

## Acoustic and Viscometric Studies of Atropine Sulphate with Life Essential 3d- Transition Metal Ions in Aqueous Medium

Sandeep Tiwari<sup>1</sup>, Brajendra Singh Kusmariya<sup>2</sup>, Anjali Tiwari<sup>3\*</sup>, V. Pathak<sup>1</sup> and A. P. Mishra<sup>3</sup>

<sup>1</sup>Department of Physical Science, M.G.C.G. Vishwavidyalaya, Chitrakoot, Satna (M.P.), India

<sup>2</sup>Department of Chemistry, Govt. Kamla Nehru Mahila Mahavidyalaya, Damoh– 470661, Inida

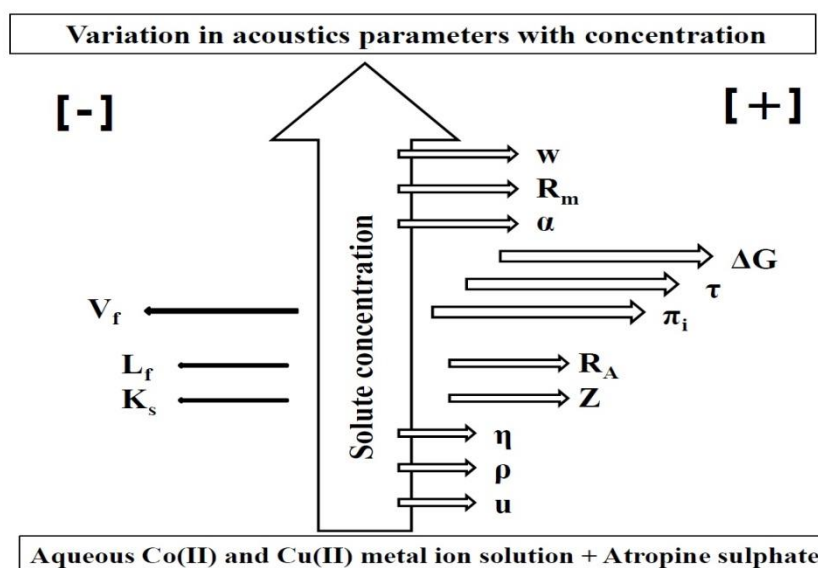
<sup>3</sup>Department of Chemistry, Dr. H. S. Gour Central University, Sagar– 470003, India

\*Corresponding author (e-mail: anjalitiwari0001@gmail.com)

In the present paper, the ultrasonic velocity  $u$ , density  $\rho$  and viscosity  $\eta$  measurements of the drug atropine sulphate in aqueous solutions of Cu(II) and Co(II) metal ions at 298.15 K/1atm at a wide range of concentrations (0.01M-0.1M) are reported. They constitute a valuable source of information viz. inter-relationship of system composition, intermolecular interactions and the physical properties of the solute and solvent investigated. The observed values of  $u$ ,  $\rho$  and  $\eta$  were found in the range of 1500-1550  $\text{ms}^{-1}$ , 1000-1040  $\text{kgm}^{-3}$  and 0.8900-1.300  $\text{Nsm}^{-2}$  respectively. The effect of concentration on  $u$ ,  $\rho$  and  $\eta$  in all ternary systems of metal ions were found to be positive. Acoustical parameters such as isentropic compressibility  $K_s$ , intermolecular free length  $L_f$ , specific acoustic impedance  $Z$ , relative association  $R_A$ , free volume  $V_f$ , internal pressure  $\pi_i$ , viscous relaxation time  $\tau$ , Gibb's free energy  $\Delta G$ , attenuation coefficient  $\alpha$ , Rao's constant  $R_m$ , and Wada's constant  $w$  were calculated from the experimental data. It was found that all the parameters increased with increasing concentration except  $V_f$ ,  $L_f$  and  $K_s$ . On the basis of the Jones-Dole equation, viscosity data were analyzed and the values of the Falkenhagen coefficient  $A$  and Jones-Dole  $B$  coefficient were evaluated. The variations in these parameters are discussed in terms of hydrophilic-hydrophilic/hydrophilic-hydrophobic interactions in these systems along with the structure-making/breaking behaviour of the drug.

**Key words:** Atropine sulphate; density; viscosity; ultrasonic velocity; Jones-Dole equation

**Graphical Abstract:**



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The acoustic and viscometric studies of liquid mixtures are important tools to correlate the binding forces between particles in liquid mixtures. These studies

provide valuable information on the nature of the interactions in these mixtures [1, 2]. In recent years, ultrasonic velocity measurements have been frequently

used to examine the nature of molecular interactions in liquid mixtures [3-4], and in aqueous and non-aqueous solutions of metal ions [5-6]. The acoustic properties of many organic, inorganic and biological compounds in different solvents have been extensively studied to evaluate some important acoustic and viscometric parameters with the help of a number of mathematical models. Baluza and Oza reported ultrasonic studies of sulphonamide derivatives in dimethylformamide solvent and evaluated various acoustic parameters. Mishra and Gautam investigated the acoustic studies of 3d-complexes of Schiff base in alcohol and discussed the solute-solvent interaction and structural effects on the solvent in solution [7-8].

The molecular interactions between biomolecules such as amino acids in aqueous solutions of metal complexes have been well studied [9-11], but very little attention has been paid to medicinally important compounds and drugs such as atropine sulphate, an anticholinergic drug [12] listed in the core medicines section of the World Health Organization's Essential Drugs List [13]. Generally, atropine is used medicinally in the form of atropine sulphate (monohydrate) ( $C_{17}H_{23}NO_3$ )<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O.

