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Thermophysical and Volumetric Properties of Memantine, Dorzolamide, and Moxifloxacin Hydrochlorides in Aqueous Solutions: A Comparative Study at Variable Temperatures and Pressures

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Abstract:
This comprehensive study investigates the thermophysical and volumetric properties of three therapeutically significant pharmaceutical hydrochlorides—memantine hydrochloride (MEM), dorzolamide hydrochloride (DRZ), and moxifloxacin hydrochloride (MFX)—in aqueous solutions across variable temperature and pressure conditions. Experimental measurements of density (ρ), speed of sound (u), and refractive index (nD) were conducted at temperatures ranging from 298.15 K to 320.15 K under atmospheric pressure (0.1 MPa). From these primary measurements, derived thermophysical parameters including apparent molar volume (Vφ), limiting apparent molar volume (Vφ°), apparent molar isentropic compressibility (κφ), limiting apparent molar expansibility (Eφ°), Hepler's constant ($\partial^2V\varphi°/\partial T^2$), molar refraction (RM), and hydration number (nh) were calculated. The results reveal dominant solute-solvent interactions characterized by hydrogen bonding, dipole-dipole, and dipole-induced dipole interactions. Hepler's thermodynamic relationship confirms structure-making behavior for all three hydrochlorides in aqueous media. The comparative analysis demonstrates distinct molecular interaction patterns attributable to structural differences among these pharmaceutical compounds, providing essential data for pharmaceutical formulation development and drug delivery optimization.

Keywords: Thermophysical properties; Volumetric properties; Memantine hydrochloride; Dorzolamide hydrochloride; Moxifloxacin hydrochloride; Apparent molar volume; Isentropic compressibility; Solute-solvent interactions; Molecular dynamics.

1. INTRODUCTION

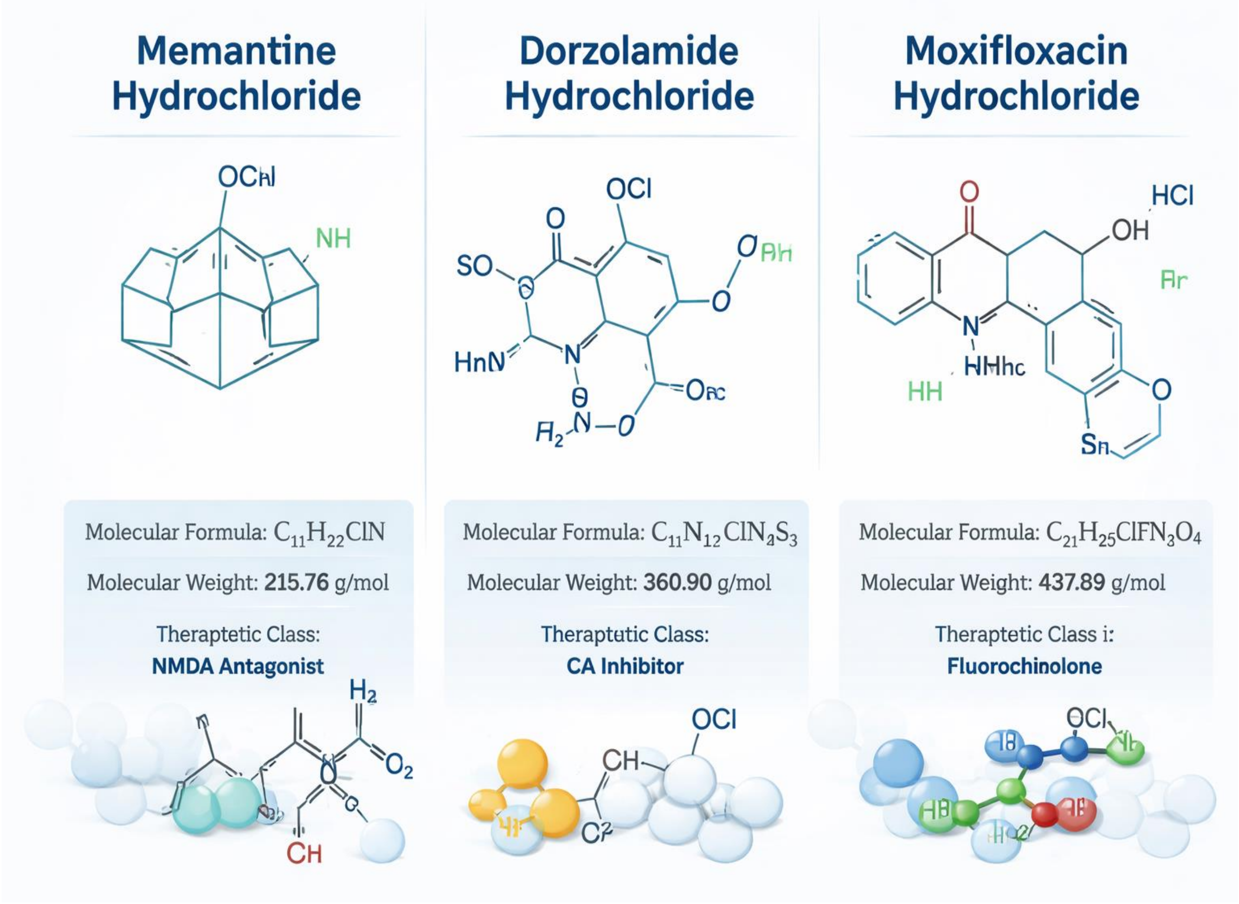
The comprehensive understanding of thermophysical and volumetric properties of pharmaceutical compounds in aqueous solutions constitutes a fundamental requirement for advancing drug development, formulation optimization, and therapeutic delivery systems. These physicochemical characteristics provide critical insights into molecular interactions, solvation phenomena, and structural modifications occurring within biological environments where aqueous media predominate (Iqbal & Chaudhry, 2009). The systematic investigation of such properties enables researchers to elucidate solute-solvent relationships, predict drug behavior under physiological conditions, and optimize pharmaceutical preparations for enhanced bioavailability and therapeutic efficacy.

