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

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Apparent molar volumes, $V_{2,\phi}$, and viscosities, η, of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-leucine, and L-phenylalanine in water and in (0.5, 1.0, 2.0, 4.0, and 5.5) mol·kg^{-1} aqueous sodium acetate solutions have been determined at 298.15 K from densities and flow time measurements, respectively. The standard partial molar volumes, V^{∞}_2, obtained from $V_{2,\phi}$, have been used to calculate the corresponding volume of transfer at infinite dilution, $\Delta_t V^{\infty}$, from water to aqueous sodium acetate solutions. *B* coefficients have been calculated using the Jones−Dole equation. The side-chain contributions to V^{∞}_2 and *B* coefficients have been calculated. The comparison of $\Delta_t V^{\infty}$ values with the literature shows that the effect of the acetate ion follows the same order as in the Hofmeister series.

Introduction

Many cations and anions of neutral salts affect the properties of proteins such as their solubility, stability, and biological activity in widely different manners.[1−2] The effectiveness of various neutral salts toward the destabilizing tendency of proteins is known as the Hofmeister series.[3] In recent years, various experimental investigations on proteins have been reported; however, the mechanism of the folding/unfolding of proteins in solution remains unclear. Furthermore, for the interpretation of the thermodynamic and transport functions accompanying the folding/unfolding processes of proteins, it is also necessary to possess the individual contributions of all of the proteins constituents. Thus, the study of low-molecular-weight model compounds such as amino acids, peptides, and their derivatives, which represent the building blocks of proteins in a variety of media, is of immense importance.

Various reports on volumetric and thermochemical properties of amino acids in mixed aqueous solutions[4−10] are available, but very few are available for amino acids in organic salt solutions.[11−13] Sodium acetate causes the salting out of acetyltetraglycine ethyl ester[14] and tends to prevent denaturation. Therefore, in continuation of our work,[8−10] we have undertaken a systematic study on the volumes and viscosities of some amino acids in aqueous sodium acetate solutions. Both of these properties are sensitive to specific interactive changes in solutions. Consequently, in the present paper, the apparent molar volumes, $V_{2,\phi}$, and viscosities, η, of glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-leucine, and L-phenylalanine in water and in aqueous sodium acetate solutions (0.5, 1.0, 2.0, 4.0, 5.5) mol·kg^{-1} have been determined by measuring the densities using a vibrating-tube digital densimeter and an Ubbelohde-type viscometer, respectively, at 298.15 K. From these data, the partial molar volumes, V^{∞}_2, and viscosity *B* coefficients have been calculated. The hydration number, n_H, side-chain contributions of amino acids, and concentration effect of sodium acetate have also been discussed in terms of various interactions.

Experimental Section

The amino acids selected for the present study—glycine, DL-α-alanine, DL-α-amino-*n*-butyric acid, L-leucine, and L-phenylalanine—were obtained from Sigma Chemical Co. These, along with sodium acetate trihydrate (AR, Sisco Research Laboratories, India), were used without further purification and dried over anhydrous $CaCl_2$ in a vacuum desiccator before use. Deionized, doubly distilled degassed water with a specific conductance of less than 10^{-6} Ω cm^{-1} was used for all of the measurements. All solutions were prepared by mass using a Mettler balance with an accuracy of ±0.01 mg.

The solution densities were measured using a vibrating-tube digital densimeter (model DMA 60/602, Anton Paar, Austria) with a precision of 1×10^{-6} g·cm^{-3} and an accuracy of 3×10^{-6} g·cm^{-3}. The details of its operation have been described elsewhere.[10] Densimeter function was checked by measuring the densities of aqueous sodium chloride solutions, which agreed well with the literature values.[15] The temperature of water around the densimeter cell was controlled to within ±0.01 K.

Viscosities were measured using an Ubbelohde-type viscometer, which was calibrated using the flow time of water from 298.15 to 318.15 K. The flow time of a constant volume of water through the capillary was measured with an electronic stop watch with a resolution of ±0.01 s and was taken as an average of at least four readings of the flow time. The temperature of the thermostat was controlled to within ±0.01 K. The viscosity of a solution, η, is calculated by using following expression:

$$\frac{\eta}{\rho} = at - \frac{b}{t}$$

where ρ is the density of the solution, t is the flow time, and a and b are the viscometer constants. The measured viscosity values are accurate up to ±0.001 mPa s.

Results and Discussion

The densities, ρ, and apparent molar volumes, $V_{2,\phi}$ of amino acids in water and in aqueous sodium acetate solutions of various molalities (m_s, molality of sodium acetate solutions, mol·kg^{-1}) at 298.15 K are given in Table 1. Apparent molar volumes of amino acids have been

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Table 1. Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions as a Function of the Molalities of Amino Acids and Sodium Acetate at 298.15 K[a]

