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Study of Intermolecular Interaction of some synthesized 3d metal complexes in solution, by ultrasonic velocity measurement

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ABSTRACT

Ultrasonic velocity and density have been measured in non- aqueous solution of the synthesized ligands viz. 5-bromosalicylidene-2-amino-4-methylbenzothiazole (BABT), 5-bromosalicylidene-2-amino-4-chlorophenol (BACP) and their metal complexes with Co(II), Ni(II) and Cu(II) in methanol at 301.15K. The value of apparent molar volume, acoustic impedance, adiabatic compressibility, inter molecular free length and molar sound velocity (Rao's constant) 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.

Key Words: 5-bromosalicylidehyde, Metal complexes, Ultrasonic velocity, Acoustical properties

INTRODUCTION

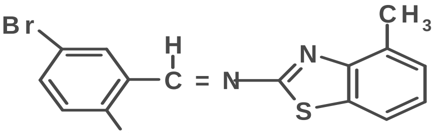
Ultrasonic is an interesting field of study which makes an effective contribution to many areas of human endeavor. In recent years, many attempts have been made in the field of physical acoustics and ultrasound on solids, liquids and gases. Drug macro molecular interactions are important phenomena in physiology such as blood membranes and intra/extra cellular fluids [1-5]. Hydrophilic and hydrophobic groups are present in almost every biological system. The cells of living organisms are composed of many kinds of complex molecules such as lipids, proteins, carbohydrates and nucleic acids. Studies of monomer units of these biopolymers may through light on complexity of these biomolecules of the metal involved with living organism, this make us to understand their relationship [6-8].

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, studied through density and ultrasonic velocity measurement, indirectly may be used to investigate the chemical behaviour/molecular interaction in such systems [9-12]. 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 [13-18]. In the present studies, the ultrasonic velocity and density in solutions of 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.

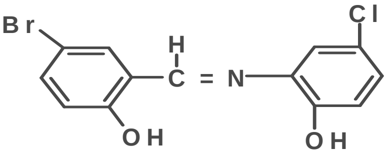
EXPERIMENTAL SECTION

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 0.6×10^{-6} S cm^{-1}. The density measurements were performed with a precalibrated bicapillary pyknometer. The complexes of 5-bromosalicylidene-2-amino-4-methylbenzothiazole (BABT), 5-bromosalicylidene-2-amino-4-chlorophenol (BACP) with 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.



BABT (Schiff base)



BACP (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 ($\O_V$) can be calculated by using following relation[12]

$$\O_V = \frac{M_2}{d_1} - \frac{d_2 - d_0}{C \times d_1} \qquad \text{……………. (1)}$$

Molar sound velocity or (Rao' constant) (R) is evaluated using the relation[13]

$$R = V \times U^{1/3} \qquad \text{……………. (2)}$$

Adiabatic compressibility (β_s) is evaluated using the formula

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

Acoustic impedance (Z) is calculated by the relation[13]

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

Intermolecular free length (L_f) is obtained using the relation

$$L_f = K \times \beta_S^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots (5)$$

Free volume V_f is the effective volume accessible to the centre of a molecule in a liquid is represented as;

$$V_f = v_m^{-b} \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

Internal pressure is represented by

$$Л_i = 2RT / (V_f V^2{}_m)^{1/3} \qquad \ldots\ldots\ldots\ldots\ldots (7)$$

RESULTS AND DISCUSSION

Complex compounds have characteristics that are favorable for the study of solute-solvent interactions, by a suitable selection of ligands and/or metal ions, the effect of factors such as the size, structures and electric charge and its distribution can be studied systematically. The result may be used to understand the nature of the ion - solvent/solute solvent interactions. These metal complexes may act as structure promoters/structure maker or breaker. The density, ultrasonic velocity, acoustic impedance, molar sound velocity (Rao's Constant), intermolecular free length and adiabatic compressibility, free volume, internal pressure and cohesive forces of metal ion and metal complexes have been presented in Table 1 and 2.

