



Studies on Conductometric Investigation of Iron (III) Octanoate in Benzene-butan-1-ol Mixture

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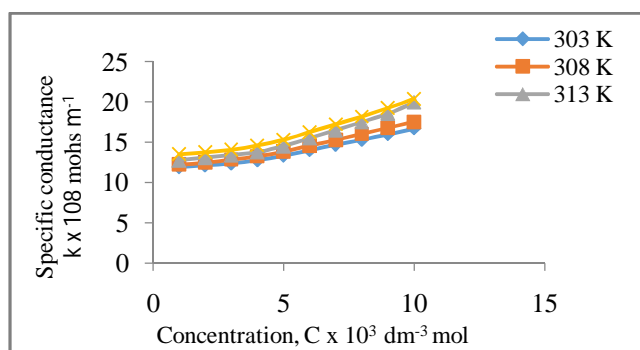
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ABSTRACT

The conductometric measurements of the solutions of the iron (III) octanoate in benzene-butan-1-ol mixture (1:1 v/v) were carried out at different temperature (303K, 308K, 313K and 318K). The investigation 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 results showed that the soap-soap interactions are weaker than 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) octanoate, Conductivity, 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 [1-20] 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 investigation of the Iron (III) octanoate in benzene-butan-1-ol mixture (1:1 v/v) were carried out at different temperatures.

MATERIALS AND METHODS

The entire chemical used were of AR grade, Iron (III) octanoate was prepared by the direct metathesis of potassium with required amount of aqueous solution of iron (III) nitrate at 50-60°C under vigorous stirring. The excess of potassium, octanoate, iron (III) nitrate and octanoic 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 (octanoate m. p. 90°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 IR 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 $\pm 0.5\%$.

RESULTS AND DISCUSSION

Conductivity: The specific conductance (k) of the solution of iron (III) octanoate 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 ($\text{C}_8\text{H}_{17}\text{COO}^-$) in dilute solutions and due to the aggregation of ionic micelles at higher soap concentrations (Table 1-4). The plot of specific conductance of soap concentration shows a break at a definite soap concentration (0.0040, 0.0041, 0.0042 dm^{-3} mol) (Table 5) corresponds to the CMC (Figure 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.

Table 1. Conductivity of iron (III) octanoate in benzene-butane-1-ol (1:1 v/v)mixture at 303K

S.No.	Concentration $C \times 10^3$ (dm^{-3} mol)	Specific Conductions. $k \times 10^8$ (mhos cm^{-1})	Molar Conductance $\mu \times 10^2$ (mhos $\text{cm}^2 \text{mol}^{-1}$)	Degree of dissociation α	Dissociation Constant $K \times 10^9$
1	1.0	11.90	11.90	0.822	69.25
2	2.0	12.10	6.10	0.422	11.85
3	3.0	12.35	4.15	0.287	6.93
4	4.0	12.75	3.18	0.221	5.29
5	5.0	13.35	2.68	0.187	5.07
6	6.0	14.00	2.34	0.166	5.30
7	7.0	14.70	2.10	0.151	5.67
8	8.0	15.30	1.91	0.140	6.17
9	9.0	16.00	1.77	0.132	6.88
10	10.0	16.70	1.66	0.125	7.53

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) octanoate can be developed using Ostwald's dilution law.

The dissociation constant (K) can be written as;

$$K = \frac{[\text{Fe}^{+3}] [\text{C}_8\text{H}_{17}\text{COO}^-]^3}{[\text{Fe}(\text{C}_8\text{H}_{17}\text{COO})_3]} = \frac{(3)^3 C^3 \alpha^4}{(1 - \alpha)} = \frac{27 C^3 \alpha^4}{(1 - \alpha)} \quad \dots(1)$$

Table 2. Conductivity of iron (III) octanoate in benzene-butane-1-ol (1:1 v/v) mixture at 308K

