Volumetric and Viscosity Properties of α-Amino Acids and Their Groups in Aqueous Sodium Caproate Solutions

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Densities and viscosities have been measured for solutions of DL-α-valine or DL-α-leucine in aqueous sodium caproate solutions at 298.15 K and 308.15 K. On the basis of these data, the apparent molar volumes ($V_{m,2}$), standard partial molar volumes ($V°_{m,2}$), standard volumes of transfer ($\Delta_t V°$), hydration number (n_H), and viscosity *B*-coefficients of DL-α-valine and DL-α-leucine have been determined. Combined with the corresponding data of glycine, DL-α-alanine, and DL-α-amino-*n*-butyric acid reported recently, it has been shown that the standard partial molar volumes and the viscosity *B*-coefficients of the amino acids vary linearly with increasing number of carbon atoms in the alkyl chain of the amino acids. These properties have been split into contributions from the zwitterionic end group (NH_3^+, COO^-) and CH_2 groups of the amino acids by using linear relations. The volumetric data suggest that sodium caproate interacts strongly with the zwitterionic end group of the amino acids, and the electrolyte has a strong dehydration effect on the amino acids. Viscosity data have been discussed on the basis of structure effects of the amino acids and their groups in the solutions.

Introduction

The behavior of proteins in mixtures is governed by many factors such as pH, solvent properties, chemical structure and surface charge distribution of proteins, and electrolyte type and concentration. The influence of electrolyte on the behavior of protein is one of the important topics in physical chemistry of the substances. It has long been known that there is a strong interaction between electrolytes and proteins,[1] which causes a departure from ideal behavior. To understand the fine details, the interactions of the building blocks of the protein with electrolytes must be studied owing to the complex structural organization of the biological macromolecules. Experimental work has been reported on the thermodynamics of amino acids in (simple salts + water).[2−15] However, there are few measurements on interactions between amino acid and organic salts.[16−20] Sodium carboxylate is known to influence the dissociation of proteins in solutions.[21] Recently, we have investigated the volumetric and viscosity properties of amino acids in aqueous sodium acetate [22,23] and in aqueous sodium butyrate.[24] As a part of the continuing studies on thermodynamic and transport properties of amino acids in aqueous sodium carboxylate solutions, the present work reports the partial molar volumes and viscosity *B*-coefficients for DL-α-valine and DL-α-leucine in aqueous solutions of (0.5, 1.0, 1.5, and 2.2) mol·kg^{-1} sodium caproate (NaC_6) at 298.15 K and 308.15 K. The contributions from the zwitterionic and CH_2 groups of the amino acids have been determined and discussed by means of the interactions between the ions and the amino acids.

Experimental Section

DL-α-Valine and DL-α-leucine (Shanghai Chem. Co., A.R.) were twice recrystallized 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. Analytical reagent grade sodium caproate (Shanghai Chem. Co.) was twice recrystallized from aqueous ethanol solutions and dried under vacuum at 383 K for 2 days before use. Water with a specific conductivity of 1.2 $\mu\Omega^{-1}\cdot cm^{-1}$ 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. The uncertainty in concentration is ± 0.0002 mol·kg^{-1}.

The sample densities were measured by an Anton Paar DMA 60/602 vibrating-tube digital densimeter. The density data determined are reproducible to $\pm 3 \times 10^{-3}$ kg·m^{-3}. Viscosity measurements were carried out with a suspended level Ubbelhode viscometer, which has an efflux time of nearly 200 s for water at 298.15 K. Flow time measurements are performed by a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. At least three time recordings were obtained, and the average value was used as the experimental flow time. The reproducibility of flow time was ± 0.02 s. The viscometer was thermostated in a Schott thermostat, the temperature of which was controlled to be (298.15 and 308.15) ± 0.005 K. The temperature around the density meter cell was controlled by circulating water from the same thermostat. The experimental details are given elsewhere.[24] The apparent molar volumes ($V_{m,2}$) of amino acids (2) were calculated from

$$V_{m,2} = (M/\rho) - (\rho - \rho_o)/(m_a\rho\rho_o) \tag{1}$$

where m_a is the molality (amount of substance of solute per mass of solvent) of amino acid in solutions; *M* is the molar mass of amino acid; and ρ and ρ_o are the densities