The values of parameters for solution of metal complexes, ligands (Schiff base) and metal chloride reflect the interaction between metal ion and ligand in methanol as solvent medium. The value of ultrasonic velocity of ligands at three different concentrations are in order BABT>BACP. In general, on comparing the metal ion system this order comes to be Cu(II)>Ni(II)>Co(II). Almost for all the three concentrations, ultrasonic velocity and density decrease on lowering the concentration.

The increase in the value of density has been attributed to increase in hydrophilic interaction. It can also be seen that the sound velocity increases or decreases depending on the structural properties of solute. Therefore the solute that increases the ultrasonic velocity is the structure maker and those decreases the sound velocity are structure breakers.

The values of apparent molar volume for Ni(II) -complexes in all the cases decrease in the order: Ni(II)- BABT>BACP. In the Co(II) complex, this order comes to be BABT>BACP, while in the copper(II) complex values of apparent molar volume are in order Cu(II) - BABT>BACP.

Variation in apparent molar volume may be accounted to the size and geometrical arrangement of metal complexes in solution. Apparent molar volume decreases with decrease in concentration of solute indicating the decrease in stacking interaction between solute and solvent molecules. Fig- show a plot of ultrasonic velocity against the concentration of solution while studying the values of ultrasonic velocity of ligands, it comes comparatively higher for the metal, [M = Co(II)/Ni(II)/Cu(II)] complexes of ligand (BABT). The values of ultrasonic velocity of various Schiff base (ligand) systems at three different concentrations follow the order: BABT>BACP. In general, on comparing the metal ion systems, this order comes to be Cu(II)>Ni(II)>Co(II), almost for all the three concentrations.

Table : 1 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 BACP, BABT, metal (Co^{II}/Ni^{II}/Cu^{II}) chlorides and their metal complexes at 301.15K.

