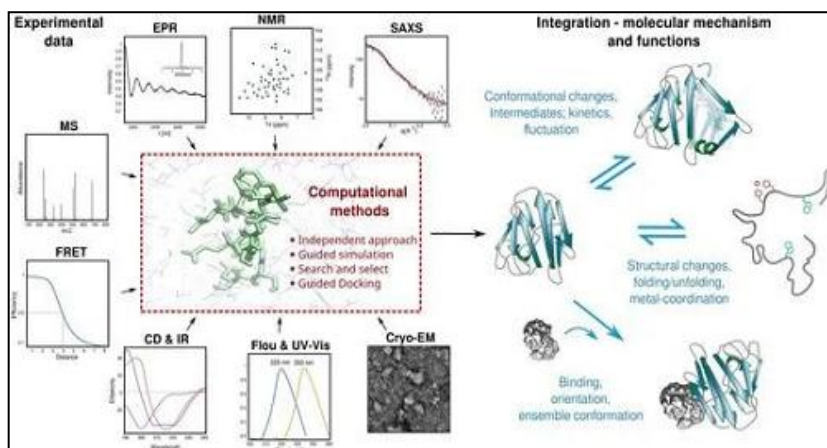




MOLECULAR INTERACTIONS AND POLARIZABILITY CONSTANTS OF SOME SUBSTITUTED COUMARIN COMPLEXES WITH LANTHANIDES METAL ION

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ABSTRACT

The ultrasonic velocity, density has been measured for the mixture of 6-ethyl7-hydroxy coumarin (E_1L_1) and 4,6-Dimethyl7-hydroxy coumarin (D_1L_2) at different concentrations in dioxane. From the experimental data different acoustical properties like apparent molar volume, apparent molar compressibility, adiabatic compressibility, intermolecular free length (L_f), relative association (RA), acoustic impedance z etc. have been calculated. These parameter obtained have been interpreted in term of solute-solvent and solute-solute interactions. Molar refraction and polarizability constant for (E_1L_1) and (D_1L_2) at different percentage of dioxane have been calculated.

KEYWORDS: acoustic impedance , experimental data.

INTRODUCTION:

Substituted coumarins, thiazoline Isooxazoles etc fall in the class of aromatic compound and the unique structural features involving coumarin oxygen and thiazoline ,trizine nitrogen sulphur makes them interesting ligand. Substituted coumarin are found to have good complexing nature. The nature and relative strength of molecular interactions between the components of liquid mixture have been successfully investigated by the ultrasonic method.¹⁻³ These interaction helps in better understanding the nature of solute and solvent i.e. whether solute modified or distorts the structure of solvent. The measurement of ultrasonic speed enable the

accurate determination of some useful acoustic and thermodynamic parameters and their excess function which are highly sensitive to molecular interactions in liquid mixture.⁴⁻⁵ Ultrasonic velocity and adsorption studies in case of electrolyte solution have led to new insight into process of ion association and complex formation.⁶⁻⁷ Sondawale and Narwade⁸ have studied ultrasonic velocity of monochloro acetic acid and trichloro acetic acid in THF and dioxane-water mixture. The nature and degree of molecular interaction in different solution depends on several factors i.e. nature of solvent structure of solute and also extends of solvation taking place in solution. The present work reflects the molecular interaction studies of Sustituted Coumarin in (E_1L_1) and (D_1L_2) water-dioxane mixture at constant temperature.

MATERIALS AND METHOD

The solvent used was purified by standard procedure⁹ solution of different concentration were prepared by dissolving known weight of substance. All weighing are made on electronic balance. Density measurement was performed with a calibrated bicapillary pykometer. The accuracy in density measurement

was found to be $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$. The speed of sound waves was obtained using variable path, single crystal interferometer (Mittal Enterprises, Model IF-18) with accuracy of $\pm 0.03\%$ and frequency 1MHz.

RESULT AND DISCUSSION

The apparent molar volume ($V_{2,\phi}$) and apparent molar compressibility $\kappa_{S,2,\phi}$ of a solution are calculated from densities (d_s) and adiabatic compressibility (β_s) of solution using the equation (1) and (2)¹⁰

$$V_{2,\phi} = \frac{M}{d_s} + \frac{1000}{md_s d_o} (d_o - d_s) \quad (1)$$

$$\kappa_{S,2,\phi} = \frac{1000(\beta_s \rho_o - \beta_o \rho)}{md_s d_o} + \frac{M \times \beta_s}{d_s} \quad (2)$$

