

## Viscosity behavior of some $\alpha$ -amino acids and their groups in water–sodium acetate mixtures

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### Abstract

Viscosities of glycine, DL- $\alpha$ -alanine, DL- $\alpha$ -amino-*n*-butyric acid, DL-valine and DL-leucine have been determined in water–sodium acetate mixtures at 298.15 and 308.15 K. The viscosity *B*-coefficients have been calculated. The corresponding activation free energies ( $\Delta\mu_2^{0\ddagger}$ ) for viscous flow have been evaluated with the help of the Feakins equation. The contributions of the charged end group ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) and  $\text{CH}_2$  groups of the amino acids to *B*-coefficient and  $\Delta\mu_2^{0\ddagger}$  have been also determined using the linear correlation between *B*-coefficient or  $\Delta\mu_2^{0\ddagger}$  and the number of carbon atoms in alkyl chains of the amino acids. The results have been interpreted in the light of the solute–solvent interactions in aqueous media.

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### 1. Introduction

Physicochemical studies of model compounds in aqueous solutions are of fundamental importance in understanding intermolecular interactions in liquids [1,2] and the effect of these compounds on water structure [3]. Tanford [4] cited evidence suggesting that the relative stability of the structure of viruses, DNA and globular proteins depend upon the molecular structure of water associated with them. Properties of amino acids in aqueous solutions have been extensively studied in order to obtain a better understanding of solute–solvent

interactions and their role on the conformational stability of proteins [5]. Even though in recent years attention has been given to their behavior in different simple salt–water mixed solvents [6–17], there are only very few studies about properties of amino acid in organic salts–water mixtures [18–20] probably due to the complex nature of their interactions. Sodium acetate ( $\text{CH}_3\text{COONa}$ ) is known to influence the dissociation of proteins in solution [21] and cause a salting-out of nonelectrolyte [22]. Therefore, it is interesting to investigate the behavior of model compounds of proteins in aqueous sodium acetate solutions.

Numerous studies have shown that the volumetric and viscosity measurements are very useful in providing information regarding solute–solute and

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solute–solvent interactions in solutions [23]. As a part of the continuing studies on the thermodynamic and transport properties of amino acids in aqueous solutions of organic salts [19,20,24–26], the present work reports the viscosity and the thermodynamic free energy of the viscous flow for the amino acids. In addition, the contributions of the charged end group ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) and  $\text{CH}_2$  groups to  $B$ -coefficients and  $\Delta\mu_2^{0\neq}$  have also been reported based on the linear correlation between  $B$ -coefficients or  $\Delta\mu_2^{0\neq}$  and the number of carbon atoms in the alkyl chains of the amino acids. The results have been interpreted in the light of solute–solvent intermolecular interactions in aqueous media.

## 2. Materials and experimental techniques

Glycine (Shanghai Chem. Co.), DL- $\alpha$ -alanine (Shanghai Chem. Co.), DL- $\alpha$ -amino-*n*-butyric acid (Shanghai Chem. Co.), DL-valine (Fluka) and DL-leucine (Baker) were recrystallized twice from aqueous ethanol solutions and dried under vacuum at 348 K for 6 h. Then they were stored over  $\text{P}_2\text{O}_5$  in a desiccator before use. Analytical reagent grade anhydrous sodium acetate (Tianjin Nankai Chem. Co.) was used after drying under vacuum at 383 K. Water with a specific conductivity of  $1.2 \mu\Omega^{-1} \text{cm}^{-1}$  was obtained by distilling deionized water from alkaline  $\text{KMnO}_4$  to remove any organic matter. All solutions were prepared freshly by weighing on the molality scale.

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

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

where  $\rho$  is the solution density,  $t$  is the flow time,  $C$  and  $K$  are the viscometer constants which were

obtained by the measurements on water at 298.15 and 308.15 K. The viscometer were thermostated using SCHOTT thermostat units which have a thermal stability of  $\pm 0.005$  K.

The density data reported in the previous papers [24,25] were used in the present work. The relative viscosities  $\eta_r = \eta/\eta_0$  were calculated from the solution and solvent viscosities, respectively.

## 3. Results

The viscosity data obtained for both solvent and solutions as a function of amino acid concentration and temperature are reported in Table 1 and Table 2. The viscosity  $B$ -coefficients for the amino acids in aqueous sodium acetate solutions were calculated from the following equation [27]

$$\eta_r = \eta/\eta_0 = 1 + Bc \quad (2)$$

where  $c$  is the molarity of amino acid in solution. Viscosity  $B$ -coefficients were obtained by the least-squares method and are given in Table 3 together with their standard deviations.