In nature, atropine is obtained from the belladonna alkaloid which is a racemic mixture of *d*- and *l*-hyocyanine in a 1:1 ratio. The *levo*-isomer of the drug is responsible for its pharmacological activity. Due to its pharmacological and medicinal benefits, atropine sulfate (monohydrate) has acquired immense importance [14]; however no data is available on its interaction with 3d metal ions in aqueous solutions. Nowadays the study of drug molecules in aqueous and mixed aqueous solutions has gained consequence as the results can help to determine their behaviour in living systems. The structure of drug molecules in solution, the intermolecular interactions and the understanding of these interactions play a key role in determining their outcome in biological systems, while other factors such as the thermodynamic properties of gases, liquids and solids are also important. In those systems, both temperature and concentration significantly affect the charge distribution of molecules, which also influences the different types of molecular interactions (ion-dipole, dipole-dipole, H-bonding etc.).

This fact prompted us to attempt the present study. The data obtained can help in the thermodynamic interpretation of molecular interactions involving atropine sulfate.

3d transition metal ions play a key role in biological systems. The role of cobalt and copper in enzymatic reactions has been proven through several *in vitro* experiments [15-16]. Cobalt and copper are trace elements which are responsible for the proper activity of

many metalloenzymes in living systems, and their imbalance is reported in many types of diseases [17].

In the present paper, the density, viscosity and ultrasonic velocity of atropine sulfate (0.01–0.10 M) in aqueous CoCl<sub>2</sub>/CuCl<sub>2</sub> (0.1, 0.05 and 0.025 M) solutions have been measured. From these experimental data, a number of thermodynamic parameters namely isentropic compressibility, intermolecular free length, specific acoustic impedance, relative association, free volume, internal pressure, viscous relaxation time, Gibb's free energy, attenuation coefficient, Rao's constant, Wada's constant, Falkenhagen coefficient *A* and Jones-Dole or viscosity *B* coefficient have been calculated. These parameters are utilized to understand the possible interactions taking place in the aqueous solutions of CoCl<sub>2</sub>/ CuCl<sub>2</sub> and atropine sulfate.

## EXPERIMENTAL

Atropine sulphate (99.0%, MW=694.34 g/mol, Sigma-Aldrich chemicals Ltd), cobalt chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O, 99.0%, MW= 237.63 g/mol, Fisher Scientific Chemicals) and copper chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O, 99.0%, MW=170.48 g/mol, Fisher Scientific Chemicals) were used to prepare the stock solutions. The requisite amount of metal salts were dissolved in the required volume of double-distilled water to prepare the 0.1, 0.05 and 0.025 M salt solutions. All the materials and reagents were kept in special air-tight bottles. Weighing was done on an electronic digital balance of 0.01 mg accuracy (Digital balance, Model: Dhona 100 DS). Ultrasonic velocity measurements were made using an ultrasonic interferometer of  $\pm 0.1\text{ms}^{-1}$  accuracy (Model M-84, supplied by M/S Mittal Enterprises, New Delhi). The measuring cell of the interferometer had a special double-walled vessel geometry with a digital thermostatic bath (Model SSI-03 Spl, supplied by M/S Mittal Enterprises, New Delhi), operating range  $-10^\circ\text{C}$  to  $85^\circ\text{C}$  with an accuracy of  $\pm 0.1^\circ\text{C}$  for maintaining the desired temperature in the double-walled measuring cell containing the liquid mixtures. The density measurements of the liquid mixtures were done using a specific gravity bottle of 25 cm<sup>3</sup> volume by the relative measurement method with  $\pm 0.01\text{kgm}^{-3}$  accuracy. The specific gravity bottle with the test mixture was immersed in the thermostatic bath. The viscosity measurements were made using an Ostwald's viscometer consisting of a vertically held U-shaped glass tube of  $3 \times 10^{-6}\text{Nm}^{-2}\text{s}$  accuracy. The relative viscosities were calculated using the following equation.

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}$$

where  $\eta_1$ ,  $\eta_2$  are viscosities of liquid 1 & 2;  $\rho_1$ ,  $\rho_2$  are densities of liquid 1 & 2;  $t_1$ ,  $t_2$  are flow time of liquid 1 & 2.

The temperature around the viscometer is maintained at  $\pm 0.01$  K in an electronically operated thermostatic water bath. The instrument was calibrated with double-distilled deionized water at the desired temperature before taking measurements. The flow rates were measured with a stopwatch of 0.1s resolution and average flow rates were selected for each series of liquid solutions [5].

### Theoretical Aspect

For understanding molecular interaction and structural changes, various parameters were derived from the ultrasonic velocity and density data. These parameters were computed using the following equations [5].

Isentropic compressibility ( $K_s$ ) is evaluated using the formula

$$K_s = \frac{1}{u^2 \times \rho} \quad (1)$$

where  $u$  is ultrasonic velocity and  $\rho$  is the density of mixture

Acoustic impedance ( $Z$ ) is calculated by the relation

$$Z = u \times \rho \quad (2)$$

Intermolecular free length ( $L_f$ ) of a solution is obtained using the following rearranged Jacobson's relationship

$$L_f = K \times K_s^{1/2} \quad (3)$$

where  $K \{(93.875+0.375T) \times 10^{-8}\}$  is a temperature-dependent constant, which does not depend on the nature of liquid.

