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Enthalpies of dilution of glycine, L-alanine and L-serine in aqueous ethylene glycol solutions at 298.15 K

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Abstract

Enthalpies of dilution of glycine, L-alanine and L-serine in aqueous ethylene glycol solutions have been measured at 298.15 K by a mixing-flow microcalorimeter. The homogeneous enthalpic interaction coefficients of the three zwitterions have been computed by least-squares fitting on the basis of the McMillan–Mayer theory. The variations of the enthalpic pairwise interaction coefficients with the mass fraction of ethylene glycol in mixtures are interpreted in terms of solute–solute and solute–solvent interactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpies of dilution; Amino acids; Enthalpic pairwise interaction coefficients; Aqueous ethylene glycol solutions

1. Introduction

There is currently a considerable amount of interest in the "non-bonding" solute–solute interactions which occur in aqueous solutions containing amino acids and other organic compounds in cell fluids or compounds with the same functional groups as those existing in biomolecules of living organism [1–9]. The principal reasons for studying such systems are directed towards problems in protein molecular biology, in particular the energetic factors controlling protein folding and assembly and interaction of substrates with the active sites of enzymes.

In our previous studies the enthalpies of dilution of some simple amino acids such as glycine, alanine and serine in aqueous solutions of DMF, ethanol, glucose, sucrose were determined by the method of mixing-flow microcalorimetry [10–17]. The results obtained were discussed from the point of view of molecular interactions on the basis of the modified McMillan–Mayer model [18]. It is well-known that the enthalpic interaction coefficients derived from this model can be considered as measures of intermolecular interactions in solution, and depend significantly on variation in solvent. As a continuation of that work, the present study is aimed at examining the homogenous enthalpic interaction coefficients of glycine, L-alanine and L-serine zwitterions in aqueous ethylene glycol solutions of different compositions.

2. Experimental

Biochemical reagent grade glycine, L-alanine, 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 ethylene glycol was used without further purification. Water was deionized and distilled using a

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quartz sub-boiling purifier. Both the aqueous ethylene glycol solutions (ethylene glycol + water) which were used as mixed solvents (mass fractions of ethylene glycol, w range from 0 to 0.50) and the aqueous amino acid–ethylene glycol solutions (amino acid + ethylene glycol + water) were prepared by mass.

The heat of dilution was measured by a mixing-flow microcalorimeter (LKB-2277 BioActivity Monitor). All the measurements were carried out at 298.15 K. The solutions were pumped through the mixing-cell at constant rates by a pair of microperpex peristaltic pumps (LKB-2132). The flow rates were determined by weighing the masses of the liquids through each pump within 3 min. The liquids passing through pumps A and B were changed in the following sequence:

1. $A_{\text{aqueous ethylene glycol solution}} + B_{\text{aqueous ethylene glycol solution}}$	baseline determined
2. $A_{\text{aqueous ethylene glycol solution}} + B_{\text{amino acid−ethylene glycol solution}}$	dilution thermal power determined
3. $A_{\text{aqueous ethylene glycol solution}} + B_{\text{aqueous ethylene glycol solution}}$	baseline re-established

The molar enthalpies of dilution $\Delta H_{\text{dil,m}}$ were calculated from the equation

$$\Delta H_{\text{dil,m}} = \frac{P(1 + m_{\text{i}}M)}{m_{\text{i}} f_2} \quad (1)$$

in which P is the dilution thermal power (μW), M the molar mass of amino acid (kg mol^{-1}), f_2 the flow rate of amino acid solution (mg s^{-1}). The final molality m_{f} were calculated from the equation

$$m_{\text{f}} = \frac{m_{\text{i}} f_2}{[f_1(m_{\text{i}}M + 1) + f_2]} \quad (2)$$

in which f_1 is the flow rate of diluent (ethylene glycol–water mixture).

