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# Investigation of Molecular Interactions of Substituted Pyrazolines and Isoxazolines in Dioxane–Water and DMF–Water Mixtures Using Ultrasonic Techniques

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**Abstract**

The ultrasonic velocities of pyrazoline, namely HBMPMPPZOLINE, and isoxazolines, namely HCMPMPIZOLINE and HBMPMPIZOLINE, in dioxane–water and DMF–water mixtures were determined at 305 K. Based on the experimental measurements, various acoustical parameters, including apparent molal volume (ϕv$\phi v$), partial molal volume (ϕv0$\phi v0$), adiabatic compressibility (ϕK$\phi K$), intermolecular free length (Lt$Lt$), and relative association, were calculated.

The observed and calculated values were analyzed to investigate molecular association and intermolecular interactions in the studied systems. The results provide insights into the nature of molecular interactions and may contribute to a better understanding of the interactions between metal ions and pyrazoline and isoxazoline compounds.

## 1. Introduction

Ultrasonic waves have emerged as an important tool for investigating the structural and physicochemical properties of matter. They have a wide range of applications in various fields, including technology, medicine, forensic science, space research, and industrial processing. In technology, ultrasonic waves are employed for flow detection, material testing, and surface cleaning. In medical science, they are widely used for diagnostic imaging, the detection of tumors and other abnormalities, fetal monitoring, physiotherapy, and certain surgical procedures.

Ultrasonic velocity and related acoustical parameters provide valuable information about molecular interactions and the structural characteristics of liquid systems. Parameters such as adiabatic compressibility, apparent molal compressibility, apparent molal volume, relative association, and solvation number are useful for understanding the nature and strength of intermolecular interactions. Studies of molecular interactions in liquids provide significant insights into molecular association, complex formation, internal pressure, and the structural arrangement of molecules. In particular, ultrasonic velocity and absorption measurements in electrolyte solutions help elucidate the mechanisms of ion association and complex formation[1-2].

Several researchers have investigated molecular interactions in different liquid systems using ultrasonic techniques. Tabhane et al[3]. studied the thermodynamic behavior of ligand mixtures containing acrolein in methanol–cyclohexane and dioxane systems using the cluster approach and Khasare's equation of state[4]. A. P. Mishra[5] investigated the ultrasonic velocities of biologically relevant systems containing $ZnCl_2$,

dextrose, and methionine in aqueous solutions. Pandey et al[6]. examined molecular interactions in ternary solutions using ultrasonic measurements, while Aswar[7] investigated interactions involving biomolecules and $Mg^{2+}$ ions in aqueous media.

The apparent and partial molal volumes of electrolyte solutions are important parameters for understanding structural interactions, including ion–ion, ion–solvent, and solute–solvent interactions. Similarly, partial molal volume and adiabatic compressibility provide useful information about the interactions of solute molecules with water and organic solvent molecules[8]. Previous studies have also examined the compressibility and apparent molal volume of electrolytes in mixed organic solvents, as well as the volumetric and compressibility properties of peptides in aqueous and aqueous–organic solvent mixtures, as reported by Khobragade et al[9].

Despite these investigations, the acoustical properties of substituted pyrazolines and isoxazolines in aqueous–organic solvent mixtures have received comparatively limited attention. Therefore, the present study focuses on the systematic investigation of substituted pyrazolines and isoxazolines in dioxane–water and N,N-dimethylformamide (DMF)–water mixtures at 305 K. Ultrasonic velocity measurements are used to evaluate relevant acoustical and volumetric parameters, including apparent molal volume, partial molal volume, adiabatic compressibility, intermolecular free length, and relative association. These parameters are analyzed to obtain a better understanding of molecular interactions, solute–solvent interactions, and molecular association in the investigated systems.

## Experimental

### *Materials and Reagents*

All analytical grade chemicals and solvents used were obtained from Merck, India. The distilled water used has a specific conductivity of about $1x10^{-6}$ $ohm^{-1}cm^{-1}$. Stock solutions of pyrazolines and isoxazolines were prepared in different percentage of dioxane-water and DMF-water mixtures. Ultrasonic velocity (2 MHz) was measured by single crystal path interferometer with an accuracy of 0.03%. The density measurements were carried out at 305° K.

