

Acoustic and volumetric properties of aqueous solution of levofloxacin nickel complexes at 308K

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Abstract

The density and ultrasonic velocity were measured for aqueous solutions of nickel complex and its ternary complex with 1,10-phenanthroline at 308 K. Using the experimental data, adiabatic compressibility, acoustic impedance, intermolecular free length and hydration number, apparent molar volume, limiting apparent molar volume, apparent molar compressibility, limiting apparent molar compressibility and their associated constants were calculated. These parameters were used to study the ion-solvent interaction in each solution.

Keywords: Ultrasonic Velocity, Hydration Number, Adiabatic Compressibility, Apparent Molar Volume, Apparent Molar Compressibility.

1. Introduction

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes provides useful information in understanding the degree and nature of interaction because intra molecular and intermolecular association related structural changes affect the ultrasonic velocity. By ultrasonic measurements, the molecular interactions in pure liquids¹⁻⁴, aqueous solution⁵⁻⁷ and liquid mixtures⁸⁻¹¹ have also been studied. Iqbal *et al*¹² have studied the apparent molar volume and adiabatic compressibility of aqueous solutions of drugs such as sodium salicylate, methyl orange, L-tryptophan, phenol and hydrochloride salts of procaine and pilocarpine and ephedrine. Naidu *et al*¹³ have reported the ultrasonic velocity; density and viscosity studies in aqueous solution of levofloxacin hemi hydrates, tacrolimus monohydrate and lisinopril dehydrate. The interaction between oral levofloxacin and multivalent cations has been described by pharmacokinetic studies¹⁴.

In the present paper levofloxacin is selected for the study as it is effective against diarrhea caused by *Escherichia Coli*, campylobacter, *Jejune* and *shigella* bacteria. It is used for testing infections of the sinuses, skin, lungs, ears, airways, bones and joints caused by susceptible bacteria. It is also used to treat urinary infections. It has been reported¹⁵⁻¹⁸ that the levofloxacin (quinolones) act as a monoionic bidentate ligand through their carboxylate and carbonyl groups. The interaction between quinolone and metal cations was based on chelation. Since the functional groups like carbonyl and carboxyl groups are required for antibacterial activity, it could be anticipated that all the quinolones could be interacting with metal ions¹⁹. The density and partial molar volume measurements of aqua-organic liquids at infinite dilution²⁰ have been found to be highly useful in understanding the structure of molecular interaction between water and organic molecules. However there are rare reports on acoustic behaviour of metal complexes of drugs. The present paper represents the acoustical and volumetric properties of nickel complexes of levofloxacin and its ternary complex with 1, 10-phenanthroline at 308 K.

2. Experimental

The hydrated salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was Anal R grade. Levofloxacin were obtained from a local pharmaceutical company. Water used in this study was double distilled water prepared by distilling water over alkaline potassium permanganate in all glass distillation flasks. All the complexes were prepared from reported methods²¹. These complexes were characterized by elemental analysis and spectroscopic methods. The ultrasonic velocity was measured by single crystal interferometer (Mittal, model-81) operating at a frequency of 2MHz. The temperature was maintained constant at 308.05K in a thermostat. The density of solutions was determined accurately using specific gravity bottle and electronic balance of accuracy (± 0.1 mg).

3. Result and discussion

The desired parameters such as adiabatic compressibility (β), inter molecular free length (L_f), acoustic impedance (Z), hydration number (n_H), limiting apparent molar compressibility (K_ϕ), apparent molar volume (V_ϕ), limiting apparent molar compressibility (K_ϕ^0), limiting apparent molar volume (V_ϕ^0) and their constants (S_k and S_v) had been studied at 308 K. Density is known to be a measure of ion-solvent and solvent-solvent interactions. The ultrasonic velocity²²⁻²³, adiabatic compressibility, acoustic impedance, intermolecular free length and hydration number²⁴ calculated with equations (1)-(4) are given as,

$$U = (\beta d)^{-1/2} \quad (1)$$

$$\beta = d^{-1}U^{-2} \quad (2)$$

$$Z = Ud \quad (3)$$

$$L_f = K_j \beta^{1/2} \quad (4)$$

$$n_H = \frac{n_1}{n_2} \left[1 - (\beta - \beta^0) \right] \quad (5)$$

Where U , β , d , Z , L_f and n_H are the ultrasonic velocity, adiabatic compressibility, density, acoustic impedance, intermolecular free length and hydration number respectively. β^0 Is the adiabatic compressibility of the solvent. K_j Is Jacobson constant = 2.0965×10^{-6}

From the density data, the apparent molar volume (V_ϕ) was calculated from the relation of the type Harned and Owen²⁵:

$$V_\phi = 1000(cd_0)^{-1}(d_0 - d) + M_2 d_0^{-1} \quad (6)$$

Where c the molar concentration of the solution is, M_2 is the molecular mass of the solute, d_0 and d are the densities of pure solvent and solution respectively.

