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Partial molar volumes of some α-amino acids in aqueous sodium acetate solutions at 308.15 K

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Abstract

The apparent molar volumes $V_{2,\phi}$ have been determined for glycine, DL-α-alanine, DL-α-amino-n-butyric acid, DL-valine and DL-leucine in aqueous solutions of 0.5, 1.0, 1.5 and 2.0 mol kg^{-1} sodium acetate by density measurements at 308.15 K. These data have been used to derive the infinite dilution apparent molar volumes $V_{2,\phi}^0$ for the amino acids in aqueous sodium acetate solutions and the standard volumes of transfer, $\Delta_t V^0$, of the amino acids from water to aqueous sodium acetate solutions. It has been observed that both $V_{2,\phi}^0$ and $\Delta_t V^0$ vary linearly with increasing number of carbon atoms in the alkyl chain of the amino acids. These linear correlations have been utilized to estimate the contributions of the charged end groups (NH_3^+,COO^-), CH_2 group and other alkyl chains of the amino acids to $V_{2,\phi}^0$ and $\Delta_t V^0$. The results show that $V_{2,\phi}^0$ values for (NH_3^+,COO^-) groups increase with sodium acetate concentration, and those for CH_2 are almost constant over the studied sodium acetate concentration range. The transfer volume increases and the hydration number of the amino acids decreased with increasing electrolyte concentrations. These facts indicate that strong interactions occur between the ions of sodium acetate and the charged centers of the amino acids. The volumetric interaction parameters of the amino acids with sodium acetate were calculated in water. The pair interaction parameters are found to be positive and decreased with increasing alkyl chain length of the amino acids, suggesting that sodium acetate has a stronger dehydration effect on amino acids which have longer hydrophobic alkyl chains. These phenomena are discussed by means of the cosphere overlap model. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Density; Apparent molar volume; α-Amino acid; Aqueous sodium acetate solutions

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1. Introduction

Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes [1–3]. The complex conformational and configurational factors affecting the structures of proteins in various solvents, make the direct interpretation from studies on proteins very difficult. Therefore, investigations of the behavior of model compounds of proteins like amino acids and peptides are of importance.

There have been many studies on the amino acid–water–salt systems. As far as the volumetric properties are concerned, the infinite dilution apparent molar volumes for some amino acids have been determined in aqueous calcium chloride [4], alkali metal halide (LiCl, NaCl, KCl, CsCl, KBr, KI) [5–8], potassium thiocyanate [9,10], ammonium chloride [11] and guanidine hydrochloride [12,13] solutions. Sodium acetate (Na^+, CH_3COO^-) is known to influence the dissociation of proteins in solution [14] and cause a salting-out of polar non-electrolytes [15]. Acetate ion has a hydrophobic methyl group and a carboxylate ion residue, its effect on amino acids should be different from the simple anions. Therefore, it is interesting to investigate the behavior of model compounds of proteins in aqueous sodium acetate solutions. As a part of the continuing studies on the thermodynamic and transport properties of amino acids in aqueous solutions of denaturing agents [13,16,17], we reported here the apparent molar volumes, infinite dilution apparent molar volumes and the standard transfer volumes for glycine (Gly), DL-α-alanine (Ala), DL-α-amino-*n*-butyric acid (Abu), DL-valine (Val) and DL-leucine (Leu) in aqueous sodium acetate solutions at 308.15 K. In addition, the infinite dilution apparent molar volumes for the zwitterionic group (NH_3^+,COO^-), CH_2 group and the other alkyl chains of the amino acids as well as the volumetric interaction parameters of the amino acids with sodium acetate have also been reported.

2. Experimental

Glycine (Shanghai Chem. Co., PR China), DL-α-alanine (Shanghai Chem. Co., PR China), DL-α-amino-*n*-butyric acid (Sigma), DL-valine (Fluka) and DL-leucine (Baker) were purified by two recrystallizations from aqueous ethanol solutions and dried under vacuum at 328 K for more than 6 h. Then they were stored over P_2O_5 in a desiccator before use. Analytical reagent grade anhydrous sodium acetate (Tianjin Nankai Chem. Co., PR China) was used as such after drying under vacuum at 383 K. Conductivity water with a conductivity of 1.2 $\mu\Omega^{-1}$ cm^{-1} obtained by distilling the deionized water from alkaline $KMnO_4$ was used thoughout. All solutions were prepared freshly by weighing on the molality scale.