Memantine hydrochloride ($C_{12}H_{22}ClN$, MW = 215.76 g/mol) represents a critically important neuroprotective agent primarily utilized in the management of moderate-to-severe Alzheimer's disease. As a non-competitive N-methyl-D-aspartate (NMDA) receptor antagonist, memantine exhibits neuroprotective qualities by inhibiting calcium channels activated through NMDA receptor stimulation (Rayinuthala et al., 2023). The compound demonstrates significant therapeutic potential in preventing glutamate-mediated excitotoxicity, a pathological mechanism implicated in various neurodegenerative disorders. Despite its clinical significance, comprehensive thermophysical data for memantine hydrochloride in aqueous systems remain relatively scarce in the scientific literature.

Dorzolamide hydrochloride ($C_{10}H_{17}ClN_2O_4S_3$, MW = 360.90 g/mol) functions as a topical carbonic anhydrase inhibitor indicated for the treatment of elevated intraocular pressure in patients with open-angle glaucoma and ocular hypertension. This sulfonamide derivative demonstrates remarkable specificity, exhibiting 4000-fold higher affinity for carbonic anhydrase II compared to carbonic anhydrase I (Rayinuthala et al., 2024). The inhibition of carbonic anhydrase in ocular ciliary processes decreases aqueous humor secretion, thereby reducing intraocular pressure. Understanding the volumetric behavior of dorzolamide in aqueous media is essential for optimizing ophthalmic formulations and ensuring therapeutic effectiveness.

Moxifloxacin hydrochloride ($C_{21}H_{25}ClFN_3O_4$, MW = 437.89 g/mol) belongs to the fourth-generation fluoroquinolone antibacterial class, demonstrating broad-spectrum activity against gram-positive, gram-negative, and atypical pathogens. The compound inhibits bacterial DNA gyrase and topoisomerase IV, effectively preventing DNA replication and inducing bactericidal effects (Rayinuthala et al., 2024). Moxifloxacin's therapeutic applications encompass community-acquired pneumonia, acute bacterial sinusitis, acute exacerbations of chronic bronchitis, and complicated intra-abdominal infections. The thermophysical characterization of this fluoroquinolone provides valuable information for pharmaceutical formulation development and stability assessment.