The V_ϕ data were fitted with an equation of the type Masson²⁶,

$$V_\phi = V_\phi^0 + S_v c^{1/2} \quad (10)$$

The apparent molar compressibility, K_ϕ can be computed from the equation²⁷,

$$K_\phi = 1000\beta c^{-1} - \beta^0 d^{-1} (1000c^{-1} - M_2) \quad (8)$$

K_ϕ Is the function of c as obtained by Gucker[27] from Debye Huckel theory²⁸ and is given by,

$$K_\phi = K_\phi^0 + S_k c^{1/2} \quad (9)$$

K_ϕ^0 Is the apparent molar compressibility and S_k is the slope.

The value of density, Ultrasonic velocity, adiabatic compressibility, acoustic impedance, intermolecular free length and hydration number of both the nickel complexes were listed in Table 1.

Table 1: The Values of Density (d), Ultrasonic Velocity (U), Adiabatic Compressibility (β), Acoustic Impedance (Z), Intermolecular Free length (L_f) and Hydration number (n_H) of $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes in Water At 308 K.

Concentration (c) moldm ⁻³	Density (d) $\times 10^3 \text{ kg m}^{-3}$	Ultrasonic velocity (U) msec ⁻¹	Adiabatic compressibility (β) $\times 10^{-7} \text{ m}^2 \text{ N}^{-1}$	Acoustic Impedance (Z) $\times 10^{-3}$ kg m ² s ⁻¹	Intermolecular free length (L_f) $\times 10^{-9}$ m	hydration number (n_H)
$[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$						
0.0099	997.71	1508.0	4.4076	1504.5	1.3919	6.6321
0.0196	996.90	1509.2	4.4085	1503.0	1.3920	2.7584
0.0291	994.51	1510.3	4.4105	1501.2	1.3923	1.0011
0.0385	992.17	1511.4	4.4125	1499.5	1.3926	0.1253
0.0477	990.26	1512.5	4.4145	1497.7	1.3930	-0.4004
$[\text{Ni}(\text{levo})(1,10\text{-phenanthroline})]\text{Cl}$						
0.0099	1000.4	1510.2	4.3829	1537.5	1.3881	37.5399
0.0197	998.80	1511.5	4.3823	1532.1	1.3879	42.1377
0.0284	996.74	1512.8	4.3336	1510.8	1.3649	52.7806
0.0388	994.96	1540.1	4.2382	1509.7	1.3576	54.7066
0.0481	991.29	1551.1	4.1933	1507.9	1.3380	54.9585

The density was found to decrease for both the nickel complexes with increase in concentration. Decrease in density indicated the decrease in solvent-solvent or ion-solvent or structure breaking property of metal complexes. The variation of ultrasonic velocity with molar concentration was shown by Figure 1.

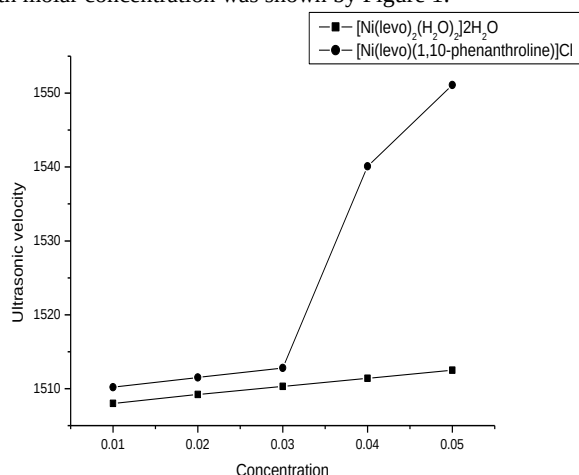


Fig. 1: Variation of Ultrasonic Velocity (U) with Concentration for $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes At 308K.