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Table 1. Solution Densities (ρ) and Apparent Molar Volumes ($V_{m,2}$) for DL-α-Valine and DL-α-Leucine in Aqueous Sodium Caproate Solutions as a Function of Molalities of Amino Acids (m_a) and Sodium Caproate (m_s) at 298.15 K and 308.15 K

m_a	ρ/(kg·m^{-3})		$V_{m,2}$/(cm^3·mol^{-1})		m_a	ρ/(kg·m^{-3})		$V_{m,2}$/(cm^3·mol^{-1})	
(mol·kg^{-1})	298.15 K	308.15 K	298.15 K	308.15 K	(mol·kg^{-1})	298.15 K	308.15 K	298.15 K	308.15 K
DL-α-Valine									
m_s = 0.5000 mol·kg^{-1}					m_s = 1.0000 mol·kg^{-1}				
0.0000	1014.396	1010.739			0.0000	1029.412	1024.963		
0.03442	1015.248	1011.566	91.38	92.33	0.03430	1030.194	1025.740	92.22	92.65
0.06562	1016.013	1012.306	91.40	92.39	0.06529	1030.894	1026.437	92.26	92.67
0.1007	1016.874	1013.148	91.34	92.25	0.09971	1031.673	1027.194	92.20	92.80
0.1505	1018.062	1014.329	91.50	92.24	0.1481	1032.744	1028.259	92.28	92.82
0.2000	1019.258	1015.518	91.43	92.08	0.1992	1033.869	1029.361	92.29	92.89
0.2528	1020.522	1016.738	91.39	92.13	0.2481	1034.956	1030.427	92.22	92.84
0.2961	1021.516	1017.702	91.48	92.25	0.2943	1035.922	1031.349	92.35	93.06
0.3478	1022.727	1018.873	91.46	92.27	0.3391	1036.888	1032.273	92.33	93.11
0.3964	1023.846	1019.988	91.47	92.22	0.3945	1038.049	1033.386	92.37	93.21
m_s = 1.5000 mol·kg^{-1}					m_s = 2.1773 mol·kg^{-1}				
0.0000	1041.883	1036.699			0.0000	1054.224	1048.717		
0.03407	1042.558	1037.381	94.14	94.30	0.03446	1054.799	1049.269	96.05	97.11
0.06559	1043.179	1038.002	94.12	94.39	0.06616	1055.319	1049.770	96.13	97.15
0.1003	1043.858	1038.679	94.13	94.46	0.1006	1055.903	1050.331	95.96	96.98
0.1503	1044.824	1039.642	94.15	94.51	0.1506	1056.689	1051.108	96.17	97.06
0.1998	1045.723	1040.582	94.39	94.57	0.1998	1057.469	1051.871	96.22	97.07
0.2503	1046.684	1041.540	94.34	94.57	0.2491	1058.291	1052.685	96.06	96.86
0.3228	1048.039	1042.784	94.32	94.91	0.3055	1059.160	1053.570	96.14	96.82
0.3742	1048.971	1043.697	94.35	94.96	0.3597	1060.026	1054.428	96.08	96.75
0.4307	1049.983	1044.729	94.38	94.92	0.4115	1060.836	1055.234	96.06	96.71
DL-α-Leucine									
m_s = 0.5000 mol·kg^{-1}					m_s = 1.0000 mol·kg^{-1}				
0.004373	1014.493	1010.833	107.64	108.72	0.01506	1029.710	1025.262	108.71	108.97
0.01462	1014.719	1011.051	107.73	108.77	0.02505	1029.902	1025.461	108.88	108.94
0.01972		1011.158		108.85	0.03033	1030.000		109.02	
0.02462	1014.931	1011.265	108.08	108.74	0.04049	1030.199	1025.760	108.95	109.08
0.03499	1015.157	1011.484	108.05	108.80	0.04553	1030.288	1025.859	109.12	109.10
0.03996	1015.259	1011.589	108.17	108.81	0.05037	1030.375	1025.957	109.23	109.03
0.04994	1015.462	1011.798	108.40	108.84	0.05602	1030.480	1026.062	109.27	109.13
0.06525	1047.832	1012.117	108.44	108.90	0.06062		1026.153		109.10
					0.06477	1030.624	1026.348	109.58	
m_s = 1.5000 mol·kg^{-1}					m_s = 2.1773 mol·kg^{-1}				
0.01510	1042.147	1036.967	109.71	109.92	0.01493	1054.427	1048.912	112.07	113.15
0.02559	1042.326	1037.148	109.85	110.09	0.02496	1054.563	1049.038	112.10	113.29
0.03192		1037.260		110.05	0.03998	1054.761	1049.222	112.22	113.49
0.04024	1042.574	1037.409	109.96	109.97	0.04527	1054.832		112.23	
0.04735	1042.695	1037.535	109.96	109.94	0.04983	1054.892	1049.344	112.21	113.52
0.05021	1042.739	1037.579	110.05	110.07	0.05566	1054.970	1049.413	112.22	113.48
0.05765	1042.870	1037.714	109.98	109.98	0.06028	1055.021	1049.466	112.39	113.58
0.06138	1042.925	1037.771	110.10	110.10	0.06450	1055.076	1049.512	112.39	113.65
0.06562	1042.993	1037.851	110.14	110.00					

