

MICELLIZATION AND PHYSICO-CHEMICAL STUDY OF TERBIUM CARBOXYLATES IN MIXED ORGANIC SOLVENT

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Abstract:

The physico-chemical properties as conductometric and viscometric estimation of the solutions of terbium caprate and terbium laurate in mixed organic solvent, benzene –DMF (7:3v/v) has been investigated at constant temperature, 40°C. Results of Conductivity measurements indicate that carboxylates in dilute solutions were weak electrolytes in behavior. Results of viscometric and molar volume estimation of carboxylates, examined by various equations were in close agreement. The result showed that in dilute solution molecules do not aggregate below CMC

Keywords: terbium caprate, terbium laurate, CMC, Conductivity, Density, Viscosity.

Introduction

The physicochemical properties and micellar behavior of metallic carboxylates long chain fatty acids are now of great interest due to their increasing application in various industrial and technical area. Much industrialization has taken place for alkali and alkaline earth and transition metal carboxylates were not much explored [1-26].

The present investigation has been initiated with the conductivities and viscosity measurement of terbium carboxylates in mixed non aqueous solvent, benzene-DMF(7:3v/v) at constant temperature to evaluate micellization, structural analysis in solution, solute-solvent interaction and various other parameters.

Experimental and Measurements:

Chemicals used to prepare terbium carboxylates were of BDH/Merk AR grade. Terbium caprate and laurate were prepared by metathesis reaction between potassium salt of capric and lauric acid, respectively with aqueous solution of terbium acetate in slight excess at 50-60°C with vigorous stirring. Excess reagents were removed by initial washing with distilled water and then with acetone.

Recrystallization of carboxylate was carried out with benzene-DMF mixed solvents. These were dried in an oven and then under reduced pressure. Melting point and elemental analysis was done to contain the purity. Absence of absorption band in the region of 3500-3000 cm^{-1} in IR spectra of carboxylates confirmed that hydroxyl group is not present.

Conductivity estimations were done with digital conductivity meter (Toshniwal CLO1.10) using dipping type conductivity cell with platinized electrodes. Densities of solutions were measured with dilatometer and viscosity measurements were done with Ostwald's type viscometer. All measurements were carried out in the mixture of benzene-DMF (7:3v/v) at constant temperature 40°C.

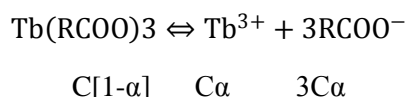
Result and Discussion

Conductivity Measurements:

Specific conductance (k) of solution of terbium caprate and terbium laurate solutions in benzene-DMF, (7:3v/v) mixture, show an increase with increase in carboxylate concentration (Table-1,2). This might be observed due to carboxylate ionization to give terbium cation and carboxylic acid anion in dilute solution and due to aggregation of ionic micelles at higher concentration. The graph of specific conductance V_s vs. carboxylate concentration shows a break at dilute concentration for caprate at 0.0056 mol/l and for laurate at 0.00050 mol/l. These intersection points correspond to the CMC of respective terbium carboxylate in solvent mixture at 40°C (fig.1). The specific conductance values decrease as chain length of terbium carboxylate increases and mobility of anion decreases.

Molar conductance (μ) of terbium carboxylate solutions in benzene-DMF mixture (7:3v/v) decreases with increase in carboxylate concentration and also with chain length, this may be due to combined effect of ion formation, solvation of ions, decrease of ion mobility and micellization, the plots of μ vs. carboxylate concentration are concave in shape as moving upwards indicate that carboxylates behave as weak electrolyte when the solutions were dilute.

Hence, dissociation of terbium caprate and laurate can be expressed using Ostwald's law:



here R for caprate is $CH_3(C_8H_{16})^-$ for laurate is $CH_3(C_{10}H_{20})^-$ C is the concentration and α is the degree of dissociation of carboxylates.

dissociation constant (k) for above equation can be expressed as-

$$k = \frac{[Tb^{3+}][RCOO^-]^3}{[Tb(RCOO)_3]} = \frac{27C^3 \cdot \alpha^4}{(1-\alpha)} \dots \dots (1)$$

