



STUDIES IN THE ACOUSTIC PARAMETERS OF 3-HYDROXY-6-CHLORO-8-SUBSTITUTED FLAVANOL

P. B. RAGHUWANSHI* and A. D. DESHMUKH

Department of Chemistry, Brijlal Biyani Mahavidyalaya, AMRAVATI – 444604 (M.S.) INDIA

ABSTRACT

Ultrasonic velocity and density measurements of 3-hydroxy-6-chloro-8-nitro flavanol (L_1) and 3-hydroxy-6-chloro-8-bromo flavanol (L_2) were carried out in three different solvents, dioxane, benzene, and ethanol, respectively for investigating solute–solvent and solute–solute interactions. These interactions were also performed at 303 K. The data obtained during the most significant acoustic parameters like, adiabatic compressibility (β), apparent molar compressibility (ϕ_k), apparent molar volume (ϕ_v), intermolecular free length (L_f) and relative association (R_A). These parameters explore solute-solute and solute-solvent interactions in different solvents. In this investigation, the comparative study of effect of solvents and effect of substituents in the solute are studied on molecular interaction of the matter.

Key words: Substituted flavanol, Solute–solvent interaction, Interferometry, Acoustic parameters.

INTRODUCTION

The ultrasonic velocity of vanadium laurate confirms that there is a significant interaction between the solute–solvent molecules in dilute solution and the carboxylate molecules do not aggregate appreciable in dilute solutions. The value of critical micelle concentration (CMC) for vanadium laurate is in agreement with those obtained from other physical parameters, the effect of concentration, chain length of soap on ultrasonic velocity and the various acoustic parameters (apparent volume, adiabatic compressibility, apparent molal compressibility, intermolecular free length, relative association, specific acoustic impedance, molar sound velocity, compressibility relative association and solvation number) been investigated.

Ultrasonic velocity and adiabatic compressibility can be measured with great accuracy and consequently provides a powerful tool for the prediction of intermolecular interaction. In view of the analytical, medicinal, agricultural, industrial and pharmaceutical

* Author for correspondence; E-mail: deshmukhashwini16@gmail.com

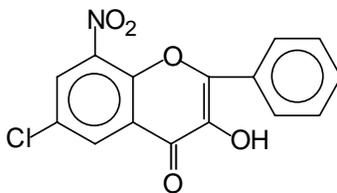
significance²⁻¹⁰. For α -Bromoacetophenones and coumaran-3-ones, it is of interest to investigate the acoustic parameters such as adiabatic compressibility along with the effect of Cu^{II} / Fe^{III} metal ion on the above system by ultrasonic interferometric technique in order to discuss intermolecular interactions.

Speeds of sound and isentropic compressibilities have been measured for binary mixtures of 1,2-ethane diol with 1-butanol, 1-hexanol or 1-octanol in the temperature range from 293.15 to 313.15 K¹¹. Various acoustic parameters¹² such as isentropic compressibility (bs), intermolecular free length (L_f), apparant molar volume (f), apparant molar compressibility $y(\text{fk})$ molar compressibility (W), molar sound velocity (R) and acoustic impedance (Z) of $\text{Cu}(\text{NO}_3)_2$ in 10%, 20% and 30% propane-2-ol + water at 303.15 K have been determined from ultrasonic velocity (V), density (r) and relative velocity (hr) of the solution. These parameters are related with the molar concentration of the solution and reflects the distortion of the structure of the solvent (i.e. propane-2-ol + water) when the solute is added to it.

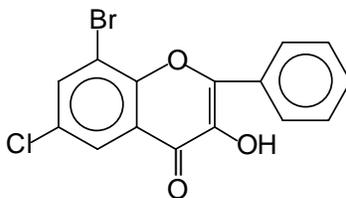
Apparant molar volume of NaCl have been studied in ethanol, methanol, propane-2-ol, dioxane, glycol and glycerol water mixture at 10,20 and 30% (W/W) within the temperature range 30⁰-40⁰C and ion solvent interaction has been inferred¹³. Taking all these things into consideration, we intended to analyze a comparative study of these ligands in ethanol and dioxane solvents to investigate protic–aprotic nature, polarity–nonpolarity, hydrogen bonding, dielectric constant and density, of solvents on solute–solvent, ion–solvents and ion–ion interactions. Hence, in this present investigation, attempt is made to understand behaviour of substituted flavanol viz. 3-hydroxyl-6-chloro-8-nitroflavanol (L_1) and 3-hydroxyl-6-chloro-8-bromo flavanol (L_2) compounds in dioxane, ethanol and benzene solvents separately in respect to β_s , ϕ_k , ϕ_v , L_f and R_A .