The apparent molal volumes $(\phi_v)$ and apparent molal adiabatic compressibility $\phi_{K(s)}$ of pyrazolines and isoxazolines in solutions are determined from density **(ds)** and adiabatic compressibility $(\beta_s)$ of solution using following equations

$$\phi_v = \left\{ \frac{(d_0-d_s) \times 10^3}{m\, d_s .\, d_0} \right\} + \frac{M}{d_s} \quad \text{---------- (1)}$$

Where M is molecular weight of the solute, m is the molality of solution, do is the density of the solvent and ds is the density of the solution.

$$\phi k_s = \left\{ \frac{(\beta_s d_0-\beta_0 d_s) \times 10^3}{m\, d_s .\, d_0} \right\} + \frac{\beta_s M}{d_s} \quad \text{------ (2)}$$

Where $\beta_s$ is the adiabatic compressibility of solution and $\beta_0$ is the adiabatic compressibility of solvent which can be calculated by

$$\beta_s = \frac{100}{U_s^2 \times d_s} \quad \text{------ (3)} \quad \text{for solution and}$$

$$\beta_0 = \frac{100}{U_0^2 \times d_0} \quad \text{------ (4)} \quad \text{for solvent}$$

Where $U_s$ & $U_0$ are the ultrasonic velocities of ultrasonic waves in solution and solvent respectively.

Knowing □s, □0 and molecular weight of pyrazoline and isoxazolines, the values of $\phi_v$ and $\phi_{K(s)}$ are calculated. The values of $\phi_v$ and $\phi_{K(s)}$ are plotted against molality (m) of pyrazoline and isoxazolines. The curve represented the least square and $\phi_v$ and $\phi_{K(s)}$ can be given as

$\phi_v = (\phi^0_v + S_v\, m)$ ------ (5)

$\phi k_s = (\phi^0 k_{(s)} + Sk_{(s)}\, m)$ ---- (6)

Where $\phi^0_v = v^o$ and $\phi^0_{K(s)} = K^0$ are the infinite dilution partial molal volumes and adiabatic partial molal compressibilities respectively. $S_v$ and $Sk_{(s)}$ are the experimental slopes.

The $\phi_{K(s)}$ and $\phi_v$ values of pyrazoline and isoxazolines in two mixed solvents are calculated and given in Table 1 to 11.

The intermolecular free length ($L_t$), specific acoustic impendence (z) and relative association ($R_A$) are calculated by using the following relations

$L_t = K\ X\ (B_s)^{1/2}$ ------ (7)

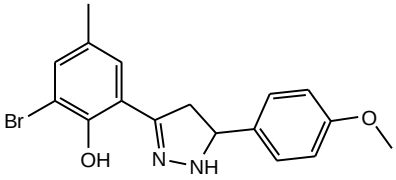
Where K is Jacobson's constant = 6.0186 X $10^4$ and

$Z = U_s\ X\ ds$ ----------(8)

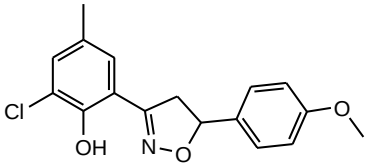
$R_A = ds/d0\ (U_0/U_s)^{1/3}$ ---------(9)

The ligands used in these investigations are

1) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} pyrazoline




2) 3-{2-hydroxy-3-chloro-5-methyl-phenyl-5(4-methoxyphenyl)}isoxazolines




3) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} isoxazolines

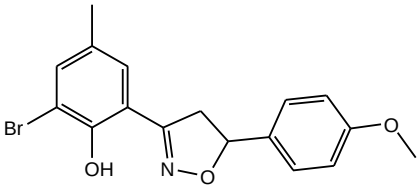



**Table No. 1**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities (□$_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_1$ (HBMPMPZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} pyrazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| % Dioxane | Conc. in | Ultrasonic velocities | Densities (ds) | Adiabatic | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|

| | mol $dm^{-3}$ | | in g $cm^{-3}$ | compressibilities ($\beta_s$) | |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1411.2 | 1.0538 | 4.76 X $10^{-5}$ | 4.15 X $10^{2}$ |
| 90 | 9.0 X $10^{-3}$ | 1427.2 | 1.0633 | 4.61 X $10^{-5}$ | 4.08 X $10^{2}$ |
| 85 | 8.5 X $10^{-3}$ | 1457.6 | 1.0604 | 4.43 X $10^{-5}$ | 4.00 X $10^{2}$ |
| 80 | 8.0 X $10^{-3}$ | 1469.0 | 1.0549 | 4.23 X $10^{-5}$ | 3.91 X $10^{2}$ |
| 75 | 7.5 X $10^{-3}$ | 1507.2 | 1.0588 | 4.17 X $10^{-5}$ | 3.88 X $10^{2}$ |
| 70 | 7.0 X $10^{-3}$ | 1535.0 | 1.0593 | 4.00 X $10^{-5}$ | 3.80 X $10^{2}$ |

