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Review

Viscosity *B*-coefficients and standard partial molar volumes of amino acids, and their roles in interpreting the protein (enzyme) stabilization

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Abstract

This review systematically surveys the viscosity *B*-coefficients and standard partial molar volumes of amino acids at various temperatures as these data are quite important for interpreting the hydration and other properties of peptides and proteins. The effect of organic solutes and various ions on the viscometric and volumetric properties of amino acids has also been discussed in terms of their kosmotropic ('structure-making') effects on the hydration of amino acids. The comparison of these effects on the amino acid hydration enables us to have a better understanding of the influence of organic solute and salt on the protein stabilization. In addition, the viscometric and volumetric behaviors of amino acid ions (cations and anions) are also summarized because these ions have recently been incorporated as part of novel ionic liquids, which have wide applications in biocatalysis and protein stabilization.

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Keywords: Amino acid; Viscosity B-coefficient; Standard partial molar volume; Ion; Protein; Ionic liquid

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1. Introduction

The stabilization of native conformations of biological macromolecules is commonly related to several non-covalent interactions including hydrogen bonding, electrostatic and hydrophobic interactions. These interactions are affected by the surrounding solutes and solvent of macromolecules; for this reason, the physico-chemical behaviors of proteins are strongly influenced by the presence of solutes. Because of direct solutesolvent interactions and/or alteration of the water structure, these solutes can change many properties of globular proteins such as their hydration, solubility, stability and the activity of enzymes [1-5]. However, due to the complex conformational and configurational three-dimensional structures of proteins, direct investigations of the solute/solvent effect on these biological macromolecules are very challenging. On the other hand, the interpretation of behaviors of model compounds such as amino acids and peptides are quite helpful in understanding the water-protein interactions in solutions. Especially, viscometric and volumetric properties (such as viscosity Bcoefficients and standard partial molar volumes) as well as changes in enthalpy and free energy in water and solutions of organic solvents or salts can provide valuable clues for comprehending the protein unfolding [6] and the hydrophobic interactions of non-polar side chains [7].

The second reason of studying viscometric and volumetric properties of amino acids is that many amino acids and their derivatives are known as compensatory (or compatible) solutes in stabilizing proteins and enhancing enzyme activity [8-10]. Since amino acids are zwitterions in aqueous solutions, their hydrations and interactions with proteins have resemblances with those of electrolytes [11]. To list a few examples, the effect of glycine and β -alanine on the activity of bovine carbonic anhydrase was found similar to that of kosmotropic acetate anion [12]. Amino acid salts were investigated as effective solutes in stabilizing the pig heart mitochondrial dehydrogenase (phm-MDH) against temperature induced changes; the order of stabilization is NaGlutamate, NaAspartate>NaGlycinate> lysine·HCl>arginine·HCl [13]. Ny-Acetyldiaminobutyrate (NADA) was observed having a stronger ability in protecting the rabbit muscle lactate dehydrogenase against thermal inactivation than ectoine or potassium diaminobutyrate [14]. Glycine, alanine and proline (as well as TAMO and betaine) showed non-perturbing or favorable effects on the enzymesubstrate and enzyme-cofactor complex formation, catalytic velocity and protein structural stability [15]. While amino acids have unique zwitterionic structures, the viscosity Bcoefficients and standard partial molar volumes of amino acids (as well as their ions) allow us to compare the ability of amino acids in stabilizing proteins.

Strongly hydrated solutes are known as kosmotropes ('structure-makers'), while weakly hydrated ones are chaotropes ('structure-breakers') [16–19]. For ionic solutes, it has been established that following the Hofmeister series, strong kosmotropic anions stabilize proteins and strong kosmotropic cations destabilize them [1,5,20–23]. The kosmotropic effect of ions and compatible solutes including amino acids on the

enzyme activity has been discussed in our recent review [10]. The kosmotropicity of ions can be quantified by the viscosity *B*-coefficients, hydration entropies, hydration volumes, heat capacities, NMR B'-coefficients, ion mobility, etc. [19,24].

The viscosity *B*-coefficients of various ions (mostly inorganic) in water and non-aqueous solutions at different temperature have been systematically reviewed by Jenkins and Marcus [25]. Although the viscosity *B*-coefficients and standard partial molar volumes of amino acids have been summarized in some articles [11,26–34], most of them are outdated and lack of systematic analysis of experiment work. Meanwhile, with the increasing application of ionic liquids (ILs) in biocatalysis (see recent reviews [35–46]) and the development of novel ionic liquids based on amino acid anions [47] or cations [48], there is also an urgent need of summarizing the viscometric and volumetric properties of amino acids, and interpreting the effect of amino acids, and their corresponding anions or cations on the protein (enzyme) stabilization.

2. Viscosity *B*-coefficients of zwitterionic amino acids in pure water

The Jones-Dole empirical equation (Eq. (1)) describes the relative viscosities of electrolyte solutions as functions of their concentrations [49]. The origin of this equation was described in details by Jenkins and Marcus [25].

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2... \tag{1}$$

where η is the viscosity of the solution and η_0 is the viscosity of the solvent. The A-coefficient (also called Falkenhagen coefficient [50], reflecting solute-solute interactions) can be calculated theoretically but are usually small (negligible for nonelectrolytes) [25]; therefore, it is often ignored in many correlations. For most salts at low concentrations [(<0.5 M)][25] or (<0.1 M for binary strong electrolytes) [51]], the D or higher coefficients can be omitted although they are necessary at higher concentrations [25]. Generally, viscosity B-coefficients reflect the solute-solvent interactions, while D-coefficients indicate the solute-solute interactions as well as the solutesolvent interactions [52]. This equation was initially developed for solutions of strong electrolytes. However, for aqueous solutions of amino acids, Eq. (1) is also valid (usually with the omission of A-coefficient, see references of Table 1) despite amino acids are weak electrolytes probably because they are zwitterionic (NH $_3^+$, COO⁻). In fact, when both A- and Dcoefficients are neglected in Eq. (1), this equation is equivalent to the Einstein's viscosity equation for non-electrolyte solutions [25]. Due to the hydrophobic alkyl groups and polar zwitterionic groups, the behavior of amino acids in solutions is somewhat between strong electrolytes and non-electrolytes [53].

In general, positive *B*-coefficients suggest kosmotropes since strongly hydrated solutes exhibit a larger change in viscosity with concentration, while negative *B*-coefficients indicate chaotropes for weakly hydrated solutes [19,25,54]. However, the *B*-coefficients may not be indicative especially for large hydrophobic solutes. For example, tetramethylammonium cation (Me₄N⁺) has a positive *B*-value as high as 0.123 [25], Download English Version:

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