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Synthesis, Characterization and acoustical parameters of some synthesized 3d metal complexes with 2-amino 4-chloro phenol

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Abstract

Ultrasonic refers to study of sound waves which are higher frequency than the human audible range. It is widely used in many application viz. medical underwater food and oil technology. Some metal complexes of Co (II), Ni(II) and Cu(II) derived from 2- hydroxyl acetophenone with 2-amino-4-chlorophenol (HACP) have been synthesized and their ultrasonic velocity and density have been measured in non- aqueous solution methanol at 301.15K. 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 . The results have been discussed in the light of solvent interaction and structure effecting metal complexes.

Keywords: Ultrasonic velocity, Density, Acoustical parameters and Metal complexes.

Introduction

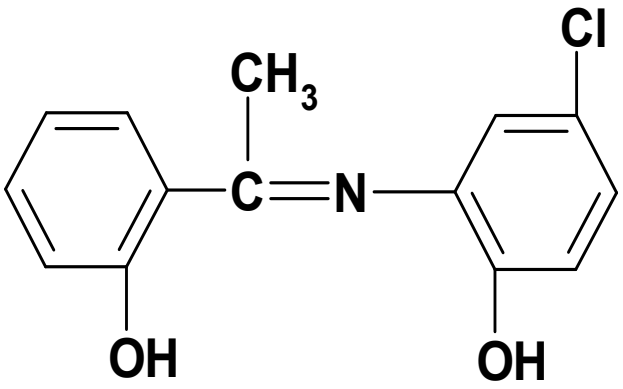
Schiff bases are used as fine chemicals, medical substrates and ligands for metal complexes. They find their industrial importance as antifungal and biological application. They are known to be important due to their various applications such as preparation of dyes, liquid crystals and powerful corrosion inhibitor[1-6]. Ultrasonic speeds and related acoustical properties of organic liquids and non aqueous electrolytic solutions are extensively useful especially in process industry[7-13].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. Velocity and absorption of ultrasonic waves play an important role in the interaction and other thermodynamic studies of liquid and liquid mixtures [7-13.] The knowledge of experimental values of these parameters serves as a versatile tool for investigating physic chemical behavior and structure of liquid [14-17]

However, due to the complexities of biological compounds, direct experimental studies are not feasible and hence several parameters viz. apparent molar volume, adiabatic compressibility, Rao's constant, (molar sound velocity), acoustic impedance, free volume, internal pressure and cohesive forces studied through density and ultrasonic velocity measurement, indirectly may be used to investigate the chemical behavior/molecular interaction in such systems. The successful application of acoustic methods to physico-chemical investigation of solution becomes possible after the development of adequate theoretical approaches and methods for precise ultrasound velocity measurements in small volumes of liquids. In the present studies, the ultrasonic velocity and density of solutions of twelve new Schiff bases and their metal complexes of Co(II),Ni(II) and 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 2-hydroxy Acetophenone with 2-amino-4-chlorophenol in Co(II), Ni(II) and 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 temperature.

STRUCTURE



HACP (Schiff base)

THEORY

The ultrasonic velocity and density data described many parameters for understanding solvent interaction and structural effect. The parameters have been computed using the following relation.

The apparent molar volume ($Ø_V$) can be calculated by using following relation

$$\emptyset_V = \frac{M_2}{d_1} - \frac{d_2 - d_0}{C \times d_1} \quad \text{..... (1)}$$

Molar sound velocity or (Rao' constant) (R) is evaluated using the relation

$$R = V \times U^{\frac{1}{3}} \quad \text{..... (2)}$$

Adiabatic compressibility (β_s) is evaluated using the formula

$$\beta_S = \frac{1}{U^2 \times d_0} \quad \text{..... (3)}$$

Acoustic impedance (Z) is calculated by the relation

$$Z = U \times d_0 \quad \text{..... (4)}$$

Intermolecular free length (L_f) is obtained using the relation

$$L_f = K \times \beta_S^{\frac{1}{2}} \quad \text{..... (5)}$$

RESULTS AND DISCUSSION:

The values of above parameters for solutions of complexes, ligands (Schiff base) and metal chlorides (Methanol as solvent) have been found to vary up to a considerable extent. This reflects molecular interactions between solute and solvent. This further indicates the interactions between metal ion and ligand using methanol as medium (solvent).On complexation the value and order of ultrasonic velocity changes. This reflects about the impact of nature and extent of interaction of both ligand and metal ions on the solute-solvent interaction. Ultrasonic velocity and density decrease on lowering the concentration. With increase in concentration of solution, the ultrasonic velocity (U), acoustic impedance (Z) and molar sound velocity (R) increase, while compressibility (βs), and inter molecular free length (L_f) decreases. The increase in ultrasonic velocity also indicates about the association among the molecules and greater solute-solvent interaction. Molar sound velocity (Rao's constant)[1] increases with increase in concentration of solute. This parameter also indicates solute-solvent interactions. Eyring and Kincaid's model for sound propagation suggests that inter molecular free length (L_f) is a predominant factor in determining the

