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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.

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

Contents

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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 solute–solvent 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 *B*-coefficients 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]. *N*γ-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 enzyme–substrate and enzyme–cofactor complex formation, catalytic velocity and protein structural stability [15]. While amino acids have unique zwitterionic structures, the viscosity *B*-coefficients 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].

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \ldots \quad (1)$$

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 non-electrolytes) [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 solute–solvent 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 *D*-coefficients 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 (Me_4N^+) has a positive *B*-value as high as 0.123 [25],

but this ion is considered as a structure-breaker as suggested by many studies [19,55–59]. Similarly, in Table 1, amino acids have relatively large *B*-coefficients, but not all of them are kosmotropic as discussed later in this review. One improvement is to divide the *B*-coefficient by the standard partial molar volume V_ϕ^o (also called 'the limiting apparent molar volume') of the solute because large molecules usually exhibit greater *B*-coefficients [25,60]. A high B/V_ϕ^o value is an indication of the formation of a primary salvation shell [61]. The B/V_ϕ^o ratio lies between 0 and 2.5 for unsolvated spherical species [62]; for example, the tetramethylammonium and betaine belong to the unsolvated category [63]. The second improvement of the *B*-coefficient is to use its first derivative over temperature. The reason is because the sign of d*B*/d*T* is more indicative in measuring the structure-making or -breaking ability than sign or quantity of the *B*-coefficient [25,60,64,65]. The negative sign of d*B*/d*T* means structure-making (kosmotropic) while the positive sign suggests structure-breaking (chaotropic). The theoretical background of d*B*/d*T* is based on the Eyring's theory of viscosity [66], i.e., a negative value of d*B*/d*T* is equivalent to the energy of activation for viscous flow being greater for the solution than for the pure solvent. The sign of d*B*/d*T* of amino acids is determined by the net effect of the hydrophobic structure stabilization by non-polar (CH_2) groups and the structure disruption by (NH_3^+, COO^-) groups [67]. For these reasons, the values of *B*, B/V_ϕ^o and d*B*/d*T* are all listed in Table 1. The hydration numbers n_H (or solvation numbers) in Table 1 illustrate the degree of hydration of amino acids by water molecules.

Glycine has *B*-coefficients increasing with temperature (positive d*B*/d*T*). Although glycine has high values of *B* and B/V_ϕ^o (suggesting a primary solvation shell formed), this simplest amino acid is classified as a structure-breaker [60,65,68]. In the series of glycine–sarcosine–dimethylglycine–betaine, an increase in *B*-values is observed but a decrease of B/V_ϕ^o ratios is also seen in Table 1. The increase of *B*-values suggests an increase of kosmotropicity. Sarcosine is a borderline ion based on the fact that its *B*-coefficients are almost independent of temperature from 5 to 20 °C [61]. However, Tsangaris and Martin [60] considered this amino acid as a structure-maker based on their observation that the *B*-coefficients decrease with *T* between 30 and 45 °C. Dimethylglycine has a rather negative d*B*/d*T* (-1.2×10^{-3} dm^3 mol^{-1} K^{-1}), qualifying this amino acid as a kosmotrope. Betaine has *B*-coefficients that are almost independent of temperature from 5 to 20 °C, suggesting this solute is not a structure-builder [61]. Meanwhile, Sandhu and Singh [69] observed positive values of d*B*/d*T* for L-proline and L-hydroxyproline implying structure-breaking. However, betaine and proline are known as two of the most important compensatory solutes (along with ectoines and *N*-acetylated ornithine/lysine) in nature with structure-making ability [8,9,70,71]. Using the near-infrared (NIR) spectroscopy measurement, Galinski et al. [70] confirmed that betaine is a structure-forming solute based on its free water factor (0.742) lower than 0.8 and its relatively high hydration number (2.9) as compared to that of glycine (2.2) (see hydration numbers in bold in Table 1).

Alanine has a negative d*B*/d*T* in pure water; thus, it is considered as a kosmotrope [72]. β-Alanine has a slightly positive d*B*/d*T* value, but smaller than that of glycine. In addition, it has a smaller hydration number than α-alanine because of a larger charge separation in β-alanine [73], which is consistent with the data of Ogawa et al. [74]. Based on these experimental data, β-alanine is a weaker kosmotrope than α-alanine. However, a contradictory result was reported by Mason et al. showing that both α- and β-alanine are structure-makers based on their differential entropies of dilution and differential activation energies for viscous flow [75]. This discrepancy was explained due to the experimental variations of the overall effect of polar groups and hydrophobic groups in amino acids [72].

Awasthi and Rastogi [76] noticed that d*B*/d*T* is positive for acidic amino acids such as DL-aspartic and DL-glutamic acids implying structure-breaking, while negative for basic amino acids such as L-histidine and L-arginine implying structure-making (Table 1). The reason was explained as the protonation of water by acidic amino acids (protic behavior) causing the breakage of hydrogen bonds and the deprotonation of water by basic amino acids (aprotic behavior) enhancing the hydrogen bonding [76]. However, arginine is well known as a perturbing (destabilizing) solute of proteins [8].

Other amino acids in Table 1 are generally kosmotropes with varying degrees of structure-making abilities [8]. *B*-coefficients of homologous series of α-amino acids were found linear with the number of carbon atoms (n_c) on their alkyl chains at certain temperatures. An early correlation of several amino acids by Daniel and Cohn [77] yielded a simple relationship of $B=0.052+0.10\times n_c$. This linearity can be further generalized into

$$B = B(NH_3^+, COO^-) + n_c B(CH_2) \quad (2)$$

where $B(NH_3^+, COO^-)$ and $B(CH_2)$ are contributions of the polar groups and the hydrophobic groups to the *B*-coefficient, respectively [78]. It has been known that the polar groups of NH_3^+ and COO^- disrupt the water structure, while hydrophobic groups of CH_2 have structure-promoting effect in stabilizing the water structure [65,72,79]. With an increase in the alkyl chain (CH_2) length in an amino acid, the contribution of $B(CH_2)$ is increased in Eq. (2), resulting in a higher *B*-coefficient and thus a higher kosmotropicity of the amino acid.

To further illustrate the relationship between the hydrophobicity of amino acids and their kosmotropicity, the *B*, B/V_ϕ^o and d*B*/d*T* were correlated with the hydrophobicity scale (log *P*), respectively, for several amino acids (Fig. 1). Log *P* is known as the partition coefficient between octanol and water [80]. At first, we compared the log *P* scale with another hydrophobicity scale known as Δf_i values [81] (for transfer of amino acid side chain from 100% organic solvent to water at 25 °C), and a linear relationship (correlation coefficient 0.925) was found between these two scales (Fig. 1). This linearity confirmed the validity of using the log *P* scale to represent the hydrophobicity of amino acids. Improved correlation coefficients were obtained in an increasing order of B/V_ϕ^o (0.412), *B* (0.881) and d*B*/d*T* (0.965). This observation demonstrated that the *B*-coefficients increase with the hydrophobicity of amino acids and d*B*/d*T* is a better hydrophobicity (and thus kosmotropicity) indicator than the *B*-

Table 1
Viscosity *B*-coefficients of amino acids at various temperatures in $dm^3\ mol^{-1}$ and dB/dT in $dm^3\ mol^{-1}\ K^{-1}$

Amino acid	*B*-coefficient at 25 °C			B/V_ϕ^o (25 °C)	$dB/dT \times 10^3$ (*T* range, °C)	n_H (25 °C)[b]	Log *P*	*B*-coefficient (at other temperature, °C)
	Selected (average)[a]	Included in average	Not included					
Glycine (Gly)	0.143	0.143,[c,g,s,u,cc,jj] 0.1427,[e] 0.149,[h] 0.146,[k] 0.135,[q] 0.137[kk]	0.14193,[l] 0.1534,[j] 0.132,[bb] 0.134[hh]	**3.31**,[nn] 3.33,[c,g] 3.31,[e,s] 3.47,[h] 3.36[k]	1.4 (15–25),[c] 1.1 (5–20),[d] 0.9 (5–35),[k] 0.45 (25–45)[jj]	2.72,[h] 2.63,[i] 2.64,[s] 3.34,[u] **2.2**,[w] 3.52 or 2.63,[y] 2.9,[z] 3.26,[aa] 3.02[gg]	−3.11,[ll] −3.00[mm]	0.1164 (5),[d] 0.1227 (5),[k] 0.1230 (10),[d] 0.129 (15),[c] 0.1273 (15),[d] 0.132 (15),[k] 0.151 (16),[x] 0.1339 (20),[d] 0.131 (30),[f] 0.137 (30),[bb,ee] 0.139 (35),[f] 0.1466 (35),[k] 0.14470 (35),[l] 0.148 (35),[n,jj] 0.153 (35),[cc] 0.142 (35),[hh] 0.144 (40),[f] 0.152 (40)[x] 0.145 (40),[bb,ee] 0.151 (45),[hh] 0.152 (45)[jj]
N-Methylglycine (sarcosine)				3.07 (20)[d]	0.07 (5–20)[d]	**2.8**[w]		0.1926 (5),[d] 0.1948 (10),[d] 0.1960 (15),[d] 0.1933 (20),[d] 0.147 (30),[f] 0.143 (35),[f] 0.136 (40)[f]
Dimethylglycine				2.62 (20)[d]	−1.2 (5–20)[d]	**2.7**[w]		0.2232 (10),[d] 0.215 (15),[d] 0.211 (20)[d]
Trimethylglycine (glycine betaine)			0.227,[bb]	2.25 (20)[d]	0.5 (5–20)[d]	**2.9**,[w]		0.2143 (5),[d] 0.2153 (10),[d] 0.2173 (15),[d] 0.2212 (20),[d] 0.175 (30),[f] 0.226 (30),[bb] 0.199 (35),[f] 0.225 (35),[bb] 0.201 (40),[f] 0.225 (45),[bb]
Alanine (Ala)	0.252	0.246,[h] 0.258,[k] 0.253,[jj] 0.247−L,[q] 0.251,[s,u] 0.250,[cc] 0.258[kk]	0.25253,[l] 0.253,[n] 0.2525,[v] 0.241[hh]	**4.17**,[nn] 4.08,[h] 4.2 5,[k] 4.15[s]	−0.8 (30–40),[g] −1.0 (5–35),[k] −0.40 (25–45)[jj]	3.49,[h] 3.43,[s] 3.17,[u] 4.65 or 3.41,[y] 3.8,[z] 2.89,[aa] 2.86[gg]	−2.74,[ll] −2.77[mm]	0.278 (5),[k] 0.269 (15),[k] 0.259 (15),[o] 0.281 (16),[x] 0.241 (30),[g] 0.240 (30),[ee] 0.250 (35),[k] 0.23633 (35),[l] 0.247 (35),[n,jj] 0.241 (35),[cc] 0.244 (35),[dd] 0.243 (35),[ee] 0.255 (35),[hh] 0.233 (40),[g] 0.247 (40),[ee] 0.238 (45),[dd] 0.257 (45),[hh] 0.245 (45)[jj]
β-Alanine	0.201	0.220,[c] 0.168,[h] 0.216[q]	0.22473,[l]	**3.44**,[nn] 3.80,[c] 2.89[h]	0.5 (15–25)[c]	**2.8,**[w] 2.97[gg]		0.215 (15),[c] 0.21620 (35),[l] 0.232 (35),[ee] 0.220 (40)[ee]
Valine (Val)	0.414	0.3811,[e] 0.447,[k] 0.4052,[m] 0.423−L[u]		**4.56**,[nn] 4.20,[e] 4.92[k]	−3.6 (5–35)[k]	3.21,[h] 3.71−L,[u] 5.18 or 3.43−L,[y] 3.9−L,[z] 3.48−L[gg]	−2.26,[ll] −2.29[mm]	0.526 (5),[k] 0.487 (15),[k] 0.418 (35)[k]
Norvaline (Nval)	(0.3710)	0.3710[p]		4.04[p]	−3.8 (15–30)[p]	5.5[p]		0.4063 (15),[p] 0.3993 (20),[p] 0.3519 (30)[p]
Leucine (Leu)	0.533	0.487,[k] 0.537−L,[s] 0.576−L[u]	0.453−L[hh]	**4.95**,[nn] 4.53,[k] 4.98−L[s]	−5.6 (5–25)[k]	4.96,[i] 4.95−L,[s] 3.87−L,[u] 7.09 or 4.96−L,[y] 5.5−L,[z] 3.56−L[gg]	−1.79,[ll] −1.72[mm]	0.599 (5),[k] 0.540 (15),[k] 0.483 (35)[k]
Isoleucine (Ilu)						3.56−L[gg]	−1.69,[ll] −1.80[mm]	
Norleucine (Nleu)	(0.4543)	0.4543[p]		4.22[p]	−4.8 (15–30)[p]	5.3[p]		0.5011 (15),[p] 0.4925 (20),[p] 0.4342 (30)[p]
Serine (Ser)	0.237	0.2072,[e] 0.278−L,[h] 0.238−L,[k] 0.225−L[q]		**3.91**,[nn] 3.43,[e] 4.60−L,[h] 3.91−L[k]	−0.2−L (5–35)[k]	3.9−L,[h] 3.33−L[gg]	−3.07,[ll] −3.00[mm]	0.2420−L (5),[k] 0.241−L (15),[k] 0.237−L (35)[k]
Threonine (Thr)	0.342	0.346−L,[o,t] 0.335−L[q]		**4.45**[nn]	0.6−L (15–25),[o,t] −3.1−L (25–35)[o,t]	3.38−L,[h] 3.53−L[gg]	−2.94,[ll] −2.83[mm]	0.340−L (15),[o,t] 0.315−L (35)[o,t]
Methionine (Met)						6.17[h]	−1.87,[ll] −2.10[mm]	

Aspartic acid (Asp)	(0.13)	0.13[ii]			4.0 (25–40)[ii]		−3.61[mm]	0.15 (30),[ii] 0.17 (35),[ii] 0.19 (40)[ii]
Asparagine (Asn)							−3.48[mm]	
Glutamic acid (Glu)	(0.29)	0.29[ii]			2.6 (25–40)[ii]	3.87−L[gg]	−0.94,[ll]	0.31 (30),[ii] 0.32 (35),[ii] 0.33 (40)[ii]
							−3.51[mm]	
Glutamine (Gln)							−3.11[mm]	
Arginine (Arg)	(0.5013)	0.5013[e]	0.36−L[ii]	4.05[e]	−2.6 (25–40)[ii]		−1.99,[ll]	0.34−L (30),[ii] 0.33−L (35),[ii] 0.32−L (40)[ii]
							−3.79[mm]	
Lysine (Lys)							−1.15,[ll]	
							−3.77[mm]	
Histidine (His)	(0.39)	0.39−L[ii]			−2.6 (25–40)[ii]		−1.91,[ll]	0.38−L (30),[ii] 0.37−L (35),[ii] 0.35−L (40)[ii]
							−2.85[mm]	
Phenylalanine (Phe)	(0.585)	0.585−L[s]		4.81−L[s]		4.94,[h] 5.22,[i]	−1.43,[ll]	
						5.14,[s] 3.71−L[gg]	−1.44[mm]	
Tyrosine (Tyr)							−2.03,[ll]	
							−2.11[mm]	
Tryptophan (Trp)							−1.11,[ll]	
							−1.15[mm]	
Proline (Pro)	0.268	0.2140,[e] 0.285−L,[o,t]		**3.24**,[nn] 2.59[e]	0.2−L (15–25),[o,t]	**2.9**,[w] 2.59−L[gg]	−2.54,[ll]	0.283−L (15),[o,t] 0.354 (30),[f] 0.269
		0.279,[q] 0.277−L[ff]			−10.8 (30–40),[f]		−2.62[mm]	(35),[f] 0.297−L (35),[ff] 0.246 (40),[f]
					2.20−L (25–45)[ff]			0.321−L (45)[ff]
Hydroxyproline	0.280	0.281,[q] 0.279−L[ff]		**3.31**[nn]	1.95−L (25–45)[ff]			0.300−L (35),[ff] 0.318−L (45)[ff]
2-Aminobutanioc acid	0.328	0.299,[h] 0.352,[k] 0.3606,[m]	0.319[n,ij]	**4.34**,[nn] 3.97,[h] 4.64,[k]	−2.3 (5–35),[k]	5.6,[p] 3.16[u]		0.402 (5),[k] 0.379 (15),[k] 0.3130
(α-amino-*n*-butyric		0.2950,[p] 0.338,[s] 0.325[u]		3.90,[p] 4.47[s]	−2.3 (15–30),[p]			(15),[p] 0.363 (15),[r] 0.3103 (20),[p]
acid) (Aaba)					−0.40 (25–45)[ij]			0.2793 (30),[p] 0.3357 (35),[k] 0.311
								(35),[n,ij] 0.313 (35),[ee] 0.300 (40),[ee]
								0.307 (45)[ij]
2-Amino-2-methylpropanoic	(0.346)	0.346[q]	0.35685[l]		−3.41 (25–35)[l]			0.32277 (35)[l]
acid (α-amino-*i*-butyric acid)								
4-Aminobutanoic acid	0.312	0.314,[c] 0.310[h]		**4.26**,[nn] 4.30,[c] 4.24[h]	−0.8 (15–25),[c]	**3.3**[w]		0.322 (15),[c] 0.329 (30),[ee] 0.299
(γ-amino-*n*-butyric acid)					−4.4 (30–40)[ee]			(35),[o] 0.316 (35),[ee] 0.285 (40)[ee]
(Gaba)								
2-Aminopentanoic acid			0.42948[l]		−2.96 (25–35)[l]			0.39992 (35)[l]
(α-amino-*n*-valeric acid)								
5-Aminopentanoic acid	(0.383)	0.383[r]		4.35[r]	−2.8 (15–35)[r]	**3.7**[w]		0.429 (15),[r] 0.373 (35)[r]
(δ-amino-*n*-valeric acid)								
(Dava)								
6-Aminohexanoic acid	0.489	0.479,[c] 0.513[ij]	0.513[n]	**4.69**,[nn] 4.61[c]	−4.2 (15–25),[c]	**3.9**[w]		0.521 (15),[c] 0.499 (35),[o,ij] 0.480
(ε-amino-*n*-caproic acid)					−1.65 (25–45)[ij]			(45)[ij]
(Eacc)								
Diglycine					8.7 (30–40)[f]			0.250 (30),[f] 0.298 (35),[f] 0.337 (40)[f]
Triglycine					7.7 (30–40)[f]			0.385 (30),[f] 0.433 (35),[f] 0.462 (40)[f]

[a]Unless indicated otherwise, amino acids in this paper are α-isomers; L for L-enantiomer and D for D-enantiomer. The select value is an average of experimental data.

