



Determination of critical micellar concentration & study molecular interactions of Terbium Decanoate in non-aqueous binary mixture

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ABSTRACT: Viscosity and density measurements of terbium decanoate in non-aqueous binary mixture show that there is marked change in the aggregation of the anionic species at critical micellar concentration (CMC) & CMC increase with increasing temperature. The values of various constants calculated from well known equations (Einstein, Vand, Moulik and Jones-Dole) indicate that there is a significant interaction between solute and solvent molecules.

Keywords: Critical micellar concentration; Solute-solvent interactions; terbium decanoate.

INTRODUCTION

Any compound formed by the reaction of a water insoluble fatty acid with a metallic radical or with an organic base may be called as “soap”. Practically the soap industry is concerned mainly with water soluble soaps which results from the interaction between fatty acids and alkali metals. Salts of fatty acids with other than alkali metals are water insoluble and termed as “metallic soaps”. Many researchers¹⁻⁴ synthesized metallic soaps by using different method & techniques. Malik et. al.⁵⁻⁶ determined the solubility of cobalt soaps in organic solvents and absorption spectra⁷ of chromium soaps in non-aqueous solvents. The behaviour of transition metal soaps in organic medium has been investigated by studying various physical properties (viz. solubility, surface tension, viscosity, refractive index, colorimetry and magnetic susceptibility) by Mehrotra and coworkers⁸⁻¹². Upadhyaya¹³ &¹⁴ determined acoustical parameters for dissociation and micellization process of lanthanide linoleates, molecular interaction and compressibility behavior of lithium soaps in benzene-methanol mixture. In present communication, some solution properties of terbium decanoate in non-aqueous binary mixture have been determined to study micelle formation and molecular interaction.

MATERIAL AND METHODS

The chemical purification of synthesis of terbium decanoate (caprate) has already communicated¹⁵. Ostwald's type viscometer was used for measuring the viscosity of terbium decanoate in a mixture of 60/40 benzene-methanol (v/v) at different temperatures. The densities were determined with the help of specific gravity bottle. All the measurements were made at 25⁰, 30⁰, 35⁰, and 40⁰C in a thermostat (Toshniwal).

RESULTS AND DISCUSSION

The density, ρ of terbium decanoate have been measured in a mixture of 60/40 benzene-methanol (v/v) at different temperatures. The density of terbium decanoate solution increases (Table 1) with increase in solute concentration. However, values of density decrease with increasing temperature. The plots of density, ρ against solute concentration, C (Figure 1) are characterized by an intersection of two straight

lines at a definite solute concentration. This concentration corresponds to critical micellar concentration, CMC at which there is a sudden change in the aggregation of solute molecules. Critical micellar concentration, CMC values are almost in good agreement with the values obtained from other physical properties [15] at different temperatures (25⁰, 30⁰, 35⁰ and 40⁰C) and mentioned in Table 2.

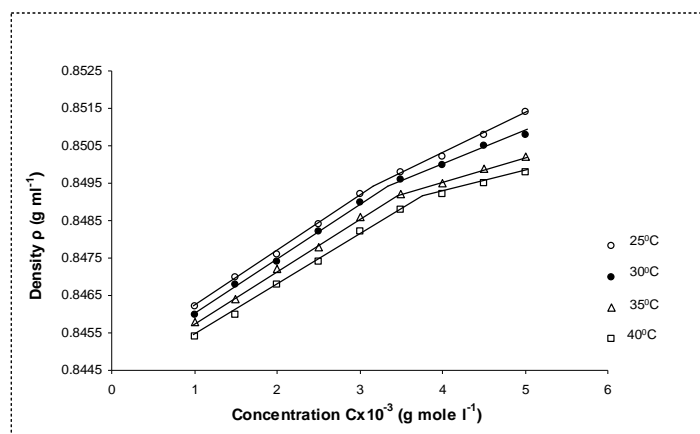


Figure 1: Density, ρ versus Concentration, C of Terbium Decanoate.