Relative association  $R_A$  gives the idea of non-ideality of solution and was obtained using following equation:

$$R_A = \frac{\rho}{\rho_0} \cdot \left(\frac{u_0}{u}\right)^{1/3} \quad (4)$$

Free volume  $V_f$  is the effective volume affable to the centre of a molecule in a liquid is represented as

$$V_f = \left[ \frac{M_{eff} \cdot u}{K \eta} \right]^{3/2} \quad (5)$$

where  $M_{eff}$  is the effective molecular weight of the mixture ( $\sum M_i x_i$ ),  $\eta$  is the viscosity and  $K$  is the temperature-independent constant ( $K = 4.281 \times 10^9$ ).

Internal pressure is represented by

$$\pi_i = bRT \left[ \frac{k\eta}{u} \right]^{1/2} \left[ \frac{\rho^{2/3}}{M_{eff}^{7/6}} \right] \quad (6)$$

where  $b$  is a constant for the cubic packing factor, which is assumed to be 2 for liquids,  $R$  is the universal gas constant and  $T$  is the temperature in K.

The viscous relaxation time  $\tau$  is obtained using the following equation:

$$\tau = \frac{4}{3} K_s \eta \quad (7)$$

Gibb's free energy is calculated from

$$\Delta G = k T \ln \left[ \frac{k T \tau}{h} \right] \quad (8)$$

where  $k$ , Boltzmann's constant ( $1.38 \times 10^{-23} \text{ JK}^{-1}$ );  $T$ , absolute temperature and  $h$ , Planck's constant ( $6.63 \times 10^{-34} \text{ Js}$ ).

Attenuation Coefficient (Absorption Coefficient)  $\alpha$  is evaluated using this equation:

$$\frac{\alpha}{f^2} = \frac{8 \pi^2 \eta}{3 \rho u^2} \quad (9)$$

where  $f$  is the frequency of the ultrasonic wave.

Molar sound velocity or Rao's constant ( $R$ ) is calculated using the relation:

$$R_m = \left( \frac{M_{eff}}{\rho} \right) u^{1/3} \quad (10)$$

Molar compressibility (Wada's constant)  $w$  is calculated using the relation:

$$w = \frac{M_{eff} \cdot K_s^{1/7}}{\rho} \quad (11)$$

### RESULTS AND DISCUSSION

The densities, viscosities and ultrasonic velocities of the aqueous Cu(II) and Co(II) metal ion solutions with atropine sulfate as a third component have been determined and are listed in table 1.

**Table 1.** Measured values of ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) of atropine sulfate drug solutions at 298.15 K

Atropine con. (M)	Metal ion Concentration (M)								
	0.1M			0.05 M			0.025M		
	$u$ ( $\text{ms}^{-1}$ )	$\rho$ (Kg $\text{m}^{-3}$ )	$\eta$ ( $\text{Nsm}^{-2}$ )	$u$ ( $\text{ms}^{-1}$ )	$\rho$ (Kg $\text{m}^{-3}$ )	$\eta$ ( $\text{Nsm}^{-2}$ )	$u$ ( $\text{ms}^{-1}$ )	$\rho$ (Kg $\text{m}^{-3}$ )	$\eta$ ( $\text{Nsm}^{-2}$ )
Cu(II) metal ion solution									
0	1518.2	1016.4	1.0164	1510.6	1011.6	0.9536	1508.4	1006.4	0.8963
0.01	1522.4	1016.6	1.0218	1516.4	1012	0.9698	1510.4	1004	0.9203
0.02	1520.8	1018	1.0392	1514.2	1012.2	0.9752	1512.2	1006.6	0.9541
0.03	1526.4	1022.2	1.0434	1520.4	1014.6	0.9987	1516.8	1009.8	0.9572
0.04	1532.6	1024.4	1.0724	1522.8	1020.2	1.0202	1518.2	1013.2	0.9868
0.05	1533.4	1024.6	1.0939	1526.8	1018.8	1.0665	1518.8	1017.8	1.0018
0.06	1534.2	1028.6	1.1303	1527.4	1021.2	1.0903	1519.2	1019.6	1.0408
0.07	1534.6	1029.4	1.1473	1528	1023.4	1.1086	1519.6	1022.8	1.0494
0.08	1535.4	1032.4	1.1506	1534.6	1026.6	1.1174	1520	1025.6	1.0629
0.09	1540.4	1032.6	1.1993	1536.6	1028.8	1.1520	1520.6	1027.6	1.0918
0.1	1542.2	1032.8	1.2264	1538	1030.4	1.1592	1521.2	1029.2	1.1256
Co(II) metal ion solution									
0	1520.2	1014.6	0.9776	1518.2	1008.8	0.951	1500.4	1006.6	0.9227
0.01	1522.2	1014.4	1.0038	1518.8	1010.4	0.9156	1504.6	1008.2	0.9346
0.02	1523.6	1015.6	1.0156	1519.6	1010.8	0.9213	1502.6	1008.4	0.9453
0.03	1524.8	1018.2	1.0394	1520.8	1012.2	0.9700	1508.2	1012.4	0.9596
0.04	1525.6	1020.4	1.0522	1521.6	1013.2	1.0290	1512.6	1012.8	0.9917
0.05	1526.8	1024.4	1.0937	1522.6	1013.8	1.0507	1516.6	1011.2	1.0164
0.06	1527.6	1025	1.1050	1524	1016.8	1.0803	1516.8	1013.2	1.0395
0.07	1528.8	1026.6	1.1281	1525.8	1019.2	1.0882	1518.8	1016.8	1.0697
0.08	1534.2	1026.8	1.1444	1526.6	1021.8	1.1016	1519.6	1018.2	1.0818
0.09	1536.8	1028	1.1511	1532.2	1023.6	1.1089	1522.8	1020.6	1.1056
0.1	1538	1030.2	1.1697	1532.4	1026.4	1.1440	1524.2	1022.8	1.1186

The values of  $u$ ,  $\rho$  and  $\eta$  increase with the increasing concentration of atropine sulfate in all ternary systems of the metal ions under investigation.