Solution densities were determined to $\pm 3 \times 10^{-6}$ g cm^{-3} with an Anton Paar DMA 60/602 Vibrating-tube digital densimeter. The temperature of the thermostated bath was controlled to 308.15 ± 0.005 K using a CT-1450 temperature controller and a CK-100 ultracryostat. The densimeter was calibrated with the known densities of water [18] and dry air [19] every day. The other details have been described previously [13,16].

3. Results and discussion

The apparent molar volumes $V_{2,\phi}$ of the amino acids were calculated from the solution densities by Eq. (1):

$$V_{2,\phi} = M/\rho - 10^3(\rho - \rho_0)/m_a \rho \rho \quad (1)$$

where M and m_a are, respectively, the molar mass and molality of the amino acid, and ρ and ρ_0 are the densities of amino acid–water–sodium acetate ternary solutions and of aqueous sodium acetate solutions, respectively. The solution densities and the calculated apparent molar volumes for the amino acids are listed in Table 1 as functions of molalities of amino acid (m_a) and of sodium acetate (m_s).

It was found that $V_{2,\phi}$ values varied linearly with amino acid molalities and could be least-square, fitted to Eq. (2)

Table 1
Solution densities ρ and apparent molar volumes $V_{2,\phi}$; for the α-amino acids in aqueous sodium acetate solutions at 308.15 K as a function of molality of amino acids

m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}
$m_s = 0.5000$			$m_s = 1.0000$			$m_s = 1.4999$			$m_s = 2.0001$		
Glycine											
0.0000	1.014023	–	0.0000	1.032663	–	0.0000	1.050031	–	0.0000	1.066790	–
0.1039	1.017106	45.00	0.06093	1.034399	45.91	0.1599	1.054398	46.52	0.06182	1.068405	47.33
0.1541	1.018586	45.01	0.1017	1.035567	45.80	0.2020	1.055541	46.50	0.1183	1.069864	47.40
0.2037	1.020042	45.01	0.1537	1.037010	45.98	0.2518	1.056876	46.53	0.1854	1.072869	47.41
0.2565	1.021569	45.08	0.2055	1.038467	45.95	0.2991	1.058119	46.61	0.2650	1.073615	47.43
0.2981	1.022760	45.13	0.2941	1.040911	46.02	0.3105	1.058444	46.54	0.2873	1.074212	47.36
0.3489	1.024213	45.16	0.3347	1.042024	46.05	0.3297	1.058936	46.60	0.3315	1.075279	47.42
0.4074	1.025876	45.20	0.4052	1.043955	46.06	0.3533	1.059582	46.55	0.3597	1.076022	47.41
$m_s = 0.5000$			$m_s = 1.0000$			$m_s = 1.4995$			$m_s = 2.0001$		
DL-α-alanine											
0.0000	1.014023	–	0.0000	1.032663	–	0.0000	1.049995	–	0.0000	1.066790	–
0.1013	1.016712	61.84	0.05817	1.034122	62.66	0.04955	1.051172	63.23	0.03246	1.067516	63.80
0.1552	1.018114	61.96	0.1952	1.037512	62.68	0.09483	1.052242	63.23	0.1497	1.070098	63.89
0.2036	1.019366	61.99	0.2432	1.038680	62.71	0.1412	1.053327	63.24	0.1970	1.071137	63.85
0.2570	1.020740	62.02	0.2999	1.040058	62.70	0.1921	1.054509	63.26	0.2422	1.072151	63.74
0.3034	1.021945	61.97	0.3384	1.040978	62.72	0.2383	1.055577	63.27	0.2998	1.073365	63.84
0.3554	1.023238	62.07	0.3846	1.042095	62.70	0.2843	1.056626	63.30	0.3186	1.073736	63.94
0.3995	1.024361	62.05	–	–	–	0.3215	1.057485	63.27	0.3487	1.074411	63.85
$m_s = 0.5000$			$m_s = 1.0000$			$m_s = 1.4999$			$m_s = 2.0001$		
DL-α-aminobutyric acid											
0.0000	1.014023	–	0.0000	1.032663	–	0.0000	1.050031	–	0.0000	1.066790	–
0.06141	1.015593	76.67	0.03174	1.033419	77.47	0.06080	1.051387	77.88	0.05825	1.068001	78.30
0.1039	1.016665	76.73	0.06066	1.034101	77.52	0.1425	1.053199	77.81	0.09640	1.068786	78.32
0.1507	1.017825	76.85	0.1507	1.036206	77.55	0.1809	1.054016	77.93	0.1965	1.070818	78.35
0.2010	1.019063	76.91	0.2044	1.037438	77.59	0.2311	1.055102	77.93	0.2423	1.071739	78.36
0.2517	1.020297	76.96	0.3309	1.040311	77.61	0.2863	1.056259	78.01	0.3071	1.072927	78.65
0.2995	1.021448	77.01	0.3950	1.041728	77.66	0.3072	1.056717	77.97	0.3263	1.073303	78.64
0.3540	1.022760	77.02	0.4442	1.042845	77.60	0.3919	1.058460	78.07	0.3639	1.074033	78.64
0.4001	1.023852	77.05	–	–	–	–	–	–	–	–	–

