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Studies on Acoustic Parameters of Some Substituted Isoxazolines and Pyrazolines in 70% Dioxane-Water Mixture and Effect on Seed Germination

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ABSTRACT

Ultrasonic velocities and densities of 3-(2-hydroxyl-4-methyl phenyl)-5-phenyl isoxazoline (L_1) and 1-phenyl-3-(2-hydroxyl-3-nitro-4-methyl phenyl)-5-phenyl pyrazoline (L_2) at different concentrations in dioxane. Different acoustic properties like partial molal volume, adiabatic compressibility, apparent molal compressibility, intermolecular free length, specific acoustic impedance and relative association etc., have been determined. These parameters obtained have been interpreted in terms of solute-solute interactions. Effect of L_1 & L_2 ligand and its complexes on germination of seeds.

Key words : Isoxazolines, Pyrazoline, 70% Dioxane-Water mixture, Seed germination.

INTRODUCTION

Ultrasonic velocity and adsorption studies in case of electrolyte solution have led to new insight into the process of ion association and complex formation[1,2]. Sondawale and Narwade[3] have studied ultrasonic velocity of peptide in binary mixture. Rohankar[4] has investigated the ultrasonic velocity of monochloro acetic acid and trichloro acetic acid in Trihydrofuron (THF) and dioxane-water mixture. Ultrasonic velocity of substituted acrylophenones and its complexes in acetone[5] and substituted thiadiazoles and carboxylate at different liquid mixture has been studied[6]. Ikhe and Narwade[7] have studied ultrasonic velocities and densities of isoxazole and pyrazole at 303 K. Naik and Narwade[8] studied metal-ligand stability constant of substituted pyrazole complexes with lanthanide metal ion.

The information about the role of metal complexes in biological systems, their concentration and presence in different equilibria is of immense importance. Greshon et al[9,10] reported that the activity of metal chelates is considerably increased as compared to that of the free metal and ligand alone on their complexation. The observation of antifungal and antibacterial activities of complexes show that they are more active as compared to free ligand and metal involved[11,12].

The biological activity of metal ion and ligand of Cu(II) complexes towards some fungi and bacteria are evaulated[13]. Rare earth metal ions, when they replace the metal ion Ca^{2+} in complex, spectral properties of the systems are modified with no change in functionalities of the complex[14]. Rare earth ions are used as probe in bio-chemistry of calcium. Zielinski et al[15] showed that, Lanthanide ion could substitute the calcium ion to produce active enzyme system.

Biological properties of some rare earth complexes have been reported by Sharma et al[16]. The pharmaceutical uses of metal complexes have been reported by many worker[17-18]. Studies on special structural requirement and complexation as a possible mode of pesticidal action have also been reported[19]. Activity of thiocynate of titanium as plant growth regulator has been reported[20].

Looking at the important role of substituted 3-(2-hydroxyl-4-methyl phenyl)-5-phenyl isoxazoline (L_1); 1-phenyl-3-(2-hydroxy-3-nitro-4-methyl phenyl)-5-phenyl pyrazoline (L_2) as antibiotic drugs, it was thought worthwhile to study the acoustic properties of L_1 and L_2 in 0.02, 0.04, 0.06, 0.08, 0.10 M in 70% dioxane-water mixture.

MATERIALS AND METHODS

The solvent used was purified by standard procedure[21]. Solutions of different concentrations were prepared by dissolving known weight of substances. All weighing were made on Mechaniki Zaktady Precyzyjnej Gdansk Balance (±0.001 g).

Density measurements were performed with a precalibrated bicapillary pyknometer. The accuracy in density measurement was found to be ±0.001 cm^{-3}.

The speed of sound waves was obtained using variable path, single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy of ±0.03% and frequency 1 MHz.

Effect of binary complexes on germination, survival and seedling height of *Triticum aestivum* (Wheat) and *Trigunella* (Methi) plants are studied. For biological study, the metal ions used are Cu(II), Ni(II) and Co(II). Ligands L_2 and L_4 are used in the present study. The applications of complexes in general are studied by dissolving it in proper solvent at desired pH or it is formed during the reaction. The biological applications are therefore studied in aqueous medium at pH 3.0, 7.0 and 9.0 and at constant ionic strength of 0.01 M potassium nitrate solution.