As concentration (M) increases, the medium becomes denser due to the increasing number of molecules in a given volume, which makes for lesser compressibility and hence higher ultrasonic velocity. In addition, the increasing number of molecules increases the fractional resistance between the layers of medium, which results in the viscosity coefficient increasing and this seems to be particle-sensitive. It has also been noted that the solutes which increase the ultrasonic velocity are structure-makers and those that decrease the ultrasonic velocity are structure-breakers. The values of ultrasonic velocity and their variation with molarities is almost the same for all the mixtures in the present study [18, 19].

Liquid water consists of a connected network structure of H-bonds (HB). Addition of ions has a strong effect on the HB-network. It is important to know the influence of an individual ion on the structure of water and the arrangement of water molecules around the different types of molecules and ions. Ions or solutes which enhance the HB-network of water are known as structure-makers while those that weaken the HB-network are known as structure-breakers. The structure-makers are considered to be strongly hydrated. They break the HB-network in the surrounding water molecules and rearrange them in an ordered hydration structure. On the contrary, structure-breaking ions interact weakly and induce a disordering in the HB network of water. A structure-breaking effect is seen when water molecules in a solution are less or not influenced by the presence of ions (Figure 1).

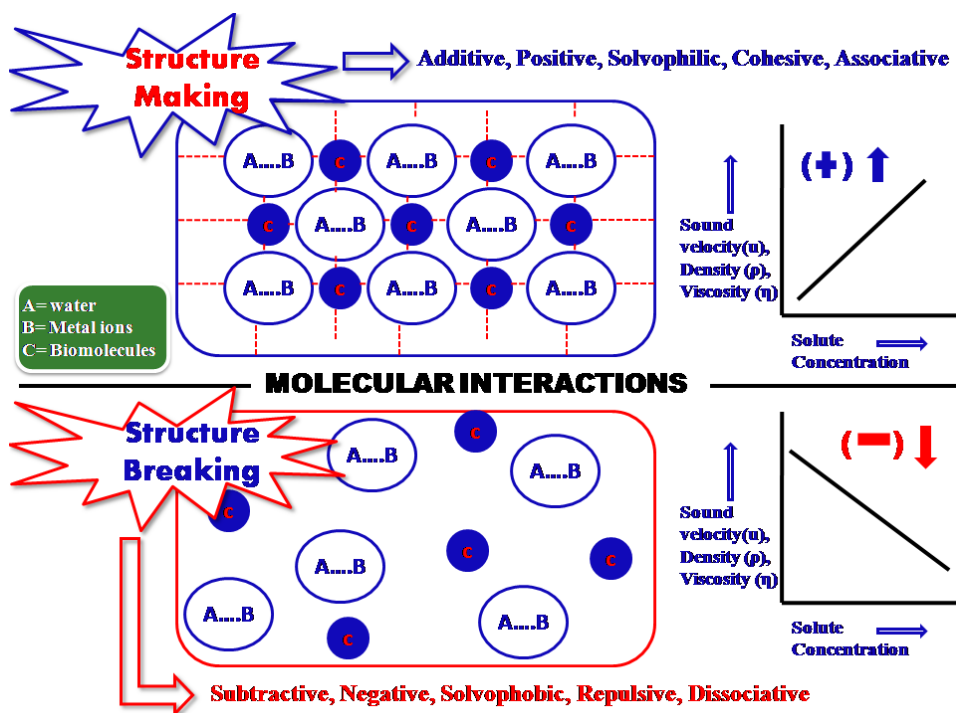


Figure 1. Structure-making and structure-breaking behaviour of solute-solvent interactions.

The increase in ultrasonic velocity with concentration may be due to the presence of interactions caused by atropine sulphate and the hydrophilic nature of aqueous Cu(II) and Co(II) metal ions [20]. Atropine sulphate in an aqueous solution of Cu(II) and Co(II) metal ions produces a greater cohesion in the solution as the concentration is increased. The increasing molecular associations in solution may be due to water structure enhancement. Furthermore, the blank spaces in water clusters may be filled with atropine sulphate molecules which results in the formation of a denser structure for metal ion solutions [21]. Density measurements represent the solvent-solvent and solvent-solute interactions. Increases in density with concentration indicate an increase in solvent-solvent and solute-solvent interactions. This may be due to fact that less

space is available for molecules owing to the presence of a larger number of solute particles in the same region. This represents the structure-making capacity of the solute in solutions which depends on the hydrophobic or hydrophilic nature of the solute [6].

The acoustical parameters such as isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , specific acoustic impedance,  $Z$ , relative association,  $R_A$ , free volume,  $V_f$ , internal pressure,  $\pi_i$ , viscous relaxation time,  $\tau$  and Gibb's free energy,  $\Delta G$ , attenuation coefficient,  $\alpha$ , Rao's constant,  $R_m$ , and Wada's constant,  $w$  of the  $\text{CuCl}_2$ ,  $\text{CoCl}_2$  and their ternary mixtures with atropine sulfate as a third component have been determined and are recorded in Tables 2-4.

