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Infinite Dilution Binary Diffusion Coefficients of Several α-Amino Acids in Water over a Temperature Range from (293.2 to 333.2) K with the Taylor Dispersion Technique

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Infinite dilution binary diffusion coefficients (D_{12}) were determined for 10 α-amino acids, glycine, alanine, α-amino-*n*-butyric acid, norvaline, valine, norleucine, leucine, isoleucine, alloisoleucine, and *tert*-leucine in water over a temperature range from (293.2 to 333.2) K with the Taylor dispersion technique. At 298.2 K, the literature data for the two α-amino acids alloisoleucine and *tert*-leucine are not available, whereas the determined D_{12} values of the others are in good agreement with the data reported previously within the experimental errors of ± 2.0 %. The D_{12} values for all α-amino acids studied were well-represented by two simple correlations, and the accuracies for the correlations were examined for each α-amino acid.

Introduction

Amino acids are of growing importance in the food and pharmaceutical industries as healthy ingredients and supplements. To produce the amino acids in reaction and extraction/separation processes efficiently, it is of great importance to estimate the mass transfer rates and design optimum chemical reactors and separators. Due to this, diffusion coefficients are one of the most fundamental quantities. These values, moreover, can provide meaningful information about intermolecular interactions because the translational motion of the molecular diffusion reflects the friction arising from intermolecular interactions between the diffusing and surrounding molecules. Hence, it is necessary and important to measure the diffusion coefficients of amino acids from not only an engineering but also a scientific viewpoint.

Binary diffusion coefficients (D_{12}) for α-amino acids, of which one structural formula is expressed as NH_2-CH(COOH)-R with an alkyl group R, in water have been measured for 50 years or more.[1−15] Lyons and Thomas determined the D_{12} values of glycine at two temperatures of (274.2 and 298.2) K.[1] Later, Longsworth measured the D_{12} values of glycine, alanine, α-amino-*n*-butyric acid, norvaline, valine, norleucine, and leucine aqueous solutions at 274.2 K[2] and at 298.2 K.[3] For glycine and alanine aqueous solutions, moreover, the D_{12} values over the temperature range from (274.2 to 310.2) K were reported by the same author.[4] At almost the same time, Gutter and Kegeles made the D_{12} measurements for an alanine aqueous solution at 298.2 K.[5] Dunlop reported the D_{12} values of glycine at 298.2 K.[6] Later, Woolf et al. examined the D_{12} data for a glycine aqueous solution at 298.2 K.[7] Ellerton et al. determined the D_{12} values of glycine, α-amino-*n*-butyric acid, and valine at 298.2 K.[8] Lemaguer et al. measured the D_{12} values for a glycine aqueous solution at 298.2 K.[9] Chang and Myerson examined the D_{12} data of glycine at three temperatures of (298.2, 308.2, and 318.2) K.[10] Paduano et al. measured the D_{12} values for a norleucine aqueous solution at 298.2 K.[11] Myerson and Lo reported the D_{12} data of glycine and valine at 298.2 K.[12] Lu and Leaist measured D_{12} values of glycine at 298.2 K.[13] Wu et al.[14] and Ma et al.[15] measured D_{12} values of several amino acids at 298.15 K and various concentrations. The reliable D_{12} values of α-amino acids are available at 298.2 K; however, accurate D_{12} data at other temperatures are extremely limited. Moreover, there are only a few reports measuring precisely the D_{12} values of α-amino acids at infinite dilution in water.

Hence, in the present study, the infinite dilution D_{12} values for α-amino acids of NH_2-CH(COOH)-R where R's are alkyl groups up to a butyl group, which are glycine (Gly), alanine (Ala), α-amino-*n*-butyric acid (Abu), norvaline (Nva), valine (Val), norleucine (Nle), leucine (Leu), isoleucine (Ile), alloisoleucine (aIle), and *tert*-leucine (*t*-Leu) in water, were measured over the temperature range from (293.2 to 333.2) K by the Taylor dispersion method. Reliable D_{12} values are presented, and the accuracies in a few simple correlations were examined.

Experimental Section

Materials. Table 1 lists the purity given by the supplier for DL-α-amino acids used in this study together with the molar mass. These reagents were used without further purification prior to the measurement. Ultrapure water produced by a Millipore Direct-Q system was used as the solvent.