In Eyring's simple model [28], the molecules move one-by-one from their equilibrium positions through their transition-states, in which intermolecular bonds are stretched, to other equilibrium positions. For a pure liquid he found the equation

$$\eta_0 = (hN_A/V_{1,\phi}^0) \exp(\Delta\mu_1^{0\neq}/RT) \quad (3)$$

where  $h$  is the Planck constant,  $N_A$  is the Avogadro's number,  $\Delta\mu_1^{0\neq}$  is the contribution per mole of solvent to the free energy of activation for viscous flow of the solution. When a solution flows, both the solute and the solvent molecules move under the shearing force. The activation energy per mole of solution can be written:

$$\Delta G^{0\neq} = x_1 \Delta\mu_1^{0\neq} + x_2 \Delta\mu_2^{0\neq} \quad (4)$$

where  $x_1$  and  $x_2$  are the mole fraction of the solvent and solute, respectively.  $\Delta\mu_2^{0\neq}$  as defined by Eq. (4) includes any change in the free energy of activation of the solvent molecules caused by the presence of the solute, as well as a contribution from the movement of the solute itself. According to the Feakins et al. the  $B$ -coefficient is related to  $\Delta\mu_2^{0\neq}$  by Eq. (5), [29]

Table 1

Viscosities  $\eta$  for  $\alpha$ -amino acid + sodium acetate + water systems as a function of molarities of amino acids ( $c$ ) and sodium acetate ( $m_s$ ) at 298.15 K

$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.4999$		$m_s = 2.0001$	
$c/\text{mol l}^{-1}$	$\eta/\text{mPa S}$	$c/\text{mol l}^{-1}$	$\eta/\text{mPa S}$	$c/\text{mol l}^{-1}$	$\eta/\text{mPa S}$	$c/\text{mol l}^{-1}$	$\eta/\text{mPa S}$
Glycine							
0.0000	1.043	0.0000	1.214	0.0000	1.411	0.0000	1.645
0.03106	1.048	0.03273	1.220	0.03227	1.419	0.03418	1.655
0.06198	1.052	0.06296	1.225	0.06120	1.424	0.06564	1.664
0.1029	1.058	0.1049	1.232	0.1026	1.433	0.1081	1.673
0.1637	1.067	0.1581	1.242	0.1544	1.444	0.1594	1.685
0.1987	1.073	0.2109	1.252	0.2131	1.457	0.2142	1.698
0.2413	1.079	0.2563	1.260	0.2529	1.465	0.2594	1.709
DL- $\alpha$ -alanine							
0.03104	1.051	0.03137	1.224	0.03199	1.424	0.03468	1.662
0.06389	1.061	0.06005	1.233	0.06148	1.435	0.06472	1.674
0.1030	1.071	0.1002	1.246	0.1019	1.449	0.1065	1.693
0.1396	1.082	0.1499	1.264	0.1536	1.470	0.1587	1.716
0.2091	1.101	0.1997	1.279	0.2021	1.488	0.2081	1.739
0.2489	1.113	0.2482	1.295	0.2494	1.508	0.2552	1.762
DL- $\alpha$ -aminobutyric acid							
0.03172	1.054	0.03281	1.229	0.03470	1.430	0.03207	1.664
0.06330	1.066	0.06256	1.243	0.06377	1.445	0.06208	1.683
0.1039	1.081	0.1035	1.261	0.1074	1.468	0.1024	1.707
0.1493	1.099	0.1543	1.284	0.1596	1.495	0.1561	1.742
0.2073	1.128	0.2084	1.309	0.2053	1.521	0.2071	1.774
0.2577	1.142	0.2578	1.331	0.2560	1.548	0.2543	1.808
DL-valine							
0.03091	1.057	0.03282	1.232	0.03215	1.433	0.03305	1.669
0.05599	1.071	0.06282	1.248	0.06149	1.451	0.06329	1.692
0.1039	1.091	0.1031	1.270	0.1006	1.477	0.1047	1.725
0.1554	1.115	0.1562	1.299	0.1524	1.510	0.1527	1.762
0.2055	1.141	0.2013	1.326	0.2024	1.544	0.2033	1.801
0.2578	1.165	0.2496	1.354	0.2507	1.578	0.2548	1.844
DL-leucine							
0.01977	1.054	0.01531	1.223	0.01560	1.423	0.01069	1.655
0.03022	1.059	0.03081	1.233	0.02613	1.432	0.02157	1.664
0.04123	1.064	0.04639	1.243	0.04208	1.443	0.03220	1.674
0.05098	1.070	0.05699	1.250	0.05286	1.452	0.04344	1.684
0.06304	1.076	0.06749	1.257	0.05772	1.456	0.04865	1.690