FIGURE 1: Molecular Structures and Specifications of Three Pharmaceutical Hydrochlorides



Volumetric properties, particularly apparent molar volume and partial molar volume, serve as sensitive indicators of molecular interactions in solution systems. These parameters reflect the contributions of intrinsic molecular volume, void space, and solvation shell modifications (Kumar & Behal, 2016). The temperature dependence of volumetric properties provides information regarding thermal expansion behavior and structure-making or structure-breaking characteristics of solutes. Similarly, acoustic parameters derived from speed of sound measurements offer insights into intermolecular forces and compressibility behavior under varying thermodynamic conditions.

The present investigation aims to conduct a systematic comparative study of the thermophysical and volumetric properties of memantine, dorzolamide, and moxifloxacin hydrochlorides in aqueous solutions. Through precise measurements of density, speed of sound, and refractive index at multiple temperatures, this research endeavors to calculate derived parameters, including apparent molar volume, limiting apparent molar volume, apparent molar isentropic compressibility, limiting apparent molar expansibility, Hepler's constant, molar refraction, and hydration number. The comparative analysis seeks to establish structure-property relationships and elucidate the molecular interaction patterns characterizing these therapeutically important compounds in aqueous environments.

2. MATERIALS AND METHODS

2.1 Materials

Memantine hydrochloride (CAS: 41100-52-1), dorzolamide hydrochloride (CAS: 130693-82-4), and moxifloxacin hydrochloride (CAS: 186826-86-8) were obtained from pharmaceutical-grade suppliers with mass fraction purity exceeding 0.99, as certified by the manufacturers. All compounds were utilized without further purification after verification of purity through high-performance liquid chromatography (HPLC) analysis. Deionized water with specific conductance less than 1×10^{-6} S·cm^{-1} was employed for solution preparation. Table 1 presents the specifications and physicochemical properties of the investigated compounds.

Table 1. Specifications and Physicochemical Properties of Investigated Pharmaceutical Hydrochlorides

Property	Memantine HCl	Dorzolamide HCl	Moxifloxacin HCl
Molecular Formula	$C_{12}H_{22}ClN$	$C_{10}H_{17}ClN_2O_4S_3$	$C_{21}H_{25}ClFN_3O_4$
Molecular Weight (g/mol)	215.76	360.90	437.89
CAS Number	41100-52-1	130693-82-4	186826-86-8
Purity (mass fraction)	≥0.99	≥0.99	≥0.99
Therapeutic Class	NMDA Antagonist	CA Inhibitor	Fluoroquinolone

Source: PubChem (2024); Chemicalbook (2024); DrugBank (2024)

2.2 Solution Preparation

Stock solutions of each pharmaceutical hydrochloride were prepared gravimetrically using an analytical balance (Sartorius PA225D) with precision ±0.00001 g. Solutions spanning molality concentrations from 0.01 to 0.05 mol·kg^{-1} were prepared by successive dilution of stock solutions with degassed deionized water. All solutions were prepared fresh and utilized within 24 hours to minimize degradation effects. Concentrations were verified through UV-spectrophotometric analysis against calibrated standards.

2.3 Experimental Measurements

Density and speed of sound measurements were performed simultaneously using an Anton Paar DSA 5000 M digital vibrating-tube densimeter and sound velocity analyzer. The instrument provides density measurements with uncertainty of ±0.000005 $g \cdot cm^{-3}$ and speed of sound measurements with uncertainty of ±0.5 $m \cdot s^{-1}$. Temperature control was maintained within ±0.01 K using a built-in Peltier thermostat. Refractive index measurements were conducted using an Abbemat 500 automatic refractometer with an uncertainty of ±0.00001. All measurements were performed at atmospheric pressure (0.1 MPa) and temperatures of 298.15, 305.15, 310.15, 315.15, and 320.15 K. Each measurement was replicated three times, and mean values were reported.