Table 2. Calculated values of isentropic compressibility,  $K_s$ , intermolecular free length,  $L_f$ , specific acoustic impedance,  $Z$  and relative association,  $R_A$  for the mixtures at 298.15K

Atropine con. (M)	Metal ion Concentration (M)											
	0.1 M				0.05 M				0.025 M			
	$k_s$ ( $10^{-10}$ $\text{m}^2\text{N}^{-1}$ )	$L_f$ ( $10^{-10}$ m)	$Z$ ( $10^6$ kg $\text{m}^{-2}\text{s}^{-1}$ )	$R_A$	$k_s$ ( $10^{-10}$ $\text{m}^2\text{N}^{-1}$ )	$L_f$ ( $10^{-10}$ m)	$Z$ ( $10^6$ kg $\text{m}^{-2}\text{s}^{-1}$ )	$R_A$	$k_s$ ( $10^{-10}$ $\text{m}^2\text{N}^{-1}$ )	$L_f$ ( $10^{-10}$ m)	$Z$ ( $10^6$ kg $\text{m}^{-2}\text{s}^{-1}$ )	$R_A$
	Cu(II) metal ion solution											
0	4.2685	0.4402	1.5430	1	4.3320	0.4435	1.5281	1	4.3671	0.4453	1.5180	1
0.01	4.2441	0.4390	1.5476	0.9992	4.2972	0.4417	1.5345	0.9991	4.3659	0.4452	1.5164	0.9971
0.02	4.2472	0.4391	1.5481	1.0010	4.3089	0.4423	1.5326	0.9998	4.3443	0.4441	1.5221	0.9993
0.03	4.1988	0.4366	1.5602	1.0039	4.2637	0.4400	1.5425	1.0008	4.3043	0.4421	1.5316	1.0015
0.04	4.1559	0.4344	1.5699	1.0047	4.2269	0.4381	1.5535	1.0058	4.2820	0.4409	1.5382	1.0045

0.05	4.1508	0.4341	1.5711	1.0047	4.2106	0.4372	1.5555	1.0035	4.2592	0.4397	1.5458	1.0090
0.06	4.1303	0.4330	1.5780	1.0084	4.1974	0.4365	1.5597	1.0057	4.2495	0.4392	1.5489	1.0107
0.07	4.1250	0.4328	1.5797	1.0091	4.1851	0.4359	1.5637	1.0078	4.2339	0.4384	1.5542	1.0137
0.08	4.1087	0.4319	1.5851	1.0119	4.1362	0.4333	1.5754	1.0095	4.2202	0.4377	1.5589	1.0164
0.09	4.0813	0.4305	1.5906	1.0110	4.1166	0.4323	1.5808	1.0112	4.2086	0.4371	1.5625	1.0183
0.1	4.0710	0.4299	1.5927	1.0108	4.1028	0.4316	1.5847	1.0125	4.1988	0.4366	1.5656	1.0197
Co(II) metal ion solution												
0	4.2648	0.4401	1.5423	1	4.3007	0.4419	1.5316	1	4.4129	0.4476	1.5103	1
0.01	4.2544	0.4395	1.5441	0.9993	4.2904	0.4414	1.5345	1.0014	4.3813	0.4460	1.5169	1.0006
0.02	4.2416	0.4388	1.5473	1.0002	4.2842	0.4410	1.5360	1.0016	4.3921	0.4466	1.5152	1.0013
0.03	4.2241	0.4379	1.5525	1.0025	4.2715	0.4404	1.5393	1.0027	4.3424	0.4440	1.5269	1.0040
0.04	4.2106	0.4372	1.5567	1.0045	4.2628	0.4399	1.5416	1.0036	4.3154	0.4426	1.5319	1.0034
0.05	4.1876	0.4360	1.5640	1.0082	4.2547	0.4395	1.5436	1.0039	4.2995	0.4418	1.5335	1.0009
0.06	4.1807	0.4357	1.5657	1.0086	4.2344	0.4385	1.5496	1.0066	4.2899	0.4413	1.5368	1.0029
0.07	4.1677	0.4350	1.5694	1.0099	4.2144	0.4374	1.5550	1.0086	4.2634	0.4400	1.5443	1.0060
0.08	4.1376	0.4334	1.5753	1.0089	4.1993	0.4366	1.5598	1.0110	4.2531	0.4394	1.5472	1.0072
0.09	4.1188	0.4324	1.5798	1.0095	4.1613	0.4347	1.5683	1.0115	4.2253	0.4380	1.5541	1.0089
0.1	4.1036	0.4316	1.5844	1.0114	4.1489	0.4340	1.5728	1.0142	4.2084	0.4371	1.5589	1.0107

**Table 3.** Calculated values of free volume,  $V_f$ , internal Pressure,  $\pi_i$ , relaxation time,  $\tau$  and Gibb's free energy,  $\Delta G$ , for the mixtures at 298.15K