Apparatus and Procedure. The D_{12} measurements were made at six different temperatures ranging from (293.2 to 333.2) K by the Taylor dispersion method. The experimental apparatus employed in this work was almost identical to that described in a previous study.[16] Some minor modifications and improvements were made here as briefly described below. The ultrapure water degassed by reducing pressure was supplied at a constant water velocity with a syringe pump (100DM, Isco). Each α-amino acid was diluted with ultrapure water at a concentration of 10.0 mol·m^{-3}. The α-amino acid aqueous solution filtered with a 2.0×10^{-7} m micropore membrane was charged into an injector (7125, Rheodyne) with $\approx 2.0 \times 10^{-8}$ m^3 sampling loop, which was immersed in a water bath at the desired temperature. After filling the solution in the sampling loop for 15 min to attain the temperature of the solution equal to that of the water

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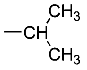
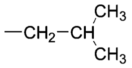
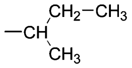
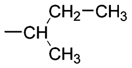
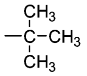
Table 1. α-Amino Acids (NH_2-CH(COOH)-R) Used in This Study

amino acid	substituent (—R)[a]	molar mass/g·mol^{-1}	purity/ %[b]	supplier
glycine (Gly)	$-H$	75.1	99	Wako
alanine (Ala)	$-CH_3$	89.1	98	Wako
α-amino-*n*-butyric acid (Abu)	$-CH_2-CH_3$	103.1	99	Tokyo Kasei
norvaline (Nva)	$-CH_2-CH_2-CH_3$	117.1	99	Acros
valine (Val)	 $-CH(CH_3)_2$	117.1	97	Aldrich
norleucine (Nle)	$-CH_2-CH_2-CH_2-CH_3$	131.2	98	Tokyo Kasei
leucine (Leu)	 $-CH_2-CH(CH_3)_2$	131.2	99	Sigma
isoleucine (Ile)	 $-CH(CH_2-CH_3)(CH_3)$	131.2	99	Acros
alloisoleucine (aIle)	 $-CH(CH_2-CH_3)(CH_3)$	131.2	99	Fluka
tert-leucine (*t*-Leu)	 $-C(CH_3)_3$	131.2	99	Fluka

[a] Two α-amino acids of Ile and aIle are the diastereomers. [b] The purity is given by the suppliers.

bath, the sample solution was loaded into a fused silica diffusion column with a 2.64×10^{-4} m inner radius, 42.12 m length, and ≈ 0.095 m coil radius (Supelco), which was immersed horizontally in the water bath. The solute concentration at the diffusion column outlet was detected with a differential refractometer (L-7490, Hitachi, Tokyo, Japan), and the refractive index time profile was recorded with an integrator (D-2500, Hitachi). The temperature fluctuation in the water bath was within ± 0.1 K during each measurement.

Analysis. According to Taylor[17] and Aris,[18] when a small amount of a solute is injected at the diffusion column inlet, the solute concentration at a distance L from the inlet is given by eqs 1 and 2:

$$C(t) = \frac{m}{\pi R_{\text{tube}}^2 \sqrt{4\pi K t}} \exp\left[-\frac{(L - ut)^2}{4Kt}\right] \qquad (1)$$

where

$$K = D_{12} + \frac{R_{\text{tube}}^2 u^2}{48 D_{12}} \qquad (2)$$

where C is the solute concentration, m is the amount of the injected solute, R_{tube} is the inner radius of the diffusion tube, t is the residence time, L is the length of the diffusion tube, and u is the average flow velocity. In the present study, two parameters of D_{12} and u were determined from the response curve by using eqs 1 and 2 as to minimize the fitting error (ϵ), defined as eq 3, between the observed and the calculated response curves ($\epsilon < 0.01$):

$$\epsilon = \left[\frac{\sum \{C_{\text{exp}}(t) - C_{\text{cal}}(t)\}^2 \Delta t}{\sum \{C_{\text{exp}}(t)\}^2 \Delta t}\right]^{1|2} \qquad (3)$$

where $C_{\text{exp}}(t)$ and $C_{\text{cal}}(t)$ are the measured and calculated concentrations, respectively; and Δt is the data acquisition interval of 0.1 min. The D_{12} value was obtained as the mean value for measurements repeated five times under each condition. The uncertainty of the D_{12} values on different runs was generally ± 1.0 % (the maximum standard deviation ≈ ± 1.7 %) and that of temperature was less than 0.1 K.

