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Thermodynamic Properties of Biologically Active Compounds: A Comprehensive Review

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Abstract: *The physico-chemical characterization of biologically active compounds (BACs) is essential for understanding their physiological behavior, formulation stability, and therapeutic efficacy. This review focuses current research on the volumetric, acoustic, and transport properties of various BACs, including amino acids, drugs, carbohydrates, and terpenes, across diverse solvent systems. Experimental parameters like density, speed of sound, and viscosity have been utilized to derive fundamental thermodynamic and transport quantities, such as partial molar volumes, isentropic compressibilities, and viscosity B-coefficients.*

Analysis of these properties through established theoretical frameworks, including the Masson and Jones-Dole equations, provides deep insights into solute-solute and solute-solvent interactions. The review highlights how solvent environments ranging from aqueous and mixed aqueous-organic systems to ionic liquids modulate the solvation behavior and hydration spheres of BACs. Temperature dependence study of these parameters further elucidates the structure-making or structure-breaking tendencies of solutes, often interpreted through Hepler's constant and the temperature derivative of the viscosity B-coefficient. This comprehensive overview underscores the role of thermo-acoustic and transport data in bridging molecular-level interactions with practical applications in pharmaceutical sciences and biochemistry.

Keywords: *physico-chemical characterization*

I. INTRODUCTION

The study of thermodynamic and transport properties of biologically active compounds (BACs) in solution is a cornerstone of modern biophysical chemistry. These properties provide a macroscopic window into the microscopic interactions occurring between solutes and their surrounding solvent environment [1, 2]. Understanding these interactions is critical for several fields, including drug design, protein stability, and the development of advanced delivery systems [3].

Drugs play an important role in human health and livestock rearing. Physicochemical properties of drugs are of great importance to understand the drug action at the molecular level. Local anesthetics drugs tend to have a vasodilator activity and therefore have a tendency to govern their own removal from the site of administration by increasing the local blood supply. These anesthetics, containing both lipophilic and hydrophilic groups, may penetrate the excitable cell and interfere with metabolic internal processes exerting their effects primarily at the excitable membrane. The excitable membranes so prepared conduct apparently normal impulses for long periods and can be blocked by local anesthetics [4]. Sodium and potassium are the primary positive ions in blood plasma and extracellular fluids. Bathe cells like sodium ions are vital in metabolic transport phenomena for nutrients and wastes in humans. They are also important in neuron function of the central nervous system across the nerve cell membrane and maintain osmoregulation between cells. Isotonic solution of sodium chloride is the component of body fluid and it contributes to the maintenance of concentration and charge difference across cell membrane. These ions through sodium and potassium channels combine with ATPase enzyme and act as active transporter pump across the concentration gradient. In nerves, drug showing fewer effects on

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sodium ion motion leads to diverse pharmacological and pharmacodynamic effects which range from anti-depressant to anti-seizure actions [5-6].

Biologically active molecules, such as amino acids, vitamins, and drugs, exhibit complex behavior in physiological environments [1], [7]. Their functionality often depends on their hydration state and their ability to interact with other biomolecules, which are reflected in their volumetric (density-based), acoustic (sound speed-based), and transport (viscosity-based) parameters [8-12]. For instance, the hydration of amino acids is a fundamental determinant of protein folding and stability [13]. Similarly, the solvation of drug molecules in aqueous or mixed solvent systems dictates their solubility, bioavailability, and pharmacokinetic profile [14], [15].

This review focuses on the systematic analysis of volumetric, acoustic, and transport properties of amino acids, drugs, and other bioactive molecules. It examines how these properties vary across different solvent systems, including pure water, mixed aqueous-organic solvents, and ionic liquids [16-18]. By synthesizing data from multiple studies, the review aims to provide a clear picture of the intermolecular forces such as hydrogen bonding, hydrophobic interactions, and ion-dipole forces that govern the behavior of BACs in solution.

II. EXPERIMENTAL AND THEORETICAL METHODS

The characterization of BACs relies on high-precision measurements of fundamental physical quantities. Recent literature emphasizes the use of advanced instrumentation to ensure data reliability across varying concentrations and temperatures.

2.1. Measurement Techniques

The primary experimental data required for these studies are density (ρ), speed of sound (u), and viscosity (η).

2.1.1 Density and Speed of Sound: Modern studies frequently utilize vibrating-tube densimeters and sound analyzers, such as the Anton Paar DSA 5000 M, which allow for simultaneous recording of density and ultrasonic speed with high precision (e.g., 10^{-6} g.cm^{-3} and ± 0.1 m·s^{-1}) [18], [21-23]. These measurements are typically conducted across a temperature range relevant to biological systems, often from 288.15 K to 323.15 K [4], [13].

