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Studies on thermodynamic and Acoustic Parameters of Iron (III) Hexanoate in Benzene-butan-1-ol mixture

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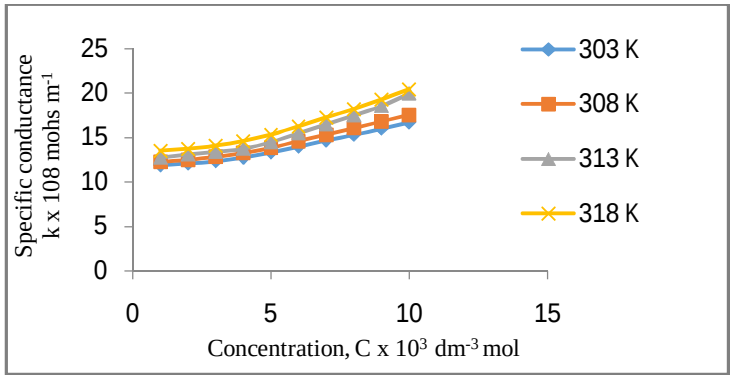
ABSTRACT

The conductometric measurements of the solutions of the iron (III) hexanoate in benzene-butan-1–ol mixture (1:1 v/v) were carried out at different temperature (303K, 308K, 313K and 318K) and ultrasonic velocity measurements of the solutions of the iron (III) hexanoate in benzene-butan-1–ol mixture (1:1 v/v) were carried out at constant temperatures, 308K. The thermodynamic of dissociation and association can be satisfactorily explained in the light of phase separation model by the conductivity measurements and the results shows that the association process is dominant over dissociation process. The ultrasonic measurements were used to evaluate various acoustic parameters. The results showed that the soap-soap interactions are weaker that soap-solvent interactions in dilute solutions and soap molecules do not aggregate below the critical micelle concentration in dilute solutions.

Graphical Abstract



Specific conductance, (k) Vs Concentration, (C) Solvent: Benzene-Butan-1-ol (1:1 v/v) mixture.

Keywords: Iron (III) hexanoate, Conductivity, Acoustic parameters C.M.C.

INTRODUCTION

In recent years metal soaps have been used in industries and various branches of technology, rubber, pharmaceuticals, detergents, lubrication, etc. The physicochemical properties of metal soaps in solutions have not been carried out systematically and few references (**1-21**) are available in this field. The applications of these metal soaps depend largely on their physical state, stability, chemical reactivity and solubility in common solvents keeping in view the manifold uses of the metal soaps, a study on micelles behavior of Iron soaps was carried out.

The present work deals with the study of micelles behavior and evaluation of various thermodynamic and acoustic parameters of the iron (III) hexanoate in benzene-butan-1–ol mixture (1:1 v/v) were carried out at different temperatures.

MATERIALS AND METHODS

All the chemical used were of AR grade, iron (III) hexanoate was prepared by the direct metathesis of potassium hexanoate with required amount of aqueous solution of iron (III) nitrate at 50-60^{o}C under vigorous stirring. The excess of potassium, hexanoate, iron (III) nitrate and hexanoic and were removed by the washing with the distilled water and acetone. The soap was re-crystallized with benzene-1-ol mixture and dried reduced pressure. The purity of soap was confirmed by determination of its melting point and elemental analysis (hexanoate m. p. 40°C, found, C=54.5, H= 8.2, Calculated, C =54.7, H = 8.4). The absence of hydroxyl in the soap molecule was confirmed by the absence of absorption maxima in the region of 3500-3000 cm^{-1} in its I.R. spectrum. The conductance of the soap solution with a digital conductivity meter (NDC 7360 and a dipping type conductivity cell with platinized electrodes was measured. The accuracy of the result was $\pm$ 0.5%.

A multi-frequency ultrasonic interferometer M-83 (Mittal Enterprises, New Delhi) was used to measure the ultrasonic velocity result was $\pm$0.2%. All measurements were made at a constant temperature (35$\pm$0.05 °C) in a thermostat.

The adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f), apparent molar compressibility (ϕ_K), was calculated by using the following relationships:

$$\eta / \eta_0 = p.t / p_0.t_0 \quad \ldots (1)$$

$$\beta = V^{-2}. \rho^{-1} \quad \ldots(2)$$

$$Z = v. \rho \quad \ldots(3)$$

$$L_f = (\beta/k)^{1/2} \quad \ldots(4)$$

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0.\beta - \rho\,\beta_0.) + \frac{M.\beta_0}{\rho_0} \quad \ldots(5)$$

Where η, η_0, ρ_0, ρ, t t_0, and β_0, β are velocity, density, time of flow and adiabatic compressibility for solvent and solution respectively; K, V, and M the temperature dependent Jacobson's constant, ultrasonic velocity and molecular weight of the soap, respectively.

RESULTS AND DISCUSSION

Conductivity: The specific conductance (k) of the solution of iron (III) hexanoate in benzene-butane-1-ol mixture (1:1 v/v) increases with increasing soap concentration which may be due to the ionization of the soap into simple metal cation (Fe^{+3}) and fatty acids anion ($C_8H_{17}COO^-$) in dilute solutions and due to the aggregation of ionic micelles at higher soap concentrations. The plot of specific conductance of soap concentration shows a break at a definite soap concentration (0.0044 dm^{-3} mol) (Table 1) corresponds to the CMC (Fig 1). The molar conductance, (μ) of the soap Solutions decreases with increasing soap concentration in dilute solution due to the combined effect of ionic atmosphere, salvation of ions, decrease of mobility and ionization and formation of micelles.

The plot of μ Vs $C^{1/2}$ is concave upward indicates that the soap behaves as a weak electrolyte in dilute solution. Hence an expression for dissociation of iron (III) hexanoate can be developed using Ostwald's dilution law.

Table 1. Values of CMC, X_{CMC} limiting molar conductance, μ_0 and dissociation constant, K of iron (III) hexanoate in benzene-butan-1-ol (1:1 v/v) mixture

S. No.	Temperature	CMC	X_{CMC} x 10^4	μ_0	K x 10^9
1.	303K	0.0042	4.17	20.00	8.43
2.	308K	0.0044	4.39	21.00	8.32
3.	313K	0.0048	4.63	22.00	8.13
4.	318k	0.0050	4.90	25.00	4.14

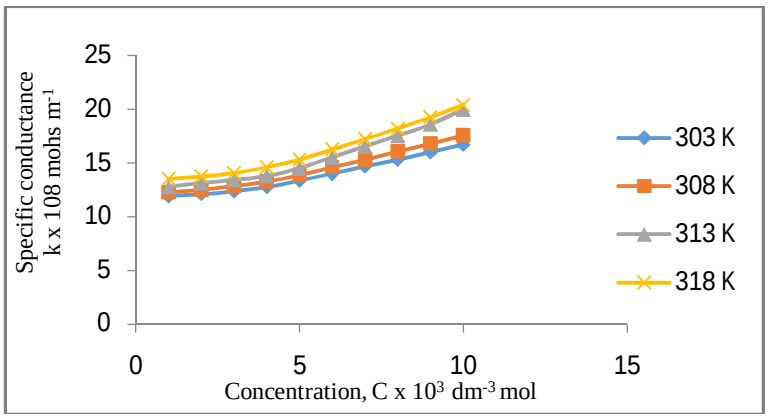


Figure 1. Specific conductance, (k) Vs Concentration, (C) Solvent: Benzene-Butan-1-ol (1:1 v/v) mixture.