Results and Discussion

Table 2 shows the D_{12}, u, and ϵ values obtained for each α-amino acid together with $DeSc^{1/2}$, where De and Sc are the Dean and Schmidt numbers, respectively:

$$De = \frac{2R_{\text{tube}} \rho u}{\eta} \left(\frac{R_{\text{tube}}}{R_{\text{coil}}}\right)^{1/2} \qquad (4)$$

$$Sc = \frac{\eta}{\rho D_{12}} \qquad (5)$$

Here, ρ is the water density,[19] η is the water viscosity,[19] and R_{coil} is the coil radius. In a higher flow velocity region than a certain value, the obtained D_{12} values are known to deviate upward from the intrinsic values due to secondary flow in the coiled diffusion column. Alizadeh et al. estimated the effects to be lower than 1.0 % in terms of the moment in the Taylor

Table 2. Determined D_{12}, u, and ϵ Together with Calculated $DeSc^{1/2}$ for α-Amino Acids[a]

amino acid	T/K	$\rho/10^3\ \mathrm{g \cdot m^{-3}}$ [b]	$\eta/10^{-3}\ \mathrm{Pa \cdot s}$ [b]	$D_{12}/10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$	$u/10^{-3}\ \mathrm{m \cdot s^{-1}}$	$10^3\epsilon$	$DeSc^{1/2}$
Gly	293.2	998.2	1.002	9.36 (0.06)	6.97 (0.01)	7.7 (0.9)	6.33 (0.03)
	298.2	997.0	0.890	10.61 (0.05)	6.98 (0.01)	7.2 (1.7)	6.31 (0.03)
	303.2	995.6	0.797	12.16 (0.08)	6.96 (0.02)	6.1 (1.0)	6.21 (0.01)
	313.2	992.2	0.653	15.04 (0.20)	7.01 (0.01)	6.9 (2.3)	6.21 (0.04)
	323.2	988.0	0.547	18.56 (0.14)	7.05 (0.01)	5.2 (0.9)	6.13 (0.03)
	333.2	983.2	0.466	22.19 (0.18)	7.09 (0.01)	6.3 (1.1)	6.09 (0.04)
Ala	293.2	998.2	1.002	8.06 (0.08)	6.94 (0.02)	7.3 (1.2)	6.79 (0.05)
	298.2	997.0	0.890	9.30 (0.05)	6.95 (0.02)	6.9 (1.4)	6.71 (0.02)
	303.2	995.6	0.797	10.41 (0.10)	6.98 (0.01)	6.1 (2.0)	6.73 (0.04)
	313.2	992.2	0.653	13.08 (0.21)	7.01 (0.00)	6.3 (1.3)	6.66 (0.05)
	323.2	988.0	0.547	16.27 (0.13)	7.05 (0.01)	5.9 (0.8)	6.54 (0.04)
	333.2	983.2	0.466	19.64 (0.16)	7.07 (0.01)	6.6 (1.0)	6.45 (0.02)
Abu	293.2	998.2	1.002	7.29 (0.08)	6.95 (0.03)	7.5 (0.9)	7.15 (0.07)
	298.2	997.0	0.890	8.39 (0.04)	6.96 (0.02)	5.9 (1.1)	7.08 (0.03)
	303.2	995.6	0.797	9.48 (0.10)	6.98 (0.01)	6.0 (1.4)	7.05 (0.05)
	313.2	992.2	0.653	12.00 (0.18)	7.02 (0.01)	6.1 (1.7)	6.95 (0.06)
	323.2	988.0	0.547	14.92 (0.23)	7.03 (0.01)	5.6 (1.3)	6.81 (0.06)
	333.2	983.2	0.466	17.96 (0.11)	7.09 (0.00)	6.9 (1.0)	6.76 (0.02)
Nva	293.2	998.2	1.002	6.77 (0.04)	6.95 (0.01)	8.6 (1.7)	7.42 (0.03)
	298.2	997.0	0.890	7.75 (0.04)	6.96 (0.01)	7.4 (1.7)	7.37 (0.02)
	303.2	995.6	0.797	8.79 (0.10)	6.97 (0.02)	6.2 (2.0)	7.31 (0.05)
	313.2	992.2	0.653	11.18 (0.16)	7.02 (0.01)	5.9 (1.0)	7.20 (0.06)
