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Thermochimica Acta 362 (2000) 1–6

thermochimica acta

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Enthalpic interactions of amino acids in aqueous glucose solutions at 298.15 K

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Received 26 January 2000; received in revised form 12 June 2000; accepted 13 June 2000

Abstract

The dilution enthalpies of L-alanine and L-serine in various aqueous glucose solutions have been determined using LKB-2277 flow microcalorimetry at 298.15 K. The homogeneous enthalpic interaction coefficients over the whole range of aqueous glucose solutions have been calculated according to the excess enthalpy concept. The results were interpreted from the point of view of solute–solute interactions involved by solvent effects.

Keywords: Dilution enthalpy; Amino acids; Aqueous glucose solutions; Enthalpic interactions

1. Introduction

It is well known that polyhydroxy compounds help in stabilizing the native conformation of globular proteins [1–3]. A lot of interpretations about water-structure modifications by polyhydroxy compounds are not identical [4–6]. Since polyhydroxy compounds have both hydrophobic and hydrophilic moieties, the promotion of water structure by hydrophobic hydration tends to cancel the effect of structure breakdown by hydrophilic sites. The highly ordered structure of water by hydrogen bonds and the structure resemblance of polyhydroxy compounds to water make the whole situation complex.

Thermodynamic functions, especially enthalpy and entropy, are significantly connected with the solvent-structure perturbations brought about by the introduction of solute. In a recent work of ours [7], the dissolution enthalpies of four typical amino acids were measured in pure water and in aqueous glucose solutions at 298.15 K, and the transfer enthalpies of these model compounds of proteins from water to various aqueous glucose solutions were calculated. It is concluded that the highly polar zwitterion groups and the OH group of serine cause the breakdown of structure in aqueous glucose solutions, and the non-polar side chain produces order in proportion to its size. Information about the interaction mechanism can be inferred from the pairwise interaction coefficients of the virial expansion of an excess thermodynamic property [8]. The physical meaning of these interaction parameters is bound to the variation of the thermodynamic property when two hydrated molecules are brought from an infinite distance to a finite distance where their hydration co-spheres are perturbed. Recently, the dilution enthalpies of glycine in various aqueous glucose and sucrose solutions [9], the dilution enthalpies of glycine in various DMF–water and ethanol–water mixtures [10] and the dilution enthalpies of L-serine in various ethano–water mixtures were

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0040-6031/00/$ – see front matter
PII: S0040-6031(00)00592-X

reported [11], and the enthalpic interaction parameters were derived from the equation

$$\Delta H_{\mathrm{dil}} = h_2(m_{\mathrm{f}} - m_{\mathrm{i}}) + h_3({m_{\mathrm{f}}}^2 - {m_{\mathrm{i}}}^2) + \ldots \quad (1)$$

Here, ΔH_{dil} is the dilution enthalpy, h_2 and h_3 are the pair and triplet enthalpic interaction parameters, respectively, and m_{i} and m_{f} the initial and final molalities, respectively. From these studies, it is found that the enthalpic pairwise interaction parameter is very sensitive to solvent variation. It is a measure of solute–solute interaction mediated by the solvent. Two effects are considered to give contributions to the enthalpic interaction coefficients: one results from the electrostatic interaction and the other from the structural interaction. The calorimetric studies allow to discover all the different structure effects. In the present work, the dilution enthalpies of L-alanine and L-serine in aqueous glucose solutions of different compositions are reported.

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 D-glucose was dried in a vacuum desiccator for 48 h at room temperature. Water was deionized and distilled using a quartz sub-boiling purifier. Both the aqueous glucose solutions (water + glucose) which were used as solvents or diluents and the amino acid solutions (amino acid + water + glucose) 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	$A_{\mathrm{ags}} + B_{\mathrm{ags}}$	baseline determined
2	$A_{\mathrm{ags}} + B_{\mathrm{aags}}$	dilution thermal power determined
3	$A_{\mathrm{ags}} + B_{\mathrm{ags}}$	baseline re-established

Here, 'ags' represents 'aqueous glucose solution', and 'aags' —'amino acid glucose'.

The dilution enthalpies ΔH_{dil} were calculated from the equation

$$\Delta H_{\mathrm{dil}} = \frac{P(1 + m_{\mathrm{i}}M)}{m_{\mathrm{i}} f_2} \quad (2)$$

where P is the dilution thermal power (μW), 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} were calculated from the equation

$$m_{\mathrm{f}} = \frac{m_{\mathrm{i}} f_2}{[f_1(m_{\mathrm{i}}M + 1) + f_2]} \quad (3)$$

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

3. Results and discussion

The experimental values of ΔH_{dil} of L-alanine and L-serine solutions together with the initial and final molalities are given in Tables 1 and 2, respectively. The uncertainties of all ΔH_{dil} 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. (1) using a least-squares procedure to obtain h coefficients (Tables 3 and 4). 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 L-alanine and L-serine in pure water are 209.59 and −740.32 J kg mol^{-2}, respectively, which are in good agreement with those obtained by other workers [12]. The variation of h_2 coefficients for the two amino acids with the mass percentages of glucose in solutions is illustrated in Fig. 1. The data for glycine are taken from Ref. [9].