3. Results and discussion

The thermodynamic formalism for the treatment of the enthalpies of dilution is based on the excess enthalpy concept. If aqueous ethylene glycol 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

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

in which $h_2, h_3, h_4, \ldots,$ are enthalpic pairwise, triplet and quadruplet interaction coefficients, respectively. The molar enthalpy of dilution ($\Delta H_{\text{dil,m}}$) of the solution from an initial molality m_{i} to a final molality m_{f}, is therefore given by

$$\Delta H_{\text{dil,m}} = H^{\text{E}}(m_{\text{f}}) - H^{\text{E}}(m_{\text{i}}) = h_2(m_{\text{f}}m_{\text{i}}) + h_3(m_{\text{f}}^2 m_{\text{i}}^2) + h_4(m_{\text{f}}^3 m_{\text{i}}^3) + \cdots \quad (4)$$

The experimental values of $\Delta H_{\text{dil,m}}$ of glycine, L-alanine and L-serine solutions together with the initial and final molalities are given in Tables 1–3, respectively. The uncertainties of all $\Delta H_{\text{dil,m}}$ values owing to duplicate runs at each initial molality and the slight variation of flow rates are within 1%. The data were fitted to Eq. (4) using a least-squares procedure to obtain the h coefficients (Tables 4–6). As there are some difficulties in the interpretation of the higher h coefficients, only the pairwise interaction coefficient h_2 are considered. The h_2 values of glycine, L-alanine and L-serine in pure water are −465.29, 209.59 and −740.32 J kg mol^{-2}, respectively, which are in good agreement with those of other workers [19].

The variations of h_2 coefficients for the three amino acids with the mass fractions of ethylene glycol in the mixed solvents are illustrated in Fig. 1. It shows that the enthalpic pairwise interaction coefficients of glycine and serine are negative and pass through a minimum at about 0.20 mass fraction of ethylene glycol, while those of alanine are positive and become less positive and even negative ($w > 0.40$) with increasing ethylene glycol concentrations in the mixed solvents.

For amino acid zwitterions in aqueous solutions, 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 solvent shell of one molecule interacting with the solvated negatively charged carboxyl group of another [20]. 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 interaction, a negative value of h_2 should be observed.

Table 1
Enthalpies of dilution of glycine in aqueous ethylene glycol solutions at 298.15 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})
$w = 0$					
0.4001	0.1304	111.39	0.3000	0.1479	64.14
0.4001	0.1702	94.64	0.3000	0.1975	43.12
0.4001	0.1968	83.14	0.2499	0.0821	72.49
0.4001	0.2239	71.84	0.2499	0.1232	54.62
0.4001	0.2635	55.36	0.2499	0.1650	36.53
0.3500	0.1146	98.87	0.2001	0.0659	59.58
0.3500	0.1722	73.84	0.2001	0.0988	44.74
0.3500	0.2302	49.57	0.2001	0.1322	30.04
0.3500	0.0983	85.77			
$w = 0.20$					
0.2015	0.1005	47.33	0.6001	0.1888	155.88
0.2015	0.0671	65.47	0.6001	0.2960	109.07
0.2015	0.1338	31.47	0.6001	0.3956	73.10
0.4026	0.1993	80.24	0.8029	0.2614	198.03
0.4026	0.1328	113.71	0.8029	0.3940	136.54
0.4026	0.2664	54.25	0.8029	0.5275	93.97
$w = 0.30$					
0.2033	0.1016	45.74	0.6017	0.2972	97.02
0.2033	0.0679	63.17	0.6017	0.1980	141.42
0.2033	0.1355	29.89	0.6017	0.3979	68.42
0.3964	0.1970	72.13	0.8025	0.3940	121.10
0.3964	0.1314	101.68	0.8025	0.5291	84.44
0.3964	0.2633	49.73	0.8025	0.2620	174.95
$w = 0.35$					
0.1999	0.1005	40.82	0.5999	0.2986	91.56
0.1999	0.0699	55.02	0.5999	0.1986	129.68
0.1999	0.1335	28.90	0.5999	0.3983	62.55
0.4006	0.2006	68.61	0.8002	0.3964	120.91
0.4006	0.1335	94.93	0.8002	0.2636	174.08
0.4006	0.2667	46.21	0.8002	0.5300	84.15
$w = 0.45$					
0.2000	0.1004	32.99	0.6003	0.2974	67.32
0.2000	0.0669	48.83	0.6003	0.1984	94.30
0.2000	0.1337	23.12	0.6003	0.3988	44.49
0.4001	0.1994	51.15	0.8000	0.3950	78.32
0.4001	0.1331	72.09	0.8000	0.2624	117.02
0.4001	0.2667	34.28	0.8000	0.5300	56.37
$w = 0.50$					
0.2005	0.1002	30.60	0.6019	0.3985	37.53
0.2005	0.1335	21.15	0.6019	0.1984	76.95
0.4014	0.1997	43.41	0.8009	0.3940	63.48
0.4014	0.1334	61.07	0.8009	0.5276	45.37
0.4014	0.2664	29.74	0.8009	0.2620	91.89
0.6019	0.2982	54.47			