m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2,\phi}$ / cm^3·mol^{-1}	m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2,\phi}$ / cm^3·mol^{-1}	m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2,\phi}$ / cm^3·mol^{-1}	m / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{2,\phi}$ / cm^3·mol^{-1}
Glycine in Water											
0.09741	1.000138	43.24	0.30165	1.006458	43.50	0.48778	1.012066	43.67			
0.20110	1.003365	43.41	0.39361	1.009246	43.58	0.59157	1.015098	43.80			
m_s/mol·kg^{-1} = 0.5[a]											
0.00000	1.023282		0.10798	1.026486	44.88	0.39095	1.034685	45.00	0.59064	1.040299	45.10
0.04978	1.024765	44.85	0.29728	1.032002	44.96	0.47324	1.037009	45.06	0.71710	1.043773	45.17
m_s/mol·kg^{-1} = 1.0											
0.00000	1.047559		0.09398	1.050182	46.11	0.47080	1.060391	46.26	0.69588	1.066255	46.35
0.03822	1.048630	46.08	0.29179	1.055611	46.16	0.60627	1.063949	46.30			
m_s/mol·kg^{-1} = 2.0											
0.00000	1.086810		0.17688	1.091252	47.62	0.37594	1.096103	47.74			
0.04993	1.088073	47.60	0.29205	1.094073	47.70	0.64681	1.102436	47.93			
m_s/mol·kg^{-1} = 4.0											
0.00000	1.123245		0.10145	1.125532	48.87	0.38916	1.131765	49.11			
0.04558	1.124282	48.76	0.32819	1.130471	49.07	0.52600	1.134619	49.20			
m_s/mol·kg^{-1} = 5.5											
0.00000	1.139165		0.15800	1.142493	49.52	0.29373	1.145404	49.53	0.51623	1.149818	49.53
0.07215	1.140694	49.50	0.23689	1.144133	49.52	0.38792	1.147223	49.54			
DL-α-Alanine in Water											
0.04360	0.998297	60.44	0.14831	1.001262	60.51	0.32973	1.006262	60.68	0.44356	1.009334	60.74
0.08036	0.999343	60.47	0.20594	1.002862	60.59	0.38631	1.007795	60.71			
m_s/mol·kg^{-1} = 0.5											
0.00000	1.023282		0.09574	1.025819	61.60	0.28498	1.030694	61.78	0.50375	1.036131	61.93
0.05216	1.024672	61.52	0.20731	1.028721	61.68	0.38764	1.033270	61.85	0.58686	1.038115	62.02
m_s/mol·kg^{-1} = 1.0											
0.00000	1.047559		0.05391	1.048894	62.40	0.29131	1.054681	62.34	0.50079	1.059640	62.34
0.03492	1.048425	62.39	0.09813	1.049987	62.35	0.37013	1.056556	62.36			
m_s/mol·kg^{-1} = 2.0											
0.00000	1.086810		0.05581	1.088024	63.49	0.34579	1.094117	63.65			
0.02944	1.087452	63.47	0.24647	1.092073	63.59	0.44753	1.096175	63.71			
m_s/mol·kg^{-1} = 4.0											
0.00000	1.123245		0.17879	1.126482	64.78	0.32326	1.128985	64.91	0.46912	1.131434	65.00
0.09928	1.125057	64.74	0.24289	1.127600	64.85	0.39117	1.130136	64.95			
m_s/mol·kg^{-1} = 5.5											
0.00000	1.139165		0.17313	1.142007	65.39	0.31388	1.144278	65.36			
0.05043	1.139999	65.41	0.23311	1.142960	65.44	0.38164	1.145348	65.37			
DL-α-Amino-*n*-butyric acid in Water											
0.03934	0.998127	75.69	0.14447	1.000993	75.63	0.23741	1.003478	75.67	0.31790	1.005602	75.68
0.08124	0.999275	75.64	0.20216	1.002543	75.64	0.28641	1.004784	75.64			
m_s/mol·kg^{-1} = 0.5											
0.00000	1.023282		0.07622	1.025204	76.53	0.14065	1.026804	76.58	0.20658	1.028446	76.49
0.04219	1.024348	76.54	0.10289	1.025874	76.50	0.17051	1.027556	76.50	0.24029	1.029264	76.53
m_s/mol·kg^{-1} = 1.0											
0.00000	1.047559		0.08090	1.049427	77.24	0.14030	1.050789	77.20	0.21449	1.052463	77.22
0.04689	1.048645	77.23	0.10696	1.050020	77.27	0.16195	1.051271	77.26	0.23051	1.052820	77.23
m_s/mol·kg^{-1} = 2.0											
0.00000	1.086810		0.10859	1.088913	78.32	0.16731	1.090043	78.27	0.21353	1.090913	78.30
0.08161	1.088393	78.33	0.14129	1.089552	78.24	0.19535	1.090583	78.24	0.21558	1.090970	78.23
m_s/mol·kg^{-1} = 4.0											
0.00000	1.123245		0.07588	1.124407	79.57	0.20372	1.126308	79.65	0.21686	1.126495	79.67
0.04602	1.123953	79.54	0.10105	1.124786	79.59	0.21128	1.126417	79.66			
m_s/mol·kg^{-1} = 5.5											
0.00000	1.139165		0.12808	1.140881	80.06	0.16274	1.141327	80.11	0.18692	1.141660	80.04
0.05001	1.139840	80.06	0.15893	1.141281	80.10	0.18221	1.141588	80.09			
L-Leucine in Water											
0.01266	0.997346	107.74	0.02274	0.997582	107.85	0.03943	0.997975	107.80	0.05611	0.998370	107.70
0.01738	0.997458	107.73	0.03028	0.997762	107.73	0.04666	0.998149	107.69			
m_s/mol·kg^{-1} = 0.5											
0.00000	1.023282		0.02222	1.023748	108.12	0.03582	1.024029	108.20	0.06294	1.024589	108.22
0.01084	1.023509	108.17	0.03320	1.023975	108.19	0.05147	1.024356	108.15			

Table 1 (Continued)

m mol·kg^{-1}	ρ g·cm^{-3}	$V_{2,\phi}$ cm^3·mol^{-1}	m mol·kg^{-1}	ρ g·cm^{-3}	$V_{2,\phi}$ cm^3·mol^{-1}	m mol·kg^{-1}	ρ g·cm^{-3}	$V_{2,\phi}$ cm^3·mol^{-1}	m mol·kg^{-1}	ρ g·cm^{-3}	$V_{2,\phi}$ cm^3·mol^{-1}
m_s/mol·kg^{-1} = 1.0											
0.00000	1.047559		0.01610	1.047849	108.78	0.02925	1.048085	108.78	0.04603	1.048386	108.77
0.01080	1.047754	108.75	0.02138	1.047945	108.73	0.03644	1.048212	108.83	0.05212	1.048494	108.78
m_s/mol·kg^{-1} = 2.0											
0.00000	1.086810		0.01657	1.087023	109.79	0.02756	1.087165	109.76	0.04403	1.087373	109.82
0.00878	1.086923	109.79	0.01841	1.087048	109.73	0.03467	1.087258	109.72	0.05118	1.087469	109.73
m_s/mol·kg^{-1} = 4.0											
0.00000	1.123245		0.00856	1.123311	110.67	0.02158	1.123408	110.78	0.04273	1.123558	110.95
0.00681	1.123298	110.61	0.01248	1.123340	110.74	0.03237	1.123485	110.89	0.05326	1.123626	111.08
m_s/mol·kg^{-1} = 5.5											
0.00000	1.139165		0.02082	1.139262	111.55	0.03076	1.139311	111.48	0.05297	1.139419	111.43
0.01497	1.139236	111.49	0.02523	1.139286	111.45	0.03749	1.139342	111.50			
L-Phenylalanine in Water											
0.01545	0.997721	121.73	0.02977	0.998343	121.74	0.04624	0.999058	121.69	0.05832	0.999577	121.74
0.02099	0.997961	121.77	0.03372	0.998516	121.69	0.05305	0.999349	121.76			
m_s/mol·kg^{-1} = 0.5											
0.00000	1.023282		0.01990	1.024090	122.57	0.03047	1.024518	122.55	0.03805	1.024823	122.58
0.00907	1.023650	122.65	0.02433	1.024270	122.58	0.03677	1.024772	122.56			
m_s/mol·kg^{-1} = 1.0											
0.00000	1.047559		0.01911	1048.272	123.62	0.02623	1.048536	123.64			
0.01040	1.047948	123.57	0.02356	1.048437	123.64	0.03276	1.048780	123.59			
0.01546	1.048136	123.62									
m_s/mol·kg^{-1} = 2.0											
0.00000	1.086810		0.01367	1.087250	124.70	0.02267	1.087539	124.69	0.02974	1.087765	124.71
0.00994	1.087130	124.71	0.01852	1.087406	124.69	0.02949	1.087759	124.65			
m_s/mol·kg^{-1} = 4.0											
0.00000	1.123245		0.01673	1.123691	125.89	0.02275	1.123851	125.89	0.02828	1.123999	125.83
0.01438	1.123620	125.88	0.01951	1.123766	125.83	0.02394	1.123882	125.90			

[a] m_s = molality of sodium acetate in water.

calculated as follows:

$$V_{2,\phi} = \frac{M}{\rho} - \left[\frac{(\rho - \rho_0)1000}{m\rho\rho_0}\right] \qquad (1)$$

where M is the molar mass of amino acid, m (mol·kg^{-1}) is the molality of amino acid, and ρ and ρ_0 are the densities of solution and solvent, respectively. The uncertainty in the determination of $V_{2,\phi}$ occurring because of the measurement of various quantities has been calculated. The uncertainty values for $V_{2,\phi}$ range from 0.053 to 0.009 cm^3·mol^{-1} for the lower (≤ 0.05 m) and higher concentration ranges for the amino acids, respectively. However, in the case of L-leucine and L-phenylalanine where the studied concentrations are small, the uncertainty values are higher. The uncertainty values in these cases range from 0.241 to 0.076 cm^3·mol^{-1} for the lower (≤ 0.01 m) and higher concentration ranges. At infinite dilution, the apparent molar volumes, $V^{\infty}{}_{2,\phi}$, and partial molar volumes, $V^{\infty}{}_2$, are identical ($V^{\infty}{}_{2,\phi} = V^{\infty}{}_2$). In the case of negligible concentration dependence of $V_{2,\phi}$ (i.e., within the uncertainty limits of the measurements), $V^{\infty}{}_2$ was determined by taking the average of all of the data points. However, where a finite concentration dependence was observed, $V^{\infty}{}_2$ was determined by least-squares fitting of the data using the following equation