$$B = (V_{1,\phi}^0 - V_{2,\phi}^0)/1000 + (V_{1,\phi}^0/1000)(\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq})/RT \quad (5)$$

It can be rearranged as follows:

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/V_{1,\phi}^0)[1000B - (V_{1,\phi}^0 - V_{2,\phi}^0)] \quad (6)$$

Table 4 gives values of  $\Delta\mu_2^{0\neq}$  for the amino acids

in aqueous sodium acetate solutions at 298.15 and 308.15 K.

According to the transition-state theory [29] every solvent molecule in one mole of solution interacts more or less strongly with the solute. Each solvent molecule must pass through the transition-state, in which it must also interact with the solute. Thus,  $\Delta\mu_2^{0\neq}$  contains the free energy of

Table 2

Viscosities  $\eta$  for  $\alpha$ -amino acid + sodium acetate + water systems as a function of molarities of amino acids ( $c$ ) and sodium acetate ( $m_s$ ) at 308.15 K

$m_s = 0.5000$		$m_s = 1.0000$		$m_s = 1.4999$		$m_s = 2.0001$	
$c / \text{mol l}^{-1}$	$\eta / \text{mPa S}$	$c / \text{mol l}^{-1}$	$\eta / \text{mPa S}$	$c / \text{mol l}^{-1}$	$\eta / \text{mPa S}$	$c / \text{mol l}^{-1}$	$\eta / \text{mPa S}$
Glycine							
0.0000	0.8390	0.0000	0.9708	0.0000	1.119	0.0000	1.293
0.03055	0.8443	0.03262	0.9749	0.03215	1.125	0.03406	1.299
0.06055	0.8461	0.06274	0.9803	0.06098	1.131	0.06540	1.306
0.1007	0.8511	0.1046	0.9863	0.1022	1.137	0.1077	1.313
0.1624	0.8593	0.1576	0.9943	0.1538	1.146	0.1588	1.324
0.1820	0.8610	0.2102	1.001	0.2123	1.156	0.2134	1.335
0.2592	0.8710	0.2554	1.008	0.2520	1.162	0.2584	1.343
DL- $\alpha$ -alanine							
0.03116	0.8450	0.03126	0.9781	0.03187	1.128	0.03455	1.306
0.06048	0.8513	0.05984	0.9857	0.06125	1.138	0.06447	1.316
0.09997	0.8595	0.09983	0.9959	0.1015	1.149	0.1061	1.329
0.1523	0.8705	0.1494	1.007	0.1530	1.163	0.1580	1.346
0.2044	0.8820	0.1992	1.021	0.2014	1.179	0.2073	1.364
0.2570	0.8939	0.2473	1.033	0.2485	1.192	0.2542	1.381
DL- $\alpha$ -aminobutyric acid							
0.03373	0.8477	0.03269	0.9821	0.03457	1.133	0.03267	1.308
0.06198	0.8559	0.06234	0.9915	0.06353	1.143	0.06184	1.320
0.1019	0.8692	0.1031	1.006	0.1070	1.161	0.1020	1.339
0.1497	0.8809	0.1538	1.028	0.1589	1.180	0.1555	1.365
0.2003	0.8962	0.2077	1.040	0.2045	1.200	0.2063	1.387
0.2489	0.9107	0.2568	1.058	0.2550	1.219	0.2534	1.410
DL-valine							
0.03272	0.8494	0.03270	0.9844	0.03203	1.135	0.03292	1.310
0.06419	0.8601	0.06260	0.9953	0.06126	1.149	0.06305	1.327
0.1054	0.8744	0.1027	1.012	0.1002	1.167	0.1043	1.349
0.1512	0.8909	0.1556	1.034	0.1518	1.192	0.1521	1.377
0.1982	0.9087	0.2006	1.053	0.2017	1.217	0.2025	1.406
0.2485	0.9276	0.2487	1.075	0.2498	1.240	0.2538	1.434
DL-leucine							
0.01456	0.8441	0.01525	0.9773	0.01554	1.129	0.01065	1.300
0.03037	0.8510	0.03070	0.9843	0.02603	1.134	0.02149	1.308
0.04538	0.8567	0.04623	0.9924	0.04191	1.143	0.03208	1.314
0.05710	0.8619	0.05679	0.9975	0.05266	1.149	0.04327	1.321
0.06608	0.8657	0.06725	1.002	0.05749	1.152	0.04846	1.325