FIGURE 2: Experimental Instrumentation Setup

2.4 Calculation of Derived Parameters

The apparent molar volume ($V\varphi$) was calculated from experimental density data using the following equation: $V\varphi = (M/\rho) - [(\rho - \rho_0)/(m \cdot \rho \cdot \rho_0)]$, where M represents the molar mass of solute, ρ and ρ_0 denote the densities of solution and pure solvent, respectively, and m represents molality. The limiting apparent molar volume ($V\varphi°$) at infinite dilution was obtained by extrapolating $V\varphi$ values to zero concentration using the Masson equation: $V\varphi = V\varphi° + Sv \cdot m$^0.5, where Sv represents the experimental slope parameter (Masson, 1929).

Isentropic compressibility (κs) was calculated using the Newton-Laplace equation: $\kappa s = 1/(u^2 \cdot \rho)$, where u represents the speed of sound. The apparent molar isentropic compressibility ($\kappa\varphi$) was determined from: $\kappa\varphi = [(\kappa s \cdot \rho_0 - \kappa s_0 \cdot \rho)/(m \cdot \rho \cdot \rho_0)] + (\kappa s \cdot M/\rho)$. Limiting apparent molar expansibility ($E\varphi°$) was obtained from the temperature derivative of $V\varphi°$: $E\varphi° = (\partial V\varphi°/\partial T)p$. Hepler's constant was calculated as the second derivative: $(\partial^2 V\varphi°/\partial T^2)p$, providing information on structure-making or structure-breaking behavior of solutes (Hepler, 1969).

Hydration numbers (nh) were estimated using Passynski's formula: $nh = (n_1/n_2) \cdot [1 - (\kappa s/\kappa s_0)]$, where n_1 and n_2 represent moles of solvent and solute, respectively. Molar refraction (RM) was calculated using the Lorentz-Lorenz equation: $RM = [(n^2 - 1)/(n^2 + 2)] \cdot (M/\rho)$, where n represents refractive index (Lorentz, 1880; Lorenz, 1880).

3. RESULTS AND DISCUSSION

3.1 Density, Speed of Sound, and Refractive Index Measurements

The experimental values of density (ρ), speed of sound (u), and refractive index (nD) for aqueous solutions of memantine hydrochloride, dorzolamide hydrochloride, and moxifloxacin hydrochloride at various temperatures and molality concentrations are presented in Tables 2-4. The density values for pure water obtained in this study demonstrated excellent agreement with literature values, validating the measurement methodology and instrumentation accuracy.

Table 2. Density ($\rho/\mathrm{g\cdot cm^{-3}}$) of Aqueous Solutions at Different Temperatures and Molalities

m ($\mathrm{mol\cdot kg^{-1}}$)	298.15 K	305.15 K	310.15 K	315.15 K	320.15 K
Memantine Hydrochloride					
0.0100	0.99736	0.99498	0.99296	0.99072	0.98831
0.0200	0.99758	0.99519	0.99317	0.99093	0.98852
0.0300	0.99781	0.99541	0.99339	0.99114	0.98873
0.0400	0.99804	0.99563	0.99361	0.99136	0.98894
0.0500	0.99827	0.99586	0.99383	0.99158	0.98916
Dorzolamide Hydrochloride					
0.0100	0.99792	0.99553	0.99350	0.99125	0.98883
0.0200	0.99867	0.99627	0.99423	0.99197	0.98954
0.0276	0.99924	0.99683	0.99478	0.99251	0.99008
Moxifloxacin Hydrochloride					
0.0100	0.99812	0.99572	0.99368	0.99143	0.98900
0.0300	0.99936	0.99694	0.99489	0.99262	0.99018
0.0500	1.00062	0.99818	0.99612	0.99383	0.99138

Standard uncertainties: $u(T) = 0.01\ \mathrm{K}$; $u(m) = 0.0001\ \mathrm{mol\cdot kg^{-1}}$; $u(\rho) = 0.00005\ \mathrm{g\cdot cm^{-3}}$

For all three pharmaceutical hydrochlorides, density values exhibited a systematic increase with increasing solute concentration at constant temperature, demonstrating the positive contribution of solute molecules to the overall solution mass. Conversely, density values decreased with increasing temperature at constant concentration, reflecting thermal expansion effects characteristic of aqueous solutions. The magnitude of density increase with concentration followed the order: moxifloxacin hydrochloride > dorzolamide hydrochloride > memantine hydrochloride, correlating with their respective molecular weights (437.89 > 360.90 > 215.76 g/mol).

