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Enthalpies of dilution of glycine, L-alanine and L-serine in aqueous potassium chloride solutions

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Abstract

The dilution enthalpies of glycine, L-alanine and L-serine in aqueous potassium chloride solutions of various molalities have been determined using LKB-2277 flow microcalorimetry at 298.15 K. The homogeneous enthalpic interaction coefficients over the whole range of aqueous potassium chloride solutions investigated have been calculated according to the excess enthalpy concept. It is found that pairwise enthalpic interaction coefficients h_2 of glycine and L-serine are all negative and become less negative with increasing of the molalities of potassium chloride, while pairwise enthalpic interaction coefficients h_2 of L-alanine are positive on which the influence of potassium chloride is not obvious. The results are interpreted from the point of view of solute–solute interactions involved by solvent effects. © 2004 Elsevier B.V. All rights reserved.

Keywords: Glycine; L-alanine; L-serine; Potassium chloride; Dilution enthalpy; Structural interactions; Electrostatic interactions

1. Introduction

The study of the thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigation [1]. Amino acids and peptides are used as probe molecules to understand the complex nature of proteins. There is information on the zwitterionic nature of amino acids in water in the literature [2–5]. The properties of proteins, such as their structure, solubility, denaturation, activity of enzymes, are greatly influenced by electrolytes [6,7]. The property of electrolyte known as structure-maker or structure-breaker has been widely used to understand the effect of electrolytes on the structure and function of both proteins and nucleic acids [3–10].

In biological fluids of living organisms, there contains a specified quantity of ions, especially sodium, potassium and chloride ions, which are indispensable for the metabolic processes of living organism to proceed [11]. Information is available on activity coefficients, enthalpies and heat capacities of aqueous amino acids in electrolytes [12–18]. But most of the research works are focus on the dissolution

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or mixing enthalpies between amino acids and electrolytes [19–22]. A survey of the literatures indicates a lack of experimental data of the dilution enthalpies of amino acid in aqueous electrolyte solutions. Glycine is the most simple amino acid in nature. L-serine is the amino acid with polar side-chain $-CH_2OH$. L-alanine is the amino acid with apolar side-chain $-CH_3$. Based on the research of polar and apolar amino acids, it is well understand the effect of hydroxyl and alkyl group on the interactions of protein's interiors. In this paper, the dilution enthalpies of glycine, L-alanine and L-serine in aqueous potassium chloride solutions of various molalities at 298.15 K and the homogeneous enthalpic interaction coefficients of glycine, L-alanine and L-serine have been reported. The results are interpreted from the point of view of electrostatic interaction and structural interaction.

2. Experimental

2.1. Reagents

Biochemical reagent grade glycine, L-alanine and L-serine were used after recrystallization from methanol–water mixtures and drying in vacuum over P_2O_5 at room temperature for at least 72 h. Analytical reagent grade KCl were recrystallized from distilled water and dried under reduced

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pressure for 72 h at 353 K. The water used for the preparation of solutions was deionized and distilled using a quartz sub-boiling purifier.

Both the aqueous salt solutions, which were used as mixed solvents (water + potassium chloride), and the amino acid solutions (amino acid + potassium chloride + water) were prepared by mass using a Hancpinc FA 1004 balance precise to ± 0.1 mg. All the solutions were degassed and used within 12 h after preparation.

2.2. Calorimetric procedure

The enthalpies of dilution for amino acids in aqueous salt solutions were measured with LKB-2277 BioActivity Monitor at 298.15 K. The solutions were pumped through the mixing-flow vessel of the calorimeter in different rates using a LKB-L010011 microperpex peristaltic pump. The variation in flow rates was less than 0.2%. The flow rates were determined by weighing the masses of the liquids through each tube within 3 min. The variation in flow rates was less than 0.1% both before and after a complete dilution experiment. The liquids passing through tubes A and B were changed in the following sequence:

- 1. A (aqueous salt solution) + B (aqueous salt solution) baseline determined;
- 2. A (aqueous salt solution) + B (amino acid solution) dilution thermal power determined;
- 3. A (aqueous salt solution) + B (aqueous salt solution) baseline re-established.