transfer of the solute from the ground to the transition-state solvents,  $\Delta G_2^0(1-1')$ . It will also contain the free energy of solute through its own viscous transition state,  $\Delta G_2^0(2-2')$ .  $\Delta G_2^0(1-1')$  can be obtained from the measured  $\Delta\mu_2^{0\neq}$  values and  $\Delta G_2^0(2-2')$ , which equal to  $\Delta\mu_1^{0\neq}$  [30]. The values of  $\Delta G_2^0(1-1')$  have been collected in Table 5.

#### 4. Discussion

The values of  $B$ -coefficient for the amino acids in aqueous sodium acetate solutions, as given in Table 3, reflect the net effects of the charged groups and the hydrophobic  $\text{CH}_2$  groups on the amino acids. These two effects can be separated by noting that the  $B$ -coefficients are linear in  $n_C$ ,

Table 3

Viscosity  $B$ -coefficients for  $\alpha$ -amino acids in aqueous sodium acetate solutions at 298.15 and 308.15 K

Amino acid	$B/\text{dm}^3 \text{mol}^{-1}$			
	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
298.15 K				
Gly	$0.1438 \pm 0.0009$	$0.1466 \pm 0.0007$	$0.1505 \pm 0.0009$	$0.151 \pm 0.002$
DL-ala	$0.268 \pm 0.001$	$0.269 \pm 0.002$	$0.272 \pm 0.002$	$0.275 \pm 0.002$
DL-abu	$0.372 \pm 0.006$	$0.3750 \pm 0.0003$	$0.377 \pm 0.001$	$0.381 \pm 0.003$
DL-val	$0.454 \pm 0.003$	$0.457 \pm 0.003$	$0.466 \pm 0.002$	$0.469 \pm 0.003$
DL-leu	$0.506 \pm 0.004$	$0.518 \pm 0.002$	$0.545 \pm 0.005$	$0.551 \pm 0.004$
308.15 K				
Gly	$0.147 \pm 0.002$	$0.151 \pm 0.001$	$0.153 \pm 0.001$	$0.1521 \pm 0.0008$
DL-ala	$0.251 \pm 0.002$	$0.257 \pm 0.001$	$0.260 \pm 0.001$	$0.266 \pm 0.004$
DL-abu	$0.341 \pm 0.003$	$0.349 \pm 0.001$	$0.352 \pm 0.003$	$0.357 \pm 0.001$
DL-val	$0.418 \pm 0.004$	$0.423 \pm 0.003$	$0.430 \pm 0.001$	$0.435 \pm 0.002$
DL-leu	$0.477 \pm 0.005$	$0.491 \pm 0.001$	$0.505 \pm 0.002$	$0.518 \pm 0.004$

the number of carbon atom in alkyl chain, i.e.

$$B = B(\text{NH}_3^+, \text{COO}^-) + n_{\text{C}} B(\text{CH}_2) \quad (7)$$

The regression parameters,  $B(\text{NH}_3^+, \text{COO}^-)$ , the charged end group contribution and  $B(\text{CH}_2)$ , the methylene group contribution to  $B$ -coefficients, are listed in Table 6. Similar linear correlation has been found for some amino acids in aqueous potassium thiocyanate [16], guanidine hydrochloride [20], urea [31] and sodium butyrate [26] solutions. However, it should be pointed out that

$B(\text{CH}_2)$  obtained here characterizes the mean contribution of CH and  $\text{CH}_3$  groups to  $B$ -coefficients of the amino acids.