of solution and the solvent, respectively. The viscosity data were obtained from relation

$$\eta = C\rho t - K\rho/t \tag{2}$$

where t is the efflux time, and C and K are the viscometer constants obtained by the measurements of flow time for water at 298.15 K and 308.15 K. The values of C and K obtained are 4.854×10^{-6} mPa·m^3·kg^{-1} and 1.979×10^{-3} mPa·s^2·m^3·kg^{-1}, respectively. The uncertainty of the viscosity measurements is better than $\pm\ 1 \times 10^{-3}$ mPa·S, and the effect of imprecision in density on the viscosity is $\pm$ 3.63×10^{-6} mPa·S.

Results

The values of density and apparent molar volume at (298.15 and 308.15) K are given in Table 1. Uncertainty in apparent molar volumes changes from 0.013 to 0.001 cm^3·mol^{-1} for DL-α-valine and from 0.025 to 0.005 cm^3·mol^{-1} for DL-α-leucine in the amino acid concentration range investigated. The data of apparent molar volume can be fitted by

$$V_{m,2} = V°_{m,2} + S_V m_a \tag{3}$$

where $V°_{m,2}$ is the apparent molar volume of the amino acids at infinite dilution which has the same meaning as the standard partial molar volume, and S_V is an experimentally determined parameter. Values of $V°_{m,2}$ have been obtained by weighted least-squares regression analysis.[25] The standard partial molar volumes for DL-α-valine and DL-α-leucine in aqueous solutions of (0.5, 1.0, 1.5, and 2.2) mol·kg^{-1} sodium caproate are presented in Table 2 along with their standard deviations.

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

$$\Delta_t V° = V°_{m,2}\ (\text{in aqueous NaC}_6) - V°_{m,2}\ (\text{in water}) \tag{4}$$

where $V°_{m,2}$ (in water) values were taken from our earlier publication.[26] The results are presented in Table 3.

The viscosity data at (298.15 and 308.15) K obtained for both solvent and solutions are reported in Table 4 as a function of amino acid concentrations. The viscosity B-coefficients for the amino acids in aqueous sodium caproate solutions can be represented by the following equation:[27]

$$\eta_r = \eta/\eta_o = 1 + Bc \tag{5}$$

Table 2. Standard Partial Molar Volumes for DL-α-Valine and DL-α-Leucine in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

amino acids	$V^\circ_{m,2}/(cm^3 \cdot mol^{-1})$			
	$m_s = 0.5\ mol \cdot kg^{-1}$	$m_s = 1.0\ mol \cdot kg^{-1}$	$m_s = 1.5\ mol \cdot kg^{-1}$	$m_s = 2.2\ mol \cdot kg^{-1}$
		298.15 K		
valine	91.38 ± 0.03	92.17 ± 0.03	94.19 ± 0.05	96.18 ± 0.06
leucine	107.73 ± 0.08	108.33 ± 0.09	109.64 ± 0.05	111.88 ± 0.06
		308.15 K		
valine	92.14 ± 0.08	92.53 ± 0.04	94.27 ± 0.05	97.22 ± 0.04
leucine	108.71 ± 0.03	109.12 ± 0.04	110.01 ± 0.08	113.10 ± 0.06

Table 3. Standard Volumes of Transfer for DL-α-Valine and DL-α-Leucine from Water to Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

amino acid	$\Delta_t V^\circ/(cm^3 \cdot mol^{-1})$			
	$m_s = 0.5\ mol \cdot kg^{-1}$	$m_s = 1.0\ mol \cdot kg^{-1}$	$m_s = 1.5\ mol \cdot kg^{-1}$	$m_s = 2.2\ mol \cdot kg^{-1}$
		298.15 K		
valine	0.41 ± 0.05	1.20 ± 0.05	3.22 ± 0.06	5.21 ± 0.07
leucine	0.32 ± 0.15	0.92 ± 0.16	2.23 ± 0.14	4.47 ± 0.14
		308.15 K		
valine	0.50 ± 0.11	0.89 ± 0.08	2.63 ± 0.09	5.58 ± 0.08
leucine	0.38 ± 0.13	0.79 ± 0.13	1.68 ± 0.15	4.77 ± 0.14