The enthalpies of dilution $\Delta_{dil}H_m$ were calculated from the equation:

$$\Delta_{\rm dil}H_m = \frac{P(1+m_{\rm i}M)}{m_{\rm i}f_2} \tag{1}$$

in which *P* is the dilution thermal power (μ W), *M* the molar mass of amino acid (kg mol⁻¹) and *f*₂ the flow rate of amino acid solution (mg s⁻¹). The final molality *m*_f was calculated from the equation:

$$m_{\rm f} = \frac{m_{\rm i} f_2}{[f_1(m_{\rm i} M_2 + 1) + f_2]} \tag{2}$$

in which f_1 is the flow rate of diluent (aqueous salt solution).

3. Results and discussion

According to the McMillan–Mayer theory [18], all the thermodynamic properties of multi-components solutions can be expressed by using a virial expansion in m which relates the non-ideal contributions of any total thermodynamic function to a series of interaction parameters. If aqueous potassium chloride solution is regarded as "solvent", the excess enthalpy per kg of solvent (H^E) of a solution containing a single amino acid at molality m is given by:

$$H^{\rm E} = h_2 m^2 + h_3 m^3 + h_4 m^4 + \cdots$$
 (3)

in which h_2 , h_3 , h_4 , etc. are the enthalpic coefficients representing pairwise and, at least notionally, triplet, quarter and higher order interactions between solvated solute species. The molar enthalpy change ($\Delta_{dil}H_m$) on diluting a solution of non-electrolytic solute from an initial molality (m_i) to a final molality (m_f) can be written as

$$\Delta_{\rm dil} H_m = H_m^{\rm E}(m_{\rm f}) - H_m^{\rm E}(m_{\rm i})$$

= $h_2(m_{\rm f} - m_{\rm i}) + h_3(m_{\rm f}^2 - m_{\rm i}^2)$
+ $h_4(m_{\rm f}^3 - m_{\rm i}^3) + \cdots$ (4)

where $H_m^E(m_i)$ and $H_m^E(m_f)$ are the molar excess enthalpies of the solute in the solutions before and after dilution.

Tables 1–3 give the experimental values ($\Delta_{dil}H_m$), together with the initial and final molalities $(m_i \text{ and } m_f)$ of glycine, L-alanine and L-serine in various aqueous potassium chloride solutions. Tables 4–6 list the coefficients of Eq. (4) that were obtained from least-squares analysis of above results. Since it is difficult to interpret the higher h coefficients, only the enthalpic pairwise coefficient h_2 is discussed here. The h_2 values of glycine, L-alanine and L-serine in pure water are -466.20, 205.36 and -740.30 J kg mol⁻², respectively, which are in good agreement with those obtained by other workers [23,24]. From Fig. 1, it can be seen that the enthalpic pair interaction coefficients of glycine and L-serine are all negative and become less negative with increasing KCl concentrations, at the same time the h_2 coefficients for L-serine are more negative than that for glycine, while pairwise enthalpic interaction coefficients h_2 of L-alanine is positive on which the influence of potassium chloride is not obvious.

It is generally accepted that the h_2 coefficients are attributable to the interaction between two solvated solute



Fig. 1. Variations in enthalpic pair interaction coefficients (h_2) of glycine, L-alanine and L-serine with the molality (m) of potassium chloride in aqueous potassium chloride solutions at 298.15 K: (\bigcirc) glycine; (\blacksquare) L-serine; (\blacktriangle) L-alanine.