Table 1 (*Continued*)

m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}	m_a/ mol kg^{-1}	ρ/ g cm^{-3}	$V_{2,\phi}$/ cm^3 mol^{-1}
$m_s = 0.5000$			$m_s = 1.0000$			$m_s = 1.4999$			$m_s = 2.0001$		
DL-valine											
0.0000	1.014023	–	0.0000	1.032663	–	0.0000	1.050031	–	0.0000	1.066790	–
0.09825	1.016374	92.01	0.03177	1.033373	92.42	0.09631	1.052026	92.60	0.05945	1.067901	93.29
0.1509	1.017605	92.00	0.1004	1.034889	92.46	0.1466	1.053040	92.69	0.09870	1.068616	93.39
0.1989	1.018746	92.00	0.1529	1.036045	92.40	0.1957	1.054025	92.71	0.1446	1.069470	93.43
0.2491	1.019900	92.04	0.1980	1.036992	92.55	0.2435	1.054951	92.81	0.1935	1.070329	93.43
0.3023	1.021114	92.06	0.2465	1.038036	92.52	0.2946	1.055969	92.76	0.2437	1.071209	93.50
0.3479	1.022155	92.05	0.2943	1.039061	92.48	0.3791	1.057606	92.78	0.2934	1.072048	93.60
0.4018	1.023368	92.05	0.3490	1.040189	92.55	0.4163	1.058362	92.68	0.3502	1.073062	93.53
–	–	–	0.4028	1.041301	92.56	–	–	–	–	–	–
$m_s = 0.4999$			$m_s = 1.0000$			$m_s = 1.4995$			$m_s = 2.0001$		
DL-leucine											
0.0000	1.014020	–	0.0000	1.032663	–	0.0000	1.049995	–	0.0000	1.066790	–
0.03015	1.014666	108.49	0.01956	1.033041	108.78	0.02494	1.050431	108.98	0.009991	1.066942	109.45
0.03795	1.014830	108.53	0.02897	1.033227	108.66	0.03030	1.050520	109.10	0.02019	1.067097	109.49
0.04580	1.014996	108.52	0.03978	1.033435.	108.68	0.03544	1.050612	109.01	0.03018	1.067251	109.40
0.05222	1.015129	108.59	0.04509	1.033529	108.86	0.04120	1.050707	109.13	0.03477	1.067321	109.42
0.05917	1.015284	108.44	0.05062	1.033639	108.78	0.04695	1.050805	109.13	0.04086	1.067411	109.48
0.06365	1.015373	108.53	0.05435	1.033710	108.79	0.05213	1.050895	109.12	0.04457	1.067464	109.54

Table 2
Infinite dilution apparent molar volumes for α-amino acids in aqueous sodium acetate solutions at 308.15 K[a]

