



Viscosity measurements of Terbium Octanoate in mixed organic solvent

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(Received 29 July, 2013, Accepted 17 August, 2013)

ABSTRACT: Viscosity measurements of terbium octanoate in mixed organic solvent shows that there is marked change in the aggregation of the anionic species at critical micellar concentration (CMC). The effects of temperature on CMC have been reported. The viscosity results have been satisfactorily explained by various equations with their parameters. The result shows that there is a significant interaction between solute and solvent molecules.

Keywords: micellar; CMC; terbium octanoate.

INTRODUCTION

Carboxylates of metals other than alkali metals are generally insoluble in water and generally called metallic soaps. Metallic soaps are carboxylates of alkaline earth and other polyvalent metals with general formula $M(O_2CR)_n$ where M is a metal in oxidation state n & R is an organic radical containing at least 6-7 carbons atoms. Several workers^[1-4] synthesized metallic soaps by using different method & techniques. Malik et. al. studied the solubility^[5], viscosity^[6] and absorption spectra^[7] 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 coworkers^[8-12]. Upadhyaya^[13, 14] determined acoustical parameters for dissociation and micellization process of lanthanide linoleates, molecular interaction and compressibility behaviour of lithium soaps in benzene-methanol mixture. In present work, some solution properties of terbium octanoate in mixed organic solvent have been determined to study micelle formation and molecular interaction.

MATERIAL AND METHODS

The chemical purification of synthesis of terbium octanoate (caprylate) has already communicated^[15]. Ostwald's type viscometer was used for measuring the viscosity of terbium octanoate 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 25^o, 30^o, 35^o, and 40^oC in a thermostat (Toshniwal).

RESULTS AND DISCUSSION

1. Density Measurements: The density, ρ of terbium octanoate has been measured in a mixture of 60/40 benzene-methanol (v/v) at different temperatures. The density, ρ of terbium octanoate solution increases (Table 1) with increase in solute concentration. However, values of density decrease with increasing temperature. The plot of density, ρ against solute concentration, C (Figure: 1) is 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 (25^o, 30^o, 35^o and 40^oC) and mentioned in Table 2.

The plot of density, ρ against solute concentration, C (Figure 1) are extrapolated to zero solute concentration and it was noticed that extrapolated values of density, ρ_0 are in agreement with the densities of the solvent mixture. It is, therefore, concluded that the solute molecules do not show appreciable aggregation below the critical micellar concentration, CMC whereas at this definite solute concentration there is a marked change in the aggregation.

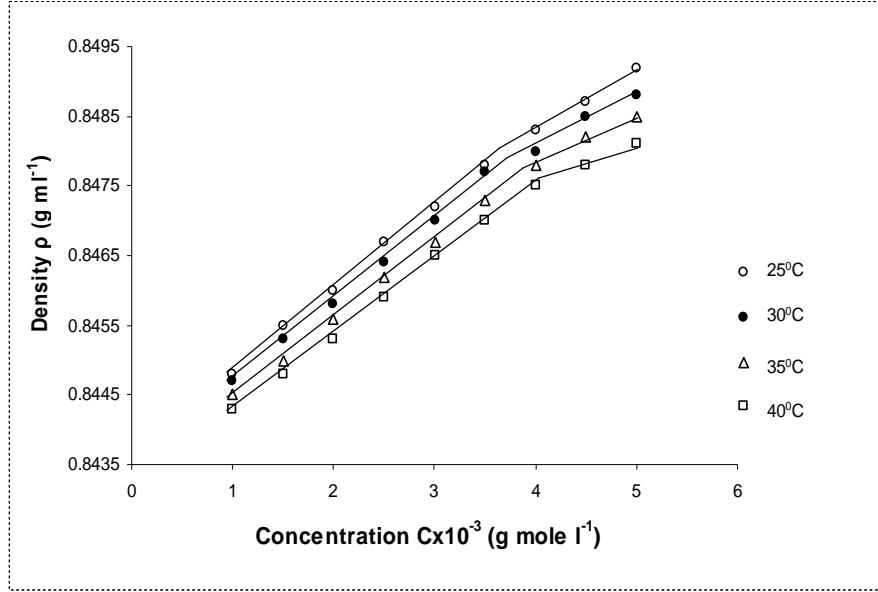


Figure 1: Density, ρ versus Concentration, C of Terbium Octanoate.

