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ACOUSTICAL STUDIES OF SOME PYRAZOLES IN DIFFERENT PERCENTAGE OF DIOXANE-WATER MIXTURE AT 303.15 K

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ABSTRACT

The acoustical properties like adiabatic compressibility (β_s), apparent molal volume (ϕv), apparent molal compressibility (ϕ_K), intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A) of some substituted pyrazoles viz. [5-(2-hydroxyphenyl)-3-(pyridin-3-yl)-4-(benzoyl)]-pyrazol, [5-(2-hydroxyphenyl)-3-(3-nitrophenyl)-4-(3-pyridinoyl)]-pyrazol, [5-(2-hydroxyphenyl)-3-(3-nitrophenyl)-(4-benzoyl)]-pyrazol and [5-(2-hydroxyphenyl)-3-(phenyl)-4-(3-pyridinoyl)]-pyrazol have been calculated from measured sound velocities (U) and densities (ρ) of their solutions of 0.01M concentrations in different percentage of dioxane-water mixture at 298.15 K. The variations in acoustical properties with increasing percentage of dioxane have been used to understand the changes in molecular interactions between water, dioxane and pyrazoles and to know the structure making and breaking property of solvent molecules on addition of dioxane in presence of pyrazoles.

Keywords: ultrasonic velocity, adiabatic compressibilities, relative association, acoustic properties, specific acoustic impedance

INTRODUCTION

Ultrasonic techniques are best studied for the physico-chemical studies of a system. Ultrasonic waves, in recent years have acquired the status of an important probe for the study of structure and properties of matter in basic science. The study of molecular interactions in liquids provides valuable information regarding internal structure, molecular association, complex formation, internal pressure etc. Ultrasonic technique reveals very weak intermolecular interactions due to its useful wavelength range. In recent years, determinations of ultrasonic velocity and absorption coefficient have furnished methods for studying molecular and structural properties of liquids. The discoveries of interferometry and optical diffraction method improved the investigation manifold, both qualitatively and quantitatively.

Many workers[1-7] have done the acoustical study by the measurement of density and ultrasonic velocity of different aqueous and non-aqueous systems at different temperatures, different concentrations of solute and in different percentage of organic solvents. In recent years, ultrasonic velocity and absorption studies in case of electrolyte solutions have led to new insight into the process of ion-association and complex formation. Density, ultrasonic velocity and viscosity measurements of pharmacologically significant drugs in methanol at 25°C have been studied by D. V. Jahagirdar et al[8]. Ultrasonic Velocity and Compressibility in Aqueous Solutions of Alkali Metal Chlorides have been studied by Hisashi Uedaira and Yasuko Suzuki[9].

No work has been reported on the ultrasonic studies of these pyrazoles in different percentage of dioxane-water mixture, which will provide the information about molecular interactions between two solvents with different compositions in the presence of solute pyrazoles. Therefore the present work is undertaken to study the acoustical behavior of these pyrazoles in 0.01M concentration in different percentage of dioxane-water mixture to discuss the interactions of unlike molecule of solvents in presence of solute. This work is in continuation with our previous work[10].

EXPERIMENTAL

Analytical reagent grade dioxane was purified by standard method[11]. 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 pyrazole of 0.01 M were prepared in different compositions of dioxane and water (75-100% of dioxane) by dissolving exact amounts of pyrazoles 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[12]. 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 ± 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.

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)

$$d = \lambda / 2 \ldots \ldots .(1)$$

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)

$$U = \lambda \times \nu_{ins.} \times 10^{3} ....(2)$$

Where, U is the sound velocity in m/sec and $\nu_{ins.}$ is the frequency of instrument (2 MHz). The acoustical properties like adiabatic compressibilities of solution (β_s) [13], relative association (R_A), intermolecular free length (L_f) and specific acoustic impedance (Z) were calculated by using equations (3-6)[14]

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

$$R_A = \frac{\rho_s}{\rho_o} \times \left(\frac{U_o}{U_s} \right)^{1/3} \quad ...(4)$$

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

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

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[15].

The apparent molal compressibility (ϕ_K) was calculated by using equation (7).

$$\phi_K = \frac{1000(\beta s.do - \beta o.ds)}{m.ds.do} + \frac{\beta s.M}{ds} ....(7)$$

Where, β_s and βo are adiabatic compressibilities of solution and solvent mixtures respectively, M is molecular weight of pyrazoles and m is the molality of solution.

The apparent molal volume, ϕv of different solutions were calculated by finding difference in densities of solvent and solution, molecular weight and molality of compounds using equation (8).