The density results for terbium decanoate have been explained by using Root's equation¹⁶:

$$\rho = \rho_0 + AC - BC^{3/2} \quad \text{--- (1)}$$

where C is the concentration of the solute, ρ and ρ₀ are densities of terbium decanoate solution and solvent mixture, respectively. The constants A and B refer to the solute-solvent and solute-solute interactions, respectively. The values of constants A and B (Table 2) have been obtained from the intercept and slope of the plot of ρ-ρ₀ / C against C^{1/2} below the CMC. The values of constants A and B for terbium decanoate decrease with increase in temperature.

The apparent molar volume¹⁷, φ_v of terbium decanoate solutions have been determined by using the relationship.

$$\phi_v = \frac{1000}{C\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \quad \text{--- (2)}$$

where C, M, ρ and ρ₀ are the concentration of solution, molecular weight of the solute, density of solution and density of organic solvent mixture, respectively. The plot of φ_v against C^{1/2} show a break at a definite solute concentration which corresponds to CMC. The partial molar volume φ_v⁰ have been obtained by extrapolating the linear plot of φ_v against C^{1/2} for dilute solutions according to Masson's equation¹⁸.

$$\phi_v = \phi_v^0 + S_v C^{1/2} \quad \text{--- (3)}$$

The limiting apparent molar volume, φ_v⁰ and experimental limiting slope, S_v are measure of solute-solvent and solute-solute interactions, respectively (Table 2). The limiting apparent molar volume, φ_v⁰ values for terbium decanoate in a mixture of 60/40 benzene-methanol (v/v) increase with increasing temperature. The presence of strong solute-solute interactions was indicated by the positive value of S_v. The values of S_v decrease with rise in temperature.

The viscosity, η of the solutions of terbium decanoate has been measured at different temperatures (25⁰, 30⁰, 35⁰ and 40⁰C). The viscosity of terbium decanoate solutions increase with increasing solute (soap) concentration. However values of viscosity decrease with rise in temperature. The plot of viscosity against the soap concentration are characterised by an intersection of two straight lines corresponds to critical micellar concentration (Table 2) (Figure 2). The plot of viscosity versus soap concentration has

been extrapolated to zero soap concentration. The extrapolated values of viscosity, η_0 are in agreement with the experimental value of viscosity of the organic solvent mixture.

The specific viscosity, η_{sp} of the Terbium Decanoate solutions in a mixture of 60/40 benzene-methanol increases with increasing the solute concentration. The plot of specific viscosity, η_{sp} versus solute concentration, C are characterised by an intersection of two straight lines at a definite solute concentration which corresponds to the critical micellar concentration, CMC.

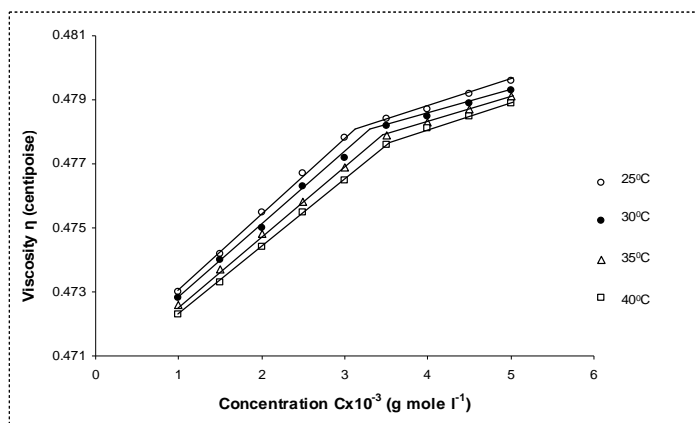


Figure: 2 Viscosity, η versus Concentration, C of Terbium Decanoate .

The viscosity results of Terbium Decanoate in a mixture of 60/40 benzene-methanol (v/v) can be satisfactorily explained by the following equations.

Einstein¹⁹,

$$\eta_{sp} = 2.5 \bar{V} C \quad \text{--- (4)}$$

Vand²⁰,

$$\frac{1}{c} = \left[\frac{0.921}{\bar{V}} \right]^{-1} 1 / \log(\eta/\eta_0) + \phi \bar{V} \quad \text{--- (5)}$$

Moulik²¹,

$$(\eta/\eta_0)^2 = M + K' C^2 \quad \text{--- (6)}$$

Jones-Dole²²,

$$\eta_{sp} / C^{1/2} = A + B C^{1/2} \quad \text{--- (7)}$$

where \bar{V} , C , ϕ , η , η_0 and η_{sp} are molar volume of the solute, concentration of solute, interaction coefficient, viscosity of solution, viscosity of organic solvent mixture and specific viscosity of solution, respectively. M and K' are Moulik's constants. The constant A and B of Jones Dole's equation signify the solute-solute and solute-solvent interactions, respectively.

