

Study of Acoustic Properties of Luminol in DMSO-Water Mixture

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Abstract: *The acoustical properties like adiabatic compressibility (β_s), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_k), intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (RA) of Luminol have been calculated from measured sound velocities (U) and densities (ρ) of their solutions of 0.01M concentrations in different percentage of DMSO-water mixture at 298.15 K. The variations in acoustical properties with increasing percentage of DMSO have been used to understand the changes in molecular interactions between water, DMSO and Luminol and to know the structure making and breaking property of solvent molecules on addition of DMSO in presence of Luminol.*

Keywords: Luminol, Acoustic Properties, Ultrasonic velocity, DMSO, Water.

1. Introduction

The solvent plays a crucial role in chemiluminescence reactions. Luminol CL in water is mostly applied for analytical purposes. The chemiluminescence of the system Luminol-DMSO has several practical applications[1], so it is also useful to know more about the spectroscopic behavior of this system. Dimethyl sulfoxide (DMSO) shows a remarkable promoting effect on the luminescent reaction of the luminol-H₂O₂ system[2]. Two luminescent processes occur when a mixed solvent of water and DMSO is used. The total luminescence increases exponentially with increasing DMSO concentration.

The Chemiluminescence of Luminol has been studied either in aqueous alkaline solutions sodium hydroxide[3] or carbonates[4]. Various solvents[5] like glycerol, glycol, pyridine, piperidine and ammonia have been used for Chemiluminescence of Lucigenin. Similarly various solvent[6]-[7], or solvent mixtures[8] have been utilized for chemiluminescence of luminol. Recently, the effect of temperature on the chemiluminescence of alcohols and aldehydes has been studied by Kher et al[9]. A very little work on Chemiluminescence of Luminol and Lucigenin in aqueous aliphatic amines[10] and aniline[11] has been reported in literature. Therefore it is important to study the effect of solvent on chemiluminescence of Luminol. Thus the present chapter deals with the study of effect of solute solvent interaction on chemiluminescence of Luminol interferometrically.

2. Experimental

Analytical reagent grade DMSO was purified by standard method[12]. Double distilled water was used for the preparation of solutions and the solutions of solutes were always used a fresh in present investigation. All the glassware's used during the experiment were of Pyrex quality. Pyknometers used for this study were of borosil make and of various volumes. Weighing was done on single pan electronic balance. Solutions of each Luminol of 0.01 M

were prepared in different compositions of DMSO and water (75-100% of DMSO) by dissolving exact amounts of Luminol in liquid mixtures. Densities of different solutions were measured by using precalibrated bicapillary pyknometer at 298.15K. Densities were determined using three different pyknometers. Using the weight of solution and volume of pyknometers, density of solution was calculated. Same procedure was followed with other two pyknometers and average of three density values was considered in calculations. Pyknometers were standardized by the standard procedure[13]. Accuracy of the balance was ± 0.001 g. Ultrasonic velocity of each solution was obtained by using variable path, single crystal interferometer (Mittal Enterprises, Model F-81) with accuracy of $\pm 0.03\%$ and frequency 2 MHz. Uncertainty in ultrasonic velocity measurements was 0.03%. The ultrasonic interferometer was calibrated with triply distilled water. The instrument was calibrated by measuring velocity of water at 298.15 K which was in good agreement with literature value. A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Densities and sound velocities of solutions were measured in different percentage of dioxane-water mixture at temperature 298.15 K.

3. Theory and Calculations

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ) in the medium, equation (1)

$$d = \lambda / 2 \dots \dots \dots (1)$$

Where, d is the distance traveled by micrometer screw to get one maxima in ammeter in mm and λ is wavelength. From the knowledge of wavelength (λ), the velocity (U) can be obtained by the relation (2)

$$U = \lambda \times \gamma_{\text{ins}} \times 10^3 \dots \dots \dots (2)$$

Where, U is the sound velocity in m/sec and γ_{ins} is the frequency of instrument (2 MHz). The acoustical properties

like adiabatic compressibilities of solution (β_s)[14], relative association (RA), intermolecular free length (Lf) and specific acoustic impedance (Z) were calculated by using equations (3-6)[15]

$$\beta_s = \frac{1}{U_s^2 \times \rho_s} \dots\dots\dots(3)$$

$$RA = \frac{\rho_s}{\rho_o} \times \left[\frac{U_o}{U_s} \right]^{1/3} \dots\dots\dots(4)$$

$$L_f = K' \sqrt{\beta_s} \dots\dots\dots(5)$$

$$Z = U_s \times \rho_s \dots\dots\dots(6)$$

Where, (U_s) and (U_o) are ultrasonic velocity in solution and solvent mixture, (ρ_s) and (ρ_o) are density of solution and solvent mixture respectively and K' is temperature dependent Jacobson's constant[16]. The apparent molal compressibility (ϕ_k) was calculated by using equation (7).

$$\phi_k = \frac{1000 (\beta_s d_o - \beta_o d_s)}{m \cdot d_s \cdot d_o} + \frac{\beta_s M}{d_s} \dots\dots\dots(7)$$