EXPERIMENTAL

All chemicals used were of A. R. grade (i) 3-Hydroxy-6-chloro-8-nitro flavanol (L_1) and (ii) 3-Hydroxy-6-chloro-8-bromo flavanol (L_2).



(i) 3-Hydroxy-6-chloro-8-nitroflavanol (L_1)

(ii) 3-Hydroxy-6-chloro-8-bromo flavanol (L_2)

1, 4-dioxane, ethanol and benzene were purified by described method¹⁴. Densities were measured with the help of bicapillary pycnometer. 0.041 M solution of ligand in ethanol, benzene and dioxane solvents were prepared separately. Weighing was made on Mechaniki Zaktady Precyzynej Gdansk balance made in Poland (± 0.001 g). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic water bath was used, where continuous stirring of water was carried out with the help of in electric stirrer and temperature variation was maintained within $\pm 0.1^\circ\text{C}$. Single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy of $\pm 0.03\%$ and frequency 1 MHz was used in the present work. The densities and ultrasonic velocity of ligands in ethanol, dioxane and benzene were measured at 303 K.

RESULTS AND DISCUSSION

In the present investigation, measurements of densities and ultrasonic velocities of L_1 and L_2 in dioxane, ethanol and benzene have been carried out and given in tables.

Table 1: Acoustic parameters for ligands in dioxane at 303 K [Freq. = 1 MHz]

Ligand	v (m sec ⁻¹)	d (Kg m ⁻³)	$\beta \times 10^{-4}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	$L_f \times 10^2$ (Å)	R_A
L_1 -Dioxane	442.72	1186.4	60.53	0.156278	-0.164202	46.84	0.952794
L_2 -Dioxane	434.54	1189.0	62.97	-0.02801	-0.144812	47.77	0.960836

Table 2: Acoustic parameters for ligands in benzene at 303 K [Freq. = 1 MHz]

Ligand	v (m sec ⁻¹)	d (Kg m ⁻³)	$\beta \times 10^{-4}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	$L_f \times 10^2$ (Å)	R_A
L_1 -Benzene	424.32	1008.0	55.99	0.519207	0.073374	44.04	1.01854
L_2 -Benzene	394.09	1008.2	64.92	0.499559	0.161851	48.50	1.044151

Table 3: Acoustic parameters for ligands in ethanol at 303 K [Freq. = 1 MHz]

Ligand	v (m sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-4}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	$L_f \times 10^2$ (Å)	R_A
L ₁ -Ethanol	436.23	949.2	49.88	7.943287	-0.130316	42.52	0.891089
L ₁ -Ethanol	405.47	937.4	57.02	9.269594	-0.047560	45.46	0.901725

Adiabatic compressibility (β)

β is one of the important properties during the study of solute–solvent interactions and represented by β . From tables and figures, it can be noted that the β values in dioxane medium are considerably and notably smaller than in alcohol medium. This may be due to nature of solvents. The parameters of solvents which directly affect the values of β , are protic nature, non-polarity, low dielectric constant (2.2) and higher density of dioxane as compared with protic nature, polarity, high dielectric constant (24.6) and lower density of ethanol, In ethanol, hydrogen bonding is possible, while it is not observed in dioxane.

β value of L₂ ligand is higher than L₁ ligand in dioxane solvent. In benzene the β value of L₂ ligand is greater than L₁ ligand and in case of ethanol, the β value for L₂ ligand is greater than L₁ ligand. These different values of L₁ and L₂ ligand is due to their different structures and due to different solvents.

For plane solution i.e. dioxane, benzene and ethanol, the β value is greater in dioxane than ethanol than benzene.

$$\text{Dioxane} > \text{Ethanol} > \text{Benzene}$$

Apparent molar compressibility (ϕ_k)

ϕ_k values for L₁ and L₂ ligands in dioxane solvent are negative, for L₂ ligand ϕ_k value is higher than L₁ ligand in dioxane solvent. ϕ_k value for L₁ and L₂ ligand in benzene solvent are positive. ϕ_k value for L₂ ligand is greater than L₁ ligand in benzene solvent. ϕ_k values for L₁ and L₂ ligand in ethanol are negative and for L₂ ligand ϕ_k value are higher than L₁ ligand in ethanol solvent.

$$\text{L-Benzene} > \text{L-Ethanol} > \text{L-Dioxane}$$

Apparent molar volume (ϕ_v)

ϕ_v is the thermodynamic property of solutions, which expresses the solute–solvent interactions, and it is obtained from the density and molality of solution and the molecular weight of the solute.