The values of molar volume, \bar{V} and interaction coefficient, ϕ obtained from Einstein's and Vand's type plot are summarized in Table 2. The molar volume obtained from the slope of Einstein's plot decreases with increasing temperature. The values of interaction coefficient, ϕ obtained from the intercept of Vand's plot decrease with increasing temperature.

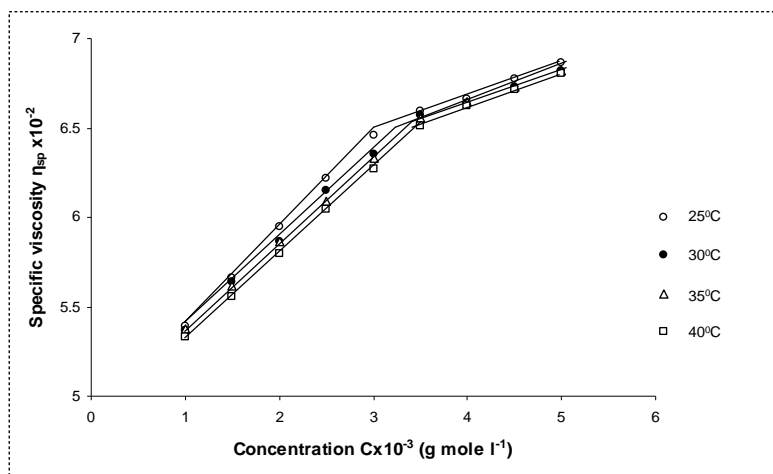


Figure: 3 Specific viscosity, η_{sp} versus Concentration, C of Terbium Decanoate.

The values of constant A (solute-solute interactions) and B (solute-solvent interactions) for Terbium Decanoate have been calculated from the intercept and slope of the Jones-Dole plot below the CMC are mentioned in Table 2. It is noticed that the values of constant A decrease with increase in temperature due to more violent thermal agitation at higher temperatures and thereby resulting in the weakening of force of attraction. The data of Table 2 indicates that the values of coefficient, B for Terbium Decanoate are positive indicating the existence of strong solute-solvent interactions. The magnitude of B decreases with rise in temperature showing that solute-solvent interactions decrease with increasing temperature. The results of Jones-Dole equation suggest that the values of constant B (solute-solvent interaction) are larger than the values of constant A (solute-solute interaction) which again confirms that the molecules of the solute do not aggregate appreciably below the CMC and there is a sudden change in aggregation above the CMC. The values of Moulik's constants, M and K' for Terbium Decanoate (Table 2) have been calculated from the intercept and slope of the plot between $(\eta/\eta_0)^2$ and C^2 . The plot of $(\eta/\eta_0)^2$ versus C^2 is linear below the CMC which indicate that the Moulik's equation is applicable to the dilute solutions. The data reported in Table 2 indicates that the Moulik's constants M and K' decrease with the rise in temperature.

Table 1: Density and viscosity data of Terbium Decanoate in a mixture of 60/40 benzene-methanol (v/v)