$$V_{2,\phi} = V^{\infty}{}_2 + S_v m \qquad (2)$$

where S_v is the experimental slope. The $V^{\infty}{}_2$ values along with their standard deviations are summarized in Table 2. The experimental values of $V^{\infty}{}_2$ for the amino acids in water agreed well with those reported in the literature.[4,16–18] The $V^{\infty}{}_2$ values for the amino acids increase with the increase in the concentration of sodium acetate. The only other report on $V^{\infty}{}_2$ values of some amino acids in aqueous sodium acetate solutions is by Wang et al.,[12] and the values have been included in Table 2 for comparison. They have studied only up to 2.0 mol·kg^{-1} of sodium acetate, whereas the present studies have been extended up to 5.5 mol·kg^{-1} of sodium acetate near the solubility of sodium acetate at 298.15 K to study the effect at higher concentrations. Their $V^{\infty}{}_2$ values in most cases are lower, except in the case of DL-α-alanine, where the values are slightly higher at some concentrations of sodium acetate. However, in case of L-leucine the present values are higher. This may be due to the different forms of leucine used presently (L-leucine) and in the literature (DL-leucine).

It is important to mention here that sodium acetate, being a salt of a weak acid and a strong base, undergoes hydrolysis and gives a basic solution. The pH of an aqueous solution of sodium acetate can be calculated by the following equation:

$$\mathrm{pH} = 14 - \frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\log c + \frac{1}{2}\mathrm{p}K_a \qquad (3)$$

where K_w is the ionic product of water, K_a is the dissociation constant of acetic acid, and c (mol·dm^{-3}) is the molarity of the sodium acetate solution. The pH values for the aqueous solutions of sodium acetate at (0.5, 1.0, 2.0, 4.0, and 5.5) mol·kg^{-1} are 9.21, 9.35, 9.49. 9.60, and 9.65, respectively at 298.15 K (molality was converted to molarity). However, a decrease in pH values has been observed upon the addition of amino acids. Although the pH values are less than the pK_a values for the amino acids studied (pK_a = glycine 9.78, DL-α-alanine 9.87, L-leucine 9.74) except for L-phenylalanine (9.31), they are very close to the range in which the second stepwise protonation takes place. Thus,

Table 2. Standard Partial Molar Volumes, V^{∞}_2, at Infinite Dilution for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

	V^{∞}_2/cm^3·mol^{-1} at various m_s/mol·kg^{-1a}					
amino acids	water	0.5	1.0	2.0	4.0	5.5
glycine	43.16 ± 0.02^b (1.07) 43.19^{c,d}	44.82 ± 0.01 (0.47) 44.60^g	46.06 ± 0.01 (0.40) 45.54^g	47.54 ± 0.03 (0.57) 47.01^g	48.75 ± 0.03 (0.89)	49.52 ± 0.01
DL-α-alanine	60.41 ± 0.01 (0.78) 60.47^c 60.52^d	61.50 ± 0.02 (0.89) 61.57^g	62.36 ± 0.03 62.01^g	63.45 ± 0.01 (0.56) 63.55^g	64.66 ± 0.01 (0.73)	65.39 ± 0.03
DL-α-amino-*n*-butyric acid	75.66 ± 0.02 75.92^f	76.52 ± 0.03 76.39^g	77.23 ± 0.02 76.79^g	78.27 ± 0.04 77.95^g	79.51 ± 0.01 (0.70)	80.08 ± 0.03
L-leucine	107.75 ± 0.06	108.17 ± 0.04	108.77 ± 0.03	109.76 ± 0.04	110.57 ± 0.02	111.48 ± 0.04
DL-leucine	107.74^c 107.76^d	107.52^g	107.63^g	108.34^g	(9.32)	
L-phenylalanine	121.73 ± 0.03 121.48^c 121.50^d 121.70^e	122.58 ± 0.03	123.61 ± 0.03	124.69 ± 0.02	125.87 ± 0.03	

[a] m_s = molality of sodium acetate in water. [b] Standard deviation; brackets contain S_v/cm^3·kg·mol^{-2}. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 4. [g] Reference 12.

Table 3. Standard Partial Molar Volumes of Transfer, $\Delta_t V^{\infty}$, at Infinite Dilution for Some Amino Acids from Water to Aqueous Sodium Acetate Solutions at 298.15 K

	$\Delta_t V^{\infty}$/cm^3·mol^{-1} at various m_s/mol·kg^{-1}a				
amino acids	0.5	1.0	2.0	4.0	5.5
glycine	1.66 ± 0.02	2.90 ± 0.02	4.38 ± 0.04	5.59 ± 0.04	6.36 ± 0.02
DL-α-alanine	1.09 ± 0.02	1.95 ± 0.03	3.04 ± 0.01	4.25 ± 0.01	4.98 ± 0.03
DL-α-amino-*n*-butyric acid	0.86 ± 0.04	1.57 ± 0.03	2.61± 0.04	3.85 ± 0.02	4.42 ± 0.03
L-leucine	0.42 ± 0.07	1.02 ± 0.07	2.01± 0.07	2.82 ± 0.06	3.73 ± 0.07
L-phenylalanine	0.85 ± 0.04	1.88 ± 0.04	2.96 ± 0.04	4.14 ± 0.04	

[a] m_s = molality of sodium acetate in water.

solutions may be equilibrium mixtures of monoprotonated and fully protonated forms; however, the population of these variously protonated forms changes within one concentration series. For a particular pH, the hydroxyl ion concentration [OH$^-$] can be obtained. In the extreme case if all of the hydroxyl ions are neutralized by the zwitterions to give fully deprotonated amino acids, then the concentration of zwitterionic forms of amino acids may be obtained by subtracting the [OH$^-$] from the actual molality of the amino acid. By considering this, the molality of the amino acid in solution changes by 2 units at the fifth place, which results in the change of $V^{\infty}_{2,\phi}$ by only 0.02 cm^3·mol^{-1}, which is within the uncertainty limits in the measurements. The change is still smaller at higher concentration. Thus, there is a fraction of fully deprotonated amino acid, but it is very small and its effect can be neglected.

From the V^{∞}_2 data, the standard partial molar volumes of transfer, $\Delta_t V^{\infty}$, at infinite dilution from water to aqueous sodium acetate solutions have been evaluated as follows:

$$\Delta_t V^{\infty} = V^{\infty}_2(\text{in aqueous sodium acetate}) - V^{\infty}_2(\text{in water}) \quad (4)$$

The $\Delta_t V^{\infty}$ values for the amino acids are summarized in Table 3 and illustrated in Figure 1.The $\Delta_t V^{\infty}$ values for the studied amino acids are positive and increase almost linearly in the lower-concentration range up to ~1.0 m_s; then the slope starts decreasing. The behavior of $\Delta_t V^{\infty}$ again becomes almost linear when the concentration of sodium acetate crosses ~2.0 m_s, although with a smaller slope. The reported[12] $\Delta_t V^{\infty}$ values for some amino acids (up to 2.0 m_s only) are also positive but consistently smaller than the present one. The comparison of the results shows that the order of transfer volumes for similar amino acids is the same as that observed presently; however, the dependence of $\Delta_t V^{\infty}$ upon the concentration of sodium acetate is different (Figure 2) from that observed presently (Figure 1). It may be noted that Wang et al.[12] have used anhydrous sodium acetate but we have used sodium acetate trihydrate. However, we are unable to provide a satisfactory explanation for this discrepancy. The more positive $\Delta_t V^{\infty}$ values in the case of glycine indicate the dominance of the effect of charged end groups, (NH_3^+ and COO^-), whereas less-positive $\Delta_t V^{\infty}$ values in the case of L-leucine indicate the effect of the hydrophobic parts. In the case of L-phenylalanine, the $\Delta_t V^{\infty}$ value is greater than that for DL-α-amino-*n*-butyric acid and L-leucine, which may be due to the difference in the hydration behavior of the aliphatic