Atropine con. (M)	Metal ion Concentration (M)											
	0.1 M				0.05 M				0.025 M			
	$V_f$ ( $10^{-6}$ $\text{m}^3\text{mol}^{-1}$ )	$\pi_i$ ( $10^6$ $\text{Nm}^{-2}$ )	$\tau$ ( $10^{-12}$ s)	$\Delta G$ ( $10^{-20}$ $\text{KJmol}^{-1}$ )	$V_f$ ( $10^{-6}$ $\text{m}^3\text{mol}^{-1}$ )	$\pi_i$ ( $10^6$ $\text{Nm}^{-2}$ )	$\tau$ ( $10^{-12}$ s)	$\Delta G$ ( $10^{-20}$ $\text{KJmol}^{-1}$ )	$V_f$ ( $10^{-6}$ $\text{m}^3\text{mol}^{-1}$ )	$\pi_i$ ( $10^6$ $\text{Nm}^{-2}$ )	$\tau$ ( $10^{-12}$ s)	$\Delta G$ ( $10^{-20}$ $\text{KJmol}^{-1}$ )
Cu(II) metal ion solution												
0	509.12	0.9198	0.5784	0.5426	549.76	0.8982	0.5508	0.5221	598.61	0.8723	0.5219	0.4995
0.01	512.19	0.9141	0.5782	0.5424	544.58	0.8973	0.5556	0.5257	582.32	0.8751	0.5357	0.5104
0.02	503.61	0.9160	0.5885	0.5498	544.23	0.8937	0.5603	0.5292	558.16	0.8851	0.5527	0.5235
0.03	508.23	0.9118	0.5841	0.5467	533.65	0.8970	0.5677	0.5347	563.62	0.8802	0.5493	0.5209
0.04	495.59	0.9168	0.5942	0.5538	523.25	0.9023	0.5749	0.5400	544.53	0.8885	0.5634	0.5315
0.05	486.07	0.9189	0.6054	0.5616	496.26	0.9135	0.5987	0.5570	537.84	0.8909	0.5689	0.5356
0.06	467.60	0.9293	0.6225	0.5733	485.07	0.9180	0.6102	0.5649	513.11	0.9022	0.5897	0.5506
0.07	461.84	0.9297	0.6310	0.5790	477.94	0.9199	0.6186	0.5707	511.94	0.9009	0.5924	0.5525
0.08	464.57	0.9258	0.6303	0.5785	479.92	0.9167	0.6163	0.5691	507.22	0.9015	0.5981	0.5566
0.09	442.89	0.9368	0.6526	0.5931	463.78	0.9246	0.6323	0.5798	492.22	0.9079	0.6126	0.5666
0.1	433.06	0.9401	0.6657	0.6014	464.48	0.9212	0.6341	0.5810	474.93	0.9158	0.6302	0.5784
Co(II) metal ion solution												
0	546.15	0.8935	0.5559	0.5259	559.01	0.8896	0.5483	0.5202	569.98	0.8858	0.5370	0.5114
0.01	531.15	0.8978	0.5694	0.5360	597.96	0.8669	0.5280	0.5043	567.09	0.8843	0.5440	0.5168
0.02	527.82	0.8965	0.5743	0.5396	598.88	0.8629	0.5292	0.5053	561.97	0.8831	0.5480	0.5199
0.03	515.38	0.9012	0.5854	0.5476	560.48	0.8791	0.5544	0.5248	558.04	0.8836	0.5538	0.5244
0.04	511.27	0.9011	0.5907	0.5514	518.42	0.8989	0.5861	0.5481	538.83	0.8903	0.5705	0.5368
0.05	487.70	0.9138	0.6106	0.5653	507.83	0.9016	0.5961	0.5551	526.44	0.8924	0.5827	0.5456
0.06	485.22	0.9119	0.6160	0.5689	492.52	0.9087	0.6099	0.5647	514.05	0.8969	0.5940	0.5536
0.07	475.43	0.9152	0.6269	0.5762	492.76	0.9061	0.6115	0.5658	498.21	0.9045	0.6081	0.5635
0.08	472.22	0.9135	0.6313	0.5792	488.80	0.9063	0.6168	0.5694	495.00	0.9035	0.6134	0.5672
0.09	473.71	0.9095	0.6321	0.5797	491.29	0.9020	0.6187	0.5707	485.20	0.9071	0.6228	0.5735
0.1	467.35	0.9111	0.6400	0.5849	473.37	0.9111	0.6348	0.5815	481.94	0.9066	0.6277	0.5768

**Table 4.** Calculated values of attenuation coefficient,  $\alpha$ , Rao’s constant,  $R_m$ , and Wada’s constant,  $w$ , for the mixtures at 298.15K