| Concentration $C \times 10^3$ (g mole l^{-1}) | Density ρ (g ml^{-1}) | Apparent molar volume ϕ_v | $(\rho - \rho_0)/C$ | Viscosity η (centipoise) | Specific viscosity $\eta_{sp} \times 10^2$ | $1/\log(\eta/\eta_0)$ | $(\eta/\eta_0)^2$ | $\eta_{sp}/C^{1/2}$ |
|--|-------------------------------------|---|---------------------|-------------------------------------|--|-----------------------|-------------------|---------------------|
| At 25°C ± 0.5°C | | | | | | | | |
| 1.0 | 0.8462 | -2522.29 | 2.800 | 0.4730 | 5.392 | 43.84 | 1.111 | 1.705 |
| 1.5 | 0.8470 | -2048.02 | 2.400 | 0.4742 | 5.659 | 41.83 | 1.116 | 1.461 |
| 2.0 | 0.8476 | -1692.32 | 2.100 | 0.4755 | 5.949 | 39.84 | 1.122 | 1.331 |
| 2.5 | 0.8484 | -1573.75 | 2.000 | 0.4767 | 6.216 | 38.18 | 1.128 | 1.243 |
| 3.0 | 0.8492 | -1494.71 | 1.933 | 0.4778 | 6.462 | 36.77 | 1.133 | 1.180 |
| 3.5 | 0.8498 | -1370.49 | 1.829 | 0.4784 | 6.595 | 36.05 | 1.136 | 1.115 |
| 4.0 | 0.8502 | -1218.05 | 1.700 | 0.4787 | 6.662 | 35.70 | 1.137 | 1.053 |
| 4.5 | 0.8508 | -1152.18 | 1.644 | 0.4792 | 6.774 | 35.13 | 1.140 | 1.010 |
| 5.0 | 0.8514 | -1099.48 | 1.600 | 0.4796 | 6.863 | 34.69 | 1.142 | 0.971 |
| At 30°C ± 0.5°C | | | | | | | | |

| | | | | | | | | |
|--|--------|----------|-------|--------|-------|-------|-------|-------|
| 1.0 | 0.8460 | -2522.89 | 2.800 | 0.4728 | 5.371 | 44.01 | 1.110 | 1.698 |
| 1.5 | 0.8468 | -2048.51 | 2.400 | 0.4740 | 5.638 | 41.98 | 1.116 | 1.456 |
| 2.0 | 0.8474 | -1692.72 | 2.100 | 0.4750 | 5.861 | 40.42 | 1.121 | 1.311 |
| 2.5 | 0.8482 | -1574.13 | 2.000 | 0.4763 | 6.151 | 38.57 | 1.127 | 1.230 |
| 3.0 | 0.8490 | -1495.06 | 1.933 | 0.4772 | 6.352 | 37.39 | 1.131 | 1.160 |
| 3.5 | 0.8494 | -1303.05 | 1.771 | 0.4782 | 6.574 | 36.16 | 1.136 | 1.111 |
| 4.0 | 0.8500 | -1218.34 | 1.700 | 0.4785 | 6.641 | 35.81 | 1.137 | 1.050 |
| 4.5 | 0.8505 | -1126.09 | 1.622 | 0.4789 | 6.731 | 35.35 | 1.139 | 1.003 |
| 5.0 | 0.8508 | -1004.87 | 1.520 | 0.4793 | 6.802 | 34.90 | 1.141 | 0.964 |
| At 35^oC ± 0.5^oC | | | | | | | | |
| 1.0 | 0.8458 | -2642.42 | 2.900 | 0.4726 | 5.373 | 43.99 | 1.110 | 1.699 |
| 1.5 | 0.8464 | -1970.14 | 2.333 | 0.4737 | 5.619 | 42.12 | 1.115 | 1.451 |
| 2.0 | 0.8472 | -1752.64 | 2.150 | 0.4748 | 5.864 | 40.41 | 1.121 | 1.312 |
| 2.5 | 0.8478 | -1527.22 | 1.960 | 0.4758 | 6.087 | 38.97 | 1.125 | 1.217 |
| 3.0 | 0.8486 | -1452.04 | 1.900 | 0.4769 | 6.332 | 37.50 | 1.130 | 1.156 |
| 3.5 | 0.8492 | -1337.40 | 1.800 | 0.4779 | 6.555 | 36.26 | 1.135 | 1.108 |
| 4.0 | 0.8495 | -1159.45 | 1.650 | 0.4783 | 6.644 | 35.79 | 1.137 | 1.051 |
| 4.5 | 0.8499 | -1047.40 | 1.555 | 0.4787 | 6.733 | 35.33 | 1.139 | 1.004 |
| 5.0 | 0.8502 | -934.03 | 1.460 | 0.4791 | 6.823 | 34.89 | 1.141 | 0.965 |
| At 40^oC ± 0.5^oC | | | | | | | | |
| 1.0 | 0.8454 | -2643.68 | 2.900 | 0.4723 | 5.330 | 44.34 | 1.109 | 1.686 |
| 1.5 | 0.8460 | -1971.07 | 2.333 | 0.4733 | 5.555 | 42.61 | 1.114 | 1.435 |
| 2.0 | 0.8468 | -1753.46 | 2.150 | 0.4744 | 5.798 | 40.85 | 1.119 | 1.297 |
| 2.5 | 0.8474 | -1527.95 | 1.960 | 0.4755 | 6.044 | 39.24 | 1.124 | 1.209 |
| 3.0 | 0.8482 | -1456.76 | 1.900 | 0.4765 | 6.267 | 37.88 | 1.129 | 1.144 |
| 3.5 | 0.8488 | -1338.04 | 1.820 | 0.4776 | 6.512 | 36.50 | 1.134 | 1.101 |
| 4.0 | 0.8492 | -1189.67 | 1.675 | 0.4781 | 6.623 | 35.90 | 1.137 | 1.048 |
| 4.5 | 0.8495 | -1047.92 | 1.555 | 0.4785 | 6.713 | 35.44 | 1.138 | 1.001 |
| 5.0 | 0.8498 | -934.48 | 1.460 | 0.4789 | 6.802 | 34.99 | 1.140 | 0.962 |