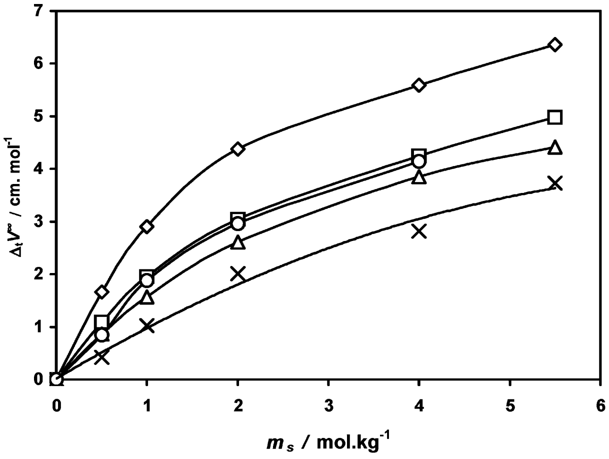

Figure 1. Standard partial molar volumes of transfer, $\Delta_t V^{\infty}$, of some amino acids vs different molalities, m_s, of sodium acetate solutions at 298.15 K: ◇, glycine; □, alanine; ○, phenylalanine; △, aminobutyric acid; ×, leucine.

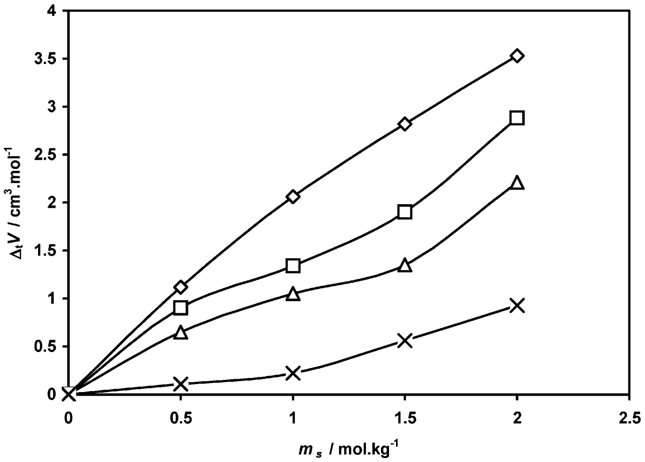

Figure 2. Standard partial molar volumes of transfer, $\Delta_t V^{\infty}$, of some amino acids vs different molalities, m_s, of sodium acetate solutions at 298.15 K: ◇, glycine; □, alanine; △, aminobutyric acid; ×, leucine.

and aromatic side chains. This is because the aromatic ring has very little influence on the structure of water because of the counterbalancing effects arising from its hydrophobic and structure-breaking character.[19−20]

The cosphere overlap model[21] can be utilized to rationalize the $\Delta_t V^{\infty}$ values in terms of solute−cosolute interactions. According to this model, when two solute particles come close enough together so that their cospheres overlap some cosphere material is displaced, and this is accompanied by the change in thermodynamic parameters. The following types of interactions can occur between amino acids and sodium acetate in solution: (1) ion−ion interactions occurring between Na^+ ions and $-COO^-$ groups of amino acids and between CH_3COO^- ions of sodium acetate and $-NH_3^+$ groups of amino acids; (2) interactions between ions (Na^+, CH_3COO^-) of sodium acetate and nonpolar (hydrophobic) groups of amino acids. The ion−ion interactions result in positive $\Delta_t V^{\infty}$ values, whereas ion−hydrophobic group interactions result in negative $\Delta_t V^{\infty}$ values. Presently observed positive $\Delta_t V^{\infty}$ values for the studied amino acids suggest that ion−ion interactions dominate the ion−hydrophobic group interactions. Because of the first type of interaction, the electrostriction of water in the neighborhood of charged end groups (NH_3^+, COO^-) of amino acids gets reduced, and this will contribute positively to the volumes of transfer. Furthermore, the increase in $\Delta_t V^{\infty}$ values with increasing sodium acetate concentration strengthens this view. The decreasing magnitude of transfer volumes from glycine to L-leucine indicates the building up of the ion−hydrophobic interactions that contribute negatively to the $\Delta_t V^{\infty}$ values. Similar observations have also been reported[12] in the literature.

Bhat and Ahluwalia[4] have reported positive partial molar heat capacities, $\Delta_t C^{\infty}_{2,p}$ and volumes of transfer, $\Delta_t V^{\infty}$ for some amino acids and peptides from water to aqueous sodium chloride solutions at 298.15 K. The positive $\Delta_t V^{\infty}$ values for amino acids increase with the concentration of sodium chloride but decrease with the increase in the size of the nonpolar side chains of amino acids in all cases, which is similar to the behavior observed presently. Wadi and Ramasami,[22] from the positive partial molal volumes and adiabatic compressibilities of transfer for glycine and DL-α-alanine from water to aqueous sodium sulfate solutions at 288.15, 298.15, and 308.15 K, have concluded that the interactions between sodium sulfate and charged centers of amino acids become stronger with increasing concentration of sodium sulfate. These results again strengthen the view that ion−ion interactions dominate the ion−hydrophobic interactions observed presently. A comparison of $\Delta_t V^{\infty}$ values for the amino acids in the presence of sodium chloride,[4] sodium sulfate[22] (only glycine and DL-alanine) (Table 4), and sodium acetate shows that the values decrease in the order $Na_2SO_4 > NaCOOCH_3 > NaCl$, which suggests that interactions are stronger between amino acids and sodium sulfate than in the case of sodium acetate and sodium chloride. The stabilizing effect on the proteins of these anions (i.e., SO_4^{2-}, CH_3COO^-, and Cl^-) also appear in the same order in the Hofmeister series[3].

The V^{∞}_2 values of the studied amino acids (except for L-phenylalanine) in water and in aqueous sodium acetate solutions vary linearly with the number of carbon atoms, n_c, in their alkyl side chains (average correlation coefficient ≥ 0.999). Similar linear correlations for the homologous series of some α-amino acids have been reported in aqueous solutions.[5,10,12] A linear regression analysis of V^{∞}_2 values versus n_c in water and in aqueous sodium acetate solutions was carried out using the following equation:

$$V^{\infty}_2 = V^{\infty}_2(NH_3^+, COO^-) + n_c V^{\infty}_2(CH_2) \qquad (5)$$

where $V^{\infty}_2(NH_3^+, COO^-)$ and $V^{\infty}_2(CH_2)$ represent the zwitterionic end groups and the methylene group contributions, respectively. The results are given in Table 5. It may be noted that the values of $V^{\infty}_2(CH_2)$ evaluated here represent the main contributions of CH and CH_3 groups to V^{∞}_2 values of amino acids. The contributions of $V^{\infty}_2(CH_2)$ and $V^{\infty}_2(NH_3^+, COO^-)$ groups to V^{∞}_2 in water agree well with the literature values.[5,10,23] The contribution of (NH_3^+, COO^-) groups to V^{∞}_2 is larger than that of the CH_2 group and increases with increasing concentration of sodium acetate, which indicates that the interactions between sodium acetate and charged end groups (NH_3^+, COO^-) of amino acids are stronger than those between sodium acetate and