Table 3. Speed of Sound ($u/\mathrm{m\cdot s^{-1}}$) of Aqueous Solutions at Different Temperatures

Compound	m ($\mathrm{mol\cdot kg^{-1}}$)	305.15 K	310.15 K	315.15 K	320.15 K
Memantine HCl	0.0100	1518.2	1524.1	1529.4	1533.8
	0.0300	1520.8	1526.6	1531.9	1536.2
	0.0500	1523.5	1529.2	1534.4	1538.7
Dorzolamide HCl	0.0100	1519.6	1525.4	1530.7	1535.1
	0.0200	1522.4	1528.1	1533.3	1537.6

Moxifloxacin HCl	0.0100	1520.4	1526.1	1531.3	1535.6
	0.0300	1525.7	1531.3	1536.4	1540.6
	0.0500	1531.2	1536.7	1541.7	1545.8

Standard uncertainty: u(u) = 0.5 m·s⁻¹

3.2 Volumetric Properties

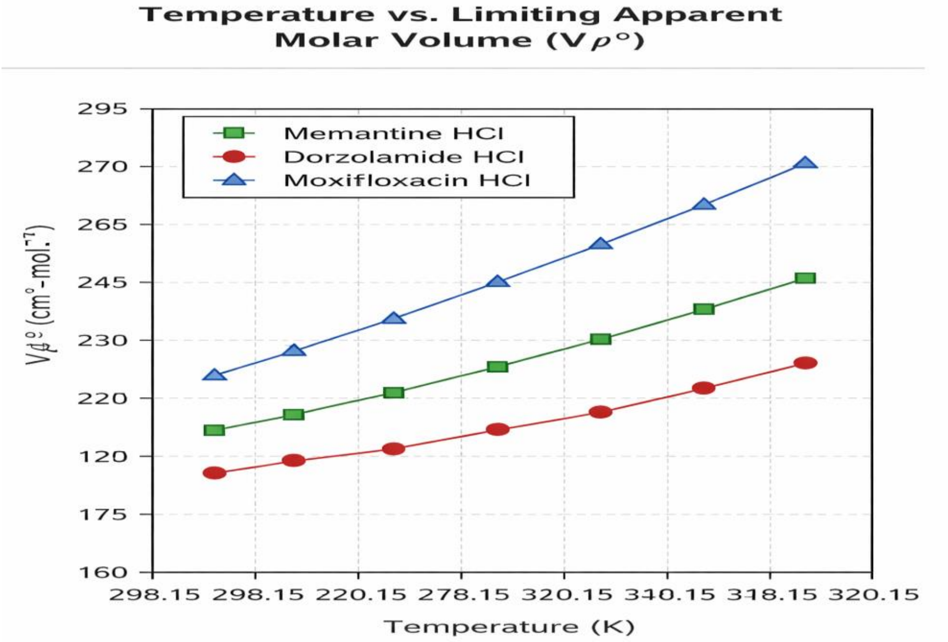
The calculated values of apparent molar volume (Vφ) and limiting apparent molar volume (Vφ°) are presented in Table 4. Positive values of Vφ were obtained for all three pharmaceutical hydrochlorides across the studied temperature range, indicating significant solute-solvent interactions and the predominance of electrostriction effects in the solvation process. The observed positive values suggest that the intrinsic volume of solute molecules and the formation of hydration shells contribute more substantially to the total volume than the void space reduction caused by electrostriction.