Table 2: various parameters obtained for Terbium Decanoate in a mixture of 60/40 benzene-methanol (v/v) at different temperatures.

| | | | | | | | | |
|---|--|------------------------|------------------------|------------------------|--|------------------------|------------------------|------------------------|
| Terbium Decanoate | Values of Critical Micellar Concentration (CMC) | | | | | | | |
| | CMC x 10³ (mol l⁻¹) From the plot of ρ versus C | | | | CMC x 10³ (mol l⁻¹) From the plot of η | | | |
| | 25^oC | 30^oC | 35^oC | 40^oC | 25^oC | 30^oC | 35^oC | 40^oC |
| | 3.10 | 3.23 | 3.37 | 3.63 | 3.07 | 3.23 | 3.43 | 3.57 |
| | The values of constant A and B obtained from the plot of ρ-ρ₀ / C versus C^{1/2} | | | | | | | |
| | Constant A | | | | Constant B | | | |
| | 3.34 | 3.28 | 3.20 | 3.14 | 51.47 | 50.00 | 47.72 | 41.77 |
| | Partial molar volume (ϕ_v⁰), experimental slope (S_v) | | | | | | | |
| | -ϕ_v⁰ x 10⁻² | | | | S_v x 10⁻⁴ | | | |
| | 27.00 | 26.00 | 25.05 | 25.00 | 5.00 | 4.83 | 4.56 | 4.47 |
| Molar volume (\bar{V}) and interaction coefficient (ϕ) obtained from Einstein and Vand's equation | | | | | | | | |

| Molar volume (\bar{V}) liter mole ⁻¹ | | | | Interaction coefficient (ϕ) | | | |
|---|-------|-------|-------|------------------------------------|-------|-------|-------|
| 2.09 | 2.04 | 2.00 | 1.95 | 70.00 | 58.00 | 50.10 | 45.00 |
| Constants M and K' obtained from the Moulik's equation | | | | | | | |
| M | | | | K' x 10 ² | | | |
| 1.112 | 1.109 | 1.108 | 1.105 | 21.54 | 18.00 | 16.00 | 15.83 |
| Values of constants A and B determined from Jones-Dole equation | | | | | | | |
| A | | | | B | | | |
| 1.778 | 1.776 | 1.774 | 1.772 | 8.01 | 7.39 | 6.55 | 4.50 |

CONCLUSION

The equations of Einstein, Vand, Moulik and Jones-Dole have a similar probability of fitting the experimental data of terbium decanoate in a mixture of 60/40 benzene-methanol (v/v). The viscosity measurement of terbium decanoate solution indicate that there is a marked change in the aggregation of the anionic species at the critical micellar concentration, the values of CMC for terbium decanoate (terbium caprate) increase with increasing temperature and results are in good agreement with other data²³⁻²⁶. The values of various constants calculated from above cited well known equations indicate that there is a significant interaction between soap and solvent molecules.

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