**Table No. 2**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_1$ (HBMPMPZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} pyrazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | -692.0 | -1.99 X $10^{-4}$ | 1.0063 | 1.487 X $10^{3}$ |
| 9.0 X $10^{-3}$ | -1695.6 | -4.34 X $10^{-4}$ | 1.0116 | 1.517 X $10^{3}$ |
| 8.5 X $10^{-3}$ | -1515.5 | -6.45 X $10^{-4}$ | 1.0017 | 1.545 X $10^{3}$ |
| 8.0 X $10^{-3}$ | -1011.7 | -9.01 X $10^{-4}$ | 0.9879 | 1.578 X $10^{3}$ |
| 7.5 X $10^{-3-}$ | -1181.9 | -10.58 X $10^{-4}$ | 0.9892 | 1.595 X $10^{3}$ |
| 7.0 X $10^{-3}$ | -1788.2 | -13.663 X $10^{-4}$ | 0.9838 | 1.620 X $10^{3}$ |

**Table No. 3**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities ($\beta_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_2$ (HCMPMPIZOLINE) 3-{2-hydroxy-3-chloro-5-methyl-phenyl-5(4-methoxyphenyl)} isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| % Dioxane | Conc. in mol $dm^{-3}$ | Ultrasonic velocities | Densities (ds) in g $cm^{-3}$ | Adiabatic | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|

| | | | | compressibilities ($\beta_s$) | |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1374.4 | 1.0679 | 4.957 X $10^{-5}$ | 4.237 X $10^{2}$ |
| 90 | 9.0 X $10^{-3}$ | 1409.6 | 1.0546 | 4.772 X $10^{-5}$ | 4.157 X $10^{2}$ |
| 85 | 8.5 X $10^{-3}$ | 1476.8 | 1.0423 | 4.399 X $10^{-5}$ | 3.991 X $10^{2}$ |
| 80 | 8.0 X $10^{-3}$ | 1539.2 | 1.0529 | 4.008 X $10^{-5}$ | 3.810 X $10^{2}$ |
| 75 | 7.5 X $10^{-3}$ | 1569.6 | 1.0562 | 3.843 X $10^{-5}$ | 3.731 X $10^{2}$ |
| 70 | 7.0 X $10^{-3}$ | 1596.8 | 1.0740 | 3.651 X $10^{-5}$ | 3.636 X $10^{2}$ |

**Table No. 4**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_2$ (HCMPMPIZOLINE) 3-{2-hydroxy-3-chloro-5-methyl-phenyl-5(4-methoxyphenyl)} isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | -1127.2 | -1.994 X $10^{-4}$ | 1.0119 | 1467.72 |
| 9.0 X $10^{-3}$ | 120.87 | -3.400 X $10^{-4}$ | 0.9909 | 1486.56 |
| 8.5 X $10^{-3}$ | 1431.21 | -7.194 X $10^{-4}$ | 0.9643 | 1539.26 |
| 8.0 X $10^{-3}$ | 290.25 | -12.840 X $10^{-4}$ | 0.9607 | 1620.02 |
| 7.5 X $10^{-3-}$ | -107.50 | -15.960 X $10^{-4}$ | 0.9576 | 1657.81 |
| 7.0 X $10^{-3}$ | -2429.31 | -20.537 X $10^{-4}$ | 0.9576 | 1714.96 |

**Table No. 5**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities ($\beta_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_3$ (HBMPMPIZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| % Dioxane | Conc. in mol $dm^{-3}$ | Ultrasonic velocities | Densities (ds) in g $cm^{-3}$ | Adiabatic compressibilities ($\beta_s$) | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1398.40 | 1.0663 | 4.795 X $10^{-5}$ | 4.167 X $10^{2}$ |
| 90 | 9.0 X $10^{-3}$ | 1422.40 | 1.0660 | 4.636 X $10^{-5}$ | 4.097 X $10^{2}$ |
| 85 | 8.5 X $10^{-3}$ | 1470.40 | 1.0826 | 4.272 X $10^{-5}$ | 3.933 X $10^{2}$ |
| 80 | 8.0 X $10^{-3}$ | 1497.60 | 1.0725 | 4.157 X $10^{-5}$ | 3.880 X $10^{2}$ |
| 75 | 7.5 X $10^{-3}$ | 1518.40 | 1.0759 | 4.031 X $10^{-5}$ | 3.821 X $10^{2}$ |
| 70 | 7.0 X $10^{-3}$ | 1555.20 | 1.0732 | 3.852 X $10^{-5}$ | 3.735 X $10^{2}$ |

