10^{-4}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.001 | 0.835 | 11.2 | 9.54 | 6.27 | 3.2 | 9.35 | 11.0 | 1.17 | 6.94 | 4.78 |
| 2 | 0.002 | 0.836 | 11.2 | 9.44 | 6.24 | 4.5 | 9.41 | 10.5 | 1.12 | 6.93 | 2.95 |
| 3 | 0.003 | 0.837 | 11.3 | 9.35 | 6.20 | 5.5 | 9.46 | 10.0 | 1.06 | 6.91 | 2.28 |
| 4 | 0.004 | 0.838 | 11.3 | 9.25 | 6.17 | 6.3 | 9.52 | 10.0 | 1.06 | 6.90 | 2.02 |
| 5 | 0.005 | 0.841 | 11.4 | 9.08 | 6.11 | 7.1 | 9.62 | 11.4 | 1.22 | 9.28 | 1.99 |
| 6 | 0.006 | 0.843 | 11.5 | 8.92 | 6.06 | 7.7 | 9.72 | 12.2 | 1.32 | 11.26 | 1.96 |
| 7 | 0.007 | 0.845 | 11.6 | 8.75 | 6.00 | 8.4 | 9.83 | 12.8 | 1.40 | 12.73 | 1.95 |
| 8 | 0.008 | 0.848 | 11.7 | 8.58 | 5.95 | 8.9 | 9.94 | 13.4 | 1.46 | 13.41 | 1.92 |
| 9 | 0.009 | 0.850 | 11.8 | 8.43 | 5.89 | 9.5 | 10.04 | 13.5 | 1.49 | 14.36 | 1.90 |
| 10. | 0.010 | 0.852 | 11.9 | 8.28 | 5.84 | 10. | 10.14 | 13.5 | 1.50 | 14.69 | 1.96 |

Thus the quantity dρ/dc is positive while dβ/dc is negative. Since the values (1/β.dβ/dc) are larger than (1/ρ.dρ/dc) for soap solutions, the concentration derivative of velocity dv/dc is positive which is in agreement with the result of other workers[8 - 9] reported for electrolytic solution. The plot of ultrasonic velocity, V vs concentration, C of manganese soaps are characterized by breaks at definite soap concentration which correspond to the CMC 0.0041 and 0.0040 for manganese myristate and stearate, respectively. The increase in ultrasonic velocity with concentration of soap can be represented by the equation

$$V = V_{\circ} + GC$$

Where G in Garnsey's[10] constant. The value of G have been calculated from the linear portions of plots V vs C and found to be $3.2\times10^{-5}$ ,$4\times10^{-5}$ and result shows that G increase with increasing chain length and molecular weight of the soaps.

The adiabatic compressibility of dilute solutions of manganese (myristate and steatrate ) soap decrease with increasing concentration and chain length of the soap.The decrease in adiabatic compressibility may be due to the fact that these soaps behave as weak electrolytes in solutions and ionize into simple metal cation $Mn^{2+}$ and fatty acid

anions, $RCOO^-$ and these ions in solution are surrounded by a layer of solvent molecule around the ions may be due to the influence of electrostatic field of ions and result in the increase in internal pressure and in lowering of the compressibility,β is found to obey bachem'S[11] relationship.

$$\beta=\beta_\circ + AC + BC^{1\cdot5}$$

Where, A and B are constants and C is the concentration of soap solutions. The constant A and B have been determined from intercept and slope of the plots of $(\beta-\beta_\circ)/c$ vs $C^{\circ\cdot5}$ and other constants are mentioned in table 3.

**Table 3**
**Values Of Various Parameters And Constants Obtained From Ultrasonic Measurements**

| S. No. | Name of soap | CMC g mol $l^{-1}$ | Apparent molar compressibility, $\varphi_k \times 10^6$ $cm^{-2}$ $dyne^{-1}$ | Constant, $S_K \times 10^6$ | Apparent molar volume, $\phi_{ov} \times 10^{-2}$ ml $mol^{-1}$ | Constant, $S_v \times 10^{-3}$ | Garnsey's constant, $G \times 10^{-5}$ | $(\beta - \beta_0)/C$ vs $\sqrt{C}$ constants | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | A | B |
| 1. | Manganese myristate | 0.0041 | 1.28 | 8.7 | 4.10 | 1.66 | 3.20 | 12.60 | 7.50 |
| 2. | Manganese stearate | 0.0040 | 1.31 | 4.4 | 7.50 | 1.11 | 4.10 | 13.10 | 8.00 |
| 3. | Iron myristate | 0.0040 | 2.24 | 7.7 | 11.40 | 2.00 | 7.70 | 19.70 | 10.00 |
| 4. | Iron stearate | 0.0035 | 3.28 | 2.5 | 19.40 | 1.67 | 9.10 | 29.50 | 13.00 |

From Debye Huckle and Masson,s theory it follows that apparent molar compressibility, $\Phi_v$ and apparent molar volume $\Phi_v$ are related to the molar concentration of the soap, c by the relationship

$$\Phi_v=\Phi^\circ_v+S_vC^{\circ\cdot5}$$

$$\Phi_v=\Phi^\circ_v+S_vC^{\circ\cdot5}$$

Where $\Phi^\circ_k$ and $\Phi^\circ_v$ are limiting apparent molar compressibility and limiting molar volume respectively, $S_v$ and $S_v$ are constants. The value of these constants (table 3) signifies a considerable soap solvent interaction in dilute soap solutions and values $\Phi^\circ_v$ are found to be increased with chain length.All the plots show breaks indicate the CMC, which are in accordance with the values obtained from other parameters.The value of solvation number, $S_v$ decrease with increasing soap concentration but decreased rapidly below the CMC with increasing soap concentration and remain constant above CMC.Variation in the value of solvation number with soap concentration are in agreement with the result proposed Prakesh etal[12].

**Conclusion**

The ultrasonic measurements results of manganese myristate and stearate confirms that there is a significant interaction between the soap and solvent molecule in dilute solution and soap molecule do not aggregate appreciably below the CMC.

**Endnotes**

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