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Enthalpic interaction of glycine in aqueous glucose and sucrose solutions at 298.15 K

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Abstract

The dilution enthalpies of glycine in aqueous glucose and sucrose solutions (0–50 wt%) at 298.15 K were measured calorimetrically. The data were fitted to virial polynomials from which the enthalpic pair interaction coefficients of glycine (h_{AA}) were evaluated. The values of h_{AA} in the two aqueous saccharide solutions are all negative and become less negative with increasing saccharide concentrations. The results are discussed in terms of solute–solute and solute–solvent interactions.

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1. Introduction

Many studies have been done on the effects of saccharides and polyols on the proteins and it was found that saccharides and polyols help in stabilizing the native conformations of globular proteins [1–9]. Some trends correlating the stabilizing potency of saccharides and polyols with the number or configuration of the hydroxy groups have also been noted [10]. However, there are numerous exceptions [11,12] and not all proteins respond equally to a given compound. Thus our understanding of the stabilization mechanism of proteins is still incomplete.

In order to understand the nature of interactions between saccharides and proteins in aqueous solutions, it is necessary to study biochemical model compounds owing to the complex structure of the biological micromolecules. Amino acids are basic components of proteins and are considered to be the model compounds of protein molecules. Dilution enthalpy is recognized as a basic thermodynamic parameter to study the interactions between two solute molecules occurring in solutions. But little data concerning dilution enthalpies of amino acids in aqueous solutions containing other model components are available. In this paper, the dilution enthalpies of glycine in aqueous glucose and sucrose solutions of different weight percentage compositions at 298.15 K have been reported.

2. Experimental

Glycine (biochemical reagent) was dried in an infrared drier until there was no significant change in mass. Glucose and sucrose (analytical reagents) were dried over P_2O_5 in a vacuum desiccator for 72 h at room temperature before use. Water was

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deionized and distilled using a quartz sub-boiling purifier.

The solutions were degassed and used within 12 h after preparation to minimize decomposition due to bacterial contamination. All solutions were prepared by weight by Mettler AE 200 balance with a precision of ±0.0001 g. The weight percents of saccharides are from 0% to 50%.

The enthalpies of dilution were measured with LKB-2277 BioActivity Monitor. The solutions were pumped through the mixing-flow cell of the calorimeter using two LKB-2132 microperpex peristaltic pumps. The variation in flow rates was less than 0.2%. The flow rates were determined by weighing samples delivered in known time. The relative mean deviation in weighing was 0.01%. The relative mean deviation of thermal powers determined was 0.3% and at last the relative mean deviation of the dilution enthalpies was less than 1%.

The dilution enthalpies ($\Delta_{\rm dil}H_{\rm m}$) can be obtained by the following equation

$$\Delta_{\rm dil}H_{\rm m} = \frac{-W \times 10^6}{f_{\rm u}C_{\rm i}}, \qquad (1)$$

where, $C_{\rm i}$ is the concentration of the solution before dilution (mol kg^{-1}); $f_{\rm u}$ is the flow rate of the solution (kg s^{-1}); W is the thermal power output (W).

3. Results and discussion

The thermodynamic formalism for the treatment of the results is based on the excess function concept [13–15]. If aqueous glucose or sucrose solutions are regarded as "solvents", the excess enthalpy per kg of solvent ($H^{\rm ex}$) of a solution containing a single non-electrolytic solute A at molality $m_{\rm A}$ is given by

$$H^{\rm ex} = h_{\rm AA}m_{\rm A}^2 + h_{\rm AAA}m_{\rm A}^3 + \cdots \qquad (2)$$

In which, $h_{\rm AA}$, $h_{\rm AAA}\ldots$ are enthalpic interaction coefficients. The molar enthalpy of dilution ($\Delta_{\rm dil}H_{\rm m}$) of the solution, from an initial molality $m_{\rm A,i}$ to a final molality $m_{\rm A,f}$, is therefore given by

$$\begin{aligned}\Delta_{\rm dil}H_{\rm m} &= H(m_{\rm A,f}) - H(m_{\rm A,i})\\ &= h_{\rm AA}(m_{\rm A,f} - m_{\rm A,i})\\ &\quad + h_{\rm AAA}(m_{\rm A,f}^2 - m_{\rm A,i}^2) + \cdots \end{aligned} \qquad (3)$$

The experimental results are given in Tables 1 and 2. These data were fitted to Eq. (3) from which enthalpic interaction coefficients were evaluated and given in Tables 3 and 4. Many of the dilution enthalpies in the literatures are expressed in terms of the relative apparent molar enthalpy (L_ϕ) of the solute. A comparison between the values of L_ϕ of glycine in pure water and those already in the literatures [16–19] is given in Fig. 1. Our results are in excellent agreement with those of other workers except for Zittle and Schmidt [19].