Where, β_s and β_o are adiabatic compressibilities of solution and solvent mixtures respectively, M is molecular weight of Luminol and m is the molality of solution. The apparent molal volume, ϕ_v of different solutions was calculated by finding difference in densities of solvent and solution, molecular weight and molality of compounds using equation (8).

$$\phi_v = \left[\frac{M}{\rho_s} \right] + \left[\frac{(\rho_o - \rho_s) \times 10^3}{m \cdot \rho_s \cdot \rho_o} \right] \dots\dots\dots(8)$$

4. Result and Discussion

Velocities, densities and calculated acoustical properties in different percentage of DMSO and in 0.01M solution at 298.15K are given in Table (1) and variation in these properties with DMSO % for one of system are shown in Figure (1-2). Existence of molecular association between the components of the liquid mixtures can be understood from the increase in ultrasonic velocity (U) with increasing percentage of DMSO. The values of adiabatic compressibility, (ϕ_s) decrease with increase in the percentage of DMSO which may be due to departure of solvent molecules around the ions[17]. The apparent molal volumes (ϕ_v) found to be increase with increase in the percentage of DMSO. It is observed that (ϕ_k) values increases with increase in the percentage of DMSO. It could also be seen that the intermolecular free length (Lf) increases with increase in the percentages of DMSO, this may be due to the weaker interaction between ions and solute molecules, which suggest the structure promoting behaviour of solute. This may also imply that the increase in free ions, showing the occurrence of ionic dissociation due to weak ion-ion

interaction. The values of relative association (RA) decrease with increase in the percentage of DMSO-water mixture, which may be due to breaking up of solvent molecules on addition of DMSO in it. Specific acoustic impedance (Z) decreases non-linearly with increase in percentage of DMSO. Studies of acoustic properties on the same line have been performed by many researchers [18]-[20].

4.1 Tables

Table 1: Acoustic Properties of Luminol in different percentage of DMSO-water mixture

% of DMSO	100.0	95.0	90.0	85.0	80.0	75.0
U_s (cm sec ⁻¹)10 ²	1414	1415	1409.	1401	1397	1392
d_s (g cm ⁻³)	0.752	0.760	0.770	0.780	0.787	0.792
B_s (bar-1) 10 ⁻⁶	66.54	65.70	65.44	65.41	65.19	65.21
L_f (A ⁰) 10 ²	4.910	4.879	4.869	4.868	4.860	4.860
Φ^0_v (cm ³ mole ⁻¹) 10 ⁵	6.521	6.238	5.885	5.575	5.357	5.196
$\phi_k(s)$ (cm ³ mole ⁻¹ bar ¹)10 ²	0.872	0.830	0.801	0.779	0.759	0.749
RA	0.770	0.778	0.790	0.801	0.808	0.814
Z (cm sec ⁻¹ g cm ⁻³) 10 ²	1062	1072	1080	1092	1098	1101

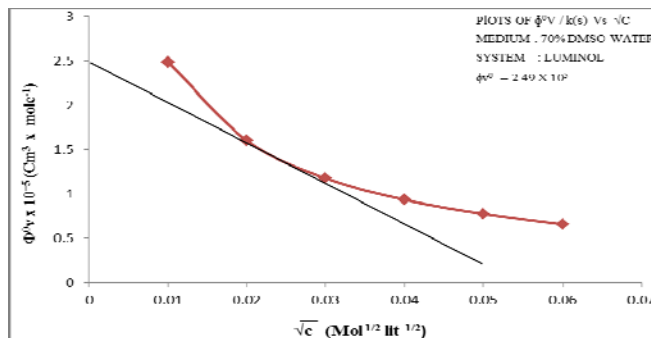


Figure 1: Plot of $\Phi^0_v \times 10^5$ Vs \sqrt{C}

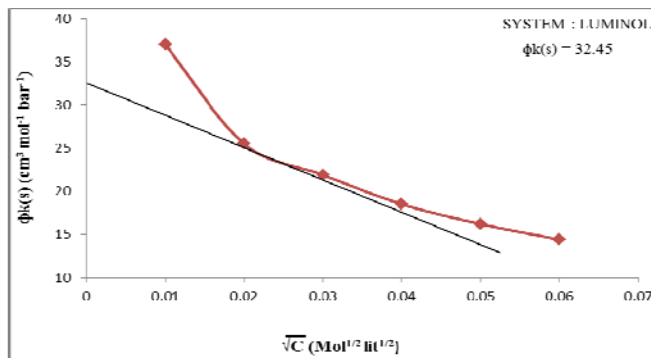


Figure2: Plot of $\Phi_k(s) \times 10^5$ Vs \sqrt{C}

5. Conclusion

It can be concluded from above study that there exist the interactions between Luminol and DMSO-water mixture. Breaking up of solvent molecules on addition of DMSO in the solution is observed. Solute-solvent interactions are more favorable than other interactions.

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