The  $B$  value of glycine increases with increasing temperature in all the solvent compositions. Since  $(\text{d}B/\text{d}T)$  is positive for a structure-breaking solute [32], we can classify glycine as a structure breaker in water–sodium acetate mixtures. The other amino acids, which have negative  $\text{d}B/\text{d}T$  values, are structure-makers. The  $\text{d}B/\text{d}T$  values obtained in this work for the groups (Table 6) confirm that

Table 4

Activation free energies,  $\Delta\mu_2^{0*}$ , for viscous flow of amino acids in aqueous sodium acetate solutions at 298.15 and 308.15 K

Amino acid	$\Delta\mu_2^{0*}/\text{kJ mol}^{-1}$			
	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
298.15 K				
Gly	$32.7 \pm 0.1$	$33.30 \pm 0.09$	$34.0 \pm 0.1$	$34.3 \pm 0.3$
DL-ala	$51.9 \pm 0.1$	$52.1 \pm 0.3$	$52.3 \pm 0.3$	$52.7 \pm 0.3$
DL-abu	$68.0 \pm 0.8$	$68.17 \pm 0.04$	$68.2 \pm 0.1$	$68.6 \pm 0.4$
DL-val	$81.1 \pm 0.4$	$81.2 \pm 0.4$	$81.9 \pm 0.3$	$82.0 \pm 0.4$
DL-leu	$90.4 \pm 0.5$	$91.5 \pm 0.3$	$94.6 \pm 0.7$	$94.9 \pm 0.5$
308.15 K				
Gly	$33.6 \pm 0.3$	$34.4 \pm 0.1$	$34.9 \pm 0.1$	$34.9 \pm 0.1$
DL-ala	$50.6 \pm 0.3$	$51.4 \pm 0.1$	$51.8 \pm 0.1$	$52.6 \pm 0.3$
DL-abu	$65.2 \pm 0.4$	$66.2 \pm 0.1$	$66.3 \pm 0.4$	$66.8 \pm 0.1$
DL-val	$78.1 \pm 0.6$	$78.5 \pm 0.4$	$79.0 \pm 0.1$	$79.4 \pm 0.3$
DL-leu	$88.7 \pm 0.7$	$90.1 \pm 0.1$	$91.5 \pm 0.3$	$92.8 \pm 0.5$

Table 5

Thermodynamic activation parameters of transfer for the amino acids from ground-state to transition-state in aqueous sodium acetate solutions at 298.15 and 308.15 K

Amino acid	$\Delta G_2^{\ddagger}(1-1')/\text{kJ mol}^{-1}$			
	$m_s = 0.5$	$m_s = 1.0$	$m_s = 1.5$	$m_s = 2.0$
298.15 K				
Gly	$23.1 \pm 0.1$	$23.31 \pm 0.09$	$23.6 \pm 0.1$	$23.5 \pm 0.1$
DL-ala	$42.3 \pm 0.1$	$42.1 \pm 0.3$	$41.9 \pm 0.3$	$41.9 \pm 0.8$
DL-abu	$58.4 \pm 0.8$	$58.18 \pm 0.04$	$57.8 \pm 0.1$	$57.8 \pm 0.4$
DL-val	$71.5 \pm 0.4$	$71.2 \pm 0.4$	$71.5 \pm 0.3$	$71.2 \pm 0.5$
DL-leu	$80.8 \pm 0.5$	$81.5 \pm 0.3$	$84.2 \pm 0.7$	$84.1 \pm 0.4$
308.15 K				
Gly	$24.3 \pm 0.3$	$24.6 \pm 0.1$	$24.8 \pm 0.1$	$24.4 \pm 0.1$
DL-ala	$41.3 \pm 0.3$	$41.6 \pm 0.1$	$41.6 \pm 0.1$	$42.1 \pm 0.3$
DL-abu	$55.9 \pm 0.4$	$56.4 \pm 0.1$	$56.1 \pm 0.4$	$56.3 \pm 0.1$
DL-val	$68.8 \pm 0.6$	$68.7 \pm 0.4$	$68.8 \pm 0.1$	$68.9 \pm 0.3$
DL-leu	$79.4 \pm 0.7$	$80.3 \pm 0.1$	$81.3 \pm 0.3$	$82.3 \pm 0.5$

Table 6

Contributions of zwitterionic group ( $\text{NH}_3^+, \text{COO}^-$ ) and  $\text{CH}_2$  group to viscosity  $B$ -coefficients of the amino acids at 298.15 and 308.15 K

