Partial Molar Volumes and Viscosities of Some α-Amino Acids in Micellar Solutions of Sodium Caprylate

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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 caprylate have been measured as a function of the concentrations of amino acid and sodium caprylate 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 volume $V°_{2,\phi}$ and standard volumes of transfer $\Delta_t V°$ have been determined for the amino acids. It has been shown that values of $V°_{2,\phi}$ and the *B* coefficient vary linearly with the increasing number of carbon atoms in the alkyl chain of the amino acids, and they were split into contributions from the zwitterionic end group (NH_3^+, COO^-) and CH_2 groups of the amino acids. From the volumetric data, it is suggested that the amino acids are solubilized in the palisade layer of sodium caprylate micelles. The viscosity properties have been interpreted in light of the solute−solvent interactions in aqueous media.

Introduction

Various biological processes involve volume changes and the hydration of molecules. Their complete understanding needs a proper idea for the state and the behavior of the molecules in the medium.[1] Because of the structural complexities of proteins and the nonfeasibility of direct thermodynamic studies, amino acids are often used as model compounds because they are building blocks of proteins.

In the past 20 years, there have been extensive thermodynamic property studies on amino acid−water−simple salt systems[2−11] but few studies on amino acids in organic salt−water mixtures,[12−16] especially for their viscosity property. In continuation of our studies on the thermodynamic and transport properties of amino acids in protein-denaturant media,[13−18] we report, in this paper, the volumetric and viscosity properties of some α-amino acids in aqueous sodium caprylate solutions at 298.15 K. Sodium caprylate (NaC_8) is a surfactant that is known to inhibit DNA synthesis and to release cytoplasmic protein, inducing fibrolast damage.[19] A previous study showed that micelles are formed in aqueous NaC_8, and its CMC is found to be 0.35 mol·dm^{-3}.[20] The aqueous sodium caprylate solutions studied here are micellar solutions. To our knowledge, the interactions between amino acids with NaC_8 have never before been determined. Therefore, it is interesting to investigate the behavior of some amino acids in micellar solutions of sodium caprylate. For this purpose, apparent molar volumes and viscosities for glycine (Gly), DL-α-alanine (Ala), DL-α-amino-*n*-butyric acid (Abu), DL-valine (Val), and DL-leucine (Leu) are determined in aqueous solutions containing (0.4, 0.6, 0.8, and 1.0) mol·kg^{-1} sodium caprylate at 298.15 K. In addition, the standard partial molar volumes and viscosity *B* coefficients for the zwitterionic (NH_3^+, COO^-) and CH_2 groups of the amino acids have also been reported. The results are discussed in terms of the solute−solvent interactions in aqueous media.

Experimental Section

Chemicals. 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 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 caprylate (Shanghai Chem. Co.) was twice recrystallized from aqueous ethanol solutions and dried under vacuum at 383 K for 2 days. 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.

Apparatus Procedures. 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 daily at 298.15 K using dry air and conductivity water. The density of pure water at 298.15 K was taken from Kell's data.[21]

Viscosity measurements were carried out with a suspended-level Ubbelohde viscometer that 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. At least three time recordings reproducible to 0.02 s were obtained, and the average value was used in the calculations. The viscosity of the 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 that were obtained by the measurements on water at (298.15 and 308.15) K.

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

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Table 1. Solution Densities (ρ) and Apparent Molar Volumes ($V_{2,\phi}$) for the α-Amino Acids in Aqueous Sodium Caprylate Solutions as a Function of the Molality of Amino Acids (m_a) and Sodium Caprylate (m_s) at 298.15 K

