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Short communication

Thermodynamics of solution of histidine

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Abstract

The enthalpies of solution of L-histidine in water at 288.15–318.15 K and 0.003–0.15 mol kg^{-1} were measured. The enthalpies of solution were found to be independent of the solute molality up to ~0.1 mol kg^{-1}. Standard enthalpies and heat capacities of solution were computed. Free energies and entropies of solution have been estimated in the temperature range studied using literature solubility data and the results of the present study. The temperature increase was found to result in a pronounced rise of the L-histidine solubility due to the significant increase of the $T\Delta S$ values. The characteristic temperatures for the thermodynamic properties of histidine aqueous solutions were estimated.
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1. Introduction

Many investigations of thermodynamic properties of amino acids in aqueous solutions have been done [1–9]. However, most of these works deal with highly soluble non-polar or aliphatic amino acids, the measurements being performed at 298.15 K. Thermodynamics of aqueous solutions of slightly soluble aromatic amino acids is scarce [1,4,5]. The present work is one of our continuing studies on thermodynamic properties of aromatic amino acid aqueous solutions [10–12]. This paper reports experimental enthalpies of solution of L-histidine in water at different temperatures and concentrations. Standard enthalpies, heat capacities, free energies and entropies of L-histidine in water in the 273–373 K temperature range are reported.

2. Experimental

L-Histidine (C$_3$H$_3$N$_2$CH$_2$CH(NH$_2$)COOH, M = 155.16 g/mol, MP Biomedicals Inc., Germany, >99%) was dried under reduced pressure at 343 K and used without further purification. The calorimetric measurements were carried out with a new isoperibol ampoule calorimeter fitted with a 70-cm^3 vessel [12]. The vessel is equipped with a calibration heater, a titanium stirrer and a thermistor. A glass ampoule containing solute is attached

to the stirrer and crushed against the vessel bottom to initiate the dissolution process. Thermistor resistance is measured by the Standard Temperature Measuring Instrument constructed by Inter Higher Educational Institute Centre of Belarus. The signal is converted to the degrees of The International Temperature Scale of 1990. The detection limit of the apparatus is of 10 μK. The temperature stability in the bath is less than 1 mK. An electrical calibration is carried out before and after each experiment. The calorimeter was tested by measuring the enthalpies of solution of potassium chloride (KCl) and 1-propanol (1-PrOH) in water at 298.15 K according to [13]. The agreement between our ($\Delta_{sol}H^m$ (m = 0.111 mol kg^{-1}) = 17.61 ± 0.02 kJ mol^{-1} for KCl and $\Delta_{sol}H^\circ$ = −10.18 ± 0.03 kJ mol^{-1} for 1-PrOH) and recommended literature values (17.58 ± 0.02 and −10.16 ± 0.02 kJ mol^{-1} for KCl and 1-PrOH, respectively) was found to be excellent [12].

3. Results and discussion

The experimental enthalpies of solution are given in Table 1. The $\Delta_{sol}H^m$ values do not depend on the solute concentration below ~0.1 mol kg^{-1}. Above ~0.1 mol kg^{-1} the dissolution process becomes less endothermic. This observation indicates enthalpically unfavourable histidine–histidine pair interaction. Thus, we calculate the standard enthalpies of L-histidine solution ($\Delta_{sol}H^\circ$) as average values in the range of the solute molalities of 0.003–0.06 mol kg^{-1}.

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Table 1
Experimental ($\Delta_{sol}H^m$, kJ mol^{-1}) and standard enthalpies of solution ($\Delta_{sol}H^\circ$, kJ mol^{-1}) of L-histidine at 288.15, 293.15, 306.15 and 318.15 K

