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Studies on apparent molar volume, viscosity and conductivity of Terbium Decanoate in methanol

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Abstract

The apparent molar volume was evaluated from the density measurements of the solutions of terbium decanoate in methanol and the results were used to determine the partial molar volume of decanoate and its variation with temperature. The viscosity results were interpreted in terms of equations proposed by Einstein, Vand, Moulik and Jones-Dole and were used to determine the molar volume. The density and viscosity results showed that there is no appreciable aggregation in dilute solutions of terbium decanoate and there is a marked change in aggregation at a definite concentration. The conductivity measurements were used to evaluate limiting molar conductance, ionization constant and various thermodynamic parameters. The conductivity results were in agreement with those of density, apparent molar volume and viscosity.

Keywords: Terbium decanoate, apparent molar volume, viscosity, conductivity, ion-ion and ion-solvent interactions

Introduction

The most striking feature of metallic carboxylates is their increasing importance in industrial and academic fields due to their unique characteristics owing to the presence of both lyophilic and lyophobic moieties in the same molecule. Although, a large amount of work has been reported on alkali, alkaline earth and transition metal carboxylates, only few studies have been performed carboxylates of lanthanides and actinides (1-18). The metallic carboxylates are largely present as metal cations and carboxylate anions in dilute solutions and many of their physical properties exhibit characteristic transitions at a definite concentration of carboxylate. The transitions are generally related to the aggregation arising due to the intrinsic amphiphilic nature of metal carboxylates. The transition region has been used to determine the definite carboxylate concentration, above which multi molecular aggregates are formed. The present work deals with the studies of the density, apparent molar volume, viscosity and conductivity of the solutions of terbium decanoate in methanol and the results were used to study the ion-solvent and ion-ion interactions and test the validity of well-known equations and models.

Methodology

All the chemicals used were of Analytical Reagent grade. Terbium decanoate was prepared by direct metathesis of potassium decanoate with slight excess of required amount of aqueous solution of terbium acetate under vigorous stirring. The purity of terbium decanoate was confirmed by its melting point, 103°C and elemental analysis. The absence of hydroxyl groups in terbium decanoate was confirmed by the absence of any peak in the region of 3000-3500 cm⁻¹ IR-spectra.

The solutions were prepared by dissolving known amounts of terbium decanoate in methanol and were kept in a thermostat at the desired temperatures. A Pyrex glass dilatometer with a 15 cm³ reservoir was used to determine the density of the solutions at constant desired temperature and the reproducibility of the results was ± 0.0002 g cm⁻³. The viscosity measurements were carried out with an Ostwald's viscometer and the probable error was below 0.3%. The conductivity measurements were made with a To shniwal Digital Conductivity Meter "Type CL 01.10A" using a dipping type conductivity cell with platinized electrodes at different constant temperatures and the accuracy of the results was $\pm 0.5\%$.

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Results and Discussion

(1) Density, ρ and Apparent molar volume ϕ_v

The density, ρ of the solutions of terbium decanoate in methanol increases with increasing decanoate concentration,

C and decrease in temperature. The plots of density, ρ Vs concentration, C are characterized by an intersection of two straight lines at a definite concentration at which there is a sudden change in the aggregation of decanoate anions. The values of this concentration (0.0042, 0.0044 and 0.0058 mol dm⁻³ at 303, 313 and 323K respectively) increase with

increase in temperature. The plots of density, ρ Vs concentration, C for dilute solutions have been extrapolated to zero decanoate concentration and the extrapolated values

of density, ρ_o , are in agreement with the experimental values of the density of the solvent. It is, therefore, concluded that the decanoate anions do not show appreciable aggregation in dilute solutions and there is a marked change in aggregation at a definite concentration of decanoate. The density results have been explained in terms of Root's equation:

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

where C is the concentration of decanoate ρ and ρ_o are the densities of the solution and solvent, respectively. The constants A and B of the Root's equation refer to the solute-solvent and solute-solute interactions, respectively and the values of A and B have been obtained from the intercept and slope of the plots of $(\rho - \rho_o)/C$ Vs $C^{1/2}$ for dilute solutions.