ϕ_v values for L₂ ligand is negative and for L₁ ligand ϕ_v value is positive. In benzene solvent, ϕ_v values for L₁ and L₂ ligand is positive and in ethanol ϕ_v values for L₁ and L₂ ligand are also positive. From table ϕ_v value in ethanol solvent is higher than benzene and than dioxane at same concentration.



ϕ_v values for L₂ in ethanol is the highest among the ligands. This may be due to the presence of electron donating nature of ligand and weak solute–solvent interaction

Intermolecular free length (L_f)

The values of L_f for L₂ ligand in dioxane solvent is higher than L₁ ligand and for benzene solvent L_f values for L₂ ligand is higher than L₁ ligand and in ethanol L_f values of L₂ ligand is higher than L₁ ligand. In all the three solvents, L_f value for L₂ ligand is higher than L₁ ligand at same concentration

The values of L_f for the ligand in ethanol show a very little variation on moving from L₁ to L₂; on changing the solvent to dioxane, the values are decreased a little. Because of the hydrogen bonded structure of ethanol, there is association of molecules in a structure leaving free length available. When a polar solute is added, it also gets associated in the structure by electrostriction thus, decreasing the free space available; therefore, in ethanol the L_f values are higher but as the size of solute increases, the L_f values slightly decreases.

In case of dioxane, because of its non-polar nature, the compact packing of molecules is already there and when polar solute is added because of its association again free space decreases, therefore, the L_f values in dioxane must be smaller as given in table.

Relative association (R_A)

R_A is an acoustic property of understanding interaction, which is influenced by two opposing factors¹⁵:

- (i) Breaking of solvent structure on addition of solute to it and
- (ii) Solvation of solutes that are simultaneously present by the free solvent molecules

The former effect results in the decrease in R_A values while the latter resulting in increases of R_A values.

The value of R_A for L_2 ligand in dioxane solvent is higher than L_1 ligand at same concentration and in benzene the R_A value for L_2 ligand is higher than L_1 ligand and in ethanol the R_A value for L_2 ligand is higher than L_1 ligand at same concentration. This higher value for L_2 ligand than L_1 ligand is due to different structures of ligand.