S.No.	Concentration $C \times 10^3$ ($\text{dm}^{-3} \text{mol}$)	Specific Conductions. $k \times 10^8$ (mhos cm^{-1})	Molar Conductance $\mu \times 10^2$ ($\text{mhos cm}^2 \text{mol}^{-1}$)	Degree of dissociation α	Dissociation Constant $K \times 10^9$
1	1.0	12.25	12.15	0.820	67.81
2	2.0	12.45	6.25	0.420	11.58
3	3.0	12.85	4.30	0.285	6.83
4	4.0	13.25	3.31	0.219	5.18
5	5.0	13.85	2.77	0.184	4.84
6	6.0	14.60	2.43	0.163	5.09
7	7.0	15.30	2.18	0.147	5.39
8	8.0	16.05	2.00	0.135	5.68
9	9.0	16.80	1.86	0.127	5.96
10	10.0	17.55	1.75	0.122	6.32

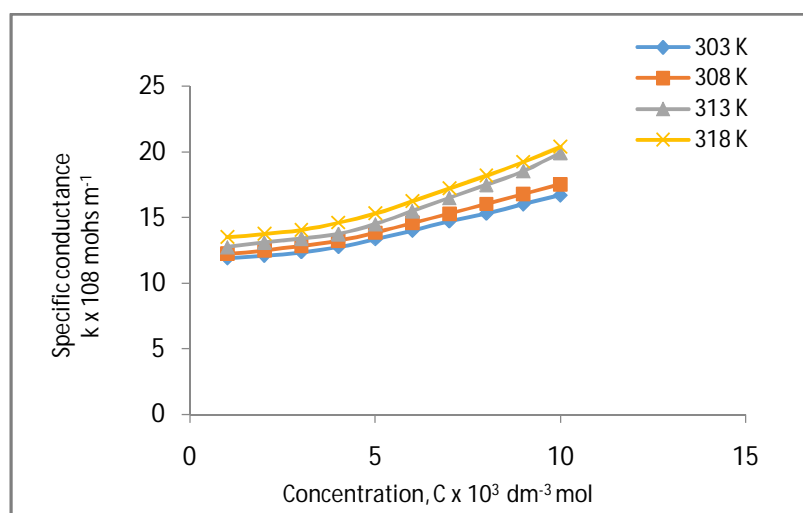


Figure 1. Specific conductance, (k) Vs Concentration, (C) Solvent: Benzene-Butan-1-ol (1:1 v/v) mixture.

Since the ionic concentrations are low and the interionic effects almost negligible, the solvation 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 finite and infinite dilution, respectively. On substituting the value of α and rearranging equation (1) can be written as;

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

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 $1/\mu$. The values of μ_0 were increases with increasing concentration (Table 5). The decrease in ionization constant, K with increasing soap concentration may be due to predominating effects of concentration as compared to that of degree of ionization.

The decrease in the value of K with increasing temperature indicates the exothermic nature of iron (III) octanoate in a mixture of benzene-butan-1-ol (1:1 v/v).

Table 3. Conductivity of iron (III) octanoate in benzene-butane-1-ol (1:1 v/v) mixture at 313K

S.No.	Concentration C x10 ³ (dm ⁻³ mol)	Specific Conductions. k x10 ⁸ (mhos cm ⁻¹)	Molar Conductance μ x 10 ² (mhos cm ² mol ⁻¹)	Degree of dissociation α	Dissociation Constant K x 10 ⁹
1	1.0	12.75	12.75	0.810	61.17
2	2.0	13.10	6.55	0.416	11.07
3	3.0	13.40	4.46	0.283	6.73
4	4.0	13.75	3.43	0.217	5.08
5	5.0	14.50	2.90	0.182	4.74
6	6.0	15.50	2.58	0.160	5.89
7	7.0	16.50	2.35	0.145	5.18
8	8.0	17.50	2.18	0.133	5.58
9	9.0	18.55	2.06	0.124	5.71
10	10.0	19.95	1.95	0.119	5.93

Table 4. Conductivity of iron (III) octanoate in benzene-butane-1-ol (1:1 v/v) mixture at 318K