Group	$B/\text{dm}^3 \text{ mol}^{-1}$			
	$m_s=0.5$	$m_s=1.0$	$m_s=1.5$	$m_s=2.0$
298.15 K				
$(\text{NH}_3^+, \text{COO}^-)$	$0.076 \pm 0.027$	$0.074 \pm 0.024$	$0.067 \pm 0.016$	$0.067 \pm 0.017$
$\text{CH}_2-$	$0.091 \pm 0.008$	$0.093 \pm 0.007$	$0.098 \pm 0.005$	$0.099 \pm 0.005$
308.15 K				
$(\text{NH}_3^+, \text{COO}^-)$	$0.079 \pm 0.017$	$0.080 \pm 0.015$	$0.077 \pm 0.013$	$0.076 \pm 0.013$
$\text{CH}_2-$	$0.083 \pm 0.005$	$0.085 \pm 0.005$	$0.087 \pm 0.004$	$0.090 \pm 0.004$

the charged end groups are structure-breakers and  $\text{CH}_2$  groups are structure-makers. In glycine the hydrophobic stabilization effect of  $\text{CH}_2$  is over-compensated by structure breaking of  $(\text{NH}_3^+, \text{COO}^-)$ . In the case of other amino acids, owing to the increase of alkyl chain, the hydrophobic stabilization is effective and we observed a negative  $\text{dB}/\text{dT}$  as a result of net structure-making effect. On the other hand,  $B$ -coefficient values of the amino acids increase with concentration of sodium acetate, indicating the promotion of liquid structure in the presence of sodium acetate.

It is interesting to note that at a given concentration of sodium acetate, the variation of the viscosity of amino acid + sodium acetate + water solutions with the concentration of amino acids can be expressed by the following equation

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

Values of the fitted parameters  $a_1$  and  $a_2$  are listed in Table 7.

The values of  $\Delta\mu_1^{0\neq}$  for 0.5, 1.0, 1.5 and 2.0 mol  $\text{kg}^{-1}$  sodium acetate solutions are 9.58, 9.99, 10.39, 10.80  $\text{kJ mol}^{-1}$  at 298.15 K and 9.35, 9.76, 10.15, 10.55  $\text{kJ mol}^{-1}$  at 308.15 K, respectively. It is evident from the data in Table 4 and Table 5 that  $\Delta\mu_2^{0\neq}$  and  $\Delta G_2^0(1-1')$  values are positive and much larger than  $\Delta\mu_1^{0\neq}$ . This suggests that the formation of the transition state is less favored in the presence of the amino acids, and the formation of the transition state is accompanied by the breaking and distortion of the intermolecular bonds. On the other hand, the values of  $\Delta G_2^0(1-$

$1')$  increase from glycine to leucine at given temperatures. Thus, more energy is need for the amino acids, which have longer alkyl chains, transferring from the ground-state solvent to the transition-state solvent. Accordingly, more solute–solvent bonds must be broken to form the transition state. Therefore  $\Delta\mu_2^{0\neq}$  should increase gradually from glycine to leucine. From the data in Table 5, the same conclusion can be drawn. Because the interactions of the charged end groups for different amino acids with sodium acetate are the same, and those of the charged end groups for different amino acids with water are also the same, it can be deduced that the increasing  $\Delta\mu_2^{0\neq}$  comes from the difference in interactions of the alkyl groups of the amino acids with sodium acetate and in those with water molecules in the solvent mixtures. The interaction between amino acids and water increases with the size of the nonpolar part of the molecule [33]. The results obtained from volumetric properties of amino acids in aqueous sodium acetate [24,25] showed that more hydrophobic amino acids undergo more dehydration effect of sodium acetate. The study on the interaction between amino acid and alkyl-chloride [13] also showed that the more the ion–dipole interaction, the more the dehydration affects. Thus, sodium acetate has larger effect on amino acids with longer alkyl chain. Palecz [34] has determined the enthalpic pair interaction coefficients values of the interaction between L- $\alpha$ -amino acids and electrolyte in water and suggested that an amino acid–NaCl interaction in water became more endothermic and grew up according to the growth

of alkyl group of side chain in the order glycine < alanine < aminobutyrate < valine < leucine. Therefore, the interactions of the alkyl groups with sodium acetate and water molecules increase with increasing alkyl chains length of the amino acids, and  $\Delta\mu_2^{0\neq}$  increase gradually from glycine to leucine.

