Apparent Molar Volumes and Viscosities of Some α-Amino Acids in Aqueous Sodium Butyrate Solutions at 298.15 K

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Densities and viscosities of aqueous solutions of α-amino acids (glycine, DL-alanine, DL-α-amino-*n*-butyric acid, DL-α-valine, and DL-α-leucine) + sodium butyrate have been measured as a function of concentrations of amino acid and electrolyte at 298.15 K. These data have been used to calculate apparent molar volumes and viscosity *B*-coefficients of the amino acids. The standard partial molar volumes, $V°_{2,\phi}$, standard volumes of transfer, $\Delta_t V°$, and hydration numbers of the amino acids have been determined. It has been shown that $V°_{2,\phi}$, $\Delta_t V°$, and the *B*-coefficient vary linearly with increasing number of carbon atoms in the alkyl chain of the amino acids, and they were split into contributions from the charged end group (NH_3^+, COO^-) and CH_2 groups of the amino acids. From the volumetric data, we found that sodium butyrate interacts strongly with the charged center of the zwitterion of the amino acids and has a strong dehydration effect on the amino acids.

Introduction

Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes.[1,2] Proteins are complex molecules, and their behavior in solutions is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interactions in systems containing smaller biomolecules, such as amino acids and peptides. Some studies[3,4] have revealed that the presence of an electrolyte drastically affects the behavior of amino acids in solutions, which can be used for their separation and purification.

There have been some investigations on the partial molar volumes and adiabatic compressibilities of amino acids in aqueous salt ($CaCl_2$, alkali-chloride, Na_2SO_4, guanidine hydrochloride, CH_3COONa) solutions.[5−10] The heat capacity and Gibbs free energy of transfer from aqueous to ionic environment have been reported.[11−15] The viscosity *B*-coefficients of some amino acids have been investigated in aqueous potassium thiocyanate (KSCN),[16,17] guanidine hydrochloride (GuHCl),[18,19] and ammonium chloride (NH_4Cl)[4] solutions.

Since there are few measurements on interactions between amino acid and organic salt, and sodium butyrate is known to influence the dissociation of proteins in solution[20] and cause a salting-out of nonelectrolytes,[21] a systematic study of the effect of sodium butyrate on the volumetric and viscometric behavior of a series of amino acids is of interest. Both these properties are sensitive to specific interactive changes in solutions. In this paper, apparent molar volumes and viscosities of some α-amino acids in sodium butyrate (NaC_4) solutions are reported. The amino acids chosen were glycine (Gly), DL-α-alanine (Ala), DL-α-amino-*n*-butyric acid (Abu), DL-valine (Val) and DL-leucine (Leu). This permits individual estimation of contributions from the zwitterionic and CH_2 groups.

Experimental Section

Glycine (Shanghai Chem. Co.), DL-α-alanine (Shanghai Chem. Co.), DL-α-amino-*n*-butyric acid (Shanghai Chem. Co.), DL-valine (Fluka), and DL-leucine (Baker) were recrystallized twice from aqueous ethanol solutions and dried under vacuum at 348 K for 6 h. Then they were stored over P_2O_5 in a desiccator before use. Water with a conductivity of 1.2 $\mu\Omega^{-1}$ cm^{-1} was obtained by distilling deionized water from alkaline $KMnO_4$ to remove any organic matter. All solutions were prepared freshly by weighing on the molality scale.

Solution densities were measured to $\pm 3 \times 10^{-6}$ g cm^{-3} with an Anton Paar DMA 60/602 vibrating-tube digital densimeter that was calibrated at 298.15 K using dry air and conductivity water daily. The density of pure water at 298.15 K was taken from Kell's datum.[22]

Viscosity measurements were carried out with a suspended level Ubbelhode viscometer which has a flow time of about 200 s for water at 298.15 K. The viscometer was calibrated with water. Flow time measurements are performed by a SCHOTT AVS 310 photoelectric time unit with a resolution of 0.01 s. The repeatability for reading was ±0.02 s. At least three time recordings reproducible to 0.02 s were obtained, and the average value was used. Viscosity of solution, η, is given by the following equation

$$\eta/\rho = Ct - K/t \qquad (1)$$

where ρ is the solution density, t is the flow time, and C and K are the viscometer constants which were obtained by the measurements on water at 25 and 35 °C.