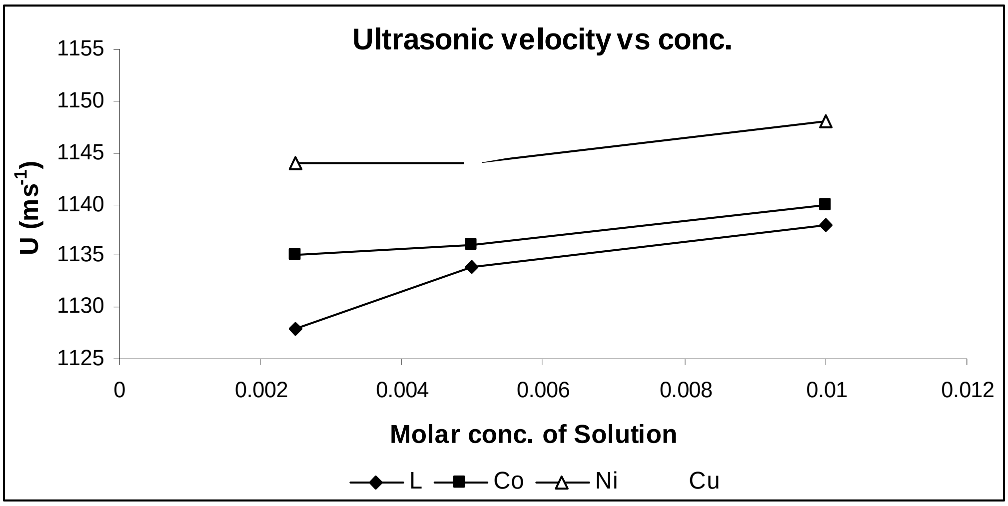
Molar Conc. dm^{-3}	$d_o x10^{-3}$ (kgm^{-3})	U (ms^{-1})	$\phi_v X10^5$ (m^3mol^{-1})	$Zx10^{-3}$ ($kgm^{-2}s^{-1}$)	$\beta_s X10^{11}$ (m^2N^{-1})	($Rx10^6$)	Sn
BACP (Ligand) ($C_{13}H_9BrClNO_2$)							
0.01	0.8132	1138	310.06	925.42	82.00	3237.12	158.43
0.005	0.8130	1134	612.06	923.07	82.20	63826.10	302.41
0.0025	0.8120	1128	720.06	915.93	82.40	74950.57	498.51
Co(II) – BACP ($C_{13}H_{13}BrClCoNO_5$)							
0.01	0.8145	1140	340.53	928.53	81.60	3557.32	160.21
0.005	0.8142	1136	462.43	924.93	81.50	4825.09	306.21
0.0025	0.8130	1135	567.46	922.75	81.50	6919.25	503.11
Ni(II) – BACP ($C_{13}H_{13}BrClNNiO_5$)							
0.01	0.8149	1148	345.54	933.32	81.60	3618.08	161.12
0.005	0.8144	1144	380.67	931.216	81.62	3981.29	307.32
0.0025	0.8140	1144	460.34	931.21	81.90	4814.53	505.21
Cu(II) – BACP ($C_{13}H_9BrClCuNO_3$)							
0.01	0.8160	1150	390.60	938.40	81.90	4092.27	162.63
0.005	0.8150	1144	422.64	932.36	81.98	4420.24	309.23
0.0025	0.8148	1150	520.66	928.87	82.10	5439.04	512.12
BABT (Ligand) ($C_{15}H_{11}BrOS$)							
0.01	0.8146	1142	320.58	930.57	81.40	3350.87	161.41
0.005	0.8140	1140	478.96	927.96	81.40	5003.42	308.31
0.0025	0.8130	1131	880.08	919.50	81.40	9169.44	428.21
Co (II) – BABT ($C_{30}H_{24}Br_2CoN_4O_4S_2$)							
0.01	0.8153	1170	380.06	953.90	81.20	4004.79	162.62
0.005	0.8150	1168	492.08	951.92	81.30	5182.22	312.21
0.0025	0.8148	1158	1010.76	943.53	81.30	10614.12	430.31
Ni(II) – BABT ($C_{30}H_{24}Br_2N_4NiO_4S_2$)							
0.01	0.8162	1182	396..86	964.74	81.00	4196.07	164.36
0.005	0.8160	1180	492.67	962.88	81.10	5206.15	315.63
0.0025	0.8149	1165	1020.96	936.32	81.30	10742.79	432.43
Cu(II) – BABT ($C_{30}H_{24}Br_2CuN_4O_4S_2$)							
0.01	0.8172	1190	398.67	972.46	80.80	4224.70	165.32
0.005	0.8167	1184	488.66	966.97	81.00	5169.60	318.11
0.0025	0.8153	1170	990.86	953.90	81.10	10440.97	436.16
$CoCl_2$- $6H_2O$							
0.01	0.8189	1135	225.67	929.45	82.60	2553.99	155.21
0.005	0.8185	1130	280.68	924.90	82.40	2923.50	304.21
0.0025	0.8180	1125	640.46	920.25	82.00	6661.05	606.56
$NiCl_2$ - $6H_2O$							
0.01	0.8187	1138	230.68	929.45	82.20	2408.37	154.22
0.005	0.8184	1135	294.74	924.90	82.00	3074.47	298.43
0.0025	0.8184	1132	880.69	920.25	82.00	9178.50	601.23
$CuCl_2$ $2H_2O$							
0.01	0.8190	1140	235.67	933.66	82.10	2461.91	154.24
0.005	0.8178	1136	340.46	933.02	81.90	3552.43	303.21
0.0025	0.8168	1134	990.45	929.25	81.80	10328.49	610.36

On complexation the value and order of ultrasonic velocity is 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 depend on free length among the molecules.

Table–2 Value of molar volume (V_m), free volume (V_f) internal pressure (π_i), cohesive forces (H) and intermolecular free length (L_f) for ligands BACP, BABT, metal ($Co^{II}/Ni^{II}/Cu^{II}$) chlorides and their metal complexes at 301.15K.