[b]Hydration number n_H (or solvation number n_s, in molecules of water per molecule of solute)$=V_\phi^o(e)/(V_e^o-V_b^o)$, where $V_\phi^o(e)$ is the electrostriction partial molar volume, V_e^o is the molar volume of electrostricted water and V_b^o is the molar volume of bulk water; the value of $(V_e^o-V_b^o)$ is −3.3 cm^3 mol^{-1} at 25 °C [11,92]; some hydration numbers were calculated from the compressibility method [11,195] or by the NIR spectroscopy method (in bold) [70]; *B*-coefficient data in the table are either taken directly or calculated from the following literatures: [c]Ref. [65], [d]Ref. [61], [e]Ref. [52], [f]in unit of kg mol^{-1} using Tsangaris-Martin equation [60] $\eta_r=1+Bm+Dm^2$ (*m*=molality, in mol kg^{-1}) from Ref. [60], [g]Ref. [72], [h]Ref. [73], [i]Ref. [11], [j]Ref. [77] (*B*-coefficient of glycine calculated from viscosity data), [k]Ref. [78], [l]in unit of kg mol^{-1} using $\eta_r=1+Bm+Dm^2$ from Ref. [75], [m]Ref. [143], [n]Ref. [235] (in duplication with [ij]Ref. [191] from the same authors), [o]Ref. [68], [p]Ref. [84], [q]Ref. [74], [r]Ref. [115], [s]Ref. [116], [t]Ref. [141], [u]Ref. [195], [v]in unit of kg mol^{-1} using $\eta_r=1+Bm+Dm^2$ from Ref. [236], [w]hydration numbers (in bold) determined by NIR spectroscopy at a solute concentration of 2 mol/kg from Ref. [70], [x]calculated from data in Ref. [237], [y]Ref. [184] (hydration numbers based on different intrinsic volumes), [z]Ref. [213], [aa]Ref. [238], [bb]in unit of kg mol^{-1} from Ref. [63], [cc]Ref. [211], [dd]Ref. [148], [ee]Ref. [149], [ff]Ref. [69], [gg]hydration numbers calculated from partial molar isothermal compressibilities by Ref. [32], [hh]Ref. [208], [ii]Ref. [76], [jj]Ref. [191] (*B*-coefficients of α-aminoisovaleric acid at 25, 35 and 45 °C are 0.414, 0.396 and 0.374, respectively; this reference provided data for α-amino-*n*-butyric acid in their Table 1, but described it as β-amino-*n*-butyric acid in text and their Fig. 1; therefore, its *B*-value at 25 °C is not included in averaging), [kk]Ref. [181], [ll]Ref. [80], [mm]experimental or calculated data from Ref. [239], [nn]calculated from selected *B*-coefficients in this table and selected V_ϕ^o values from Table 2.

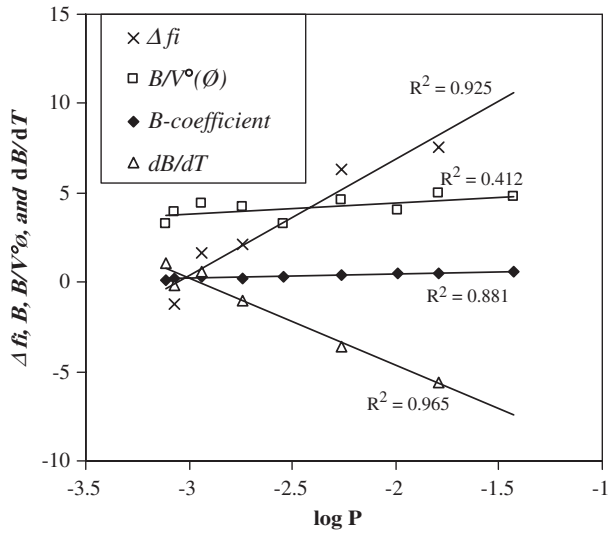

Fig. 1. Correlations of Δf_i, B, B/V_ϕ^o and dB/dT with log P respectively at 25 °C (log P values from Ref. [80]; Δf_i values from Ref. [81]; B, B/V_ϕ^o and dB/dT values from Table 1; amino acids included are Gly, Ala, Val, Leu, Ser and Thr).

value. Surprisingly, the B/V_ϕ^o values are not as indicative as B-coefficients in terms of measuring hydrophobicity.

It is important to notice that some ω-amino acids (such as γ-aminobutyric acid, δ-aminovaleric acid and ε-aminocaproic acid in Table 1) have high values of B, B/V_ϕ^o and hydration numbers, as well as negative values of dB/dT. Therefore, they are known as compensatory solutes with structure-enforcing effect [65,68,70]. It was also found that γ-amino acids are more structure-making than their α-isomers based on the more negative differential entropies of dilution in aqueous solutions of γ-amino acids than those of α- and β-ones [82].

The importance of D-coefficients has not been fully understood, but they increase with the increase of number of CH_2 groups [73]. The D-coefficients of amino acids in alkali-chloride solutions were reported almost the same as those in water [74]. Therefore, the D-coefficients are not discussed in the present review.

3. Standard partial molar volumes of amino acids in pure water

The standard partial molar volume (V_ϕ^o) equals the partial molar volume of a solute at infinite dilution; therefore, it is also called the limiting partial molar volume. At infinite dilution, the solute–solute interaction is negligible; therefore, the standard partial molar volume and its temperature-dependence provide valuable information of the solute–solvent interactions [32,83,84]. The apparent molar volume (V_ϕ, $cm^3 \cdot mol^{-1}$) can be calculated using accurate density data through the following equation.

$$V_\phi = 1000(1 - d/d_0)/c + M/d_0 \quad (3)$$

where d and d_0 are densities of the solution and water in $g \cdot cm^{-3}$, c is the molar concentration of the solution in M ($mol \cdot dm^{-3}$) and M is the molar mass of the solute in $g \cdot mol^{-1}$. Zamyatnin [34] explained the derivation of the above equation and the difference between the partial volume and the apparent volume. In dilute solutions, the apparent volume is approximately equal to the partial one; at infinite dilution, these two volumes are equal. Therefore, the standard partial molar volume is often obtained from the extrapolation of the apparent molar volume (V_ϕ) to an infinite dilution using the following linear equation,

$$V_\phi = V_\phi^o + S_v m \quad (4)$$

where m is the concentration of amino acid often in molality ($mol\ kg^{-1}$), S_v is the slope indicating solute–solute interactions and is also known as the volumetric pairwise interaction coefficient v_{AA} [85].

The volumetric properties of solutions of amino acids, peptides and proteins have been investigated over sixty years; a very early systematic study was conducted by Cohn and Edsall [86]. Therefore, compared to the limited data of viscosity B-coefficients of amino acids, there are plenty values of the standard partial molar volumes. Table 2 summarized these data at various temperatures along with the averaged values at 25 °C as selected values.

The V_ϕ^o data are often embedded with important information of solute hydrophobicity, hydration properties and solute–solvent interactions [84,87–89]. The derivatives of the standard partial molar volume with temperature reflect the hydrophobicity of the solute (so-called Hepler [90] hydrophobicity criteria) [83,84]: if $(\partial V_\phi^o/\partial T)_P > 0$ and $(\partial^2 V_\phi^o/\partial T^2)_P < 0$, the solute is hydrophilic where $(\partial V_\phi^o/\partial T)_P$ actually is the partial molar expansibility and, if $(\partial V_\phi^o/\partial T)_P < 0$ and $(\partial^2 V_\phi^o/\partial T^2)_P > 0$, the solute is hydrophobic. According to this criteria and based on the positive first derivatives and negative second derivatives for three amino acids (i.e. α-amino-*n*-butyric acid, norvaline and norleucine), Romero and Negrete [84] suggested that the hydrophilic interactions between water and three amino acids are stronger than the hydrophobic interactions, but are decreasing with the increasing length of hydrophobic chains. Meanwhile, since $(\partial C_p^\circ/\partial P)_T = -T(\partial^2 V_\phi^o/\partial T^2)_P$, a negative value of $(\partial^2 V_\phi^o/\partial T^2)_P$ seems to associate with a structure-breaking solute and a positive one is associated with a structure-making solute [32,90]. According to this scale, Banipal and Kapoor [32] suggested that, except L-proline, most amino acids (glycine, alanine, β-alanine, L-valine, L-leucine, L-isoleucine, L-serine, L-phenylalanine, L-threonine, L-glutamic acid and α-amino-*n*-butyric acid) are structure-breakers based on negative values of $(\partial^2 V_\phi^o/\partial T^2)_P$. However, this classification is inconsistent with the previous discussion on their B-coefficients, implying the limitation of this scale.

The hydration number n_H (or solvation number n_s, in molecules of water per molecule of solute) explicitly reveal the hydration degree of a solute in water. The hydration number generally increases with the size of the amino acid in water or solutions (Tables 1, 5, 6 and 7). A relatively high hydration number of L-glutamic acid was attributed to the presence of charged side-chain, while a low hydration number of L-proline was explained due to its cyclic structure causing less water

molecules in the electrostricted state [32]. The hydration number can be calculated from the volumetric properties using the following equation [11].

$$n_H = V_\phi^o(e)/(V_e^o - V_b^o) \quad (5)$$

where $V_\phi^o(e)$ is the electrostriction partial molar volume (also called the free, void or dead volume [91]), V_e^o is the molar volume of electrostricted water and V_b^o is the molar volume of bulk water, the value of $(V_e^o - V_b^o)$ is -3.3 cm^3 mol^{-1} at 25 °C [11,92]. The hydration numbers can also be calculated from the second temperature derivative of the partial molar volume or partial molar compressibility [93]. The hydration numbers calculated from different methods (such as methods based on volume, compressibility and viscosity [94–96]) are not always consistent as shown in Table 1. The $V_\phi^o(e)$ can be calculated from the standard partial molar volume (V_ϕ^o) and the intrinsic partial molar volume (V_{in}^o, which can be approximated by the van der Waals volume V_w or molecular volume V_M [91]; or assumed to consist of two terms: van der Waals volume V_w and the volume due to packing effects V_p [11]) using the following equation [73,91,92,97].

$$V_\phi^o(e) = V_\phi^o - V_{in}^o \quad (6)$$

It is important to realize that the electrostriction partial molar volume, $V_\phi^o(e)$ represents the contraction of water in the vicinity of charged groups caused by solute–solvent interactions, resulting in a decrease in the overall water volume in the presence of amino acids [93]. Edsall and Wyman [98] suggested that smaller ions produce greater electrostriction of the solvent due to the stronger electric field near the ions and thus the increased orientation and compression effects. They also indicated that the amino group causes more electrostriction than the carboxyl group does.

The intrinsic volumes of some amino acids have been reported in several references [73,99,100] and can be obtained through several methods: (1) converting the densities (ρ_r) of dry amino acids [100] using $V_{in}^o = (0.7/0.634)(M_r/\rho_r)$ where M_r is the molar mass of amino acid [11,101]; (2) assuming they are equal to the partial molar volumes of equivalent amides [11,77,99,102]; or (3) substituting with van der Waals volumes (V_w), which can be estimated from the group contribution methods [91,103].

The theoretical models of partial molar volume can be grouped into three categories: (1) models based on intrinsic or van der Waals volumes, (2) group-contribution models and (3) models based on the Kirkwood–Buff theory.

3.1. Models based on intrinsic or van der Waals volumes

The intrinsic volume is the volume of a hypothetical ion without charge, and is considered by the scaled particle theory [104] as the volume associated with the free energy of cavity formation in liquids [104,105]. Based on the scaled particle theory, which assumes the solute dissolution as a step-wise process: creating a cavity in the solvent for the solute molecule and allowing solute molecule to interact with surrounding solvent molecules, a thermodynamic model can be written in the following equation [93],

$$V_\phi^o = V_c + V_I + \beta_{T0} RT \quad (7)$$

where V_c is the partial molar volume of cavity formation, V_I is the volume change due to the solute–solvent interactions, β_{T0} is the coefficient of isothermal compressibility of the solvent, R is the universal gas constant and T is the absolute temperature. The cavity volume (V_c) consists of two contributions [93,106],

$$V_c = V_M + V_v \quad (8)$$

where V_M is the geometric volume occupied by the solute molecule and can be substitute by the van der Waals volume (V_w) for low molecular weight solute [93]; V_v is so-called the 'empty' volume for the void space near the solute molecule. This model (Eq. (7)) clearly indicates the temperature dependence of the standard partial molar volume since the temperature is known to strongly influence the hydration of amino acids [30,107].

Studies [87,108] also suggested the standard partial molar volume is made up of three terms: the intrinsic molar volume V_{in}, electrostriction partial molar volume $V_\phi^o(e)$ and so-called molar structural volume ΔV_{st} (reflecting the structure-making or structure-breaking ability of a solute [24]).

$$V_\phi^o = V_\phi^o(e) + V_{in}^o + \Delta V_{st} \quad (9)$$

where the electrostriction contribution $V_\phi^o(e)$ is negligible for large singly charged ions (such as tetraalkylammonium, pyridinium, imidazolium). However, it is known that amino acids cause electrostriction of solvent molecules [109]; therefore, the $V_\phi^o(e)$ may not be negligible for some amino acids. The major effect of the solvent molecules on the electrostrictive volume is believed to arise from the positively charged amino group [110].

The standard partial molar volumes can also be related to the van der Waals volumes (V_w) directly [111,112],

$$V_\phi^o = aV_w + b \quad (10)$$

where a and b are empirical constants for a homologous series. This equation is suitable for molecules with chain-like structures such as amino acids [112]. A similar equation with an additional term is described in the following [30],

$$V_\phi^o = aV_w + b + V_I \quad (11)$$

where V_I is the interaction volume resulting from solute–solvent molecules. Comparing Eq. (11) with (9), it is noticeable that the V_I term is similar to the structural volume ΔV_{st} term.