The densimeter and viscometer were thermostated using SCHOTT thermostat units which have a thermal stability of ±0.005 K.

Results and Discussion

The density data measured for the aqueous amino acids + sodium butyrate + water solutions at 298.15 K are given

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Table 1. Solution Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, for the α-Amino Acids in Aqueous Sodium Butyric Solutions As a Function of Molalities of Amino Acids and Sodium Butyrate at 298.15 K[a]

m	ρ	$V_{2,\phi}$	m	ρ	$V_{2,\phi}$	m	ρ	$V_{2,\phi}$	m	ρ	$V_{2,\phi}$
mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}	mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}	mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}	mol kg^{-1}	g cm^{-3}	cm^3 mol^{-1}
Glycine											
	$m_s = 0.50000$			$m_s = 1.0000$			$m_s = 1.5000$			$m_s = 2.0001$	
0.0000	1.016240		0.0000	1.033679		0.0000	1.049354		0.0000	1.064093	
0.03241	1.017218	44.62	0.03236	1.034601	45.91	0.03333	1.050261	46.79	0.03477	1.064971	48.19
0.06205	1.018102	44.73	0.06191	1.035434	46.01	0.06297	1.051054	46.95	0.06817	1.065817	48.13
0.1027	1.019310	44.78	0.1022	1.036577	45.95	0.1023	1.052129	46.77	0.1047	1.066732	48.15
0.1519	1.020784	44.70	0.1553	1.038067	45.98	0.1528	1.053464	46.93	0.1585	1.068101	48.03
0.2015	1.022241	44.76	0.2070	1.039492	46.08	0.2030	1.054793	46.96	0.2087	1.069363	48.01
0.2462	1.023554	44.79	0.2579	1.040917	46.03	0.2550	1.056168	46.97	0.2721	1.070953	47.97
0.3014	1.025156	44.83	0.3077	1.042290	46.05	0.2942	1.057210	46.94	0.3258	1.072301	47.93
0.3204	1.025709	44.84	0.3314	1.042937	46.07	0.3200	1.057889	46.94	0.3637	1.073257	47.89
0.3897	1.027678	44.94	0.3648	1.043852	46.07	0.3532	1.058759	46.94	0.4221	1.074705	47.87
DL-α-Alanine											
	$m_s = 0.50000$			$m_s = 1.0000$			$m_s = 1.5000$			$m_s = 2.0001$	
0.0000	1.016240		0.0000	1.033679		0.0000	1.049354		0.0000	1.064093	
0.03145	1.017088	61.51	0.03196	1.034489	62.43	0.03221	1.050 132	62.94	0.03392	1.064859	63.71
0.05998	1.017854	61.51	0.06136	1.035168	62.38	0.06154	1.050837	62.93	0.06658	1.065595	63.71
0.09943	1.018909	61.51	0.1010	1.036223	62.45	0.1001	1.051763	62.89	0.1010	1.066360	63.76
0.1514	1.021293	61.50	0.1499	1.037439	62.49	0.1518	1.052988	62.94	0.1509	1.067467	63.77
0.1970	1.021495	61.52	0.2010	1.038697	62.52	0.2039	1.054211	62.98	0.2037	1.068627	63.79
0.2516	1.022940	61.48	0.2499	1.039883	62.58	0.2533	1.055363	63.00	0.2520	1.069679	63.81
0.2983	1.024156	61.49	0.2961	1.041024	62.53	0.2949	1.056322	63.03	0.3088	1.070943	63.72
0.3246	1.024818	61.56	0.3272	1.041758	62.59	0.3240	1.057007	62.99	0.3614	1.072079	63.73
0.3631	1.025828	61.52	0.3592	1.042537	62.57	0.3547	1.057709	63.01	0.4127	1.073183	63.73
DL-α-Aminobutyric Acid											
	$m_s = 0.50000$			$m_s = 1.0000$			$m_s = 1.5000$			$m_s = 2.0001$	
0.0000	1.016240		0.0000	1.033679		0.0000	1.049354		0.0000	1.064093	
0.03146	1.017056	76.29	0.03220	1.034466	76.83	0.03127	1.050077	77.23	0.03427	1.064836	77.97
0.06008	1.017792	76.34	0.06201	1.035192	76.82	0.06061	1.050755	77.19	0.06632	1.065510	77.93