$m_s = 0.4000$ mol·kg^{-1}			$m_s = 0.6000$ mol·kg^{-1}			$m_s = 0.8001$ mol·kg^{-1}			$m_s = 0.9999$ mol·kg^{-1}		
m_a	ρ	$V_{2,\phi}$	m_a	ρ	$V_{2,\phi}$	m_a	ρ	$V_{2,\phi}$	m_a	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						
0.0000	1.009386		0.0000	1.013938		0.0000	1.017850		0.0000	1.021436	
0.02978	1.010262	45.47	0.03068	1.014810	46.34	0.02946	1.018641	47.80	0.03064	1.022237	48.41
0.05923	1.011119	45.57	0.06167	1.015687	46.37	0.05881	1.019432	47.72	0.06086	1.023027	48.38
0.09786	1.012253	45.49	0.09386	1.016583	46.51	0.1011	1.020558	47.77	0.09899	1.024019	48.36
0.1481	1.013703	45.56	0.1491	1.018119	46.58	0.1458	1.021767	47.64	0.1456	1.025266	48.11
0.1974	1.015101	45.69	0.1954	1.019416	46.52	0.1964	1.023134	47.53	0.1996	1.026686	48.04
0.2481	1.016587	45.56	0.2433	1.020743	46.53	0.2472	1.024508	47.44	0.2481	1.027993	47.86
0.2978	1.018025	45.51	0.2971	1.022141	46.80	0.2968	1.025837	47.40	0.2941	1.029215	47.78
0.3153	1.018510	45.56	0.3323	1.023136	46.69	0.3306	1.026773	47.28	0.3214	1.030004	47.55
0.3549	1.019643	45.54	0.3919	1.024786	46.61	0.3508	1.027328	47.23	0.3549	1.030879	47.55
					DL-Alanine						
0.03148	1.010230	61.89	0.02962	1.014685	63.29	0.03052	1.018590	64.05	0.03036	1.022144	64.84
0.06295	1.011070	61.90	0.05897	1.015428	63.20	0.06055	1.019318	64.03	0.06065	1.022853	64.74
0.1025	1.012112	61.98	0.09460	1.016316	63.27	0.09946	1.020255	64.03	0.09804	1.023723	64.72
0.1526	1.013430	61.99	0.1461	1.017608	63.19	0.1520	1.021553	63.78	0.1486	1.024914	64.57
0.2015	1.014699	62.05	0.1945	1.018784	63.33	0.2017	1.022746	63.79	0.1980	1.026115	64.28
0.2510	1.015954	62.17	0.2488	1.020157	63.16	0.2515	1.023960	63.69	0.2271	1.026773	64.36
0.3097	1.017453	62.20	0.2855	1.021040	63.22	0.3016	1.025143	63.73	0.2485	1.027303	64.22
0.3383	1.018216	62.10	0.3182	1.021861	63.15	0.3326	1.025903	63.65	0.2952	1.028372	64.26
0.3713	1.019039	62.15	0.3467	1.022561	63.14	0.3589	1.026531	63.64	0.3247	1.029090	64.15
									0.3586	1.029899	64.07
					DL-Aminobutyric Acid						
0.03008	1.010166	76.65	0.03115	1.014687	78.26	0.02909	1.018520	79.02	0.03008	1.022103	79.67
0.06010	1.010938	76.71	0.06221	1.015429	78.27	0.05603	1.019140	78.98	0.05993	1.022762	79.65
0.09888	1.011934	76.67	0.1017	1.016359	78.36	0.09231	1.019968	79.00	0.09824	1.023606	79.61
0.1499	1.013214	76.80	0.1514	1.017542	78.28	0.1425	1.021108	78.98	0.1506	1.024768	79.49
0.1987	1.014404	76.98	0.2027	1.018750	78.24	0.1934	1.022290	78.81	0.1981	1.025816	79.43
0.2502	1.015703	76.90	0.2491	1.019851	78.16	0.2411	1.023360	78.82	0.2474	1.026931	79.24
0.3287	1.017555	77.14	0.3018	1.021053	78.22	0.2756	1.024104	78.92	0.2984	1.028023	79.29
0.3653	1.018455	77.10	0.3363	1.021863	78.17	0.3050	1.024786	78.82	0.3252	1.028630	79.19
			0.3749	1.022762	78.13	0.3419	1.025613	78.79	0.3583	1.029357	79.15
					DL-Valine						
0.02976	1.010114	91.99	0.02939	1.014595	93.75	0.03157	1.018515	94.68	0.02997	1.021205	95.13
0.05990	1.010847	92.00	0.05848	1.015244	93.70	0.06311	1.019176	94.68	0.05975	1.022653	95.06
0.09965	1.011809	91.97	0.09565	1.016062	93.75	0.1036	1.020025	94.63	0.09745	1.023342	95.05
0.1467	1.012915	92.12	0.1405	1.017041	93.77	0.1538	1.021080	94.52	0.1471	1.024438	94.86
0.1962	1.014079	92.16	0.1970	1.018290	93.65	0.2033	1.022130	94.38	0.1969	1.025467	94.69
0.2470	1.015229	92.31	0.2451	1.019339	93.61	0.2531	1.023189	94.24	0.2483	1.026502	94.67
0.2931	1.016311	92.24	0.2869	1.020219	93.66	0.3063	1.024273	94.26	0.2958	1.027409	94.79
0.3300	1.017147	92.27	0.3233	1.021022	93.57	0.3482	1.025159	94.16	0.3269	1.028051	94.68
			0.3471	1.021547	93.52	0.3769	1.025752	94.13	0.3530	1.028597	94.59
					DL-Leucine						
0.009655	1.009591	109.04	0.009950	1.014123	111.26	0.009965	1.018012	113.09	0.009717	1.021585	113.66
0.02471	1.009912	108.96	0.02491	1.014389	111.65	0.02488	1.018242	113.54	0.02482	1.021811	113.85
0.03974	1.010223	109.12	0.03987	1.014642	112.06	0.03986	1.018463	113.89	0.03992	1.022019	114.31
0.05001	1.010449	108.92	0.04998	1.014801	112.42	0.04983	1.018616	113.88	0.04972	1.022158	114.37
0.05515	1.010549	109.08	0.05511	1.014874	112.68	0.05468	1.018670	114.23	0.05496	1.022222	114.57
0.05957	1.010637	109.14	0.06104	1.014970	112.75	0.06051	1.018745	114.42	0.06048	1.022292	114.70
0.06490	1.010738	109.31	0.06281	1.014999	112.75	0.06105	1.018757	114.36	0.06431	1.022333	114.89
0.06987	1.010863	108.99	0.06991	1.015088	113.18	0.06381	1.018805	114.25	0.06932	1.022400	114.93
						0.06954	1.018869	114.55			