3.2. Group-contribution models

Similar to Eq. (2), the individual contributions of polar group (NH_3^+, COO^-) and hydrophobic group (CH_2) to the standard

Table 2
Standard partial molar volumes (V_ϕ^o) of amino acids at different temperatures in $cm^3\ mol^{-1}$

Amino acid	Standard partial molar volume (V_ϕ^o) at 25 °C			V_ϕ^o (other temperature, °C)[b]
	Selected (average)[a]	Included in average	Not included	
Glycine (Gly)	43.18	42.9,[d] 43.5,[e,y,vv,jjj] 43.19,[f,o,dd,xxx] 43.20,[g] 43.25,[i,z] 43.3,[k] 43.18,[l] 42.89,[m] 43.16,[n] 43.14,[p,fff] 43.26,[bb,xx,ppp] 43.217,[s] 43.199,[u] 43.15,[x] 42.54,[oo] 43.2,[pp,ttt] 43.27,[rr] 43.23,[bbb] 43.24,[eee] 43.30,[ggg] 43.2,[hhh] 43.22,[kkk,uuu] 43.62,[lll] 42.54,[qqq] 43.12,[rrr] 42.48,[yyy]	43.26,[q] 43.3,[v] 43.5,[ee] 43.33,[ii] 42.48,[kk] 42.9[nnn]	41.1 (5),[c] 41.9 (5),[e] 41.07 (5),[f] 41.25 (5),[rrr] 41.9 (10),[c] 42.3 (15),[c] 42.5 (15),[d] 42.6 (15),[e] 42.29 (15),[f] 42.54 (15),[g] 42.4 (15),[k] 42.35 (15),[q,xx] 42.48 (15),[bb] 42.37 (15),[rr] 42.37 (15),[rrr] 42.7 (18),[pp] 42.8 (20),[c] 43.36 (20),[ooo] 43.39 (24),[h c] 39.5 (30),[ddd] 43.59 (30),[kkk] 43.89 (30),[ooo] 44.2 (35),[e] 43.81 (35),[f,uuu] 43.85 (35),[g] 43.8 (35),[k] 44.12 (35),[q,xx] 43.90 (35),[nn] 43.98 (35),[rr] 41.7 (35),[ddd] 43.79 (35),[eee,kkk] 44.95 (35),[iii] 43.69 (35),[rrr] 44.52 (35),[www] 43.87 (35),[zzz] 43.9 (40),[k] 44.01 (40),[bb] 44.0 (40),[pp] 42.6 (40),[ddd] 44.15 (40),[kkk] 44.52 (40),[ooo] 44.00 (40),[zzz] 44.00 (45),[f] 44.17 (45),[eee] 44.15 (45),[zzz] 44.91 (50),[ooo] 44.25 (50),[zzz] 44.3 (55),[k] 44.51 (55),[bb] 44.2 (55),[pp] 44.25 (55),[eee] 45.40 (60),[ooo] 44.38 (60),[zzz] 44.47 (70)[zzz]
N-Methylglycine (sarcosine)	(62.28)	62.28[aa,vv]	52.6[v]	61.1 (5),[c] 62.0 (10),[c] 62.4 (15),[c] 62.8 (20)[c]
Dimethylglycine	(82.20)	81.20,[aa,vv]		79.1 (5),[c] 79.6 (10),[c] 79.9 (15),[c] 80.4 (20)[c]
Trimethylglycine (glycine betaine)	97.6	97.50,[vv] 97.7 [jjj]		97.0 (5),[c] 97.3 (10),[c] 97.7 (15),[c] 98.4 (20)[c]
Alanine (Ala)	60.48	60.7,[e] 60.52−L,[f] 60.30,[g] 60.6,[i] 60.4−L,[k] 60.23,[m] 60.41,[n] 60.50,[o] 60.53,[xx] 60.609,[t] 60.47,[w,cc] 60.36,[x] 60.3,[y] 60.45−L,[z] 60.47−L,[o,bb,ppp] 60.43−D,[o] 60.42,[dd] 60.19−L,[oo] 60.42−L,[rr] 60.50−L,[bbb] 60.49,[eee] 60.71,[fff] 60.8,[hhh] 60.68,[lll] 60.74−D,[lll] 60.19−L,[qqq] 60.40,[rrr] 60.35,[sss] 60.5,[ttt] 60.37,[uuu] 60.43−L,[xxx] 60.92−L[yyy]	60.53,[q] 60.6,[v] 60.6,[ee] 60.54,[ii] 60.92−L,[kk] 60.2[nnn]	59.4 (5),[e] 58.64−L (5),[f] 58.81 (5),[rrr] 60.0 (15),[e] 59.73−L (15),[f] 60.10 (15),[g] 59.9−L (15),[k] 59.89 (15),[q,xx] 59.67−L (15),[bb] 59.67−L (15),[rr] 59.77 (15),[rrr] 60.01−L (20),[ooo] 60.62−L (24),[h] 60.68−D (24),[h] 59.8 (30),[ddd] 60.63−L (30),[ooo] 61.4 (35),[e,ddd] 60.96−L (35),[f] 61.06 (35),[g] 60.9−L (35),[k] 61.27 (35),[q,xx] 60.44−L (35),[nn] 60.88−L (35),[rr] 61.01 (35),[eee] 60.96 (35),[rrr] 61.00 (35),[uuu] 61.99 (35),[www] 61.16 (35),[zzz] 61.2−L (40),[k] 61.14−L (40),[bb] 62.9 (40),[ddd] 61.22−L (40),[ooo] 61.35 (40),[zzz] 61.46−L (45),[f] 61.31 (45),[eee] 61.46 (45),[zzz] 61.61−L (50),[ooo] 61.61 (50),[zzz] 61.6−L (55),[k] 61.53−L (55),[bb] 62.10−L (60),[ooo] 61.85 (60),[zzz] 62.24 (70)[zzz]
β-Alanine	58.41	57.9,[d] 58.6,[i] 58.20,[m] 58.723,[t] 58.28,[w] 58.5,[y] 58.3,[pp] 58.71,[xx] 58.25,[bbb] 58.37,[eee] 58.38,[ggg] 58.9,[jjj] 58.26[sss]	58.71,[q] 58.7,[v] 58.9,[ee]	57.0 (15),[d] 57.48 (15),[q,xx] 57.6 (18),[pp] 59.2 (30),[ddd] 59.06 (35),[q,xx] 60.9 (35),[ddd] 58.85 (35),[eee] 59.25 (35),[zzz] 59.1 (40),[pp] 62.0 (40),[ddd] 59.54 (40),[zzz] 59.19 (45),[eee] 59.75 (45),[zzz] 59.84 (50),[zzz] 59.2 (55),[pp] 60.03 (60),[zzz] 60.18 (70)[zzz]
Valine (Val)	90.87	90.9,[e] 90.81−L,[f] 90.79,[l] 91.48,[m] 90.78−L,[o,bbb] 91.04,[q] 90.77,[s] 90.70−L,[x] 90.65−L,[dd] 90.79−L,[hh] 90.80−L,[aaa] 90.98−L,[eee] 90.87−L[vvv,xxx]	91.3,[v] 90.91[ii]	89.8 (5),[e] 89.03−L (5),[f] 90.2 (15),[e] 89.96−L (15),[f] 89.43 (15),[q] 90.08−L (15),[aaa] 89.15−L (20),[ooo] 90.98−L (24),[h] 90.87−D (24),[h] 90.22−L (30),[ooo] 91.7 (35),[e] 91.51−L (35),[f] 91.61 (35),[q] 91.55−L (35),[eee] 91.42 (35),[zzz] 91.67−L (40),[aaa] 90.91−L (40),[ooo] 91.58 (40),[zzz] 91.93−L (45),[f] 91.93−L (45),[eee] 92.65−L (50),[ooo] 91.96 (50),[zzz] 92.57−L (55),[aaa] 92.98−L (60),[ooo] 92.12 (60),[zzz] 92.25 (70)[zzz]
Norvaline (Nval)	91.74	91.87,[j] 91.61,[m] 91.77,[r] 91.70,[dd]	93.2[nnn]	91.10 (15),[j] 90.53 (15),[r] 91.03 (20),[r] 92.05 (24),[h] 92.21 (30),[r] 92.68 (35)[j]

Table 2 (*continued*)

Amino acid	Standard partial molar volume (V_ϕ^o) at 25 °C			V_ϕ^o (other temperature, °C)[b]
	Selected (average)[a]	Included in average	Not included	
Leucine (Leu)	107.69	107.5,[e] 107.76−L,[f] 107.75−L,[n] 107.74 −L,[o,x] 107.75−L,[w] 107.83−L,[dd] 107.57 −L,[hh] 107.59−L,[rr] 107.73−L,[aaa] 107.77 −L,[eee,fff] 107.48−L[vvv]	107.5,[v] 107.74[ii]	105.8 (5),[e] 105.61−L (5),[f] 106.7 (15),[e] 106.58−L (15),[f] 106.71−L (15),[rr] 106.81 −L (15),[aaa] 107.96−L (24),[h] 108.4 (35),[e] 108.80−L (35),[f] 108.40−L (35),[rr] 108.41 −L (35),[eee] 109.00−L (40),[aaa] 109.37−L (45),[f] 109.38−L (45),[eee] 110.18−L (55)[aaa]
Isoleucine (Ilu)	105.71	105.73−L,[f] 105.80−L,[dd] 105.45−L,[hh] 105.76−L,[aaa] 105.79−L[eee]	106.81−D[mmm]	103.65−L (5),[f] 104.80−L (15),[f] 104.90 −L (15),[aaa] 105.13−L (20),[ooo] 106.31 −L (30),[ooo] 106.54−L (35),[f] 106.47−L (35),[eee] 107.13−L (35),[www] 107.04−L (40),[aaa] 107.19−L (40),[ooo] 107.32 −L (45),[f] 107.42−L (45),[eee] 108.06−L (50),[ooo] 108.09−L (55),[aaa] 109.36−L (60)[ooo]
Norleucine (Nleu)	107.60	107.62,[j] 107.6−L,[k] 107.13,[m] 107.58,[r] 107.72,[w] 107.93,[dd]	108.4,[v] 108.02,[ii] 110.3[nnn]	106.90 (15),[j] 107.0−L (15),[k] 106.20 (15),[r] 106.88 (20),[r] 107.95 (24),[h] 108.22 (30),[r] 108.16 (35),[j] 109.2−L (40),[k] 110.8 −L (55)[k]
Serine (Ser)	60.56	60.9−L,[e] 60.61,[j] 60.8−L,[k] 60.43,[l] 60.46 −L,[m] 60.62−L,[z,dd] 60.66−L,[bb] 60.26 −L,[oo,qqq] 60.72−L,[bbb] 60.60−L,[eee] 60.32,[rrr] 60.55,[sss] 60.53−L[yyy]	60.3,[v] 60.8,[ee] 60.53−L,[kk] 61.28[mmm]	59.6−L (5),[e] 58.37 (5),[rrr] 60.3−L (15),[e] 59.78 (15),[j] 59.8−L (15),[k] 59.70−L (15),[bb] 59.66 (15),[rrr] 59.64−L (20),[ooo] 60.27−L (30),[ooo] 62.1−L (35),[e] 61.37 (35),[j] 60.73−L (35),[nn] 61.15−L (35),[eee] 61.07 (35),[rrr] 61.96−L (35),[www] 61.7−L (40),[k] 61.63−L (40),[bb] 61.39−L (40),[ooo] 61.86−L (45),[eee] 62.36−L (50),[ooo] 62.2 −L (55),[k] 62.22−L (55),[bb] 63.53−L (60)[ooo]
Threonine (Thr)	76.81	76.58−L,[m] 76.90−L,[bb] 76.83−L,[dd,tt] 76.86−L,[hh] 76.59−L,[xx] 76.94−L,[bbb] 76.88−L,[eee] 76.84[rrr]		75.24 (5),[rrr] 76.18−L (15),[bb] 76.03−L (15),[xx] 76.20 (15),[rrr] 75.16−L (20),[ooo] 76.30−L (30),[ooo] 77.71−L (35),[xx] 77.49 −L (35),[eee] 77.33 (35),[rrr] 78.04 (35),[www] 77.93−L (40),[bb] 77.31−L (40),[ooo] 78.24 −L (45),[eee] 78.85−L (50),[ooo] 78.52−L (55),[bb] 79.55−L (60)[ooo]
Cysteine (Cys)	73.45	73.3−L,[k] 73.44−L,[o] 73.62−L[hh]		72.5−L (15),[k] 74.7−L (40),[k] 75.0−L (55),[k]
Methionine (Met)	105.25	104.83,[f] 105.2−L,[k] 105.32,[m] 105.35,[o] 105.57−L,[dd] 105.3−L,[hh] 105.21[jj]	105.91[mmm]	101.41 (5),[f] 103.89 (15),[f] 104.0−L (15),[k] 103.8 (15),[jj] 105.85 (35),[f] 108.11−L (35),[www] 107.0−L (40),[k] 107.02 (40),[jj] 106.51 (45),[f] 108.1−L (55),[k] 108.47 (55),[jj]
Aspartic acid (Asp)	73.65	73.83,[o] 74.8−L,[dd] 71.79−L,[hh] 74.78−L,[ss] 73.05[sss]		72.84−L (15),[ss] 75.84−L (35),[nn] 75.98−L (40),[ss] 77.11−L (55),[ss]
Asparagine (Asn)	77.36	77.29−L,[ff] 77.2−L,[k] 77.63−L,[gg] 77.18 −L,[hh] 77.52−L[uu]	78−L,[ww] 79.49−L[mmm]	74.03−L (5),[ff] 76.0−L (15),[k] 75.87−L (15),[ff] 76.28−L (15),[gg] 78.42−L (35),[ff] 78.8−L (40),[k] 79.07−L (40),[gg] 79.32−L (45),[ff] 79.5−L (55),[k] 80.48−L (55)[gg]
Glutamic acid (Glu)	88.97	89.0−L,[k] 85.88,[o] 89.85−L,[dd] 89.36−L,[hh] 90.06−L,[ss] 89.64−L[eee]		87.8−L (15),[k] 88.52−L (15),[ss] 89.70−L (35),[nn] 90.60−L (35),[eee] 90.8−L (40),[k] 91.62−L (40),[ss] 91.30−L (45),[eee] 91.8−L (55),[k] 92.84−L (55)[ss]
Glutamine (Gln)	93.80	93.8−L,[k] 93.56−L,[m,ff] 93.61−L,[dd] 93.90 −L,[gg] 94.36−L[hh]		90.13−L (5),[ff] 92.3−L (15),[k] 92.05−L (15),[ff] 92.29−L (15),[gg] 94.72−L (35),[ff] 94.9−L (40),[k] 95.14−L (40),[gg] 95.54−L (45),[ff] 96.3−L (55),[k] 96.25−L (55)[gg]
Arginine (Arg)	124.55	123.71,[l] 127.34−L,[o] 123.86−L,[dd] 123.7 −L,[hh] 124.12−L[jj]		122.29−L (15),[jj] 124.10−L (20),[ooo] 126.40−L (30),[ooo] 131.10−L (35),[www] 125.51−L (40),[jj] 127.36−L (40),[ooo] 130.51−L (50),[ooo] 126.51−L (55),[jj] 131.34−L (60)[ooo]
Lysine (Lys)	(108.71)	108.71−L[hh]	108.5[ee]	

(continued on next page)

Table 2 (*continued*)