0.09964	1.018809	76.32	0.1024	1.036164	76.86	0.1002	1.051653	77.28	0.1002	1.066209	78.10
0.1513	1.020126	76.31	0.1492	1.037284	76.88	0.1519	1.052820	77.30	0.1508	1.067262	78.11
0.1997	1.021347	76.33	0.1979	1.038443	76.88	0.2017	1.053921	77.37	0.2031	1.068325	78.19
0.2485	1.022574	76.32	0.2502	1.039652	76.97	0.2539	1.055064	77.42	0.2530	1.069343	78.19
0.2978	1.023779	76.39	0.3034	1.040894	76.96	0.3096	1.056253	77.52	0.3047	1.070379	78.23
0.3291	1.024565	76.35	0.3241	1.041364	76.99	0.3386	1.056888	77.51	0.3755	1.071784	78.25
0.3640	1.025423	76.36	0.3516	1.042006	76.98	0.3733	1.057631	77.53	0.4041	1.072350	78.25
DL-Valine											
	$m_s = 0.50000$			$m_s = 1.0000$			$m_s = 1.5000$			$m_s = 2.0001$	
0.0000	1.016240		0.0000	1.033679		0.0000	1.049354		0.0000	1.064093	
0.03324	1.017058	91.37	0.03154	1.034409	91.62	0.03116	1.050029	91.92	0.03377	1.064760	92.58
0.06299	1.017788	91.35	0.06146	1.035100	91.57	0.06110	1.050672	91.94	0.06546	1.065382	92.58
0.1043	1.018800	91.28	0.1023	1.036029	91.63	0.1001	1.051506	91.92	0.09914	1.066037	92.60
0.1584	1.020092	91.38	0.1508	1.037139	91.56	0.1518	1.052595	91.96	0.1498	1.066994	92.73
0.2132	1.021409	91.34	0.2008	1.038252	91.61	0.1703	1.052964	92.07	0.1994	1.067921	92.80
0.2580	1.022472	91.33	0.2474	1.039260	91.73	0.2019	1.053646	91.96	0.2497	1.068846	92.87
0.3333	1.024236	91.33	0.2906	1.040199	91.75	0.2521	1.054666	92.04	0.3051	1.069856	92.91
0.3555	1.024788	91.22	0.3214	1.040882	91.72	0.3063	1.055754	92.10	0.3730	1.071066	92.98
0.3879	1.025544	91.21	0.3558	1.041611	91.77	0.3394	1.056400	92.17	0.4182	1.071876	92.98
						0.3694	1.057021	91.12			
DL-Leucine											
	$m_s = 0.50000$			$m_s = 1.0000$			$m_s = 1.5000$			$m_s = 2.0001$	
0.0000	1.016240		0.0000	1.033679		0.0000	1.049354		0.0000	1.064093	
0.01815	1.016641	107.55	0.01499	1.033982	107.87	0.009355	1.049 527	108.13	0.009760	1.064256	108.42
0.02716	1.016728	107.70	0.02505	1.034186	107.84	0.01911	1.049704	108.28	0.01972	1.064419	108.54
0.03178	1.016940	107.62	0.03977	1.034479	107.93	0.02460	1.049806	108.23	0.02980	1.064585	108.56
0.03651	1.017044	107.60	0.04476	1.034577	107.96	0.02910	1.049886	108.29	0.02476	1.064502	108.55
0.04093	1.017140	107.62	0.04989	1.034685	107.86	0.03432	1.049980	108.31	0.03938	1.064742	108.58
0.04547	1.017238	107.65	0.05507	1.034783	107.96	0.03889	1.050063	108.32	0.03461	1.064661	108.64
0.05077	1.017354	107.64	0.06006	1.034886	107.90	0.04502	1.050173	108.34	0.04946	1.064903	108.65
0.05494	1.017445	107.64				0.04902	1.050247	108.32	0.04510	1.064834	108.61
0.06319	1.017625	107.64									

[a] m_s stands for the molality of sodium butyrate in water.

in Table 1. Apparent molar volumes of the amino acids were calculated as

$$V_{2,\phi} = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0 \qquad (2)$$

where m is the molality of amino acid in solutions, M is the molar mass of amino acid, and ρ_0 is the density of the solvent (aqueous solution of sodium butyrate). The reported apparent molar volume data for the amino acids (Table 1)