As for the  $B$ -coefficient,  $\Delta\mu_2^{0\neq}$  also vary linearly with  $n_C$ . The regression of  $\Delta\mu_2^{0\neq} - n_C$  data using Eq. (9) gives  $\Delta\mu_2^{0\neq}(\text{NH}_3^+, \text{COO}^-)$  and  $\Delta\mu_2^{0\neq}(\text{CH}_2)$  as the respective contributions of  $(\text{NH}_3^+, \text{COO}^-)$  and the  $\text{CH}_2$  groups.

$$\Delta\mu_2^{0\neq} = \Delta\mu_2^{0\neq}(\text{NH}_3^+, \text{COO}^-) + n_C \Delta\mu_2^{0\neq}(\text{CH}_2) \quad (9)$$

It can be seen from Table 8 that  $\Delta\mu_2^{0\neq}(\text{CH}_2)$  decreases whereas  $\Delta\mu_2^{0\neq}(\text{NH}_3^+, \text{COO}^-)$  increases from 298.15 to 308.15 K, giving a positive and

Table 8

Contributions of zwitterionic group  $(\text{NH}_3^+, \text{COO}^-)$  and  $\text{CH}_2$  group to the activation free energies of the amino acids at 298.15 and 308.15 K

Group	$\Delta\mu_2^{0\neq}/\text{kJ mol}^{-1}$			
	$m_s=0.5$	$m_s=1.0$	$m_s=1.5$	$m_s=2.0$
298.15 K				
$(\text{NH}_3^+, \text{COO}^-)$	$21.4 \pm 3.6$	$21.6 \pm 3.2$	$21.0 \pm 2.2$	$21.4 \pm 2.2$
$\text{CH}_2^-$	$14.5 \pm 1.1$	$14.5 \pm 1.0$	$15.1 \pm 0.7$	$15.0 \pm 0.7$
308.15 K				
$(\text{NH}_3^+, \text{COO}^-)$	$21.9 \pm 2.3$	$22.6 \pm 2.2$	$22.5 \pm 1.8$	$22.6 \pm 1.8$
$\text{CH}_2^-$	$13.8 \pm 0.7$	$13.8 \pm 0.7$	$14.1 \pm 0.5$	$14.2 \pm 0.6$

negative  $\Delta S_2^{0\neq}$  values, respectively. Similar trends are observed in aqueous guanidine hydrochloride [20] and urea [13]. The positive  $\Delta S_2^{0\neq}(\text{CH}_2)$  shows that the transition state is attained by considerable

Table 7

Coefficients  $a_1$  and  $a_2$  of Eq. (8) for  $\alpha$ -amino acids in aqueous sodium acetate solutions at 298.15 and 308.15 K

Amino acid	298.15 K			308.15 K		
	$a_1$	$a_2$	$\sigma^a$	$a_1$	$a_2$	$\sigma^a$
$m_s=0.5$						
Gly	$1.0429 \pm 0.0003$	$0.142 \pm 0.002$	0.0003	$0.8397 \pm 0.0007$	$0.139 \pm 0.005$	0.0009
DL-ala	$1.0433 \pm 0.0004$	$0.258 \pm 0.003$	0.0005	$0.8385 \pm 0.0002$	$0.248 \pm 0.001$	0.0002
DL-abu	$1.0417 \pm 0.0018$	$0.365 \pm 0.012$	0.0022	$0.8389 \pm 0.0009$	$0.330 \pm 0.006$	0.0010
DL-val	$1.0439 \pm 0.0009$	$0.428 \pm 0.006$	0.0011	$0.8378 \pm 0.0003$	$0.409 \pm 0.002$	0.0003
DL-leu	$1.0437 \pm 0.0005$	$0.483 \pm 0.011$	0.0004	$0.8383 \pm 0.0003$	$0.487 \pm 0.006$	0.0003
$m_s=1.0$						
Gly	$1.2139 \pm 0.0001$	$0.1455 \pm 0.0007$	0.0001	$0.9709 \pm 0.0004$	$0.148 \pm 0.003$	0.0005
DL-ala	$1.2142 \pm 0.0006$	$0.261 \pm 0.004$	0.0007	$0.9708 \pm 0.0004$	$0.250 \pm 0.003$	0.0005
DL-abu	$1.2152 \pm 0.0003$	$0.356 \pm 0.002$	0.0004	$0.9722 \pm 0.0022$	$0.333 \pm 0.014$	0.0027
DL-val	$1.2139 \pm 0.0002$	$0.438 \pm 0.002$	0.0003	$0.9706 \pm 0.0005$	$0.407 \pm 0.003$	0.0006
DL-leu	$1.2139 \pm 0.0002$	$0.514 \pm 0.004$	0.0002	$0.9702 \pm 0.0005$	$0.482 \pm 0.012$	0.0005
$m_s=1.5$						
Gly	$1.4120 \pm 0.0003$	$0.145 \pm 0.002$	0.0004	$1.1203 \pm 0.0004$	$0.146 \pm 0.003$	0.0005
DL-ala	$1.4118 \pm 0.0004$	$0.263 \pm 0.003$	0.0005	$1.1199 \pm 0.0005$	$0.251 \pm 0.003$	0.0006
DL-abu	$1.4123 \pm 0.0002$	$0.359 \pm 0.002$	0.0003	$1.1196 \pm 0.0004$	$0.335 \pm 0.003$	0.0005
DL-val	$1.4123 \pm 0.0003$	$0.441 \pm 0.002$	0.0003	$1.1202 \pm 0.0003$	$0.409 \pm 0.002$	0.0003
DL-leu	$1.4118 \pm 0.0006$	$0.529 \pm 0.014$	0.0005	$1.1196 \pm 0.0004$	$0.495 \pm 0.001$	0.00003
$m_s=2.0$						
Gly	$1.6476 \pm 0.0003$	$0.141 \pm 0.002$	0.0003	$1.2930 \pm 0.0003$	$0.148 \pm 0.002$	0.0004
DL-ala	$1.6464 \pm 0.0004$	$0.263 \pm 0.002$	0.0005	$1.2945 \pm 0.0005$	$0.252 \pm 0.002$	0.0007
DL-abu	$1.6443 \pm 0.0005$	$0.370 \pm 0.003$	0.0006	$1.2936 \pm 0.0004$	$0.340 \pm 0.003$	0.0005
DL-val	$1.6448 \pm 0.0004$	$0.449 \pm 0.003$	0.0005	$1.2927 \pm 0.0005$	$0.410 \pm 0.003$	0.0006
DL-leu	$1.6446 \pm 0.0003$	$0.556 \pm 0.008$	0.0003	$1.2932 \pm 0.0004$	$0.501 \pm 0.011$	0.0003