	323.2	988.0	0.547	13.94 (0.17)	7.03 (0.01)	6.8 (1.2)	7.04 (0.04)
	333.2	983.2	0.466	16.90 (0.08)	7.08 (0.01)	6.3 (1.0)	6.96 (0.02)
Val	293.2	998.2	1.002	6.76 (0.11)	6.95 (0.02)	7.0 (1.1)	7.42 (0.08)
	298.2	997.0	0.890	7.77 (0.05)	6.95 (0.01)	6.7 (1.0)	7.35 (0.03)
	303.2	995.6	0.797	8.91 (0.06)	6.97 (0.01)	5.9 (1.9)	7.26 (0.04)
	313.2	992.2	0.653	11.24 (0.10)	7.01 (0.01)	6.0 (0.4)	7.18 (0.03)
	323.2	988.0	0.547	14.02 (0.15)	7.05 (0.01)	7.2 (1.6)	7.04 (0.04)
	333.2	983.2	0.466	17.03 (0.16)	7.09 (0.01)	6.6 (1.2)	6.94 (0.04)
Nle	293.2	998.2	1.002	6.41 (0.08)	6.94 (0.03)	7.6 (1.5)	7.62 (0.07)
	298.2	997.0	0.890	7.36 (0.05)	6.98 (0.02)	7.2 (1.3)	7.58 (0.04)
	303.2	995.6	0.797	8.27 (0.11)	6.66 (0.07)	9.2 (1.3)	7.20 (0.08)
	313.2	992.2	0.653	10.70 (0.05)	6.83 (0.01)	7.5 (0.6)	7.17 (0.02)
	323.2	988.0	0.547	13.16 (0.19)	7.04 (0.01)	7.6 (1.4)	7.26 (0.05)
	333.2	983.2	0.466	15.99 (0.15)	7.08 (0.00)	7.7 (1.4)	7.16 (0.04)
Leu	293.2	998.2	1.002	6.41 (0.06)	6.87 (0.02)	7.6 (1.6)	7.53 (0.05)
	298.2	997.0	0.890	7.35 (0.07)	6.95 (0.03)	5.8 (1.9)	7.55 (0.06)
	303.2	995.6	0.797	8.24 (0.03)	6.91 (0.06)	8.5 (1.0)	7.48 (0.07)
	313.2	992.2	0.653	10.71 (0.06)	6.76 (0.10)	6.2 (0.8)	7.09 (0.12)
	323.2	988.0	0.547	13.28 (0.15)	7.05 (0.00)	7.9 (0.9)	7.23 (0.04)
	333.2	983.2	0.466	15.98 (0.15)	7.08 (0.01)	5.4 (1.1)	7.16 (0.03)
Ile	293.2	998.2	1.002	6.41 (0.06)	6.94 (0.01)	8.6 (1.2)	7.62 (0.04)
	298.2	997.0	0.890	7.44 (0.11)	6.95 (0.02)	7.3 (1.1)	7.50 (0.08)
	303.2	995.6	0.797	8.36 (0.09)	6.77 (0.09)	8.0 (1.6)	7.28 (0.09)
	313.2	992.2	0.653	10.70 (0.11)	7.02 (0.01)	6.8 (1.2)	7.36 (0.05)
	323.2	988.0	0.547	13.33 (0.16)	7.05 (0.00)	6.1 (1.1)	7.22 (0.05)
	333.2	983.2	0.466	16.17 (0.13)	7.09 (0.00)	7.1 (0.8)	7.12 (0.03)
aIle	293.2	998.2	1.002	6.42 (0.08)	6.91 (0.04)	8.4 (0.8)	7.58 (0.08)
	298.2	997.0	0.890	7.38 (0.11)	6.91 (0.06)	7.8 (1.7)	7.50 (0.11)
	303.2	995.6	0.797	8.44 (0.08)	6.98 (0.01)	6.3 (1.2)	7.48 (0.04)
	313.2	992.2	0.653	10.70 (0.10)	7.00 (0.01)	6.4 (0.8)	7.35 (0.03)
	323.2	988.0	0.547	13.26 (0.16)	7.05 (0.00)	6.3 (1.7)	7.22 (0.06)
	333.2	983.2	0.466	16.08 (0.04)	7.07 (0.01)	8.6 (0.9)	7.13 (0.02)
t-Leu	293.2	998.2	1.002	6.31 (0.08)	6.93 (0.03)	7.9 (0.7)	7.67 (0.07)
	298.2	997.0	0.890	7.29 (0.05)	6.97 (0.01)	7.6 (0.6)	7.60 (0.03)
	303.2	995.6	0.797	8.46 (0.07)	6.94 (0.02)	6.9 (2.1)	7.42 (0.04)
	313.2	992.2	0.653	10.61 (0.13)	7.00 (0.01)	5.9 (1.1)	7.38 (0.05)
	323.2	988.0	0.547	13.33 (0.11)	7.05 (0.01)	5.8 (1.6)	7.22 (0.03)
	333.2	983.2	0.466	16.11 (0.13)	7.09 (0.01)	6.4 (1.6)	7.14 (0.03)