The values of $(\rho - \rho_o)/C$ are constant for dilute solutions indicating that there is solute-solute interaction ($B=0$) in dilute solutions. However, the values of constant B (solute-solute interaction) are positive above a definite concentration of decanoate indicating a sudden increase in solute-solute interaction at this concentration. The values of constant B (1.85, 1.56 and 1.43 at 303, 313 and 323°K, respectively) decrease with rise in temperature.

The apparent molar volume, ϕ_v has been evaluated by the relationship:

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

where M , ρ , ρ_o and C represent the molecular weight of terbium decanoate, density of solution, density of solvent and concentration of decanoate, respectively.

The values of apparent molar volume ϕ_v remain almost constant for dilute solutions but decrease (become more negative) with increasing decanoate concentration above a definite concentration (Fig.1). The negative values of ϕ_v suggest that there is a decrease in molar volume when decanoate is added to the solution and this may be due to the phenomenon of electrostriction in which the cations, Tb³⁺ with a strong electric field pack solvent molecule around themselves in a smaller volume than in the bulk of solvent. The values of the limiting apparent molar volume or partial molar volume of solute, ϕ_v^o have been obtained by

extrapolating the plots of ϕ_v Vs $C^{1/2}$ (Fig.2) of Masson's equation (19) for dilute solutions:

$$\phi_v = \phi_v^o + S_v \cdot C^{1/2} \quad (3)$$

where S_v , is a constant representing the variation of apparent molar volume with decanoate concentration. The values of ϕ_v^o (-634.47, -636.01 and -637.55 ml mol⁻¹ at 303, 313 and 323°K, respectively) decrease (become more negative) with increase in temperature and the decrease in ϕ_v^o is about 0.154 ml mol⁻¹ deg⁻¹ for dilute solutions of terbium decanoate in methanol. The values of S_v , are almost equal to zero for dilute solutions below the concentration at which aggregation begins but are negative for more concentrated solutions.

(2) Viscosity, η :

The viscosity, η and specific viscosity, η_{sp} of the solutions of terbium decanoate in methanol increase with increasing concentration of decanoate as well as with the rise in temperature (Fig.2). The plots of η Vs C (Fig.3) and η_{sp} Vs C are characterized by an intersection of two straight lines at a definite decanoate concentration at which there is a sudden change in the aggregation of decanoate anions. The plots of η Vs C (Fig.3) have been extrapolated to zero concentration of terbium decanoate and the extrapolated values of viscosity, η_o are in agreement with the viscosity of methanol (solvent). The viscosity results were interpreted in terms of equations proposed by Einstein (20), Vand (21), Moulik (22) and Jones-Dole (23):

$$\text{Einstein: } \eta_{sp} = 2.5 \bar{V} \cdot C$$

$$\text{Vand: } 1/C (0.921/\bar{V})^{-1} [1/\log(\eta/\eta_o)] + \phi \bar{V}.$$

$$\text{Moulik: } (\eta/\eta_o)^2 = M + KC^2$$

$$\text{Jones-Dole: } \eta_{sp}/C^{1/2} = A + BC^{1/2}$$

Where

\bar{V} , C , ϕ , η , η_o and η_{sp} are molar volume, concentration of decanoate, interaction coefficient, viscosity of solution, viscosity of solvent and specific viscosity, respectively. M and K are Moulik's constants and A and B refer to Jones-Dole's constants, respectively.

The plots of η_{sp} Vs C for dilute solutions are linear with intercept almost equal to zero indicating that the Einstein's equation is applicable to dilute solutions of decanoate in methanol. The values of molar volume, \bar{V} have been calculated from the slope of the plots of η_{sp} Vs C (Table 1).