Aminoacids	$m_s = 0.5$		$m_s = 1.0$		$m_s = 1.5$		$m_s = 2.0$	
	$V^0_{2,\phi}$/ cm^3 mol^{-1}	S_V/ cm^3 mol^{-2}kg	$V^0_{2,\phi}$/ cm^3 mol^{-1}	S_V/ cm^3 mol^{-2}kg	$V^0_{2,\phi}$/ cm^3 mol^{-1}	S_V/ cm^3 mol^{-2}kg	$V^0_{2,\phi}$/ cm^3 mol^{-1}	S_V/ cm^3 mol^{-2}kg
Glycine	44.90(2)	0.73(8)	45.91(2)	0.38(10)	46.45(5)	0.37(19)	47.36(3)	0.17(12)
Alanine	61.83(4)	0.59(16)	62.68(2)	0.09(9)	63.21(1)	0.22(5)	63.84(6)	–
Aminobu-tyric acid	76.65(4)	1.12(14)	77.49(2)	0.34(8)	77.79(4)	0.68(17)	78.17(7)	1.29(29)
Valine	91.98(2)	0.20(6)	92.41(3)	0.38(13)	92.72(7)	–	93.28(4)	0.86(18)
Leucine	108.52(5)	–	108.76(8)	–	108.90(8)	4.73(211)	109.46(5)	–

[a] Values in parentheses are S.D. × 100.

$$V_{2,\phi} = V_{2,\phi}^0 + S_V m_a \tag{2}$$

where $V_{2,\phi}^0$ is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_V is the corresponding experimental slopes of the $V_{2,\phi}$ vs. m_a plots. In the cases where there was no dependence with m_a, $V_{2,\phi}^0$ were calculated by taking an average of all the data points. The regression coefficients of Eq. (2) for the α-amino acids in aqueous solutions of 0.5, 1.0, 1.5 and 2.0 mol kg^{-1} sodium acetate are represented in Table 2 along with their standard deviations. The standard volumes of transfer, $\Delta_t V^0$, for the amino acids from water to aqueous sodium acetate solutions are listed in Table 3. They were calculated from Eq. (3):

$$\Delta_t V^0 = V_{2,\phi}^0(\text{in aqueous CH}_3\text{COONa}) - V_{2,\phi}^0(\text{in water}) \tag{3}$$

where $V_{2,\phi}^0$ (in water) is the infinite dilution apparent molar volume for the amino acids in water [20].

3.1. Contributions of the zwitterionic end group, CH_2 group and the other alkyl chains of the α-amino acids to $V_{2,\phi}^0$

It is interesting to note that variations of $V_{2,\phi}^0$ with the number of carbon atoms in the alkyl chain of the amino acids are linear (average correlation coefficients $R \geq 0.9998$). A similar linear correlation has been reported for the homologous series of ω-amino acids in aqueous potassium thiocyanate solutions [10] and of α-amino acids in aqueous guanidine hydrochloride solutions [13]. This linear relation could be reasonably represented by Eq. (4):

$$V_{2,\phi}^0 = V_{2,\phi}^0(\text{NH}_3^+,\text{COO}^-) + n_c V_{2,\phi}^0(\text{CH}_2) \tag{4}$$

where n_c is the number of carbon atoms in the alkyl chain of the α-amino acids, $V_{2,\phi}^0((\text{NH}_3^+,\text{COO}^-)$ and $V_{2,\phi}^0(\text{CH}_2)$ are, respectively, zwitterionic end groups and the methylene group contributions to $V_{2,\phi}^0$. Values of $V_{2,\phi}^0((\text{NH}_3^+,\text{COO}^-)$ and $V_{2,\phi}^0(\text{CH}_2)$ calculated by a least-square regression analysis are listed in Table 4. Since the alkyl chains of the homologous series of α-amino acids investigated in this work are as follows: CH_2– (gly), CH_3CH– (ala), $\text{CH}_3\text{CH}_2\text{CH}$– (abu), $\text{CH}_3\text{CH}_3\text{CHCH}$– (val) and $\text{CH}_3\text{CH}_3\text{CHCH}_2\text{CH5}$– (leu), the $V_{2,\phi}^0(\text{CH}_2)$ value obtained in this way characterize the mean contribution of CH and CH_3 groups to $V_{2,\phi}^0$ of the α-amino acids. Based on the assumptions:

$$V_{2,\phi}^0(\text{CH}_3) = 1.5\, V_{2,\phi}^0(\text{CH}_2) \tag{5}$$

$$V_{2,\phi}^0(\text{CH}) = 0.5\, V_{2,\phi}^0(\text{CH}_2) \tag{6}$$

suggested by Hakin and co-workers [21,22], the contribution of the other alkyl chains of the α-amino acids can be calculated. The results are also given in Table 4.