Table-1: Measured sound velocities (Us), densities (ρ_s) and calculated acoustic properties of substituted pyrazoles in different % of dioxane-water mixture at 298.15 K in 0.01M solutions

% of dioxane	75	80	85	90	95	100
[5-(2-hydroxyphenyl)-3-(pyridin-3-yl)-4-(benzoyl)]-pyrazol [HPPBP]						
Us (m/s)	1419.62	1435.67	1448.95	1469.57	1486.34	1502.72
ρ_s ($\times 10^3$ kg/m^3)	0.9561	0.9542	0.9503	0.9474	0.9428	0.9392
βs ($\times 10^{-10}$ m^2 N^{-1})	5.1898	5.0845	5.0123	4.8875	4.8011	4.7150
L_f ($\times 10^{-11}$ m)	4.6856	4.6379	4.6048	4.5471	4.5068	4.4662
ϕv ($\times 10^3$cm^{3}mole^{-1})	0.2214	0.2427	0.2648	0.2761	0.2880	0.3210
ϕ_K ($\times 10^{-6}$ m^{2}N^{-1})	0.0147	0.0115	0.0097	0.0073	0.0049	0.0028
R_A	0.9934	0.9907	0.9891	0.9876	0.9854	0.9831
Z ($\times 10^3$ kg m^{-2}s^{-1})	1357.30	1369.92	1376.94	1392.27	1401.32	1411.35
[5-(2-hydroxyphenyl)-3-(3-nitrophenyl)-4-(3-pyridinoyl)]-pyrazol [HPNPPP]						
Us (m/s)	1423.42	1428.6	1446.95	1468.37	1481.28	1508.57
ρ_s ($\times 10^3$ kg/m^3)	0.9568	0.9549	0.9509	0.9478	0.9431	0.9396
βs ($\times 10^{-10}$ m^2 N^{-1})	5.1584	5.1312	5.0229	4.8934	4.8325	4.6766
L_f ($\times 10^{-11}$ m)	4.6714	4.6591	4.6097	4.5499	4.5214	4.4479
ϕv ($\times 10^3$cm^{3}mole^{-1})	0.1952	0.2165	0.2490	0.2814	0.3040	0.3263
ϕ_K ($\times 10^{-6}$ m^{2}N^{-1})	0.0143	0.0120	0.0098	0.0074	0.0053	0.0024
R_A	0.9932	0.9930	0.9902	0.9883	0.9868	0.9822
Z ($\times 10^3$ kg m^{-2}s^{-1})	1361.93	1364.17	1375.90	1391.72	1397.00	1417.45
[5-(2-hydroxyphenyl)-3-(3-nitrophenyl)-(4-benzoyl)]-pyrazol [HPNPBP]						
Us (m/s)	1421.65	1437.48	1452.76	1475.35	1491.46	1504.95
ρ_s ($\times 10^3$ kg/m^3)	0.9569	0.9551	0.9512	0.9481	0.9434	0.9397
βs ($\times 10^{-10}$ m^2 N^{-1})	5.1707	5.0670	4.9813	4.8460	4.7652	4.6986
L_f ($\times 10^{-11}$ m)	4.6769	4.6298	4.5905	4.1569	4.4899	4.4584
ϕv ($\times 10^3$cm^{3}mole^{-1})	0.1837	0.1945	0.2163	0.2486	0.2711	0.3146
ϕ_K ($\times 10^{-6}$ m^{2}N^{-1})	0.0144	0.0113	0.0094	0.0068	0.0045	0.0026
R_A	0.9938	0.9912	0.9891	0.9870	0.9849	0.9836
Z ($\times 10^3$ kg m^{-2}s^{-1})	1360.38	1372.94	1381.87	1398.78	1407.04	1414.20
[5-(2-hydroxyphenyl)-3-(phenyl)-4-(3-pyridinoyl)]-pyrazol [HPPPP]						
Us (m/s)	1416.75	1437.65	1451.53	1471.21	1485.62	1498.64
ρ_s ($\times 10^3$ kg/m^3)	0.9561	0.9542	0.9503	0.9472	0.9425	0.9391
βs ($\times 10^{-10}$ m^2 N^{-1})	5.2109	5.0705	4.9945	4.8776	4.8073	4.7413
L_f ($\times 10^{-11}$ m)	4.6951	4.6315	4.5966	4.5425	4.5097	4.4786
ϕv ($\times 10^3$cm^{3}mole^{-1})	0.2214	0.2424	0.2648	0.2972	0.3199	0.3317
ϕ_K ($\times 10^{-6}$ m^{2}N^{-1})	0.0149	0.0114	0.0096	0.0072	0.0050	0.0030
R_A	0.9941	0.9902	0.9885	0.9870	0.9852	0.9839
Z ($\times 10^3$ kg m^{-2}s^{-1})	1354.55	1371.81	1379.39	1393.53	1400.20	1407.37