[a] The standard deviation determined from five measurements is given in parentheses. [b] The density ρ and the viscosity η for water were quoted from the literature.[19]

dispersion when $DeSc^{1/2} < 8$.[20] As shown in Table 2, the calculated $DeSc^{1/2}$ values are always lower than 8 for all the α-amino acids. The experimental errors were estimated to be less than 2.0 % (with standard deviations of 1.0 %).

As described in the Introduction, there have been many reports of precise D_{12} measurements for α-amino acids in water at 298.2 K. Table 3 shows a comparison between the determined D_{12} values and the limiting D_{12} data, which are the extrapolated D_{12} values at zero solute concentration, published in the literature for α-amino acids in water at 298.2 K. As far as we know, no data for two α-amino acids, aIle and *t*-Leu, are available in the literature. The present data are almost consistent with the values reported previously within the experimental error, except for isoleucine for which the reason is not known. Therefore, the D_{12} values in this study can be regarded as infinite dilution for all the α-amino acids studied.

To examine the effects of molar mass on the D_{12} values of α-amino acids in water, let us return to Table 2. At each temperature, the D_{12} values decrease with increasing molar mass, and there are no recognizable differences in the D_{12} values

Table 3. Comparison of D_{12} Values for α-Amino Acid in Water at 298.2 K between Experimental and Literature Values[a]

amino acid	reference	method	$D_{12}/10^{-10}$ m^2·s^{-1}
Gly	Lyons and Thomas[1]	G	10.64
	Longsworth[3,4]	R	10.55
	Dunlop[6]	G	10.60
	Woolf et al.[7]	G	10.59
	Ellerton et al.[8]	G	10.61
	Ma et al.[15]	L	10.62
	present study	T	10.61
Ala	Longsworth[3,4]	R	9.10
	Gutter and Kegeles[5]	G	9.15
	Ma et al.[15]	L	9.24
	present study	T	9.30
Abu	Longsworth[3]	R	8.29
	Ellerton et al.[8]	G	8.31
	Ma et al.[15]	L	8.32
	present study	T	8.39
Nva	Longsworth[3]	R	7.68
	present study	T	7.75
Val	Longsworth[3]	R	7.73
	Ellerton et al.[8]	G	7.72
	Ma et al.[15]	L	7.50
	present study	T	7.77
Nle	Longsworth[3]	R	7.25
	Paduano et al.[11]	G	7.26
	present study	T	7.36
Leu	Longsworth[3]	R	7.26
	present study	T	7.35
Ile	Ma et al.[15]	L	7.75
	present study	T	7.44

[a] The listed D_{12} values of Ma et al.[15] were estimated by the least-squares method with the parabolic function of each amino acid concentration. G, Gouy interference method; L, laser holographic interference method; R, Rayleigh interference method; T, Taylor dispersion.

between the two valine isomers and between the five leucine isomers containing the two diastereomers. Wu et al. studied D_{12} data for three amino acids of L-proline, L-threonine, and L-arginine in water at 298.2 K by a metallic diaphragm cell method.[14] They explained the differences in the D_{12} values for the amino acid aqueous solutions by the effects of molecular size and polarity of the amino acids. In the present study, the polarity is estimated to be unchanged for every α-amino acid because their isoelectric points are almost equivalent. Hence, the polarity effect on the present D_{12} values seems to be indiscernible. The molecular size, on the other hand, is effective because their volumes become larger as the alkyl chains R in the α-amino acids grow longer. The present results indicate that the D_{12} data are strongly dependent on the molecular size and almost independent of the molecular shape.