It can be seen from Table 4 that $V_{2,\phi}^0(\text{CH}_2)$ values for the amino acids are not sensitive to the concentration of sodium acetate. The same trend has been observed by Wadi and Goyal [10] in

Table 3
Standard volumes of transfer for amino acids from water to aqueous sodium acetate solutions at 308.15 K[a]

Amino acids	$\Delta_t V^0/\text{cm}^3\text{mol}^{-1}$			
	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
Glycine	0.70(6)	1.71(6)	2.25(8)	3.16(7)
Alanine	0.51(6)	1.35(4)	1.89(4)	2.52(10)
Aminobutyric acid	0.45(8)	1.29(7)	1.59(8)	1.97(10)
Valine	0.34(7)	0.77(8)	1.08(10)	1.65(8)
Leucine	0.19(14)	0.43(15)	0.57(15)	1.13(14)

[a] Values in parentheses are S.D. × 100.

Table 4
Contributions of zwitterionic group (NH_3^+,COO^-), CH_2 group and other alkyl chains to the infinite dilution apparent molar volume in aqueous sodium acetate solutions at 308.15 K[a]

Group	$V^0_{2,\phi}$/$cm^3 mol^{-1}$			
	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
(NH_3^+,COO^-)	29.6(0.7)	30.8(0.7)	31.5(0.7)	32.3(0.6)
CH_2–	15.7(0.2)	15.5(0.2)	15.4(0.2)	15.4(0.2)
CH_3CH–	31.4(0.3)	31.0(0.3)	30.8(0.3)	30.8(0.3)
CH_3CH_2CH–	47.1(0.4)	46.5(0.3)	46.2(0.4)	46.2(0.3)
$(CH_3)_2CHCH$–	62.8(0.4)	62.0(0.4)	61.6(0.4)	61.6(0.4)
$(CH_3)_2CHCH_2CH$–	78.5(0.5)	77.5(0.4)	77.0(0.5)	77.0(0.4)

[a] Values in paretheses are S.D. values.

aqueous KSCN solutions. The average value of 15.5 ± 0.2 cm^3 mol^{-1} derived from this work is very close to the values of 15.3 and 15.6 reported at 308.15 K for the amino acids in aqueous and aqueous KSCN solutions [10]. Values of $V^0_{2,\phi}(NH_3^+,COO^-)$ are larger than those of $V^0_{2,\phi}(CH_2)$ and increase with increasing sodium acetate concentration. These results indicate that the interactions of ions (Na^+ and CH_3COO^-) with zwitterionic groups of the amino acids are much stronger than those with hydrophobic CH_2 groups.

3.2. Standard transfer volumes of the α-amino acids

It is evident from Fig. 1 that $\Delta_t V^0$ values are positive and increase linearly with increasing concentration of sodium acetate. In the amino acid–sodium acetate–water ternary system, the following interactions may be occurring: (a) ion-charged group interactions between Na^+ and the COO^- group of the amino acids and between CH_3COO^- and the NH_3^+ group of the amino acids; (b) ion-non-polar group interactions between Na^+, CH_3COO^- and the non-polar groups of the amino acids. According to the cosphere overlap model [23], the ion-charged group interactions would lead to a positive $\Delta_t V^0$, whereas ion-non-polar group interactions will result in a negative $\Delta_t V^0$. The overall $\Delta_t V^0$ values obtained experimentally consist of these two opposite contributions. Since positive $\Delta_t V^0$ values were observed for all the amino acids studied, we concluded that the contribution of ion-charged group interactions to $\Delta_t V^0$ dominates that of ion-non-polar group interactions. This also explains the higher $\Delta_t V^0$ values observed at higher molalities of sodium acetate for the amino acids.