Molar Conc. dm^{-3}	$V_m X10^3$	$V_f X10^7$	$\pi_i X10^{-8}$	$HX10^{-3}$	$L_f \times 10^{-10}$
BACP (Ligand) ($C_{13}H_9BrClNO_2$)					
0.01	400.885	0.6222	14.369	57.603	0.8442
0.005	400.984	0.6219	14.520	58.222	0.8468
0.0025	401.477	0.6204	14.708	59.049	0.8492
Co(II) - BACP ($C_{13}H_{13}BrClCoNO_5$)					
0.01	931.860	1.151	41.972	39.112	0.8363
0.005	932.203	1.150	41.988	39.150	0.8378
0.0025	933.579	1.147	42.105	39.350	0.8378
Ni(II) - BACP ($C_{13}H_{13}BrClNNiO_5$)					
0.01	931.402	1.152	41.894	39.020	0.8228
0.005	932.774	1.150	41.898	39.039	0.8263
0.0025	932.432	1.147	41.913	39.081	0.8291
Cu(II) – BACP ($C_{13}H_9BrClCuNO_3$)					
0.01	936.274	1.140	42.779	40.074	0.8430
0.005	937.432	1.137	42.825	40.145	0.8451
0.0025	937.653	1.137	42.822	40.152	0.8463
BABT (Ligand) ($C_{15}H_{11}BrOS$)					
0.01	425.975	0.5511	18.177	77.429	0.8607
0.005	426.280	0.5503	18.370	78.307	0.8607
0.0025	426.810	0.5508	18.379	78.443	0.8825
Co(II) - BABT ($C_{30}H_{24}Br_2CoN_4O_4S_2$)					
0.01	917.453	1.188	39.417	36.163	0.8335
0.005	917.791	1.187	39.479	36.233	0.8352
0.0025	918.016	1.186	39.483	36.246	0.8385
Ni(II) - BABT ($C_{30}H_{24}Br_2N_4NiO_4S_2$)					
0.01	916.442	1.190	39.264	35.983	0.8310
0.005	916.666	1.191	39.283	36.009	0.8362
0.0025	917.904	1.186	39.522	36.277	0.8373
Cu(II) - BABT ($C_{30}H_{24}Br_2CuN_4O_4S_2$)					
0.01	921.439	1.177	40.132	36.979	0.8190
0.005	922.003	1.176	40.188	37.053	0.8310
0.0025	923.586	1.172	40.420	37.331	0.8362
$CoCl_2 .6H_2O$					
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