Table 2. Standard Partial Molar Volumes for α-Amino Acids in Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	$m_s = 0.5$[b]		$m_s = 1.0$		$m_s = 1.5$		$m_s = 2.0$	
	$V°_{2,\phi}$	S_V	$V°_{2,\phi}$	S_V	$V°_{2,\phi}$	S_V	$V°_{2,\phi}$	S_V
amino acid	$cm^3\ mol^{-1}$	$m^3\ mol^{-2}\ kg$	$cm^3\ mol^{-1}$	$m^3\ mol^{-2}\ kg$	$cm^3\ mol^{-1}$	$m^3\ mol^{-2}\ kg$	$cm^3\ mol^{-1}$	$m^3\ mol^{-2}\ kg$
glycine	44.58(4)	0.87(16)	45.96(3)	0.30(11)	46.91(5)	0.10(24)	48.17(4)	−0.74(8)
alanine	61.49(2)	0.10(8)	62.44(3)	0.40(12)	62.93(1)	0.23(6)	63.78(3)	−0.13(14)
aminobutyric acid	76.29(2)	0.20(7)	76.78(2)	0.62(9)	77.18(2)	0.99(8)	78.06(5)	0.52(20)
valine	91.46(4)	−0.57(18)	91.51(4)	0.72(5)	91.83(3)	0.88(12)	92.61(4)	0.94(15)
leucine	107.62(4)	0.42(101)	107.90(2)	0.14(11)	108.21(4)	2.63(131)	108.47(5)	0.41(27)

[a] Values in parentheses are standard deviation × 100. [b] m_s stands for the molality of sodium butyrate in water.

Table 3. Contributions of (NH_3^+, COO^-) and CH_2 Groups to the Standard Partial Molar Volume in Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	$V°_{2,\phi}$[b]/($cm^3\ mol^{-1}$)				
group	$m_s = 0$[b]	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
(NH_3^+, COO^-)	28.3(0.5)[c]	29.5(0.6)	31.0(0.7)	32.0(0.7)	33.4(0.6)
CH_2	15.8(0.2)[c]	15.6(0.2)	15.3(0.2)	15.1(0.2)	14.9(0.2)

[a] Values in parentheses are standard deviations. [b] m_s stands for the molality of sodium butyrate in water. [c] From ref 23.

were found to be adequately presented by the linear equation

$$V_{2,\phi} = V°_{2,\phi} + S_V m \qquad (3)$$

where $V°_{2,\phi}$ is the infinite dilution apparent molar volume, which has the same meaning as the standard partial molar volume, and S_V is the experimental slope. The regression coefficients of eq 3 for the α-amino acids in aqueous solutions of (0.5, 1.0, 1.5, and 2.0 mol kg^{-1}) sodium butyrate are presented in Table 2 along with their standard deviations.

Note that $V°_{2,\phi}$ values of the studied homologous series of α-amino acids vary linearly with the number of carbon atoms (n_c) in their alkyl chains at 298.15 K. A similar linear correction has been observed for some α- and α,ω-amino acids in aqueous ammonium chloride,[4] and the homologous series of α- or ω-amino acids in guanidium chloride or potassium thiocynate solutions.[9,16] A linear regression analysis of the $V°_{2,\phi}$ values as a function of n_c at different sodium butyrate concentrations using

$$V°_{2,\phi} = V°_{2,\phi}(NH_3^+,COO^-) + n_c V°_{2,\phi}(CH_2) \qquad (4)$$

gives $V°_{2,\phi}(NH_3^+,COO^-)$, the zwitterionic end group contribution, and $V°_{2,\phi}(CH_2)$, the methylene group contribution. These results are listed in Table 3. It should be pointed out that the $V°_{2,\phi}(CH_2)$ value obtained here characterizes the mean contribution of CH and CH_3 groups to $V°_{2,\phi}$ of the α-amino acids.

