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Synthesis, Spectral, Magnetic behavior and Acoustical parameters of synthesized Cu(II) metal complexes with 4-Nitrobenzylidene.

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Abstract

Metal complexes play a variety of important roles in physical, chemical biological systems. The importance of copper as an essential element can be estimated by the wide range of copper proteins and enzymes playing different role in biological system. Ultrasonic propagation parameters yield valuable information regarding the behavior of liquid systems, because intermolecular association, dipolar interactions, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity. Metal complexes of Cu(II) derived from 4-Nitrobenzylidene with 2-aminothiazole (NBAT) have been synthesized and their ultrasonic velocity and density have been measured in non- aqueous solution methanol at room temperature. The value of apparent molar volume, acoustic impedance, adiabatic compressibility, inter molecular free length, molar sound velocity (Rao's constant), free volume, internal pressure and cohesive forces have been calculated from density and ultrasonic velocity data.

Keywords: Ultrasonic velocity, Density, Acoustical parameters of Cu(II) Metal complexes.

Introduction

Coordination chemistry can find a use in medicine in a number of ways. Coordination compounds can be used in the treatment, management or dignosis of disease. Complex can be formed in the body to handle dysfunction due to metal poisoning.[1-12] Free copper ions are harmful for the body but when it forms a reactive oxygen complex that can be used for several applications. Copper is the essential element which plays an inevitable role in various chemical,biological and environmental systems. Ultrasonic velocity of a solution is an important property from which some structural features of liquid or solutions are reflected,eg intermolecular interactions and distances.[13-30] Velocity and absorption of ultrasonic waves play an important role in the interaction and other acoustical studies of liquid and liquid mixtures.[31-35] In the present studies, the ultrasonic velocity and density of solutions of NBAT Schiff bases and their metal complexes of Cu(II) have been measured and various acoustical parameters have been calculated in non-aqueous medium

EXPERIMENTAL

All the used chemicals were of Anal R grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were obtained from Loba Chemie. All solutions were prepared in fresh (by weight) double distilled water, degassed by boiling, having conductance less $0.6x10^{-6}$ S cm^{-1}. The density measurements were performed with a precalibrated bicapillary pyknometer. The complexes 4-Nitrobenzylidene with 2-aminothiazole in Cu(II) were studied. The solutions of varying concentration of metal complexes were prepared on molarity basis. The ultrasonic velocity of the solution was measured by using M-84 (Mittal Enterprises, New Delhi) instrument of a frequency of 2MHz with an accuracy of 0.03% at constant temperate.

THEORETICAL:

Apparent molar volume has been calculated from the density data using the expression:

$$\phi_v = \frac{M_2}{d_1} - \frac{1000}{C}\left[\frac{d_0-d_1}{d_1}\right] \quad (1)$$

Where C is the molarity, d_0 and d_1 are the densities of solution and solvent respectively, and M_2 is the molecular weight of the solute.

Molar sound velocity, molar compressibility, acoustic impedance and intermolecular free length have been computed using the following relations.

$$R = V.U.^{1/3} \quad 2$$

$$\beta_S = \frac{1}{U^2.d_0} \quad 3$$

$$W = V.\ \beta_S^{-1/7} \quad 4$$

$$L_f = K.\ \beta_S \quad 5$$

$$Z = U.d_0 \quad 6$$

where R, V, U, β_S, β_S^0, K, W and L_f are the molar sound velocity, molar volume, ultrasonic velocity, adiabatic compressibility of solution, adiabatic compressibility of solvent, Jacobson constant, molar compressibility and intermolecular free length respectively.

Synthesis of 4-Nitrobenzylidene with 2-aminothiazole (NBAT)

The ligand-NBAT has been synthesized by adding the methanolic solution of 4-Nitrobenzaldehyde (0.01 mole) to the methanolic solution of 2-aminothiazole (0.01 mole) in 1:1 ratio. The reaction mixture is refluxed on a water bath for about 5-6 hours. The product is brown in colour. It has been recrystallized with methanol and purity is checked by TLC using silica gel.

