Thermochimica Acta, 180 (1991) 199–202
Elsevier Science Publishers B.V., Amsterdam

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

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(Received 21 August 1990)

ABSTRACT

The enthalpies of dissolution of glycine in aqueous 0.5, 1.0, 1.5, 2.0 and 2.5 mol kg^{-1} H_2O solutions of NaCl, KCl, CsCl, NaI, KI, CsI, $NaNO_3$ and KNO_3 were measured at 298.15 K. The glycine molecule–electrolyte enthalpic pair interaction coefficients were determined using standard solution enthalpies of glycine in water and aqueous solutions of electrolytes.

INTRODUCTION

Amino acids have been quite useful as models for understanding the thermodynamic behaviour of peptides and proteins in aqueous solution [1]. It is well known that salts have striking and specific effects on the conformation and properties of proteins and nucleic acids [2–5], on enzyme activity [6] and on the rates of macromolecular transformation reactions [7]. Therefore, the thermodynamic aspects of the interaction of amino acids with salts have been of interest for some time [8–10].

In the present study the enthalpies of solution of glycine in aqueous uni-univalent electrolyte solutions were determined. The results were analysed using the McMillan–Mayer formalism [11,12] to calculate the enthalpy pair interaction coefficients for aqueous glycine + aqueous dissociated electrolyte.

EXPERIMENTAL

Glycine (G) (Sigma) was recrystallized from distilled water and dried in vacuo over P_2O_5 at room temperature for at least 72 h before use.

NaCl, KCl, CsCl (Merck "puriss"), $NaNO_3$ and KNO_3 (POCh Poland "puriss") were crystallized from distilled water and dried at 373 K.

NaI, KI and CsI (Merck "puriss") were crystallized from a 1 : 1 water : acetone mixture and dried under reduced pressure at 333 K.

0040-6031/91/$03.50

The concentrations of the solvents were determined by weight.

The measurements of the enthalpies of solution were carried out in an "isoperibol" calorimeter [13], at 298.15 K. The accuracy of the measurements is estimated to be better than 0.6%.

RESULTS AND DISCUSSION

The enthalpies of dissolution of glycine in aqueous solutions of electrolytes from 0.5 to 2.5 mol electrolyte (kg water)$^{-1}$ in the glycine concentrations range of 0.004–0.02 mol G (kg solvent)$^{-1}$ were measured at 298.15 K.

On the basis of the solution enthalpy values, the standard enthalpies of solution of glycine in aqueous solutions of electrolytes were determined graphically (Table 1).

The enthalpies of dissolution of glycine in the aqueous solutions of electrolytes show that the endothermic effect of dissolution decreases as the electrolyte concentration increases (Table 1).

The enthalpic pair interaction coefficients of glycine molecule–dissociated electrolyte in water were estimated on the basis of the dissolution enthalpy of glycine in water–salt mixtures measured in this work. In order to calculate the νh_{GE} coefficients, a method similar to those described by Friedman and Krishman [11], Desnoyers et al. [14] and Heuvelsland et al. [15] was used. The standard enthalpy of solution, $\Delta H_{\mathrm{m}}^{\ominus}$, of glycine in water–electrolyte was presented as a function

$$\Delta H_{\mathrm{m}}^{\ominus}(\mathrm{G\ in\ W+E}) = \Delta H_{\mathrm{m}}^{\ominus}(\mathrm{G\ in\ W}) + 2\nu h_{\mathrm{GE}} m_{\mathrm{E}} + 3\nu h_{\mathrm{GEE}} m_{\mathrm{E}}^{2} + \ldots$$

where E is the electrolyte, $\Delta H_{\mathrm{m}}^{\ominus}$ (G in W) denotes the standard enthalpy of solution of glycine in pure water ($\Delta H_{\mathrm{m}}^{\ominus} = 14.20$ kJ mol^{-1}) [16], ν is the number of ions which the electrolyte dissociates and m_{E} is the electrolyte content (in mol kg^{-1}).

TABLE 1

Standard enthalpies of solution ($\Delta H_{\mathrm{m}}^{\ominus}$) for glycine in aqueous electrolyte solutions at 298.15K

m_{E} (mol kg^{-1})	$\Delta H_{\mathrm{m}}^{\ominus}$ (kJ mol^{-1})							
	NaCl	KCl	CsCl	NaI	KI	CsI	$NaNO_3$	KNO_3
0.5	13.74	13.75	13.74	13.28	13.27	13.28	13.27	13.28
1.0	13.34	13.35	13.29	12.42	12.39	12.42	12.40	12.41
1.5	12.92	12.96	12.93	11.56	11.52	11.56	11.56	11.53
2.0	12.58	12.68	12.59	10.78	10.76	10.81	10.72	10.76
2.5	12.34	12.35	–	9.98	9.95	–	10.00	10.05

TABLE 2

Enthalpic pair interaction coefficients for glycine–electrolyte in water solutions at 298.15 K

Salt	$(h_{GM^+} + h_{GX^-})$ (J kg mol^{-1})
NaCl	−480 (−504) [a]
KCl	−470 (−490) [a]
CsCl	−490 (−508) [a]
NaI	−940
KI	−945 (−962) [a]
CsI	−950
$NaNO_3$	−950
KNO_3	−935

[a] From Ref. 10.

Hence:

$$\left[\Delta H_m^\ominus(\text{G in W} + \text{E}) - \Delta H_m^\ominus(\text{G in W})\right] m_E^{-1} = 2\nu h_{GE} + 3\nu h_{GEE} m_E + \cdots$$

The enthalpic pair interaction coefficients between a molecule of glycine and a molecule of the electrolyte of the 1 : 1 type, $\nu h_{GE} = (h_{GM^+} + h_{GX^-})$, were determined graphically. The values of $(h_{GM^+} + h_{GX^-})$ obtained in this way are listed in Table 2. For comparison, the enthalpic pair interaction coefficients reported by Lilley et al. [10] are also listed in Table 2.

For the chloride and iodide salts the change of cation (Na^+, K^+ or Cs^+) does not exert any influence on the values of the enthalpic pair interaction coefficients between glycine and the electrolyte (Table 2). The carboxylic group, which has a negative charge, interacts with the cations so strongly that water–cation and water–glycine electrostatic interactions do not meet the competition with these. Thus, a glycine molecule does not distinguish the alkali cations.

A small ion with high charge density, Li^+ is the exception to the rule and its behaviour is different [10].

In the case of anions interacting with a glycine–NH_3^+ group, the size of the hydrated anion differentiates the force of electrostatic interactions existing between the molecule of glycine and anion in a water solution.

Additional investigations of the enthalpy of solution of glycine in $NaNO_3$ and KNO_3 aqueous solutions (Tables 1 and 2) have confirmed the above mentioned suggestion concerning the "lack of differentiation" among alkali cations by the carboxylate group of glycine.

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