Table 2
Enthalpies of dilution of L-alanine in aqueous ethylene glycol solutions at 298.15 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})
$w = 0$					
0.1018	0.0514	−9.04	0.2998	0.0992	−41.02
0.2004	0.0999	−19.29	0.3968	0.1970	−40.68
0.2004	0.1331	−12.99	0.3968	0.2369	−33.14
0.2004	0.0665	−26.99	0.3968	0.1566	−49.93
0.2998	0.1489	−30.46	0.3968	0.1307	−55.25
0.2998	0.1793	−24.62	0.6020	0.2886	−65.90
0.2998	0.1187	−37.64	0.6020	0.1900	−87.76
$w = 0.10$					
0.1993	0.1000	−19.64	0.5999	0.2978	−57.40
0.1993	0.0669	−24.66	0.5999	0.1981	−78.47
0.1993	0.1333	−18.06	0.5999	0.3979	−38.16
0.4000	0.1996	−38.91	0.8003	0.3946	−78.40
0.4000	0.1332	−50.20	0.8003	0.2620	−107.87
0.4000	0.2664	−25.39	0.8003	0.5287	−54.36
$w = 0.20$					
0.1500	0.0755	−29.03	0.4499	0.2247	−39.64
0.1500	0.0504	−14.92	0.4499	0.1493	−51.11
0.1500	0.1004	−14.31	0.4499	0.2994	−27.23
0.3000	0.1505	−28.42	0.5931	0.2945	−51.32
0.3000	0.1003	−31.95	0.5931	0.1955	−35.60
0.3000	0.2002	−17.26	0.5931	0.3933	−33.47
$w = 0.30$					
0.1498	0.0755	−10.62	0.4499	0.1499	−38.25
0.2999	0.1504	−18.96	0.4499	0.2993	−21.05
0.2999	0.1003	−21.70	0.5997	0.2980	−43.71
0.2999	0.2002	−12.69	0.5997	0.1981	−60.62
0.4499	0.2244	−29.75	0.5997	0.3978	−30.59
$w = 0.40$					
0.1500	0.0757	−4.01	0.4501	0.1498	−39.70
0.1500	0.0507	−3.60	0.4501	0.3000	−21.04
0.1500	0.1005	−3.62	0.6000	0.2983	−40.84
0.3000	0.1507	−11.32	0.6000	0.1988	−52.86
0.3000	0.2005	−9.12	0.6000	0.3983	−27.76
0.4501	0.2247	−30.28			
$w = 0.50$					
0.1500	0.0750	−2.42	0.4500	0.2224	−27.81
0.1500	0.1000	−4.55	0.4500	0.1479	−35.73
0.3000	0.1493	−17.13	0.4500	0.2978	−20.89
0.3000	0.0994	−20.82	0.5997	0.2953	−34.99
0.3000	0.1993	−13.18	0.5997	0.1959	−46.29

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.