Table 4. Standard Partial Molar Volumes of Transfer, $\Delta_t V^{\infty}$, at Infinite Dilution for Some Amino Acids from Water to Aqueous Sodium Chloride and to Sodium Sulfate Solutions at 298.15 K

	$\Delta_t V^{\infty}$/ cm^3·mol^{-1} at various m_s/mol·kg^{-1} [a]					
	in sodium chloride[b]				in sodium sulfate[c]	
amino acids	1.0	2.0	3.0	4.0	0.5	1.0
glycine	1.35 ±0.09	1.60 ±0.26	2.20 ±0.23	2.16 ±0.47	2.95	4.50
DL-α-alanine	0.78 ±0.22		1.06 ±0.77		2.60	4.06
DL-α-amino-*n*-butyric acid	0.38 ±0.58		0.83 ±0.51			
L-leucine	0.44 ±0.39		0.54 ±0.55			

[a] m_s = molality of sodium chloride and sodium sulfate in water. [b] Reerence 4. [c] Reference 22.

Table 5. Contribution of (NH_3^+, COO^-) and (R) Groups to the Standard Partial Molar Volumes, V^{∞}_2, for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

	V^{∞}_2/cm^3·mol^{-1} at various m_s/mol·kg^{-1}[a]					
groups	water	0.5	1.0	2.0	4.0	5.5
(NH_3^+, COO^-)	27.59 ± 0.65 27.80[b] 27.72[c] 28.30[d]	29.40 ± 0.51 [29.60][e]	30.65 ± 0.44 [30.60]	32.09 ± 0.38 [32.40]	33.49 ± 0.35	34.14 ± 0.41
$-CH_2$	16.06 ± 0.21 15.30[b] 15.99[c] 15.80[d]	15.77 ± 0.16 [15.60]	15.62 ± 0.14 [15.40]	15.51 ± 0.12 [15.10]	15.41 ± 0.10	15.44 ± 0.13
$-CHCH_3$	32.12 ± 0.30 31.98[c]	31.54 ± 0.23	31.24 ± 0.20	31.02 ± 0.17	30.82 ± 0.14	30.88 ± 0.18
$-CHCH_2CH_3$	48.18 ± 0.36 47.97[c]	47.31 ± 0.28	46.86 ± 0.24	46.53 ± 0.21	46.23 ± 0.17	46.32 ± 0.22
$-CHCH_2CH(CH_3)_2$	80.30 ± 0.47 79.95[c]	78.85 ± 0.36	78.10 ± 0.31	77.55 ± 0.27	77.05 ± 0.22	77.20 ± 0.29

[a] m_s = molality of sodium acetate in water. [b] Reference 5. [c] Reference 10. [d] Reference 23. [e] Reference 12.

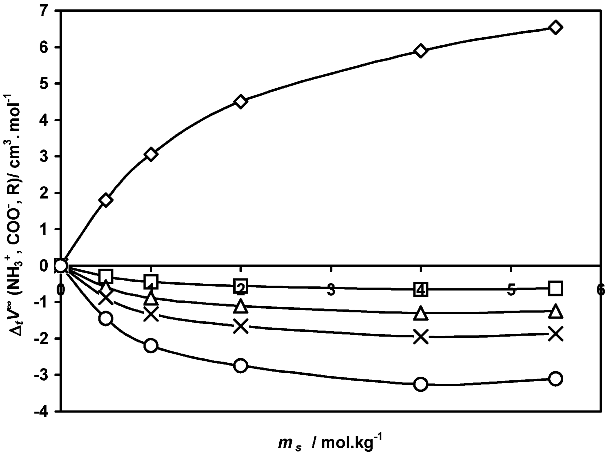

Figure 3. Contributions of (◇) NH_3^+, COO^-; (□) $-CH_2$; (△) $-CHCH_3$; (×) $-CHCH_2CH_3$; and (○) $CHCH_2CH(CH_3)_2$ groups to standard partial molar volumes of transfer, $\Delta_t V^{\infty}$, vs different molalities, m_s of sodium acetate solutions at 298.15 K.

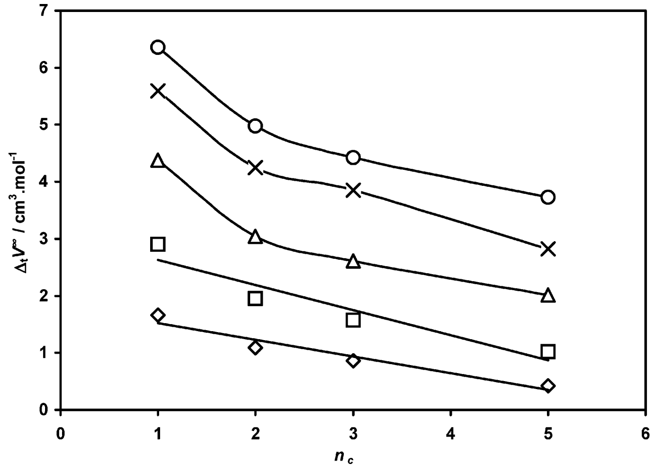

Figure 4. Standard partial molar volumes of transfer, $\Delta_t V^{\infty}$, of some amino acids vs number of carbon atoms, n_c, in the alkyl chain of amino acids at 298.15 K: ◇, 0.5 m_s; □, 1.0 m_s; △, 2.0 m_s; ×, 4.0 m_s; ○, 5.5 m_s.

CH_2 groups. The $V^{\infty}_2(CH_2)$ values are almost insensitive to the concentration of sodium acetate, and similar observations have been reported by other workers in different cosolutes.[5,12] However, the contribution from side chains increases with the increasing size of side chains of amino acids.

The standard partial molar volumes of transfer of zwitterionic end groups [$\Delta_t V^{\infty}(NH_3^+, COO^-)$] and alkyl side-chain groups [$\Delta_t V^{\infty}(R)$] of amino acids from water to aqueous sodium acetate solutions have been calculated as follows:

$$\Delta_t V^{\infty}(NH_3^+, COO^-) \text{ or } \Delta_t V^{\infty}(R) = V^{\infty}_2(NH_3^+, COO^-) \text{ or } V^{\infty}_2(R) \text{ (in aqueous sodium acetate)} - V^{\infty}_2(NH_3^+, COO^-) \text{ or } V^{\infty}_2(R) \text{ (in water)} \quad (6)$$

where R = $-CH_2$, $-CHCH_3$, $-CHCH_2CH_3$, and $-CHCH_2CH(CH_3)_2$. The results are illustrated in Figure 3. The contribution of (NH_3^+, COO^-) to $\Delta_t V^{\infty}$ is positive, and its magnitude increases with increasing concentration of sodium acetate. The contributions of R to $\Delta_t V^{\infty}$ values are negative for the amino acids, and their magnitude increases with the increasing size of alkyl side chains of amino acids. Figure 4 shows the dependence of $\Delta_t V^{\infty}$ values upon n_c, and this behavior may be considered to be linear at 0.5 and 1.0 m_s of sodium acetate, where as at higher concentrations of sodium acetate the dependence of $\Delta_t V^{\infty}$ is nonlinear. Wang et al.[12] have treated the dependence of $\Delta_t V^{\infty}$ upon n_c for similar amino acids as linear up to 2.0 m_s. In light of eq 5, the slopes and intercepts corresponding to the above behavior will represent the contribution of CH_2 groups and charged end groups to $\Delta_t V^{\infty}$. Therefore, the contributions of charged end groups (NH_3^+, COO^-) are positive, and those of CH_2 groups are negative. From these observations, the overall positive $\Delta_t V^{\infty}$ values suggest that the effect of charged end groups dominates that of the alkyl side chains.