S.No.	Concentration C x10 ³ (dm ⁻³ mol)	Specific Conductions. k x10 ⁸ (mhos cm ⁻¹)	Molar Conductance μ x 10 ² (mhos cm ² mol ⁻¹)	Degree of Dissociation α	Dissociation Constant K x 10 ⁹
1	1.0	13.50	13.50	0.794	52.90
2	2.0	13.75	7.00	0.411	10.46
3	3.0	14.05	4.78	0.281	6.42
4	4.0	14.60	3.68	0.216	4.89
5	5.0	15.30	3.06	0.180	4.42
6	6.0	16.25	2.70	0.158	5.81
7	7.0	17.22	2.45	0.142	5.05
8	8.0	18.19	2.26	0.132	5.23
9	9.0	19.25	2.11	0.121	5.51
10	10.0	20.40	2.00	0.117	5.72

Table 5. Values of CMC, X_{CMC} limiting molar conductance, μ₀ and dissociation constant, K of iron (III) octanoate in benzene-butane-1-ol (1:1 v/v) mixture

S. No.	Temperature	CMC	X _{CMC} x 10 ⁴	μ ₀	K x 10 ⁹
1.	303K	0.0040	4.17	14.50	5.22
2.	308K	0.0041	4.39	15.00	4.75
3.	313K	0.0042	4.63	15.50	4.10
4.	318k	0.0044	4.91	17.00	3.60

The value of degree of dissociation, α at different soap concentrations have been calculated by assuming it as equal to the conductance ratio, μ/μ₀ and using the value μ₀ obtained from the plots of μ³.C³ Vs 1/μ. The values of degree of dissociation (α<0.4) show that the soap behaves as a weak electrolyte in these solutions.

The values of dissociation constant K calculated by using equation (1) (Table 1 to 4). The calculated values of dissociation constant exhibit a drift with increasing soap concentration which may be partly due to the fact that the degree of dissociation, α is not equal to the conductance ratio, μ/μ₀ but mainly due to the fact that the activity co-efficient of the ions are not exactly equal to the unity. The deviations at higher soap concentrations may be due to the failure of Debye-Huckel's activity equation. The relation between dissociation constant, K and heat of dissociation, ΔH_D⁰ can be expressed as:

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

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

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

The values of changes in free energy, ΔG_D^0 and entropy, ΔS_D^0 per moles for the dissociation process (Table 2) have been calculated using the relationships:

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

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

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:

$$\Delta G_A^0 = 2RT \log X_{CMC} \quad \dots(6)$$

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:

$$X_{CMC} = \frac{n_s}{n_o} \quad \dots (7)$$

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

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

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

The values of ΔH_A^0 have been obtained from the slope of linear plot of $\log X_{CMC}$ Vs $1/T$ and are recorded in (Table 2).

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

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

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.

APPLICATION

The study of micelles behavior and evaluation of various investigation of the Iron (III) octanoate in benzene-butan-1-ol mixture (1:1 v/v) at different temperatures will help its application as a catalyst in chemical reaction.

CONCLUSION

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.

