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Ultrasonic and Viscosity Studies of Zirconyl Laurate in Benzene-Methanol Mixture

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ABSTRACT

The ultrasonic and viscosity measurements of Zirconyl Laurate in benzene-methanol mixture (4:1 v/v) have been at carried out at constant temperature and the result were used to evaluate the critical micelle concentration (CMC), soap-solvent interaction and various allied parameters. The values of CMC for zirconyl laurate obtained from the ultrasonic measurements are in agreement with the results obtained from viscosity measurements. The various acoustic parameters (adiabatic compressibility, intermolecular free length, specific acoustic impedance, solvation number, apparent molar compressibility, molar sound velocity and molar sound compressibility) for zirconyl laurate have been evaluated by ultrasonic measurements. The results of viscosity measurements have been explained in terms of well known equations.

Keywords- Zirconyl laurate, ultrasonic velocity, CMC, acoustic parameters and viscosity.

I. INTRODUCTION

Recently, the emphasis has been laid on the study of metal soaps on account of their important role in technological and academic fields while major developments have taken place in the study of alkali, alkaline earth and first series of transition metal soaps, the investigations on second series of transition metal soaps remained almost untouched inspite of their widespread applications in various industries [1-10]. The physico-chemical characteristics and structures of soaps can be controlled upto some extent by the methods and conditions of their preparation, therefore information on the nature and structure of metal soaps is of great significance for their uses in various industries under different conditions.

The present work deals with the ultrasonic velocity and viscosity measurements of solutions of zirconyl laurate in mixture of benzene-methanol (4:1 v/v). The results have been used to determine the critical micelle concentration (CMC), soap-solvent interactions and various acoustical parameters.

II. RESULT AND DISCUSSION

Ultrasonic Measurements:

The variation of ultrasonic velocity and soap concentration follows the relationship

$$v = v_o + GC$$

where v_o is the ultrasonic velocity in the solvent and G is Garney's constant [15] . The plots (Fig. 1) of ultrasonic velocity Vs soap concentration are characterized by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC. The value of CMC was found to be 0.037 M for zirconyl laurate in benzene-methanol mixture (4:1 v/v). The micellization is mainly caused by the energy change due to dipole-dipole interactions between the polar head groups of soap molecules and the micelles are held together by Vander Waals forces acting between hydrocarbon chains of parallel layers and by strong dipole-dipole interactions between polar heads. The extrapolated values of v_o (1095.8 ms^{-1}) was found in close agreement with the velocity in pure solvent mixture (1095.5 ms^{-1}), indicating that the soap molecules do not aggregate upto an appreciable extent below CMC. The value of Garney's constant was found to be 90 for the solvent mixture.

The values of the adiabatic compressibility, β, of the solution of zirconyl laurate decreases with increase in soap concentration (Table-1). The decrease in adiabatic compressibility may be due to the ionization of soap molecues into zirconyl cation (ZrO^{2+}) and laurate anions ($C_{11}H_{23}COO^-$).

The ions in the solutions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic fields of the ions and thus the internal pressure increases which lowers the compressibility of the solutions i.e. the solutions become harder to compress.[16]

The adiabatic compressibility of the soap solutions obey Bachem's relationship. [17]

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$$\beta = \beta_o + AC - BC^{3/2}$$

A and B are constants, C is the molar concentration of the soap, and β_o is the adiabatic compressibility of the solvent mixture. The values of A ($- 4.20 \times 10^{10}$) and B (8.22×10^{10}) were obtained from the intercept and the slope of the plots of $(\beta - \beta_o/C)$ Vs $C^{1/2}$ for the solutions.

It follows from Debye-Huckel's theory that the apparent molar compressibility, ϕ_k , is related to the molar concentration of the soap by the relationship

$$\phi_k = \phi_k^o + S_k C^{1/2}$$

where f_k^o is the apparent molar compressibility of the solvent and S_k (10.34×10^7) were evaluated from the intercept and the slope of the linear plots of ϕ_k Vs $C^{1/2}$ below CMC.