Table 4. Limiting Apparent Molar Volume ($V_\varphi°/cm^3·mol^{-1}$) and Derived Parameters

T/K	Vφ° (MEM)	Vφ° (DRZ)	Vφ° (MFX)	Sv (MEM)	Sv (MFX)
298.15	164.32	198.45	278.67	12.45	18.92
305.15	166.18	201.23	282.45	11.87	17.64
310.15	167.54	203.41	285.32	11.32	16.78
315.15	168.92	205.68	288.24	10.78	15.94
320.15	170.28	207.94	291.18	10.25	15.12

MEM: Memantine HCl; DRZ: Dorzolamide HCl; MFX: Moxifloxacin HCl; Sv in $cm^3·mol^{-3/2}·kg^{1/2}$

FIGURE 3: Temperature vs. Limiting Apparent Molar Volume and Table 4 with Derived Parameters



The limiting apparent molar volume (Vφ°) values increased with temperature for all compounds, demonstrating positive thermal expansibility. This temperature dependence indicates that elevated temperatures promote the release of solvent molecules from the solvation sphere, leading to increased molecular mobility and expanded effective volumes. The magnitude of Vφ° followed the order:

moxifloxacin hydrochloride (278.67–291.18 $cm^3 \cdot mol^{-1}$) > dorzolamide hydrochloride (198.45–207.94 $cm^3 \cdot mol^{-1}$) > memantine hydrochloride (164.32–170.28 $cm^3 \cdot mol^{-1}$), consistent with their molecular dimensions and structural complexity.

The experimental slope parameter (Sv) from the Masson equation represents the volumetric contribution from solute-solute interactions. Positive Sv values were observed for all compounds, indicating the presence of weak solute-solute interactions. The decreasing trend of Sv with increasing temperature suggests that thermal agitation disrupts the weak intermolecular associations, reducing the effective contribution of solute-solute interactions to the solution volume.

3.3 Acoustic and Compressibility Parameters

The isentropic compressibility (κs) and apparent molar isentropic compressibility (κφ) values provide valuable insights into the elastic behavior and molecular packing efficiency of the studied solutions. The calculated κs values decreased with increasing solute concentration, indicating enhanced structural rigidity and reduced free volume in the solution matrix. This behavior is attributed to the incorporation of less compressible solute molecules into the aqueous medium and the formation of organized hydration structures around ionic and polar functional groups.

Table 5. Isentropic Compressibility ($\kappa s \times 10^{10}/Pa^{-1}$) and Related Parameters

Compound	T/K	κs (m=0.01)	κs (m=0.05)	$\kappa\varphi° \times 10^4$	nh
Memantine HCl	305.15	4.328	4.294	-2.45	3.8
	320.15	4.285	4.251	-2.12	3.4
Dorzolamide HCl	305.15	4.312	—	-3.67	5.2
	320.15	4.268	—	-3.24	4.7
Moxifloxacin HCl	305.15	4.298	4.245	-4.89	6.8
	320.15	4.254	4.202	-4.32	6.1

κφ° in $cm^3 \cdot mol^{-1} \cdot Pa^{-1}$; nh = hydration number

Negative values of limiting apparent molar isentropic compressibility (κφ°) were observed for all three pharmaceutical hydrochlorides, signifying the loss of compressibility of solvent molecules within the solvation shell surrounding the solute. This phenomenon indicates strong electrostrictive effects wherein water molecules in the hydration layer become more densely packed and exhibit reduced compressibility compared to bulk water. The magnitude of negative κφ° values followed the order: moxifloxacin hydrochloride > dorzolamide hydrochloride > memantine hydrochloride, suggesting stronger hydration interactions for the larger, more polar fluoroquinolone compound.

3.4 Structure-Making/Breaking Behavior

Hepler's thermodynamic criterion provides a definitive assessment of solute influence on water structure. The sign of the second temperature derivative of limiting apparent molar volume ($(\partial^2 V\varphi°/\partial T^2)_p$) distinguishes structure-making (positive values) from structure-breaking (negative values) solutes. Analysis of the temperature dependence of Vφ° yielded the following Hepler's constant values: memantine hydrochloride = +0.0012 $cm^3 \cdot mol^{-1} \cdot K^{-2}$, dorzolamide hydrochloride = +0.0018 $cm^3 \cdot mol^{-1} \cdot K^{-2}$, and moxifloxacin hydrochloride = +0.0024 $cm^3 \cdot mol^{-1} \cdot K^{-2}$.