m^a	$\Delta_{sol}H^m$	m	$\Delta_{sol}H^m$
288.15 K		293.15 K	
0.005560	13.80	0.008882	13.90
0.01275	13.78	0.01765	13.97
0.01792	13.76	0.01801	14.02
0.01847	13.83	0.02017	13.95
0.01904	13.76	0.02245	13.93
0.02165	13.65	0.1121	13.67
$\Delta_{sol}H^\circ = 13.76 \pm 0.05^b$		$\Delta_{sol}H^\circ = 13.95 \pm 0.04$	
306.15 K		318.15 K	
0.003302	14.66	0.009980	15.71
0.006683	14.69	0.01765	15.79
0.01133	14.73	0.01956	15.79
0.02783	14.78	0.02103	15.76
0.02928	14.73	0.1018	15.57
0.02944	14.84	$\Delta_{sol}H^\circ = 15.76 \pm 0.04$	
0.05805	14.72		
0.1184	14.47		
$\Delta_{sol}H^\circ = 14.74 \pm 0.05$			

^{a} Moles of the solute per 1 kg of water.
^{b} Errors represent twice standard deviation from the mean value.

Analysis of the temperature dependence of the $\Delta_{sol}H^\circ$ values given in Table 1 were performed with the second-order polynomial equation:

$$\Delta_{sol}H^\circ(T) = \Delta_{sol}H^\circ(\Theta) + \Delta_{sol}C_p^\circ(\Theta)(T - \Theta)$$
$$+ 0.5\left(\frac{\partial \Delta_{sol}C_p^\circ}{\partial T}\right)[(T - \Theta)^2] \qquad (1)$$

where $\Delta_{sol}H^\circ(T)$ and T (current temperature, K) are variables, $\Delta_{sol}H^\circ(\Theta)$ and $\Delta_{sol}C_p^\circ(\Theta)$ are the enthalpy and heat capacity parameters desired at a reference temperature Θ (K), respectively. The equation parameters thus have a clear physical meaning. The $\Delta_{sol}H^\circ$ values of 14.22 ± 0.06 and 15.34 ± 0.07 kJ mol^{-1} at 298.15 and 313.15 K, respectively [11], have also been included in the calculation. The $\Delta_{sol}C_p^\circ$ values obtained are positive and increase as the temperature increases (see Table 2). The heat capacity of L-histidine solution at 298.15 K is small (57 ± 2 J mol^{-1} K^{-1}) but larger than that for more hydrophilic alanine (19 ± 4 J mol^{-1} K^{-1}) [4], and noticeably smaller than the heat capacity of solution of hydrophobic L-phenylalanine (189 J mol^{-1} K^{-1}) [10]. In the previous study [11] we estimated the heat capacity of L-histidine solution near 306 K to be about 75 ± 7. The data given in Table 2 confirm this estimation.

Nozaki and Tanford [1] reported the solubility of many amino acids in water. Since L-histidine is slightly soluble in water at 298.15 K (4.33 g per 100 g of water or $X_2 = 0.00500$ mol fraction of the amino acid) [1], we can represent the limiting activity coefficient of the solute as:

$$\gamma^\infty \approx \frac{1}{X_2} \qquad (2)$$

Then the standard free energy of solution and temperature changes of the limiting activity coefficients are defined by the

Table 2
Coefficients of Eq. (1) ($\Delta_{sol}H^\circ(\Theta)$, kJ mol^{-1}; $\Delta_{sol}C_p^\circ(\Theta)$, J mol^{-1} K^{-1}; $\partial \Delta_{sol}C_p^\circ/\partial T$, J mol^{-1} K^{-2}) and solubility X_2 (mol fractions) of L-histidine in water at different temperatures

Θ	$\Delta_{sol}H^\circ(\Theta)$	$\Delta_{sol}C_p^\circ(\Theta)$	$\partial \Delta_{sol}C_p^\circ/\partial T$	X_2
273.15	13.42(0.08)^a	7(6)	2.0(0.2)	0.00302
283.15	13.59(0.03)	27(4)	2.0(0.2)	0.00372
293.15	13.96 (0.01)	47(2)	2.0(0.2)	0.00454
303.15	14.54 (0.01)	68(1)	2.0(0.2)	0.00550
313.15	15.31 (0.01)	88(2)	2.0(0.2)	0.00665
323.15	16.29(0.03)	108(4)	2.0(0.2)	0.00802
333.15	17.47(0.08)	128(6)	2.0(0.2)	0.00968
343.15	18.86(0.15)	149(8)	2.0(0.2)	0.0117
353.15	20.45(0.24)	169(10)	2.0(0.2)	0.0142
363.15	22.24(0.35)	189(12)	2.0(0.2)	0.0174
373.15	24.23(0.48)	210(14)	2.0(0.2)	0.0214