Table 1	
Enthalpies of dilution of glycine in aque	ous potassium chloride solutions at 298.15 K

m (KCl) (mol kg ⁻¹)	$m_{\rm i}~({\rm mol}{\rm kg}^{-1})$	$m_{\rm f} ({\rm mol}{\rm kg}^{-1})$	$\Delta_{\rm dil} H_m \ ({\rm J} {\rm mol}^{-1})$	$m_{\rm i}~({\rm mol}{\rm kg}^{-1})$	$m_{\rm f}~({\rm molkg^{-1}})$	$\Delta_{\rm dil} H_m \ ({\rm J} {\rm mol}^{-1})$
0	0.1053	0.0521	23.28	0.2723	0.1337	58.40
	0.1439	0.0708	32.32	0.2898	0.1425	61.35
	0.1786	0.0881	38.97	0.3046	0.1492	63.47
	0.2081	0.1026	45.18	0.3319	0.1630	69.21
	0.2330	0.1147	50.04	0.3555	0.1745	73.89
	0.2461	0.1212	51.99	0.4206	0.2062	85.03
0.2001	0.2305	0.1148	45.96	0.5294	0.2615	98.09
	0.2673	0.1332	51.01	0.5757	0.2834	104.67
	0.2988	0.1484	59.06	0.6689	0.3294	118.52
	0.3302	0.1635	64.63	0.7133	0.3507	124.98
	0.3720	0.1848	71.46	0.7607	0.3743	131.31
	0.4081	0.2025	77.72	0.8379	0.4122	140.35
	0.4747	0.2358	88.50			
0.3796	0.2574	0.1265	47.38	0.5904	0.2873	99.27
	0.3198	0.1565	57.87	0.6576	0.3194	108.68
	0.3571	0.1748	64.05	0.7055	0.3422	114.95
	0.4107	0.2009	72.38	0.7449	0.3606	120.98
	0.4587	0.2240	79.88	0.8016	0.3885	127.25
	0.5071	0.2474	87.01	0.8912	0.4310	138.46
	0.5537	0.2696	93.90			
0.6107	0.2345	0.1131	39.09	0.6104	0.2921	90.59
	0.2718	0.1310	44.42	0.6612	0.3148	98.22
	0.3157	0.1519	50.81	0.6979	0.3331	102.37
	0.3716	0.1784	59.10	0.7445	0.3554	106.96
	0.4358	0.2092	68.19	0.7986	0.3804	113.67
	0.4916	0.2354	75.73	0.8902	0.4230	124.12
	0.5611	0.2683	84.90			
0.8445	0.1784	0.0834	26.57	0.5957	0.2769	81.78
	0.2319	0.1079	34.90	0.6602	0.3034	90.85
	0.2870	0.1334	42.90	0.7221	0.3284	99.34
	0.3471	0.1624	50.54	0.7856	0.3611	104.04
	0.4096	0.1911	58.98	0.8557	0.3940	110.69
	0.4749	0.2191	68.45	0.9085	0.4183	116.08
	0.5312	0.2456	75.05			
1.0107	0.1809	0.0860	25.44	0.5935	0.2775	76.04
	0.2397	0.1129	33.67	0.6554	0.3075	81.62
	0.2974	0.1398	41.30	0.7197	0.3355	89.51
	0.3560	0.1672	48.43	0.7820	0.3631	95.99
	0.4145	0.1947	55.89	0.8485	0.3973	101.37
	0.4672	0.2197	61.44	0.9018	0.4202	106.28
	0.5279	0.2482	68.32			
1.3855	0.1862	0.0893	21.76	0.5941	0.2802	63.49
	0.2282	0.1078	27.13	0.6634	0.3123	69.48
	0.2825	0.1341	32.83	0.7286	0.3450	73.81
	0.3426	0.1625	39.06	0.7886	0.3682	80.61
	0.4035	0.1908	45.62	0.8622	0.4040	85.61
	0.4626	0.2186	51.43	0.9125	0.4264	89.81
	0.5291	0.2498	57.65			

molecules and very sensitive to solvent variation. The interaction of non-electrolyte with electrolyte consists of electrostatic and structural interactions. Lilley et al. [25] considered the interactions between electrolyte and amino acids consist of three effects: (a) electrostatic interaction; (b) partial desolvation of solutes; (c) solvent reorganization [19]. The latter two effects belong to the class of structural interactions. Desonyers and co-workers [26] gave a general discussion for structural interactions, and thought that in most cases the net effect of the co-sphere overlap on the hydration structure is destructive. Structural interactions make quite a large contribution to the enthalpic function, and sometimes surpasses the effect of electrostatic interaction even predominate [25,27,28]. It can be concluded that the interactions of the ions of electrolyte with the polar groups of non-electrolyte are electrostatic, accompanied by partial