2.1.2 Viscosity: Capillary viscometers, such as Ubbelohde or Ostwald types, are standard for measuring the flow time of solutions, which is then converted to kinematic and dynamic viscosity [24, 25].

2.1.3 Other Techniques: Some studies incorporate electrolytic conductivity to probe ion association in ionic liquid systems [15] and refractive index measurements to determine molar refractions [23], [32]. Electronic absorption spectra are occasionally used to provide complementary evidence of molecular interactions [14], [3].

2.2. Theoretical Models and Data Analysis

The measured raw data are processed using several established semi-empirical models to extract limiting parameters that represent infinite dilution behavior.

2.2.1 Masson Equation: Used to analyze the concentration dependence of apparent molar volume V_ϕ:

$$V_\phi = V_\phi^0 + S_V m$$

where V_ϕ^0 is the limiting apparent molar volume (representing solute-solvent interactions) and S_V is the experimental slope (representing solute-solute interactions) [32].

2.2.2 Jones-Dole Equation: Applied to viscosity data:

$$\eta_{\mathrm{r}} = 1 + A\sqrt{C} + BC$$

where the *A*-coefficient relates to ion-ion interactions and the *B* coefficient (viscosity B-coefficient) reflects the size of the solute and its interaction with the solvent [12], [32]. The temperature derivative dB/dT is a key indicator of the solute's structure-making ($dB/dT < 0$) or structure-breaking ($dB/dT > 0$) effect on the solvent [1], [14].

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2.2.3 Hepler's Constant: The values of $\partial^2 V_\phi^0 / \partial T^2$ can be useful in determination of structure making or structure breaking tendency of solute in aqueous solutions. According to the observation of Hepler [27] the sign of $\partial^2 V_\phi^0 / \partial T^2$ determines the structure maker or structure breaker tendency of particular solute dissolved in solvent. He suggests that structure-making solutes will have positive $\partial^2 V_\phi^0 / \partial T^2$, whereas for structure-breaking solutes, $\partial^2 V_\phi^0 / \partial T^2$ will be negative. [7], [10].

2.2.4 Redlich-Kister Equation: Often used for binary and ternary mixtures to correlate excess molar volumes and viscosity deviations across the full composition range [12].

2.2.4 Co-sphere Overlap Model: A qualitative framework used to interpret transfer properties, where the interaction between solute and co-solute is explained by the overlap of their respective hydration or solvation spheres [7], [19].

III. VOLUMETRIC PROPERTIES

Volumetric properties provide direct information about the space occupied by a solute and the resulting changes in solvent structure.

3.1. Partial Molar Volumes and Transfer Quantities

The limiting apparent molar volume $\left(V_\phi^0\right)$ is a critical parameter that represents the volume change upon adding one mole of solute to an infinite amount of solvent. For amino acids and drugs, V_ϕ^0 is generally positive and increases with temperature, reflecting the expansion of the solute and its hydration shell [13], [16].

Transfer volumes $\left(\Delta_{tr} V_\phi^0\right)$ are used to study the effect of co-solutes (e.g., salts, sugars, or ionic liquids). For example, the transfer of amino acids like L-serine and L-threonine from water to aqueous ionic liquid solutions results in positive $\Delta_{tr} V_\phi^0$ values [7]. This is typically explained by the dehydration of the solute's polar groups due to the presence of the co-solute, leading to a net increase in volume as water molecules are released from the electrostricted hydration shell into the bulk solvent [7], [16].

3.2. Expansivity and Solvation Behavior

Partial molar expansibilities $E_\phi^0 = \left(\partial V_\phi^0 / \partial T \right)$ and their derivatives provide insights into the thermal stability of the solvation shell. A positive E_ϕ^0 suggests that the solute-solvent interactions are sensitive to temperature [10], [18]. In studies of alpha-hydroxy acids and sodium benzoate, volumetric data confirmed that hydrophobic associations and specific solute-solvent interactions are the dominant forces governing stability and formulation efficacy [19].

The thermal expansion coefficient $\left(\alpha^*\right)$ of can be calculated using following equation:

$$\alpha^* = \frac{1}{V_\phi^0} \left[\frac{\partial V_\phi^0}{\partial T} \right]_P$$

It has been observed by Cabani et al. [28] that the coefficient of thermal expansion $\left(\alpha^*\right)$ can be used to interpret the solute- solvent interactions.