The density results of terbium octanoate have been explained in terms of Root's equation ^[16]:

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

Where C is the concentration of the solute, ρ and ρ_0 are densities of terbium octanoate 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 $\rho - \rho_0 / C$ against $C^{1/2}$ below the CMC. The values of constants A and B for terbium octanoate decrease with increase in temperature.

The apparent molar volume ^[17], ϕ_v of terbium octanoate in a mixture of 60/40 benzene-methanol (v/v) have been calculated 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 ρ_0 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_v^0 have been obtained by extrapolating the linear plot of ϕ_v against $C^{1/2}$ for dilute solutions according to Masson's equation ^[18].

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

The limiting apparent molar volume, ϕ_v^0 and experimental limiting slope, S_v are measure of solute-solvent and solute-solute interactions, respectively (Table 2). The limiting apparent molar volume, ϕ_v^0 values for terbium octanoate 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.

2. Viscometric measurements: The viscosity, η of the solutions of terbium octanoate in a mixture of 60/40 benzene-methanol (v/v) has been measured at different temperatures (25^o, 30^o, 35^o and 40^oC). The viscosity, η of the solutions of terbium octanoate increase with increasing 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 octanoate 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 is characterized by an intersection of two straight lines at a definite solute concentration which corresponds to the critical micellar concentration, CMC.

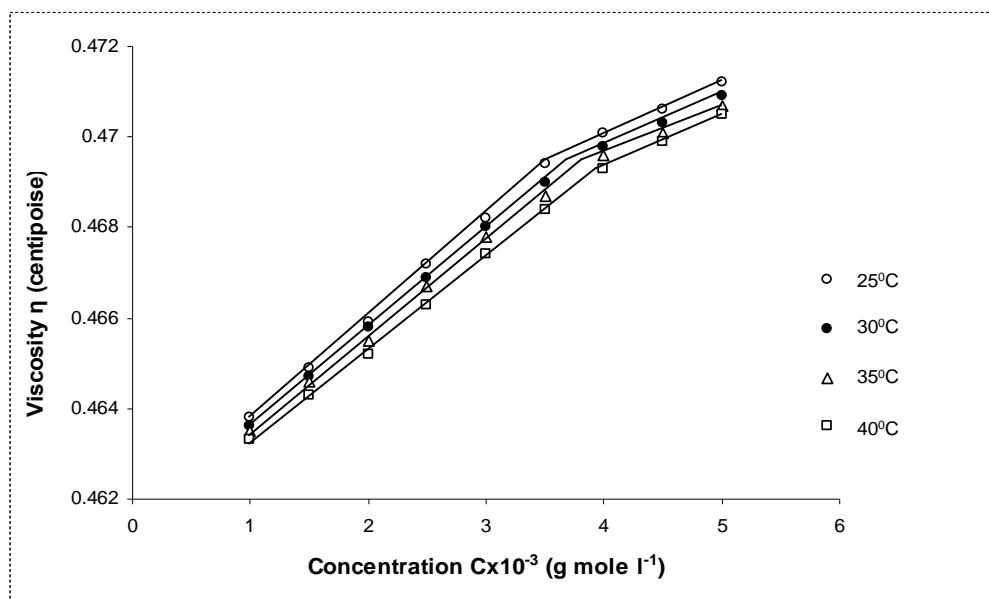


Figure 2: Viscosity, η versus Concentration, C of Terbium Octanoate.

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

Einstein^[19],

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

Vand^[20],

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

Moulik^[21],

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

Jones-Dole ^[22],

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

Where \bar{V} , C, ϕ , η , η_0 and η_{sp} are molar volume of the solute, concentration of solute, interaction coefficient, viscosity of 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 summarised 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.