Amino acid	Standard partial molar volume (V_ϕ^o) at 25 °C			V_ϕ^o (other temperature, °C)[b]
	Selected (average)[a]	Included in average	Not included	
Histidine (His)	98.86	98.8−L,[k] 98.79,[o] 98.3−L,[dd] 98.89−L,[ff] 99.14−L,[gg,hh] 98.98−L,[ll] 98.81[rrr]	99.3[ee]	95.48−L (5),[ff] 95.76 (5),[rrr] 97.3−L (15),[k] 96.95−L (15),[ff] 97.65−L (15),[ll] 97.77 (15),[rrr] 99.9−L (35),[k] 100.07−L (35),[ff] 99.42 (35),[rrr] 100.35−L (35),[www] 100.4 −L (40),[k] 100.51−L (40),[ll] 101.05−L (45),[ff] 101.6−L (55),[k] 101.58−L (55)[ll]
Phenylalanine (Phe)	121.80	121.50−L,[f] 122.06,[j] 121.7−L,[k] 122.40,[m] 121.73−L,[n] 121.48,[o] 121.49−L,[x] 122.2 −L,[dd] 121.92−L,[hh] 122.03−L,[ll] 121.32 −L,[eee] 121.74[sss]	121.2,[v] 121.3,[ee] 127.65−L[mmm]	118.28−L (5),[f] 120.43−L (15),[f] 121.37 (15),[j] 120.3−L (15),[k] 120.58−L (15),[ll] 117.14−L (20),[ooo] 119.52−L (30),[ooo] 122.77−L (35),[f] 122.51 (35),[j] 122.82−L (35),[eee] 123.5−L (40),[k] 123.55−L (40),[ll] 121.79−L (40),[ooo] 123.90−L (45),[f] 123.75 −L (45),[eee] 123.84−L (50),[ooo] 124.9−L (55),[k] 125.49−L (55),[ll] 125.03−L (60)[ooo]
3,4-Dihydroxy-phenylalanine (Dopa)	126.06	126.35−L,[ll] 125.76[ttt]		124.10−L (15),[ll] 126.34−L (40),[ll] 128.71 −L (55)[ll]
Tyrosine (Tyr)	124.58	124.33−L,[f] 124.4−L,[dd] 125.02−L[ll]	123−L[hh]	118.47−L (5),[f] 120.92−L (15),[f] 122.82 −L (15),[ll] 126.63−L (35),[f] 127.33−L (40),[ll] 127.48−L (45),[f] 128.52−L (55)[ll]
Tryptophan (Trp)	143.83	143.38−L,[f] 143.7−L,[k] 143.91−D,[o] 143.8,[dd] 144.0−L,[hh] 143.78−L,[ll] 144.24 −L[mm]	144.1[ee]	139.62−L (5),[f] 141.38−L (15),[f] 141.6−L (15),[k] 141.99−L (15),[ll] 144.66−L (35),[f] 145.6−L (40),[k] 146.23−L (40),[ll] 145.43 −L (45),[f] 147.8−L (55),[k] 147.90−L (55)[ll]
Proline (Pro)	82.69	82.50−L,[f] 82.5−L,[k] 82.56,[l] 82.83−L,[o] 82.63−L,[dd] 82.65−L,[hh] 82.61−L,[jj] 83.13 −L,[xx] 82.87,[ccc] 82.61−L[eee]	81.0[v,ee]	80.43−L (5),[f] 81.57−L (15),[f] 81.71−L (15),[jj] 81.93−L (15),[xx] 83.22−L (35),[f] 83.62−L (35),[xx] 83.10−L (35),[eee] 85.13 −L (35),[www] 83.6−L (40),[k] 83.64−L (40),[jj] 83.86−L (45),[f] 83.88−L (45),[eee] 84.5−L (55),[k] 84.46−L (55)[jj]
Hydroxyproline	84.47	84.49−L,[dd] 84.45[ccc]	84.4[v,ee]	
2-Aminobutanioc acid (α-amino-*n*-butyric acid)	75.60	75.8,[e] 75.24,[m] 75.66,[o,ggg] 75.92,[p] 75.64,[j,r] 75.62,[s] 75.54,[w] 75.50,[dd] 75.95,[qq] 75.51,[ss] 75.38,[sss] 75.4[ttt]	75.64,[q] 76.5,[ee] 75.85,[ii] 76.35,[eee] 77.2[nnn]	74.4 (5),[e] 75.1 (15),[e] 74.78 (15),[j,q] 74.44 (15),[r] 74.67 (15),[ss] 74.98 (20),[r] 75.92 (24),[h] 75.89 (30),[r] 76.3 (30),[ddd] 76.2 (35),[e] 76.03 (35),[j,q] 76.9 (35),[ddd] 76.61 (35),[eee] 76.34 (40),[ss] 77.4 (40),[ddd] 76.82 (45),[eee] 77.01 (55)[ss]
2-Amino-2-methylpropanoic acid (α-amino-*i*-butyric acid)	(77.54)	77.54[bbb]	77.2,[v] 78.1,[ee] 77.65[ii]	
4-Aminobutanoic acid (γ-amino-*n*-butyric acid)	73.21	73.1,[d,pp] 73.17,[m] 73.02,[w] 73.5,[y] 73.35,[xx] 73.23[ggg]	73.53,[q] 73.4,[v] 73.26[ii]	72.2 (15),[d] 71.25 (15),[q,xx] 72.4 (18),[pp] 71.2 (30),[ddd] 74.18 (35),[q,xx] 71.6 (35),[ddd] 74.1 (40),[pp] 72.8 (40),[ddd] 73.7 (55)[pp]
2-Aminopentanoic acid (α-amino-*n*-valeric acid)	(92.7)	92.7[jjj]	92.7[ee]	
5-Aminopentanoic acid (δ-amino-*n*-valeric acid)	87.86	87.33,[m] 88.01,[j] 87.58,[w] 88.3,[y,pp] 87.65[ggg]	88.01,[q] 87.9,[v] 87.65[ii]	87.38 (15),[j,q] 87.3 (18),[pp] 88.32 (35),[j,q] 89.1 (40),[pp] 88.7 (55)[pp]
2-Amino-*n*-hexanoic acid (α-aminocaproic acid)	–		108.4[ee]	
6-Amino-*n*-hexanoic acid (ε-aminocaproic acid)	104.22	103.9,[d] 104.35,[i] 104.17,[m] 104.02,[w] 104.7,[y] 104.3,[pp] 104.20,[xx] 104.09[ggg]	102.6,[v] 104.31,[ii] 104.9[ee]	103.0 (15),[d] 103.02 (15),[xx] 103.1 (18),[pp] 104.88 (35),[xx] 105.2 (40),[pp] 105.2 (55)[pp]
Diglycine	76.42	76.8,[i] 76.63,[p] 76.34,[s] 76.27,[z] 76.23,[dd] 76.29,[gg] 76.27,[qq] 76.76,[zz] 76.30,[ppp] 76.28[rrr]	77.2,[ee] 76.60,[ii] 76.6[nnn]	73.60 (5),[rrr] 75.25 (15),[gg] 75.22 (15),[rrr] 76.73 (35),[nn] 78.71 (35),[iii] 77.10 (35),[rrr] 77.81 (35),[zzz] 77.59 (40),[gg] 78.20 (40),[zzz] 78.47 (45),[zzz] 78.62 (50),[zzz] 77.96 (55),[gg] 78.91 (60),[zzz] 79.15 (70)[zzz]
Triglycine	112.09	111.81,[z] 112.11,[dd] 111.92,[yy] 112.51[zz]	113.5,[ee] 112.66,[ii] 111.9[nnn]	114.93 (35)[iii]

partial molar volume can be identified through the following linear relationship.

$$V_\phi^o = V_\phi^o(NH_3^+, COO^-) + n_c V_\phi^o(CH_2) \quad (12)$$

Through linear regression calculations, the polar group contribution V_ϕ^o (NH_3^+, COO^-) and hydrophobic group contribution V_ϕ^o (CH_2) were obtained to analyze the interactions of (amino acid)–water [78] and (amino acid)–water–(other solute) [113–116].

Based on the additivity principle, Gianni and Lepori proposed a contribution method [91,117] for estimating the standard partial molar volumes of various α-, β-, ω-amino acids in aqueous solutions at 25 °C with relatively high accuracies. A similar approach for calculating V_ϕ^o at 25 °C was proposed by Millero and co-workers [11]. Another simple group-contribution method proposed by Hakin et al. [118,119] allows the prediction of standard partial molar volumes (so-called 'standard-state apparent molar volumes') of amino acids at various temperatures based on the trends in group contributions at several temperatures (i.e. 15, 25, 40 and 55 °C).

Based on the theoretical model by Edward and Farrell [120], the group-contribution model is often expressed as.

$$V_\phi^o = \frac{4}{3}\pi(r_w + \Delta)^3 + \sum_Y n_Y \sigma^*(Y) \quad (13)$$

where r_w is the van der Waals radius, Δ is a constant (Δ=0.53 Å), n_Y is the number of Y groups in the molecule, σ*(Y) is the shrinkage parameter representing the volume change of group Y and is always negative. Further implementations of this model were completed by Cabani et al. [28], Shahidi et al. [121], Ogawa et al. [122] and Singh and Kishore [106].

The equation of state of Helgeson, Kirkham and Flowers (HKF) has been widely used in predicting the standard partial molar volumes and heat capacities of amino acids at different temperatures and pressures [123–125]. A group-contribution model based on HKF was constructed to calculate several properties (such as standard partial molar volumes, standard molar entropies, enthalpies of formation, Gibbs free energies of formation, compressibilities and standard heat capacities) of aqueous biomolecules over a wide temperature range [126].

3.3. Models based on the Kirkwood–Buff solution theory

The Kirkwood–Buff solution theory [127] provides an infrastructure for evaluating thermodynamic properties of solutions, including the partial molar volume. There are a number of thermodynamic models developed based on this theory for calculating the partial molar volumes of amino acids, such as the one-dimensional reference interaction site model (1D-RISM) derived by combining the modified RISM method with the Kirkwood–Buff theory [105,128], and three-dimensional RISM (3D-RISM) [129]. Imai et al. [105] described the background and development of this type of models.

3.4. Other models

Other methods used for predicting the partial molar volumes of amino acids include Leyendekkers' model derived from the Kirkwood–Fuoss theory [130], molecular modeling techniques [131] and the correlation between the apparent molar volumes of amino acids with van der Waals and molecular volumes [132]. A detail discussion of these models is beyond the objective of this review.

The partial molar volumes of amino acids are temperature- and pressure-dependent. Cabani et al. [133] proposed a polynomial correlation for the temperature dependence of standard partial molar volumes of a number of amino acids, peptides and related compounds. Their correlation can be simply expressed as,

$$V_\phi^o = V_\phi^o(25\ °C) + \alpha^o(t - 25\ °C) + \beta^o(t - 25\ °C)^2 + \gamma^o(t - 25\ °C)^3 \quad (14)$$

where t is the temperature in °C, α°, β° and γ° are correlation constants reported in their paper [133]. This correlation is consistent with the observation by Kikuchi et al. that the partial molar volumes of amino acids in dilute aqueous solutions increase with the temperature [27]. A similar correlation equation [32,134] is written as

$$V_\phi^o = a + bT + cT^2 \quad (15)$$

Notes to Table 2:

L for L-enantiomer, D for D-enantiomer, others are DL racemates; [a]average of experimental values; [b]standard partial molar volumes at other temperatures; [c]Ref. [61], [d]Ref. [65], [e]Ref. [78], [f]Ref. [27], [g]Ref. [238], [h]Ref. [205], [i]Ref. [77], [j]Ref. [240] (volumes of ω-aminocaprylic acid are 134.36, 135.43 and 136.15 at 15, 25 and 35 °C respectively), [k]apparent molar volumes at a concentration of 3 mg/ml from Ref. [30], [l]average values from Ref. [52], [m]Ref. [73], [n]Ref. [116], [o]Ref. [11], [p]Ref. [241], [q]Ref. [115] (some data in duplication with [xx]Ref. [141] and [j]Ref. [240] from the same group), [r]Ref. [84], [s]Ref. [143], [t]Ref. [144], [u]Ref. [99], [v]Ref. [242] (cited from Ref. [86] or estimated from densities), [w]Ref. [243], [x]Ref. [182], [y]Ref. [112] (other amino acids not included in this table are other α,ω-aminocarboxylic acids up to 11-aminoundecanoic acid, and carboxylic acids of cyclopentane and cyclohexane analogues), [z]Ref. [244] (other peptides not included), [aa]Ref. [245], [bb]Ref. [123], [cc]Ref. [236], [dd]Ref. [29], [ee]Ref. [102] (apparent molal volumes of amino acids at 0.25 m of concentration; other amino acids not included are α-aminoisovaleric acid, α-aminoisocaproic acid, β-aminobutyric acid, γ-aminovaleric acid and most cyclic amino acids such as pyridine, piperazine and piperidine), [ff]Ref. [154], [gg]Ref. [119] (other dipeptides not included), [hh]Ref. [202], [ii]averaged experimental values from Ref. [28], [jj]Ref. [246], [kk]Ref. [179], [ll]Ref. [126] (V_ϕ^o values of L-tyrosine and L-dopa seemed independent of concentration due to their low solubilities in water), [mm]Ref. [147] (other drug molecules not included), [nn]Ref. [101], [oo]Ref. [199], [pp]Ref. [93] (other amino acids not included in this table are 7-aminoheptanoic acid, 8-aminooctanoic acid and 11-aminoundecanoic acid), [qq]Ref. [184], [rr]Ref. [216], [ss]Ref. [118], [tt]Ref. [247] (other amino acids not included in this table are β-alanine, β-phenylalanine, isoserine and more), [uu]Ref. [248], [vv]Ref. [110] (betaines of α,ω-aminocarboxylic acids are not included in this table), [ww]Ref. [249] (data of peptides are not included), [xx]Ref. [141], [yy]Ref. [225] (other tripeptides not included), [zz]Ref. [250], [aaa]Ref. [124], [bbb]Ref. [74, 122], [ccc]Ref. [74], [ddd]Ref. [156], [eee]Ref. [32], [fff]Ref. [208], [ggg]Ref. [153] (other amino acids not included are 3-aminobutanoic acid, 8-aminooctanoic acid and 11-aminoundecanoic acid), [hhh]Ref. [181], [iii]Ref. [251] (several peptides were also reported), [jjj]Ref. [98] (the value of γ-amino-*n*-valeric acid is 90.0), [kkk]Ref. [252], [lll]extrapolation from partial molal volumes in Ref. [253], [mmm]extrapolation from partial molal volumes re-calculated from the density data in Ref. [254] (asparagine is in hydrate form: L-asparagine·H_2O), [nnn]values in D_2O from Ref. [137], [ooo]Ref. [255], [ppp]Ref. [169], [qqq]Ref. [256], [rrr]Ref. [200], [sss]Ref. [138], [ttt]Ref. [173], [uuu]Ref. [139], [vvv]Ref. [257], [www]Ref. [97], [xxx]Ref. [95], [yyy]Ref. [201], [zzz]Ref. [258].

where a, b and c are constants and T is the absolute temperature. The partial molar volumes of aqueous α-alanine, β-alanine and proline under hydrothermal conditions (25 to 250 °C) and pressures up to 20.0 MPa were determined by Clarke and Tremaine [125]. They observed that the standard partial molar volumes increase with temperature but decrease at temperatures above 125 °C due to a lower critical temperature in the solution than that in water.

The apparent molar volume of amino acids is also pressure-dependent. Bridgman and Dow [135] measured the volumes of aqueous solutions of amino acids (glycine, α-aminobutyric and ε-aminocaprotic acid) at pressures up to ~10,000 atm. However, they observed the contamination of their solutions after a run. The apparent molar volumes of glycine and its uncharged isomer glycolamide, alanine and its uncharged isomer lactamide, and glycylglycine were studied Yayanos [136] at 25 °C and at pressures up to 1000 atm. The apparent molar volumes of dipolar amino acids and glycylglycine were found increasing with pressure, while those of the uncharged isomers decreasing with pressure. The rate of change with pressure was believed to be concentration- and pressure-dependent.

The partial molar volumes of amino acids and peptides in D_2O were not shown significantly different from values in H_2O although the thickness of the 'empty' volume layer surrounding the solute molecule in D_2O is slightly larger that in H_2O [137].