It can be seen from Tables 2 and 3 that $V°_{2,\phi}(CH_2)$ values for the amino acids decrease and that $V°_{2,\phi}(NH_3^+,COO^-)$ and $V°_{2,\phi}$ values increase with increasing concentrations of sodium butyrate. These results indicate that the interactions between ($CH_3CH_2CH_2COO^-$, Na^+) and the charged end groups (NH_3^+, COO^-) of the amino acids are the main contribution to $V°_{2,\phi}$ values of amino acids, and they are much stronger than those between ($CH_3CH_2CH_2COO^-$, Na^+) and CH_2 groups in the alkyl chain of α-amino acids.

The standard volumes of transfer for the amino acids from water to aqueous sodium butyrate solutions were calculated from the relation

$$\Delta_t V° = V°_{2,\phi}(\text{in aqueous } NaC_4) - V°_{2,\phi}(\text{in water}) \qquad (5)$$

Table 4. Standard Volumes of Transfer for Amino Acids from Water to Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	$\Delta_t V°/(cm^3\ mol^{-1})$			
amino acid	$m_s = 0.5$[b]	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
glycine	1.10(4)	2.45(4)	3.43(5)	4.69(4)
alanine	0.82(4)	1.77(5)	2.26(4)	3.11(5)
aminobutyric acid	0.55(13)	1.04(13)	1.44(13)	2.32(14)
valine	0.49(5)	0.54(5)	0.86(5)	1.64(5)
leucine	0.21(13)	0.49(13)	0.80(13)	1.06(14)

[a] Values in parentheses are standard deviation × 100. [b] m_s stands for the molality of sodium butyrate in water.

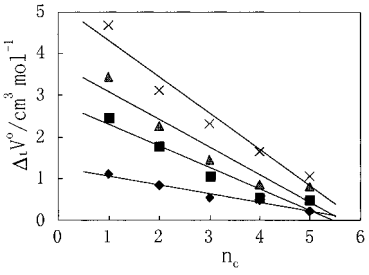

Figure 1. Relation between $\Delta_t V°$ and n_c in aqueous sodium butyrate solution at 298.15 K: ◆, 0.5 m; ■, 1.0 m; ▲, 1.5 m; ×, 2.0 m.

where $V°_{2,\phi}$(in water) values were taken from the literature.[23] The results have been presented in Table 4. It is evident that $\Delta_t V°$ values from water to aqueous NaC_4 are positive and increase with increasing concentration of NaC_4. As seen from Figure 1, reasonable linear relations exist between $\Delta_t V°$ for the amino acids and the number of carbon atoms in their alkyl chains. Compared with eq 4, it is evident that the intercept and slope of the straight line represent the contributions of the zwitterionc end group and the CH_2 group to $\Delta_t V°$, respectively. It is clear that the contribution of the CH_2 group to $\Delta_t V°$ is negative and that of the zwitterionic group is positive. The overall positive $\Delta_t V°$ observed in this work for the amino acid can be thought of as the effect of the zwitterionic portion of the amino acids dominating that of the alkyl chain. This conclusion supports our results of the standard partial molar volumes. Because of the interactions of the ions (Na^+, $CH_3CH_2CH_2COO^-$) and the zwitterionic group of the amino acids, the electrostriction of water molecules lying in the vicinity of the NH_3^+ and COO^- centers of the amino acids would get reduced and consequently lead to a positive volume contribution. With increasing NaC_4 concentration, this interaction will become stronger and therefore $\Delta_t V°$ increases.

The number of water molecules (n_H) hydrated to the amino acid can be estimated from the electrostriction partial molar volume $V°_{2,\phi}$(elect)[24] by

$$n_H = V°_{2,\phi}(\text{elect})/(V°_e - V°_b) \qquad (6)$$

Table 5. Hydration Number, n_H, for Amino Acids in Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	n_H			
amino acid	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
glycine	2.2	1.8	1.5	1.1
alanine	3.1	2.8	2.7	2.4
aminobutyric acid	3.5	3.1	2.8	2.4
valine	3.2	3.2	3.1	2.9
leucine	5.0	4.9	4.8	4.7

[a] m_s stands for the molality of sodium butyrate in water.

where $V°_e$ is the molar volume of electrostricted water and $V°_b$ is the molar volume of bulk water. The values of ($V°_e - V°_b$) are calculated to be -3.3 cm^3 mol^{-1} at 298.15 K.[24] The $V°_{2,\phi}$(elect) values can be calculated[25] from the intrinsic partial molar volume of the amino acid $V°_{2,\phi}$(int)[26,27] and the $V°_{2,\phi}$ values determined experimentally

$$V°_{2,\phi}(\text{amino acid}) = V°_{2,\phi}(\text{int}) + V°_{2,\phi}(\text{elect}) \qquad (7)$$

The obtained n_H values are included in Table 5. It can be seen that n_H for a given amino acid varies with solvent composition, showing a tendency to decrease with an increase in the concentration of sodium butyrate. This supports the view[6] that electrolytes have a dehydration effect on the amino acids in solutions.