It can be seen that the enthalpic pair interaction coefficients of glycine and serine are negative and become less negative with increasing glucose concentrations, while those of alanine are positive and pass through a maximum at about 20% of glucose. In the ternary solutions, there are mainly three kinds of interactions which are expected to contribute to h_2 coefficient. The first is the kind of interactions of ionic or hydrophilic nature between two solvated zwitterions which give endothermic contribution to h_2. The

Table 1
Dilution enthalpies of alanine in aqueous glucose 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})
wt. = 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
wt. = 10%					
0.2002	0.0997	−24.51	0.3003	0.1188	−41.83
0.2002	0.1202	−21.11	0.4066	0.1333	−64.24
0.2002	0.0796	−30.70	0.4066	0.2010	−47.43
0.2002	0.0665	−31.91	0.4066	0.2421	−38.07
0.3003	0.1490	−34.99	0.4066	0.1602	−57.22
0.3003	0.1793	−28.56	0.5994	0.2869	−73.05
0.3003	0.0989	−47.67	0.5994	0.1884	−97.60
wt. = 20%					
0.1019	0.0506	−13.04	0.3049	0.1504	−40.26
0.1019	0.0403	−16.77	0.3049	0.1000	−55.50
0.1019	0.0609	−12.16	0.4020	0.2649	−35.52
0.1999	0.0990	−27.27	0.4020	0.1975	−53.75
0.1999	0.0659	−39.03	0.4020	0.1312	−73.86
0.1999	0.1324	−18.41	0.6014	0.2896	−83.26
0.3049	0.2016	−28.22	0.6014	0.3907	−58.00
wt. = 30%					
0.1018	0.0333	−17.84	0.3003	0.1971	−34.84
0.1018	0.0500	−17.08	0.4004	0.1291	−75.07
0.1018	0.0397	−18.15	0.4004	0.1951	−56.63
0.2004	0.0983	−30.64	0.4004	0.2621	−40.19
0.2004	0.0651	−37.01	0.6003	0.2880	−92.17
0.2004	0.1318	−21.68	0.6003	0.3891	−67.71
0.3003	0.1467	−42.75	0.6003	0.3103	−80.00
0.3003	0.0972	−56.84			
wt. = 40%					
0.1049	0.0524	−20.12	0.4034	0.2660	−44.50
0.1049	0.0697	−16.68	0.4034	0.2398	−50.97
0.1049	0.0628	−20.30	0.4034	0.1300	−80.11
0.2031	0.1012	−32.99	0.6008	0.3940	−60.01
0.2031	0.1346	−28.91	0.6008	0.1948	−108.00
0.2031	0.1214	−32.51	0.6008	0.2951	−78.39
0.4034	0.1994	−59.35	0.6008	0.2500	−95.01
wt. = 50%					
0.1020	0.0501	−31.01	0.4018	0.1948	−57.84
0.1020	0.0665	−22.52	0.4018	0.1288	−69.11
0.1020	0.0602	−29.00	0.4018	0.2616	−47.02
0.2014	0.0984	−34.03	0.6029	0.2902	−80.11
0.2014	0.1321	−27.78	0.6029	0.1915	−101.10
0.2014	0.0652	−40.52	0.6029	0.3906	−65.21

Table 2
Dilution enthalpies of serine in aqueous glucose 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})
wt. = 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
wt. = 10%					
0.1019	0.0497	34.22	0.4001	0.1934	114.60
0.1019	0.0329	47.56	0.4001	0.1272	156.19
0.1019	0.0666	24.79	0.4001	0.2600	77.92
0.2006	0.0973	62.90	0.6004	0.2878	158.90
0.2006	0.0643	85.59	0.6004	0.1892	216.00
0.2006	0.1309	43.44	0.6004	0.3882	107.40
wt. = 20%					
0.1065	0.0521	32.03	0.3975	0.1921	98.05
0.1065	0.0699	18.94	0.3975	0.1271	138.80
0.1065	0.0345	49.88	0.3975	0.2591	44.98
0.2030	0.0992	55.14	0.6024	0.2895	133.03
0.2030	0.0655	80.94	0.6024	0.1912	188.74
0.2030	0.1329	37.39	0.6024	0.3911	94.88
wt. = 30%					
0.1055	0.0517	20.07	0.3919	0.1254	111.97
0.1055	0.0693	13.43	0.3919	0.2557	49.47
0.2045	0.0995	42.38	0.6005	0.2886	109.99
0.2045	0.1336	26.24	0.6005	0.1905	156.85
0.3919	0.1897	79.47	0.6005	0.3883	72.57
wt. = 40%					
0.1050	0.0512	15.15	0.4037	0.1285	89.86
0.1050	0.0688	11.41	0.4037	0.2619	42.71
0.2049	0.0995	33.53	0.5982	0.2859	82.15
0.2049	0.1337	25.25	0.5982	0.1882	113.32
0.4037	0.1943	61.12	0.5982	0.3863	52.76
wt = 50%					
0.1948	0.0946	24.21	0.4074	0.2373	36.03
0.1948	0.0627	33.76	0.4987	0.2402	50.00
0.1948	0.1143	21.16	0.4987	0.1586	68.00
0.4074	0.1962	41.29	0.5985	0.2857	50.55
0.4074	0.1295	57.30	0.5985	0.1770	70.26