Fig: (1-2) M(II) - BACP Complexes



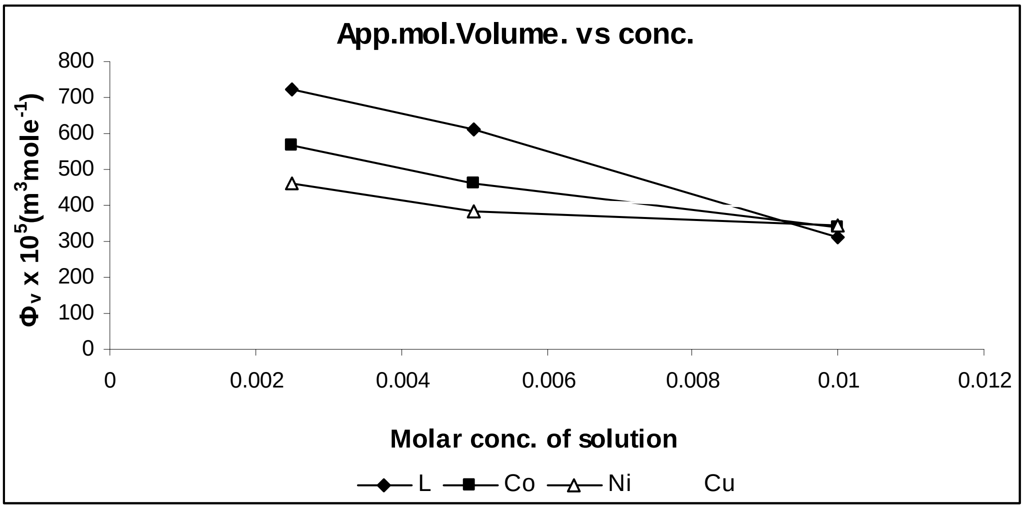
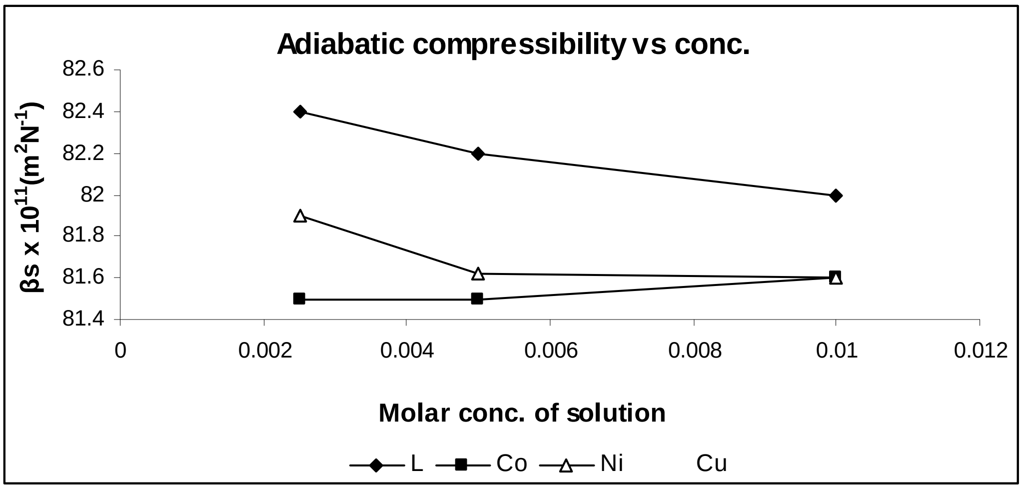
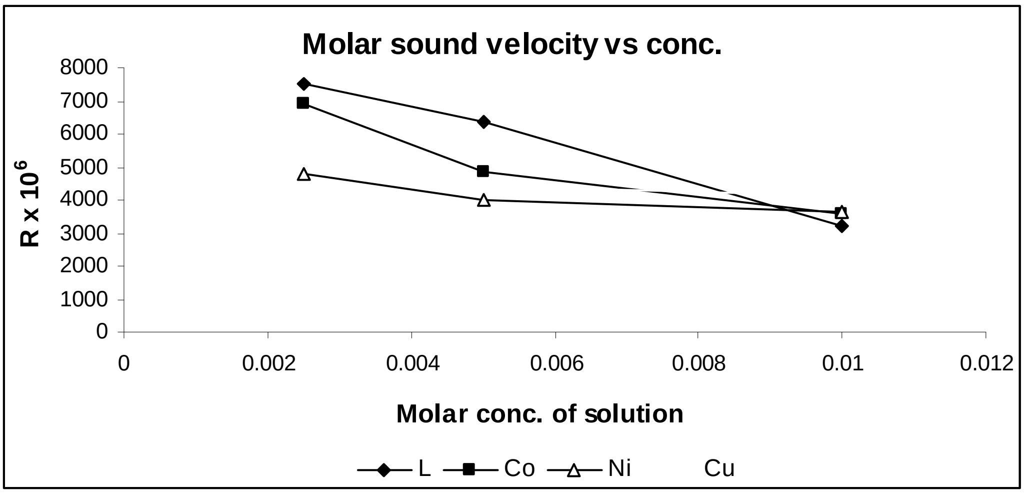