Results and Discussion

The density data measured for the amino acids + sodium caprylate + water systems at 298.15 K are given in Table 1 as a function of the molality of amino acid (m_a) and sodium caprylate (m_s). Apparent molar volumes, $V_{2,\phi}$, of the amino acids were calculated from the solution densities, ρ, using the equation

$$V_{2,\phi} = \frac{M}{\rho} - \frac{1000(\rho - \rho_o)}{m_a \rho \rho_o} \qquad (2)$$

where M is the molar mass of amino acid and ρ_o is the density of aqueous sodium caprylate solutions. Calculated apparent molar volumes for the amino acids are also listed in Table 1. The results can be fit by the equation

$$V_{2,\phi} = V^\circ_{2,\phi} + S_V m_a \qquad (3)$$

where $V^\circ_{2,\phi}$ is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_V is an experimentally determined parameter. Values of $V^\circ_{2,\phi}$ have been evaluated by weighted least-squares regression analysis.[22] The standard partial molar volumes for the amino acids in aqueous solutions of (0.4, 0.6, 0.8, and 1.0) mol·kg^{-1} sodium caprylate are represented in Table 2 along with their standard deviations.

Table 2. Standard Partial Molar Volumes for the α-Amino Acids in Aqueous Sodium Caprylate Solutions at 298.15 K

	$V^\circ_{2,\phi}$/cm^3·mol^{-1}			
amino acids	$m_s = 0.4$ mol·kg^{-1}	$m_s = 0.6$ mol·kg^{-1}	$m_s = 0.8$ mol·kg^{-1}	$m_s = 1.0$ mol·kg^{-1}
glycine	45.63 ± 0.06	46.50 ± 0.08	47.91 ± 0.03	48.62 ± 0.05
alanine	61.97 ± 0.05	63.35 ± 0.04	64.00 ± 0.05	64.79 ± 0.06
amino-butyric acid	76.61 ± 0.04	78.35 ± 0.03	79.01 ± 0.04	79.72 ± 0.03
valine	92.00 ± 0.05	93.85 ± 0.04	94.72 ± 0.03	95.01 ± 0.07
leucine	108.95 ± 0.11	110.75 ± 0.10	112.89 ± 0.10	113.25 ± 0.09