**Table No. 6**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of dioxane-water mixture at 303 K.**

System $L_3$ (HBMPMPIZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)}isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: Dioxane-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | -718.05 | -3.288 X $10^{-4}$ | 1.0021 | 1440.00 |
| 9.0 X $10^{-3}$ | -740.56 | -5.199X $10^{-4}$ | 0.9964 | 1516.27 |
| 8.5 X $10^{-3}$ | -2543.11 | -10.168X $10^{-4}$ | 1.0010 | 1591.85 |
| 8.0 X $10^{-3}$ | -1586.06 | -11.168 X $10^{-4}$ | 0.9855 | 1606.17 |
| 7.5 X $10^{-3-}$ | -2107.59 | -14.207X $10^{-4}$ | 0.9841 | 1633.34 |
| 7.0 X $10^{-3}$ | -1489.80 | -17.494 X $10^{-4}$ | 0.9737 | 1669.04 |

**Table No. 7**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities ($\phi_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_1$ (HBMPMPZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} pyrazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| % Dioxane | Conc. in mol $dm^{-3}$ | Ultrasonic velocities | Densities (ds) in g $cm^{-3}$ | Adiabatic compressibilities ($\phi_s$) | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1520.8 | 0.9867 | 4.381 X $10^{-5}$ | 398.36 |
| 90 | 9.0 X $10^{-3}$ | 1542.4 | 0.9912 | 4.240X $10^{-5}$ | 391.90 |
| 85 | 8.5 X $10^{-3}$ | 1611.2 | 0.9726 | 3.960X $10^{-5}$ | 378.74 |
| 80 | 8.0 X $10^{-3}$ | 1611.2 | 0.9950 | 3.871X $10^{-5}$ | 374.46 |
| 75 | 7.5 X $10^{-3}$ | 1628.8 | 0.9825 | 3.836X $10^{-5}$ | 372.76 |
| 70 | 7.0 X $10^{-3}$ | 1651.2 | 1.032 | 3.554X $10^{-5}$ | 358.80 |

**Table No. 8**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_1$ (HBMPMPZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)} pyrazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | 149.02 | -3.570 X $10^{-4}$ | 0.9907 | 1500.47 |
| 9.0 X $10^{-3}$ | -381.1 | -5.578X $10^{-4}$ | 0.9906 | 1528.82 |
| 8.5 X $10^{-3}$ | 1850.4 | -8.354X $10^{-4}$ | 0.9580 | 1567.05 |
| 8.0 X $10^{-3}$ | -3200.00 | -11.160X $10^{-4}$ | 0.9800 | 1603.24 |
| 7.5 X $10^{-3-}$ | -305.82 | -11.730X $10^{-4}$ | 0.9642 | 1600.29 |
| 7.0 X $10^{-3}$ | -6338.08 | -19.178X $10^{-4}$ | 1.0906 | 1704.03 |

**Table No. 9**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities ($\phi_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_2$ (HCMPMPIZOLINE) 3-{2-hydroxy-3-chloro-5-methyl-phenyl-5(4-methoxyphenyl)}isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| % Dioxane | Conc. in mol $dm^{-3}$ | Ultrasonic velocities | Densities (ds) in g $cm^{-3}$ | Adiabatic compressibilities ($\phi_s$) | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1523.20 | 1.06790.9715 | 4.436 X $10^{-5}$ | 4.008 X $10^{2}$ |
| 90 | 9.0 X $10^{-3}$ | 1560.00 | 1.0039 | 4.093X $10^{-5}$ | 3.850 X $10^{2}$ |
| 85 | 8.5 X $10^{-3}$ | 1625.60 | 1.0129 | 3.735 X $10^{-5}$ | 3.678 X $10^{2}$ |
| 80 | 8.0 X $10^{-3}$ | 1678.40 | 1.0232 | 3.461 X $10^{-5}$ | 3.545 X $10^{2}$ |
| 75 | 7.5 X $10^{-3}$ | 1694.40 | 1.0253 | 3.397 X $10^{-5}$ | 3.507 X $10^{2}$ |
| 70 | 7.0 X $10^{-3}$ | 1699.20 | 1.0261 | 3.375 X $10^{-5}$ | 3.416 X $10^{2}$ |