Preparation of the metal complexes:

Metal complexes have been synthesized by the addition of the methanolic solution of the appropriate metal salt $MCl_2 .XH_2O$ (0.01 mole) to a methanolic solution of Schiff base 4-Nitrobenzylidene-2-aminothiazole (0.01 mole) in 1:2 ratio and the mixture is refluxed on water bath for about 5 hours. The refluxate was kept overnight. The resulting coloured precipitated complex is washed with ethanol followed by petroleum ether and dried under reduced pressure over anhydrous $CaCl_2$ in a dessicator. The complexes are stable and soluble in methanol, ethanol and acetone.

RESULTS AND DISCUSSION:

The analytical and physical data of the metal chelates are presented in Table-1. Elemental analysis of the complexes indicates the stoichiometry to be 1:2 metals: ligand (Schiff base). The molar conductance in methanol (10^{-3} m), of the complexes are 41.9 Ohm^{-1} cm^2 mol^{-1} respectively for Cu(II) complexes. This indicates the non-electrolytic nature.In the IR spectrum, the $\nu_{C=N}$ band of the free ligand at 1611 cm^{-1} has shifted to lower wave numbers (1580$\pm$10 cm^{-1}) in the complexes, suggesting the metal coordination with the azomethine nitrogen. The ligand exhibited a sharp band at 825 cm^{-1} due to C-S-C group. Its position in the spectra of complexes has been observed at 806$\pm$5 cm^{-1} indicating the involvement of ring sulphur atom in coordination. An intense band at 1574 cm^{-1} in Schiff base ligand due to C=N cyclic of thiazole ring, does not alter in the spectra of complexes. This rule out the participation of (C=N cyclic) group in coordination. IR data suggest that metal coordinates through N & S donor atoms of Schiff base. This results a four membered metal chelated ring structure. In literature based on the experimental data, there are several references where such four membered ring structures have been observed and proposed. However, these may not be considered much more stable. The ligand (Schiff base) is bidentate. A band around 3405$\pm$6 cm^{-1} in the spectra of complexes is assignable to stretching of water. A new band at 481$\pm$7 cm^{-1} has been assigned to νM-N vibration in the complexes. Although ligands having oxygen and nitrogen as the donor atoms are by far the most studied, the interest in sulphur donor chelating agents has grown over the years and the number of chemical studies in the area has increased considerably. The interest in complexes of these ligand systems now covers a full gamut of areas ranging from general considerations to metal-sulphur bonding and electron delocalization in transition metal complexes and potential biological activity and their practical applications. 2-Aminothiazole comprises a well known group of nitrogen and sulphur donors which have been extensively used for complex formation in the recent past.The Cu(II)-complex a single broad band appears at 13322 cm^{-1} corresponding to transition ^2Eg-^2T_2g. The various ligand field parameters viz., 10Dq, λ and LFSE have been calculated and values are: 13319 cm^{-1}, (-)384 and 95.47 kJ mol^{-1} respectively. Ligand field parameters and magnetic moment (1.93 B.M.) data substantiate for the octahedral geometry of this complex.Values of ultrasonic velocity are comparatively higher for the cupper metal complexes of 4-nitrobenzylidene-2-aminothiazole (NBAT) ligand. The values of ultrasonic velocity of various Schiff base (ligand) systems at three different concentrations. Ultrasonic velocity and density decrease on lowering the concentration. With increase the concentration of solution, the ultrasonic velocity (U), acoustic impedance (Z) and molar sound velocity (R) increase while compressibility and intermolecular free length decrease. Eyring and Kincaid's model for sound propagation suggests that the intermolecular free length (**lf**) is a predominant factor in determining the variation of ultrasonic velocity in solution. Extent of compressibility gives the information of ion-solvent molecular attraction and the resultant compactness. The adiabatic compressibility values are comparatively lower for NBAT+Cu ligand-metal complexes. In this way NBAT+Cu metal complexes are in more compressed solvation behaviour, stereo-arrangement of ligand around the metal ion, non-spherical 3d-ions radii and change in co-ordination number. In other words, the bulky chelate rings of the ligands make the metal complexes hard to compress. A tight or dense solvation layer (primary and secondary) around an ion leads to decrease in βs. The lowering of $\boldsymbol{\beta}$s varies with the effective size of entering ligands in the metal complexes as the metal ion remains the same. Higher values of ultrasonic velocity and acoustic impedance, and lower value of adiabatic compressibility for ligand-complexes may be due to ligand's structural effect. This makes the metal complex Cu-NBAT slightly more compact. Cu-NBAT ligand-metal complex is more stable. This may be due to electron withdrawing tendency of NO_2 group than Cl group.