As the ionic concentrations of carboxylates are low and the inter ionic interactions are almost negligible, so the solution will not deviate much from ideal behavior and the ion activities can be taken as approximately equal to their concentrations. The degree of dissociation can be replaced by ratio of conductance (μ/μ_0) and equation can be written as

$$\mu^3 c^3 = \frac{k\mu_0^3}{27\mu} - \frac{k\mu_0^3}{27} \dots \dots (2)$$

Here μ and μ_0 are molar conductance at finite and infinite dilutions. The values of specific conductance (k) and μ_0 were obtained from the slope $\left(\frac{k\mu_0^3}{27}\right)$ and intercept $\left(-\frac{k\mu_0^3}{27}\right)$ of the linear part of the plot of $\mu^3 c^3$ vs $1/\mu$.

The value of degree of dissociation α indicate that in dilute solutions, both carboxylates behave as weak electrolyte (Table-3). The value of k decreases as chain length of carboxylate ion increases.

Density and Viscosity Measurements:

The density of carboxylate solutions increases as there is increase in concentration (Table-4, fig2) and results were evaluated by application of Root's equation:

$$e = e_0 + AC - BC^2 \dots \dots \dots (3)$$

Where e_0 and e are the densities of the solvent and solution, respectively constant A and B represents the ion-solvent and ion-ion interactions, the values for terbium caprate and laurate were obtained from the intercept and slope of the plot $(e - e_0)/c$ Vs $c^{1/2}$. The results show that the ion solvent interaction is more than the ion-ion interaction when carboxylate solution is dilute.

The viscosity (η) and specific viscosity (η_{sp}) of the solution in benzene-DMF (7:3 v/v) of terbium caprate and laurate at 40°C as concentration increases (Table-4) and the graph of viscosity vs carboxylate concentration shows a break of two lines at definite carboxylate concentrations that represent the CMC of carboxylates (fig. 3). These values agree with that observed from conductivity measurement under similar conditions. The result of viscosity indicates that carboxylate molecules do not aggregate appreciably below CMC whereas above CMC there is a distinct change in the aggregation of the carboxylate molecules.

The viscosity results have been expressed in terms of equation proposed by Einstein²⁷ and Vond²⁸, Moulik²⁹ and Jones-Dole³⁰. Values for molar values evaluated from these equations were found to be coherent indicating both equations can be applied below CMC. The results were in agreement with other rare earth metal carboxylates^{31,32}. Moulik's constant M and K (Table) obtained from the linear plot of $(\frac{\eta}{\eta_0})^2$ Vs C^2 below CMC and values increase as chain length of fatty acid constituent. Constant A of Jones-Dole expression indicates the solute-solvent interaction dominates over solute-solute interaction in these solutions.

Conclusion

The results of conductivity, viscosity and density reveal carboxylates of terbium behave as weak electrolytes in dilute solution below CMC. The value of CMC shows that micellization of carboxylates starts at a definite concentration and below that these are appreciably ionized in solution.

Table 1: Conductivity measurements of terbium caprate in benzene-DMF(7:3 v/v) at 40°C

S. NO.	Concentration, $c \times 10^3 \text{ dm}^3$	Specific conductance, $k \times 10^6 (\text{m} \eta_0 \text{ cm}^{-1})$	Molar conductance, $\mu (\text{m} \eta_0 \text{ cm}^{-2} \text{ mol}^{-1})$	Degree of dissociation, α	Dissociation constant, $k \times 10^9$
1.	2.1	3.42	1.63	0.4015	10.86
2.	2.3	3.58	1.56	0.3842	11.37
3.	2.5	3.67	1.47	0.3621	11.62
4.	2.6	3.77	1.45	0.3571	12.00
5.	2.8	3.91	1.40	0.3448	12.79
6.	2.9	3.97	1.37	0.3374	12.88
7.	3.1	4.10	1.32	0.3251	13.31
8.	3.3	4.24	1.28	0.3153	14.01
9.	3.6	4.49	1.25	0.3079	16.36

10.	3.8	4.60	1.21	0.2980	16.64
11.	4.2	4.92	1.17	0.2882	19.39
12.	4.5	5.13	1.14	0.2882	21.27
13.	5.0	5.56	1.11	0.2808	25.95
14.	5.5	5.81	1.06	0.2734	28.25
15.	6.2	6.14	0.99	0.2611	30.06
16.	7.1	6.53	0.92	0.2438	32.94
17.	7.7	6.86	0.89	0.2266	33.45
18.	8.3	7.13	0.86	0.2192	35.28
19.	9.1	7.48	0.82	0.2020	42.45
20.	10.0	7.70	0.77	0.1823	56.47