It is interesting to notice that most experimental measurements (Table 2) were done at concentrations greater than 0.01 m; therefore, the linearity was observed as shown in Eq. (4). However, Romero and Munar [138] determined the volume behavior of several amino acids at lower concentrations (< 0.01 m) and found out the apparent molar volumes sharply deviate from the linear relationship of Eq. (4). At this lower concentration region, they observed that apparent molar volumes of α- and β-alanine dramatically decrease with the increase of concentration, while those of serine, phenylalanine aspartic acid and α-amino-*n*-butyric acid increase with the concentration. According to this report, the standard partial molar volume extrapolated from the apparent molar volume (V_ϕ) based on Eq. (4) may not be the 'real' value at infinite dilution. Lark et al. [139] also noticed a sharp increase of apparent molar volumes of transfer from water to NaCl solutions with the increase of concentration (up to 0.05 m). Both papers explained the 'unusual' behavior was due to the strong solute–solute interactions in the dilute region. Lark et al. [139] suggested that the following correlation should be used at low concentrations (up to 0.06 m) instead of Eq. (4),

$$V_\phi = V_\phi^o + S_v m^{1/2}. \tag{16}$$

4. Relationship between *B*-coefficients and standard partial molar volumes

There is a linear relationship between ionic B-coefficients and the ionic standard partial molar volumes [25]. Major contributions to the B-coefficient are from the volume of solute in the solution, plus a water-structure contribution if water is the solvent. Such a relationship was described by Krumgalz [140] for large hydrophobic ions as

$$B/\mathrm{dm^3\ mol^{-1}} = 2.5(V_\phi^o/\mathrm{dm^3\ mol^{-1}}) + B_{str} \tag{17}$$

The B_{str} term can be omitted for non-aqueous solvents. However, a general linear formula shown below is more representative for many aqueous and non-aqueous systems.

$$B/\mathrm{dm^3\ mol^{-1}} = aV_\phi^o + b \tag{18}$$

Similarly, this correlation relationship between B and V_ϕ^o is also applicable to amino acids in aqueous solutions [65,78], as well as in aqueous solutions containing salts [68,79,92,114,116,141], or organic solutes (such as 1,4-dioxane [94]) at various temperatures.

The correlation using selected B-coefficients ($\mathrm{dm^3\ mol^{-1}}$) from Table 1 and selected V_ϕ^o ($\mathrm{dm^3\ mol^{-1}}$) from Table 2 resulted in a=4.99, b=−0.0693 and a correlation coefficient of 0.873 (17 amino acids involved in the correlation. They are Gly, Ala, Val, Nval, Leu, Nleu, Ser, Thr, Glu, Arg, His, Phe, Pro, Aaba, Gaba, Dava and Eacc).

5. Viscometric and volumetric properties of cations and anions of amino acids

The zwitterionic amino acids exhibit higher B-coefficients than those uncharged isomers. For example, the B-value of glycine at 25 °C (from Table 1) is about 0.03–0.04 unit ($\mathrm{dm^3\ mol^{-1}}$) higher than that of glycolamide (0.1041 at 20 °C [61], 0.104 at 25 °C [142]); the B-coefficient of α-alanine at 25 °C (0.252 from Table 1) is about 0.05 unit higher than that of lactamide (0.1984) [143]. In terms of standard partial molar volumes at 25 °C, glycine (V_ϕ^o=43.18 $\mathrm{cm^3\ mol^{-1}}$ from Table 2) has a smaller V_ϕ^o than glycolamide (57.6 [112] or 56.156 [99]) and α-alanine (60.48 from Table 1) has a smaller volume than lactamide (72.7 [112] or 73.508 [144]), indicating the charged isomers are more hydrated. Charles [145] noticed that the B-coefficient of a base is about 0.10–0.18 unit higher than that of its conjugated acid for several carboxylic acids, tetraalkylammonium and amino acids. According to data from Refs. [60,145] as shown in Table 3, the decreasing order of B-coefficients and kosmotropicity is: $Gly^- \gg Gly^+ > Gly$, $Ala^- > Ala$, betaine > $betaine^+$. However, the B-coefficient of $betaine^+$ at 16 °C was calculated from a negative B-value of betainium chloride [60], which was considered 'unacceptable' [63]. Bhattacharyya and Sengupta [63] reported the order of B-coefficients as $B_{anion} > B_{cation} > B_{zwitterion}$ for both glycine and betaine systems. As conjugated acids or bases of amino acids, the cations and anions seem to have greater B-coefficients and thus higher kosmotropicity than the zwitterionic amino acids. Meanwhile, dB/dT is positive for glycine, but are negative for both glycinate and glycinium ions [63], further confirming the latter two are kosmotropic. The B-value was found to be almost temperature-independent (25–45 °C) for betaine, but is negative for betaine cation [63]. This observation classifies betaine as neither a structure-maker nor a structure-breaker, but its cation as a structure-maker. The similar structure promotion was also demonstrated by Laurence and Wolfenden [146] in the case of

Table 3
B-coefficients ($dm^3\ mol^{-1}$) and standard partial molar volumes (V_ϕ^o, $cm^3\ mol^{-1}$) of amino acid ions

Amino acid and ions	*B* ($dm^3\ mol^{-1}$)	V_ϕ^o at 25 °C ($cm^3\ mol^{-1}$)	Amino acid and ions	*B* ($dm^3\ mol^{-1}$)	V_ϕ^o at 25 °C ($cm^3\ mol^{-1}$)
Gly	0.143 (25), 0.144 (40)	43.18	L-Lys$^+$		101.37,[e] 101.47,[f] 101.46,[h]
Gly$^-$	0.242 (25),[n] 0.24 (18),[a] 0.27 (40),[a]	47.5,[d] 50.39,[i] 49.1,[k] 49.51,[m] 46.7,[n] 50.49[o]	Lys$^+$		102.6,[g] 100.97,[j]
Gly$^+$	0.160 (25),[n] 0.151 (40) [b]	47.5,[d] 45.38,[i] 43.7,[k] 40.7,[l] 43.92,[m] 42.7,[n] 42.28[o]	Arg	0.5013 (25)	124.55
Gly betaine	0.2173 (15)[c]	97.6	L-Arg$^+$		116.55,[e] 116.76,[h] 116.49,[f]
Gly betaine$^+$	−0.04 (16),[c] 0.241 (25)[n]	97.55,[i] 97.45,[m] 99.7,[n]	Arg$^+$		118.13,[j]
Ala	0.252 (25), 0.233 (40)	60.48	His	0.39 (25)	98.86
Ala$^-$	0.38 (18),[a] 0.37 (40),[a]	63.4,[d] 66.51[o]	L-His$^+$		90.49,[f]
Ala$^+$		65.3,[d] 63.52[o]	His$^+$		89.73,[j]
Val	0.414 (25)	90.87	Gaba[p]	0.312 (25)	73.23[o]
Val$^-$		92.8,[d]	Gaba$^-$		82.21[o]
Val$^+$		96.7,[d]	Gaba$^+$		77.35[o]
Asp	0.13 (25)	73.65	Dava[q]	0.383 (25)	87.65[o]
Asp$^-$/Asp^{2-}		69.0 (Asp$^-$),[d] 70.63−L (Asp$^-$),[f] 69.1 (Asp^{2-}),[d]	Dava$^-$		97.16[o]
Asp$^+$		78.4,[d]	Dava$^+$		93.53[o]
Glu	0.29 (25)	88.97	Eacc[k]	0.489 (25)	104.35,[k]
L-Glu$^-$		85.99,[f]	Eacc$^-$		112.7,[k] 113.45[o]
Lys		108.71	Eacc$^+$		112.1,[k] 111.02[o]

Numbers in parenthesis are temperatures of *B*-coefficients; although the standard partial molar volumes of amino acid salts are available at other temperatures in the following literatures, they are not included in this table due to the lack of V_ϕ^o values of counter ions (such as Cl^-, Na^+) at these temperatures; if no references indicated, *B*-coefficients and V_ϕ^o values of zwitterionic amino acids are selected values from Tables 1 and 2, respectively; [a]Ref. [145], [b]calculated using *B*(Gly·HCl, 40 °C)=0.16 from Ref. [60] and *B*(Cl^-, 40 °C)=0.009 from Ref. [25], [c]calculated using *B*(betaine·HCl, 16 °C)=−0.06 and *B*(Cl^-, 16 °C)=−0.02 both from Ref. [60], [d]averaged apparent molar volumes at 0.25 m of concentration (NOT at infinite dilution) from Ref. [102], [e]based on the additivity using data of amino acid hydrochloride (other temperatures not included) from Ref. [259] and $V_\phi^o(Cl^-)$=23.3 at 25 °C (same value used in other calculations) [24]; [f]based on the additivity using data of monosodium or monohydrochloride salts of amino acids from Ref. [154] (values at other temperatures not included) and $V_\phi^o(Na^+)$=−6.7 at 25 °C (same value used in other calculations) [24]; [g]calculated from Ref. [30], [h]calculated from Ref. [29], [i]collections of Gianni and Lepori [117], [j]calculated from Ref. [247], [k]Ref. [77] (Eacc=ε-aminocaproic acid or 6-amino-*n*-hexanoic acid), [l]based on V_ϕ^o(Gly·HCl, 25 °C)=63.959 which was obtained through a linear extrapolation of apparent molar volume data in Ref. [88], [m]calculated from Ref. [222], [n]calculated from Ref. [63] using *B*(Na^+)=0.085 and *B* (Cl^-)=−0.005 [25], $V_\phi^o(Cl^-)$ and $V_\phi^o(Na^+)$ values from above, [o]from or calculated from Ref. [153] (other ions not included are cations and anions from 8-aminooctanoic acid and 11-aminoundecanoic acid), [p]Gaba=γ-amino-*n*-butyric acid (4-aminobutanoic acid), [q]Dava=δ-amino-*n*-valeric acid (5-aminopentanoic acid).

acetate anion (B_{Ac^-}=0.245 and B_{HAC}=0.117). The *B*-values of amino acid ions can not be simply obtained from the *B*-coefficients of amino acids based on the additivity because amino acids are weak carboxylic acids and weak bases of amines, and they do not dissociate completely in water. Instead, since the salts of amino acids are generally considered completely dissociated [102] (shown in the following two equations where A is the zwitterionic amino acid), the *B*-coefficients of amino acid ions can be calculated from *B*-values of their corresponding salts following the additivity method [147].

$$A{\cdot}HCl \rightarrow AH^+ + Cl^- \quad (19)$$

$$A^-Na^+ \rightarrow A^- + Na^+ \quad (20)$$

Bhattacharyya and Sengupta [148,149] determined the *B*-coefficients of glycine, α- and β-alanine, 2-aminobutyric acid (butyrine) and 4-aminobutyric acid in water, 0.1 N NaOH and 0.1 N HCl, respectively, at temperatures between 30 and 45 °C. Their results illustrated that the *B*-coefficients for these amino acids follow the sequence $B(H_2O) > B(NaOH) > B(HCl)$. One might figure out $B_{zwitterion} > B_{anion} > B_{cation}$ for amino acid systems using the *B*-values of Na^+ and Cl^-; however, such a sequence is inconsistent with the previous discussion. The possible problem is that the *B*-coefficient of cations and anions can not be simply deduced from such systems based on the additivity because of the presence of HCl or NaOH molecules in solutions of amino acid salts. In addition, although the predominated species in 0.1 N HCl (pH 1.2) and 0.1 N NaOH (pH 12.4) are glycine cations and anions, respectively, there are zwitterions of glycine as well. As evidenced by the NMR spectra of ^{15}N-enriched glycine at different pHs [150], the predominated species were found to be glycine cations (99.99%) at pH 0.5, zwitterions at pH 6.4 and the anions (99.99%) at pH 13.6. In another approach, Bhattacharyya and Sengupta [151] measured the *B*-coefficients of glycine, β-alanine and 4-aminobutyric acid at pH=pK_1 (in HCl) and pH=pK_2 (in NaOH), respectively, at 30 °C. Relying on the assumption that the contributions of two forms of amino acids (either zwitterions + cations or zwitterions + anions) to the *B*-coefficients at pH=pK_1 and pH=pK_2 are identical, they subtracted the *B*-coefficient in pure water from those in HCl and NaOH solutions respectively, resulting in $B_{zwitterion} \gg B_{anion} \sim B_{cation}$ for glycine and $B_{zwitterion} \gg B_{anion} > B_{cation}$ for the other two amino acids. However, they forgot the presence of HCl or NaOH molecules (they were not completely consumed by the reactions) and their contributions; in addition, the additivity principle of *B*-coefficients may not be applicable to such mixture systems.

The standard partial molar volumes of amino acid ions can also be calculated from the data of hydrochlorides and alkali

salts based on the additivity shown in Eqs. (19) and (20) [152]. The general trend of the standard partial molar volumes of most amino acids (Tables 3 and 4) is in a decreasing order of V_ϕ^o(anion) > V_ϕ^o(cation) > V_ϕ^o(zwitterions) [153]. But there are some exceptions (such as valine, aspartic acid, arginine and histidine). The apparent molar volumes of ions of some amino acids (e.g. Gly^+, Ala^+, Val^+, Glu^+, Asp^+) are greater than the zwitterions. It was explained that the electrostriction of amino acid ions is slightly greater than that of zwitterions [102]. However, the standard partial molar volumes of Asp^-, Asp^{2-}, L-Arg^+ and L-His^+ are smaller than their zwitterionic amino acids. Meanwhile, there seems no simple relationship between the *B*-coefficients of amino acid ions and their standard partial molar volumes. The standard partial molar volumes of L-Asp^-, L-Glu^-, L-Lys^+, L-Arg^+ and L-His^+ were also reported increasing with the temperature [154].

Table 4 summarized the standard partial molar volumes of α,ω-amino acids as well as their corresponding cations and anions. The V_ϕ^o values are in the increasing order of zwitterion < cation < anion for each amino acid. As explained in the previous section, since the *B*-coefficients increase with the standard partial molar volumes for homologous solutes, the *B*-coefficients are in an increasing order of zwitterion < cation < anion for each amino acid (such as glycine in Table 3). Therefore, the anion of an amino acid is more kosmotropic than its cation and itself. Lepori and Mollica [153] concluded that the interactions between two polar end-groups (NH_3^+ and COO^-) of ω-aminocarboxylic acids decrease with the increase of methylene units in between, but do not vanish even they are separated by 10 methylene units. However, Shahidi [155] argued that the dissociation of α,ω-aminocarboxylic acids follows different processes (Eqs. (21) and (22)) instead of Eqs. (19) and (20).

$$A{\cdot}HCl \rightarrow A + HCl \tag{21}$$

$$A^-Na^+ + H_2O \rightarrow A + NaOH \tag{22}$$

According to Eqs. (21) and (22), the additivity calculations of *B*-coefficients and partial molar volumes based on Eqs. (19) and (20) might be in question.

Table 4
Standard partial molar volumes (V_ϕ^o, $cm^3\ mol^{-1}$) of α,ω-amino acids [$NH_3^+(CH_2)_nCOO^-$] and their anions and cations[a] at 25 °C

Amino acid	V_ϕ^o	Cation	V_ϕ^o	Anion	V_ϕ^o
$n=1$	43.30	$n=1$	45.38	$n=1$	50.39
2	58.38	2	60.70	2	66.27
3	73.23	3	77.45	3	82.11
4	87.65	4	93.63	4	97.06
5	104.09	5	111.12	5	113.35
6	120.0	6	126.18	6	128.53
7	136.03	7	143.93	7	145.48
8	151.3	8	158.15	8	160.67
9	167.3	9	174.49	9	176.62
10	183.00	10	191.50	10	193.0

[a] Collections of Gianni and Lepori [117]; Shahidi [155] reported similar results for hydrochlorides and sodium salts of α,ω-amino acids.

Bhattacharya and Sengupta [156] further examined the standard partial molar volumes of amino acids in water, 0.1 N NaOH and 0.1 N HCl, respectively, and found that V_ϕ^o(NaOH) > V_ϕ^o(HCl) > V_ϕ^o(H_2O). The authors suggested the series of V_ϕ^o(anion) > V_ϕ^o(cation) > V_ϕ^o(H_2O) based on the additivity although they neglected the effect of remaining NaOH and HCl on the partial molar volumes. Abbate et al. [152] observed a similar sequence in 1 M solutions of HCl and NaOH as V_ϕ^o(NaOH) > V_ϕ^o(HCl) > V_ϕ^o(H_2O). However, they realized that in order to calculate the partial molar volumes of amino acid ions, the H^+ contribution (for example, $V_\phi^o = -5.2\ cm^3\ mol^{-1}$ at 22 °C [157] and a variety of other values [158]), or OH^- ($V_\phi^o = -0.2\ cm^3\ mol^{-1}$ at 25 °C [159,160]) and H_2O (for example, $V_\phi^o = 6.6\ cm^3\ mol^{-1}$ at 25 °C [34]) contributions should be considered in acidic and basic solutions, respectively, as shown in the following equations.

$$V_\phi^o(\text{cation}) = V_\phi^o(\text{HCl}) + V_\phi^o(H^+) \tag{23}$$

$$V_\phi^o(\text{anion}) = V_\phi^o(\text{NaOH}) + V_\phi^o(OH^-) - V_\phi^o(H_2O) \tag{24}$$

A similar approach by Rao et al. [161] derived the formulas for calculating the partial molar volumes of amino acid ions in acidic or basic solutions by considering the contributions by H^+, or OH^- and H_2O. They reported the partial molar volumes of several amino acids (Gly, Ala, Asp, Glu, Lys and Arg) and their singly or multiply charged ions at 20 °C, showing a general agreement with those in literatures (calculated from amino acid salts).