Table 4. Viscosities (*η*) for (Amino Acids + Sodium Caproate + Water) Systems as a Function of Concentrations of Amino Acids (*c*) and Sodium Caproate (m_s) at 298.15 K and 308.15 K

$m_s = 0.5000\ mol \cdot kg^{-1}$		$m_s = 1.0000\ mol \cdot kg^{-1}$		$m_s = 1.5000\ mol \cdot kg^{-1}$		$m_s = 2.1773\ mol \cdot kg^{-1}$	
c / $mol \cdot dm^{-3}$	η / mPa·S	c / $mol \cdot dm^{-3}$	η / mPa·S	c / $mol \cdot dm^{-3}$	η / mPa·S	c / $mol \cdot dm^{-3}$	η / mPa·S
			DL-α-Valine (298.15 K)				
0.0000	1.212	0.0000	1.607	0.0000	2.102	0.0000	3.187
0.03481	1.229	0.03519	1.632	0.03538	2.133	0.03620	3.241
0.06616	1.246	0.06680	1.656	0.06789	2.164	0.06928	3.293
0.1012	1.264	0.1017	1.681	0.1035	2.198	0.1050	3.353
0.1506	1.292	0.1504	1.717	0.1543	2.249	0.1564	3.431
0.1992	1.319	0.2013	1.754	0.2042	2.299	0.2065	3.508
0.2506	1.349	0.2495	1.789	0.2546	2.350	0.2561	3.593
			DL-α-Leucine (298.15 K)				
0.004434	1.197	0.01548	1.619	0.01571	2.117	0.01571	3.213
0.01481	1.220	0.02572	1.628	0.02658	2.129	0.02624	3.231
0.02491	1.226	0.04149	1.640	0.04174	2.146	0.04195	3.257
0.04036	1.235	0.05156	1.648	0.05201	2.157	0.05223	3.274
0.05038	1.241	0.06198	1.657	0.06350	2.171	0.06310	3.292
0.06572	1.251						
			DL-α-Valine (308.15 K)				
0.0000	0.956	0.0000	1.240	0.0000	1.601	0.0000	2.402
0.03468	0.969	0.03504	1.258	0.03520	1.625	0.03600	2.444
0.06592	0.981	0.06651	1.273	0.06755	1.648	0.06892	2.481
0.1008	0.995	0.1012	1.291	0.1030	1.673	0.1045	2.527
0.1501	1.015	0.1497	1.316	0.1535	1.709	0.1556	2.577
0.1985	1.035	0.2004	1.343	0.2032	1.745	0.2054	2.632
0.2497	1.057	0.2484	1.370	0.2533	1.781	0.2548	2.690
			DL-α-Leucine (308.15 K)				
0.004418	0.958	0.01542	1.249	0.01563	1.613	0.01563	2.421
0.01475	0.962	0.02561	1.254	0.02645	1.622	0.02610	2.434
0.02482	0.967	0.04131	1.263	0.04153	1.634	0.04173	2.453
0.04021	0.974	0.05134	1.269	0.05179	1.642	0.05195	2.466
0.05020	0.978	0.06171	1.275	0.06324	1.651	0.06276	2.479
0.06548	0.985						

where *c* is the molarity of amino acid in solutions. Viscosity *B*-coefficients were obtained by the least-squares method and are given in Table 5 together with their standard deviations.

Discussion

It is well-known that the amino acids exist in different ionic forms depending on the environment. There are several forms of amino acids, viz., the fully protonated amino acids (A^+), the zwitterionic form ($A^\pm$), and the fully deprotonated amino acid (A^-); and the relative concentrations of these different forms depend strongly on the pH of the medium. Sodium caproate is a salt formed by a weak acid and a strong base, which can be hydrolyzed and gives a basic solution. It has been calculated that the pH values of aqueous solutions of (0.5, 1.0, 1.5, and 2.2) $mol \cdot kg^{-1}$ sodium caproate are 9.27, 9.43, 9.51, and 9.59, respectively, at 298.15 K. Therefore, a part of zwitterionic amino acids change into the fully deprotonated amino acids in aqueous sodium caproate solutions. In the extreme case, if all of the hydroxyl ions in aqueous sodium caproate solutions are neutralized by the zwitterions to give the fully deprotonated amino acids, then the concentration of zwitterionic forms of amino acids may be obtained by subtracting the