It is found that $V^\circ_{2,\phi}$ values of the studied homologous series of α-amino acids vary linearly with the number of

Table 3. Standard Partial Molar Volumes of Zwitterionic (NH^+_3, COO^-) and CH_2 Groups of the Amino Acids in Aqueous Sodium Caprylate Solution at 298.15 K

	$V°_{2,\phi}$/cm^3·mol^{-1}			
group	$m_s = 0.4$ mol·kg^{-1}	$m_s = 0.6$ mol·kg^{-1}	$m_s = 0.8$ mol·kg^{-1}	$m_s = 1.0$ mol·kg^{-1}
(NH^+_3, COO^-)	30.0 ± 0.7	30.9 ± 0.6	31.5 ± 1.0	32.4 ± 1.1
CH_2−	15.7 ± 0.2	15.9 ± 0.2	16.1 ± 0.3	16.0 ± 0.3

Table 4. Standard Partial Molar Volumes of Transfer for the Amino Acids from Water to Aqueous Sodium Caprylate Solutions at 298.15 K

	$\Delta_t V°$/cm^3·mol^{-1}			
amino acid	m_s=0.4 mol·kg^{-1}	$m_s = 0.6$ mol·kg^{-1}	$m_s = 0.8$ mol·kg^{-1}	$m_s = 1.0$ mol·kg^{-1}
glycine	2.15 ± 0.06	3.02 ± 0.08	4.43 ± 0.04	5.14 ± 0.05
alanine	1.30 ± 0.06	2.68 ± 0.06	3.33 ± 0.06	4.12 ± 0.07
aminobutyric acid	0.87 ± 0.14	2.61 ± 0.13	3.27 ± 0.14	3.98 ± 0.13
valine	1.03 ± 0.06	2.88 ± 0.06	3.75 ± 0.05	4.04 ± 0.08
leucine	1.54 ± 0.17	3.34 ± 0.16	5.48 ± 0.16	5.84 ± 0.16

carbon atoms (n_c) in their alkyl chains at 298.15 K. A similar linear correlation has been observed for some α- and α,ω-amino acids in aqueous ammonium chloride,[8] guanidium chloride,[12,13] sodium acetate,[14,15] and sodium butyrate[16] solutions. A linear regression analysis of the $V°_{2,\phi}$ values as a function of n_c at different sodium caprylate concentrations using

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

gives $V°_{2,\phi}(NH_3^+, COO^-)$, for the zwitterionic end group, and $V°_{2,\phi}(CH_2)$, the methylene group contributions. These results are listed in Table 3. It can be seen that $V°_{2,\phi}(CH_2)$ values for the amino acids are not sensitive to the concentration of sodium caprylate. The same trend has been observed in aqueous sodium acetate and sodium butyrate[14−16] solutions. Values of $V°_{2,\phi}(NH_3^+, COO^-)$ are larger than those of $V°_{2,\phi}(CH_2)$ and increase with increasing sodium caprylate concentration. These results indicate that the interactions of sodium caprylate with zwitterionic end group of the amino acids are much stronger than those with hydrophobic CH_2 groups.

The standard volumes of transfer, $\Delta_t V°$, for the amino acids from water to micellar solutions of sodium caprylate are listed in Table 4. They were calculated from the relation

$$\Delta_t V° = V°_{2,\phi}(\text{in aqueous } NaC_8) - V°_{2,\phi}(\text{in water}) \quad (5)$$

where $V°_{2,\phi}$(in water) is the infinite dilution apparent molar volume for the amino acids in water, and its value can be found in one of our previous papers.[23] It is evident that $\Delta_t V°$ values from water to sodium caprylate solutions are positive and increase with increasing concentration of sodium caprylate. The positive $\Delta_t V°$ values can be explained by the fact that sodium caprylate interacts directly through electrostatic interactions with the zwitterionic end group of the amino acids, thereby leading to a volumetric reduction in the electrostriction of the solvent and a positive partial molar volume of transfer. With increasing sodium caprylate concentration, this interaction will become stronger; therefore, $\Delta_t V°$ increases.

