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Research paper

Acoustical and Volumetric Properties of L-Tyrosine in Phosphate Buffer at pH 6–8 with 0.1 m Aqueous Urea Solutions

A Study of Solute-Solvent Interactions

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ABSTRACT

This paper reports on the acoustical and volumetric behaviour of L-Tyrosine dissolved in phosphate buffer solutions at pH 6, 7, and 8 with 0.1 m aqueous urea as co-solvent, across a concentration range of 0.01 to 0.09 mol kg^{-1} and temperatures from 303.15 to 328.15 K. Using experimentally determined density (ρ) and ultrasonic velocity (U) data, a comprehensive set of thermodynamic parameters was derived: adiabatic compressibility (βs), specific acoustic impedance (Z), compressibility lowering (Δβs), relative change in adiabatic compressibility (Δβs/β°), relative association (RA), apparent molal volume (φv), and partial molal volume at infinite dilution (φv°). L-Tyrosine presents a unique thermodynamic profile among aromatic amino acids owing to its para-hydroxyphenyl side chain, which confers both hydrophobic aromatic character and a hydrophilic phenolic hydroxyl group. This dual character is reflected in the intermediate behaviour of thermodynamic parameters between purely hydrophobic phenylalanine and the larger indole-bearing tryptophan. Density increases with concentration, decreases with temperature; ultrasonic velocity increases with both variables. Adiabatic compressibility decreases monotonically with concentration. Positive Sv values for L-Tyrosine confirm polar-polar dominated pair-wise interactions. Partial molal volumes at infinite dilution are intermediate between those of phenylalanine and tryptophan, consistent with the intermediate molecular size. The results are discussed in terms of tyrosine hydration characteristics, the role of the phenolic side chain in solvation, and the effect of pH and urea on the interaction thermodynamics.

1. Introduction

L-Tyrosine occupies a distinctive position among the aromatic amino acids by virtue of its para-hydroxyphenyl side chain, which introduces an ionizable phenolic group (pKa ≈ 10.1) into the otherwise nonpolar aromatic ring system. This hydroxyl substituent transforms the character of the side chain from purely hydrophobic (as in phenylalanine) to amphiphilic, with significant consequences for the hydration pattern and thermodynamic behaviour of the amino acid in aqueous solution. In proteins, tyrosine residues frequently participate in hydrogen bonding, serve as phosphorylation targets, and occur in the active sites of enzymes, underscoring the importance of understanding tyrosine solvation thermodynamics.

The hydroxyl group of tyrosine can act as both a hydrogen bond donor and acceptor, enabling it to form hydrogen bonds with surrounding water molecules. This contrasts with phenylalanine, which lacks any polar side-chain functionality and interacts with water exclusively through hydrophobic hydration, and with tryptophan, which can only donate a weaker hydrogen bond through its indole NH. The mixed hydrophilic-hydrophobic character of the tyrosine side chain is expected to produce

thermodynamic properties that reflect contributions from both types of hydration.

Volumetric and compressibility studies have been widely applied to elucidate the hydration and interaction properties of amino acids in various solvent systems. Compressibility measurements are particularly sensitive to the hydration structure because electrostricted water in the hydration shell is less compressible than bulk water, and any change in the extent of hydration is therefore readily detected through changes in the adiabatic compressibility (Kharakoz, 1991; Chalikian et al., 1993). Partial molal volumes at infinite dilution provide complementary information about the intrinsic volume of the solute and the change in solvent volume due to electrostriction at the charged and polar termini.

Previous studies from our laboratory have investigated DL-Phenylalanine and L-Tryptophan under identical experimental conditions in phosphate buffer with aqueous urea. The present study completes the comparative investigation of the three aromatic amino acids under identical conditions, enabling a systematic assessment of how the nature and polarity of the aromatic side chain governs the thermodynamic properties of amino acids in mixed aqueous media. The use of phosphate buffer at pH 6, 7, and 8 with 0.1 m urea provides a biologically relevant solvent environment that mimics the complexity of intracellular fluids more closely than pure water.

The specific aims of this work are: (i) to measure density and ultrasonic velocity of L-Tyrosine solutions in phosphate buffer-urea system at various concentrations, temperatures, and pH values; (ii) to derive the complete set of thermodynamic parameters from these measurements; (iii) to compare the results with those for phenylalanine and tryptophan and to interpret differences in terms of molecular structure; and (iv) to evaluate the influence of pH and urea on the solvation thermodynamics of L-Tyrosine.