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IV. ACOUSTIC AND COMPRESSIBILITY PROPERTIES

Acoustic measurements, specifically the speed of sound, are highly sensitive to the structural changes and the "tightness" of the solvent around the solute.

4.1. Isentropic Compressibility and Hydration

Isentropic compressibility $\left(\kappa_S\right)$ and apparent molar isentropic compressibility $\left(K_\phi\right)$ are derived from density and speed of sound data. For most BACs in aqueous solutions, κ_S decreases with increasing concentration and temperature [20], [13]. This decrease is attributed to the fact that the water molecules in the hydration shell of the solute are less compressible than those in the bulk solvent due to the strong electrostatic field of the solute (electrostriction) [10]. The limiting apparent molar isentropic compressibility $\left(\kappa_\phi^0\right)$ and its transfer counterpart $(\Delta_{tr} K_\phi^0)$ are used to quantify hydration numbers $\left(n_H\right)$ [7], [10]. For instance, in ternary systems containing acetaminophen and ionic liquids, transfer compressibility values were positive, indicating the dominance of hydrophilic-hydrophilic interactions and the dehydration effect of the ionic liquid on the drug [7].

4.2. Thermo-Acoustic Parameters

Beyond compressibility, researchers derive several other parameters to characterize the internal state of the solution:

Free Volume (V_f) and Internal Pressure (P_i): These parameters are used to study molecular interaction dynamics. In aqueous amino acid solutions, variations in V_f and P_i provide a measure of the "available" space and the cohesive forces within the liquid matrix [1], [30].

Acoustic Impedance (Z) and Intermolecular Free Length (L_f): These indicate the ease with which sound waves travel through the medium and the distance between molecules, respectively. A decrease in L_f usually points to stronger intermolecular interactions [8], [14], [15].

Nonlinear Parameters: Some studies explore Gruneisen parameters and Bayer's non linearity parameter to explain anharmonicity and structural information in aqueous biomaterials like L-arginine and L-methionine [13].

V. TRANSPORT PROPERTIES

Transport properties describe the dynamics of solutes and the resistance to flow or movement within the solvent.

5.1. *Activation parameters of viscous flow* and Jones-Dole Coefficients

Viscosity measurements are essential for determining the viscosity B-coefficient. For many biologically active solutes, such as amino acids in the presence of drugs like cefepime or levocetirizine, the B-coefficient is positive, indicating that these solutes act as "structure makers" or "structure breakers" depending on the temperature dependence [3-4].

The viscosity data can analyzed on the basis of Eyring transition state theory. Activation parameters, Gibbs energy of activation per mole of solute and per mole of solvent have been evaluated by using Feakins *et al* [29]. According to this theory, the Jones Dole viscosity *B*-coefficient is given by the relation:

$$\Delta\mu_2^{0\#} = \left(\Delta\mu_1^{0\#}\right) + \frac{RT}{\bar{V}_1^0}\left[B - \left(\bar{V}_1^0 - \bar{V}_2^0\right)\right]$$

where $\Delta\mu_2^{0\#}$ is the contribution per mole of solute to the free energy of activation for viscous flow of solution and $\Delta\mu_1^{0\#}$ is the free energy of activation per mole of the solvent. $\bar{V}_1^0\left(= M / \rho_0\right)$ is the molar volume of the solvent, M is the molar mass of solvent and ρ_0 is density of the solvent and $\bar{V}_2^0\left(= V_\phi^0\right)$ is the limiting partial molar volume of solute. $\Delta\mu_1^{0\#}$ is calculated from the relation:

$$\Delta\mu_1^{0\#} = RT.\ln\left\{ \eta_0 \bar{V}_1^0 \big/ hN_a \right\}$$

Where, *h* is Planck's constant, *N*$_a$ is Avogadro's number and η_0 is viscosity of water.

According to Feakins *et al*., $\Delta\mu_2^{0\#} > \Delta\mu_1^{0\#}$ for solutes having positive viscosity *B*-coefficients indicates stronger ion-solvent interactions, suggesting the formation of a transition state which is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure.

The calculations of entropy $\left(\Delta S_2^{0\#}\right)$ and enthalpy $\left(\Delta H_2^{0\#}\right)$ of activation per mole of viscous flow can be calculated using following equations.

$$\Delta S_2^{0\#} = -\mathrm{d}\left(\frac{\Delta\mu_2^{0\#}}{\mathrm{d}T}\right)$$

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T\bullet\Delta S_2^{0\#}$$

The B/V_ϕ^0 values are important indicators as to whether a particular solute is solvated or unsolvated, a value between 0-2.5 points to unsolvated species, and any higher value tends to solvated ones.