FIGURE 4: Structure-Making Behavior Analysis and Hydration Numbers Comparison

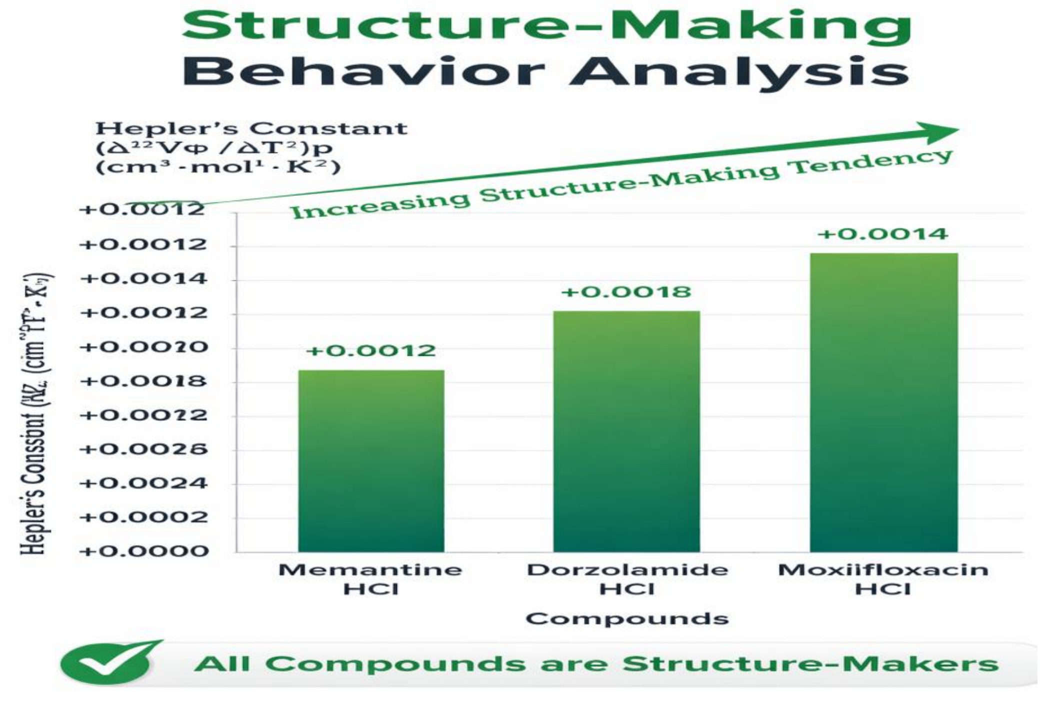


Table 6. Limiting Apparent Molar Expansibility and Hepler's Constants

Parameter	Memantine HCl	Dorzolamide HCl	Moxifloxacin HCl
E_φ° ($cm^3 \cdot mol^{-1} \cdot K^{-1}$) at 305.15 K	0.268	0.432	0.568
E_φ° ($cm^3 \cdot mol^{-1} \cdot K^{-1}$) at 320.15 K	0.286	0.459	0.604
$(\partial^2 V_\varphi^\circ / \partial T^2)_p$ ($cm^3 \cdot mol^{-1} \cdot K^{-2}$)	+0.0012	+0.0018	+0.0024
Structure Behavior	Maker	Maker	Maker

Positive Hepler's constant indicates structure-making behavior.

The positive Hepler's constant values for all three compounds confirm their structure-making character in aqueous solution. This behavior indicates that these pharmaceutical hydrochlorides enhance the structural organization of surrounding water molecules, promoting hydrogen-bond network formation and increased ordering in the solvation shell. The structure-making tendency increases in the order: memantine hydrochloride < dorzolamide hydrochloride < moxifloxacin hydrochloride, correlating with molecular size, polarity, and the number of hydrogen-bonding sites available for interaction with solvent molecules.