The dissociation constant (K) can be written as;

$$K = \frac{[Fe^{+3}]\ [C_{11}H_{23}COO^-]^3}{[Fe(C_{11}H_{23}COO)_3]} = \frac{(3)^3\ C^3\alpha^4}{(1-\alpha)} = \frac{27\ C^3\ \alpha^4}{(1-\alpha)} \quad \ldots(1)$$

Since the ionic concentrations are low and the inter ionic effects almost negligible, the salvation will not deviate much from the ideal behavior and so the activity of ions can be taken as almost equal to their concentration. The degree of dissociation (α) may be replaced by conductance at ratio. μ / μ_0, where μ and μ_0 are the molar conductance at finite and infinite dilution, respectively. On substituting the value of α and rearranging equation (1) can be written as;

$$\mu^3C^3 = \frac{K\,\mu_0^4}{27\,\mu} - \frac{K\mu_0^3}{27} \quad \ldots (2)$$

The values of K and μ_0 were obtained from the slope ($K\,\mu_0^4/27\mu$) and intercept ($K\mu_0^3/27$) of the linear portion of the plot of $\mu^3.C^3$ Vs $1/\mu$ and found to be 2.4×10^{-5} and 1.86×10^{-4}mho $m^2.mol^{-1}$, respectively.

The value of degree of dissociation α lie in the range between 0.640 to 0.102 indicating that soap behaves as a weak electrolyte in dilute solution.

The values of dissociation constant, K calculated by using equation (1), (Table 1) also show that the iron (III) hexanoate behave as a weak electrolyte in the mixture of benzene-butan-1-ol. The relation between dissociation constant, K and heat of dissociation, , ΔH_D^0 can be expressed as:

$$\frac{d \ln K}{dT} = \frac{\Delta H_D^0}{RT^2}$$

$$\text{or} \quad \log K = \frac{-\Delta H_D^0}{2.303RT} + \text{constant} \quad \ldots(3)$$

The value of the heat of dissociation, ΔH_D^0 was obtained from the slop of plot of log K Vs 1/T are recorded in (Table 2). The negative values of ΔH_D^0 also indicate that the dissociation of iron (III) soaps in an exothermic process.

Table 2. Thermodynamic parameters of iron (III) hexanoate in benzene-butan-1-ol (1:1 v/v) mixture heat of dissociation and association (K. J. mol^{-1}) of iron (III) hexanoate

S. No.	Iron (III) hexanoate	$-\Delta H_D^0$	$+\Delta H_A^0$
1.	303 K	23.09	52.38
2.	308 K	26.98	61.40
3.	313 K	30.91	70.52
4.	318 K	37.26	79.77

The values of changes in free energy, ΔG_D^0 and entropy, ΔS_D^0 per moles for the dissociation process (Table 3, 4) have been calculated using the relationships:

$$\Delta G_D^0 = -RT \log K_D \quad \ldots(4)$$

$$\Delta S_D^0 = \frac{[\Delta H_D^0 - \Delta G_D^0]}{T} \quad \ldots(5)$$

Table 3. Entropy change of iron (III) hexanoate for dissociation and association process

S. No.	Iron (III) hexanoate	$-\Delta S_D^0 \times 10^2$	$+\Delta S_A^0 \times 10^2$
1.	303 K	43.56	98.4
2.	308 K	43.62	99.2
3.	313 K	43.72	99.7
4.	318 K	46.84	100.2

Table 4. Free energy change of iron (III) hexanoate for dissociation and association process

S. No.	Iron (III) hexanoate	+ ΔG_D^0	- ΔG_A^0
1.	303 K	10.02	22.85
2.	308 K	11.71	26.66
3.	313 K	13.42	30.62
4.	318 K	16.18	34.63