CONCLUSIONS:

The coordination chemistry with its growing list of applications, has paved the way to the preparation of new compounds which may possess some definite predetermined properties and thus show promising prospects in the realm of medicine and molecular biology. The application of Schiff bases and their metal chelates in the field of industry, agriculture and medicine are well known. Ultrasonic technique is a powerful and effective tool for investigation of properties of polymer solutions and behavior of polymer chains under the influence of ultrasonic field. A background knowledge of phenomenon of chelation and interaction in solutions helps in understanding the stabilization, of drug and its mechanistic path for targeted drug delivery and drug toxicity. In the present investigation, density and ultrasonic velocity have been measured in non-aqueous solution of synthesized 3d metal complexes viz NBAT with Cu(II) at room temperature. The results were used to test the applicability of simple equation for the ultrasonic velocity and density of electrolytic solutions, and their acoustical parameters have been used to study the interaction in solution. The results show that equation can yield good prediction for the densities and ultrasonic velocity of electrolytic solutions.

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TABLE - 1

ANALYTICAL AND PHYSICAL DATA OF LIGAND AND METAL COMPLEXES

Comp. No.	Compounds/ Molecular Formulae		Elemental Analysis; Found/(Calc.)%					
	Mol.Wt [Colour]	M.Pt. / (dec)^{0}C	C	H	N	M	μ_{eff}	Ω_M
1	($C_{10}H_7N_3SO_2$) 233.0 [Blackish green]	92	51.40 (51.60)	2.84 (3.00)	18.30 (18.02)	-	-	-
2	[$Cu(C_{10}H_7N_3SO_2)_2Cl_2$] $2H_2O$ 636.54 [Green]	158	37.50 (37.68)	2.37 (2.83)	13.80 (13.27)	9.38 (9.84)	1.94	41.9

TABLE – 2

ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF THE SCHIFF BASE WITH METAL COMPLEXES

Comp. No.	Metal Complex	Transition	Band Cm^{-1}	Parameters 10 Dq,B, β, ν_2/ν_1,λ, LFSE
1	Cu(II)–NBAT Complex	^2Eg–^2T_2g	13322	13319, (-)384, 95.47

TABLE-4 VALUES OF DENSITY, ULTRASONIC VELOCITY, APPREANT MOLAR VOLUME, ACOUSTIC IMPEDENCE, ADIABATIC COMPRESSIBLITY, RAO'S CONSTANT, and WADA'S CONSTANT AND INTERMOLECULAR FREE LENGTH FOR 4-NITROBENZYLIDENE-2-AMINOTHIAZOLE AT 301K.

Conc. mol/litre	do x 10^{-3} kg m^{-3}	U mS^{-1}	$\phi v x 10^5$ $m^3 mol^{-1}$	Z x 10^{-3} $kgm^{-2}S^{-1}$	βs x 10^{11} m^2N^{-1}	$Rx10^6$	$Wx10^6$	L_f A^0
NBAT (Schiff base)								
0.01	0.8139	1142	355.80	930.91	93.90	2994.78	5577.52	0.8639
0.005	0.8135	1140	674.31	928.09	94.40	2993.37	5575.08	0.8688
0.0025	0.8133	1138	1303.71	924.51	95.12	2990.85	5571.28	0.8754
NBAT+Cu (II) Complex								
0.01	0.8154	1187	429.77	968.83	86.88	8266.84	15373.48	0.7991
0.005	0.8151	1186	771.14	966.01	87.33	8262.92	15367.31	0.8037
0.0025	0.8147	1181	1436.15	961.37	88.14	8256.32	15356.73	0.8108