We direct our attention to the enthalpic pair interaction coefficients. From Tables 3 and 4, it can be seen that the enthalpic pair interaction coefficients of glycine both in aqueous glucose and sucrose solutions are negative and become less negative with increasing saccharide concentrations Fig. 2. This indicates that there are two different interactions present in solutions. One is the interaction between two solvated zwitterions which gives endothermic contribution to $h_{\rm AA}$. There are many studies [5,20,21] which support the idea that glycine is a net structure breaker due to its highly polar zwitterion portion. Some authors [22–24] concluded that polyhydroxy compounds have a structure-breaking effect in aqueous glycine. Using above description, the interaction between two glycine molecules increases with increasing saccharide concentrations, which leads to larger endothermic contribution to $h_{\rm AA}$ with increasing saccharide concentrations. On the other hand, a solute molecule can also interact with solvent molecules because $h_{\rm AA}$ is a measure of the solvent mediated solute–solute interaction. The types of interactions between saccharides and amino acids molecules can be classified as follows [25]:

1. Hydrophilic ionic group interactions between the OH group of the saccharides and the zwitterionic center of the amino acids, which leads negative to $h_{\rm AA}$.
2. Hydrophilic–hydropholic interactions between the OH group of the saccharides and non-polar groups of the amino acids, which leads positive to $h_{\rm AA}$.

For glycine in aqueous saccharides solutions, hydrophilic ionic group interactions are predominant over hydrophilic–hydropholic interactions [25]. With the increase of the saccharide concentrations, the hydrophilic–hydropholic interactions also increase gradually and cancel part of the hydrophilic ionic

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

$m_{\mathrm{i,glycine}}$ (mol kg^{-1})	m_{f} (mol kg^{-1})	$\Delta H_{\mathrm{dil,m}}$ (J mol^{-1})	$m_{\mathrm{i,glycine}}$ (mol kg^{-1})	m_{f} (mol kg^{-1})	$\Delta H_{\mathrm{dil,m}}$ (J mol^{-1})
Glucose wt = 0					
0.1980	0.1006	43.42	0.6012	0.2984	113.14
0.1980	0.1339	28.57	0.6012	0.3986	74.80
0.1980	0.0673	58.01	0.6012	0.1988	153.38
0.4101	0.2047	81.86	0.7956	0.3939	134.23
0.4101	0.2729	54.44	0.7956	0.5267	93.53
0.4101	0.1365	110.82	0.7956	0.2620	193.84
Glucose wt = 10%					
0.2045	0.1019	37.51	0.6036	0.2996	94.16
0.2045	0.1360	25.36	0.6036	0.4003	63.40
0.2045	0.0683	49.71	0.6036	0.2002	128.19
0.4040	0.2013	68.46	0.8051	0.3986	119.07
0.4040	0.2684	45.35	0.8051	0.5330	79.00
0.4040	0.1343	92.10	0.8051	0.2659	162.40
Glucose wt = 20%					
0.2030	0.1018	30.15	0.5985	0.2972	72.56
0.2030	0.1356	19.37	0.5985	0.3971	50.16
0.2030	0.0681	36.90	0.5985	0.1981	99.36
0.4010	0.2003	53.77	0.8047	0.3980	91.99
0.4010	0.2669	36.35	0.8047	0.5321	62.61
0.4010	0.1336	71.21	0.8047	0.2649	127.31
Glucose wt = 30%					
0.2006	0.1006	22.71	0.5983	0.2974	53.84
0.2006	0.1339	14.87	0.5983	0.3965	37.37
0.2006	0.0672	27.02	0.5983	0.1980	74.90
0.4035	0.2013	39.82	0.8065	0.3983	67.25
0.4035	0.2685	28.06	0.8065	0.5325	46.21
0.4035	0.1343	53.91	0.8065	0.2648	94.73
Glucose wt = 40%					
0.1548	0.0776	12.75	0.4529	0.3015	21.30
0.1548	0.1034	7.23	0.4529	0.1510	40.73
0.1548	0.0520	14.99	0.6016	0.1995	49.19
0.3023	0.1515	22.41	0.6016	0.2991	36.19
0.3023	0.2016	15.34	0.6016	0.3992	25.68
0.4529	0.1803	36.00	0.7983	0.3824	44.80
0.4529	0.2261	30.33	0.7983	0.5153	30.86
Glucose wt = 50%					
0.3018	0.1518	13.87	0.4958	0.2476	20.31
0.3018	0.2015	10.10	0.5995	0.2384	27.22
0.3018	0.1214	17.07	0.5995	0.1997	31.60
0.4029	0.2017	17.86	0.5995	0.3982	16.23
0.4029	0.2684	11.89	0.8039	0.3857	24.26
0.4958	0.1659	28.44	0.8039	0.5207	17.00
0.4958	0.3301	14.68			