Compared with $V°_{2,\phi}$, $\Delta_t V°$, and n_H values of the amino acids in aqueous sodium acetate,[10] it is found that $V°_{2,\phi}$(in NaC_4) and $\Delta_t V°$(in NaC_4) are larger than those in aqueous sodium acetate (NaC_2) solutions and that n_H values in aqueous NaC_4 are smaller than that in aqueous NaC_2. In general, the interaction between amino acid and sodium butyrate (or sodium acetate) can be classified into (a) ion−ion interactions between Na^+ and the COO^- group of the amino acids and those between $CH_3CH_2CH_2COO^-$ (or CH_3COO^-) of NaC_4 (or NaC_2) and the NH_3^+ group of the amino acid and (b) interactions between ion and nonpolar groups of the amino acids. It is noted that $V°_{2,\phi}(CH_2)$ in aqueous NaC_4 is close to that in aqueous NaC_2 solutions,[10] while $V°_{2,\phi}(NH_3^+,COO^-)$ in this work is larger than that in NaC_2 solutions. So the difference in volumetric properties and hydration number observed above mainly comes from the difference in interaction (a) and, accordingly, the interaction between carboxylic ion and the NH_3^+ group of the amino acids. Butyrate ion has a bigger hydrophobic hydration sphere and a larger destructive effect on the hydration sphere of NH_3^+ of the amino acids than acetate ion. The electrostriction of water caused by the NH_3^+ group of the amino acids will be largely reduced, which results in a larger increase in volume and a decrease in n_H values. The study of the dissociation of protein with aliphatic acid salts also indicated that sodium butyrate has larger binding constants than sodium acetate on Haman Hemoglobin A.[20]

Bhat and Ahluwalia[13] studied the transfer volumes of some amino acids from water to aqueous sodium chloride solutions at 298.15 K. We found that, for glycine, DL-α-alanine, and DL-α-amino-*n*-butyric acid, values of $\Delta_t V°$ from water to 1 mol kg^{-1} and 2 mol kg^{-1} aqueous NaCl solutions are smaller than those to the same concentrations of aqueous sodium acetate and sodium butyrate solutions. This indicates that the interactions between carboxylate anion and the amino acids are stronger than those between Cl^- and the amino acids.

The viscosity data for the amino acids in aqueous sodium butyrate solutions at 298.15 K are given in Table 6. At a given concentration of NaC_4, the variation of the viscosity

Table 6. Viscosity η for the α-Amino Acid in Aqueous Sodium Butyrate Solutions As a Function of Concentrations of Amino Acid and Sodium Butyrate at 298.15 K[a]