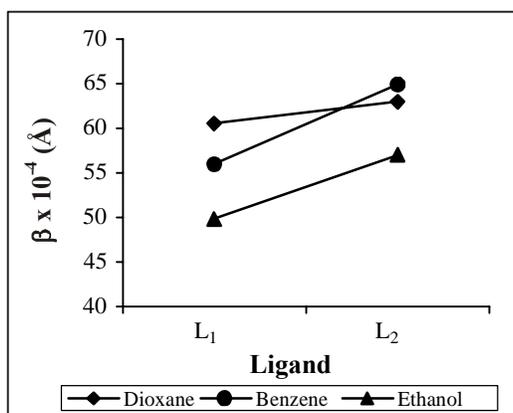


Fig. 1: Adiabatic compressibility (β) of L_1 and L_2

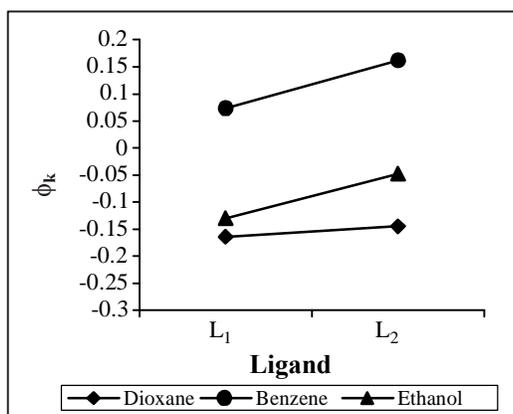


Fig. 2: Apparent molar compressibility (ϕ_k) of L_1 and L_2

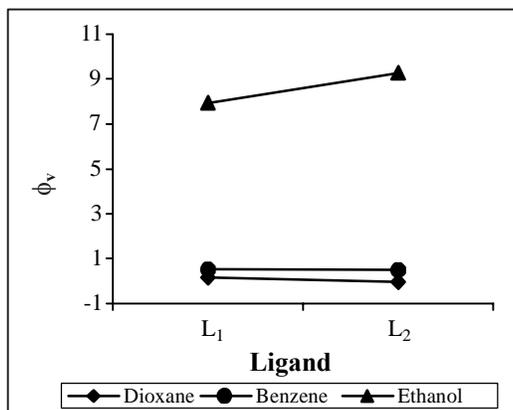


Fig. 3: Apparent molar volume (ϕ_v) of L₁ and L₂

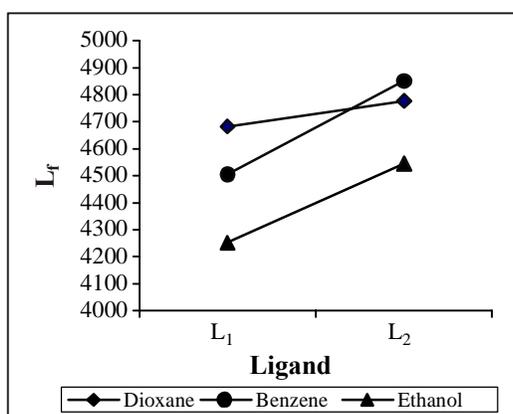


Fig. 4: Intermolecular free length (L_r) of L₁ and L₂

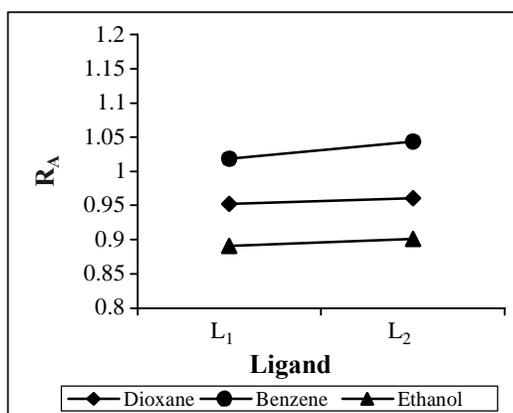


Fig. 5: Relative association (R_A) of L₁ and L₂

ACKNOWLEDGEMENT

The authors thank the Principal, Dr. S. B. Lohiya, Brijlal Biyani Science College Amravati for providing necessary facilities and for kind cooperation of Prof. V. D. Thakre, Head, Dept. of Chemistry, G.V.I.S.H. Amravati.

REFERENCES

1. S. H. Kulshrestha and P. S. Verghese, *Oriental J. Chem.*, **23**, 177 (2007).
2. B. K. Sharma, G. P. Pokhriyal and S. K. Sharma, *Organic Chemistry-II*, Goel Publishers, Meerut (1991) p. 385.
3. S. K. Ghosh, *Advanced General Organic Chemistry*, New Central Book Agency, Kolkata (2003) p. 1381.
4. I. L. Finar, *Organic Chemistry–Vol. I*, 6th Ed, ELBS and Longmann, London (1973) p. 749.
5. A. N. Nesmeyanov and N. A. Nesmeyanov, *Fundamental of Organic Chemistry*, Vol. III, MIR Publishers, Moscow (1977) p. 318.
6. D. R. Williams, *Proc. Summer Comput. Simul. Cont.*, **2**, 92 (1984).
7. Website : <http://www.Inpharm.com>, CHEMADA Fine Chemicals (2001).
8. C. L. Border (Jr.), D. M. Perez, M. W. Lattery, A. J. Kondow, J. Brahm, M. B. Fenderson, G. L. Brelsford and V. B. Pett, *Bio-Org. Chem.*, **17**, 96 (1986).
9. G. Arabaci, P. Yi, H. Fu, M. E. Morter, K. D. Beebe and D. Pei, *Bio-Org. and Med. Chem. Lett.*, **12**, 3047 (2002).
10. M. Kidwai, R. Kumar, A. Shrivastava and H. P. Gupta, *Bio-Org. Chem.*, **26**, 289 (1998).
11. E. Zorebaski and E. Dec, *J. Mol. Liq.*, **168**, 61-68 (2012).
12. S. B. Mishra, S. K. Nayak, A. K. Pattnaik and P. K. Mishra, *Abstract of Volume*, **8(2)**, (2012).
13. C. K. Rath, N. C. Raut, S. P. Das and P. K. Mishra, *Abstract of Volume*, **8(2)** (2012).
14. A. I. Vogel, *Textbook of Practical Organic Chemistry*, 4th Ed., ELBS and Longman, London (1978) p. 264.
15. H. Eyring and J. F. Kincaid, *J. Chem. Phys.*, **6**, 728 (1977).

Revised : 28.01.2013

Accepted : 30.01.2013