Table 2
Enthalpies of dilution of glycine in aqueous sucrose solutions at 298.15 K

$m_{\mathrm{i,glycine}}$ (mol kg^{-1})	m_{f} (mol kg^{-1})	$\Delta H_{\mathrm{dil,m}}$ (J mol^{-1})	$m_{\mathrm{i,glycine}}$ (mol kg^{-1})	m_{f} (mol kg^{-1})	$\Delta H_{\mathrm{dil,\ m}}$ (J mol^{-1})
Sucrose wt = 0					
0.1980	0.1006	43.42	0.6012	0.2984	113.14
0.1980	0.1339	28.57	0.6012	0.3986	74.80
0.1980	0.0673	58.01	0.6012	0.1988	153.38
0.4101	0.2047	81.86	0.7956	0.3939	134.23
0.4101	0.2729	54.44	0.7956	0.5267	93.53
0.4101	0.1365	110.82	0.7956	0.2620	193.84
Sucrose wt = 10%					
0.2017	0.1018	38.68	0.6026	0.3020	100.30
0.2017	0.1350	26.07	0.6026	0.4011	66.39
0.2017	0.0684	53.09	0.6026	0.2016	125.77
0.4064	0.2046	72.04	0.8079	0.4021	127.84
0.4064	0.2712	47.91	0.8079	0.5366	84.35
0.4064	0.1369	97.05	0.8079	0.2686	171.83
Sucrose wt = 20%					
0.2007	0.1017	31.40	0.6032	0.3026	82.18
0.2007	0.1347	21.60	0.6032	0.4023	55.47
0.2007	0.0681	43.14	0.6032	0.2018	112.52
0.4049	0.2039	58.25	0.8011	0.3994	101.18
0.4049	0.2706	36.90	0.8011	0.5327	67.99
0.4049	0.1366	81.38	0.8011	0.2665	139.73
Sucrose wt = 30%					
0.2025	0.1029	26.23	0.5992	0.3020	62.73
0.2025	0.1364	17.82	0.5992	0.4015	43.13
0.2025	0.0691	34.76	0.5992	0.2021	87.49
0.4010	0.2048	45.31	0.7987	0.4002	76.92
0.4010	0.2691	31.17	0.7987	0.5330	52.98
0.4010	0.1364	62.08	0.7987	0.2684	106.41
Sucrose wt = 40%					
0.3042	0.1509	27.22	0.4992	0.2471	39.68
0.3042	0.2013	19.85	0.4992	0.3302	28.64
0.3042	0.1006	39.20	0.5973	0.1976	61.66
0.4033	0.2001	33.34	0.5973	0.2961	45.14
0.4033	0.2672	24.53	0.5973	0.3953	31.83
0.4033	0.1336	46.37	0.8038	0.3867	54.12
0.4992	0.1647	55.46	0.8038	0.2551	74.17
Sucrose wt = 50%					
0.3007	0.1507	15.26	0.5012	0.2502	20.14
0.3007	0.2002	10.29	0.5981	0.1995	32.19
0.4006	0.1350	22.61	0.5981	0.3972	16.35
0.4006	0.2001	17.19	0.5981	0.2984	23.34
0.4006	0.2665	12.25	0.8121	0.3900	34.92
0.5012	0.1673	27.97	0.8121	0.5254	24.12
0.5012	0.3331	14.39	0.8121	0.2568	43.05

