Thermochimica Acta, 173 (1990) 295–299
Elsevier Science Publishers B.V., Amsterdam

ENTHALPIES OF SOLUTION OF GLYCINE IN SOLUTIONS OF AQUEOUS UREAS AT 298.15 K

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(Received 9 May 1990)

ABSTRACT

Enthalpies of dissolution of glycine in aqueous 0.5, 1.0, 1.5 and 2.0 mol kg^{-1} H_2O solutions of urea, monoethylurea, 1,3-dimethylurea, thiourea and hydroxyurea were measured at 298.15 K. The standard enthalpies of glycine dissolution in water and aqueous non-electrolyte solutions and the enthalpic pair coefficients of glycine–ureas in water were calculated.

INTRODUCTION

Thermodynamic properties of aqueous solutions of amino acids are of current interest as a means of allowing better understanding of complex biochemical systems. Urea is a strong denaturant of many globular proteins [1,2]; therefore recently there has been a growing interest in determining the thermodynamic properties of aqueous solutions of urea + organic substances which contain constituents of the proteins [3–6].

Here we report the enthalpies of solution at 298.15 K of glycine in aqueous solutions of urea and hydrophylic or hydrophobic urea derivatives. The results have been analysed, using the McMillan–Mayer formalism [7], to determine the enthalpy pair interaction coefficients for aqueous glycine + aqueous ureas.

EXPERIMENTAL

Urea (U), monoethylurea (MEU), 1,3-dimethylurea (DMU), thiourea (TU) and hydroxyurea (HU) (Fluka) were crystallized from ethanol and dried under reduced pressure at 333 K. Glycine (G) (Sigma) was recrystallized from distilled water and dried in vacuum over P_2O_5 at room temperature for at least 72 h before use. The concentrations of the solvents were determined by weight. The measurements of the enthalpies of solution were carried out in an isoperibol calorimeter [8] at a temperature of 298.15 K.

0040-6031/90/$03.50

TABLE 1

The enthalpies of solution of glycine in water and aqueous urea solutions at 298.15 K

H_2O		0.5 mol U (kg $H_2O)^{-1}$		1.0 mol U (kg $H_2O)^{-1}$		1.5 mol U (kg $H_2O)^{-1}$		2.0 mol U (kg $H_2O)^{-1}$	
m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})
0.0000	14.20	0.0000	13.83	0.0000	13.47	0.0000	13.15	0.0000	12.86
0.0042	14.18	0.0052	13.85	0.0058	13.46	0.0046	13.17	0.0056	12.89
0.0061	14.24	0.0078	13.77	0.0080	13.50	0.0052	13.12	0.0077	12.81
0.0075	14.16	0.0084	13.90	0.0088	13.39	0.0091	13.16	0.0084	12.85
0.0078	14.26	0.0092	13.81	0.0099	13.47	0.0105	13.21	0.0118	12.79
0.0102	14.23	0.0121	13.90	0.0129	13.42	0.0115	13.07	0.0123	12.87
0.0152	14.12	0.0138	13.77	0.0137	13.53	0.0151	13.17	0.0145	12.92

RESULTS AND DISCUSSION

Enthalpies of dissolution of glycine in water and in aqueous solutions of ureas from 0.5 to 2.0 mol urea (kg water)$^{-1}$, in the range of glycine concentrations 0.004–0.02 mol G (kg solvent)$^{-1}$, were measured at 298.15 K (Tables 1–5).

The values of enthalpies of dissolution of glycine in the aqueous solutions of urea (Table 1) exhibit a decrease of the endothermic effect of dissolution with increasing urea concentration. The same effect is caused by hydrophilic urea derivatives (Tables 4 and 5).

The substitution of urea hydrogen atoms by a larger alkyl radical (e.g. monoethylurea) or by a larger number of radicals (e.g. 1,3-dimethylurea) makes the endothermic effect greater because of an increase of hydrophobic hydration (Tables 2 and 3).