RESULTS AND DISCUSSION

The apparent molal volume and apparent molal compressibility have been calculated from Eqns. (1) and (2).[22]

$$\phi_v = \frac{1000\,(d_0 - d_s)}{m\, d_s\, d_0} + \frac{M}{d} \qquad \text{..........................} (1)$$

$$\phi_k = \frac{1000\,(\beta_s\, d_0 - \beta_0\, d_s)}{m\, d_s\, d_0} + \frac{\beta_s\, M}{d_s} \qquad \text{..........................} (2)$$

where, d_0 and d_s represent densities of solvent and solution respectively, m is the molality, M is the molecular weight of solute, β_s and β_0 are the adiabatic compressibilities of solution and solvent respectively. Specific acoustic impedance (z), relative association (R_A) and free length (L_f) are the functions of ultrasonic velocity and are computed by Eqns. (3)-(5).[23]

$$z = U_s d_s \qquad \text{.........................} (3)$$

$$R_A = \frac{d_s}{d_0}\left(\frac{U_0}{U_s}\right)^{1/3} \qquad \text{.........................} (4)$$

$$L_f = K \sqrt{\beta_s} \qquad \text{.........................} (5)$$

where, U_0 and U_s are velocity of ultrasonic wave in solvent and solution and K is Jacobson's constant (6.0186×10^4)

The values of ϕ_v, ϕ_{ks}, β_s, d_s, L_f, z and R_A obtained in present investigation at different concentrations are presented in Table-1. It could be seen from table-1 that intermolecular free length decreases with increase in the concentration of L_1 and L_2 in dioxane and hence increase in ultrasonic velocity with increasing concentration of L_1 and L_2.

Table-1 : Values of different parameters of L_1 and L_2 in 1,4-dioxane from ultrasonic study.

Parameters	**Conc. M mol dm^{-3}**				
	0.02	**0.04**	**0.06**	**0.08**	**0.10**
L_1					
d_s (g cm^{-3})	1.01247	1.01781	1.0205	1.0244	1.0295
$U_0 \times 10^3$ (m/s^{-1})	1090.851	1091.85	1091.95	1092.00	1092.15
$\beta_s \times 10^{-5}$ (bar^{-1})	4.754	5.015	5.250	5.555	5.785
$L_f \times 10^{-2}$	0.05201	0.0462	0.0419	0.0395	0.03550
ϕ_v (cm^3 mol^{-1})	192.55	248.33	245.86	248.41	261.342
ϕ_{ks} (cm^3 mol^{-1} bar^{-1})	1.9255	1.3400	1.0968	0.2486	0.6166
R_A	1.66766	1.9484	1.9998	2.1254	2.25061
$z \times 10^4$ (m s^{-1} g^{-3})	1220.74	1377.239	1650.39	1705.55	1755.65
L_2					
d_s (g cm^{-3})	1.0837	1.1889	1.1614	1.1312	1.1341
$U_0 \times 10^3$ (m/s^{-1})	1090.850	1091.80	1091.90	1091.95	1092.00
$\beta_s \times 10^{-5}$ (bar^{-1})	5.06071	4.6584	4.9398	5.3170	4.8015
$L_f \times 10^{-2}$	0.04488	0.04346	0.04334	0.04330	0.04320
ϕ_v (cm^3 mol^{-1})	344.156	313.697	321.142	329.75	328.88
ϕ_{ks} (cm^3 mol^{-1} bar^{-1})	1.74003	1.4604	1.5857	1.7527	1.7554
R_A	2.03918	2.2043	2.2424	2.2885	2.2955
$z \times 10^4$ (m s^{-1} g^{-3})	463.353	1597.53	1533.32	1458.59	1535.86

This indicates that there is strong interaction between ion and solvent molecule, suggesting a structure promoting behaviour of the added solute. This may also imply that there is decrease in number of free ions, 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 ions[24] supporting strong ion-solvent interaction. It is observed from table-1 that apparent molal volume and adiabatic compressibility increases with decrease in the concentration. Partial molar adiabatic compressibility and viscosity of some amino acids have been studied in aqueous glycerol solution at 298.15 K.[25] Ultrasonic study of glycine in binary aqueous solution of mannose, maltose, raffinose at different temperatures have been studied by Amalendru Pol et al.[26]

The positive value of ϕ_{ks} shows strong electrostatic force in the vicinity of ions, causing electrostatic solution of ions. The relative association is influenced by two factors: i) the breaking up of the solvent molecule on addition of electrolyte to it and ii) solvated ions that the simultaneously present.

Table – 2 Effect of Ligand and Complexes on Germination and Survival of (*Triticum aestivum*) Wheat seed.

Ligand : L_1 μ = 0.1 M pH = 3.0

Parameters	Effect of			Effect of Complexes with Ligand (L_1)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	40	50	70	50	50	50	Ligand > Ni(II) > Co(II) > Cu(II) Ligand is having an excellent function as a plant growth regulator
% Survival after 8 days	55	60	62	62	65	60	
Root length (mm)	12.00	15.10	12.00	12.00	15.10	12.50	
Shoot length (mm)	18.00	19.70	19.50	17.00	17.40	17.20	
Seedling height (mm)	30.00	34.80	30.60	28.00	31.45	28.80	
Root Shoot Ratio	0.666	0.695	0.620	0.607	0.553	0.607	
Leaf Length (mm)	12.50	15.25	19.25	12.20	12.40	12.20	

Table – 3 Effect of Ligand and Complexes on Germination and Survival of (*Triticum aestivum*) Wheat seed.