The partial specific quantities are primarily independent of the size of the solute and reflect the ratio of the effect of the hydrophilic hydration on the hydrophobic hydration, whereas the partial molar quantities are the reflection of the net changes in both hydrations.[24] The standard partial specific volumes, ν^{∞}_2 ($\nu^{\infty}_2 = V^{\infty}_2/M$, where M is the molar mass of the amino acid) for studied amino acids in aqueous sodium acetate solutions are illustrated in Figure 5. The increase in ν^{∞}_2 values from glycine to L-leucine both in water and in aqueous sodium acetate solutions is due to the effect of the size of the side chains of the amino acids. Furthermore, the values of ν^{∞}_2 also increase with the concentration of sodium acetate, again suggesting the dominance of the interactions between ions of sodium acetate and charged centers of amino acids. The variation

Table 6. Pair and Triplet Interaction Coefficients for Some Amino Acids in Aqueous Sodium Acetate Solutions at 298.15 K

amino acids	$V_{XY}{}^{a}$/cm^3·mol^{-2}·kg	$V_{XYY}{}^{a}$/cm^3·mol^{-3}·kg^2	R
glycine	1.3686	−0.0990	0.972
DL-α-alanine	0.9298	−0.0596	0.986
DL-α-amino-*n*-butyric acid	0.7909	−0.0480	0.996
L-leucine	0.5210	−0.0231	0.989
L-phenylalanine	0.9941	−0.0796	0.997

[a] V_{XY} and V_{XYY} are the pair and triplet interaction coefficients.

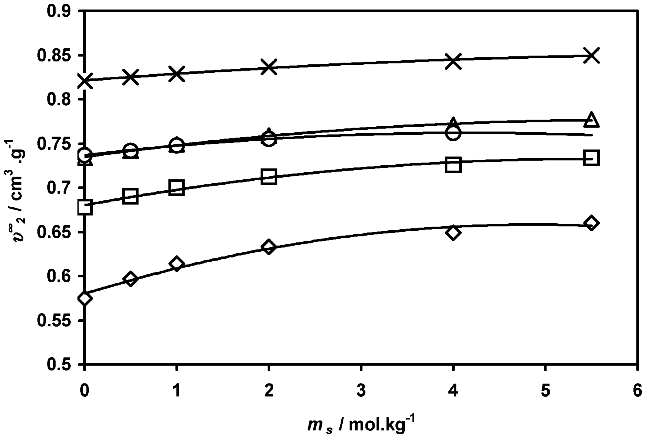

Figure 5. Partial specific volumes, $\nu^{\infty}{}_2$, of some amino acids vs different molalities, m_s, of sodium acetate solutions at 298.15 K: ◇, glycine; □, alanine; ○, phenylalanine; △, aminobutyric acid; ×, leucine.

of $\nu^{\infty}{}_2$ with the concentration of sodium acetate for the studied amino acids tends to be linear as the size of side chains increases, which is evident from the almost complete linear behavior of L-leucine. This may be attributed to the negative contribution from the alkyl side chains of amino acids whose magnitude increases with the size of the side chain. The $\nu^{\infty}{}_2$ values for L-phenylalanine in water and aqueous sodium acetate solutions lie those for between DL-α-alanine and DL-α-amino-*n*-butyric acid, which is again indicative of the distinct hydration behavior of aromatic side chains in comparison to that of aliphatic side chains.

McMillan and Mayer proposed a theory[25] of solutions that permits the formal separation of the effects due to interactions between the pair of solute molecules and those due to interactions between two or more solute molecules. According to this treatment, at infinite dilution $\Delta_t V^{\infty}$ can be expressed as

$$\Delta_t V^{\infty} = 2V_{XY}m_s + 3V_{XYY}m_s{}^2 + ... \qquad (7)$$

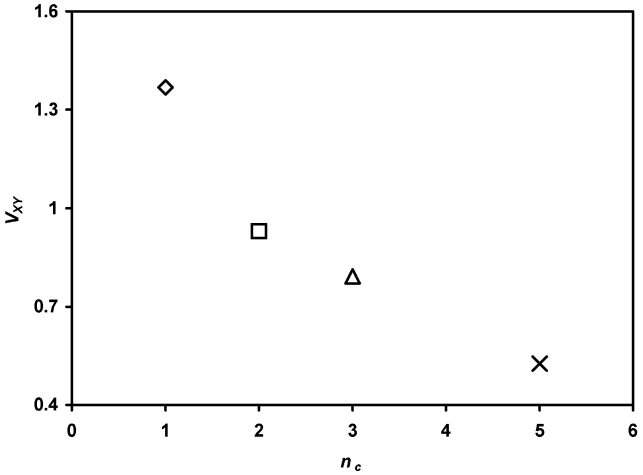

Figure 6. Pair interaction coefficient, V_{XY}, of some amino acids vs number of carbon atoms, n_c, in the alkyl side chain of amino acids at 298.15 K: ◇, glycine; □, alanine; △, aminobutyric acid; ×, leucine.

Table 7. Hydration Number, n_H, for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

	n_H at various m_s/mol·kg^{-1a}					
amino acids	water	0.5	1.0	2.0	4.0	5.5
glycine	2.64	2.14	1.76	1.31	0.94	0.71
	2.63^b	[2.20]^c	[1.90]	[1.50]		
DL-α-alanine	3.43	3.10	2.84	2.51	2.14	1.92
	3.41^b	[3.10]	[3.0]	[2.50]		
L-lecuine	4.95	4.83	4.64	4.34	4.10	3.82
DL-leucine	4.96^b	[5.0]	[5.0]	[4.8]		
L-phenylalanine	5.14	4.89	4.57	4.25	3.89	
	5.22^b					

[a] m_s = molality of sodium acetate in water. [b] Reference 16. [c] Reference 12.

where X stands for amino acids and Y stands for sodium acetate. V_{XY} and V_{XYY} are pair and triplet interaction coefficients, respectively (Table 6). V_{XY} and V_{XYY} are positive and negative, respectively, for the studied amino acids; however, the magnitude of both decreases with the size of the alkyl chain of amino acids (except for L-phenylalanine). The large positive magnitude of V_{XY} in comparison to that of V_{XYY} shows that interactions between sodium acetate and amino acids are mainly pairwise. The decrease in V_{XY} values from glycine to L-leucine may be due to the difference in the interactions of sodium acetate with the alkyl side chains of amino acids because the interactions between charged centers of different amino acids and sodium acetate remain almost the same. Thus, the destruction of hydration spheres of alkyl side chains (hydrophobic groups) of amino acids in aqueous sodium acetate solutions plays an important role in affecting the transfer volumes. From these observations, it may be said that the amino acids with the longer hydrophobic alkyl side chains undergo a stronger dehydration effect in the presence of sodium acetate. Thus, in case of L-leucine the loss of hydrophobically hydrated water molecules will be more than in the case of glycine, and these observations are in line with reported values.[12]

The dependence of pair interaction coefficients, V_{XY} (Figure 6), on the alkyl side-chain length is not linear, and the decrease is sharp initially (glycine to DL-α-alanine) and then becomes flat. This indicates that the influence of the additional CH$_2$ group decreases at increasing side-chain length, an effect similar to that observed by Palecz[7] from enthalpic pair interaction coefficients.