Table 3
Enthalpic interaction coefficients of glycine in aqueous glucose solutions

Glucose (wt%)	h_{AA} (J kg mol^{-2})	h_{AAA} (J kg mol^{-2})	h_{AAAA} (J kg mol^{-2})	m_i (mol kg^{-1})	r
0	−465.29	127.22	−27.28	0.20–0.80	0.9983
10	−376.00	91.82	−21.33	0.20–0.81	0.9998
20	−277.51	42.26	2.84	0.20–0.80	0.9989
30	−218.65	44.87	−3.82	0.20–0.81	0.9982
40	−131.41	−1.10	26.81	0.15–0.80	0.9956
50	−84.94	−5.19	31.45	0.30–0.80	0.9907

Table 4
Enthalpic interaction coefficients of glycine in aqueous sucrose solutions

Sucrose (wt%)	h_{AA} (J kg mol^{-2})	h_{AAA} (J kg mol^{-2})	h_{AAAA} (J kg mol^{-2})	m_i (mol kg^{-1})	r
0	−465.29	127.22	−27.28	0.20–0.80	0.9983
10	−397.40	143.38	−71.05	0.20–0.81	0.9967
20	−342.78	96.16	−22.79	0.20–0.80	0.9989
30	−253.15	57.31	−4.23	0.20–0.80	0.9988
40	−193.95	67.48	−6.52	0.30–0.80	0.9965
50	−73.38	0.21	−0.69	0.30–0.81	0.9916

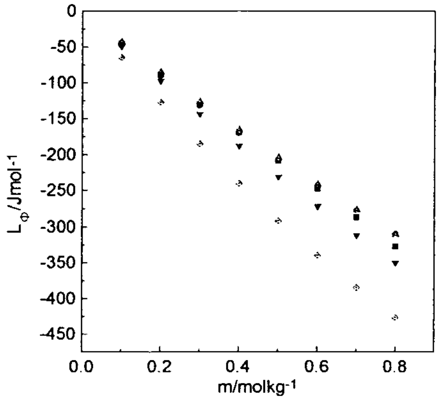

Fig. 1. The apparent relative molar enthalpies of glycine in aqueous solution at 298.15 K: (■) this work; (▼) Ref. [16]; (▲) Ref. [17]; (•) Ref. [18]; (◆) Ref. [19].

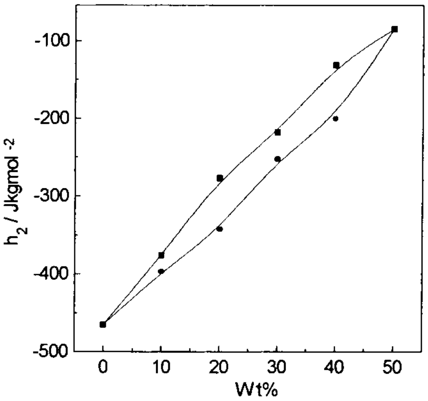

Fig. 2. Enthalpic pair interaction coefficients of glycine in aqueous sugar solutions: (■) glucose; (●) sucrose.

group interactions [25]. The experimentally observed less negative values of h_{AA} indicate that hydrophilic ionic group interactions are predominant over hydrophilic–hydropholic interactions and solute–solute interactions.

The behavior of glycine in aqueous glucose is different from that in aqueous sucrose. The enthalpic pair interaction coefficients of glycine in glucose are larger than those in sucrose solutions of the same concentrations when saccharide concentrations are between 0 and 40 wt%, but less than that in aqueous sucrose solution when saccharide concentration is 50 wt%. This may be due to the fact that for solutions of the same concentration, aqueous sucrose solutions contain about twice the number of OH groups compared to aqueous glucose solutions, which leads to larger hydrophilic ionic group interactions in sucrose solutions than that in glucose solutions when saccharide concentrations are between 0 and 40 wt%, and also leads to larger hydrophilic–hydropholic interactions in sucrose solutions than that in glucose solutions when saccharide concentration is 50 wt%.

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