The ultrasonic velocity increased smoothly with concentration in $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$. But increase in ultrasonic velocity occurred steadily in case of $[\text{Ni}(\text{levo})(1,10\text{-phenanthroline})]\text{Cl}$. The increase in ultrasonic velocity for both the nickel complexes may be due to molecular association caused by cohesive forces²⁹.

The adiabatic compressibility (β) is a measure of intermolecular association or repulsion calculated from the measured ultrasonic velocity (U) and density (d). The β values were found to increase in $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and decrease in $[\text{Ni}(\text{levo})(1,10\text{-phenanthroline})]\text{Cl}$ (Figure 2).

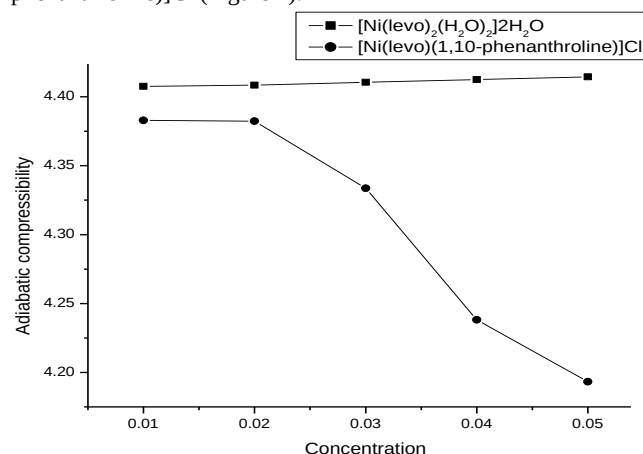


Fig. 2: Variation of Adiabatic Compressibility (β) with Concentration for $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes At 308K.

Decrease in adiabatic compressibility in $[\text{Ni}(\text{levo})(1,10\text{-phenanthroline})]\text{Cl}$ might be due to close association between water molecules i.e. solvent-solvent interaction and also electrostriction³⁰. The increase in β values for $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ complex with increase in concentration of solution may be due to

collection of water molecules around ions³¹. This implies significant solute-solvent interaction in $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$.

The value of acoustic impedance (Z) decreased with increase in concentration for both the complexes in water. When concentration of solute increases, the thickness of oppositely charged ionic atmosphere may increase due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with increase in concentration in both the systems investigated.

It was found that intermolecular free length increased on increasing the concentration of $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and decreased in $[\text{Ni}(\text{levo})(1, 10\text{-phenanthroline})]\text{Cl}$. The increase in L_f values was due to greater force of interaction between complex and water molecule by forming hydrogen bonding.

The hydration number was increasing with increase in concentration due to strong solute-solvent interaction. There was regular increase in hydration number with increase in concentration in case of $[\text{Ni}(\text{levo})(1, 10\text{-phenanthroline})]\text{Cl}$ which indicates the increase in size of secondary layer of hydration i.e. the solvent molecules forms strong co-ordination bond in primary layer. The hydration number in primary layer corresponds to co-ordination number and it is concentration independent. But the hydration number in secondary layer is concentration dependent. So increase in hydration with concentration indicated that water molecules are strongly attached in secondary layer.

Table 2: The Values of Concentration, Apparent Molar Volume (V_ϕ), Limiting Apparent Molar Volume (V_ϕ^0) and Experimental Slope (S_v) of $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes In Water At 308K.

Concentration (c) mol dm ⁻³	Apparent molar vol- ume (V _φ) x10 ³ m ³ mol ⁻¹	Limiting appar- ent molar vol- ume (V _φ ⁰) m ³ mol ⁻¹	S _v m ³ kg ^{1/2} mol ^{3/2}
[Ni(levo) ₂ (H ₂ O) ₂]2H ₂ O			
0.0099	0.6083	0.578	0.3443
0.0196	0.6874		
0.0291	0.7530		
0.0385	0.8258		
0.0477	0.8654		
[Ni (levo)(1,10-phenanthroline)]Cl			
0.0099	0.2332	0.225	0.7265
0.0197	0.3768		
0.0284	0.4681		
0.0388	0.5984		
0.0481	0.6804		

From Table 2 it was observed that apparent molar volume increased with concentration in both systems indicating the existence of solute-solvent interaction. The value of limiting apparent molar volume and experimental slope were positive in both systems shown by Figure 3.