In the pairwise interaction of other amino acids, interactions relating to the side-chains will be significant. The contributions of these interactions to h_2 depend on the nature of the side-chain. For amino acids with apolar side-chains, positive contributions to h_2 arise from both the interactions between

Table 3
Enthalpies of dilution of L-serine in aqueous ethylene glycol solutions at 298.15 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta H_{dil,m}$ (J mol^{-1})
$w = 0$					
0.1004	0.0490	38.48	0.3084	0.0984	139.93
0.1004	0.0324	51.70	0.3084	0.1490	104.81
0.1004	0.0657	26.95	0.4035	0.1948	133.81
0.2012	0.0977	71.99	0.4035	0.1283	178.50
0.2012	0.1315	49.66	0.6012	0.2876	180.76
0.2012	0.0646	96.21	0.6012	0.1893	248.33
$w = 0.10$					
0.1500	0.0754	58.64	0.4498	0.2240	148.15
0.1500	0.0504	79.08	0.4498	0.1493	202.74
0.1500	0.1004	39.62	0.4498	0.2992	98.62
0.2998	0.1500	107.08	0.5999	0.2976	185.09
0.2998	0.1001	147.25	0.5999	0.1976	255.75
0.2998	0.2000	70.55	0.5999	0.3977	124.07
$w = 0.20$					
0.1500	0.0759	64.60	0.4492	0.2252	149.10
0.1500	0.0507	87.38	0.4492	0.1504	205.82
0.1500	0.1007	42.36	0.4492	0.2998	94.80
0.3000	0.1509	106.43	0.5997	0.2993	176.33
0.3000	0.1011	149.06	0.5997	0.1993	255.36
0.3000	0.2008	74.14	0.5997	0.3988	123.66
$w = 0.30$					
0.1499	0.0760	65.22	0.4501	0.2259	140.89
0.1499	0.0509	85.61	0.4501	0.1506	202.19
0.1499	0.1007	44.03	0.4501	0.3005	98.59
0.3000	0.1514	104.93	0.5997	0.2999	184.09
0.3000	0.1010	146.43	0.5997	0.1998	248.77
0.3000	0.2009	74.80	0.5997	0.3992	120.53
$w = 0.40$					
0.1459	0.0724	62.15	0.4498	0.2245	156.55
0.1459	0.0483	87.92	0.4498	0.2988	103.10
0.1459	0.0969	43.19	0.6001	0.2981	163.53
0.2999	0.1483	94.73	0.6001	0.1975	242.16
0.2999	0.0989	138.65	0.6001	0.3975	115.16
0.2999	0.1984	68.58			
$w = 0.50$					
0.1500	0.0759	49.87	0.4499	0.2253	121.11
0.1500	0.0507	59.38	0.4499	0.1502	173.72
0.1500	0.1008	30.37	0.4499	0.3002	85.44
0.3003	0.1510	101.39	0.5999	0.1989	196.72
0.3003	0.2012	77.81	0.5999	0.3993	95.95

hydrated hydrocarbon chains and those between the hydrated side-chains and the ionic groups. The positive value of h_2 for L-alanine suggests that interactions involving the methyl groups dominate over the zwitterion–zwitterion interactions. For amino acids with side groups that can participate in hydrogen bonding on pairwise interaction, the contribution to h_2 should be negative. 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 + ethylene glycol + water), the overall effect on

Table 4
Enthalpic pairwise interaction coefficients of glycine in aqueous ethylene glycol solutions at 298.15 K

w (Ethylene glycol)	h_2 (J kg mol^{-2})	h_3 (J kg^2 mol^{-3})	h_4 (J kg^3 mol^{-4})	m_i (mol kg^{-1})	r
0	−465.29	127.22	−27.28	0.20–0.80	0.9983
0.20	−582.77	378.81	−195.96	0.20–0.80	0.9981
0.30	−526.26	345.02	−170.18	0.20–0.80	0.9966
0.35	−503.01	368.35	−221.42	0.20–0.80	0.9972
0.45	−414.46	358.25	−190.37	0.20–0.80	0.9945
0.50	−324.22	265.30	−128.15	0.20–0.80	0.9978