The D_{12} value of a neutral molecule in liquid has often been correlated with T, η, and the molar volume at the normal boiling point (V_b) by empirical correlations (e.g., Wilke−Chang and Tyn−Calus) on the basis of the hydrodynamic model that a solute sphere moves through a continuum solvent.[21] Most correlations, however, cannot apply to α-amino acid solution systems because the zwitterions of the amino acids make it extremely difficult to estimate V_b. Sanchez et al. found that eq 6 represented the D_{12} data for binary organic liquid mixtures:[22]

$$\ln(D_{12}/\mathrm{m^2{\cdot}s^{-1}}) = A + \frac{B}{(T/\mathrm{K})} \tag{6}$$

where A and B are constants. Figure 1 shows the semi-logarithmic plot of D_{12} versus $1000T^{-1}$, according to eq 6. The vertical error bars represent the standard deviations of the D_{12} values determined by five repeated runs. As depicted, eq 6 is effective. Table 4 lists the constants A and B in eq 6 obtained by least-squares fitting together with the average absolute deviations (AAD) and the maximum absolute deviations (MAD). Here, the absolute deviation (AD) is defined by

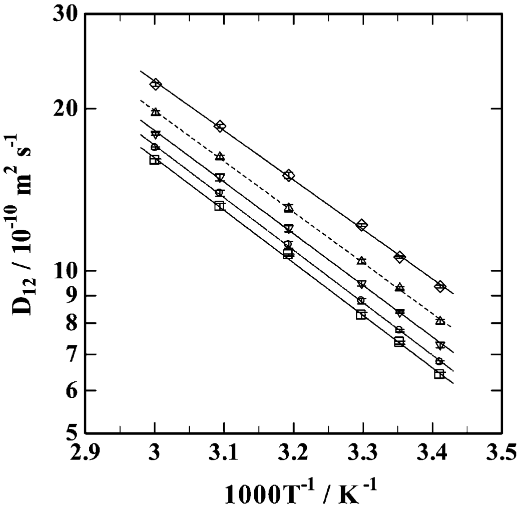


Figure 1. D_{12} value vs $1000T^{-1}$ for ◇, Gly; △, Ala; ▽, Abu; ○, Nva; and □, Nle in water. The solid lines represent the regression of the experimental data to eq 6.

Table 4. Constants *A* and *B* in Equation 6 for α-Amino Acid in Water

amino acid	A	B	AAD/%	MAD/%
Gly	−13.66	−2086	0.936	1.556
Ala	−13.59	−2150	0.570	1.479
Abu	−13.60	−2177	0.695	1.692
Nva	−13.53	−2219	0.596	1.166
Val	−13.50	−2226	0.823	1.719
Nle	−13.60	−2214	0.846	1.643
Leu	−13.58	−2220	1.111	1.632
Ile	−13.54	−2230	0.795	1.869
aIle	−13.60	−2211	0.902	1.922
t-Leu	−13.50	−2245	1.264	2.587
Gly[a]	−12.95	−2305	1.404	2.819
Ala[a]	−12.82	−2389	1.517	3.129

[a] The values were determined for the data reported by Longsworth.[4]

$$\mathrm{AD} = \left|\frac{D_{12,\mathrm{exp}} - D_{12,\mathrm{cal}}}{D_{12,\mathrm{exp}}}\right| \tag{7}$$

where $D_{12,\mathrm{exp}}$ and $D_{12,\mathrm{cal}}$ are the values measured experimentally and calculated by eq 6 with the constants A and B, respectively. Although the constants A and B in eq 6 for all amino acid aqueous solutions are not available in the literature, the constants A and B listed in Table 4 are fairly close to those for alkanolamine aqueous solutions reported by Snijder et al.[23] and Chang et al.[24] The AAD and MAD values are mostly less than 1.0 % and 2.0 %, respectively.

Funazukuri and Nishio reported that the accuracy in eq 8 was better than those in the various predictive correlations published in the literature (i.e., Wilke−Chang, Hayduk−Laudie, Nakanishi, Hayduk−Minhas, and Siddiqi−Lucas) for C_5-monoalcohol aqueous solutions:[25]

$$\frac{(D_{12}/\mathrm{m^2{\cdot}s^{-1}})}{(T/K)} = \alpha(\eta/\mathrm{Pa{\cdot}s})^{\beta} \tag{8}$$

where α and β are constants. By substituting $\alpha = k_B/6\pi r$ and $\beta = -1$, where k_B is the Boltzmann constant and r is the radius of the solute sphere, one can obtain the well-known Stokes−Einstein equation. Figure 2 shows the logarithmic plot of $D_{12}T^{-1}$ versus η according to eq 8. The vertical error bars represent