Fig: (3-5) M(II) - BACP Complexes





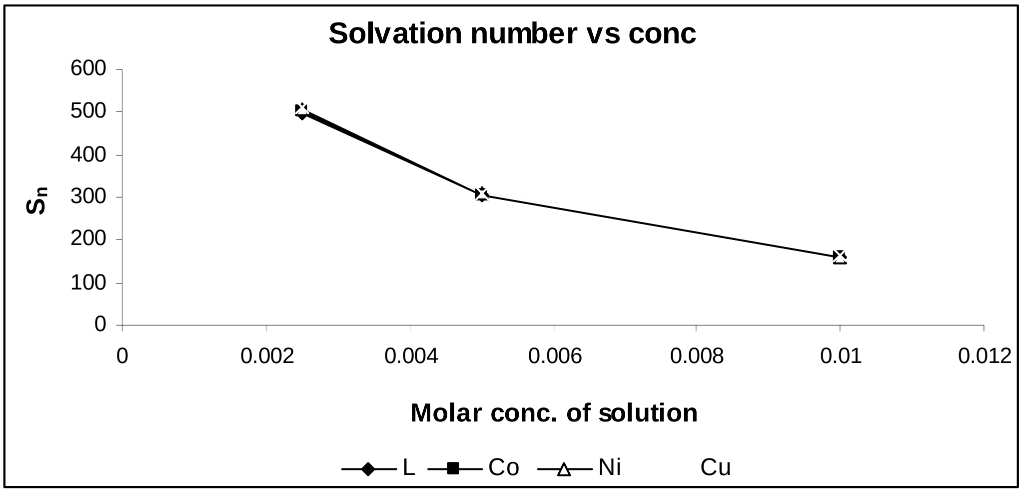
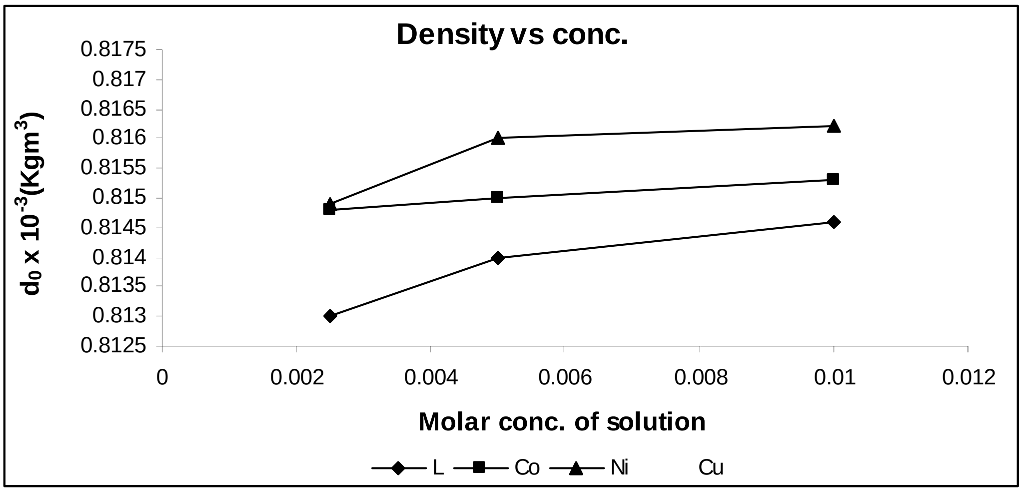