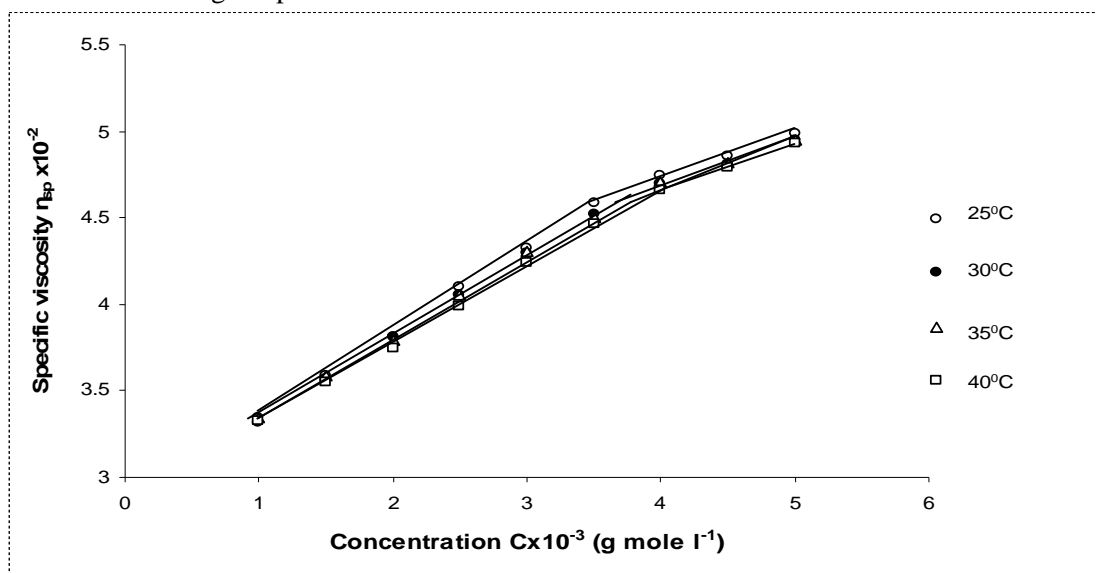


Figure 3: Specific viscosity, η_{sp} versus Concentration, C of Terbium Octanoate.