<sup>a</sup> Standard deviations of the fit.

Table 9

Parameters  $A_1$  and  $A_2$  of Eq. (10) for the amino acids in aqueous sodium acetate solutions at 298.15 and 308.15 K

$m_s$ (mol kg <sup>-1</sup> )	$-A_1/\text{dm}^3 \text{ mol}^{-1}$	$A_2$	$R^a$	$\sigma^b$
298.15 K				
0.5	$0.097 \pm 0.040$	$5.8 \pm 0.5$	0.989	0.025
1.0	$0.111 \pm 0.036$	$6.1 \pm 0.4$	0.992	0.022
1.5	$0.135 \pm 0.026$	$6.4 \pm 0.3$	0.996	0.016
2.0	$0.145 \pm 0.025$	$6.6 \pm 0.3$	0.997	0.015
308.15 K				
0.5	$0.076 \pm 0.026$	$5.2 \pm 0.3$	0.994	0.016
1.0	$0.088 \pm 0.022$	$5.5 \pm 0.3$	0.996	0.014
1.5	$0.101 \pm 0.019$	$5.7 \pm 0.2$	0.997	0.011
2.0	$0.115 \pm 0.020$	$5.9 \pm 0.2$	0.997	0.012

<sup>a</sup>  $R$  the correlation coefficient.

<sup>b</sup>  $\sigma$  the standard deviations of the fit.

solvent–solute bond breaking. For polar ( $\text{NH}_3^+$ ,  $\text{COO}^-$ ) groups, the solute–solvent bonds will be made in the transition state.

Moreover, it is observed that  $B$ -coefficients show a linear correlation with the standard partial molar volumes  $V_{2,\phi}^0$  reported previously [24,25] for the  $\alpha$ -amino acids in aqueous sodium acetate solutions. That means

$$B = A_1 + A_2 V_{2,\phi}^0 \quad (10)$$

The coefficients  $A_1$  and  $A_2$  are given in Table 9 together with their standard deviations and the correlation coefficients. The  $A_2$  value reflects the size and shape of the solute and lies between 0 and 2.5 for unsolvated spherical species [35]. It can be noted from Table 9 that the value is greater than 2.5 and increases with molality of sodium acetate at given temperatures. This can be explained that if one assumes that the increase in viscosity is predominately due to the increased resistance offered by the more structured solvent to the moving amino acid moiety, though solvation effects may also contribute.

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