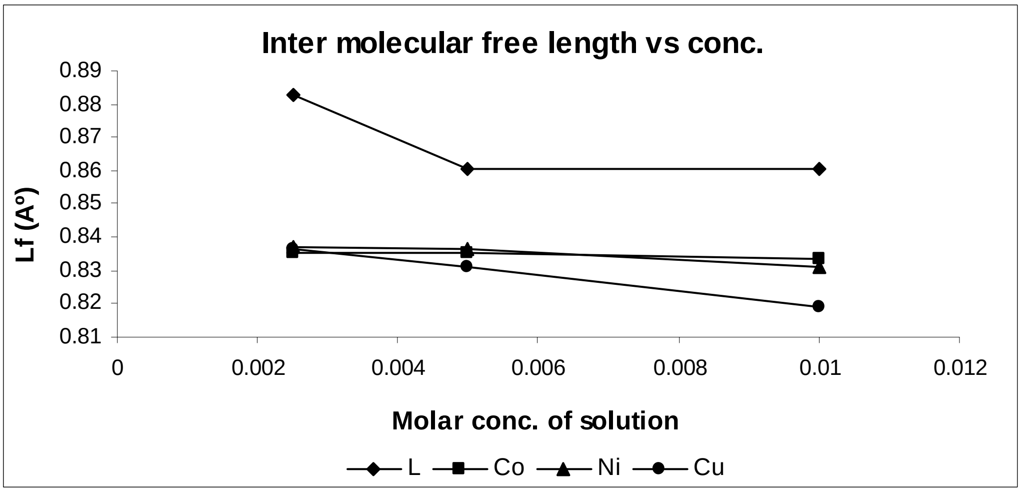
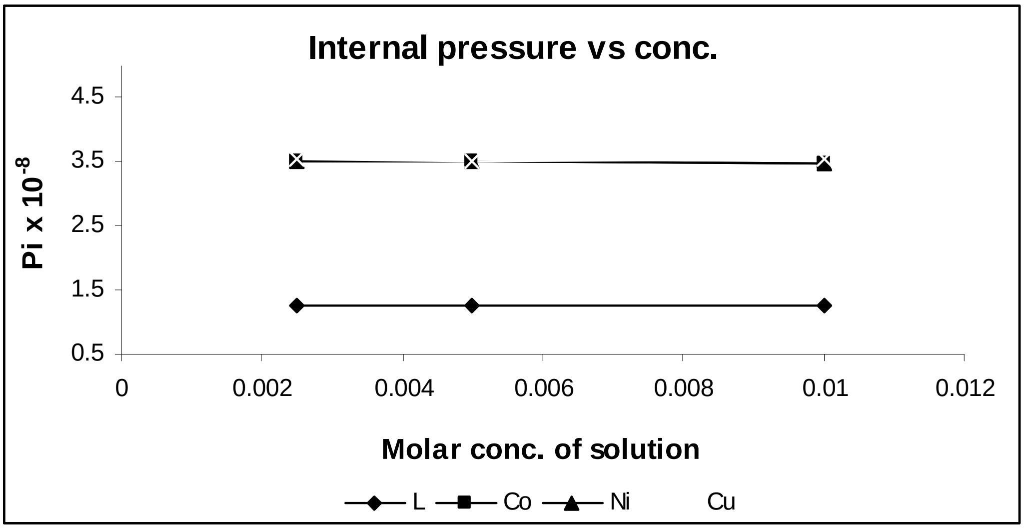