In Fig. 2, we have plotted $\Delta_t V^0$ values for the homologous series of α-amino acids against the number of carbon atoms in their alkyl chains. Good linear relations have been observed. Compared with Eq. (4), it is expected that the intercepts and slopes of these straight lines represent the contributions of zwitterionic end group and CH_2 group to $\Delta_t V^0$, respectively. Obviously, the contribution of CH_2 group to $\Delta_t V^0$ is negative and that of the zwitterionic group is positive. This experimental result supports the above molecular interpretation from the cosphere overlap model.

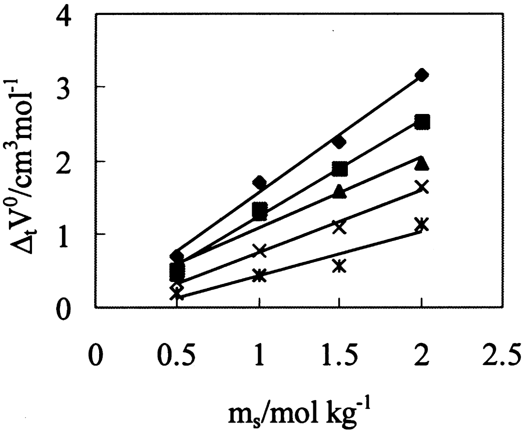

Fig. 1. Plot of the standard volumes of transfer of amino acids vs. molality of sodium acetate. ◆ glycine, ■ alanine, ▲ aminobutyric acid, ×valine, * leucine.

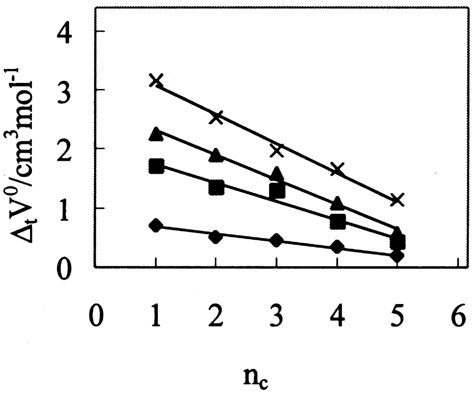

Fig. 2. Variation of the standard volumes of transfer of amino acids as a function of number of carbon atoms, n_c, in the alkyl chain of the amino acids at 308.15 K ◆ $m_s = 0.5$, ■ $m_s = 1.0$ ▲ $m_s = 1.5$, ×$m_s = 2.0$.

3.3. The number of water molecule hydrated to the amino acid

The standard partial molar volumes of the amino acids can be expressed by a simple model [24]:

$$V^0_{2,\phi}(\text{amino acid}) = V^0_{2,\phi}(\text{int}) + V^0_{2,\phi}(\text{elect}) \qquad (7)$$

where $V^0_{2,\phi}$ (int) is the intrinsic partial molar volume of the amino acid, and $V^0_{2,\phi}$(elect) is the electrostriction partial molar volume due to the hydration of the amino acid. The $V^0_{2,\phi}$(int) is made up of two terms, the van der waals volume and the volume due to packing effects. According to the suggestion of Millero et al. [25], the values of $V^0_{2,\phi}$(int) for the amino acids can be estimated from crystal molar volumes:

$$V^0_{2,\phi}(\text{int}) = (0.7/0.634)V^0_{2,\phi}(\text{cryst}) \qquad (8)$$

where 0.7 is the packing density for molecules in organic crystals, and 0.634 is the packing density for random packing spheres. The crystal molar volume can be calculated by Eq. (9):

$$V^0_{2,\phi}(\text{cryst}) = M/\rho(\text{cryst}) \qquad (9)$$

where, ρ(cryst) is the crystal density of the amino acids. Since crystal density has a very small change with temperature, we assume that ρ(cryst) data at 298.15 K from Berlin and Pallansh [26] can be approximately used in the present case (308.15 K). The $V^0_{2,\phi}$ (elect) can be estimated from the experimentally measured $V^0_{2,\phi}$ values by Eq. (10):

$$V^0_{2,\phi}(\text{elect}) = V^0_{2,\phi}(\text{amino acid}) - V^0_{2,\phi}(\text{int}) \qquad (10)$$