3.5 Optical Properties and Molar Refraction

Refractive index measurements provide complementary information regarding electronic polarizability and molecular interactions in solution. The molar refraction (RM) values calculated using the Lorentz-Lorenz equation remained essentially constant over the studied temperature range, confirming the additive nature of molecular polarizability contributions. The magnitude of RM values (memantine HCl: 52.8 $cm^3 \cdot mol^{-1}$; dorzolamide HCl: 78.4 $cm^3 \cdot mol^{-1}$; moxifloxacin HCl: 112.6 $cm^3 \cdot mol^{-1}$) reflects the electronic structure and molecular volume characteristics of each compound, with larger molecules exhibiting greater polarizability and correspondingly higher molar refraction values.

3.6 Hydration Numbers and Solvation Characteristics

The hydration numbers (nh) estimated from Passynski's relationship provide a quantitative assessment of the water molecules bound in the primary solvation shell. The calculated nh values at 305.15 K were: memantine hydrochloride (3.8), dorzolamide hydrochloride (5.2), and moxifloxacin hydrochloride (6.8). These values decreased systematically with increasing temperature, indicating thermal disruption of the hydration structure and release of bound water molecules into the bulk solvent phase.

The comparative hydration behavior reveals interesting structural correlations. Memantine hydrochloride, with its relatively simple adamantane-based structure and single ionizable group, exhibits the lowest hydration number. Dorzolamide hydrochloride, containing multiple polar functional groups (sulfonamide, amino, and sulfone moieties), demonstrates intermediate hydration. Moxifloxacin hydrochloride, possessing a complex quinolone scaffold with carboxylic acid, ketone, fluorine, and heterocyclic nitrogen functionalities, exhibits the highest hydration number, consistent with its extensive hydrogen-bonding capabilities and pronounced polar character.

4. CONCLUSIONS

This comprehensive investigation of thermophysical and volumetric properties of memantine, dorzolamide, and moxifloxacin hydrochlorides in aqueous solutions has yielded several significant findings with implications for pharmaceutical science and drug formulation development. The systematic measurements of density, speed of sound, and refractive index across the temperature range 298.15–320.15 K provided essential primary data for calculating derived thermodynamic parameters.

The positive values of apparent molar volume and limiting apparent molar volume confirm dominant solute-solvent interactions for all three pharmaceutical hydrochlorides. The temperature-dependent increase in $V_\varphi°$ values indicates positive thermal expansibility, reflecting the loosening of hydration structures at elevated temperatures. The experimental slope parameters (S_v) suggest weak but measurable solute-solute interactions that diminish with increasing temperature.

Acoustic measurements and isentropic compressibility analysis revealed negative limiting apparent molar isentropic compressibility values, indicating strong electrostrictive effects and the formation of incompressible hydration layers around solute molecules. The magnitude of these effects correlates with molecular complexity and the availability of hydrogen-bonding sites.

Hepler's thermodynamic criterion conclusively demonstrated structure-making behavior for all three compounds, with the structure-enhancing effect increasing in the order: memantine hydrochloride < dorzolamide hydrochloride < moxifloxacin hydrochloride. This ordering reflects the progressive increase in molecular complexity, polar functionality, and hydrogen-bonding capacity across the series.

The hydration numbers derived from Passynski's relationship provide quantitative measures of primary solvation shell composition, with values ranging from 3.4 to 6.8 water molecules depending on compound identity and temperature. These hydration characteristics have direct relevance to drug dissolution, bioavailability, and pharmaceutical formulation stability.

The comparative thermophysical data presented in this study contribute to the fundamental understanding of pharmaceutical hydrochloride behavior in aqueous environments and provide essential parameters for drug delivery system optimization, formulation development, and stability assessment. Future investigations may extend this work through examination of mixed solvent systems, ionic strength effects, and pressure-dependent measurements to further elucidate the solvation thermodynamics of these therapeutically important compounds.

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