second is the kind of interactions of hydrophobic nature between two solvated zwitterions which give exothermic contribution to h_2. The third is the kind of interactions between amino acid molecule and solvent molecule which may give endothermic or exothermic contribution to h_2 according to their natures. The types of interactions between glucose and amino acid molecules can be classified as follows [9,13]:

1. Hydrophilic–ionic interactions between the OH group of the glucose and the zwitterionic centers of amino acids, which lead to a negative contribution to h_2.
2. Hydrophilic–hydrophobic interactions between the OH group of the glucose and non-polar groups of amino acids, which lead to a positive contribution to h_2.

Table 3
Enthalpic pairwise interaction coefficients of alanine in aqueous glucose solutions at 298.15 K

Glucose (wt.%)	h_2 (J kg mol^{-2})	h_3 (J kg mol^{-2})	h_4 (J kg mol^{-2})	m_i (J kg mol^{-2})	r (mol kg^{-1})
0	209.59	11.01	−4.81	0.10–0.60	0.9997
10	262.98	−111.86	114.92	0.20–0.60	0.9985
20	320.64	−149.36	137.99	0.10–0.60	0.9983
30	260.75	−30.76	70.99	0.10–0.60	0.9922
40	224.41	114.96	−143.52	0.10–0.60	0.9955
50	139.85	74.93	−4.82	0.10–0.60	0.9923

Table 4
Enthalpic pairwise interaction coefficients of serine in aqueous glucose solutions at 298.15 K

Glucose (wt.%)	h_2 (J kg mol^{-2})	h_3 (J kg mol^{-2})	h_4 (J kg mol^{-2})	m_i (J kg mol^{-2})	r (mol kg^{-1})
0	−740.32	195.21	−15.53	0.10–0.60	0.9997
10	−676.59	261.48	−99.23	0.10–0.60	0.9997
20	−585.42	132.59	56.42	0.11–0.60	0.9941
30	−560.61	271.45	−102.49	0.11–0.60	0.9992
40	−344.32	−26.14	163.14	0.11–0.60	0.9966
50	−227.56	−5.70	127.93	0.20–0.60	0.9930

For glycine and serine in aqueous glucose solutions, hydrophilic–ionic interactions are predominant over hydrophilic–hydrophobic interactions, resulting in negative values of h_2 over the whole range of glucose concentration. With increasing glucose concentrations, the hydrophilic–hydrophobic interactions increase gradually and cancel part of the hydrophilic–ionic interactions, which leads to less negative values of h_2.

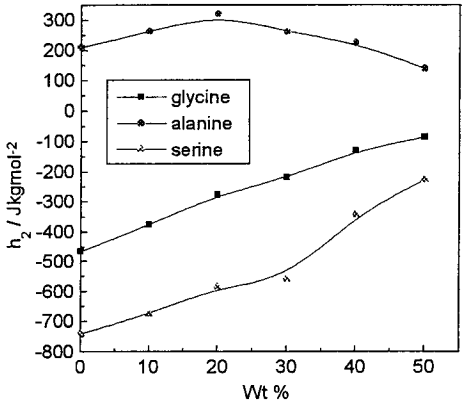

Fig. 1. The variation of enthalpic pair interaction coefficients of glycine, L-alanine and L-serine in aqueous glucose solutions at 298.15 K.

For alanine in aqueous glucose solutions, hydrophilic–hydrophobic interactions prevail over hydrophilic–ionic interactions, leading to positive values of h_2 over the whole range of glucose concentration. With the increase of glucose concentrations, the hydrophilic–ionic interactions increase significantly and cancel part of the hydrophilic–hydrophobic interactions, which leads to the maximum value of h_2 at about 20% of glucose.

Acknowledgements

The authors are grateful to the National Science Foundation of China and to the National Education Committee of China for financial support (No. 29773041).

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