Atropine con. (M)	Metal ion Concentration (M)								
	0.1 M			0.05 M			0.025 M		
	$\alpha$ ( $10^{-12}$ Hz)	$R_m$	$w$ ( $10^{-6}$ )	$\alpha$ ( $10^{-12}$ Hz)	$R_m$	$w$ ( $10^{-6}$ )	$\alpha$ ( $10^{-12}$ Hz)	$R_m$	$w$ ( $10^{-6}$ )
Cu(II) metal ion solution									
0	45.710	0.2066	823.80	43.526	0.2057	822.79	41.242	0.2059	823.91
0.01	45.695	0.2081	829.12	43.910	0.2072	827.98	42.335	0.2078	831.45
0.02	46.503	0.2092	832.95	44.277	0.2085	832.88	43.674	0.2088	834.39
0.03	46.163	0.2099	834.47	44.866	0.2097	835.76	43.410	0.2097	836.63
0.04	46.958	0.2111	837.64	45.435	0.2100	836.26	44.520	0.2105	838.95
0.05	47.843	0.2125	842.39	47.316	0.2119	842.30	44.961	0.2109	840.06
0.06	49.192	0.2131	844.00	48.219	0.2128	845.29	46.601	0.2119	843.56
0.07	49.865	0.2143	848.50	48.887	0.2137	848.54	46.814	0.2126	846.00
0.08	49.813	0.2151	850.94	48.700	0.2147	850.80	47.265	0.2135	848.60
0.09	51.572	0.2166	855.70	49.968	0.2157	854.01	48.414	0.2144	851.99
0.1	52.605	0.2179	860.48	50.109	0.2168	857.78	49.799	0.2155	855.76
Co(II) metal ion solution									
0	43.929	0.2084	832.31	43.092	0.2073	828.86	42.902	0.2058	826.39
0.01	44.997	0.2099	837.97	41.392	0.2084	833.08	43.147	0.2070	830.62
0.02	45.387	0.2111	842.06	41.586	0.2097	837.82	43.748	0.2083	835.57
0.03	46.260	0.2120	844.88	43.656	0.2108	841.58	43.906	0.2091	837.35
0.04	46.683	0.2130	848.05	46.217	0.2120	845.84	45.090	0.2106	842.00
0.05	48.257	0.2135	849.57	47.104	0.2133	850.34	46.046	0.2125	848.20
0.06	48.677	0.2148	853.98	48.198	0.2142	852.73	46.987	0.2135	851.75
0.07	49.540	0.2159	857.50	48.320	0.2151	855.60	48.053	0.2142	853.76
0.08	49.891	0.2175	862.18	48.741	0.2160	858.42	48.478	0.2153	857.65
0.09	49.955	0.2187	866.15	48.619	0.2172	861.90	49.221	0.2163	860.74
0.1	50.573	0.2196	869.13	50.008	0.2180	864.28	49.603	0.2173	864.03

To understand the structural changes and molecular interactions in solutions, viscosity is an important parameter which is influenced to a certain extent by the change in structure of solvent or solution, unlike velocity and density.

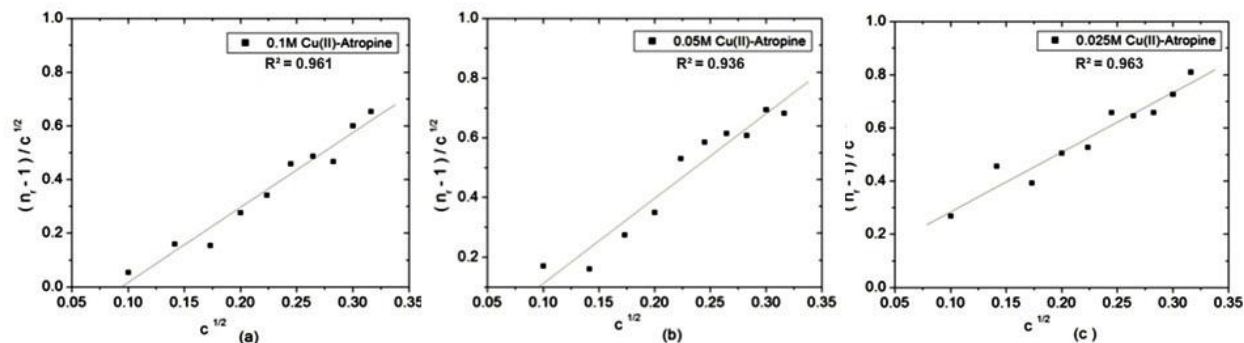
The viscosity data were analyzed using the Jones-Dole equation:

$$\frac{(\eta_r - 1)}{c^{1/2}} = A + Bc^{1/2} \dots\dots\dots (12)$$

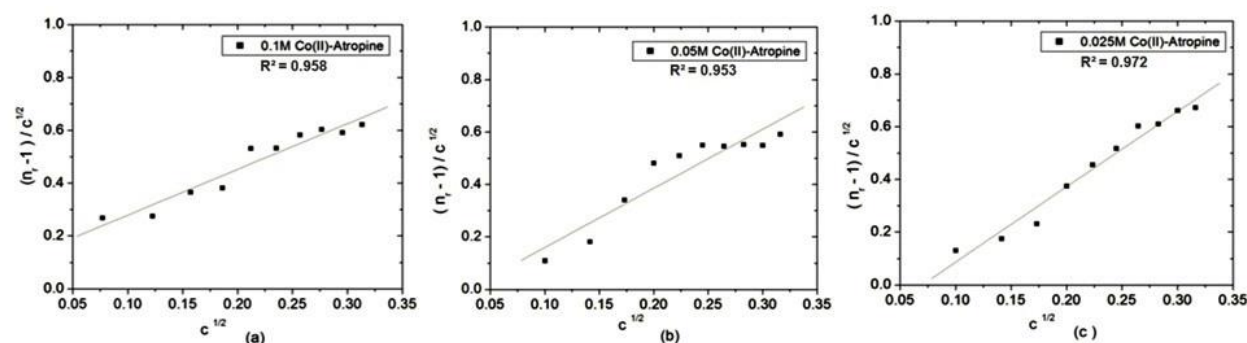
Where  $\eta_r$  is the relative viscosity ( $\eta / \eta_0$ ),  $A$  is called the Falkenhagen coefficient which represents the ionic interactions and  $B$  is the Jones-Dole coefficient that depends on particle size and the nature of solute-solvent interactions which are calculated from linear plots of  $(\eta_r - 1)/c^{1/2}$  versus  $c^{1/2}$  for atropine sulphate in aqueous solutions of Cu(II) and Co(II) metal ions at 298.15 K (Table 5) [22-23].