Fig: (6-8) M(II) - BABT Complexes







The adiabatic compressibility values are comparatively lower in ligand- metal complexes (BABT-Cu), in comparison to other metal chelates. The (BABT-Cu) metal complexes are in more compressed state than others. On comparing the adiabatic compressibility of metal complexes, the order comes to be Co(II)-BACP>Cu(II)-BACP>Ni(II)-BACP> Co(II)-BABT>Ni(II)-BABT>Cu(II)-BABT.

The difference in βs may be accounted to the nature of ligand (relatively weak or strong field), solvation behavior, 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 ring of the ligand makes the metal complexes hard to compress. The change in trend may be attributed to the activation energy of solvation, influence of size and distorted geometry of metal ion-polyhedron. The decrease in βs values with increasing concentration of solute might be due to aggregation of solvent molecules around the solute molecules. The above order of βs follows that βs depend upon the solvation layer formed around the metal complexes.

Further Mishra *et al*. used this model and observed that the overlap of co-sphere of two ionic species produce an increase in volume whereas overlap of hydrophilic and hydrophobic group results, decrease in volume. Higher value for ultrasonic velocity and acoustic impedance and lower value of adiabatic compressibility for ligand metal complex may be due to ligand structural effect.

The computed other parameters like free volume and internal pressure are given in Table 2. The free volume is found to decrease with lowering in concentration. The internal pressure is found to increase with lowering in concentration. An inverse trend as expected has been seen in free volume changes. Free volume decreases in order Ni(II)-BACP>Co(II)-BACP>Cu(II)-BACP>Ni(II)-BABT>Co(II)-BABT>Cu(II)-BABT. The internal pressure is a sensitive parameter of solute and solvent interaction, and gives both the attractive and repulsive molecular interactions. The internal pressure of the solutions increases with lowering in concentration. Internal pressure provides a very important remark for the study of structure and nature of molecular interactions in liquids. The results are reported in table A comparative account of values of internal pressure among various complexes is as follows: Co(II)-BACP>Cu(II)-BACP>Co(II)-BABT>Ni(II)-BABT>Cu(II)-BABT.

On comparing the value of internal pressure of different metal ions with same ligand, it has been found that the ligand BACP and BABT show similar behaviour i.e. Co(II)>Ni(II)>Cu(II). Further the decrease in free volume and increase in internal pressure with rise in concentration of metal complexes in all the systems clearly show the inceasing magnitude of molecular interactions.

In the solid phase, the ligands act as monodentate/bidentate chelating agents and have C=N linkage. The ligands coordinate with the metal through the N and/or O donor. Here the complexes exhibit 4 or 6 coordination number and metal to ligand stoichiometry in 1:2. Such biomimetic and bio-synergistic studies of metal chelates in solution may be useful in understanding the interaction of metal chelated bimolecule in the body system. The studies on these lines may govern and guide for the subject and bio-molecular dynamics in animal physiology vis-à-vis inorganic medicinal chemistry.

CONCLUSION

In the present investigation, density and ultrasonic velocity have been measured in non-aqueous solution of synthesized 3d metal complexes viz BABT- Co(II), Ni(II), Cu(II) and BACP - Co(II), Ni(II), Cu(II) at 301.15 K. 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 301.15 K.

Such biomimetic and bio-synergistic studies of metal chelates in solution may be useful in understanding the interaction of metal chelated biomolecules in the body system. The studies on these lines may govern and guide for the subjects and problems, viz pharmacokinetics and bio-molecular dynamics in animal physiology vis-à-vis inorganic medicinal chemistry.

REFERENCES

[1] P Aasthess, and J P Shukla, *Ultrasonics*, **2003.** 10, 241.
[2] T J Mason, *The use of ultrasound in chemistry and sono chemistry*, **1989.**
[3] W Kauzmann *Adv. Protein chem*. **1959,** 14, 1.

[4] J D Pandey, P Chandra, D Chand and AK Nain *Phys. Chem. Liq.,* **2009,** 47, 195.
[5] J D Pandey, K Mishra, RD Rai, and A Shukla, *Thermochim. Acta*, **1987,** 117, 245.
[6] AP Mishra and H Purwar *J. Pure. Appl. Ultrasonic,* **2006,** 28,138.
[7] AP Mishra and SK Gautam *Indian Chem. Soc.,* **2002,** 79,725.
[8] AP Mishra and SK Gautam *Indian J. Chem.*, **2001**, 40A, 100.
[9] Rubnia Farooq and Faiza rehman et al., *World App. Sci. J.,* **2009,** 6(2), 234.
[10] U N Dash, G Roy, S Mohanty and M Ray, *Indian J. of Pure and App. Phys.,* **2007,** 45,151.
[11] A Ali Nabi F*Acta phy. Chim. Sin.,* **2008,** 24, 47.
[12] C Dey Nibran J Bhuyan, and I Haque, *J. of Sol. Chem.,* **1997,** 6, 26.
[13] H Eyring and J F Kincaid *J. Chem. Phy.,* **1928,** 6, 620.
[14] J D Pandey, AKShukla,NTripathi and G P Dubey *Journal of Physics*, **1993,** 40(2), 81.
[15] G J Price ,*Ultrasonics Sono Chemistry,* **1996,** 3,229.
[16] J D Pandey, V Sanguri DK Dwivedi, *J. Mol. Liq.,* **2008,** 141, 1-7.
[17] AK Nain, R Sharma, A Ali and S Gopal *J.mol.liq.,* **2009,**144(3), 124.
[18] D Bhatnagar D Josi C L Jain, *Indian J. Pure and App. Phys,* **2010**, 48, 31.