Table 5. Viscosity *B*-Coefficients for DL-α-Valine and DL-α-Leucine in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

amino acid	$B/(\mathrm{dm^3 \cdot mol^{-1}})$			
	$m_s = 0.5\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 1.0\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 1.5\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 2.2\ \mathrm{mol \cdot kg^{-1}}$
		298.15 K		
valine	0.446 ± 0.004	0.454 ± 0.001	0.458 ± 0.004	0.476 ± 0.008
leucine	0.491 ± 0.001	0.501 ± 0.001	0.509 ± 0.005	0.520 ± 0.001
		308.15 K		
valine	0.414 ± 0.003	0.418 ± 0.003	0.439 ± 0.002	0.471 ± 0.004
leucine	0.450 ± 0.002	0.459 ± 0.003	0.493 ± 0.002	0.511 ± 0.002

Table 6. Contributions of Zwitterionic (NH_3^+, COO^-) and CH_2 Groups to the Standard Partial Molar Volumes for the Amino Acids in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

group	$V°_{m,2}/(\mathrm{cm^3 \cdot mol^{-1}})$			
	$m_s = 0.5\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 1.0\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 1.5\ \mathrm{mol \cdot kg^{-1}}$	$m_s = 2.2\ \mathrm{mol \cdot kg^{-1}}$
		298.15 K		
(NH_3^+, COO^-)	29.8 ± 0.6	31.4 ± 0.6	33.4 ± 0.4	35.0 ± 0.4
CH_2^-	15.5 ± 0.2	15.3 ± 0.2	15.3 ± 0.1	15.4 ± 0.1
		308.15 K		
(NH_3^+, COO^-)	30.1 ± 0.7	31.3 ± 0.7	33.2 ± 0.5	35.0 ± 0.5
CH_2^-	15.7 ± 0.2	15.5 ± 0.2	15.3 ± 0.1	15.6 ± 0.2

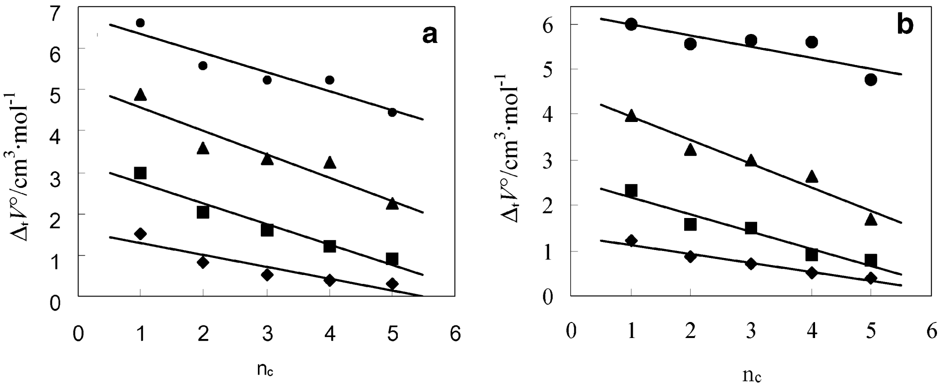

Figure 1. Linear relationship between $\Delta_t V°$ and n_c in aqueous sodium caproate solutions at 298.15 K (a) and 308.15 K (b): ◆, 0.5 $\mathrm{mol \cdot kg^{-1}}$; ■, 1.0 $\mathrm{mol \cdot kg^{-1}}$; ▲, 1.5 $\mathrm{mol \cdot kg^{-1}}$; ●, 2.2 $\mathrm{mol \cdot kg^{-1}}$.

hydroxyl ion concentration from the actual molality of the amino acids. Following the calculations of Banipal et al.,[20] we found that the molality of the amino acids in solution changes by 3 units at fifth place in this case. This results in the change of $V°_{m,2}$ by only 0.02 $\mathrm{cm^3 \cdot mol^{-1}}$, which is within the uncertainty limits in the measurements. Therefore, there is a very small fraction of fully deprotonated amino acid, but its effect is neglectable.