c	η	c	η	c	η	c	η
mol L^{-1}	mPa S	mol L^{-1}	mPa S	mol L^{-1}	mPa S	mol L^{-1}	mPa S
Glycine							
$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.5000$		$m_s = 2.0001$	
0.0000	1.136	0.0000	1.436	0.0000	1.793	0.0000	2.235
0.03288	1.142	0.03340	1.444	0.03492	1.804	0.03694	2.107
0.06288	1.147	0.06381	1.449	0.06588	1.811	0.07229	2.117
0.1038	1.153	0.1051	1.458	0.1068	1.822	0.1108	2.125
0.1533	1.161	0.1593	1.469	0.1592	1.836	0.1673	2.140
0.2029	1.170	0.2119	1.481	0.2109	1.848	0.2198	2.158
0.2475	1.177	0.2633	1.492	0.2643	1.863	0.2856	2.171
DL-α-Alanine							
$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.5000$		$m_s = 2.0001$	
0.0000	1.136	0.0000	1.436	0.0000	1.793	0.0000	2.235
0.03190	1.146	0.03293	1.448	0.03373	1.809	0.03601	2.256
0.06073	1.154	0.06317	1.458	0.06432	1.824	0.07053	2.277
0.1004	1.167	0.1037	1.474	0.1044	1.843	0.1067	2.299
0.1524	1.183	0.1535	1.494	0.1577	1.869	0.1589	2.330
0.1978	1.196	0.2051	1.516	0.2111	1.895	0.2138	2.360
0.2518	1.213	0.2542	1.536	0.2615	1.921	0.2636	2.400
DL-α-Aminobutyric Acid							
$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.5000$		$m_s = 2.0001$	
0.0000	1.136	0.0000	1.436	0.0000	1.793	0.0000	2.235
0.03189	1.149	0.03320	1.453	0.03273	1.815	0.03636	2.265
0.06078	1.161	0.06378	1.469	0.06329	1.835	0.07018	2.293
0.1005	1.178	0.1050	1.490	0.1043	1.861	0.1057	2.323
0.1520	1.199	0.1524	1.516	0.1575	1.896	0.1585	2.367
0.1999	1.219	0.2014	1.542	0.2082	1.931	0.2125	2.412
0.2478	1.240	0.2535	1.572	0.2610	1.970	0.2636	2.455
DL-Valine							
$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.5000$		$m_s = 2.0001$	
0.0000	1.136	0.0000	1.436	0.0000	1.793	0.0000	2.235
0.03368	1.152	0.03251	1.457	0.03260	1.819	0.03581	2.272
0.06364	1.168	0.06317	1.476	0.06374	1.844	0.06921	2.309
0.1050	1.188	0.1048	1.504	0.1040	1.877	0.1045	2.343
0.1586	1.216	0.1537	1.535	0.1570	1.920	0.1570	2.400
0.2125	1.248	0.2037	1.570	0.2078	1.965	0.2080	2.450
0.2560	1.271	0.2499	1.604	0.2582	2.011	0.2593	2.504
DL-Leucine							
$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.5000$		$m_s = 2.0001$	
0.0000	1.136	0.0000	1.436	0.0000	1.793	0.0000	2.235
0.01840	1.146	0.01548	1.447	0.009807	1.803	0.01037	2.249
0.02752	1.152	0.02582	1.455	0.02001	1.812	0.02094	2.260
0.03696	1.157	0.04093	1.466	0.03043	1.822	0.03160	2.272
0.04598	1.163	0.05129	1.474	0.04063	1.831	0.04172	2.284
0.05550	1.167	0.06167	1.481	0.05115	1.841	0.05233	2.297

[a] m_s stands for the molality of sodium butyrate in water.

of amino acid + NaC_4 + water solutions with the concentration of amino acids can be expressed by the following equation

$$\eta = a_1 \exp(a_2 c) \qquad (8)$$

where η is the viscosity of the solution and c is the molarity of amino acid in solutions. Values of the fitted parameters a_1 and a_2 are listed in Table 7.

The relative viscosities η_r can be represented by the relation[28]

$$\eta_r = \eta/\eta_0 = 1 + Bc \qquad (9)$$

where η_0 is the viscosity of solvent. The B-coefficients of the amino acids obtained by a least squares procedure are given in Table 8.

The B values given in Table 8 reflect the net structural effects of the charged groups and the hydrophobic CH_2

Table 7. Coefficients a_1 and a_2 of Eq 8 for α-Amino Acids in Aqueous Sodium Butyrate at 298.15 K[a]

amino acid	a_1	a_2	σ[b]
	$m_s = 0.5$[c]		
glycine	1.1366(0.0003)	0.141(0.002)	0.0004
DL-alanine	1.1366(0.0004)	0.259(0.003)	0.0006
DL-aminobutyric acid	1.1365(0.0003)	0.352(0.002)	0.0004
DL-valine	1.1348(0.0008)	0.443(0.004)	0.0010
DL-leucine	1.1361(0.0009)	0.493(0.021)	0.0007
	$m_s = 1.0$		
glycine	1.4363(0.0004)	0.144(0.002)	0.0006
DL-alanine	1.4341(0.0007)	0.270(0.003)	0.0009
DL-aminobutyric acid	1.4358(0.0004)	0.356(0.002)	0.0004
DL-valine	1.4357(0.0008)	0.441(0.003)	0.0010
DL-leucine	1.4360(0.0004)	0.504(0.007)	0.0004
	$m_s = 1.5$		
glycine	1.7948(0.0005)	0.140(0.002)	0.0006
DL-alanine	1.7932(0.0002)	0.263(0.008)	0.0003
DL-aminobutyric acid	1.7934(0.0008)	0.357(0.003)	0.0011
DL-valine	1.7924(0.0008)	0.443(0.003)	0.0010
DL-leucine	1.7940(0.0002)	0.504(0.004)	0.0002
	$m_s = 2.0$		
glycine	2.2098(0.0015)	0.123(0.004)	0.0019
DL-alanine	2.2342(0.0024)	0.266(0.007)	0.0030
DL-aminobutyric acid	2.2369(0.0007)	0.354(0.002)	0.0009
DL-valine	2.2394(0.0017)	0.433(0.005)	0.0022
DL-leucine	2.2367(0.0006)	0.503(0.008)	0.0006