Table 2					
Enthalpies of dilution of L-serine in	n aqueous	potassium	chloride	solutions	at 298.15 K

m (KCl) (mol kg ⁻¹)	$m_{\rm i}~({\rm mol}{\rm kg}^{-1})$	$m_{\rm f}~({\rm molkg^{-1}})$	$\Delta_{\operatorname{dil}} H_m \ (\operatorname{J} \operatorname{mol}^{-1})$	$m_i \pmod{\mathrm{kg}^{-1}}$	$m_{\rm f}~({\rm molkg^{-1}})$	$\Delta_{\rm dil} H_m \ ({\rm J} {\rm mol}^{-1})$
0	0.0791	0.0388	27.74	0.2769	0.1352	90.01
	0.1119	0.0549	38.54	0.3039	0.1481	98.03
	0.1427	0.0699	48.42	0.3320	0.1619	105.80
	0.1672	0.0819	56.32	0.3606	0.1754	114.15
	0.1967	0.0963	65.67	0.3835	0.1867	120.02
	0.2222	0.1086	73.81	0.4123	0.2001	128.75
	0.0851	0.0440	25.03	0.2653	0.1370	73.53
	0.1073	0.0556	31.14	0.2898	0.1496	79.46
	0.1347	0.0689	40.31	0.3133	0.1617	85.29
0.3149	0.1618	0.0837	46.51	0.3459	0.1784	93.97
	0.1882	0.0973	53.831	0.3728	0.1922	99.75
	0.2153	0.1111	61.05	0.3985	0.2057	104.85
	0.2432	0.1254	68.06			
	0.0840	0.0451	23.02	0.2736	0.1460	69.95
	0.1104	0.0592	30.08	0.2994	0.1597	76.09
	0.1398	0.0749	37.37	0.3251	0.1722	82.36
0.4040	0.1671	0.0896	44.34	0.3513	0.1871	87.19
	0.1922	0.1029	50.54	0.3769	0.2003	93.26
	0.2205	0.1180	57.28	0.3983	0.2118	97.51
	0.2483	0.1327	64.18			
	0.0833	0.0424	22.63	0.2632	0.1329	67.70
	0.1086	0.0553	29.09	0.2878	0.1452	73.44
	0.1370	0.0699	36.82	0.3085	0.1554	78.32
0.5019	0.1663	0.0848	43.72	0.3396	0.1720	83.98
	0.1957	0.0990	51.82	0.3684	0.1864	90.05
	0.2199	0.1115	57.01	0.3960	0.2002	96.08
	0.2402	0.1214	62.23			
	0.0813	0.0422	19.24	0.2654	0.1374	60.30
	0.1099	0.0572	25.90	0.2947	0.1524	66.61
	0.1299	0.0676	30.57	0.3175	0.1644	70.68
0.7045	0.1542	0.0802	36.16	0.3458	0.1786	76.73
	0.1834	0.0954	42.70	0.3728	0.1926	82.83
	0.2093	0.1086	48.36	0.3969	0.2051	86.02
	0.2349	0.1218	53.90			
	0.0822	0.0427	18.81	0.2660	0.1375	57.30
	0.1054	0.0546	24.02	0.2937	0.1514	63.14
	0.1304	0.0677	29.36	0.3227	0.1667	68.01
0.8524	0.1558	0.0809	34.71	0.3502	0.1802	74.40
	0.1879	0.0974	41.40	0.3758	0.1933	78.47
	0.2144	0.1110	46.89	0.4018	0.2068	82.52
	0.2388	0.1236	51.70	011010	0.2000	02102
	0.0854	0.0452	16.60	0.2616	0 1377	50.48
	0.1087	0.0575	21.01	0.2909	0.1531	55.41
1 0220	0.1346	0.0710	26 39	0.3180	0 1660	61.30
1.0220	0.1573	0.0832	30.75	0.3473	0.1825	65.41
	0.1373	0.0032	36.39	0.3734	0.1025	60.30
	0.1005	0.1120	41 0 7	0.3734	0.1950	73 12
	0.2404	0.1268	46.47	0.3711	0.2004	15.72
	0.2101	0.1200				