6. Viscometric and volumetric properties of amino acids in aqueous solutions of salts and organic solutes

The study of solute effect on the volumetric and viscosity properties of amino acids is of great importance because biological fluids are not pure water after all, and solutes (salts and organic solutes) have a significant impact on the protein (enzyme) stability and activity [5,10,22,162–164]. The following two sections discuss the changes of *B*-coefficients and standard partial molar volumes of amino acids in solutions of salts and organic solutes respectively in terms of their effects on the hydration of amino acids.

6.1. Salt aqueous solutions

The temperature dependence of *B*-coefficients of amino acids is helpful in quantifying the kosmotropicity of amino acids in salt solutions. For example, α-alanine is a structure breaker in Na_2SO_4 solutions based on its positive d*B*/d*T*, while β-alanine is a structure maker in Na_2SO_4 solutions although it is chaotropic in water [65,68] and KSCN solutions [68].

Generally, *B*-coefficients of amino acids increase with the salt concentration as illustrated in those references of Table 5. It is more convenient to use the difference between *B*-coefficient of an amino acid in a certain concentration of salt and *B*-coefficient of the same amino acid in pure water, so-called *B*-

Table 5
Viscosity *B*-coefficients of transfer ($dm^3\ mol^{-1}$) from water to salt solutions and hydration numbers (in parenthesis) in salt solutions at 25 °C

Salt	Gly	Ala	Val	Leu	Ser	Aaba	Gaba	DG
H_2O	(**3.52 or 2.63**),[r] (**2.9**),[s] (**3.26**)[t]	(**4.65 or 3.41**),[r] (**3.8**),[s] (**2.89**)[t]	L-(**5.18 or 3.43**),[r] L-(**3.9**)[s]	L-(**7.09 or 4.96**),[r] L-(**5.5**)[s]				
Na_2SO_4 (1.0 m)	0.006[a]	−0.017[a]	0.059[a]			0.016[a]	0.014[a]	
Na acetate (1.0 m)	0.011,[b] 0.004,[c] (**1.76**)[b]	0.017,[b] 0.018,[c] (**2.84**)[b]	0.076[c]	0.008−L,[b] 0.031−DL,[b,c] (**4.64**−L)[b]		0.028,[b] 0.056[c]		
Na acetate (4.0 m)	0.011,[b] (**0.94**)[b]	0.018,[b] (**2.14**)[b]		0.015−L,[b] (**4.10**−L)[b]		0.030[b]		
Na butyrate (1.0 m)	0.003, (**1.8**)[h]	0.018, (**2.8**)[h]	0.079, (**3.2**)[h]	0.025, (**4.9**)[h]		0.050, (**3.1**)[h]		
Na caproate (1.0 m)	−0.001,[i] (**1.6**)[j]	0.011,[i] (**2.7**)[j]	0.073,[j] (**3.0**)[j]	0.014,[j] (**4.8**)[j]		0.039,[i] (**2.9**)[j]		
Na caprylate (1 m)	0.061[f]	0.062[f]	0.111[f]	0.095[f]		0.079[f]		
LiCl (1 m)	−0.001[u]	0.008−L[u]			0.010−L[u]			
NaCl (1 m)[u] (0.02–0.10 M at 30 °C)[aa]	0.012,[u] −0.0392 (0.02 M),[aa] 0.0508 (0.06 M),[aa] 0.0225 (0.10 M)[aa]	0.009−L[u]			0.017−L[u]			
KCl (1 m)	0.003,[u] −0.022[y]	0.001−L,[u] −0.030[y]		−0.045−L[y]	0.016−L[u]			
KSCN (1.0 m)	0.008,[e] 0.016[q]	0.020,[e] −0.012[q]					0.016[e,q]	
KSCN (5.0 m)	0.047[q]	0.004[q]					0.041[q]	
NH_4Cl (~1.25 m)	2.0 m NH_4Cl 0.084,(**2.39**)[g]	0.107,(**2.97**)[g]	(**2.68**) [g]		0.063−L, (**3.31**−L)[g]		0.030[g]	
$CaCl_2$ (3.0 m)	0.080, (**0.3**)[d]	0.090, (**1.1**)[d]	0.163, (**1.5**)[d]	0.125, (**3.8**)[d]	0.110−L, (**2.4**−L)[d]	0.143, (**3.4**)[d]		
$MgCl_2$ (0.02–0.10 M at 30 °C)[aa]	0.295 (0.02 M),[aa] 0.060 (0.06 M),[aa] 0.082 (0.10 M)[aa]							
$BaCl_2$ (1.0 m)	−0.350[y]	−0.051[y]		−0.092−L[y]				
Urea (0.1 m)	−0.027[x]		−0.075[x]		−0.073[x]			
Urea (0.84 M)	0.0245[p]	−0.134[p]	−0.224[p]					
Urea (4.44 M)	0.175[p]	−0.222[p]	0.0351[p]					
Urea (5 m)	0.044[k]	0.037[k]	0.090[k]	0.032[k]	0.061−L[k]	0.068[k]		
Acetonitrile[l] (5–20% w/w, about 1.2–5 m)	5%: 0.005, 10%: 0.017, 15%: 0.027, 20%: 0.046	5%: 0.006, 15%: 0.010, 20%: 0.020						
DMF[m] (5–25% w/w, about 1–4.3 m)	5%: −0.001, 15%: 0.007, 25%: 0.018	5%: 0.0018, 15%: 0.0034, 24%: 0.0099						
Methanol[z] (5–45% w/w, about 1.6–14 M)	5%: −0.009, 25%: −0.036, 45%: 0.006	5%: −0.026, 15%: −0.046, 45%: −0.018				5%: −0.032, 25%: −0.057, 45%: −0.038		
Dioxane (2.5–25.0% w/w)[cc]	5.0%: 0.007, (**3.45**), 10.0%: 0.0015, (**3.44**), 25.0%: 0.024, (**3.19**)	5.0%: 0.023, (**4.64**), 10.0%: 0.021, (**4.63**), 25.0%: 0.033, (**4.51**)	5.0%: −0.005−L, (**5.18**) 10.0%: 0.004−L, (**5.43**), 25.0%: 0.019−L, (**5.42**)	5.0%: −0.003−L, (**6.73**), 10.0%: 0.001−L, (**7.61**), 25.0%: 0.017−L (**7.40**)				
Dioxane (5–40%, w/w)[bb]	5%: 0.006, 10%: 0.002, 20%: 0.020, 40%: 0.062	5%: 0.004, 20%: 0.024						
n-Propanol (1 m)[n]	0.011, (**2.57**)	0.028 (**2.67**)	0.017−L (**3.24**)	0.049−L (**2.82**)		0.022 (**2.97**)		−0.029
n-Propanol (5 m)[n]	−0.033	−0.033	−0.062−L	−0.149−L		−0.027		−0.054
1,2-Propanediol (1 m)[o]	0.010	0.014		0.116−L		0.047		
D-Glucose (0.83 m) [v]	0.022	0.027−L						
Glucose (1.0 m)[y]	0.005	0.006		0.026−L				
Sucrose (1.0 m)[y]	0.008	0.009		0.117−L				
GnH^+Cl^- (6 m)[w]	0.069	0.074	0.089	−0.006	0.096−L	0.091		

For abbreviations of amino acids, see Table 1; DG = diglycine; salt concentrations normally in the unit of m for molality (mol kg^{-1}) unless indicated in M for molarity (mol L^{-1}); [a]Ref. [115], [b]from or calculated from Ref. [116], [c]Ref. [79], [d]Ref. [165], [e]Ref. [68], [f]Ref. [114], [g]calculated from Ref. [73], [h]Ref. [92], [i]Ref. [260], [j]Ref. [167], [k]Ref. [183], [l]glycine data at 25 °C and alanine data at 30 °C calculated from Ref. [72], [m]Ref. [180], [n]Ref. [195], [o]Ref. [113], [p]calculated from Ref. [261] using *B*-coefficients of 0.143, 0.252 and 0.414 for Gly, Ala and Val in pure water (Table 1), respectively, [q]calculated from Ref. [141], [r]Ref. [184] (hydration numbers based on different intrinsic volumes), [s]Ref. [213], [t]Ref. [238], [u]Ref. [74], [v]Ref. [211], [w]GnH^+Cl^- = guanidine HCl (or guanidinium chloride) calculated from data in Ref. [67] using selected *B*-coefficients in water from Table 1, [x]calculated from data in Ref. [262] and selected *B*-coefficients in water from Table 1, [y]Ref. [208], [z]Ref. [191] (the standard partial molar volumes of L-serine and L-threonine were determined by Sandhu et al. [263] in 10–30 wt.% methanol solutions), [aa]calculated from *B*-coefficients of glycine at 30 °C from Ref. [50] using averaged *B*-value of glycine in water (0.135) at 30 °C from data in Table 1, [bb]calculated from Ref. [181], [cc]Ref. [94] (hydration numbers shown here were calculated from the volume method; this reference also reported hydration numbers calculated from the compressibility method and viscosity method).

coefficient of transfer (B_{tr}), when comparing the effect of different salts. The B_{tr} data for various salt solutions are shown in Table 5.

Table 5 illustrates that kosmotropic anions (e.g. sulfate, acetate, butyrate, caproate and caprylate) and compatible solutes (e.g. glucose, sucrose and polyols) do not seem to have much influence on the B_{tr} because they are strongly hydrated and do not interact strongly with amino acids. Especially, when the concentration of CH_3COONa increased from 1.0 m to 4.0 m, B_{tr} is basically unchanged. However, strong kosmotropic cations (such as Mg^{2+}, Ca^{2+} and Ba^{2+}, comparing data of 3.0 m $CaCl_2$ with 4.0 m CH_3COONa in Table 5) significantly change B_{tr}, suggesting these cations strongly interact with amino acids. In $CaCl_2$ solutions, both the zwitterionic (NH_3^+, COO^-) and hydrophobic (CH_2) groups showed negative dB/dT values, implying both groups are structure-makers [165]. It is known that Ca^{2+} strongly salts in the peptide group while SO_4^{2-} does not, although both ions salt out non-polar group [20]. The salt-in is due to the interaction of Ca^{2+} with the peptide group whereas the salt-out is due to the strong hydration of these kosmotropic ions. The B_{tr} values of glycine and L-alanine in 1 mol kg^{-1} electrolytes at 25 °C were observed in an increasing order for cations: $Mg^{2+} < Na^+ < K^+$ and for anions: $Cl^- < Br^-$ [166]. One conclusion drawn from these data is that strongly hydrated ions (kosmotropes) have less effect on the *B*-coefficients of amino acids than weakly hydrated ones (chaotropes).

The individual contributions of polar groups (NH_3^+ and COO^-) [i.e. $B(NH_3^+, COO^-)$] and non-polar (hydrophobic) CH_2 groups [i.e. $B(CH_2)$] of amino acids are also informative in identifying the effect of salts on both groups. For example, in 6 mol kg^{-1} aqueous guanidine hydrochloride solution, $dB(NH_3^+, COO^-)/dT$ was found positive indicating the structure-breaking effect of polar groups, while $dB(CH_2)/dT$ was negative indicating the structure promotion of non-polar groups [67].

On the other hand, the standard partial molar volumes (V_ϕ^o) of amino acids in salt solutions allow us to better understand the salt effect on the hydration of amino acids. Similarly, for the convenience of comparison, the standard partial molar volumes of transfer (V_{tr}^o) is defined as the difference between the standard partial molar volume in solution and that in pure water. Strongly hydrated ions have small even negative values of V_ϕ^o, for example, V_ϕ^o values for strongly hydrated Al^{3+} and weakly hydrated K^+ are −58.7 and 3.5 cm^3 mol^{-1} [159,160], respectively. The positive number of the transfer volumes indicates the hydration number of amino acids is reduced upon the addition of solutes [74]. Therefore, a higher V_{tr}^o value actually means the amino acid is more dehydrated in the solution. As a general rule, the volume of transfer increases with the salt concentration (Table 6) indicating that the high ionic strength 'dehydrates' amino acids [92,167]. Through inspecting data in Table 6, it is noticeable that the volumes of transfer (V_{tr}^o) are typically high in solutions containing strongly hydrated ion (such as SO_4^{2-}, Ca^{2+}, CH_3COO^-, butyrate, caproate and caprylate) and usually low in solutions of weakly hydrated ions (such as Cl^-, Br^-, SCN^-, NH_4^+ and Et_4N^+). These results suggest that amino acids are less hydrated in solutions containing strongly hydrated ions because these ions tend to take more water molecules to hydrate themselves, leaving amino acids with less water molecules. In fact, the dehydration effect of ions on amino acids is considered as one of the most important reasons of salting-out amino acids [168]. Based on the hydration numbers of amino acids in salt solution, Yan et al. concluded that caproate has larger dehydration effect on the amino acids than butyrate and acetate [92,167]. An increase of *B*-coefficients with increase in salt concentration and of the transfer volume from water to NH_4Cl solutions was observed and explained due to the strong interactions of NH_4^+ and Cl^- ions with the head groups (COO^- and NH_3^+) of amino acids rather than with non-polar groups [73]. The NH_4Cl salt imposed a structure-breaking effect on the hydrogen-bonded structure of water in its vicinity. Positive transfer volumes were observed in solutions of tetra-*n*-alkylammonium bromides, and $[Bu_4N]Br$ salt caused a larger increase in the transfer volumes of amino acids or peptides than $[Me_4N]Br$ and $[Et_4N]Br$ (Table 6) [169]. The $[Et_4N]Br$ salt is known to destabilize proteins such as lysozyme [170], and it was explained that the denaturing action of tetraalkylammonium halides was due to the binding of the denaturants to the protein being stronger than the exclusion of cosolvent from the protein surface [171,172]. The above phenomena indicate that larger tetra-*n*-alkylammonium cations cause more dehydration of amino acids, which is consistent with the fact that large hydrophobic cations are more kosmotropic due to the hydrophobic hydration [24]. Badarayani and Kumar [169] suggested that ions experiencing hydrophilic hydration have stronger effect on the amino acid hydration than those ions experiencing hydrophobic hydration. Ogawa et al. [74] also noticed that the alkali chlorides have a dehydration effect on the amino acids, and the order of decreasing dehydration effect is: $Na^+ > K^+ > Li^+$. This sequence was explained by the difference in the interaction of the alkali cations with the amino acid; Li^+ ion has a stronger interaction with amino acids because of its smaller crystal radius, causing higher electrostriction effect and thus a higher partial molar volume of amino acid [74]. However, a contradictory result reported by Basumallick et al. [173] suggested that for the same amino acid, the difference of volumes of transfer in solutions of various alkali halides is negligible. By further examining the data of volumes of transfer (V_{tr}^o) and hydration numbers in Table 6 and considering that both Na^+ and Et_4N^+ cations are borderline ions (having little effect on the water structure), the series of ions in a decreasing ability in 'dehydrating' amino acids is obtained as:

$$\text{Cation: } Ba^{2+} > Mg^{2+} > Ca^{2+} > Na^+ > K^+ > Li^+ > NH_4^+$$

$$\text{Anion: caprylate}^- > SO_4^{2-} > \text{caproate}^- > \text{butyrate}^- > \text{acetate}^- > Cl^- > Br^- > SCN^-$$

This order is consistent with the Hofmeister series of salting out proteins [5,10,20,163]. The volumes of transfer in 6.0 M or m guanidine HCl (GnH^+Cl^-) solution are close to those in 5.0 m KSCN (Table 6), indicating these two salts have similar abilities in affecting the hydration of amino acids. In fact, both guanidinium (GnH^+) and SCN^- are well known protein

Table 6
Standard partial molar volumes of transfer (V_{tr}^{o}, cm^3 mol^{-1}) from water to salt solutions and hydration numbers (n_H, in parenthesis and bold) in salt solutions at 25 °C