Using values of $V°_{2,\phi}$ for the amino acids in 1.0 mol·kg^{-1} aqueous sodium acetate,[15] sodium butyrate,[16] sodium caproate,[24] and sodium caprylate solutions at 298.15 K, we plotted $V°_{2,\phi}$ values for the homologous series of α-amino acids against the number of carbon atoms (n_s) in a hydrocarbon chain of carboxylate anions in Figure 1 (taking alanine and leucine as examples). It is obvious that the

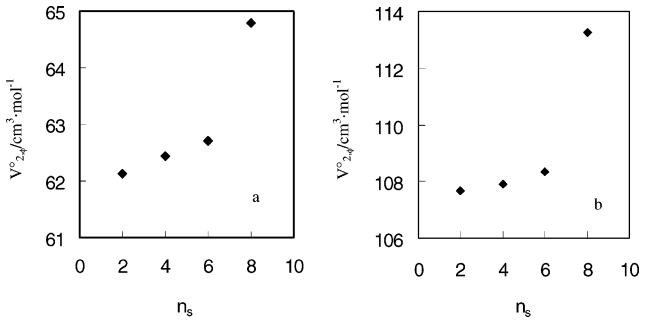

Figure 1. Relation between the standard partial molar volume of alanine (a) and leucine (b) in 1.0 mol kg^{-1} sodium carboxylate solutions and the number of carbon atom (n_s) in their alkyl chains at 298.15 K.

values of $V°_{2,\phi}$ for given amino acids in short-chain sodium carboxylate solutions (NaC_2, NaC_4, and NaC_6) increase almost linearly with increasing side-chain length of the carboxylate anion. However, there is an exception to $V°_{2,\phi}$- (in NaC_8). These values in aqueous NaC_8 solutions are much larger than the corresponding values in other salt solutions. From the comparison of $\Delta_t V°$ values of the amino acids in different sodium carboxylate solutions, it is found that at a given concentration of aqueous sodium caprylate solution (say, 1.0 mol·kg^{-1}) $\Delta_t V°$(in NaC_8) values are much larger than those in aqueous NaC_2, NaC_4, and NaC_6 solutions, thus indicating that the interactions of the amino acids with NaC_8 are different from those with NaC_2, NaC_4, and NaC_6. Because aqueous sodium caprylate is micellar in solution, there exist the interactions of the amino acids with not only ions but also micellar molecules of sodium caprylate. Vikingstad[25,26] investigated the partial molar volumes of *n*-alcohols, *n*-diols, sodium alkylcarboxylates, and disosium-alkyldicarboxylates in micellar solutions of sodium alkylcarboxylate (NaC_8−NaC_{12}). He found that the partial molar volumes of these compounds in micellar solutions are much larger than those in aqueous solutions. This clearly indicates a hydrocarbon surrounding for these polar molecules in the micellar solutions. It is now generally accepted that more polar solutes tend to be solubilized in the palisade layer of the micelle.

As polar molecules, some portions of the amino acids are probably solubilized in the palisade layer of the micelle. This conclusion can also be drawn from the values of $V°_{2,\phi}$-(NH_3^+, COO^-) and $V°_{2,\phi}(CH_2)$ in micellar solutions of sodium caprylate. In aqueous sodium acetate, sodium butyrate, and sodium caproate solutions, the mean value of $V°_{2,\phi}(CH_2)$ is (15.3 ± 0.2) cm^3·mol^{-1} at 298.15 K. However, (15.9 ± 0.2) cm^3·mol^{-1} is found for $V°_{2,\phi}(CH_2)$ in sodium caprylate micellar solutions at the same temperature. It has been reported that $V°_{2,\phi}(CH_2)$ in the hydrocarbon core of a micelle is (17.1 ± 0.1) cm^3·mol^{-1},[26] so the amino acids are probably solubilized in the outer layer of the micelles but not in the micellar core. The possible reason is that compared with NaC_{10} or NaC_{12} the molecules of NaC_8 in micelles are less restricted and considerable water penetrates into the micelles. The surroundings for hydrophobic chain of the amino acids solubilized in the micelles are not pure hydrocarbons. However, because of the electrostatic interaction between zwitterionic end groups of the amino acids and the molecules of the micelle, the repulsion among the molecules of the palisade layer decreases, leading to closer packing of the surfactant molecules. This prevents the amino acids from entering the hydrocarbon core of the micelle. Vikingstad[26] also found that $V°_{2,\phi}(CH_2)$ is somewhat smaller in the outer layer than