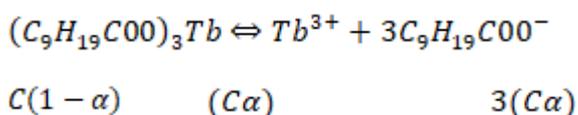
The plots of $(1/C)$ Vs $[1/\log(\eta/\eta_o)]$ are linear which shows that the Vand's equation is applicable to these solutions and the values of molar volume obtained from the Einstein's

plots (Table 1). The molar volume, \bar{V} increases while the interaction coefficient, ϕ decreases (become more negative) with the increase in temperature (Table 1). The plots of $(\eta/\eta_0)^2$ vs C^2 show concentration of decanoate at which there a break at a definite sudden change in is aggregation of anions. The plots are linear below this definite concentration indicating that the Moulík's equation is applicable to these solutions. The values of Moulík's constants, M and K were obtained from the intercept and slope of the plots of $(\eta/\eta_p)^2$ vs C^2 and the results show that the constant M remains almost constant while the constant K increases with increase in temperature (Table 1). The viscosity results have also been explained in terms of Jones-Dole's equation.

The plots of $\rho_{sp}/c^{1/2}$ vs $C^{1/2}$ are characterized by an intersection of two straight lines at a definite concentration of decanoate. The constants A and B have been evaluated from the intercept and slope of the Jones-Dole's plots (Table 1). The values then of constant A (solute-solute interaction) are smaller than those of B (solute-solvent interaction) indicating that there is no appreciable aggregation in dilute solutions and there is a marked change in aggregation at a definite decanoate concentration. The viscosity results are in accordance with those of density and apparent molar volume.

(3) Conductivity and Thermodynamic parameters

The specific conductance, k of the solutions of terbium decanoate in methanol increases with increasing decanoate concentration, C and temperature (Fig.3). The increase in specific conductance may be due to the ionisation of terbium decanoate into Tb^{3+} and $C_9H_{19}COO^-$ ions in dilute solutions and due to the association of anions at higher decanoate concentrations. The plots of specific conductance, k Vs decanoate concentration, C (Fig.4) are characterised by an intersection of two straight lines at a definite concentration indicating the association of anions. The results (Table 2) show that the values of the concentration, at which association begins, increase with the increase in temperature association occurs when the energy released as a result of aggregation of anions is sufficient to overcome the repulsion between the ionic head groups and to balance the decrease accompanying aggregation. The molar conductance, μ of solutions decreases with increasing concentration of the plots of molar conductance, μ Vs square root of decanoate concentration, $C^{1/2}$ are root not linear and the values of limiting molar conductance, μ_0 cannot be obtained by usual extrapolation method indicating that the Debye-Huckel-Onsagar's equation is not applicable to the solutions in methanol. However, an expression for the ionisation of terbium decanoate in methanol may be obtained in Ostwald's manner. If C is the concentration in mol l^{-1} and α is the degree of ionisation, the molar concentrations of different species can be expressed as:



The ionisation constant, K , for the above equilibrium may be written as:

$$K = \frac{[Tb^{3+}][C_9H_{19}COO^-]^3}{[Tb(C_9H_{19}COO)_3]} = \frac{(C\alpha).(3C\alpha)^3}{C(1-\alpha)}$$

$$K = \frac{27C^3\alpha^4}{1-\alpha}$$

The interionic effects in dilute solutions may be neglected since the ionic concentrations are low and the dilute solutions do not deviate appreciably from ideal behavior. The ionic activities may be taken as almost equal to concentrations and the degree of ionisation, α may expressed as equal to the conductance ratio, μ/μ_0 where μ_0 are the molar conductance, at a finite and infinite concentrations, respectively. On substituting the value of α and rearranging equation (1) may be written as:

$$\mu^3 C^3 = (K\mu_0^4 / 27\mu) - (K\mu_0^3 / 27)$$

The values of ionisation constant, K and limiting molar conductance, μ_0 have been obtained from the intercept, $(-K\mu_0^3 / 27)$ and slope, $(K\mu_0^4 / 27)$ of the plots of $\mu^3 C^3$ vs $1/\mu$ for dilute solutions. The results (Table-2) show that the values of limiting molar conductance, μ_0 increase while of ionisation constant, K decrease with the rise in temperature indicating the exothermic nature of ionization of terbium decanoate in methanol. The values of ionisation constant, K at different concentrations of decanoate have been evaluated using equation (1) and assuming the degree of Ionisation, α as equal to the conductance ratio, μ/μ_0 and using the value of μ_0 obtained from the plots of $\mu^3 C^3$ Vs $1/\mu$. The plots of ionisation constant K Vs decanoate constant, concentration, C (Fig.3) show that the ionisation constant decreases rapidly in dilute solutions but increases at higher concentrations of decanoate. The results