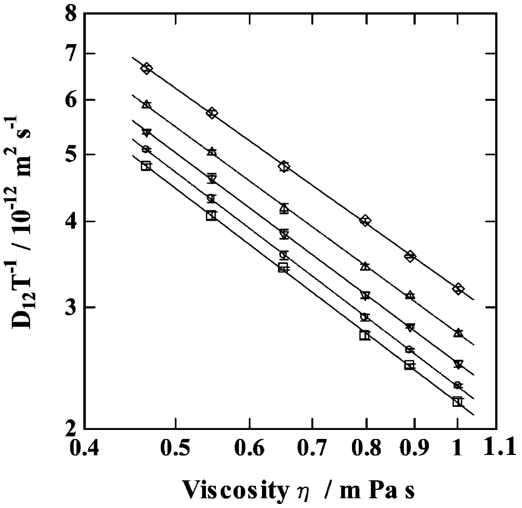


Figure 2. Logarithmic plot of $D_{12}T^{-1}$ vs η for α-amino acids in water. The key is the same as that in Figure 1. The solid lines represent the regression of the experimental data to eq 8.

Table 5. Constants α and β in Equation 8 for α-Amino Acid in Water

amino acid	$10^{15}\alpha$	β	AAD/%	MAD/%
Gly	4.121	−0.963	0.393	0.768
Ala	2.798	−0.998	0.434	0.979
Abu	2.270	−1.014	0.243	0.431
Nva	1.790	−1.036	0.262	0.507
Val	1.751	−1.040	0.194	0.439
Nle	1.730	−1.034	0.409	1.110
Leu	1.680	−1.038	0.652	1.610
Ile	1.635	−1.043	0.324	0.718
aIle	1.753	−1.033	0.151	0.258
t-Leu	1.521	−1.052	0.629	1.203
Gly[a]	4.359	−0.954	0.047	0.099
Ala[a]	2.815	−0.995	0.017	0.027

[a] The values were determined for the data reported by Longsworth.[4]

the standard deviations of the $D_{12}T^{-1}$ values calculated from the standard deviations of the D_{12} values. The logarithmic plots of $D_{12}T^{-1}$ versus η give a straight line for each α-amino acid (see the lines in Figure 2). Table 5 lists the constants α and β in eq 8 together with the AAD and MAD values obtained by eq 7. The constant α obviously decreases with increasing molar mass; whereas the constant β remains a constant of ≈ -1, as shown in our the previous study.[25] This result indicates that the predominant factor in the translational motion of α-amino acids in water is the macroscopic viscosity of solution. The AAD and MAD values are less than 0.7 % and 1.6 %, respectively. Comparing the AADs and MADs in both eq 8 and eq 6, eq 8 is more accurate than eq 6 for all the α-amino acids.

Longsworth has previously reported the D_{12} values of Gly and Ala in water at temperatures ranging (274.2 to 310.2) K, as mentioned in the Introduction.[4] In a similar manner, we can obtain the constants *A* and *B* (see in Table 4) and the constants α and β (see in Table 5) on the basis of the data reported by Longsworth. As observed in this study, the AAD and MAD values in eq 8 are also smaller than those in eq 6. As compared with our results, although the obtained constants *A* and *B* obviously differ from the present values, the constants α and β are nearly consistent with the present values. These results indicate that the correlation in eq 8 with a single set of constants α and β represents well the D_{12} data for α-amino acid aqueous solutions over a wide temperature range.

Conclusions

The D_{12} values of α-amino acids at infinite dilution in water were measured at (293.2 to 333.2) K with the Taylor dispersion technique. The measured D_{12} values were in fairly good agreement with infinite dilution D_{12} data published in the literature within the experimental error of 2.0 %. All the D_{12} values decreased with increasing molar mass at each temperature. The D_{12} were found to be strongly dependent on the molecular size, and almost independent of the molecular shape. The present D_{12} data were correlated with T and η. For every α-amino acid in the temperature range studied and at (274.2 to 310.2) K reported by Longsworth, the accuracy of the correlation in eq 8 ($D_{12}T^{-1} = \alpha\eta^{\beta}$) was found to be better than that of the correlation in eq 6 ($\ln D_{12} = A + B/T$).

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