Table 5
Enthalpic pairwise interaction coefficients of L-alanine in aqueous ethylene glycol solutions at 298.15 K

w (Ethylene glycol)	h_2 (J kg mol^{-2})	h_3 (J kg^2 mol^{-3})	h_4 (J kg^3 mol^{-4})	m_i (mol kg^{-1})	r
0	209.59	11.01	−4.81	0.10–0.60	0.9997
0.10	198.11	−26.25	26.28	0.15–0.60	0.9953
0.20	156.85	−71.76	99.66	0.15–0.60	0.9924
0.30	113.93	−4.53	64.41	0.15–0.60	0.9887
0.40	−17.90	395.50	−310.62	0.15–0.60	0.9902
0.50	−34.78	462.46	−428.11	0.15–0.60	0.9940

Table 6
Enthalpic pairwise interaction coefficients of L-serine in aqueous ethylene glycol solutions at 298.15 K

w (Ethylene glycol)	h_2 (J kg mol^{-2})	h_3 (J kg^2 mol^{-3})	h_4 (J kg^3 mol^{-4})	m_i (mol kg^{-1})	r
0	−740.32	195.21	−15.53	0.10–0.60	0.9997
0.10	−852.64	395.80	−180.92	0.15–0.60	0.9997
0.20	−927.60	574.89	−294.70	0.15–0.60	0.9977
0.30	−914.13	655.19	−417.13	0.15–0.60	0.9986
0.40	−730.29	134.69	107.10	0.15–0.60	0.9807
0.50	−693.62	336.25	−325.96	0.15–0.60	0.9809

h_2 reflects the equilibrium among the following superimposed processes.

- Direct interaction between two zwitterions resulting in exothermic or endothermic effect which depends on the nature of the side-chain group.
- Interaction between the polar portion of zwitterion and the hydroxyl groups of ethylene glycol (an exothermic process).
- Interaction between the non-polar portion of alanine zwitterion and the hydroxyl groups of ethylene glycol (an endothermic process).
- Interaction between the non-polar portions of alanine zwitterion and ethylene glycol molecule (an endothermic process).
- A partial dehydration of the hydration shell of the amino acid zwitterion (an endothermic process).
- A partial dehydration of the hydration shell of the hydroxyl groups of ethylene glycol (an endothermic process).

The positive values of h_2 for alaine–alanine interaction in ethylene glycol–water mixtures rich in water (Table 5) testify to the predominance of endothermic processes over the effect of direct interaction of the polar portion of alanine acid zwitterion with the hydroxyl groups of ethylene glycol. The predominance decreases gradually with the increasing concentration of ethylene glycol in the mixtures, leading to less positive and even negative values of h_2 coefficients.

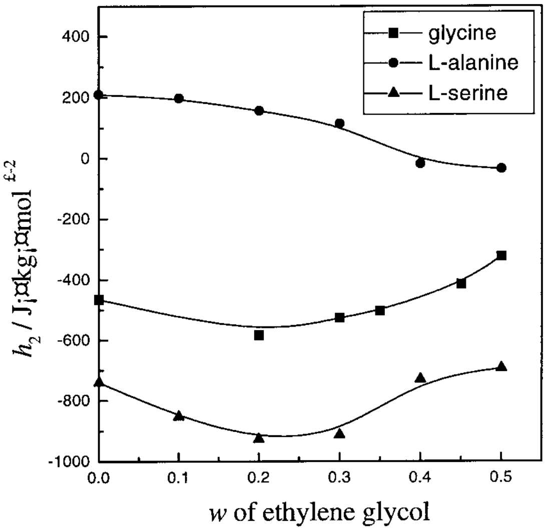

Fig. 1. The variations in h_2 of glycine, L-alanine and L-serine with the mass fractions of ethylene glycol in mixed solvents at 298.15 K.

The negative values of h_2 for glycine–glycine and serine–serine interactions in ethylene glycol–water mixtures (Table 5) testify to the predominance of exothermic processes over endothermic processes. The effect is most prevailing at about 0.20 mass fraction of ethylene glycol, leading to a minimum of h_2 coefficients.

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