$$\alpha = 0.7 \text{ to } 0.2 \text{ and } K = 6 \text{ to } 18 \times 10^{-8}$$

show that terbium decanoate behaves as a moderate electrolyte in methanol. The relation between the ionisation constant, K and heat of ionization, ΔH_I can be expressed as:

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

$$\log K = \frac{-\Delta H_I}{2303RT} + \text{constant}$$

The value of the heat of ionisation, $\Delta H_I (-9.57 \text{ kJ mol}^{-1})$ has been obtained from the plot of $\log K$ VS $1/T$ for the solutions of terbium decanoate in methanol. The negative value of ΔH_I confirms exothermic nature of the ionisation process. The values of changes in free energy, ΔG_I and entropy, ΔS_I per mole for the ionisation process (Table 3) have been evaluated using the relationships:

$$\Delta G_I = -RT \ln K$$

$$\Delta S_I = \frac{\Delta H_I - \Delta G_I}{T}$$

and the values of ΔG_I and ΔS_I are recorded in Table-3. The standard free energy of association per mole of monomer, ΔG_A for the phase separation model (24,25) can be expressed as :

$$\Delta G_A = 2RTX_C$$

where X_C is the concentration, at which association begins, expressed as a mole fraction and defined as:

$$X_C = \frac{n_s}{n_o + n_s}$$

Since the number of moles of solute (n_s) are small as compared to the number of moles of the solvent (n_o), X_C can be written as:

$$X_C = \frac{n_s}{n_o}$$

The standard enthalpy changes of association per mole of monomer for the phase separation model 24, 25 ΔH_A is given as

$$\frac{d(\ln X_C)}{dt} = \frac{\Delta H_A}{2RT^2}$$

$$\log X_C = -\frac{\Delta H_A}{2(2.303)} + \text{constant}$$

The value of ΔH_A has been obtained from the slope of the plot of $\log X_C$ VS $1/T$ and was found to be 2.87 kJ mol^{-1} for the dilute solutions of terbium decanoate in methanol. The standard entropy changes for the association process, ΔS_A has been evaluated by using the relationship:

$$\Delta S_A = \frac{\Delta H_A - \Delta G_A}{T}$$

The positive values of ΔS_A and negative values of ΔG_A and the negative values of ΔG_I and positive values of ΔS_I (Table-3) indicate that the association process is dominant over the ionisation process.

It is, concluded that the thermodynamics of ionisation and association can be satisfactorily explained in the light of phase separation model from conductivity measurements.

Table 1: Values of molar volume, \bar{V} , interaction coefficient, ϕ , constants M and K (from Moulik's equation and constants A and B (From Jones-Dole's equation)

Temperature	\bar{V}		ϕ	Moulik's equation		Jones Dole's equation	
	Einstein's Equation	Vand's Equation		M	K	A	B
303	6.06	6.12	-30.12	1.016	2285	+0.075	8.09
313	7.07	8.01	-40.04	1.017	3284	+0.048	7.39
323	9.09	9.02	-50.56	1.025	3714	+0.008	6.42

Table 2: Values of molar volume, \bar{V} , interaction coefficient, ϕ , constants M and K of terbium decanoate in methanol

Temperature (K)	CMC (Mol l ⁻¹)	X _c X10 ⁴	μ_o	K X 10 ⁸
303	0.0042	1.70	6.74	10.6
308	0.0046	1.87	7.16	10.3
313	0.0049	2.00	8.00	9.5
318	0.0054	2.23	8.33	8.9
323	0.0058	2.39	9.40	7.9