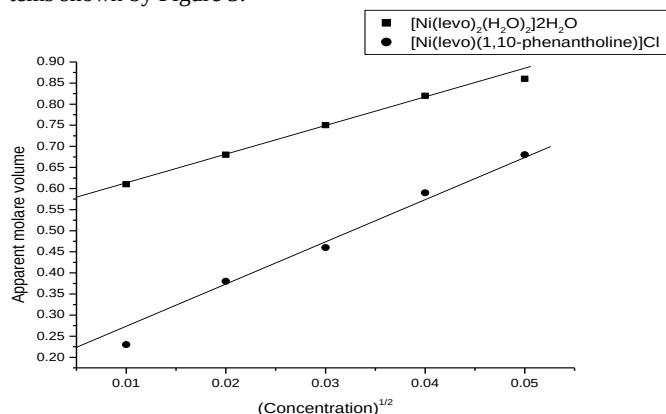


Fig. 3: Variation of Apparent Molar Volume (V_ϕ) with $C^{1/2}$ for $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes At 308K.

It indicates the ion-dipolar interaction in both aqueous solutions. The lower positive value of S_v in $[\text{Ni}(\text{levo})(1, 10\text{-phenanthroline})]\text{Cl}$ indicated strong solute-solvent interaction.

Table 3: The Values of Concentration, Apparent Molar Compressibility (K_ϕ), Limiting Apparent Molar Compressibility (K_ϕ^0) and Experimental Slope (S_k) of $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes In Water At 308K.

Concentration (c) mol dm ⁻³	Apparent molar compressibility (K _φ) x10 ³ m ³ mol ⁻¹	Limiting appar- ent molar com- pressibility (K _φ ⁰) m ³ mol ⁻¹	S _k m ³ kg ^{1/2} mol ^{3/2}
[Ni(levo) ₂ (H ₂ O) ₂]2H ₂ O			
0.0099	1.9801	1.832	0.6248
0.0196	2.3523		
0.0291	2.7682		
0.0385	3.0297		
0.0477	3.4035		
[Ni (levo)(1,10-phenanthroline)]Cl			
0.0099	1.6550	1.553	0.4040
0.0197	1.8621		
0.0284	2.1233		
0.0388	2.3381		
0.0481	2.5901		

The value of apparent molar compressibility (K_ϕ) was increased with increase in concentration in both systems shown Table 3. It shows strong electrostatic attractive force in the vicinity of ions. It may be concluded that strong molecular association was found in $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ with higher positive K_ϕ values.

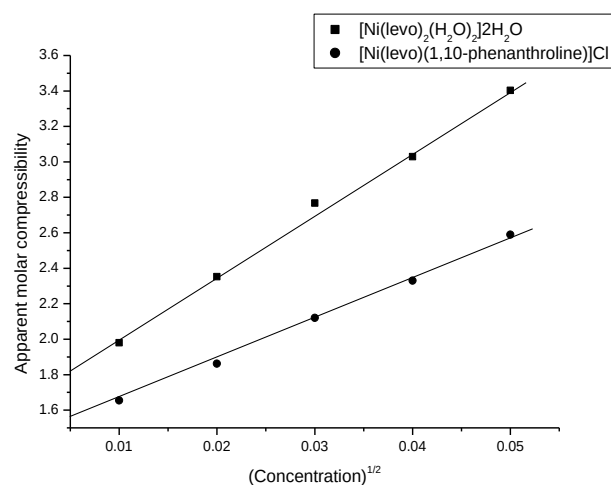


Fig. 4: Variation of Apparent Molar Compressibility (K_ϕ) with $C^{1/2}$ For $[\text{Ni}(\text{Levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{Levo})(1,10\text{-Phenanthroline})]\text{Cl}$ Complexes 308K.

The value of K_ϕ^0 and S_k were obtained in Figure 4. The higher positive K_ϕ^0 and S_k value also indicates strong solute-solute interaction. The solute-solvent interaction is enhanced with chelation.

4. Conclusion:

Acoustical and volumetric properties of aqueous solutions of $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{Ni}(\text{levo})(1, 10\text{-phenanthroline})]\text{Cl}$ at 308K was studied. From the experimental data solute-solvent and solute-solute interaction were studied. It was concluded that there was weak solute-solvent interaction in $[\text{Ni}(\text{levo})_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ system and strong solute-solvent interaction in $[\text{Ni}(\text{levo})(1, 10\text{-phenanthroline})]\text{Cl}$ system.

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