The number of water molecules, n_H, bound to the amino acids was calculated using the method reported by Millero et al.[16]

$$n_H = \frac{V^{\infty}{}_2(\text{elect})}{V^{\infty}{}_e - V^{\infty}{}_b} \qquad (8)$$

Table 8. Relative Viscosities, η_r, for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions as a Function of Concentrations of Amino Acids and Sodium Acetate at 298.15 K

$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r	$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r	$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r
Glycine in Water					
0.06012	1.0087	0.15802	1.0232	0.25780	1.0364
0.10856	1.0148	0.21529	1.0290	0.34331	1.0506
m_s/mol·kg^{-1} = 0.5[a]					
0.19800	1.0285	0.39298	1.0573	0.58836	1.0874
0.30010	1.0440	0.47391	1.0682	0.71026	1.1113
m_s/mol·kg^{-1} = 1.0					
0.19928	1.0285	0.39767	1.0584	0.61696	1.0957
0.30141	1.0452	0.48219	1.0764	0.70514	1.1101
m_s/mol·kg^{-1} = 2.0					
0.11540	1.0123	0.31267	1.0461	0.50862	1.0797
0.19049	1.0263	0.40076	1.0586	0.68005	1.1130
m_s/mol·kg^{-1} = 4.0					
0.19882	1.0264	0.36295	1.0597	0.57413	1.0872
0.28486	1.0414	0.42794	1.0687		
m_s/mol·kg^{-1} = 5.5					
0.17840	1.0273	0.32915	1.0481	0.43243	1.0823
0.26630	1.0379	0.43243	1.0662		
DL-α-Alanine In Water					
0.06650	1.0156	0.34544	1.0737	0.49658	1.1214
0.12286	1.0311	0.39707	1.1041	0.55811	1.1473
m_s/mol·kg^{-1} = 0.5					
0.09738	1.0268	0.28646	1.0795	0.49953	1.1267
0.20939	1.0516	0.38716	1.1059	0.57896	1.1561
m_s/mol·kg^{-1} = 1.0					
0.03649	1.0103	0.20700	1.0507	0.37857	1.1020
0.10214	1.0279	0.29946	1.0810	0.50800	1.1374
m_s/mol·kg^{-1} = 2.0					
0.11469	1.0316	0.26338	1.0702	0.47176	1.1247
0.18726	1.0523	0.36704	1.1042		
m_s/mol·kg^{-1} = 4.0					
0.11071	1.0255	0.26808	1.0683	0.42719	1.1201
0.19825	1.0497	0.35474	1.0961		
m_s/mol·kg^{-1} = 5.5					
0.05723	1.0144	0.26102	1.0696	0.42274	1.1134
0.19471	1.0484	0.34940	1.0899		
DL-α-Amino-*n*-butyric acid in Water					
0.03911	1.0097	0.14249	1.0490	0.23254	1.0795
0.08051	1.0265	0.19854	1.0648	0.27953	1.0960
m_s/mol·kg^{-1} = 0.5					
0.07753	1.0260	0.14235	1.0496	0.20802	1.0776
0.10445	1.0366	0.17218	1.0623	0.24135	1.0886
m_s/mol·kg^{-1} = 1.0					
0.04893	1.0183	0.14533	1.0543	0.22086	1.0792
0.08420	1.0313	0.16746	1.0602	0.23705	1.0885
0.11108	1.0403				
m_s/mol·kg^{-1} = 2.0					
0.08808	1.0325	0.15173	1.0545	0.20883	1.0795
0.11694	1.0429	0.17928	1.0660	0.22792	1.0850
m_s/mol·kg^{-1} = 4.0					
0.05148	1.0174	0.13864	1.0513	0.23292	1.0867
0.11248	1.0420	0.18798	1.0685	0.23895	1.0878
m_s/mol·kg^{-1} = 5.5					
0.08951	1.0278	0.14421	1.0519	0.20417	1.0748
0.11858	1.0420	0.17846	1.0686		
L-Leucine in Water					
0.01260	1.0068	0.03009	1.0164	0.04629	1.0249
0.01730	1.0095	0.03915	1.0209	0.05561	1.0296
0.02262	1.0126				
m_s/mol·kg^{-1} = 0.5					
0.00841	1.0043	0.02149	1.0118	0.03237	1.0178
0.01434	1.0078	0.02623	1.0136	0.03629	1.0200

Table 8. (Continued)

$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r	$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r	$\frac{c}{\mathrm{mol{\cdot}dm^{-3}}}$	η_r
		m_s/mol·kg^{-1} = 1.0			
0.00978	1.0053	0.02032	1.0118	0.03330	1.0183
0.01498	1.0082	0.02712	1.0146	0.03934	1.0211
		m_s/mol·kg^{-1} = 2.0			
0.00953	1.0052	0.01996	1.0116	0.05528	1.0301
0.01797	1.0098	0.02985	1.0168		
		m_s/mol·kg^{-1} = 4.0			
0.00960	1.0053	0.02418	1.0136	0.05942	1.0330
0.01400	1.0077	0.04774	1.0260		
		m_s/mol·kg^{-1} = 5.5			
0.02365	1.0133	0.03490	1.0191	0.04250	1.0239
0.02865	1.0158				
		L-Phenylalanine in Water			
0.01076	1.0063	0.01953	1.0115	0.02932	1.0170
0.01392	1.0093	0.02399	1.0138	0.03523	1.0203
		m_s/mol·kg^{-1} = 0.5			
0.00927	1.0047	0.02483	1.0149	0.03746	1.0224
0.02032	1.0119	0.03107	1.0186	0.03875	1.0234
		m_s/mol·kg^{-1} = 1.0			
0.01088	1.0064	0.01997	1.0119	0.02738	1.0170
0.01616	1.0095	0.02460	1.0148	0.03417	1.0202
		m_s/mol·kg^{-1} = 2.0			
0.01079	1.0065	0.02008	1.0127	0.03192	1.0189
0.01483	1.0090	0.02457	1.0150	0.03219	1.0192
		m_s/mol·kg^{-1} = 4.0			
0.01612	1.0096	0.02185	1.0132	0.02680	1.0159
0.01875	1.0118	0.02547	1.0151		

[a] m_s = molality of sodium acetate in water.

Table 9. Viscosity *B*-Coefficients for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

amino acids	B/dm^3·mol^{-1} at various m_s/mol·kg^{-1a}					
	water	0.5	1.0	2.0	4.0	5.5
glycine	0.143 ± 0.005 0.143^{b,c} 0.146^d	0.150 ± 0.005 [0.144]^e	0.154 ± 0.006 [0.147]	0.157 ± 0.011 [0.151]	0.154 ± 0.008	0.147 ± 0.005
DL-α-alanine	0.251 ± 0.01 0.253^{b,c} 0.258^d	0.265 ± 0.009 [0.268]	0.268 ± 0.007 [0.269]	0.272 ± 0.007 [0.275]	0.269 ± 0.011	0.263 ± 0.009
DL-α-amino-*n*-butyric acid	0.338 ± 0.008 0.352^d	0.363 ± 0.01 [0.372]	0.366 ± 0.006 [0.375]	0.371 ± 0.007 [0.381]	0.368 ± 0.003	0.365 ± 0.01
L-leucine	0.537 ± 0.006	0.543 ± 0.012	0.545 ± 0.006	0.551 ± 0.008	0.552 ± 0.006	0.556 ± 0.007
DL-leucine	0.487^d	[0.506]	[0.518]	[0.551]		
L-phenylalanine	0.585 ± 0.007	0.598 ± 0.007	0.600 ± 0.008	0.603 ± 0.007	0.601 ± 0.007	