Table 2: Conductivity measurements of terbiumlauratein benzene-DMF (7:3%) mixture at 40°C

S.No.	Concentration, $\text{cx}10^3\text{dm}^3$	Specific conductance $\text{k}\times10^6(\text{m}\eta_0\text{cm}^{-1})$	Molar conductance $\mu (\text{m}\eta_0\text{cm}^{-2}\text{mol}^{-1})$	Degree of dissociation α	Dissociation constant $\text{k}\times10^9$
1.	2.1	3.18	1.51	0.3963	10.22
2.	2.3	3.29	1.43	0.3753	10.42
3.	2.5	3.41	1.36	0.3569	10.64
4.	2.6	3.48	1.33	0.3491	10.79
5.	2.8	3.57	1.28	0.3359	11.06
6.	2.9	3.64	1.25	0.3281	11.36
7.	3.1	3.75	1.20	0.3150	11.86
8.	3.3	3.88	1.17	0.3071	12.46
9.	3.6	4.07	1.13	0.2966	13.86
10.	3.8	4.18	1.10	0.2887	14.47
11.	4.2	4.45	1.03	0.2782	16.60
12.	4.5	4.62	1.00	0.2703	18.00
13.	5.0	4.90	0.98	0.2572	19.90
14.	5.5	5.13	0.93	0.2441	21.10
15.	6.2	5.45	0.88	0.2310	23.83
16.	7.1	5.82	0.82	0.2152	26.41
17.	7.7	6.10	0.79	0.2073	28.72
18.	8.3	6.38	0.77	0.2021	32.89
19.	9.1	6.72	0.74	0.1942	35.91
20.	10.0	7.14	0.71	0.1864	40.06

Table 3: Value of CMC, μ_o and k of terbium

S.No.	Carboxylate	CMC	μ_o	$K*10^9$
1.	Caprate	0.0056	4.06	28.24
2.	Laurate	0.0050	3.81	26.36