Fig.(1): Us versus % dioxane

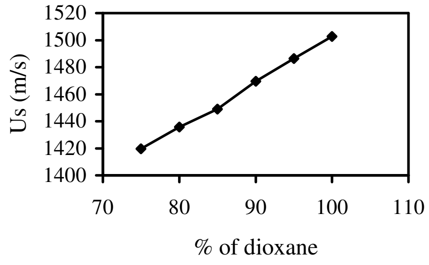


Fig.(2): ρs versus % dioxane

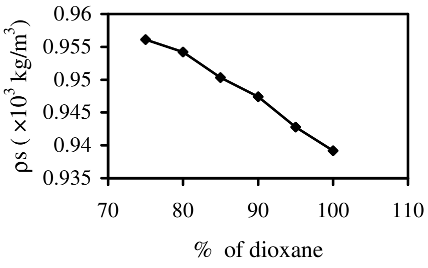


Fig.(3): Bs versus % dioxane

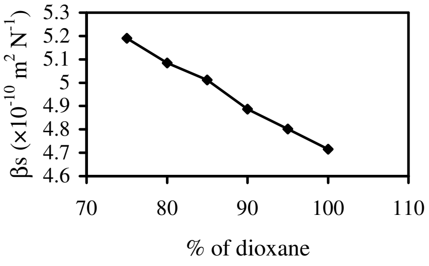


Fig.(4): Lf versus % dioxane

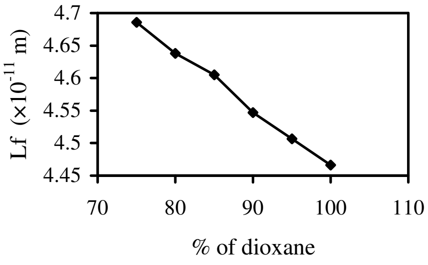


Fig.(5): ϕ v versus % dioxane

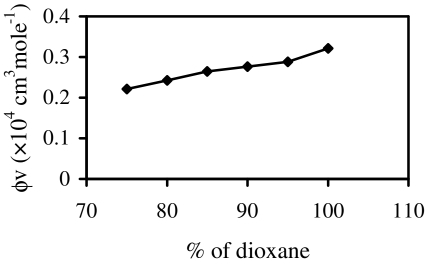


Fig.(6): ϕ_K versus % dioxane

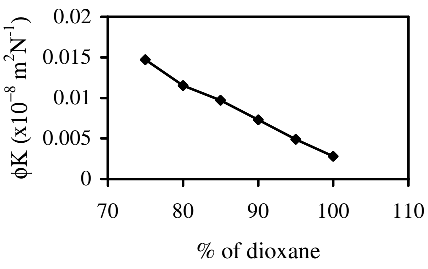


Fig.(7): R_A versus % dioxane

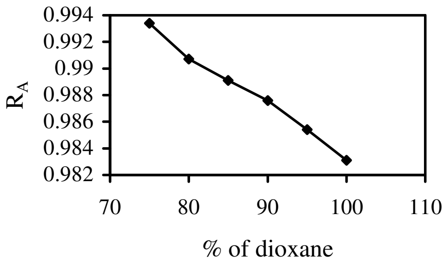
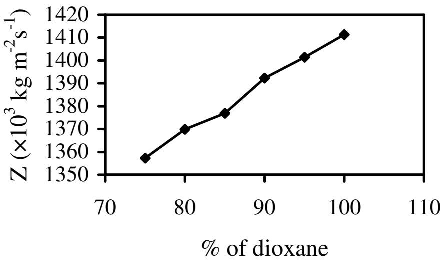


Fig.(8): Z versus % dioxane



Figures (1-8): Variation of sound velocity, density and different acoustical properties in different % of dioxane-water mixture for HPPBP

$$\phi v = \left(\frac{M}{\rho_s}\right) + \left[\frac{(\rho_o - \rho_s).10^3}{m.\rho_s.\rho_o}\right] ....(8)$$

RESULTS AND DISCUSSION

Velocities, densities and calculated acoustical properties in different percentage of dioxane and in 0.01M solution at 298.15K are given in Table (1) and variation in these properties with dioxane % for one of system are shown in Figure (1-8).

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 dioxane[16]. The values of adiabatic compressibility, βs decrease with increase in the percentage of dioxane which may be due to departure of solvent molecules around the ions[17]. The apparent molal volumes (ϕv) found to be increase with increase in the percentage of dioxane. It is observed that (ϕ_k) values decrease with increase in the percentage of dioxane. It could also be seen that the intermolecular free length (Lf) decrease with increase in the percentages of dioxane, 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 (R_A) decrease with increase in the percentage of dioxane -water mixture, which may be due to breaking up of solvent molecules on addition of dioxane in it. Specific acoustic impedance (Z) increases non-linearly with increase in percentage of dioxane. Studies of acoustic properties on the same line have been performed by many workers[18-20].

CONCLUSIONS

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

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