^{a} Values in brackets represent the standard deviation of coefficients obtained. The standard deviation of the fit is 0.02 kJ mol^{-1}.

following equations:

$$\Delta_{sol}G^\circ = RT \ln \gamma^\infty \approx RT \ln\left(\frac{1}{X_2}\right) \qquad (3)$$

$$\ln \gamma^\infty(T_2) - \ln \gamma^\infty(T_1) \approx \ln \frac{X_2(T_1)}{X_2(T_2)} = -\frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta_{sol}H^\circ}{T^2}\,dT \qquad (4)$$

Thus, using the temperature dependence of the enthalpies of solution and the experimental solubility in water at 298.15 K [1], we are able to calculate solubility, standard free energies and entropies of L-histidine solution in a wide temperature range.
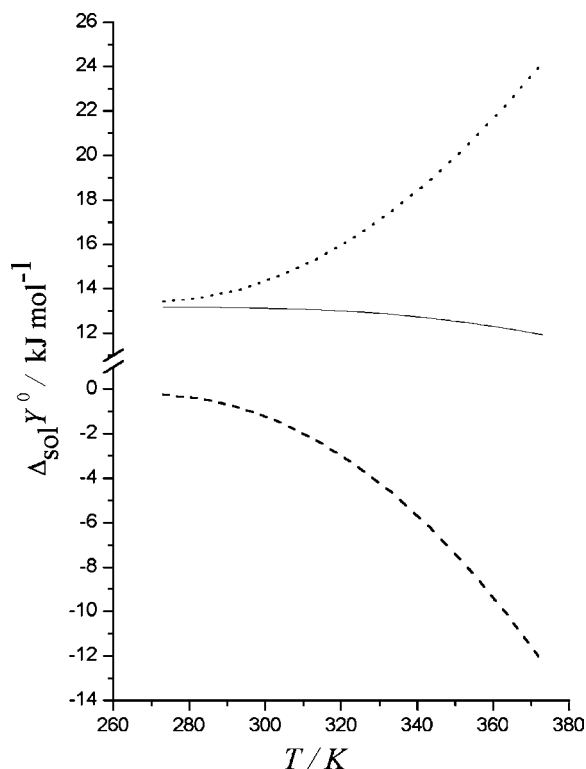

Fig. 1. Enthalpic $\Delta_{sol}H^\circ$ (dotted line) and entropic terms ($-T\Delta_{sol}S^\circ$) (dash line) in the free energies $\Delta_{sol}G^\circ$ (solid line) of solution of L-histidine in water.

Table 2 shows that the temperature increase causes a rise of solubility, as it is usually observed for solids. Fig. 1 compares the enthalpic $\Delta_{sol}H^{\circ}$ and entropic $(-T\Delta_{sol}S^{\circ})$ terms to the free energy of solution. The first term is seen to be positive, but the second one is negative. Both of them rise in absolute value as the temperature is increased, however the entropic term shows a stronger temperature dependence, which results in enhancing solubility (see Table 2). Fig. 1 clearly indicates that the entropic term is close to zero near the freezing point of liquid water and, therefore, $\Delta_{sol}H^{\circ} \approx \Delta_{sol}G^{\circ}$. An interesting situation is observed near the boiling point of water, where $\Delta_{sol}G^{\circ} = T\Delta_{sol}S^{\circ}$ and, therefore, $\Delta_{sol}H^{\circ} = 2T\Delta_{sol}S^{\circ}$. A simple analysis of the temperature dependence of the enthalpic and entropic terms indicates that both functions have minima near 270 K. Thus, the standard heat capacity of L-histidine solution should be close to zero near the freezing point of pure water, i.e. the partial molar heat capacity of L-histidine at infinite dilution equals the heat capacity of the solid.

Acknowledgements

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