Salt (*c*)	Gly	Ala	Val	Leu	Ser	Aaba	Gaba	DG	TG
H_2O	(**3.26**),[c] (**3.52 or 2.63**),[u] (**2.9**)[v]	(**2.89**),[c] (**4.65 or 3.41**),[u] (**3.8**)[v]	L-(**5.18 or 3.43**),[u] L-(**3.9**),[v] L-(**5.15 or 3.40**)[cc]	L-(**7.09 or 4.96**),[u] L-(**5.5**),[v] L-(**7.17 or 5.04**)[cc]					
Na_2SO_4 (1.0 M or m)	4.59,[a] 4.50,[c] 4.2,[f] (**1.18**)[c]	4.05,[a] 4.06,[c] 3.9,[f] (**1.13**)[c]	4.28−L,[a] 4.1[f]	3.47−L[a]	5.08[a]	3.6[f]	4.7[f]	5.58[a]	
Na_2SO_4 (2 m)	6.90[dd]						1.71[dd]		
Na acetate (1.0 M or m)	2.19,[a] 2.9,[b] 2.06,[q] (**1.76**),[b] (**1.9**)[q]	1.92,[a] 1.95,[b] 1.34,[q] (**2.84**),[b] (**3.0**)[q]	1.64−L,[a] 0.55,[q] (**3.2**)[q]	0.53−L,[a] 1.02−L,[b] 0.22,[q] (**4.64−L**),[b] (**5.0**)[q]	2.44[a]	1.57,[b] 1.05,[q] (**3.2**)[q]		3.62[a]	3.70[a]
Na butyrate (1.0 m)	2.45, (**1.8**)[h]	1.77, (**2.8**)[h]	0.54, (**3.2**)[h]	0.49, (**4.9**)[h]		1.04, (**3.1**)[h]			
Na caproate (1.0 m)	3.00,[i] (**1.6**)[j]	2.04,[i] (**2.7**)[j]	1.20,[j] (**3.0**)[j]	0.92,[j] (**4.8**)[j]		1.04,[i] (**2.9**)[j]			
Na caprylate (1.0 m)	5.14[k]	4.12[k]	4.04[k]	5.84[k]		3.98[k]			
LiCl (1.0[w] or 0.8[aa] m)	1.45,[w] 1.1,[aa] (**2.5**)[aa]	1.09−L,[w] 1.1,[aa] (**2.2**)[aa]			1.43−L[w]	1.0,[aa] (**2.3**)[aa]			
NaCl (1.0 m or M)	1.35,[l,x] 1.97,[p] 1.85,[s] 1.82,[w] 1.07[bb]	0.78,[l] 1.77−L,[p] 1.58−L,[w] 0.69,[x] 1.09[bb]	0.87−L,[l]	0.44−L,[l] 0.63−L[x]	2.50,[p] 2.02−L[w]	0.38[l]		2.57,[l] 2.38[p]	2.80[l]
NaCl (3.0 m)	2.20[l]	1.06[l]	1.02−L,[l]	0.54−L[l]		0.83[l]		4.33[l]	
NaBr (1.0 m)	4.60−L (0.05 m),[ee] (**1.24**)[ee]		0.82−L,[cc] (**3.15**)[cc]	1.24−L,[cc] (**4.66**)[cc]					
KCl (1.0[w,x] or 0.8[aa] m)	1.66,[w] 1.57,[x] 1.3,[aa] (**2.5**)[aa]	1.47−L,[w] 1.43,[x] 1.4,[aa] (**2.2**)[aa]		0.30−L[x]	2.04−L[w]	1.2,[aa] (**2.3**)[aa]			
KCl (3.0 m)	3.91[d]	3.61[d]	3.25[d]						
KBr (0.8 m)[aa]	1.2,[aa] (**2.5**)[aa]	1.2,[aa] (**2.2**)[aa]				1.1,[aa] (**2.4**)[aa]			
KI (0.8 m)[aa]	1.1,[aa] (**2.5**)[aa]	1.1,[aa] (**2.2**)[aa]				1.0,[aa] (**2.4**)[aa]			
CsCl (0.8 m)[aa]	1.1,[aa] (**2.6**)[aa]	1.1,[aa] (**2.2**)[aa]				1.0,[aa] (**2.4**)[aa]			
NaSCN (1.0 M)	1.16[a]	1.19[a]	1.81−L[a]	0.77−L[a]	1.44[a]			1.19[a]	2.23[a]
KSCN (1.0 m)	1.37[e,r]	1.33[e,r]					1.61[e,r]		
KSCN (5.0 m)	3.81[e,r]	3.69[e,r]					4.13[e,r]		
NH_4Cl (1.25 m)	*c*=1.0 m 1.09, (**2.39**)[g]	1.72, (**2.97**) [g]	1.84, (**2.68**) [g]		1.96−L, (**3.31−L**)[g]				
$[Me_4N]Br$ (1.13 m)	0.96[z]	0.20−L[z]						1.23[z]	
$[Et_4N]Br$ (1.0 M)[m] (1.2 m)[z]	1.20, (**2.5**),[m] 1.04[z]	0.02−L,(**3.8**),[m] 0.12−L[z]	−1.52−L, (**4.4**)[m]	−2.24−L, (**6.2**)[m]		−1.01[m]		0.93[z]	
$[Bu_4N]Br$ (0.73 m)	1.23[z]	0.48−L[z]						1.76 (0.59 m)[z]	
$CaCl_2$ (1.0 m)	2.98[x]	3.36[x]		2.73−L[x]					
$CaCl_2$ (3.0 m)	7.39, (**0.3**)[d]	7.50, (**1.1**)[d]	6.19, (**1.5**)[d]	4.23, (**3.8**)[d]	6.75−L, (**2.4−L**)[d]	5.47, (**3.4**)[d]			
$MgCl_2$ (*c*)	4.36 (0.918 m),[n] 4.63 (0.8 m),[y] (**1.23**)[y]	5.33−L (0.816 m),[n] 2.88 (0.8 m),[y] (**2.55−L**)[y]	−0.39−L (0.4 m),[y] (**3.52−L**)[y]	8.91−L (0.818 m)[n]					
$BaCl_2$ (1.0 m)	6.23[x]	6.44[x]		0.58−L[x]					
GnH^+Cl^- (1 m)[s], (6.0 M)[o] (6.0 m)[t,dd]	0.66,[s] 4.50,[o] 4.42,[t] 3.63[dd]	4.16[t]	4.35,[o] 3.91[t]	3.31[t]	4.67,[o] 4.05−L[t]	3.94[t]	4.39[dd]		

For abbreviations of amino acids, see Table 1; DG=diglycine, TG=triglycine; salt concentrations normally in the unit of m for molality (mol kg^{-1}) unless indicated in M for molarity (mol L^{-1}); [a]salts in 1.0 M from Ref. [106], [b]from or calculated from Ref. [116] (lower volumes of transfer in 1.0 m sodium acetate were reported at 35 °C [175]), [c]salts in 1.0 m and data calculated from Ref. [238], [d]taken or re-taken from Ref. [165], [e]Ref. [68], [f]Ref. [115], [g]calculated from Ref. [73], [h]Ref. [92], [i]Ref. [260], [j]Ref. [167], [k]Ref. [114], [l]concentration in m from Ref. [241], [m]Ref. [172], [n]Ref. [216], [o]GnH^+Cl^-=guanidine HCl (or guanidinium chloride) from Ref. [52], [p]concentration in M from Ref. [264], [q]salts in 1.0 m from Ref. [168], [r]Ref. [141] (some data in duplication with [e]Ref. [68] from the same group), [s]volumes of transfer of 0.1 m amino acids (NOT infinite dilution) to 1 m aqueous solvents at 24 °C from Ref. [205], [t]Ref[265], [u]Ref. [184] (hydration numbers based on different intrinsic volumes), [v]Ref. [213], [w]concentration in m from Ref. [74], [x]Ref. [208] (concentrations of all salts and non-electrolytes are 1.0 m), [y]Ref. [266] (hydration numbers calculated from different methods were also reported; values at 15 and 35 °C were reported recently [267]), [z]calculated from Ref. [169], [aa]Ref. [173], [bb]NaCl in 0.725 m from Ref. [139] (data in 35 °C also reported), [cc]Ref. [257] (n_H in water calculated from different equations as shown in the reference; n_H in NaBr solutions included here were from one of the equations), [dd]Ref. [268] (more ω-amino acid data at 15 and 25 °C also reported in this reference and another paper by Kumar [269]), [ee]Ref. [96] (data of L-glycine in Me_4NI and NaI solutions were also reported; however, the volumes of transfer in all salt solutions seem unusually large).

denaturants because they tend to strongly interact with the protein [20,174]. The volumes of transfer in GnH^+Cl^- solution are generally larger than the corresponding values in urea solution (Table 7) because GnH^+Cl^- is known as a stronger protein denaturant than urea. The strong interaction between GnH^+Cl^- and amino acids was due to three contributions [52]: hydrogen-bond forming between >N–H group of the guanidinium ion and the >C=O group of the amino acid, ion pairing between $-COO^-$ group of the amino acid and the $=NH_2^+$ group of the guanidinium ion, and ion pairing between $-NH_3^+$ of the amino acid and Cl^- of GnH^+Cl^-.

The thermal denaturation study of hen egg white lysozyme and α-lactalbumin in aqueous salt solutions further confirmed that the proteins are stabilized by kosmotropic CH_3COO^- and SO_4^{2-}, but destabilized by chaotropic SCN^- as indicated by Singh and Kishore [106]. They also summarized the order of volumes of transfer (V_{tr}^o) of amino acids and peptides from water to 1 M aqueous sodium salts (CH_3COO^-, SO_4^{2-} and SCN^-) as two series:

Series1: glutamate > serine > glycine≈alanine > valine > leucine

Series2: triglycine > diglycine > glycine

The salts impose stronger dehydration effect on the amino acids or peptides that are on the more left side of the above series. Series 1 is consistent with the hydrophobicity of amino acids: more hydrophilic an amino acid is, the higher the volume of transfer it has. Other data in Table 6 also confirmed that more hydrophilic amino acids undergo more dehydration effect by sodium acetate. Glutamate is negative charged and thus the most hydrophilic species than any others; serine contains a –OH group and thus is more hydrophilic (due to H-bonding with water); other amino acids (from left to right in series 1) are more hydrophobic with the increase of alkyl chain length. Interestingly, series 2 indicates that peptides are more dehydrated by salts than the amino acid. A comparable series was observed in the decreasing order for the transfer volumes of amino acids from water to alkali-chloride solutions as [74]

Series3: L-serine > L-threonine > β-alanine > glycine > L-alanine

In the presence of kosmotropic ions (such as SO_4^{2-}, Ca^{2+}, CH_3COO^-, butyrate, caproate and caprylate), the amino acids with longer alkyl chains have larger hydration numbers. Besides being larger molecules (which accommodates more coordination water molecules), amino acids with longer hydrophobic chains are more structure-making than those with short chains as suggested by Table 1, and thus are more kosmotropic and hydrated. The presence of other kosmotropic ions can further enhance the water-structure.

It is important to mention that the conventional explanation of the above series was based on the cosphere overlap model [176] in terms of solute–cosolute interactions, and suggested that strongly hydrated ions (such as sulfate [115], acetate [116], butyrate [92], caproate and caprylate [114,167]) have stronger interactions with polar groups of (NH_3^+ and COO^-) amino acids causing dehydration of amino acids, implying that weakly hydrated ions have weaker interactions with amino acids. However, it is known that kosmotropic anions (such as SO_4^{2-}) do not salt in the polar peptide group, but rather salt out non-polar groups of proteins [20]. On the other hand, protein denaturants (such as weakly hydrated SCN^-) salt in the peptide group, and both GnH^+ and SCN^- strongly interact with the protein and enzyme [20,174,177]. Meanwhile, the ion interactions with the polar peptide group is considered as a non-specific ion–dipole interaction due to the significant dipole moment of peptide groups [178], which means such ion effect depends on the ionic strength, rather than the Hofmeister series. If, as suggested by the conventional explanation, the kosmotropic ions strongly interact with the polar groups of amino acids, then they must have strong interactions with the polar peptide group rather than the hydrophobic group of proteins. A further implication of the conventional explanation is that these interactions are ionic strength-dependent and do not follow the Hofmeister series.

In summary, based on the volumetric and viscosity studies of amino acids in salt solutions, strongly hydrated (kosmotropic) ions (cations and anions) tend to 'dehydrate' amino acids, while weakly hydrated (chaotropic) ions have a better chance in interacting with amino acids. Meantime, kosmotropic cations (such as Ca^{2+}) may also have considerable interactions with amino acids.

6.2. Organic aqueous solutions

Organic solutes have a considerable impact on the volumetric and viscosity properties of amino acids. The viscosity behavior of amino acids is more complicated in organic solutions than in salt solutions. The *B*-coefficients of amino acids increase with the concentration of some solutes (type 1 or non-compatible solutes), such as acetonitrile [72], dimethylformamide (DMF) [179,180], 1,4-dioxane [181,182] and urea [183]; however, in solutions of other solutes (such as some hydroxyl groups containing compounds like methanol [69], *n*-propanol [184] and 1,2-propanediol [113]) (type 2 or compatible solutes), the *B*-values increase at low concentrations (e.g. <1.0 mol kg^{-1}), then decrease with the concentration. As discussed by Banipal et al. [182], non-hydrogen bonded 1,4-dioxane is weakly hydrated and may be considered as a (weak) structure-breaker. On the other hand, polyols and sugars are known as compatible solutes to stabilize the native conformation of globular proteins [10,15,185–190]. The effect of methanol on *B*-coefficients of amino acids [69,191] and electrolytes [192] showed that a small amount of methanol (up to 20–25% w/w) [69,191] enhances the mixture structure, and *B*-coefficients of amino acids and electrolytes decrease with the increase concentration of methanol. It is known that a low concentration of methanol [69,191] and ethanol [193] in water improves the three dimensional polymeric structure of water although a high concentration tends to break the water

Table 7
Standard partial molar volumes of transfer (V_{tr}^{o}, cm^3 mol^{-1}) from water to organic solutions and hydration numbers (in parenthesis) in organic solutions at 25 °C