Ligand : L_1 μ = 0.1 M pH = 5.0

Parameters	Effect of			Effect of Complexes with Ligand (L_1)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	55	58	58	65	58	57	Co(II) > Cu(II) > Ligand > Ni(II) Co(II) is having an excellent function as a plant growth regulator
% Survival after 8 days	60	62	65	65	70	75	
Root length (mm)	10.00	10.25	10.30	12.60	11.80	12.45	
Shoot length (mm)	16.00	17.00	18.70	19.75	18.50	18.25	
Seedling height (mm)	28.00	29.20	31.00	34.30	31.30	32.70	
Root Shoot Ratio	0.571	0.582	0.580	0.575	0.591	0.558	
Leaf Length (mm)	12.00	12.25	15.00	15.50	14.10	15.00	

Table – 4 Effect of Ligand and Complexes on Germination and Survival of (*Triticum aestivum*) Wheat seed.

Ligand : L_1 μ = 0.1 M pH = 7.0

Parameters	Effect of			Effect of Complexes with Ligand (L_1)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	50	50	50	60	80	80	Co(II) > Ni(II) > Cu(II) > Ligand Co(II) is having an excellent function as a plant growth regulator
% Survival after 8 days	62	65	69	70	72	80	
Root length (mm)	12.00	8.90	9.75	9.00	9.60	9.70	
Shoot length (mm)	16.45	12.75	17.00	17.10	18.20	17.30	
Seedling height (mm)	32.45	25.65	30.75	30.10	31.80	31.00	
Root Shoot Ratio	0.729	0.698	0.573	0.526	0.527	0.560	
Leaf Length (mm)	13.00	10.75	12.80	13.00	14.25	13.25	

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

Table – 5 Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed.

Ligand : L_2 μ = 0.1 M pH = 3.0

Parameters	Effect of			Effect of Complexes with Ligand (L_2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	70	72	60	75	70	81	Co(II) > Cu(II) > Ligand > Ni(II) Co(II) is having an excellent function as a plant growth regulator
% Survival after 8 days	68	72	75	80	82	85	
Root length (mm)	5.25	5.15	5.00	5.85	5.80	5.88	
Shoot length (mm)	7.15	6.00	6.50	7.00	7.10	7.35	
Seedling height (mm)	30.00	28.00	29.15	30.15	30.00	31.75	
Root Shoot Ratio	0.734	0.858	0.769	0.835	0.816	0.748	
Leaf Length (mm)	9.50	8.85	8.00	7.55	8.15	8.00	

Table – 6 Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed.

Ligand : L_2 μ = 0.1 M pH = 5.0

Parameters	Effect of			Effect of Complexes with Ligand (L_2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	60	60	60	72	75	80	Co(II) > Ni(II) > Cu(II) > Ligand Co(II) is having an excellent function as a plant growth regulator
% Survival after 8 days	65	68	70	75	80	82	
Root length (mm)	5.19	4.99	5.00	5.25	5.60	5.60	
Shoot length (mm)	7.25	7.75	7.80	7.00	7.85	7.80	
Seedling height (mm)	30.00	28.00	31.25	31.00	30.10	30.00	
Root Shoot Ratio	0.715	0.643	0.641	0.750	0.713	0.717	
Leaf Length (mm)	9.00	9.15	9.25	9.00	9.50	9.55	

Table – 7 Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed.

Ligand : L_2 μ = 0.1 M pH = 7.0

Parameters	Effect of			Effect of Complexes with Ligand (L_2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	50	60	65	70	75	85	Co(II) > Cu(II) > Ni(II) > Ligand Co(II) is having an excellent function as a plant growth regulator
% Survival after 8 days	50	60	65	68	75	80	
Root length (mm)	5.12	5.25	5.55	5.65	5.80	5.50	
Shoot length (mm)	7.35	7.15	7.25	7.30	7.30	7.30	
Seedling height (mm)	30.00	28.00	31.00	28.50	32.00	32.50	
Root Shoot Ratio	0.696	0.734	0.765	0.760	0.799	0.881	
Leaf Length (mm)	9.80	9.90	0.95	0.97	9.96	9.88	

It is clear from Table 2 to 7 that, in case of *Triticum aestivum* (Wheat), with increasing the pH value, percentage of germination and percentage of survival increased, but in case of *Trigunella* (Methi), reversed effect was observed with increase the pH value. The percentage germination in all treatments increases for Co(II) complex as compared to rest of the complexes and ligands.

From Table 2 to 7 clearly indicate that, root length increases with increasing pH value, but in the Co(II)-L_2 complex the root length decreases with increase in the pH value.

It could seen from Table 2 to 7 that root-soot ratio in all the systems for pH 3.0, 5.0 and 7.0 showed abnormal behaviour which may be due to not orderly germination.

The changes in the growth pattern of root and soot were studied by the proportional growth in both the cases. The root and soot ratio reflect the same and represent the development in root and soot simultaneously. It is observed from all table that Co(II)-L_2 complexes showed better plant growth regulators for *Triticum aestivum* (Wheat) and *Trigunella* (Methi) plants.

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