Table 5. Viscosities η for α-Amino Acid + Sodium Caprylate +Water Systems as Functions of the Molarity of Amino Acids (c) and Molality of Sodium Caprylate (m_s) at 298.15 K

m_s = 0.4000 mol·kg^{-1}		m_s = 0.6000 mol·kg^{-1}		m_s = 0.8001 mol·kg^{-1}		m_s = 0.9999 mol·kg^{-1}	
c/ mol·L^{-1}	η/ mPa·S	c/ mol·L^{-1}	η/ mPa·S	c/ mol·L^{-1}	η/ mPa·S	c/ mol·L^{-1}	η/ mPa·S
Glycine							
0.0000	1.204	0.0000	1.422	0.0000	1.704	0.0000	2.069
0.03002	1.209	0.03106	1.429	0.02994	1.715	0.03125	2.079
0.05963	1.214	0.06235	1.437	0.05969	1.726	0.06198	2.091
0.09834	1.221	0.09476	1.445	0.1024	1.738	0.1006	2.110
0.1485	1.230	0.1502	1.458	0.1474	1.752	0.1477	2.131
0.1974	1.241	0.1963	1.471	0.1980	1.769	0.2019	2.156
0.2476	1.250	0.2439	1.482	0.2486	1.789	0.2504	2.175
DL-Alanine							
0.03172	1.213	0.02998	1.433	0.03100	1.719	0.03095	2.088
0.06329	1.224	0.05957	1.445	0.06139	1.736	0.06171	2.107
0.1028	1.237	0.09534	1.459	0.1006	1.757	0.09950	2.130
0.1525	1.253	0.1467	1.482	0.1532	1.786	0.1503	2.164
0.2008	1.269	0.1948	1.502	0.2026	1.816	0.1997	2.202
0.2494	1.289	0.2483	1.526	0.2519	1.843	0.2498	2.230
DL-Aminobutyric Acid							
0.03030	1.217	0.03151	1.438	0.02954	1.724	0.03065	2.089
0.06039	1.229	0.06277	1.455	0.05678	1.742	0.06092	2.115
0.09905	1.249	0.1023	1.477	0.09327	1.767	0.09955	2.148
0.1495	1.269	0.1517	1.504	0.1434	1.806	0.1520	2.198
0.1975	1.291	0.2022	1.533	0.1939	1.840	0.1992	2.230
0.2478	1.316	0.2477	1.559	0.2407	1.870	0.2477	2.275
DL-Valine							
0.02996	1.220	0.02972	1.441	0.03204	1.730	0.03049	2.094
0.06013	1.236	0.05897	1.461	0.06385	1.760	0.06068	2.127
0.09967	1.257	0.09611	1.485	0.1044	1.794	0.09860	2.163
0.1461	1.284	0.1406	1.516	0.1543	1.831	0.1481	2.228
0.1945	1.313	0.1961	1.557	0.2030	1.875	0.1974	2.266
0.2437	1.341	0.2428	1.589	0.2515	1.926	0.2477	2.324
DL-Leucine							
0.009735	1.210	0.01008	1.429	0.01013	1.715	0.009914	2.078
0.02487	1.220	0.02518	1.442	0.02525	1.730	0.02528	2.099
0.03993	1.229	0.04025	1.454	0.04038	1.748	0.04059	2.117
0.05021	1.235	0.05039	1.464	0.05042	1.758	0.05050	2.130
0.05534	1.239	0.05553	1.467	0.05531	1.759	0.05578	2.136
0.06999	1.249	0.07032	1.478	0.07021	1.775	0.07024	2.154

in the core. Meanwhile, sodium cations are at the micellar surface and are surrounded by a water layer.[27] When the zwitterionic end groups interact with sodium cations and the micelles of caprylate anions, some of the previously electrostricted water molecules around these centers return to their normal structure. This gives rise to an increase in $V°_{2,\phi}(NH_3^+, COO^-)$. It can be seen from the discussion above that in micellar solutions of sodium caprylate the amino acids interact not only with ions and water but also with the micellar molecules of sodium caprylate. In aqueous sodium carboxylate solutions, the interactions between the amino acids and free caprylate anions increase with increasing side-chain length of the carboxylate anion.[24] Therefore, the interaction of sodium caprylate with amino acids is stronger than those of sodium acetate, sodium butyrate, and sodium caprylate. These interactions give rise to the larger increase in $V°_{2,\phi}$ of amino acids and their groups in micellar solution of sodium caprylate.