For the aggregation process, the standard free energy of micellization (per mole of monomer) ΔG_A^0 for the phase separation model is given by the relationship:

$$\Delta G_A^0 = 2RT \log X_{CMC} \qquad \ldots 6)$$

Where X_{CMC} is the CMC expressed as a mole fraction and defined as:

$$X_{CMC} = \frac{n_s}{n_s + n_o}$$

Since, the number of moles of free surfactant, n_s are small as compared to the number of mole of solvent, n_o, X_{CMC} can be written as:

$$X_{CMC} = \frac{n_s}{n_o} \qquad \ldots (7)$$

The standard entropy change of association per moles of monomer for the phase separation model, ΔH_A^0 is given as:

$$\frac{d \ln X_{CMC}}{dT} = \frac{\Delta H_A^0}{2RT^2}$$

$$\log X_{CMC} = \frac{\Delta H_A^0}{2(2.303RT)} + \text{constant} \qquad \ldots (8)$$

The values of ΔH_A^0 have been obtained from the slope of linear plot of log X_{CMC} Vs 1/T

The standard change for the association process, ΔS_A^0 has been calculated by relationship:

$$\Delta S_A^0 = \frac{[\Delta H_A^0 - \Delta G_A^0]}{T} \qquad \ldots (9)$$

The positive values of ΔS_A^0 and negative values of ΔS_D^0 and negative values of ΔG_A^0 and positive values of ΔG_D^0 indicates that the association process is dominant over dissociation process.

It is therefore, concluded that the thermodynamics of dissociation and association can be satisfactorily explained in the light of phase separation model by the conductivity measurements and the results shows that the association process is dominant over dissociation process.

Ultrasonic Measurement: The ultrasonic velocity, (V) of the solutions of iron (III) hexanoate in benzene-butan-1-ol (1:1v/v) increase with increasing in the soap concentration. The plot of V Vs C indicates a break at a definite soap concentration (0.044 dm^{-3} mol) (Figure 2). This corresponds to the CMC of soap. The plot of V Vs C was extrapolated to the zero soap concentration and the extrapolated values of the ultrasonic velocity, Vo (1082.0 m. s^{-1}), have been found in close agreement with the experimental value of the velocity of the solvent mixture (1082.0 m. s^{-1}) (Table 5).

Table 5. Ultrasonic velocity measurements of iron (III) hexanoate in benzene-butan-1-ol (1:1 v/v) mixture at 308 K

S. No.	Concentration C x 10^3 (dm^{-3} mol.)	Velocity, V (m. $s.^{-1}$)	Adiabatic Compressibility β x 10^{10} ($m.^2$ N^{-1})	Free length L_f x 10^{-2} (A^0)	Specific Acoustic impedance, Z x 10^{-10} (Kg. $m.^{-2}$ $s.^{-1}$)	Molar compressibility ($m.^5 mol^{-1}$ N^{-1} Kg^{-1})
1.	1.0	1098.5	8.20	82.25	1.09	17.00
2.	2.0	1105.3	8.07	81.95	1.10	16.00
3.	3.0	1111.5	7.93	81.45	1.11	15.00
4.	4.0	1118.6	7.79	80.95	1.12	14.00
5.	5.0	1142.6	7.14	79.55	1.14	15.10
6.	6.0	1165.6	6.55	78.25	1.16	16.30
7.	7.0	1185.7	6.05	77.15	1.18	17.50
8.	8.0	1210.8	5.35	76.12	1.20	18.70
9.	9.0	1235.7	4.84	75.09	1.22	19.80
10.	10.0	1255.8	4.25	74.02	124	20.90

The variation of ultrasonic velocity, (V) with soap concentration, (C) for the dilute soap solution below of the CMC follows the relationship:

$$V = V_o + G.\ C$$

Where G is the Garney's constant. The values of Garney's constant, obtained from the slope of the plot of V Vs C below the CMC was found to be 4.00 x 10^3 m^2 mol^{-1} s^{-1}.

The adiabatic compressibility, β of the solution of iron (III) haxanoate soaps decreases with increase soap concentration and the decrease may be attributed to the fact that the soap in dilute solutions behave as a weak electrolyte and are ionized into iron (III) cations, Fe^{+3} and fatty acid anions ($C_6H_{13}COO^-$) as indicated by the conductivity measurements. The ions are surrounded by a layer of solvent molecules around the ions is due to the influence of the electrostatic field of ions and thus the internal pressure increases which the adiabatic compressibility (β) of the solutions i.e. the solutions become harder to compress.