Values of $V°_{m,2}$ in Table 2 show a tendency to increase with increasing molality of sodium caproate at given temperatures. Using values of $V°_{m,2}$ obtained in this study and those of glycine, alanine, and aminobutyric acid reported in our previous work,[28] linear relation can be observed between $V°_{m,2}$ for the amino acids and the number of carbon atoms (n_c) in their alkyl chains in each solvent system. This linear variation is represented by

$$V°_{m,2} = V°_{m,2}(NH_3^+, COO^-) + n_c V°_{m,2}(CH_2) \qquad (6)$$

where $V°_{m,2}(NH_3^+, COO^-)$ and $V°_{m,2}(CH_2)$ are the zwitterionic end group and the methylene group contribution to $V°_{m,2}$, respectively. The values of $V°_{m,2}(NH_3^+, COO^-)$ and $V°_{m,2}(CH_2)$, calculated by a least-squares regression analysis, are listed in Table 6. Since the alkyl chains of homologous series of the α-amino acids are CH_2- (glycine), CH_3CH- (alanine), CH_3CH_2CH- (aminobutyric acid), CH_3CH_3CHCH- (valine), and $CH_3CH_3CHCH_2CH$- (leucine), the value of $V°_{m,2}$ (CH_2) obtained by this procedure characterize the mean contribution of CH_3- and CH- groups to $V°_{m,2}$ of the amino acids.

It can be seen from Table 6 that $V°_{m,2}(CH_2)$ values for the amino acids is close to the value of 15.3 $\mathrm{cm^3 \cdot mol^{-1}}$ obtained from studies of aqueous solution of amino acid[13] at 298.15 K. This indicated the balance of the interactions between the hydrophobic and hydrophilic groups of sodium caproate and CH_2- group of amino acid. On the other hand, the $V°_{m,2}(NH_3^+, COO^-)$ values are larger than those of $V°_{m,2}(CH_2)$ and increase with increasing sodium caproate concentration. These results suggest that the interactions of the ions of sodium caproate with the zwitterionic groups of the amino acids are much stronger than those with CH_2- groups.

As seen from Table 3, $\Delta_t V°$ values of DL-α-valine and DL-α-leucine from water to aqueous sodium caproate are positive and increase with increasing concentration of NaC_6. It can be observed from Figure 1 that 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 6, it is evident that the intercept and slope of the straight line represent the contributions of zwitterionic end group and CH_2 group to $\Delta_t V°$, respectively. It is clear that the contribution of 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 acids stressed importance of the interaction between sodium caproate and the zwitterionic portion of the amino acids.

Table 7. Values of Hydration Number (n_H) for Amino Acids in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

	n_H			
amino acids	$m_s = 0.5$ mol·kg^{-1}	$m_s = 1.0$ mol·kg^{-1}	$m_s = 1.5$ mol·kg^{-1}	$m_s = 2.2$ mol·kg^{-1}
	298.15 K			
glycine	2.1	1.6	1.1	0.6
alanine	3.1	2.7	2.3	1.7
aminobutyric acid	3.4	2.9	2.4	1.9
valine	3.2	3.0	2.4	1.8
leucine	4.9	4.8	4.4	3.7
	308.15 K			
glycine	1.6	1.3	0.9	0.4
alanine	2.4	2.2	1.8	1.1
aminobutyric acid	3.2	2.9	2.4	1.8
valine	3.0	2.4	2.0	1.2
leucine	3.8	3.8	3.5	2.8

Because of this interaction, the electrostriction of water molecules lying in the vicinity of the NH_3^+ and COO^- centers of the amino acids would be reduced and consequently lead to a positive volume contribution. With increasing NaC_6 concentrations, this interaction will become stronger and, therefore, $\Delta_t V°$ increases.

The number of water molecules (n_H) hydrated to the amino acids can be estimated from the electrostriction partial molar volume $V°_{m,2}$(elect) by[29]

$$n_H = V°_{m,2}(\text{elect})/(V°_e - V°_b) \qquad (7)$$

where $V°_e$ is the molar volume of electrostricted water and $V°_b$ is the molar volume of bulk water. The value of ($V°_e - V°_b$) is calculated to be (−3.3 and −4.0) cm^3·mol^{-1} at 298.15 K and 308.15 K, respectively.[22,29] The $V°_{m,2}$(elect) values can be calculated[30] from the intrinsic partial molar volume $V°_{m,2}$(int) of the amino acid[31,32] and the $V°_{m,2}$ values determined experimentally:

$$V°_{m,2}(\text{amino acid}) = V°_{m,2}(\text{int}) + V°_{m,2}(\text{elect}) \qquad (8)$$

The obtained n_H values are included in Table 7. It can be seen that n_H for a given amino acid varies with solvent composition, showing a tendency to decrease with increasing concentration of sodium caproate. This supports the view[8] that electrolytes have dehydration effect on the amino acids in solutions.