**Table No. 10**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_2$ (HCMPMPIZOLINE) 3-{2-hydroxy-3-chloro-5-methyl-phenyl-5(4-methoxyphenyl)} isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | -1591.46 | -0.4979 | 1.0065 | 1479.78 |
| 9.0 X $10^{-3}$ | -5402.90 | -1.0717 | 1.0316 | 1566.08 |
| 8.5 X $10^{-3}$ | -6787.60 | -1.5973 | 1.0268 | 1646.57 |
| 8.0 X $10^{-3}$ | -8564.20 | -2.0686 | 1.0372 | 1663.31 |
| 7.5 X $10^{-3-}$ | -9322.40 | -3.3110 | 1.0283 | 1720.86 |

| | | | | |
|---|---|---|---|---|
| 7.0 X $10^{-3}$ | -10128.53 | -2.5122 | 1.0258 | 1738.62 |

**Table No. 11**

**Ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities ($\beta_s$) and intermolecular free length ($L_t$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_3$ (HBMPMPIZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)}isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| % Dioxane | Conc. in mol $dm^{-3}$ | Ultrasonic velocities | Densities (ds) in g $cm^{-3}$ | Adiabatic compressibilities ($\beta_s$) | Inter molecular free length ($L_t$) |
|---|---|---|---|---|---|
| 95 | 9.5 X $10^{-3}$ | 1510.4 | 0.9987 | 4.389 X $10^{-5}$ | 398.72 |
| 90 | 9.0 X $10^{-3}$ | 1588.8 | 1.0190 | 3.887 X $10^{-5}$ | 375.23 |
| 85 | 8.5 X $10^{-3}$ | 1641.6 | 1.0177 | 3.646 X $10^{-5}$ | 363.41 |
| 80 | 8.0 X $10^{-3}$ | 1678.4 | 1.0216 | 3.477 X $10^{-5}$ | 354.89 |
| 75 | 7.5 X $10^{-3}$ | 1699.2 | 1.0241 | 3.381 X $10^{-5}$ | 349.95 |
| 70 | 7.0 X $10^{-3}$ | 1652.8 | 1.0379 | 3.526 X $10^{-5}$ | 357.38 |

**Table No. 12**

**Apparent molal volume ($\phi_v$), apparent adiabatic compressibility ($\phi k_s$), specific acoustic impendence (z) and relative association ($R_A$) at different concentrations of ligand in different percentage of DMF-water mixture at 303 K.**

System $L_3$ (HBMPMPIZOLINE) 3-{2-hydroxy-3-bromo-5-methyl-phenyl-5(4-methoxyphenyl)}isoxazoline

Ultrasonic frequency: 2MHz Temperature: 303 K Medium: DMF-water

| Conc. in mol $dm^{-3}$ | Apparent molal volume ($\phi_v$) | Apparent adiabatic compressibility ($\phi k_s$) | Relative association ($R_A$) | Specific acoustic impendence (z) |
|---|---|---|---|---|
| 9.5 X $10^{-3}$ | -3208.40 | -0.56171 | 1.0248 | 1508.43 |
| 9.0 X $10^{-3}$ | -5634.44 | -1.2553 | 1.0283 | 1618.98 |
| 8.5 X $10^{-3}$ | -5832.45 | -1.6011 | 1.0159 | 1670.65 |
| 8.0 X $10^{-3}$ | -6693.53 | -1.9142 | 1.0122 | 1714.65 |
| 7.5 X $10^{-3}$- | -7488.25 | -2.1797 | 1.0106 | 1740.15 |
| 7.0 X $10^{-3}$ | -9908.96 | -2.1974 | 1.0337 | 1715.44 |

**Table No. 13**

**Limiting apparent molal volume (□□$_v$) and limiting molal compressibility (□□$k_s$) of different ligands in Dioxane-water and DMF-water mixture at 303 K.**

| Sr.No. | System | □□$k_s$ | □□$_v$ |
|---|---|---|---|
| 1 | $L_1$ (Dioxane-water) | -16.00 | -2200.00 |
| 2 | $L_2$ (Dioxane-water) | -22.50 | ------ |
| 3 | $L_3$ (Dioxane-water) | -11.50 | ------ |
| 4 | $L_1$ (DMF-water) | ------ | -7600.00 |
| 5 | $L_2$ (DMF-water) | -3.70 | -12000.00 |
| 6 | $L_3$ (DMF-water) | -2.25 | -10300.00 |