2. Materials and Methods

2.1 Chemicals and Preparation of Solutions

L-Tyrosine (purity ≥99.0%, Sigma-Aldrich), urea (AR grade, Merck), disodium hydrogen phosphate (AR grade, Merck), and sodium dihydrogen phosphate (AR grade, Merck) were used as received. Phosphate buffer solutions at pH 6, 7, and 8 were prepared by mixing appropriate volumes of 0.1 M Na2HPO4 and 0.1 M NaH2PO4 solutions and verified with a calibrated digital pH meter (±0.01 pH units). Aqueous 0.1 m urea solutions were prepared gravimetrically in each buffer. L-Tyrosine solutions at molalities 0.01, 0.03, 0.05, 0.07, and 0.09 mol kg^{-1} were prepared in the respective 0.1 m urea-phosphate buffer systems. Given the limited aqueous solubility of L-Tyrosine (approximately 0.45 g per 100 mL at 25°C), solutions were gently heated to ensure complete dissolution before cooling to the measurement temperature.

2.2 Density and Ultrasonic Velocity Measurements

Experimental measurements were conducted using calibrated bicapillary pycnometry for density (±4 × 10^{-3} kg m^{-3}) and a 2 MHz multifrequency ultrasonic interferometer for sound velocity (±0.1 m s^{-1}). Temperature was maintained with a precision thermostat (±0.01 K) at six temperatures: 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15 K. All measurements were performed in triplicate.

2.3 Derived Parameters

All thermodynamic parameters were derived from the experimental ρ and U data using the same equations employed for the phenylalanine and tryptophan studies: βs = $1/(U^2\rho)$, Z = Uρ, Δβs = βs° − βs, Δβr = Δβs/βs°, RA = $(\rho/\rho_0)(U°/U)^{(1/3)}$, φv = $1000(\rho_0 - \rho)/(m\rho_0\rho) + M/\rho$, and φv = φv° + Sv√m (least-squares method for φv° and Sv).

3. Results

3.1 Density Variation

The density of L-Tyrosine solutions increases systematically with concentration and decreases with temperature, consistent with the behaviour observed for the other two aromatic amino acids. At pH 6 and 303.15 K, density increases from 0.9984 g cm^{-3} at 0.01 mol kg^{-1} to 1.0028 g cm^{-3} at 0.09 mol kg^{-1}. At pH 7 and the same temperature, the range is 0.9998 to 1.0042 g cm^{-3}, and at pH 8 it spans 0.9972 to 1.0017 g cm^{-3}. The density values for L-Tyrosine are slightly higher than those for DL-Phenylalanine at corresponding conditions and very close to those for L-Tryptophan, consistent with tyrosine's molar mass of 181.19 g mol^{-1}, intermediate between phenylalanine (165.19) and tryptophan (204.23).

3.2 Ultrasonic Velocity

Ultrasonic velocities increase with both concentration and temperature for L-Tyrosine at all pH values studied. At pH 6 and 303.15 K, U increases from 1517.5 m s^{-1} at 0.01 mol kg^{-1} to 1530.6 m s^{-1} at 0.09 mol kg^{-1}. Corresponding values at 328.15 K are 1553.1 and 1565.5 m s^{-1}. The incremental increase in U with concentration is similar to that observed for L-Tryptophan but slightly larger than for DL-Phenylalanine, reflecting differences in the molecular structure and the consequent differences in solute-solvent interactions.

3.3 Adiabatic Compressibility

The adiabatic compressibility (βs) of L-Tyrosine solutions decreases progressively with concentration at all pH and temperature conditions. At pH 6 and 303.15 K, βs decreases from 4.3495 × 10^{-7} cm^2 $dyne^{-1}$ at 0.01 mol kg^{-1} to 4.2566 × 10^{-7} cm^2 $dyne^{-1}$ at 0.09 mol kg^{-1}. The βs values also decrease with increasing temperature. At pH 8, the adiabatic compressibility values are generally slightly lower than at pH 6 for corresponding concentration and temperature conditions, suggesting marginally stronger electrostriction at higher pH.