Table 3: Thermodynamic parameters of terbium decanoate in methanol

Temperature (K)	Ionisation		Association	
	ΔG_I (kJmol ⁻¹)	$-\Delta S_I \times 10^2$ (kJK ⁻¹ mol ⁻¹)	$-\Delta G_I$ (kJmol ⁻¹)	$\Delta S_I \times 10^2$ (kJK ⁻¹ mol ⁻¹)
303	40.46	10.22	43.73	15.4
308	41.20	10.29	43.97	15.2
313	42.08	10.41	44.33	15.1
318	42.91	10.51	44.46	14.9
323	43.91	10.65	44.79	14.8

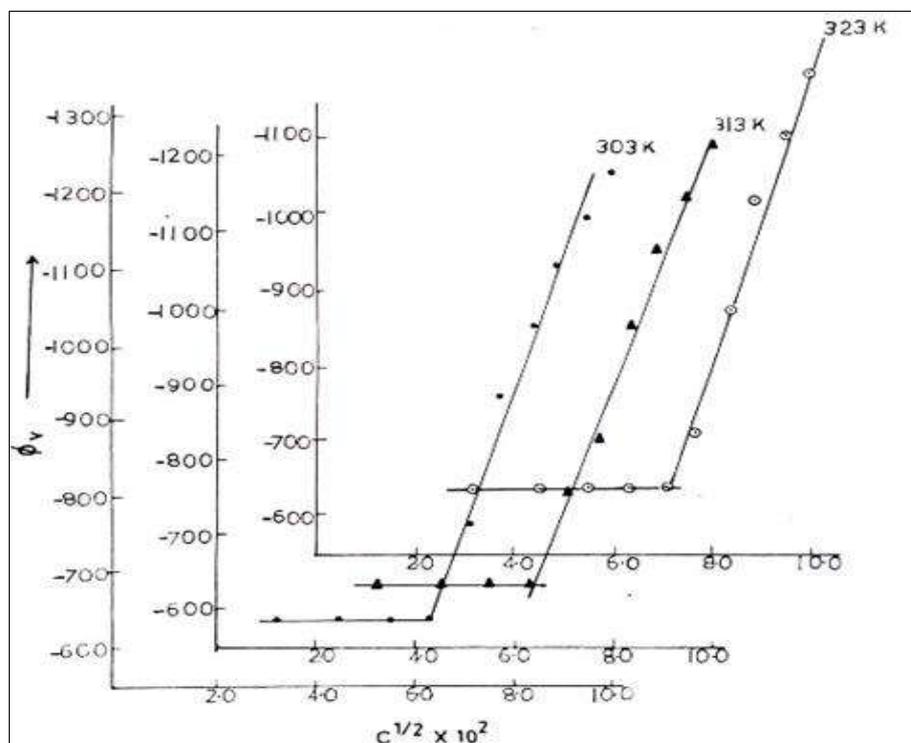


Fig 1: Apparent molar volume, ϕ_v Vs $C^{1/2}$

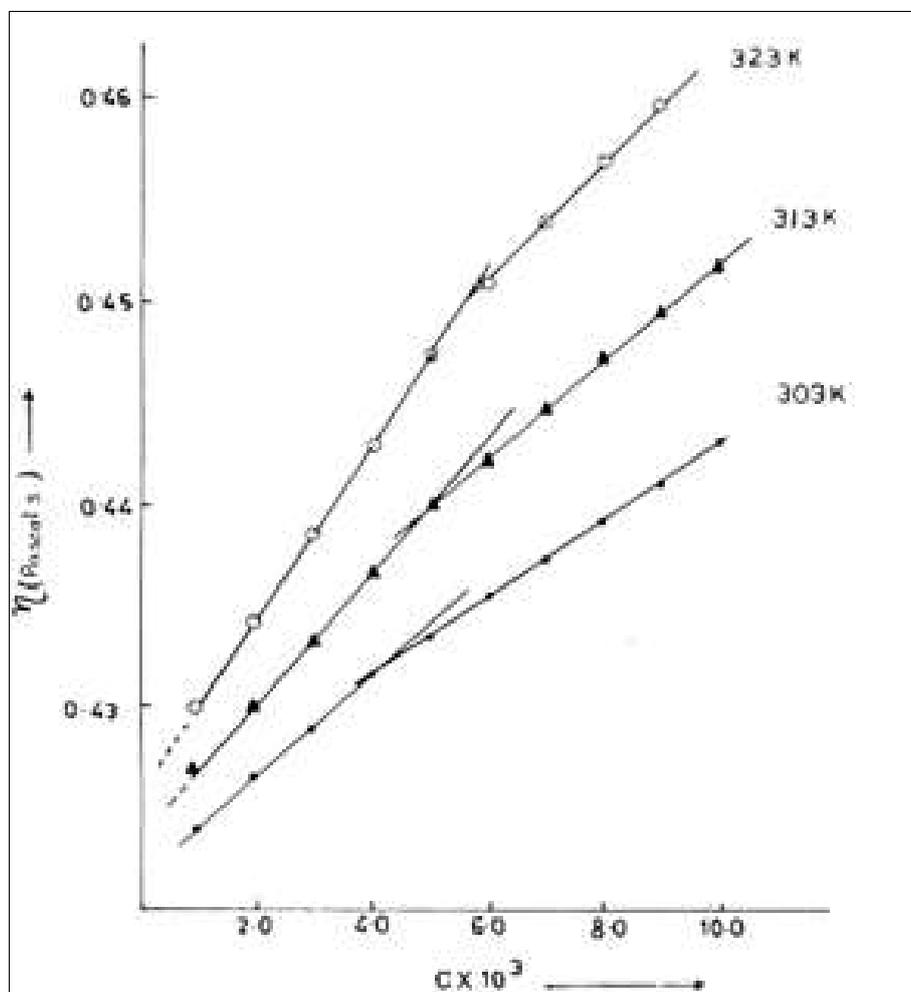


Fig 2: Viscosity, η Vs Carboxylate concentration, c

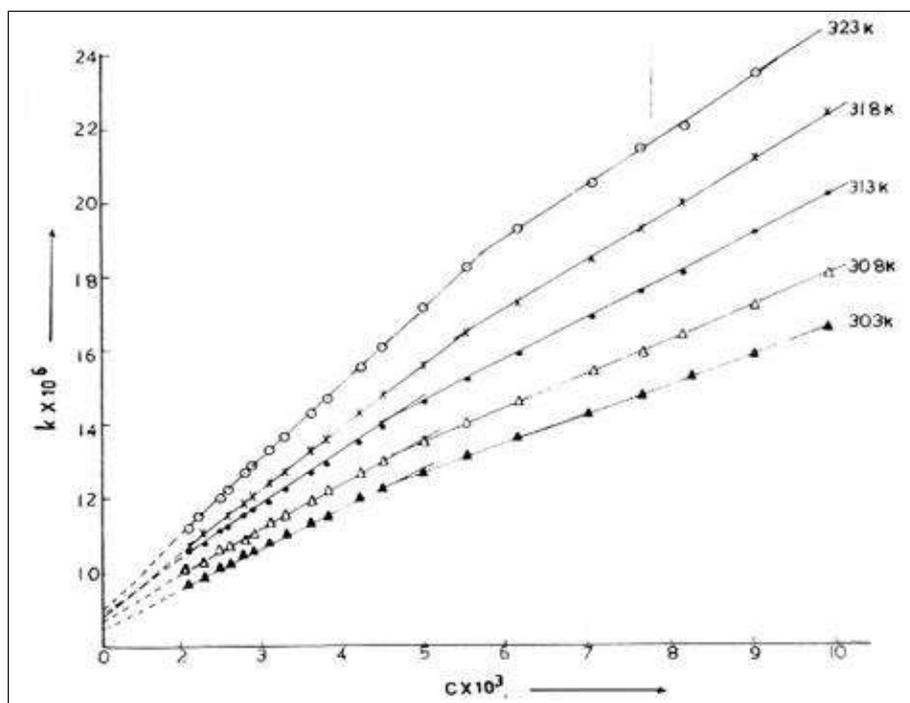


Fig 3: Specific conductance, k Vs carboxylate concentration, c

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