desolvation of the solutes, whereas the interactions with the apolar groups are mainly structural.

Gallardo et al. [29] have measured the homogeneous enthalpic pairwise parameters of some amino acids in water and given two modules of the association for the α -amino acids. One is in a side-by-side manner and the other in a head-on-fashion. For zwitterionic amino acids in solution, the configuration likely to contribute most to the pairwise interaction is that in which the molecular association is side-on with the positively charged amino group and its associated co-sphere of one amino acid interacting with the solvated negatively charged carboxyl group of the second molecule [30]. Such strong electrostatic interactions are expected to result in a coalescence of the solvation shells of the charged groups, with a subsequent relaxation of solvent molecules to the bulk solvent. If this effect dominates the pairwise inter-

Table 3						
Enthalpies of dilution	of L-alanine in	aqueous	potassium	chloride	solutions	at 298.15 K

m (KCl) (mol kg ⁻¹)	$m_{\rm i}~({\rm mol}{\rm kg}^{-1})$	$m_{\rm f}~({\rm mol}{\rm kg}^{-1})$	$\Delta_{\rm dil} H_m \ ({\rm J} { m mol}^{-1})$	$m_{\rm i}~({\rm mol}{\rm kg}^{-1})$	$m_{\rm f}~({\rm molkg^{-1}})$	$\Delta_{\rm dil} H_m \ ({\rm J} { m mol}^{-1})$
0	0.1440	0.0688	-15.46	0.5500	0.2608	-61.56
	0.2177	0.1044	-23.77	0.5729	0.2716	-64.15
	0.2731	0.1306	-30.12	0.6342	0.2999	-71.15
	0.3523	0.1680	-39.21	0.6609	0.3121	-74.77
	0.3979	0.1897	-43.79	0.6975	0.3297	-77.97
	0.4633	0.2204	-51.49	0.7481	0.3524	-84.15
	0.1649	0.0779	-19.15	0.5373	0.2510	-64.15
	0.2091	0.0988	-23.86	0.5943	0.2770	-69.90
	0.2670	0.1259	-31.04	0.6496	0.3026	-76.51
0.2022	0.3196	0.1502	-37.82	0.6977	0.3233	-82.47
	0.3753	0.1762	-44.05	0.7573	0.3510	-89.65
	0.4307	0.2018	-50.59	0.8043	0.3723	-95.51
	0.4802	0.2242	-56.72			
	0.1648	0.0783	-18.43	0.5344	0.2507	-62.34
	0.2287	0.1085	-25.98	0.5397	0.2531	-62.94
	0.2713	0.1283	-31.17	0.6377	0.2980	-74.13
0.3062	0.2921	0.1381	-33.96	0.6970	0.3251	-81.02
	0.3655	0.1720	-42.57	0.7394	0.3450	-86.34
	0.4462	0.2096	-51.72	0.8009	0.3725	-93.69
	0.4996	0.2346	-58.03			
	0.1470	0.0699	-17.72	0.5840	0.2736	-70.64
	0.2154	0.1023	-25.65	0.6255	0.2924	-75.52
	0.2932	0.1387	-35.52	0.6932	0.3236	-83.40
0.4027	0.3535	0.1665	-42.49	0.7427	0.3463	-89.52
	0.4093	0.1897	-50.70	0.7436	0.3469	-89.35
	0.4631	0.2181	-56.10	0.8116	0.3782	-97.20
	0.5209	0.2449	-62.27			
	0.1562	0.0746	-18.66	0.5319	0.2514	-64.84
	0.2167	0.1036	-25.97	0.5865	0.2763	-71.65
	0.2594	0.1244	-30.78	0.6470	0.3049	-78.67
0.5247	0.3120	0.1486	-37.70	0.7026	0.3308	-85.55
	0.3645	0.1733	-44.12	0.7357	0.3456	-89.85
	0.4210	0.2000	-51.09	0.8079	0.3769	-99.39
	0.4708	0.2232	-57.70			
	0.1438	0.0695	-18.18	0.5191	0.2481	-67.55
	0.2076	0.1005	-26.23	0.5766	0.2758	-75.14
	0.2567	0.1236	-33.25	0.6345	0.3029	-83.05
0.8578	0.3054	0.1470	-39.67	0.6950	0.3299	-91.09
	0.3661	0.1764	-47.54	0.7511	0.3559	-98.43
	0.4109	0.1976	-52.73	0.8029	0.3811	-104.83
	0.4687	0.2251	-60.88			
	0.1487	0.0701	-20.08	0.5204	0.2424	-71.22
	0.2015	0.0955	-26.46	0.5794	0.2710	-78.64
0.9987	0.2558	0.1205	-34.90	0.6308	0.2938	-85.88
	0.3088	0.1446	-42.13	0.7817	0.3623	-106.93
	0.3580	0.1678	-48.92	0.8416	0.3906	-113.77
	0.4160	0.1951	-56.93	0.9009	0.4172	-121.47
	0.4668	0.2201	-63.23			