Where d_o and d_s represent densities of solvent and solution respectively, m is molality and M is the molecular weight of solute β_s and β_o are the adiabatic compressibility of solution and solvent respectively. The adiabatic compressibility, specific acoustic impedance (Z), relative association (RA) and intermolecular free length (L_f) are calculated using equation (3) and (6)¹¹

$$\beta_s = 100 / U_s^2 \times d_s \text{ (for solution)} \dots\dots\dots 3a$$

$$\text{and } \beta_o = 100 / U_o^2 \times d_s \text{ (for solvent)} \dots\dots\dots 3b$$

$$L_f = K \times \beta \dots\dots\dots (4)$$

$$Z = U_s \times d_s \dots\dots\dots (5)$$

$$RA = \dots\dots\dots (6)$$

Where U_o and U_s are velocity of ultrasonic wave in solvent and solution and k is the Jacobson's constant (6.0186×10^4).

The value of d_s , L_f , Z , and RA are obtained in present investigation at different concentration are presented in table 1 and 2. It could be seen from table 1 that intermolecular free length decreases with increase in concentration of (E_1L_1) and (D_1L_2) in dioxane and hence increase in ultrasonic velocity with increase in concentration of (E_1L_1) and (D_1L_2). This indicates that there is strong interaction between ion and solvent molecular suggesting a structure promoting behavior of added solute this may also imply that there is decrease in number of free ion showing the occurrence of ionic association due to strong ion-ion interaction.

The increase of β_s with decrease in concentration of solution may be due to aggregation of solvent molecule around ion¹² supporting strong solute-solvent interaction. The apparent molar volume and adiabatic compressibility increases with decrease in concentration. Partial molar volume, adiabatic compressibility and velocity of some amino acid have been studied in aqueous glycerol solution at 298.15 K¹³. Ultrasonic study of glycine in binary aqueous solution of mannose, maltose at different temperature have been studied by Amalendra Pol et. al.¹⁴ Ultrasonic velocity of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in propan-2-ol + Water at 303.15K solvent has been studied by S.B.Mishra et. al.¹⁵. Molecular interaction measurement in binary mixture at 303 K have been studied by G.R. Bedre et. al.¹⁶

The position value of apparent molar volume and compressibility shows strong electrostatic force in the vicinity of ions causing electrostatic solution of ion. The relative association is influenced by two factors

- 1) The breaking up of solvent molecule on addition of electrolyte to it.
- 2) Solvated ion that simultaneously present.

The increase of RA with concentration suggests solvation of ions predominates over the breaking up of the solvents aggregates on addition of substance. It is observed from table-1 that there is linear variation of RA and Z values with respect to the concentration of solution. The lower value of RA signifies the weak association between the solvent and solute.

**Table-1. Acoustic Properties at different concentration H₂L₁ System:- Ligand H₂L₁ Temp. 30 ± 0.1 °C
Medium:-100 % dioxane**

M. Conc. (mole lit ⁻¹)	ds (g·cm ⁻³)	U _s × 10 ³ (m/sec)	B _s × 10 ⁻⁵ (bar ⁻¹)	l _f × 10 ² (Å ⁰)	(cm ³ mole ⁻¹)	(cm ³ mole ⁻¹ bar)	RA	z × 10 ⁴
0.02	1.0163	1420	4.6769	1.01858	1102.78	1.6525	99.92	1452.48
0.04	1.0158	1435	4.5789	1.01848	725.15	-0.9889	99.84	1465.64
0.06	1.0140	1441	4.9833	1.01891	658.37	-4.2879	99.78	1467.24
0.08	1.0128	1462	4.7952	1.01871	436.04	-4.2879	99.64	1487.56
0.10	1.0114	1470	4.3712	1.01825	329.10	-3.8262	99.38	1494.57

**Table-2. Acoustic Properties at different concentration H₂L₂ System:- Ligand H₂L₁ Temp. 30 ± 0.1 °C
Medium:-100 % dioxane**

M. Conc. (mole lit ⁻¹)	ds (g·cm ⁻³)	U _s × 10 ³ (m/sec)	B _s × 10 ⁻⁵ (bar ⁻¹)	l _f × 10 ² (Å ⁰)	(cm ³ mole ⁻¹)	(cm ³ mole ⁻¹ bar)	RA	z × 10 ⁴
0.02	1.0493	1395	6.7472	1.01756	1158.2	-1.8295	100.4	1450.0
0.04	1.0468	1313	5.6840	1.01631	970.5	-1.6462	99.80	1333.3
0.06	1.0451	1328	5.81426	1.01763	870.6	-1.8479	99.68	1346.5
0.08	1.0439	1146	5.79845	1.01762	613.3	-1.8381	99.38	1363.3
0.10	1.0423	1169	5.13433	1.01562	643.2	-1.6372	99.40	1384.6

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