variation of ultrasonic velocity in solution. Increase or decrease in ultrasonic velocity depends on free length among the molecules. Extent of compressibility gives the information of ion-solvent molecular attraction and the resultant compactness. It is a measure of an ion capacity to attract solvent molecules. The increase and decrease of βs values may be ascribed to two effects. (1) The decrease in compressibility caused by the introduction of in-compressible molecules of ions and (2) the addition of solute affects the structure of solvent which results in an increase in compressibility. The adiabatic compressibility values are comparatively lower in ligand-metal complexes (HACP-Cu), in comparison to other metal chelates. The (HACP-Cu(II)) metal complexes are in more compressed state than others.The solvation number is useful in understanding the structure making and structure breaking tendency of solute in a solvent. On comparing the values of solvation number of metal ion, ligand and corresponding metal complex, it has been found that the metal complex is more solvated than the ligand and their metal ions. The value of solvation number for the ligand has been found more than metal ions. This may tentatively be accounted to the placement of solvent molecules in the interstitial spaces, occurring in the metal chelate. Solvation number decreases in the order Cu(II)-HACP> Co(II)-HACP>Ni(II)-HACP.On comparing the values of solvation number of different metal ions with same ligand, it has been found that the ligand HACP, show similar behavior i.e. Cu(II)>Ni(II)>Co(II) .This different behaviour of ligand may be attributed to effect of LFSE, solvation energies and constitutional and structural changes in symmetry. As observed the solvation number decreases with increase in concentration of solution, this may be due to increased solute molecules and also to electrostriction effect.Higher values of ultrasonic velocity and acoustic impedance and lower value of adiabetic compressibility for ligand-complexes may be due to ligand's structural effect. In present studies Cu(II)-HACP complex has been found maximum .

CONCLUSIONS:

In the present investigation, density and ultrasonic velocity have been measured in non-aqueous solution of synthesized 3d metal complexes viz HACP with Co(II), Ni(II), 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. From the behavior of acoustical parameters, it can be concluded that solute-solvent interaction gets weakened with lowering concentration of room teperature.

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Table : Value of density (d_o), ultrasonic velocity(U), apparent molar volume (ϕ_v), acoustic impedance (Z), adiabatic compressibility (β_s), Rao's Constant (R) and intermolecular free length (L_f) for ligands HACP metal ($Co^{II}/Ni^{II}/Cu^{II}$) chlorides and their metal complexes at 301.15K.

Molar Conc. dm^{-3}	$d_o x10^{-3}$ (kgm^{-3})	U (ms^{-1})	$\phi_v X10^5$ (m^3mol^{-1})	$Zx10^{-3}$ ($kgm^{-2}s^{-1}$)	$\beta_s X10^{11}$ (m^2N^{-1})	($Rx10^6$)	Sn
HACP (Ligand) ($C_{18}H_{14}ClNO$)							
0.01	0.8148	1142	485	936.17	80.50	2555.0	163.59
0.005	0.8142	1140	590	929.50	80.52	2554.13	321.69
0.0025	0.8140	1139	706	927.30	80.58	2551.08	593.71
Co(II) – HACP ($C_{36}H_{32}Cl_2CoN_2O_5$)							
0.01	0.8157	1174	554	957.56	81.66	5977.28	169.73
0.005	0.8155	1172	834	954.53	81.72	5972.50	342.60
0.0025	0.8153	1170	1012	953.48	81.78	59.68.32	634.86
Ni(II) – HACP ($C_{36}H_{28}Cl_2N_2NiO_3$)							
0.01	0.8160	1177	533	962.24	81.64	5982.99	175.36
0.005	0.8159	1175	780	960.38	81.67	5980.12	340.37
0.0025	0.8156	1173	1016	958.64	81.73	5978.14	656.67
Cu(II) - HACP ($C_{36}H_{28}Cl_2CuN_2O_5$)							
0.01	0.8160	1182	524	963.11	81.61	6027.80	177.47
0.005	0.8159	1175	829	955.35	81.63	6014.67	348.46
0.0025	0.8156	1171	971	951.01	81.68	6007.82	643.73
$CoCl_2 .6H_2O$							

0.01	290.279	0.01186	39.525	11.473	0.8751
0.005	290.421	0.01185	39.575	11.493	0.8849
0.0025	290.599	0.01184	39.602	11.513	0.8932
$NiCl_2 .6H_2O$					
0.01	290.350	0.01186	39.545	11.516	0.8722
0.005	290.456	0.01185	39.625	11.720	0.8789
0.0025	290.456	0.001185	39.624	11.863	0.8888
$CuCl_2 .2H_2O$					
0.01	208.156	0.02307	10.448	21.790	0.8620
0.005	208.730	0.02295	10.561	21.805	0.8703
0.0025	208.998	0.2289	10.572	21.903	0.8810