Compared with n_H values of the amino acids in aqueous sodium acetate (NaC_2)[22,23] and in aqueous sodium butyrate (NaC_4),[24] it is found that n_H values in aqueous NaC_6 are smaller than those in aqueous NaC_2 and in aqueous NaC_4 solutions. In general, the interaction between amino acid and sodium carboxylate can be classified into: (a) ion−ion interactions between Na^+ and the COO^- group of the amino acids and those between carboxylate anion and the NH_3^+ group of the amino acid; (b) interactions between ion and nonpolar groups of the amino acids. It is noted that $V°_{m,2}(CH_2)$ in aqueous NaC_6 is close to those in aqueous NaC_2/NaC_4 solutions,[22−24] while $V°_{m,2}(NH_3^+, COO^-)$ in aqueous NaC_6 is larger than those in NaC_2/NaC_4 solutions. Therefore, the difference in volumetric properties and hydration number observed above mainly comes from the difference in interaction (a). Because the interactions of Na^+ with the COO^- group of the amino acids are the same for the amino acids in aqueous sodium carboxylates, the interaction between carboxylic anion and the NH_3^+ group of the amino acids will be responsible for this difference. Caproate anion has bigger hydrophobic hydration sphere and larger destructive effect on hydration sphere of NH_3^+ of the amino acids than acetate and butyrate anions. The electrostriction of water caused by the NH_3^+ group of the amino acids will be largely reduced, which results in decrease in n_H values. Recently, we obtained the order[28] for interaction between the carboxylate anion and the amino acid: $CH_3(CH_2)_4COO^- > CH_3(CH_2)_2COO^- > CH_3COO^-$. From the comparison of hydration number, the same order can be obtained. It seems appropriate to conclude that sodium caporate has larger dehydration effect on the amino acids in solutions.

In the previous work,[33] we found that values of $V°_{m,2}$ for a given amino acid in aqueous solutions of some sodium carboxylates (NaC_2, NaC_4, and NaC_6) almost increase linearly with increasing side chain length of the carboxylate anion. Based on this fact and the linear relations shown in eq 6, the values of $V°_{m,2}$ for the amino acids can be correlated with the concentration of sodium carboxylate (m_s), the number of carbon atom (n_c) in alkyl chain of the amino acids, and the number of carbon atom (n_s) in hydrocarbon chain of the carboxylate anions by

$$V°_{m,2} = b_1 + b_2 m_s + b_3 n_c + b_4 m_s n_s + b_5 m_s n_c + b_6 n_s n_c + b_7 n_c n_s m_s \qquad (9)$$

The parameters obtained by least-squares analysis are as follows: $b_1 = 28.43$ cm^3·mol^{-1}, $b_2 = 1.455$ cm^3·kg^{-1}·mol^{-2}, $b_3 = 15.96$ cm^3·mol^{-1}, $b_4 = 0.2634$ cm^3·kg^{-1}·mol^{-2}, $b_5 = -0.5288$ cm^3·kg^{-1}·mol^{-2}, $b_6 = -0.07970$ cm^3·mol^{-1}, $b_7 = 0.06651$ cm^3·kg^{-1}·mol^{-2} at 298.15 K; and $b_1 = 28.59$ cm^3·mol^{-1}, $b_2 = 1.475$ cm^3·kg^{-1}·mol^{-2}, $b_3 = 16.10$ cm^3·mol^{-1}, $b_4 = 0.2447$ cm^3·kg^{-1}·mol^{-2}, $b_5 = -0.4887$ cm^3·kg^{-1}·mol^{-2}, $b_6 = -0.08744$ cm^3·mol^{-1}, $b_7 = 0.07152$ cm^3·kg^{-1}·mol^{-2} at 308.15 K. The standard deviations of the fit are 0.59 at (298.15 and 308.15) K. This empirical equation can be used to calculate $V°_{m,2}$ values of the amino acids studied in aqueous NaC_2, NaC_4, and NaC_6 solutions within a certain concentration (<2.0 mol·kg^{-1}) of sodium carboxylates. It can also be used to predict $V°_{m,2}$ values of the amino acids in aqueous sodium propionate and sodium pentanoate solutions. This is useful from a practical point of view.