The intermolecular free length, L_f decreases while specific acoustic impedance, Z increases with the increasing soap concentration which indicates that there is a significant interaction between soap and solvent molecules due to which the structural arrangement is considerably affected [18]. The increase in the value of Z with increasing C can be explained on the basis of a lyophobic interaction between soap and solvent molecules while increases the intermolecular distance, opening relatively wide gaps between the molecules and becoming the main cause of impedance in the propagation of ultrasound waves. The plots of L_f Vs C and Z Vs C show a break at the CMC value of the soap.

The solvation number, S_n decreases above CMC with increasing soap concentration may be due to an enhanced incorporation of solvent molecules above CMC, reducing the repulsive forces acting between the heads of the ionic micelles. The molar sound velocity, R and molar compressibility, W of the solutions of zirconyl laurate increase with increase in concentration

The results of the ultrasound velocity measurements confirm that there is a significant interaction between soap and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably below the CMC.

Viscosity Measurements:

The viscosity, η and specific viscosity, η_{sp} of the solutions of zirconyl laurate in a mixture of benzene-methanol (4:1 v/v) increase with increasing soap concentration (Table-2) which may be due to the increasing tendency of the soap molecules to form aggregates with the increasing soap concentration. The plots of viscosity, η Vs soap concentration, C (Fig.-2) are characterised by an intersection of two straight lines at definite soap concentration which corresponds to the CMC of zirconyl soaps (0.038 M) and are in agreement with the values obtained from other micellar properties.

The viscosity results confirm that there is no appreciable aggregation below the CMC whereas there is a sudden increase in the aggregation at the CMC of the soap.

The viscosity results have been interpreted on the basis of equations proposed by Einstein [19], Vand [20]. Moulik [21] and Jones-Dole [22]:

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

Vand : $(1/C) = \left(\frac{0.921}{\bar{V}}\right)^{-1} \frac{1}{\log\left(\eta/\eta_0\right)} + \phi\,\bar{V}$

Moulik : $\left(\eta/\eta_0\right)^2 = M + K\,C^2$

Jones-Dole : $\eta_{sp}/\sqrt{C} = A + B\sqrt{C}$

where $\bar{V}$, C , ϕ , η , η_o and η_{sp} are the molar volume of the soap (1 mol^{-1}), concentration of the soap (mol dm^{-3}), interaction coefficient, viscosity of the solution (PaS), viscosity of the solvent (PaS) and specific viscosity, respectively. M and K are Moulik's constants. The constant A and B of Jones-Dole's equation refer to soap-soap and soap-solvent interactions, respectively.

The plots of specific viscosity, η_{sp} Vs soap concentration, C below the CMC are linear with intercept almost equal to zero which shows that the equation proposed by Einstein is applicable to dilute solutions of zirconyl laurate. The values of molar volume, $\bar{V}$ are obtained from the slope of Einstein's plots (0.62 mol^{-1} is in close agreement with the value obtained from the slope of the plot of Vand's equation (0.64 mol^{-1}) for the solution of zirconyl laurate in benzene-methanol (4:1 v/v).

The values of constants M (1.028) and K (72.00) of Moulik's equation are obtained from the intercept and slope of the plots of $\left(\eta/\eta_0\right)^2$ Vs C^2 for dilute solutions.

The plots of $\eta_{sp}/\sqrt{C}$ Vs $\sqrt{C}$ are characterised by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of the soap. The values of constants A (0.008) and B (1.38) of Jones-Dole's equation have been obtained from the intercept and slope of the plots of below the CMC. The values of constant B are larger than those of A which confirms that the soap molecules do not show appreciable aggregation below the CMC and there is a marked change in aggregation of soap molecules at the CMC.

The values of CMC obtained from the ultrasonic and viscosity measurements are in close agreement. It is therefore concluded that the viscosity results for dilute solutions of zirconyl laurate may be satisfactorily explained in terms of equations proposed by Einstein, Vand, Moulik and Jones-Dole.

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Table-1 : Ultrasonic velocity and acoustic parameters of zirconyl laurate in benzene-methanol (4:1 v/v) mixture at (40±0.05)°C.