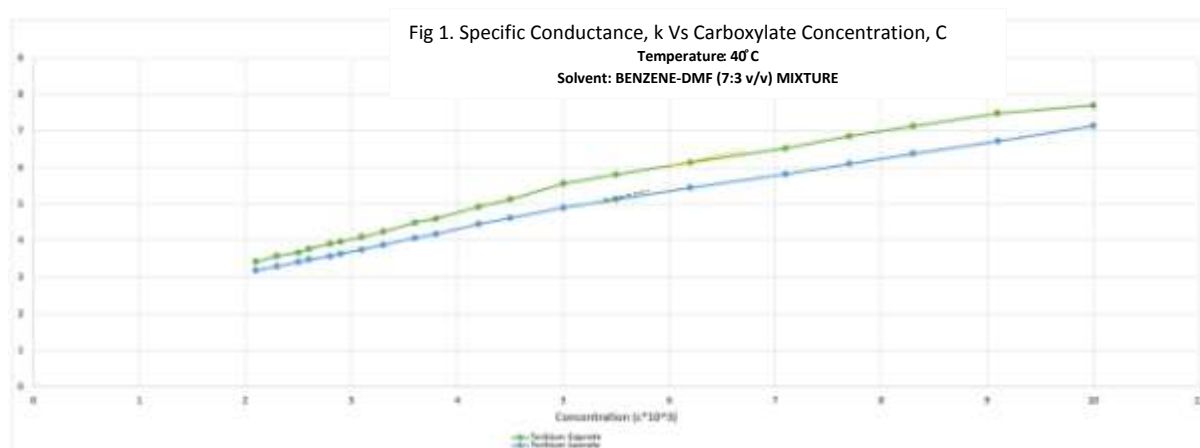


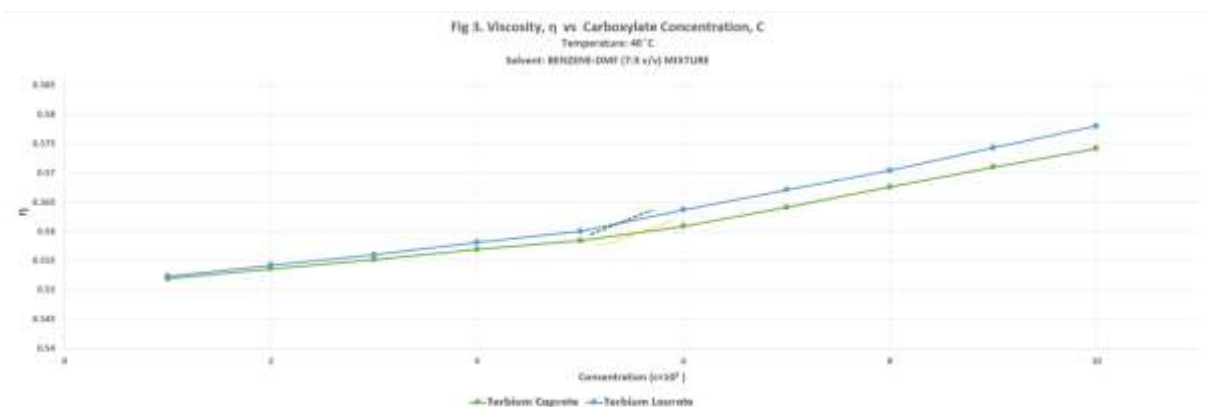
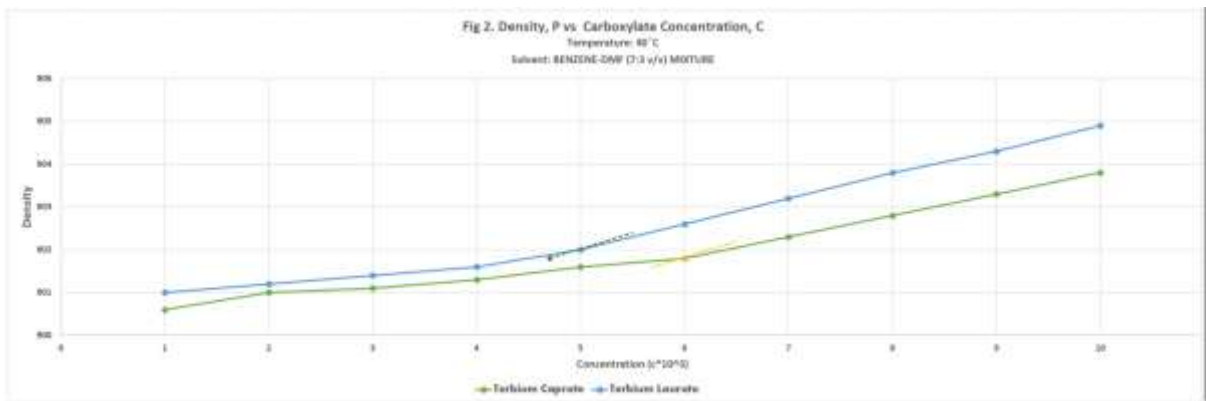
Table 4: Density and Viscosity Measurements of Terbium Carboxylates in Benzene-DMF (7:3v/v) at 40°C

Caprate

S.No.	Concentration $c \times 10^3$ ($dm^3 mol$)	Density ρ (kgm^{-3})	Viscosity η
1.	1.0	900.6	0.5519
2.	2.0	901.0	0.5536
3.	3.0	901.1	0.5552
4.	4.0	901.3	0.5569
5.	5.0	901.6	0.5584
6.	6.0	901.8	0.5509
7.	7.0	902.3	0.5641
8.	8.0	902.8	0.5676
9.	9.0	903.3	0.5710
10.	10.0	903.8	0.5742

Laurate

S.No.	Concentration $c \times 10^3$ (dm ³ mol)	Density ρ (kgm ⁻³)	Viscosity η
1.	1.0	901.0	0.5523
2.	2.0	901.2	0.5542
3.	3.0	901.4	0.5560
4.	4.0	901.6	0.5581
5.	5.0	902.0	0.5600
6.	6.0	902.6	0.5637
7.	7.0	903.2	0.5671
8.	8.0	903.8	0.5704
9.	9.0	904.3	0.5743
10.	10.0	904.9	0.5780



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