The decrease in volume due to electrostriction can be related to the number of water molecules (n_H) hydrated to the amino acids [27] by Eq. (11):

$$n_H = V^0_{2,\phi}(\text{elect})/(V^0_E - V^0_B) \qquad (11)$$

where V^0_E is the molar volume of electrostricted water and V^0_B is the molar volume of bulk water at 308.15 K. Following the procedure described by Millero et al. [25], we found that at 308.15 K:

$$V^0_E - V^0_B = -4.0 \text{ cm}^3 \text{ mol}^{-1} \qquad (12)$$

Therefore, as an approximation, the hydration number of water molecules can be obtained by Eq. (13):

$$n_H = V^0_{2,\phi}(\text{elect})/(-4.0) \qquad (13)$$

Thus, obtained $V^0_{2,\phi}$(elect) and n_H values are included in Table 5 except for aminobutyric acid

Table 5
Values of $V^0_{2,\phi;}$(elect) and hydration number, n_H, for amino acids in aqueous sodium acetate solutions at 308.15 K

Amino acids	$m_s = 0.5$		$m_s = 1.0$		$m_s = 1.5$		$m_s = 2.0$	
	$V^0_{2,}$(elect)	n_H	$V^0_{2,\phi}$(elect)	n_H	$V^0_{2,\phi}$(elect)	n_H	$V^0_{2,\phi}$(elect)	n_H
Glycine	−6.97	1.7	−5.96	1.5	−5.42	1.4	−4.51	1.1
Alanine	−9.91	2.5	−9.07	2.3	−8.53	2.1	−7.90	2.0
Valine	−11.26	2.8	−10.25	2.6	−9.71	2.4	−8.80	2.2
Leucine	−15.53	3.9	−15.28	3.8	−15.14	3.8	−14.58	3.6

Table 6
Volumetric interaction parameters in amino acids-sodium acetate-H_2O solutions at 308.15 K

Amino acid	V_{as}/cm^3 mol^{-2} kg	V_{ass}/cm^3 mol^{-2} kg^2	V_{asss}/cm^3 mol^{-2} kg^3
Glycine	0.405	−0.012	0.0030
Alanine	0.232	0.084	−0.0213
Aminobutyric acid	0.223	0.081	−0.0277
Valine	0.208	−0.037	0.0134
Leucine	0.166	−0.088	0.0300

whose crystal molar volume datum is not available. It can be seen that n_H for a given amino acid decreases with increasing concentration of sodium acetate. This shows that sodium acetate has a dehydration effect on the amino acids. This is consistent with the observed increase in $V_{2,\phi}^0$ with increasing sodium acetate concentrations.

3.4. Volumetric interaction parameters

The standard transfer volumes of the amino acids can be expressed by the following equation [28]:

$$\Delta_t V^0 = 2_v V_{as} \cdot m_s + 3_v V_{ass} \cdot m_s^2 + 4_v V_{asss} \cdot m_s^3 \quad (14)$$

where, v is the number of moles of ions into which the electrolyte dissociates. V_{as}, V_{ass} and V_{asss} are, respectively, the pair, triplet and tetrad volumetric interaction parameters, m_s is the molality of electrolyte. Using Eq. (14), various volumetric interaction parameters were calculated and are given in Table 6. It can be seen from Table 6 that all pair volumetric interaction parameters V_{as} are positive and are larger than V_{ass} and V_{asss} values. This shows that the interactions between amino acids and sodium acetate are mainly pair interactions. In addition, V_{as} decreases from glycine to leucine. Because the interaction contribution of type (a) expressed above are the same for different amino acids, the decreasing V_{as} comes from the difference in interaction contribution of type (b), that is to say, the interactions of the alkyl groups of the amino acids with sodium acetate. Among the amino acids studied, leucine with the longest alkyl chain is expected to lose the maximum amount of its hydrophobically hydrated water molecules due to the overlap of hydration cospheres of (CH_3COO^-, Na^+) and hydrophobic chain of the amino acids, which lead to a smaller transfer volume and accordingly a smaller V_{as}. The loss of hydrophobically hydrated water molecules decreases gradually with decreasing length of the alkyl chain of the amino acids. Glycine has a larger V_{as} value owing to its shorter alkyl chain. These results show that more hydrophobic amino acids undergo more dehydration effect of sodium acetate.

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