S. No.	C (mol dm^{-3})	ρ (kg m^{-3})	v (m s^{-1})	$\beta \times 10^{10}$ (m^2 N^{-1})	L_f (A°)	$Z \times 10^{-5}$ (kg m^{-2} s^{-1})	S_n (C.G.S. Unit)	$-\phi_k \times 10^7$ (m^5 N^{-1} kg^{-1} mol^{-1})	$R \times 10^4$ {m^3 mol^{-1} (ms^{-1})$^{1/3}$}	$W \times 10^4$ {m^3 mol^{-1} (N/m^2)$^{1/7}$}
1	0.01	846.2	1096.7	9.825	38.56	9.280	4.72	4.566	7.566	14.200
2	0.02	847.0	1097.6	9.800	38.51	9.296	4.09	3.999	7.601	14.267
3	0.03	847.8	1098.5	9.775	38.46	9.313	3.89	3.811	7.634	14.332
4	0.04	848.8	1099.6	9.744	38.40	9.333	3.99	3.925	7.667	14.395
5	0.05	849.8	1101.4	9.700	38.32	9.360	4.42	4.253	7.701	14.460
6	0.06	851.1	1103.0	9.658	38.23	9.388	4.65	4.497	7.733	14.522
7	0.07	852.3	1104.7	9.614	38.15	9.415	4.86	4.683	7.764	14.582
8	0.08	853.4	1106.5	9.571	38.06	9.443	4.99	4.796	7.798	14.647
9	0.09	854.7	1108.2	9.527	37.97	9.472	5.12	4.920	7.829	14.708
10	0.10	855.8	1110.0	9.484	37.89	9.499	5.21	4.986	7.862	14.771

Table-2: Density and viscosity of zirconyl laurate in benzene-methanol (4:1 v/v) mixture at (40±0.05)°C.

S. No.	C (mol dm^{-3})	ρ (kg m^{-3})	$(\rho - \rho_o)/C$	$\eta \times 10^3$ (Pas)	$\eta_{sp} \times 10^2$	$\eta_{sp}/\sqrt{C}$	$(\eta/\eta_o)^2$	$1/\log(\eta/\eta_o)$
1	0.01	846.2	100.0	0.4585	1.55	0.155	1.031	149.67
2	0.02	847.0	90.0	04652	3.03	0.125	1.062	77.03
3	0.03	847.8	86.7	0.4715	4.44	0.256	1.091	53.12
4	0.04	848.8	90.0	0.4785	5.98	0.299	1.123	39.64
5	0.05	849.8	92.0	0.4872	7.91	0.359	1.164	30.26
6	0.06	851.1	98.3	0.4959	9.83	0.401	1.206	24.55
7	0.07	852.3	101.4	0.5048	11.81	0.445	1.250	20.63
8	0.08	853.4	102.5	0.5140	13.84	0.489	1.296	17.76
9	0.09	854.7	105.6	0.5228	15.79	0.526	1.341	15.70
10	0.10	855.8	106.0	0.5317	17.76	0.562	1.387	14.08

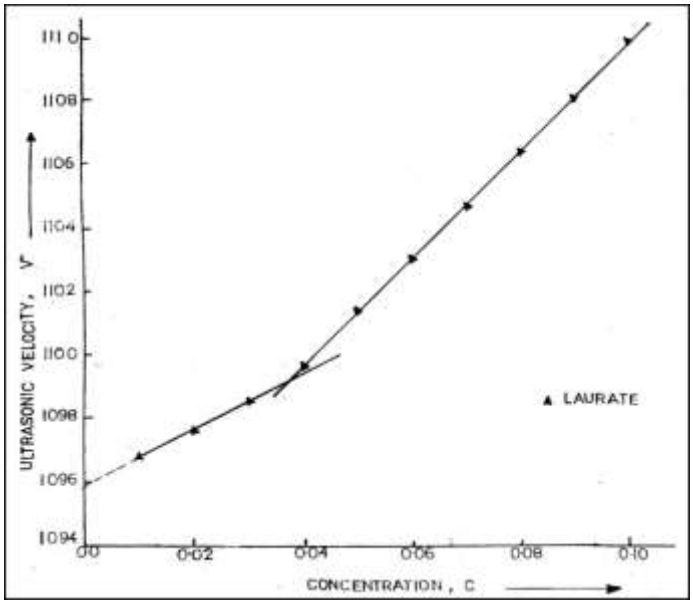

Fig. 1: Ultrasonic velocity Vs concentration of zirconyl laurate in benzene-methanol mixture (4:1 v/v) at (40±0.05)°C