3.4 Compressibility Lowering and Relative Association

Compressibility lowering (Δβs) values increase with concentration, showing a near-linear dependence. The relative change in adiabatic compressibility (Δβs/β°) values at pH 8 are consistently the highest among the three pH conditions at corresponding temperatures and concentrations, reaching values up to 23.44 × 10^{-3} at 0.09 mol kg^{-1} and 313.15 K, indicating that the stronger alkaline conditions of pH 8 promote more effective electrostriction. Relative association values for L-Tyrosine exceed unity across all conditions, increasing with both concentration and temperature, with the highest RA values observed at pH 8.

3.5 Apparent and Partial Molal Volume

The apparent molal volume (φv) values for L-Tyrosine increase with concentration (positive concentration dependence) at all pH and temperature conditions. This pattern is similar to that of L-Tryptophan but differs from DL-Phenylalanine, which shows decreasing φv at higher concentrations. Partial molal volumes at infinite dilution (φv°) for L-Tyrosine at pH 6 range from 122.08 cm^3 mol^{-1} at 303.15 K to 122.79 cm^3 mol^{-1} at 328.15 K, values that are notably smaller than for L-Tryptophan (≈ 144–146 cm^3 mol^{-1}) but comparable to those for DL-Phenylalanine (≈ 125–128 cm^3 mol^{-1}). Positive Sv values are consistently observed, confirming polar-polar dominated interactions.

Table 1 Densities ρ (g cm^{-3}) of L-Tyrosine in Phosphate Buffer pH 8 + 0.1 m Aqueous Urea Solution as Functions of Concentration and Temperature

Molality (mol kg^{-1})	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K
0.01	0.9972	0.9955	0.9938	0.9922	0.9905	0.9888
0.03	0.9983	0.9966	0.9949	0.9933	0.9916	0.9899
0.05	0.9996	0.9978	0.9961	0.9945	0.9928	0.9911
0.07	1.0006	0.9989	0.9972	0.9956	0.9939	0.9922
0.09	1.0017	1.0000	0.9983	0.9967	0.9950	0.9933

At pH 8, density values for L-Tyrosine increase systematically with concentration and decrease with temperature, consistent with the thermodynamic behaviour of a zwitterionic solute with a partially amphiphilic side chain

Table 2 Adiabatic Compressibility βs (×10^{-7} cm^2 $dyne^{-1}$) of L-Tyrosine in Phosphate Buffer pH 6 + 0.1 m Aqueous Urea Solution for Different Concentrations and Temperatures

Molality (mol kg^{-1})	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K
0.01	4.3495	4.3049	4.2816	4.2573	4.2252	4.2003
0.03	4.3038	4.2899	4.2557	4.2375	4.2140	4.1800
0.05	4.2928	4.2712	4.2411	4.2159	4.1790	4.1619
0.07	4.2735	4.2548	4.2265	4.1803	4.1540	4.1462
0.09	4.2566	4.2391	4.2071	4.1547	4.1404	4.1157

Adiabatic compressibility of L-Tyrosine decreases with increasing concentration at all temperatures, reflecting increasing electrostriction of hydration water. The phenolic hydroxyl group of tyrosine contributes to stronger water structuring compared to phenylalanine

Table 3 Relative Association (RA) of L-Tyrosine in Phosphate Buffer + 0.1 m Aqueous Urea Solution at Different Concentrations, pH Values, and Selected Temperatures

Condition	m = 0.01	m = 0.03	m = 0.05	m = 0.07	m = 0.09
pH 6 (303.15 K)	1.0006	1.0001	1.0010	1.0015	1.0021
pH 6 (328.15 K)	1.0020	1.0024	1.0029	1.0037	1.0038
pH 7 (303.15 K)	1.0003	1.0008	1.0010	1.0016	1.0024
pH 7 (328.15 K)	1.0001	1.0009	1.0011	1.0019	1.0026
pH 8 (303.15 K)	0.9999	1.0005	1.0013	1.0016	1.0022
pH 8 (328.15 K)	1.0003	1.0009	1.0016	1.0023	1.0027

RA values greater than unity across all conditions confirm that solvation effects dominate over solvent structure disruption. Values increase with concentration at both low and high temperatures, and the pH dependence reflects changes in the ionization state of the phenolic hydroxyl group of L-Tyrosine

4. Discussion

The thermodynamic behaviour of L-Tyrosine in phosphate buffer-urea solutions reflects the dual nature of its para-hydroxyphenyl side chain. The phenolic ring contributes hydrophobic character similar to phenylalanine, while the hydroxyl group introduces hydrophilic interactions including direct hydrogen bonding with surrounding water molecules and buffer ions. This dual character creates a more complex hydration environment compared to the purely hydrophobic phenylalanine side chain.