**Table 5.** Coefficients of the Jones-Dole equation for atropine sulphate in 0.1 M, 0.05 M and 0.025 M aqueous solution of Cu(II) and Co(II) metal ions at 298.15 K

Metal ion concentration (M)	A	B
<b>Atropine sulphate (0.01 M-0.1 M) + Cu(II) metal ion</b>		
0.1	-0.261	2.785
0.05	-0.172	2.844
0.025	0.059	2.248
<b>Atropine sulphate (0.01 M-0.1 M) + Co (II) metal ion</b>		
0.1	-0.206	2.484
0.05	-0.768	4.806
0.025	0.129	2.106



**Figure 2.** Plots of  $(\eta_r-1)/c^{1/2}$  versus  $c^{1/2}$  for atropine sulphate with (a) 0.1 M, (b) 0.05 M and (c) 0.025 M Cu(II) metal ion aqueous solutions.



**Figure 3.** Plots of  $(\eta_r-1)/c^{1/2}$  versus  $c^{1/2}$  for atropine sulphate with (a) 0.1 M, (b) 0.05 M and (c) 0.025 M Co(II) metal ion aqueous solutions.

The John-Dole equation usually expresses the variation of  $\eta_r$  with concentration, and observed values of viscosity coefficients support the structure-making behavior. It is observed from Table 5 that values of the *A* coefficient are found to be either negative or positive and are smaller in magnitude, which indicate weak solute-solute interactions. The *B* coefficient values are comparatively larger and positive in both Cu(II) and Co(II) systems which indicate stronger solute-solvent interactions compared with solute-solute interactions, and this introduces order in the system. This may indicate that metal ions in the system disturb the existing solvent structure and form a more stable arrangement (Figure 2-3) [24-26]. Generally, solute-solvent interactions increase with increasing concentration, as shown in other parameters. However, the obtained results show an irregular trend. Initially, values of the coefficient *B* increase with increasing concentration and then later decrease.

The values of isentropic compressibility ( $K_s$ ) decrease with an increase in concentration of atropine sulphate in aqueous solutions of Cu(II) and Co(II) metal ions [27]. This may happen because the solvent molecules accumulate around the solute molecules. Similar results for intermolecular free length ( $L_f$ )

suggest that a strong interaction is occurring between solute and solvent [28-29]. This can be attributed to the tight packing of molecules in the system which causes an increase in ultrasonic velocity and suggests a structure-making tendency of atropine sulphate with Cu(II) and Co(II) metal ions in aqueous solutions (Table 2). The behaviour of acoustic impedance (*Z*) may be responsible for the propagation of ultrasonic waves [30]. The specific acoustic impedance values increase with an increase in concentration, which is quite similar to the trend for ultrasonic velocity (Table 2). The increase in *Z* suggests strong solute-solvent interaction through hydrogen bonding [31].

The relative association ( $R_A$ ) is influenced either by the breaking-up of solvent structures on addition of solutes or the solvation of solutes. The former results show a decreasing trend and the latter results show an increasing trend in relative association ( $R_A$ ). The  $R_A$  values show a positive change with increasing concentration which is slightly greater than one. It may be suggested that the solvation of the solutes predominate over the breaking-up of the solvent structure. At very low concentrations the observed decreasing trend is due to the breaking up of the solvent on addition of atropine sulphate (Table 2). The



increasing values of  $R_A$  with concentration suggest that solvation of solutes is more dominant over the breaking of the solvent structures [32].

The free volume ( $V_f$ ) values decrease with the increase in solute concentration, with slight deviations. The higher values of free volume indicate a weak solute-solvent interaction and vice-versa. The internal pressure ( $\pi_i$ ) values decrease at a lower concentration of solute and increase at a higher concentration of solute. This decrease may be due to the loosening of cohesive forces leading to the break-up of the solvent structure. An increasing value suggests the strengthening of cohesive forces may be due to the formation of the solvent structure. The values of viscous relaxation time ( $\tau$ ) and Gibb's free energy ( $\Delta G$ ) increase with an increase in solute concentration, which shows that the molecular interactions take place between solute-solvent molecules and become stronger with increasing solute concentration [33]. The Gibb's free energy ( $\Delta G$ ) values suggest the closer packing of molecules due to the H-bonding between unlike molecules in the solutions (Table 3) [30]. The Rao's constant ( $R_m$ ), Wada's constant ( $w$ ) and attenuation coefficient ( $\alpha$ ) values also show an increasing trend with the increase in solute concentration. This may be due to the presence of a higher number of particles in the same space which leads to a more compact packing of the medium, thus increasing interactions (Table 4) [19, 29, 33].

### CONCLUSIONS

A systematic acoustic and viscometric study of atropine sulphate with Cu(II) and Co(II) metal ions in aqueous solution has been carried out over a wide concentration range. The acoustical data provides important information on solute-solvent interactions in solutions. From the experimental findings, different parameters viz.  $K_s$ ,  $L_f$ ,  $Z$ ,  $R_A$ ,  $V_f$ ,  $\pi_i$ ,  $\tau$ ,  $\Delta G$ ,  $\alpha$ ,  $R_m$ ,  $w$ , Falkenhagen Coefficient,  $A$  and Jones-Dole coefficient,  $B$  were evaluated and the results indicate the existence of solute-solvent (hydrophilic-ionic group) interactions in these mixtures. The existence of hydrophilic solute-solvent interactions supports the structure-making tendency and occurs predominantly at higher concentrations while structure-breaking is observed at lesser concentrations of solute. Hence, it is evident from the above study that acoustic and viscometric studies serve as powerful tools in understanding the molecular interactions present in these solutions.

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