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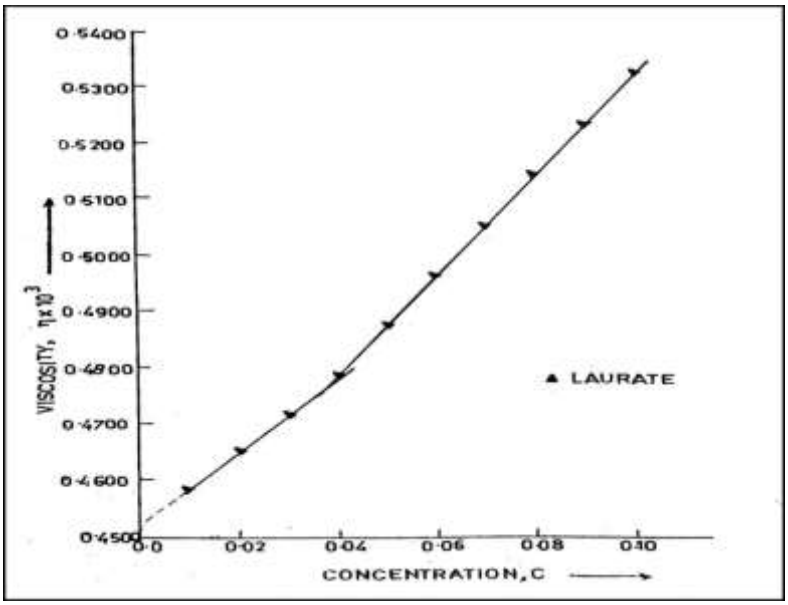

Fig. 2: Viscosity Vs concentration of zirconyl laurate in benzene-methanol mixture (4:1 v/v) at (40±0.05)ºC

III. EXPERIMENTAL

The chemicals used were of AR/BDH grade. Zirconyl laurate was prepared by direct metathesis of the potassium laurate with a slight excess of zirconium oxychloride solution under vigorous stirring. The precipitated soap was washed several times with distilled water and finally with methanol and acetone to remove excess of metal salt. The purity of the soap was checked by elemental analysis and IR Spectra. The melting point of the purified zirconyl laurate was 167ºC. The solution of different concentration of zirconyl laurate was prepared in benzene-methanol mixture (4:1 v/v) and kept for one hour in a thermostat at constant temperature (40±0.05ºC).

The ultrasonic velocity measurements of the solutions were performed with a multi frequency ultrasonic interferometer (M-83 Mittal Enterprises, New Delhi) at a frequency of 1 MHz at (40±0.05ºC). The uncertainty of the velocity measurements was ±0.2%. The density and viscosity of the solutions of zirconyl laurate were measured with dilatometer and Ostwald viscometer respectively at (40±0.05ºC) and accuracy of the result was ±0.3%.

IV. CALCULATIONS

Various acoustic parameters such as adiabatic compressibility (β), specific acoustic impedance (Z) [11], Intermolecular free length (L_f) [12], apparent molar compressibility, (ϕ_k), molar sound velocity, (R), molar sound compressibility (W) [13] and solvation number (S_n) [14], were calculated using the relationships :

$$\beta = v^{-2}\rho^{-1}$$

$$Z = v\rho$$

$$L_f = (\rho/K)^{1/2}$$

$$\emptyset_k = \frac{1000}{C\rho_o}(\rho_o\beta - \beta_o\rho) + \frac{M\beta_o}{\rho_o}$$

$$R = \frac{\bar{M}}{\rho} v^{1/3}$$

$$W = \frac{\bar{M}}{\rho}\beta^{-1/7} \quad \left[\bar{M} = \frac{n_oM_o + nM}{n_o + n}\beta^{-1/7}\right]$$

$$S_n = \frac{n_o}{n}\left(1 - \frac{\bar{v}\beta}{n_o\bar{v}_o\beta_o}\right)$$

where v_o , v ; ρ_o ; ρ ; β_o , β ; and $\bar{v}_o$, $\bar{v}$ are the ultrasonic velocity, density, adiabatic compressibility and molar volume of the solvent and solution, respectively; n_o , n and M_o , M are the number of mole and molecular mass of solvent and solute respectively; K and C are the temperature dependent Jacobson's constant and concentration.

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