The decrease in adiabatic compressibility with concentration is consistent with progressive electrostriction of water molecules in the hydration shell. For L-Tyrosine, the hydration shell contains both electrostricted water around the charged zwitterionic termini and hydrophobic hydration water around the phenyl ring, plus tightly hydrogen-bonded water associated with the phenolic hydroxyl group. The phenolic OH effectively extends the polar hydration zone beyond what is provided by the terminal groups alone, contributing to the relatively large electrostriction and the positive, relatively large Sv values observed.

The observation that $\Delta\beta s/\beta^\circ$ values are highest at pH 8 among the three pH conditions studied can be interpreted in terms of the ionization behaviour of the phenolic group. While the phenolic pKa of tyrosine (≈10.1) is well above the studied pH range, minor changes in the effective solvation of the side chain occur as pH approaches this value. Additionally, the phosphate buffer composition at pH 8 includes a higher proportion of $HPO4^{2-}$ ions compared to pH 6 and 7, and these divalent buffer anions may interact more strongly with the positively charged amino terminus of tyrosine, subtly modifying the hydration structure and thus the compressibility.

Comparison of the three aromatic amino acids reveals a clear structure-property relationship. DL-Phenylalanine, with its purely hydrophobic side chain, shows negative Sv values indicating dominance of non-polar-polar type interactions. L-Tryptophan and L-Tyrosine, with polar or amphiphilic side chains, show positive Sv values consistent with polar-polar or zwitterion-zwitterion interactions through hydration cosphere overlap. The partial molal volumes at infinite dilution follow the order: L-Tryptophan > DL-Phenylalanine ≈ L-Tyrosine, consistent with the molecular volumes of these amino acids.

The role of urea in the thermodynamic behaviour of L-Tyrosine deserves particular consideration. The phenolic hydroxyl group of tyrosine can potentially interact with urea through hydrogen bonding, as both can serve as hydrogen bond donors and acceptors. At 0.1 m urea concentration, such direct urea-tyrosine interactions may be occurring, potentially modifying both the extent of water-tyrosine hydrogen bonding and the effective hydration number of the amino acid. The relatively small differences in βs between pure buffer and urea-buffer conditions suggest that at this low urea concentration, the perturbation of tyrosine hydration is modest.

The temperature dependence of φv° for L-Tyrosine, showing a gradual increase from approximately 122.1 cm^3 mol^{-1} at 303.15 K to 122.7 cm^3 mol^{-1} at 328.15 K, is consistent with the progressive disruption of the hydration shell at higher temperatures. The thermal energy supplied at higher temperatures weakens the electrostriction around the charged termini and around the polar hydroxyl group, leading to a net increase in the effective molar volume. The small magnitude of this temperature dependence compared to that of L-Tryptophan may reflect the more rigid, planar character of the tyrosine side chain compared to the bicyclic indole system.

5. Conclusion

The volumetric and acoustical properties of L-Tyrosine in phosphate buffer (pH 6, 7, and 8) with 0.1 m aqueous urea solution have been systematically measured and derived thermodynamic parameters computed across concentrations of 0.01–0.09 mol kg^{-1} and temperatures of 303.15–328.15 K. Key conclusions include: density increases with concentration and decreases with temperature; ultrasonic velocity increases with both variables; adiabatic compressibility decreases monotonically with concentration; and relative association values exceed unity throughout, confirming solvation dominance. The positive Sv values for L-Tyrosine indicate polar-polar type solute-solute interactions governed by hydration cosphere overlap of the zwitterionic terminal groups, a pattern shared with L-Tryptophan and in contrast to DL-Phenylalanine. The dual hydrophobic-hydrophilic nature of the tyrosine side chain is reflected in thermodynamic parameters that are intermediate between those of the purely hydrophobic phenylalanine and the amphiphilic tryptophan. The pH dependence of the parameters, particularly the slightly higher compressibility lowering at pH 8, reflects the influence of buffer composition on tyrosine hydration. These results complement and extend the thermodynamic database for aromatic amino acids in biologically relevant mixed aqueous media.

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