**Results and Discussion**

The experimental and calculated values of ultrasonic velocities ($U_s$), densities (ds), adiabatic compressibilities (□$_s$), apparent adiabatic compressibility (□$k_s$), relative association ($R_A$), specific acoustic impendence (z), apparent molal volume (□$_v$) and intermolecular free length ($L_t$) for pyrazolines and isoxazolines are tabulated in Table No. 1 to 12. These values have been used to discuss the interactions of unlike molecules of solvent in presence of solute. The variation of ultrasonic velocity in solution depends on the intermolecular free length on mixing on the basis of a model for sound propagation proposed by Erying and Kincaid[i].

The graphs are plotted between □$k_s$ versus mole fraction of organic solvent and are found to be linear over the entire range of mole fraction except one of the point. In each plot, one of the points is significantly away from the linearity. Therefore □$k_s$ measurements for these organic substances are limited for those mole fractions where linearity is being followed and this seems the range of dilute solutions.

Linear pattern of the graphs is observed in dioxane-water and DMF-water as shown in graph no. 1 to 3. The plot between □$_v$ and mole fraction of organic solvents are shown in graph no. 4 to 6 and shows that □$_v$ values varies inversely with percentage / mole fraction of organic solvent.

The plot between □$k_s$ and mole fraction of organic solvents indicates that □$k_s$ values increases with increasing percentage / mole fraction of organic solvent. Pankanti and Jahagirdar[ii] have investigated apparent molal compressibility for amino acids in dioxane-water and acetone-water media. It is observed that □$k_s$ decreases upto 40% organic solvent-water mixture.

Present work reveals the increase in (□$k_s$) values above 70% organic solvent –water mixture (Table 1 to 12). This fact shows that □$k_s$ increases at higher percentage of organic solvent –water mixture. This suggests that loss of compressibility of water due to electrostatic forces in the vicinity of ions causing electro-strictive hydration of ions. The apparent molal volume (□$_v$) has been calculated from density data of solution using equation (2). The data obtained are in well agreement with Messon equation as the plot of □$_v$ against $(c)^{1/2}$ or mole fraction is linear. The □$_v$ values of substituted pyrazoline and isoxazolines are found to increase with increasing percentage of organic solvent –water mixture. Das[iii] studied the apparent molal volume (□$_v$) of univalent ions up to 30% dioxane-water mixture and reported that □$_v$ values of these ions increases with increase in dioxane content in dioxane-water mixture. In the present investigation it is found that the values of □$_v$ values are higher in dioxane-water mixture as compared to DMF-water mixture due to decreasing dielectric constant of medium[iv]. It can be explained by postulating that the [polar –OH group interact with the surrounding organic solvent-water mixture through dipole-dipole interaction in such away that the surrounding water losses its own compressibility to certain extent.

The $k_s$ values are found to be decrease in the following order of organic solvent-water mixture – dioxane-water< DMF-water, which suggest that pyrazoline and isoxazolines are extensively hydrated in dioxane-water mixture than DMF-water mixture. This can be explained on the basis of higher polarity of dioxane-water mixture than DMF-water mixture. Dipole induced- dipole interactions between unlike molecules are more in dioxane-water mixture.

In the present investigation, the values of $L_t$, $R_A$ and Z are also evaluated (Table 1 to 12). It could be seen from above table that intermolecular free length increase linearly with increasing concentration of pyrazoline and isoxazolines. This indicates that there are significant interactions between ions and solvent molecules suggesting structure-promoting behaviour of added electrolyte molecule. This may also imply that decrease in number of free ions showing the occurrence of ionic association due to strong ion-ion interactions. Relative association ($R_A$) is influenced by two factors-

1) the breaking up of solvent molecules on addition of electrolyte to it. And

2) the solvation of ions that simultaneously present the former resulting in decrease and later increase of relative association.

The increase of $R_A$ with concentration suggest that solvation of ions predominates over the breaking up of solvent aggregates (water-water, water-dioxane and water-DMF) on addition of pyrazoline and isoxazolines. It is observed from the table that there is linear variation of $R_A$ signifies the weaker association between solvent and solute molecules.

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