These parameters quantify the energy barrier that must be overcome for the liquid to flow [5], [10]. In dioxane systems, $\Delta\mu$ has been shown to decrease linearly with concentration and temperature, while in THF systems, the trend can differ, highlighting the strong role of the solvent [5], [14].

Conductometric and Diffusion Studies

For ionic BACs or systems involving ionic liquids, conductivity measurements provide data on ion mobility and association. The low concentration Chemical Model (LCCM) is used to estimate limiting molar conductivities (Λ^0) and ion association constants (K_a) [15]. For [OMIm]Br in aqueous acetaminophen, the association process was found to be endothermic and entropy-driven, indicating that the breakdown of the solvation shell is a prerequisite for ion pairing [15]. Furthermore, compilations of diffusion data for carbohydrates like pentoses and hexoses are critical for modeling transport in biological membranes [33].

VI. COMPARATIVE ANALYSIS OF BIOACTIVE COMPOUNDS

The behavior of BACs is highly specific to their chemical structure and the nature of the solvent.

6.1. Amino Acids and Peptides

Amino acids (e.g., glycine, L-alanine, L-valine) serve as model compounds for proteins. Their volumetric and acoustic properties in various media (pure water, aqueous salts like $BaCl_2$, or drugs) reveal the relative strengths of ionic, hydrophilic, and hydrophobic interactions [1], [32]. For example, the interaction of L-arginine with D-fructose in aqueous solutions suggests significant intermolecular interactions that may affect the heat-denaturation temperature of proteins [22]. The presence of ionic liquids typically enhances the structure-making ability of amino acids through the cosphere overlap effect [21, 7].

6.2. Drugs and Pharmaceutical Additives

Pharmaceuticals like acetaminophen, cefepime, and levocetirizine exhibit distinct solvation patterns. Acetaminophen shows a strong dehydration effect in the presence of ionic liquids [7]. Levocetirizine dihydrochloride interactions with amino acids like L-proline and L-valine are dominated by hydrophobic associations, which have implications for its

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stability in drug delivery platforms [14]. Preservatives such as sorbic acid and parabens are studied in mixed glycols or isopropanol to optimize their solubility and efficacy in food and pharma products [31], [34].

6.3. Carbohydrates and Terpenes:

Carbohydrates (sugars like glucose, sucrose, and lactose) are often used as co-solutes to stabilize proteins or modulate drug behavior [2], [13]. Their own volumetric and transport properties are well-documented, with virial expansion models providing recommended parameters for aqueous solutions [20, 26, 33]. Terpenes (citral, limonene, linalool), used as biofuel additives or in fragrances, show behavior dominated by dispersive interactions in nonpolar solvents like chloroform, though citral can form hydrogen bonds [13].

VII. GAPS AND FUTURE DIRECTIONS

While the current literature provides an extensive database for binary and some ternary systems, several research gaps remain:

Complex Physiological Mixtures: Most studies focus on simplified models (1-2 co-solutes). Future research should aim to characterize BACs in more complex, multicomponent systems that better mimic physiological fluids (e.g., blood plasma).

Extreme Conditions: There is limited data on properties at high pressures or extreme pH levels, which are relevant for industrial processing and certain biological environments.

Computational Integration: While some studies use DFT to validate experimental results [7], a more robust integration of molecular dynamics (MD) simulations with thermo-acoustic data would provide a more detailed molecular-level picture of solvation.

Nanostructured Solvents: The behavior of BACs in deep eutectic solvents (DES) or specialized nano-emulsions is an emerging area with significant potential for enhancing drug solubility.

VIII. CONCLUSION

The volumetric, acoustic, and transport properties of biologically active compounds offer a wealth of information regarding molecular interactions in solution. By combining precision measurements of density, speed of sound, and viscosity with rigorous theoretical models like Masson and Jones-Dole equations, researchers can determine the solvation state, hydration numbers, and structural effects of various solutes.

The findings across the reviewed literature consistently highlight the sensitivity of these properties to solvent composition and temperature. Amino acids and drugs generally exhibit complex solvation behavior that is significantly modulated by the presence of co-solutes like sugars, salts, and ionic liquids. This knowledge is not only fundamentally important for biophysics but also practically essential for optimizing the formulation, stability, and delivery of pharmaceutical and food products. Continued research into more complex systems and the integration of computational modeling will further advance our understanding of these vital biochemical properties.

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