Solvent	Gly	Ala	Val	Leu	Ser	Glu	Aaba	DG
H_2O	(**3.52 or 2.63**),[e] (**2.9**),[f] (**3.26**),[o] (**2.63**)[y]	(**4.65 or 3.41**),[e] (**3.8**),[f] (**2.89**),[o] L-(**3.43**)[y]	L-(**5.18 or 3.43**),[e] L-(**3.9**),[f] L-(**3.40**)[y]	L-(**7.09 or 4.96**),[e] L-(**5.5**)[f]				
Ethanol (1.09 m)[z]	0.21	−0.18−L			1.33−L			
2-Chloro-ethanol (1 M, 35 °C)[a]	0.85	0.50−L			0.53−L	0.49		1.65
Ethylene glycol (1.6 m)[u]	0.58	0.21−L			0.50−L			
Glycerol (1.09 m)[b] (1.0 m)[d,m]	1.02,[b] 0.34,[d] 0.62[m]	0.42−L,[b] 0.19,[d] 0.33−L[m]	−0.26−L,[d] 0.18−L[m]	−0.82−L,[d] 0.15−L[m]	0.95−L[b]		0.14[m]	
1,2-Propanediol (1.0 m)[c]	0.25	0.03		−1.14−L			−0.59	
1,2-Propanediol (6.0 m)[c]	2.15	0.85		0.76−L			−0.16	
n-Propanol (1.0 m)[e]	0.27 (**3.44 or 2.55**)	0.01 (**4.64 or 3.41**)	−1.26−L (**5.56 or 3.81**)	−1.81−L (**7.64 or 5.51**)			−1.26	−0.09
Mannitol (1.0 m)[m]	1.33	1.19−L, 1.18−D	0.93−L, 0.97−D	0.53−L			0.81	
Sorbitol (1.0 m)[m]	1.33	1.25−L, 1.13−D	1.08−L, 0.96−D	0.84−L			0.74	
Triton X-100 (0.1 m)[f]	0.28 (**2.8**)	0.19 (**3.7**)	0.40−L (**3.8−L**)	0.15−L (**5.4−L**)			−0.13	
DMF (~1 m)[g] (0.86 m)[p]	−0.017,[g] 0.06[p]	−0.1,[g] −1.70−L[p]			−0.14−L[p]			
D-Glucose (0.2 M)[h]	−3.0	−14.7	−3.2		−7.3−L			
Glucose (1.0[q] or 1.11[v] m)	1.48,[q] 1.86[v]	0.90,[q] 1.16−L[v]		0.60−L[q]	1.91−L[v]			
Sucrose (1.0 m)	1.82[q]	0.92[q]		0.80−L[q]				
Sucrose (5–25% w/w or 0.146–0.732 m)[y]	5%: 0.81, (**2.38**), 15%: 1.26, (**2.25**), 25%: 3.14, (**1.68**)	5%: −1.26−L, (**3.81**), 15%: −0.83−L, (**3.68**), 25%: −0.03−L, (**3.44**)	5%: −0.16−L, (**3.45**), 15%: 0.79−L, (**3.16**), 25%: 0.38−L, (**3.28**)					
1,4-Dioxane (5–40% w/w or 0.57–4.5 m)[r,s]	5%: 0.8,[r] 0.22,[s] 10%: 0.6,[r] 0.26,[s] 20%: 0.8,[r] 0.51,[s] 40%: 2.2[r]	5%: 6.5,[r] 0.03,[s] 10%: 0.17,[s] 20%: 1.2[r], 0.35[s]	5%: 0.01−L,[s] 10%: −0.85−L,[s] 20%: −1.71−L[s]	5%: 1.17−L,[s] 10%: −1.72−L,[s] 20%: −1.47−L[s]				
DMSO (0.9[i] or 0.15[w] M)	0.30,[i] 0.00[w]	−0.27−L,[i] −0.10[w]			0.42,[i] 0.36[w]			0.16,[i] −0.02[w]
Urea (0.84 M)[j]	0.31	1.46	0.46					
Urea (1 m)[l,m]	0.69,[l] 0.66[m]	0.40−L[l]	0.25−L[l]		0.65−L[l]			
Urea (3 m)[x]	1.40	1.22		0.99			1.26	2.15
Urea (4.44 M)[j]	4.00	2.29	1.15					
Urea (5 m)[aa]	2.26	1.81	1.15	0.91	1.78−L		1.40	
Urea (6 M[n] or 6 m[x])	4.3,[n] 2.38[x]	3.4,[n] 2.25[x]		1.82[x]			1.95[x]	3.19[x]
Urea (8 M)[k]	4.08	3.75−L	3.29−L	3.43−L	4.35−L	5.84−L		
Urea (8 m)[l]	2.85	2.60−L	2.30−L		3.34−L			
SDS (1.0 m)[t]	2.43	1.92	2.16	3.63				3.34
CATB (1.0 m)[t]	0.93	0.14	0.31	0.45				0.85

For abbreviations of amino acids, see Table 1; DG = diglycine, TG = triglycine; salt concentrations normally in the unit of m for molality (mol kg^{-1}) unless indicated in M for molarity (mol L^{-1}); [a]Ref. [101], [b]Ref. [199], [c]Ref. [113], [d]Ref. [196], [e]Ref. [184] (hydration numbers based on different intrinsic volumes), [f]Ref. [213] (Triton X100 as a surfactant is a polydisperse synthesis of *p*-(1,1,3,3-tetramethyl-butyl) phenoxypoly(oxyethyleneglycol) containing 9.5 oxyethylene units per molecule in average), [g]Ref. [180], [h]Ref. [210], [i]Ref. [264], [j]Ref. [261], [k]calculated from Ref. [202], [l]Ref. [122], [m]volumes of transfer of 0.1 m amino acids (NOT infinite dilution) to 1 m aqueous solvents at 24 °C from Ref. [205], [n]calculated from Ref. [270], [o]Ref. [238], [p]Ref. [179], [q]Ref. [208] (volumes of transfer of L-alanine and L-valine at 15 and 35 °C were also reported [134]), [r]calculated from Ref. [181], [s]Ref. [182] (V_{ϕ}^{o} values of some L-amino acids were also reported by Jahagirdar and Pankanti [271]), [t]Ref. [207] (SDS = sodium dodecyl sulfate, CTAB = cetyltrimethylammonium bromide), [u]calculated from Ref. [272], [v]calculated from Ref. [256], [w]Ref. [200], [x]Ref. [204] (other peptides also reported), [y]Ref. [95], [z]Ref. [201] (data at ethanol concentrations of 5–45% w/w were reported), [aa]Ref. [203] (values also reported at other temperatures such as 5, 15 and 35 °C).

structure. Given their negative values of dB/dT, three saccharides (e.g. D-glucose, maltose and maltotriose) are considered to be structure-makers with an increasing ability of D-glucose < maltose < maltotriose [194]. Amino acids have relatively high volumes of transfer in glucose and sucrose solutions (Table 7), suggesting amino acids are less hydrated in these solutions, which is similar to the situation in kosmotropic salt solutions. A possible explanation of the difference between types 1 and 2 solutes is that the type 1 solutes interact strongly with amino acids rather than with water, causing stronger solvation of amino acids and thus higher B-coefficients observed at high concentrations of these organic solutes; the type 2 solutes at high concentrations interact strongly with water rather than with amino acids because of the H-bond formation between hydroxyl groups and water molecules, which is confirmed by the decreasing hydration numbers with the increase of solute concentrations (for example, the case of *n*-propanol [195]).

The temperature dependence of *B*-coefficients of amino acids in organic solutions depends on several factors including the individual amino acids, organic solutes and solute concentrations. In general, with the addition of structure-breaking solute, the kosmotropicity of amino acids in such solutions decreases. For example, *B*-values of glycine increase with temperature in 5–20% (w/w) acetonitrile aqueous solutions (suggesting glycine is a structure breaker), while those of DL-alanine decrease with temperature at a low concentration (e.g. 5% w/w) of acetonitrile (suggesting alanine is a structure maker), but increase at high concentrations of acetonitrile (e.g. 15% and 20% w/w) (suggesting acetonitrile is a structure breaker) [72]. The dB/dT values in methanol solutions (5–25% w/w) are positive for glycine and alanine, but negative for α-aminoisovaleric acid and a mixed situation for ε-aminocaproic acid [191]. Overall, the structure-making ability of amino acids is reduced in methanol–water solutions; glycine is a more effective structure-breaker in the presence of methanol [191]. Glycine and alanine were classified as structure breakers in aqueous dioxane solution since dioxane behaves as a structure breaker [181].

As shown in Table 5, the *B*-coefficients of transfer (B_{tr}) of amino acids are larger in the presence of type 1 solutes (such as urea, acetonitrile, D-glucose and DMF) than type 2 ones (*n*-propanol, 1,2-propanediol, ethylene glycol, glycerol, glucose and sucrose). The larger increase of *B*-values in type 1 solutes is due to the stronger interaction of these solutes with amino acids, resulting in a stronger solvation of amino acids not only by water molecules but also by these solutes. An evidence is that urea is known as a protein denaturant because it strongly interacts with proteins [174]. Type 2 solutes can be compatible solutes of proteins. Glycerol is an biophysically important polyhydroxy compound [196] and is considered as a moderate protein stabilizer [174]. For example, the use of alcohols (2–5% v/v) as co-solvents exhibited a strong effect on the activity of Herpes simplex virus type 1 (HSV-1) protease. An increasing enzyme activity was reported in alcohols in the order of ethanol<methanol<trifluoroethanol and isopropyl alcohol<ethyl glycol<glycerol<[197]. Polyols were also reported to increase the thermo-stability of halophilic enzymes in an increasing order of glycerol<erythritol<xylitol<sorbitol, and the overall hydroxyl group concentration was related to the effectiveness of polyols on the stabilization [198]. Various sugars (glucose, sucrose, fructose, xylose, deoxyribose, ribose, lyxose and arabinose) were found being able to stabilize lysozyme (hen egg white) from the thermal denaturation [190].

From the aspect of volumetric properties of amino acids in organic solutions, Table 7 showed that the standard partial molar volumes of transfer (V_{tr}^{o}) are generally smaller than those in salt solutions (Table 6). V_{tr}^{o} increases with the increasing concentration of organic solute for both type 1 (such as DMF [180]) and type 2 solutes (such as glycerol [196,199]), suggesting organic solutes at high concentrations could strip water molecules from amino acids in varying degrees. However, the volumes of transfer of type 1 solutes (such as DMF, DMSO, 1,4-dioxane, urea and surfactants in Table 7) are usually smaller than type 2 solutes (such as various alcohols), which indicates that amino acids are more hydrated in type 1 solutes than in type 2 solutes. This observation further implies that type 1 solutes have stronger interactions with amino acids (rather than water) than type 2 compatible ones do. As a commonly used polar aprotic solvent, dimethyl sulfoxide (DMSO) influences the protein secondary structures at high concentrations; however, when used at low concentrations (<0.15 M), it showed little effect on the volumes of transfer of amino acids (Table 7) [200], which is similar to the case of methanol. In ethanol–water mixtures, the effectiveness of amino acids in enhancing the water structure in the water-rich region was found in a decreasing order of L-serine>glycine>L-alanine; however, in the ethanol-rich environment, a different order was observed as glycine>L-alanine>L-serine [201]. On the other hand, urea is known to have specific interactions with side chain polar groups of proteins [202]; volumetric studies indicated urea molecules interact strongly with the polar groups (NH_3^+ and COO^-) of amino acids [203] and the peptide group (CONH) of peptides [204]. The volumes of transfer of amino acids in several organic solvents (some data in Tables 6 and 7) were observed in an increasing order of glycerol<mannitol<sorbitol<urea<Gn HCl<NaCl [205]. In general, this sequence is consistent with the increasing structure-breaking ability of these solutes except NaCl. Sodium chloride has the highest value because salts usually have higher volumes of transfer than organic solutes do (Tables 6 and 7). As a matter of fact, NaCl is a non-perturbing salt because both the cation and anion are borderline ions [24]. Surfactants are known as protein destabilizers due to their strong binding with protein molecules [206]. Based on Table 7, the volume of transfer values in 1.0 m SDS (sodium dodecyl sulfate) are much larger than those in 1.0 m CTAB (cetyltrimethylammonium bromide), suggesting that amino acids and peptides are more dehydrated by SDS than by CTAB [207].

Relatively higher volumes of transfer of amino acids in 1.0 m of glucose and sucrose solutions [208] than those in urea solutions [122,205] (Table 7) indicates that amino acids are less hydrated in sugar solutions than in urea solutions. This is consistent with the conclusion observed in salt solutions that kosmotropic or compatible solutes dehydrate amino acids. It is known that a "nonhydrophobic" effect of denaturing agents of the urea–guanidinium class makes a major contribution to their denaturing effectiveness toward proteins by decreasing the activity coefficients of exposed amide and peptide groups in the denatured protein. Similar conclusions are drawn from the effects of these compounds on the solubility [209]. Sugars stabilize proteins because they enhance the water structure in the immediate vicinity of the protein molecules; the structure-making effect was related to the number of equatorial hydroxyl groups in the sugar molecules [190].

Several amino acids have considerably negative V_{tr}^{o} values in 0.2 M D-(+)-glucose solution (Table 7) [210], implying that the amino acids are strongly hydrated in the solution but D-glucose is rather chaotropic [212]. When D-glucose is present, the hydrophilic–ionic and hydrophilic–hydrophilic interactions (resulting in negative dB/dT for NH_3^+ and COO^- groups) are pronounced more than hydrophilic–hydrophobic interactions

(causing positive dB/dT for CH_2 groups) [210], indicating a strong interaction between D-glucose and amino acids. Therefore, D-glucose is a non-compatible solute and should be classified as a type 1 solute. Interestingly, glycine was classified as a structure-maker, while L-serine and valine were structure-breakers in aqueous D-glucose solutions based on the signs of dB/dT [210], which seems inverted from what has been observed in pure water. However, a different result showed that glycine is a structure-breaker (dB/dT>0), while L-alanine is a structure-maker (dB/dT<0) in both pure water and aqueous D-glucose solutions [211]. Wiggins [212] pointed out that D-glucose is a chaotrope, while L-glucose is a kosmotrope. Therefore, D-glucose can salt in polar groups causing negative dB/dT and salt out non-polar groups causing positive dB/dT. The longer is the side chain of amino acid, the more positive is dB/dT, which could explain the above inversion. Contradictorily, the B-coefficient of D-glucose was found decreasing from 0.436 $dm^3\ mol^{-1}$ at 25 °C to 0.419 $dm^3\ mol^{-1}$ at 35 °C, classifying D-glucose as a structure-maker in pure water [211].

As an application of the volumetric properties, Singh and Kishore [213] observed small transfer volumes of several amino acids from water to 0.05–0.4 mol kg^{-1} TX-100,[1] indicating an overall balance in the interactions of zwitterionic/hydrophilic groups of the amino acids with the hydrophilic groups of TX-100, and of the hydrophobic/ionic/hydrophilic groups of the amino acids with the hydrophobic groups of TX-100. The partial specific volume of transfer of lysozyme from water to 0.4 mol kg^{-1} TX-100 is $-(0.036\pm0.001)cm^3\ g^{-1}$, which is a small negative value indicating a balance of hydrophobic and hydrophilic interactions in the lysozyme-aqueous TX-100 system [213].

To better understand the solute–solvent interactions, Kozak et al. [214] distinguished the interactions between two solute molecules from those among three or more solute molecules based on the McMillan–Mayer solution theory. This model has been implemented for the standard partial molar volume of transfer, and was applied in various solution systems [54,56,134,139,175,182,215,216]. This general expression of this model is,

$$V_{tr}^{o} = 2V_{AB}m_B + 3V_{ABB}m_B^2 + 4V_{ABBB}m_B^3 + \ldots \quad (25)$$

where V_{AB}, V_{ABB} and V_{ABBB} are the pair, triplet and quartet interaction coefficients respectively, and m_B is the molality of the cosolute.

Interestingly, in order to mimic the specific interactions between amino acid chains, Rao et al. [217] measured the partial molar volumes of mixtures of amino acids at 20 °C. They interpreted the volumetric behaviors of mixtures in terms of interactions between ionogenic side chains. Another interesting paper reported the volumetric behavior of amino acids in 0.15 M DMSO+2.0 M NaCl aqueous solutions [200] and the major contribution to the volumes of transfer was believed due to the high concentration of salt NaCl.

[1] Triton X100 as a surfactant is a polydisperse synthesis of *p*-(1,1,3,3-tetramethyl-butyl)phenoxypoly(oxyethyleneglycol) containing 9.5 oxyethylene units per molecule in average.

7. Conclusions

Wiggins suggested that D-amino acids are kosmotropes, while L-isomers are chaotropes [212]. However, due to experimental variations, the viscometric and volumetric differences (Tables 1 and 2) between enantiomers cannot be consistently distinguished. Dipaola and Belleau [205] reached the same conclusion that the standard partial molar volumes of transfer and heat capacities are not distinguishable between L- and D-isomers of amino acids.

To minimize the influence of charged end groups of amino acids, at least two attempts have been made: (1) use amino acid derivatives such as *N*-acetyl [29,85,218–221] or *N*-methyl [222,223] amino acid amides, or cyclic dipeptides [224]; (2) use oligopeptides so that the charged groups are far away from each other [225–228].

The partial molar volumes of amino acids can be used to calculate the volumes of amino acid residues. There are two types of volumes of amino acid residues: real volume (to estimate the real volume of protein in solution) and hypothetical volume (assuming amino acid residues do not involve in intramolecular interactions in protein). These two volumes can be estimated from the volume of amino acid using the following equations [34].

$$V_\phi^o(\text{real volume}) = V_\phi^o - 7.4\ cm^3\ mol^{-1} \quad (26)$$

$$V_\phi^o(\text{hypothetical volume}) = V_\phi^o - 8.4\ cm^3\ mol^{-1} \quad (27)$$

Using the values of amino acid residues, it is possible to calculate the partial molar volumes of peptides and proteins based on the group contribution methods [34,229–233].

In summary, the viscometric and volumetric properties of amino acids discussed in this review could help us interpret the behaviors of peptides and proteins in aqueous solutions. In addition, they enable us to have a better understanding of why some amino acids are protein and enzyme stabilizers, although not all amino acids and short peptides stabilize globular proteins [234].

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