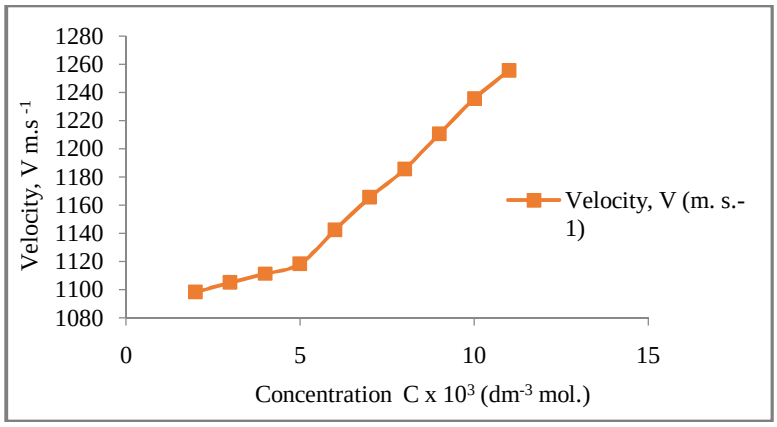


Figure 2. Ultrasonic Velocity (V) Vs Concentration (C) Solvent:benzene-Butan-1-ol (1:1v/y) Mixture, Temp. 308K

The adiabatic compressibility, (β) of the soap solutions is the found to obey Bachem's relationship;

$$\beta = \beta_0 + AC + BC^{3/2} \qquad \ldots(10)$$

Where β_0 is adiabatic compressibility of the solvent, C is the soap concentration and A and B are constant. The values of A (8.40) and B (278.96) where obtained from the intercept and slope of the plot of $\beta\beta_0$ / C Vs $C^{1/2}$.

The value of the specific acoustic impedance (Z) increases, while of intermolecular free length (L_f) decreases with increasing soap concentration for the solutions of the iron (III) hexanoate in benzene-butan-1-ol mixture. The plot of Z Vs C and L_f Vs C where extrapolated to zero soap concentration and the extrapolated values obtained for Z^o and $L_f{}^o$ where found to be (1.08×10^{-10} Kg. m^{-2}–s^{-1}) and (82.90 A^o) respectively. The increase in the value of the specific acoustic impedance (Z) with the soap concentration (C) can be the explained on the basis of lyophobic interaction between the soap and solvent molecules which increases the intermolecular distance making relatively wider gaps between the molecules and thus becoming a cause of impedance in propagation of ultrasound waves.

The apparent molar compressibility (Φ_K) decreases with increases in soap . It follows from the Debye-Huckel's theory that the apparent molar compressibility ($\Phi_{K)}$ is related to the concentration (C) by the relations:

$$\Phi_k = \Phi_k{}^0 + S_K C^{1/2}$$

Where $\Phi_k{}^0$ is the apparent molar compressibility of the solvent and S_k is a constant. The value of S_k and Φ_k were obtained from the slope and intercept of plots of Φ_k Vs $c^{1/2}$ and were found to be (0.666) and ($1.80\ m^5\ mol^{-1}\ N^{-1}\ Kg^{-1}$) respectively.

APPLICATION

The information about micelles behavior and evaluation of various thermodynamic and acoustic parameters of the iron (III) hexanoate in benzene-butan-1–ol mixture (1:1 v/v) at different temperatures will help to use it as a fungicide and insecticide.

CONCLUSION

The result of ultrasonic velocity measurements also shows that the soap behaves as a simple weak electrolyte in dilute solutions. The result conform that there is a significant interaction between the soap and the solvent molecules in dilute soap solutions and the soap molecules do not aggregate appreciably in the dilute solutions below the CMC.

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