REFERENCES

- [1]. Susan Verghese P Control of pyrethrum against the tomato disease caused by aphids, *Int. J. Curr.Res. Chem. Pharma. Sci.*, **2015**, 2(10), 40-44.
- [2]. N. Sidhardhan and Susan Verghe, Environmental Friendly Herbicides-Fatty acid metallic Salts on weed (Parthenium hysterphorous and Moss, *Int. J. Curr. Res. Chem. Pharma. Sci.*, **2015**, 2(4) 1-14.
- [3]. D. Jain, J. Susan, S. Nisha, Insecticidal effect of the mixture of Potassium soap and pyrethroids on Potato Leaf roll virus (PLRV) found on Potato plants, *J. Applicable Chem.*, **2013**, 2(3), 518-525.
- [4]. Dheeraj Jain, Susan Verghese, Environmental Friendly Pesticides-Fatty acid Metallic salts and Pyre thyroids, *Int. JSRR*, **2013**, 2, 1,43-51.
- [5]. Suleman, P. Susan.Verghe, F. M. Prasad, Ultrasonic study of vanadium myristate in liquor ammonia, *J. Indian. Chem. Soc.*, **2008**, 85, 852-856.
- [6]. F. M. Prasad, Suleman, Hemant, P. S. Verghese, Infra red Studies of Vanadium Carboxylate, *Oriental Journal of Chemistry*, **2007**, 23(3), 1139-1141.
- [7]. F. M. Prasad, Suleman, S. P. Verghese, Hemant, K Structural studies of Vanadium soap in solid state by X-ray diffraction analysis, *J. Material Science Research India*, **2007**, 4(2), 535-538.
- [8]. Suleman, P. Susan.Verghe, F. M. Prasad, H. Kulshrestha, Ultrasonic study of vanadium Palmitate in liquor ammonia, *J. Ind. Council. Chem.*, **2007**, 24, 2, 21-24.
- [9]. Suleman, H. Kulshrestha, P. Susan Verghese, Measurements of acoustic parameters of vanadium laurate inliquid ammonia by ultrasonic inferometer, *Oriental Journal of Chemistry*, **2007**, 23, 1, 177-182.
- [10]. Suleman, S.Verghe, F. M. Prasad, Thermo-gravimetric analysis of vanadium carboxylates in solid state, *J. Indian Council of Chemists*, **2006**, 23(2), 106-110.
- [11]. Sunder Singh Tomar, Deepak Kulshrestha, Suleman, Monika Singh, Renu Sharma, Susan .Verghe, Thermodynamic and conductometric investigation on product of oil crops and cadmium soaps in Benzene-dimethyl formamide solvent mixture, *Ad. Plants. Sci.*, **2006**, 19, 11, 357-363.
- [12]. Suleman, S. Verghese, F. M. Prasad, Thermo-gravimetric analysis of vanadium carboxylates in solid state, *J. Indian Council of Chemists*, **2006**, 23(2), 106-110.
- [13]. K. Deepak, S. S. Tomar, R, Sharma, Ashok, P. S. Verghese., Studies on Molar volume, Rheology and Acoustic parameters of transition metal carboxylates in Organic solvents, *J. Indian Council of Chemists*, **2005**, 22(1), 54-61.
- [14]. K. Smriti, S. Verghese, L. Chandreshwor, Studies of Molar volume, Rheology of Cerous carboxylates in benzene-xylene mixture. *J.Tenside Surfactants, Germany*, **2003**, 40(2), 108-111.
- [15]. Sunder Singh Tomar, Deepak Kulshrestha, Susan Verghese P, Thermogravimetric analysis of cadmium caroxylate in solid state *J. Tenside Surfactants, Germany*, **2003**, 40(6), 108-111.

- [16]. S. Verghese, K. N. Mehrotra, A Kumar, Properties of cobalt soaps in Benzene-methanol mixture, *J. Tenside, detg.*, **2000**, 37(4), 249-251.
- [17]. K. N. Mehrotra, S. Verghese, Molar volume, rheology and Ultrasonic studies of Nickel myristate in a Benzene-methanol mixture, *J. Tenside detg.*, **1999**, 36(1), 192-195.
- [18]. K. N. Mehrotra, A. K. Kulshrestha, S. Verghese, Investigation of cobalt stearate in the solid state and in solution in a Benzene-methanol mixture, *J. Tenside detg.*, **1999**, 36(4).
- [19]. Deepak Kulshrestha, Gyan Prakash, Ashok Kumar and S. Verghese P Studies on molar volume, rheology and conductance of iron (111)hexanoate in benzene –butan-1-ol mixture, *JICC*, **2008**, 25(2), 1-4
- [20]. K N Mehrotra, Mamta Jain and G L Bagel, S Verghese P Thermal, magnetic, spectroscopic and solubility behavior of nickel myristate, *Polish J. Chem., Poland*, **1994**, 68, 807-816.