The values of constant A (solute-solute interactions) and B (solute-solvent interactions) for terbium octanoate 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 octanoate 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 octanoate (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: Einstein, Vand, Moulik and Jones-Dole treatment of viscosity data of Terbium Octanoate 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	0.8448	-962.13	1.400	0.4638	3.342	70.04	1.068	1.056
1.5	0.8455	-962.12	1.400	0.4649	3.587	65.33	1.073	0.926
2.0	0.8460	-843.56	1.300	0.4659	3.810	61.58	1.078	0.852
2.5	0.8467	-867.27	1.320	0.4672	4.100	57.31	1.083	0.820
3.0	0.8472	-804.04	1.267	0.4682	4.323	54.41	1.088	0.789
3.5	0.8478	-792.74	1.257	0.4694	4.590	51.30	1.094	0.776
4.0	0.8483	-754.63	1.225	0.4701	4.746	49.66	1.097	0.751
4.5	0.8487	-698.64	1.178	0.4706	4.857	48.55	1.099	0.724
5.0	0.8492	-677.56	1.160	0.4712	4.991	47.28	1.102	0.706
At 30°C ± 0.5°C								
1.0	0.8447	-1080.95	1.500	0.4636	3.321	70.48	1.067	1.050
1.5	0.8453	-962.36	1.400	0.4647	3.566	65.72	1.073	0.921
2.0	0.8458	-843.76	1.300	0.4658	3.811	61.56	1.078	0.852
2.5	0.8464	-820.04	1.280	0.4669	4.056	57.91	1.083	0.811
3.0	0.8470	-804.23	1.267	0.4680	4.301	54.67	1.088	0.785
3.5	0.8477	-826.82	1.286	0.4690	4.524	52.04	1.092	0.765
4.0	0.8480	-725.16	1.200	0.4698	4.702	50.11	1.096	0.744
4.5	0.8485	-698.81	1.178	0.4703	4.814	48.97	1.098	0.718
5.0	0.8488	-630.29	1.120	0.4709	4.947	47.68	1.101	0.700
At 35°C ± 0.5°C								
1.0	0.8445	-1199.98	1.600	0.4635	3.344	69.99	1.067	1.057
1.5	0.8450	-962.70	1.400	0.4646	3.590	65.29	1.073	0.927
2.0	0.8456	-903.38	1.350	0.4655	3.790	61.89	1.077	0.848
2.5	0.8462	-867.79	1.320	0.4667	4.058	57.86	1.083	0.811
3.0	0.8467	-804.52	1.267	0.4678	4.303	54.65	1.088	0.786
3.5	0.8473	-793.22	1.257	0.4687	4.504	52.27	1.092	0.761
4.0	0.8478	-755.09	1.225	0.4696	4.705	50.09	1.096	0.744
4.5	0.8482	-699.04	1.178	0.4701	4.816	48.95	1.099	0.718
5.0	0.8485	-630.52	1.120	0.4707	4.949	47.66	1.101	0.699
At 40°C ± 0.5°C								
1.0	0.8443	-1437.94	1.800	0.4633	3.323	70.44	1.067	1.051
1.5	0.8448	-1121.42	1.533	0.4643	3.546	66.08	1.072	0.916
2.0	0.8453	-963.16	1.400	0.4652	3.747	62.60	1.076	0.838
2.5	0.8459	-915.68	1.360	0.4663	3.992	58.82	1.081	0.798
3.0	0.8465	-884.03	1.333	0.4674	4.237	55.48	1.086	0.774
3.5	0.8470	-827.51	1.286	0.4684	4.460	52.77	1.091	0.754
4.0	0.8475	-785.12	1.250	0.4693	4.661	50.54	1.095	0.737
4.5	0.8478	-699.39	1.178	0.4699	4.795	49.86	1.098	0.715
5.0	0.8481	-630.81	1.120	0.4705	4.929	47.86	1.101	0.697

Table 2: Various parameters obtained for terbium octanoate in a mixture of 60/40 benzene-methanol (v/v) at different temperatures.

Terbium Octanoate	Values of Critical Micellar Concentration (CMC)							
	CMC x 10 ³ (mol l ⁻¹) From the plot of ρ versus C				CMC x 10 ³ (mol l ⁻¹) From the plot of η versus C			
	25 ^o C	30 ^o C	35 ^o C	40 ^o C	25 ^o C	30 ^o C	35 ^o C	40 ^o C
	3.57	3.63	3.80	4.00	3.50	3.70	3.83	3.97
	The values of constant A and B obtained from the plot of $\rho - \rho_0 / C$ versus C ^{1/2}							
	Constant A				Constant B			
	2.25	2.00	1.90	1.82	40.09	38.12	35.63	32.73
	Partial molar volume (ϕ_v^0), experimental slope (S_v)							
	- $\phi_v^0 \times 10^{-2}$				$S_v \times 10^{-4}$			
	13.90	11.95	11.45	11.15	1.37	1.00	0.81	0.79
	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)			
	2.05	2.00	1.97	1.92	85.00	80.00	77.50	75.10
	Constants M and K' obtained from the Moulik's equation							
	M				K' x 10 ²			
	1.069	1.066	1.065	1.062	16.25	15.28	14.06	12.50
	Values of constants A and B determined from Jones-Dole equation							
	A				B			
1.084	1.077	1.075	1.071	5.42	5.13	4.85	4.44	

CONCLUSION

It is concluded that the equations of Einstein, Vand, Moulik and Jones-Dole have a similar probability of fitting the experimental data of terbium octanoate in a mixture of 60/40 benzene-methanol (v/v). The viscosity measurement of terbium octanoate 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 octanoate (terbium caprylate) increase with increasing temperature and results are in good agreement with other data [23-25]. 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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