[a] Values in parentheses are standard deviations. [b] Standard deviations of the fit. [c] m_s stands for the molality of sodium butyrate in water.

Table 8. Viscosity *B*-Coefficients for α-Amino Acids in Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	B/(dm^3 mol^{-1})			
amino acid	$m_s = 0.5$[b]	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
glycine	0.1438(0.7)	0.146(1)	0.147(1)	0.1492(0.8)
alanine	0.2655(0.7)	0.269(4)	0.270(1)	0.2727(0.3)
aminobutyric acid	0.367(1)	0.369(2)	0.371(2)	0.3738(0.2)
valine	0.457(5)	0.460(4)	0.461(4)	0.466(3)
leucine	0.494(5)	0.512(2)	0.522(1)	0.533(7)

[a] Values in parentheses are standard deviation × 1000. [b] m_s stands for the molality of sodium butyrate in water.

Table 9. Contributions of (NH_3^+, COO^-) and CH_2 Groups to Viscosity *B*-Coefficients of the Amino Acids in Aqueous Sodium Butyrate Solutions at 298.15 K[a]

	B/(dm^3 mol^{-1})			
group	$m_s = 0.5$[b]	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
(NH_3^+, COO^-)	0.078(30)	0.074(25)	0.072(22)	0.071(20)
CH_2	0.089(9)	0.092(7)	0.094(7)	0.096(6)

[a] Values in parentheses are standard deviation × 1000. [b] m_s stands for the molality of sodium butyrate in water.

groups on the amino acids. These two effects can be separated by noting that the *B*-coefficients are linear in n_c, that is

$$B = B(NH_3^+,COO^-) + n_c B(CH_2) \qquad (10)$$

The regression parameters, $B(NH_3^+,COO^-)$, the zwitterionic group contribution, and $B(CH_2)$, the methylene group contribution to the *B*-coefficient, are listed in Table 9. It can be seen from Table 9 that values of $B(NH_3^+,COO^-)$ decrease while $B(CH_2)$ values increase with increasing concentration of NaC_4 in solutions, indicating that the zwitterionic groups break while CH_2 groups enhance the structures of the aqueous salt solutions.

Moreover, it is observed that *B*-coefficients show a linear correlation with the standard partial molar volumes $V^\circ_{2,\phi}$ for the α-amino acids in aqueous NaC_4 solutions. The coefficients b_1 and b_2 of the equation

$$B = b_1 + b_2 V^\circ_{2,\phi} \qquad (11)$$

are given in Table 10 together with their standard deviations and correlation coefficients. Similar correlations for α-amino acids in guanidine hydrochloride solution[19] and α-amino acids in water[28] and in aqueous KSCN[17] were observed. This correlation is not unexpected, taking into account that both the viscosity *B*-coefficient and the standard partial molar volume reflect the solute−solvent interaction in solutions.

Table 10. Coefficients b_1 and b_2 of Eq 11 for Amino Acids in Aqueous Sodium Butyric Solution at 298.15 K[a]

m_s/(mol kg^{-1})	$-b_1$/(dm^3 mol^{-1})	b_2	R[b]
0.5	0.091(0.046)	5.7(0.6)	0.985
1.0	0.112(0.041)	6.0(0.5)	0.989
1.5	0.126(0.038)	6.2(0.5)	0.991
2.0	0.144(0.034)	6.4(0.4)	0.994

[a] Values in parentheses are standard deviation. [b] Correlation coefficient.

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