action, a negative value of h_2 should be observed. Furthermore, the reorganization of solvent due to the coalescence of solvation spheres of the interacting charged groups is also expected to make a negative contribution to h_2 . These effects play an dominant role in the pairwise interaction of glycine as it has no "side-chain-on" carbon. The structural interaction, arising from the apolar side group on the α -carbon, will make positive contribution to h_2 . The exact contribution

will depend on the nature of the side-groups involved. Since the apolar part of glycine is shortest, the structural interaction between a pair of glycine molecules is relatively weak. Hence, the values of h_2 for glycine in water are negative (Fig. 1).

In the pairwise association of L-alanine and L-serine, interactions involving the side-chains will be significant. For L-alanine with apolar side-chain $-CH_3$, positive con-

Table 4								
Enthalpic interaction	coefficients	of	glycine	in	aqueous	potassium	chloride	solutions

m (KCl) (mol kg ⁻¹)	$h_2 (\mathrm{Jkgmol^{-2}})$	$h_3 (\rm J kg^2 mol^{-3})$	$h_4 (\mathrm{Jkg^3mol^{-4}})$	$m_{\rm i} ({\rm mol} {\rm kg}^{-1})$	r
0	-466.20	126.72	-38.73	0-0.40	0.9995
0.2001	-443.50	92.89	-6.55	0-0.90	0.9997
0.3796	-376.93	63.80	-4.14	0-0.90	0.9999
0.6107	-323.84	48.42	-1.30	0-0.90	0.9999
0.8445	-305.08	48.39	-1.54	0-0.90	0.9998
1.0107	-287.38	59.38	-9.41	0-0.90	0.9999
1.3855	-265.11	80.82	-22.63	0-0.90	0.9999