TABLE 2

The enthalpies of solution of glycine in aqueous monoethylurea solutions at 298.15 K

0.5 mol MEU (kg H_2O)$^{-1}$		1.0 mol MEU (kg H_2O)$^{-1}$		1.5 mol MEU (kg H_2O)$^{-1}$		2.0 mol MEU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})
0.0000	14.54	0.0000	14.79	0.0000	15.04	0.0000	15.21
0.0042	14.56	0.0052	14.80	0.0049	15.03	0.0053	15.24
0.0049	14.50	0.0061	14.86	0.0059	15.13	0.0069	15.31
0.0081	14.55	0.0069	14.77	0.0068	15.08	0.0071	15.16
0.0086	14.62	0.0094	14.71	0.0089	15.04	0.0081	15.15
0.0102	14.48	0.0121	14.81	0.0102	15.00	0.0111	15.21
0.0135	14.54	0.0151	14.79	0.0135	14.95	0.0142	15.17

TABLE 3

The enthalpies of solution of glycine in aqueous 1,3-dimethylurea solutions at 298.15 K

0.5 mol DMU (kg H_2O)$^{-1}$		1.0 mol DMU (kg H_2O)$^{-1}$		1.5 mol DMU (kg H_2O)$^{-1}$		2.0 mol DMU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})
0.0000	14.58	0.0000	14.91	0.0000	15.25	0.0000	15.46
0.0049	14.62	0.0059	14.90	0.0050	15.23	0.0049	15.49
0.0059	14.65	0.0063	15.00	0.0062	15.29	0.0053	15.46
0.0063	14.50	0.0089	14.97	0.0075	15.34	0.0082	15.54
0.0079	14.59	0.0094	14.83	0.0079	15.17	0.0084	15.37
0.0101	14.54	0.0121	14.85	0.0108	15.24	0.0115	15.48
0.0134	14.57	0.0132	14.93	0.0132	15.21	0.0162	15.42

TABLE 4

The enthalpies of solution of glycine in aqueous thiourea solutions at 298.15 K

0.5 mol TU (kg H_2O)$^{-1}$		1.0 mol TU (kg H_2O)$^{-1}$		1.5 mol TU (kg H_2O)$^{-1}$		2.0 mol TU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})
0.0000	13.53	0.0000	12.95	0.0000	12.36	0.0000	11.86
0.0048	13.55	0.0056	12.92	0.0045	12.36	0.0048	11.88
0.0075	13.50	0.0085	12.97	0.0072	12.44	0.0060	11.82
0.0092	13.51	0.0089	12.95	0.0084	12.34	0.0073	11.77
0.0099	13.47	0.0120	13.02	0.0098	12.28	0.0089	11.87
0.0105	13.60	0.0131	12.93	0.0125	12.39	0.0121	11.94
0.0178	13.57	0.0139	12.92	0.0141	12.34	0.0149	11.87

TABLE 5

The enthalpies of solution of glycine in aqueous hydroxyurea solutions at 298.15 K

0.5 mol HU (kg H_2O)$^{-1}$		1.0 mol HU (kg H_2O)$^{-1}$		1.5 mol HU (kg H_2O)$^{-1}$		2.0 mol HU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})	m	$-\Delta H_m$ (kJ mol^{-1})
0.0000	13.63	0.0000	13.20	0.0000	12.82	0.0000	12.36
0.0051	13.65	0.0042	13.24	0.0053	12.84	0.0049	12.37
0.0058	13.56	0.0056	13.18	0.0075	12.76	0.0059	12.33
0.0082	13.69	0.0071	13.16	0.0091	12.82	0.0079	12.44
0.0085	13.59	0.0078	13.26	0.0095	12.91	0.0082	12.27
0.0121	13.69	0.0101	13.12	0.0129	12.77	0.0109	12.42
0.0142	13.59	0.0152	13.23	0.0134	12.80	0.0143	12.32

TABLE 6

Enthalpic pair interaction coefficients for glycine + urea derivatives in water at 298.15 K

Solutes	h_{xy} (J kg mol^{-2})
G + TU	−680
G + HU	−550
G + U	−390
G + MEU	+360
G + DMU	+400

On the basis of the solution enthalpy values obtained, standard enthalpies of solution of glycine in aqueous solutions of urea and urea derivatives were determined graphically (Tables 1–5).

Using the standard enthalpies of transfer determined in this paper the enthalpic pair interaction coefficients for the glycine molecule–urea derivative molecule were calculated [8,9].

The enthalpic pair coefficients of glycine–urea interactions obtained in this way are listed in Table 6. The $h_{G,U}$, $h_{G,TU}$ and $h_{G,HU}$ values for the solutions of urea and hydrophilic urea derivatives are negative, in contrast with those of the alkylureas.

Replacement of a hydrogen atom in the urea molecule by an alkyl group leads to a diminished share of the hydrophilic properties of the molecule of substituted urea. This is reflected in both the enthalpies of solution of glycine in aqueous urea (Tables 2 and 3) and the positive values of the enthalpic pair interaction coefficients of the glycine–alkylurea molecule (Table 6).

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