The viscosity data for the amino acids in aqueous sodium caprylate solutions at 298.15 K are given in Table 5. The relative viscosities, η_r, can be represented by the relation[28]

$$\eta_r = \frac{\eta}{\eta_o} = 1 + Bc \qquad (6)$$

where η_o is the viscosity of solvent. The B coefficients of the amino acids obtained by a least-squares procedure are given in Table 6.

The B values given in Table 6 reflect the net structural effects of the charged groups and the hydrophobic CH_2 groups on the amino acids. These two effects can be separated by noting that the B coefficients are linear in n_c:

$$B = B(NH_3^+, COO^-) + n_c B(CH_2) \qquad (7)$$

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 7. It is found that the B values of the amino acids and their groups in aqueous NaC_8 are larger than those in water and in aqueous NaC_2, NaC_4 and NaC_6[16,18,24] solutions. The B coefficient is a measure of solute−solvent interactions. This fact suggests the increased structure-making tendency of the amino acids and their groups in the presence of NaC_8. This is consistent with the conclusion obtained from volumetric properties.

Moreover, it is interesting that there is a linear correlation between the B coefficients and the standard partial molar volumes $V°_{2,\phi}$ for the α-amino acids in aqueous NaC_8 solutions:

$$B = A_1 + A_2 V°_{2,\phi} \qquad (8)$$

Coefficients A_1 and A_2 are given in Table 8 together with their standard deviations. This correlation is not unexpected, taking into account that both the viscosity B coefficient and the standard partial molar volume reflect the solute−solvent interactions in solutions.

Table 6. Viscosity B Coefficients for the α-Amino Acids in Aqueous Sodium Caprylate Solutions at 298.15 K

	B/dm^3·mol^{-1}			
amino acid	m_s = 0.4 mol·kg^{-1}	m_s = 0.6 mol·kg^{-1}	m_s = 0.8 mol·kg^{-1}	m_s = 1.0 mol·kg^{-1}
glycine	0.154 ± 0.001	0.175 ± 0.001	0.196 ± 0.002	0.204 ± 0.003
alanine	0.274 ± 0.003	0.291 ± 0.003	0.320 ± 0.003	0.313 ± 0.004
amino-butyric acid	0.371 ± 0.003	0.387 ± 0.002	0.406 ± 0.003	0.398 ± 0.005
valine	0.463 ± 0.003	0.481 ± 0.004	0.502 ± 0.006	0.492 ± 0.008
leucine	0.529 ± 0.003	0.574 ± 0.006	0.604 ± 0.009	0.582 ± 0.006

Table 7. Viscosity B Coefficients of Zwitterionic (NH_3^+, COO^-) and CH_2 Groups of Amino Acids in Aqueous Sodium Caprylate Solutions at 298.15 K

	B/dm^3·mol^{-1}			
group	m_s = 0.4 mol·kg^{-1}	m_s = 0.6 mol·kg^{-1}	m_s = 0.8 mol·kg^{-1}	m_s = 1.0 mol·kg^{-1}
(NH_3^+, COO^-)	0.076 ± 0.019	0.085 ± 0.009	0.106 ± 0.011	0.117 ± 0.007
CH_2−	0.094 ± 0.006	0.099 ± 0.003	0.100 ± 0.003	0.094 ± 0.002

Table 8. Coefficients A_1 and A_2 of Equation 10 for the Amino Acids in Aqueous Sodium Caprylate at 298.15 K

m_s/mol·kg^{-1}	$-A_1$/dm^3·mol^{-1}	A_2	σ^a
0.4	0.103 ± 0.032	6.0 ± 0.4	0.019
0.6	0.107 ± 0.013	6.2 ± 0.2	0.008
0.8	0.089 ± 00018	6.2 ± 0.2	0.011
1.0	0.072 ± 0.015	5.8 ± 0.2	0.009

[a] Standard deviation of the fit.

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