[a] m_s = molality of sodium acetate in water. [b] Reference 5. [c] Reference 6. [d] Reference 23. [e] Reference 13.

where V^∞_e is the molar volume of electrostricted water and V^∞_b is the molar volume of bulk water. The value[16] of ($V^\infty_e - V^\infty_b$) is ~ −3.3 cm^3·mol^{-1} at 298.15 K. The electrostriction partial molar volume, V^∞_2(elect) can be estimated from experimentally measured V^∞_2 values by the following equation:

$$V^\infty_2(\text{elect}) = V^\infty_2(\text{amino acid}) - V^\infty_2(\text{int}) \qquad (9)$$

The intrinsic volume, V^∞_2(int), consists of two terms: the van der Waals volume and the void volume. V^∞_2(int) can be obtained from crystal volume data.[16] The n_H values are given in Table 7 (except for DL-α-amino-*n*-butyric acid, whose crystal molar volume datum is not available). The literature values[16] for the studied amino acids in water have been included in Table 7, and good agreement is found. The n_H values for the amino acids in the presence of sodium acetate are less than in water and decrease with increasing concentration of sodium acetate, which suggests that sodium acetate has a dehydration effect on the amino acids. Other workers have reported[11,12] similar observations that electrolytes have a dehydration effect on amino acids.

The viscosity data for amino acids studied in water and in aqueous sodium acetate solutions at 298.15 K are given in Table 8. The relative viscosities, η_r ($\eta_r = \eta/\eta_0$, where η and η_0 are the viscosities of solution and solvent, respectively), have been used to calculate the viscosity B coefficients using the Jones−Dole equation

$$\eta_r = 1 + Bc \qquad (10)$$

where c is molarity (calculated from molality data). The values of B-coefficients have been summarized in Table 9. For glycine and DL-α-alanine, good agreement was observed

Table 10. Contribution of (NH_3^+, COO^-) and (CH_2) Groups to *B* Coefficients for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

	B/dm^3·mol^{-1} at various m_s/mol·kg^{-1}[a]					
groups	water	0.5	1.0	2.0	4.0	5.5
(NH_3^+, COO^-)	0.048 ± 0.006 0.039[b] 0.074[c]	0.063 ± 0.012 [0.076][d]	0.067 ± 0.012 [0.074]	0.069 ± 0.012 [0.067]	0.065 ± 0.011	0.054 ± 0.010
$-CH_2$	0.098± 0.002 0.094[b] 0.088[c]	0.097 ± 0.004 [0.091]	0.097 ± 0.004 [0.093]	0.098± 0.004 [0.099]	0.098 ± 0.004	0.101 ± 0.003

[a] m_s = molality of sodium acetate in water. [b] Reference 5. [c] Reference 23. [d] Reference 13.

between the present and literature values[5−6,23] in water and in aqueous sodium acetate solutions.[13] In the case of DL-α-amino-*n*-butyric acid, the present values are slightly lower in water and in sodium acetate than those reported by Yan et al.[13] However, in the case of L-leucine, the present values are higher in comparison to the literature values available for DL-leucine. Furthermore, the order of increase of *B*-coefficient values with the concentration of sodium acetate is similar to the reported values.[13] Similarly, some differences have also been observed in the case of volumes, as mentioned previously. The *B*-coefficient measures the size and shape effects as well as the structural effect induced by solute−solvent interactions.[26] The *B*-coefficient values for amino acids in both water and in aqueous sodium acetate solutions follow the order glycine < DL-α-alanine < DL-α-amino butyric acid < L-leucine < L-pheyalanine.

From the above order, it is clear that magnitude of the *B* coefficient increases with increasing molar mass and size of the alkyl side chains of amino acids. The *B*-coefficient values are larger in aqueous sodium acetate solutions than those in water in all cases. The values increase with the concentration of sodium acetate up to ~2.0 m_s and then start to decrease; this decrease becomes smaller and smaller with the increasing size of alkyl side chains. The *B*-coefficient values in the presence of sodium acetate, which are higher than those in water, indicate the promotion of liquid structure in the presence of sodium acetate. The *B*-coefficient values for the amino acids reflect the net structural effects of the charged end and the hydrophobic CH_2 groups on the amino acids. These two effects can be separated by noting the linear relationship[5,13,23] of *B* coefficients with the number of carbon atom, n_c:

$$B = B(NH_3^+, COO^-) + n_c B(CH_2) \qquad (11)$$

The values of the charged end-groups contribution, $B(NH_3^+, COO^-)$, and the methylene group contribution, $B(CH_2)$, to the *B*-coefficients are given in Table 10. Such linear correlation[11,13] has also been observed in other solutes for these amino acids. The contribution of the $B(CH_2)$ group to the *B*-coefficient is larger than the contribution of $B(NH_3^+, COO^-)$ groups. Furthermore, it may be seen that the contribution of $B(NH_3^+, COO^-)$ groups is more in the presence of sodium acetate than in water, and the values increase up to ~2.0 m_s and then start to decrease.

The *B*-coefficients for the studied amino acids in aqueous sodium acetate solutions also show a linear correlation[6,13,23] with $V^\infty{}_2$ as follows:

$$B = A_1 + A_2 V^\infty{}_2 \qquad (12)$$

Coefficients A_1 and A_2 are given in Table 11 along with their standard deviations and correlation coefficients. Similar observations have been reported for amino acids in different solvents.[11,13,23] The A_2 values depend on the size and shape of the solute and their values lie between 0 and 2.5 for unsolvated spherical species, but the present A_2 values are greater than 2.5 and increase slightly with the increasing concentration of sodium acetate. This may be rationalized by considering that the increase in viscosity is predominantly due to the increase in solvent structure, which offer more resistance to the movement of solute particles (amino acids), although solvation effects will also contribute.

Table 11. Coefficients A_1 and A_2 for Some Amino Acids in Water and in Aqueous Sodium Acetate Solutions at 298.15 K

	$-A_1$/dm^3 mol^{-1}	A_2	R[b]	sd
water	0.098 ± 0.019 0.079 ± 0.03[c]	5.70 ± 0.22 [5.51 ± 0.47][c]	0.998 0.989[c]	0.014
0.5 [a]m_s	0.095 ± 0.023 [0.097 ± 0.040][d]	5.79 ± 0.26 [5.8 ± 0.5][d]	0.997 [0.989][d]	0.017
1.0 m_s	0.097 ± 0.025 [0.111 ± 0.036]	5.79 ± 0.28 [6.10 ± 0.4]	0.996 [0.992]	0.018
2.0 m_s	0.102 ± 0.029 [0.145 ± 0.025]	5.83 ± 0.32 [6.60± 0.3]	0.995 [0.997]	0.020
4.0 m_s	0.115 ± 0.031	5.86 ± 0.34	0.995	0.022
5.5 m_s	0.170 ± 0.017	6.57 ± 0.22	0.999	0.010

[a] m_s = molality of sodium acetate in water. [b] Correlation coefficient. [c] Reference 23. [d] Reference 13.

In conclusion, various thermodynamic parameters for the studied amino acids in aqueous sodium acetate solutions suggest that ion−ion interactions are much stronger than ion−hydrophobic group interactions over the entire concentration range of sodium acetate. The ion−nonpolar (hydrophobic) group interactions increase from glycine to L-leucine with the increasing size of the alkyl side chain of amino acids. L-Phenylalanine has shown distinct hydration behavior due to the aromatic ring in the side chain. A comparison of $\Delta_t V^\infty$ values with the literature values has shown that the acetate ion follows the same order as in the Hofmeister series.

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