Combination of the *B*-coefficient values for valine and leucine given in Table 5 with those for glycine, alanine, and aminobutyric acid in the same electrolyte solutions[28]

Table 8. Contributions of Zwitterionic (NH_3^+, COO^-) and CH_2 Groups to Viscosity *B*-Coefficients of the Amino Acids in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

	B/(dm^3·mol^{-1})			
group	$m_s = 0.5$ mol·kg^{-1}	$m_s = 1.0$ mol·kg^{-1}	$m_s = 1.5$ mol·kg^{-1}	$m_s = 2.2$ mol·kg^{-1}
		298.15 K		
(NH_3^+, COO^-)	0.072 ± 0.026	0.070 ± 0.025	0.085 ± 0.024	0.103 ± 0.028
CH_2^-	0.089 ± 0.008	0.091 ± 0.007	0.089 ± 0.007	0.089 ± 0.008
		308.15 K		
(NH_3^+, COO^-)	0.085 ± 0.024	0.091 ± 0.023	0.099 ± 0.016	0.112 ± 0.022
CH_2^-	0.078 ± 0.007	0.078 ± 0.007	0.082 ± 0.005	0.084 ± 0.007

Table 9. Parameters A_1 and A_2 of Equation 11 for the Amino Acids in Aqueous Sodium Caproate Solutions at 298.15 K and 308.15 K

m_s/mol·kg^{-1}	$-A_1$/(dm^3·mol^{-1})	A_2	R^a	σ^b
		298.15 K		
0.5	0.097 ± 0.041	5.7 ± 0.5	0.988	0.026
1.0	0.117 ± 0.040	5.9 ± 0.5	0.989	0.024
1.5	0.110 ± 0.038	5.9 ± 0.5	0.991	0.022
2.2	0.099 ± 0.046	5.8 ± 0.6	0.987	0.027
		308.15 K		
0.5	0.063 ± 0.038	5.0 ± 0.5	0.986	0.024
1.0	0.066 ± 0.038	5.0 ± 0.5	0.987	0.023
1.5	0.078 ± 0.026	5.3 ± 0.3	0.995	0.015
2.2	0.077 ± 0.036	5.4 ± 0.4	0.991	0.021

[a] Correlation coefficient. [b] Standard deviations of the fit.

shown that *B*-coefficients increase in the following order:

glycine < alanine < aminobutyric acid < valine < leucine

In fact, *B*-coefficients of the homologous series of α-amino acids vary linearly with the number of carbon atoms on their alkyl chains at a given temperature. Similar to eq 6, the linear relation can be represented by

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

The regression parameters $B(\mathrm{NH_3}^+, \mathrm{COO}^-)$ and $B(\mathrm{CH_2})$, which indicate the contributions of the zwitterionic and the methylene groups to the *B*-coefficient, are listed in Table 8. It should be pointed out that $B(\mathrm{CH_2})$ obtained here characterizes the mean contribution of CH and CH_3 groups to *B*-coefficients of the amino acids.

The *B* values of valine and leucine decrease with increasing temperature in all the solvent compositions. Since $(\mathrm{d}B/\mathrm{d}T)$ is negative for a structure-making solute,[34] we can classify valine and leucine as structure makers in water−sodium caproate mixtures. The $\mathrm{d}B/\mathrm{d}T$ values obtained in this work for the groups (Table 8) confirm that the charged end groups are structure-breakers and CH_2 are structure-makers. On the other hand, *B*-coefficient values of the amino acids increase with concentration of sodium caproate, indicating the promotion of liquid structure in the presence of sodium caproate.

Moreover, it is observed that *B*-coefficients show a linear correlation with the standard partial molar volumes $V^\circ_{\mathrm{m},2}$ for the α-amino acids in aqueous NaC_6 solutions. The coefficients A_1 and A_2 of the equation

$$B = A_1 + A_2 V^\circ_{\mathrm{m},2} \qquad (11)$$

are given in Table 9 together with their standard deviations and correlation coefficients. Similar correlations for α-amino acids in aqueous guanidine hydrochloride,[18] KSCN,[15] sodium acetate,[23] and sodium butyrate[24] solutions have been reported. This correlation is not unexpected, taking into account that both viscosity *B*-coefficient and standard partial molar volume reflect the solute−solvent interactions in solutions.

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