Table 5

Enthalpic interaction coefficients of L-serine in aqueous potassium chloride solutions

m (KCl) (mol kg ⁻¹)	$h_2 (\mathrm{J kg mol^{-2}})$	$h_3 (J kg^2 mol^{-3})$	$h_4 (\mathrm{Jkg^3mol^{-4}})$	$\overline{m_{\rm i} ({\rm mol} {\rm kg}^{-1})}$	r
0	-709.19	194.12	-52.91	0-0.40	0.9999
0.2149	-652.53	201.67	-65.93	0-0.40	0.9998
0.4040	-596.64	113.9	22.06	0-0.40	0.9999
0.4957	-574.69	119.81	28.74	0-0.40	0.9993
0.7045	-520.88	109.76	3.32	0-0.40	0.9998
0.8524	-433.49	-60.63	189.61	0-0.40	0.9998
1.0220	-393.94	-101.74	246.93	0-0.40	0.9998

tributions to h_2 arise from both the interactions between hydrated hydrocarbon chains [30] and those between the hydrated side-chains and the ionic groups [31]. For L-serine with side-chain functional group –OH that can participate in hydrogen bonding, the contributions to h_2 stemming from hydroxyl group–hydroxyl group and hydroxyl group–zwitterionic head group interactions should be negative [32,33]. The fact that the value of h_2 for L-serine is more negative than that for glycine supports this view.

In the ternary solutions under investigation (amino acid + potassium chloride + water), the cation and the anion of electrolyte will undergo electrostatic interactions with the COO^- and NH_3^+ groups of amino acids, respectively, and make a negative contribution to h_2 . As is known, in aqueous solutions, hydration sheaths with defined water molecule order are formed around dissolved molecules or ions. The direct interaction provokes partial dehydration of the ions hydration shells, this being an endothermic process and also another endothermic effect resulting from the removal of a number of water molecules from the hydration shell of the polar head of the amino acid [11]. Therefore the partial dehydration to h_2 . The

larger concentration of KCl, the more the structure of water will be disrupted, the more positive the contribution from desolvation will be. In conclusion, the pairwise enthalpic interaction coefficients h_2 of glycine and L-serine become less negative with increasing of the molalities of potassium chloride.

The positive values of h_2 of L-alanine suggest that interactions involving alkyl side-chains dominate over the zwitterion-zwitterion interactions. The partial dehydration of solutes gives positive contribution to h_2 of L-alanine in aqueous potassium chloride solutions. The domination of interactions involving alkyl groups changes little with increasing of the molalities of potassium chloride, so the influence of potassium chloride on h_2 of L-alanine is not obvious.

For the interaction between electrolyte and zwitterionic ion, Kirkwood [34,35] proposed an electrostatic theory to estimate the contribution of electrostatic to the pairwise interaction parameters. A feature of the Kirkwood approach is the dominant role played by the dipole moment of the amino acid in determining the pairwise interaction parameters. For L-serine with side-chain functional group –OH, the dipole

Table 6

Enthalpic interaction coefficients of L-alanine in aqueous potassium chloride solutions

$\overline{m (\text{KCl}) (\text{mol} \text{kg}^{-1})}$	$h_2 (\mathrm{Jkgmol^{-2}})$	$h_3 (\mathrm{J}\mathrm{kg}^2\mathrm{mol}^{-3})$	$h_4 (\mathrm{Jkg^3mol^{-4}})$	$m_{\rm i} ({\rm mol} {\rm kg}^{-1})$	r
0	205.36	18.89	-14.10	0-0.75	0.9999
0.2022	241.91	-26.62	12.94	0-0.80	0.9998
0.3062	249.41	-41.07	21.42	0-0.80	0.9999
0.4027	234.53	-5.86	-1.95	0-0.80	0.9998
0.5247	244.08	-15.44	6.57	0-0.80	0.9999
0.8578	250.81	4.95	-6.13	0-0.80	0.9999
0.9987	259.48	3.89	-8.83	0-0.80	0.9999

moment is larger than that of glycine, the electrostatic interaction of L-serine is stronger than that of glycine. In addition, hydroxyl group of L-serine can participate in hydrogen bonding in aqueous potassium chloride solutions. The above contributions to h_2 should be negative, so the h_2 coefficients for L-serine are more negative than that for glycine.

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