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STANDARD ENTHALPIES OF FORMATION OF THE PHENYLALANINE ISOMERS AND THE PRODUCTS OF THEIR DISSOCIATION IN AQUEOUS SOLUTIONS

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The heats of dissolution of the crystalline *L*-phenylalanine and *D,L*-phenylalanine in water and potassium hydroxide solutions at 298.15 K which were determined by direct calorimetric method are reported. These heats made available calculations the standard enthalpies of the phenylalanine isomers and the products of their dissociation in aqueous solutions.

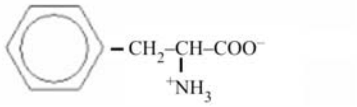
Keywords: *aminoacids, calorimetry, dissociation, thermodynamic characteristics*

Introduction

The systematic determinations of the main thermodynamic parameters for a series of bioligands like amino acids, peptides, hydroxy-acids and complexons with different functional groups are carried out in our laboratory [1–7].

Application of theoretical achievements and experimental methods of modern chemistry of solutions to biological objects has considerable importance for understanding mechanisms of intra-body proceeded processes.

The aliphatic amino acids were researched in detail. Standard enthalpies of formation of crystalline amino acids, the products of their dissociation in aqueous solutions were determined previously [8–10]. But the study of aromatic amino acids also is very interesting and useful for research investigations. Moreover, the thermodynamic parameters of solutions of these substances were investigated to a lesser extent, than aliphatic amino acids. In this connection the phenylalanine ($HPhe^{\pm}$) was choused as objects of the present study. It has such formula:



Value of dissolution enthalpies of crystalline *D,L*-phenylalanine in water at 298.15 K was reported by Rodante [8]: $\Delta_{sol}H^0=7.699$ kJ mol^{-1}. Data of others thermodynamic parameters are absent in literature.

The aim of this work is to determine the standard enthalpies of the phenylalanine isomers and the products of their dissociation in aqueous solutions from the dissolution heat effects of the isomers of amino acid in water and potassium hydroxide solutions at 298.15 K.

Experimental

Chromatographically homogeneous crystalline preparations of the *L*-phenylalanine (‘Panreac Sintesis’, Spain) and *D,L*-phenylalanine (Russia) were used. Noncarbonated potassium hydroxide solutions were prepared from the chemically pure reagent according to the standard procedure [11].

Heats of the dissolution of the crystalline isomers of amino acid in water and potassium hydroxide solutions were measured in an ampoule calorimeter equipped with an isothermal shell and automatic recorder of temperature. The calorimeter was calibrated by electric current. The volume of the calorimetric liquid was 50.02 mL; the amino acid samples were weight on a VLR-200 balance to $5\cdot10^{-5}$ g. The experimental data obtained are summarized in Table 1. The uncertainty in $\Delta_{sol}H$ was calculated at a 0.95 confidence level. The equilibrium composition of the solutions was computed on a Celeron(R) CPU 2.40 GHz computer with using the program ‘RRSU’ [12].

Results and discussion

The process of dissolution of the phenylalanine isomers in water can be represented as follows:

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Table 1 Heat effects of dissolution ($\Delta_{sol}H$) and formation ($\Delta_f H_0$) of *L*-phenylalanine and *D,L*-phenylalanine in water at 298.15 K (kJ mol^{-1})

Isomer	q/g	$m\cdot 10^{-3}$	n	$\Delta_{sol}H$	$-\Delta_f H^0$
L-Phe	0.01067	1.298	41822	8.07	458.1
	0.05162	6.237	8903	7.38	459.1
	0.07170	8.660	6408	8.30	458.2
	0.07672	9.270	6014	8.32	458.2
D,L-Phe	0.01000	1.210	45868	7.78	452.6
	0.03096	3.747	14878	8.05	452.3
	0.05100	6.172	8997	8.04	452.3
	0.07071	8.558	6488	8.43	451.9

q is the phenylalanine sample mass (g); m is the molality (mol HPhe$^{\pm}$/1000 g H_2O); n is the degree of dilution (mol HPhe$^{\pm}$/mol H_2O); $-\Delta_f H^0 \equiv -\Delta_f H^0$(HPhe$^{\pm}$, sln, H_2O, stand. cond., hyp.undiss., 298.15 K)

$$\mathrm{HPhe}^{\pm}_{(cr)} + \mathrm{nH_2O} = \mathrm{HPhe}^{\pm}(\mathrm{sln, nH_2O}) \quad (1)$$

The standard enthalpies of formation of investigated amino acid at various degrees of dilution were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln,nH_2O}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{cr}, 298.15\ \mathrm{K}) &+ \\ +\Delta_{sol} H^0(\mathrm{HPhe}^{\pm}, \mathrm{cr}, 298.15\ \mathrm{K})&\end{aligned} \quad (2)$$

where $\Delta_f H^0$(HPhe$^{\pm}$, cr, 298.15 K) is the standard enthalpy of formation of the crystalline phenylalanine; $\Delta_{sol} H^0$(HPhe$^{\pm}$, cr, 298.15 K) is the heat of dissolution of the amino acid. The calculation results are listed in Table 1.

The standard enthalpies of formation of the crystalline isomers of phenylalanine were calculated from experimentally measured enthalpies of combustion.

The reaction of combustion of the crystalline amino acid can be represented as follows:

$$\begin{aligned}C_9H_{11}O_2N_{(cr)} + 10\ 3/4O_{2(gas)} &= 9CO_{2(gas)} + \\ + 5\ 1/2H_2O_{(liq)} &+ 1/2N_{2(gas)}\end{aligned} \quad (3)$$

The standard enthalpies of combustion of investigated amino acid were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{cr}, 298.15\ \mathrm{K}) &= \\ = 9\Delta_f H^0\ (\mathrm{CO_2}, \mathrm{gas}, 298.15\ \mathrm{K}) &+ \\ + 5.5\Delta_f H^0(\mathrm{H_2O}, \mathrm{liq}, 298.15\ \mathrm{K}) &- \\ - \Delta_c H^0(\mathrm{HPhe}^{\pm}, \mathrm{cr}, 298.15\ \mathrm{K})&\end{aligned} \quad (4)$$

where $\Delta_c H^0$(HPhe$^{\pm}$, cr, 298.15 K) are the standard enthalpies of combustion *D,L*-phenylalanine and *L*-phenylalanine [11]: $\Delta_c H^0$(*D,L*-HPhe$^{\pm}$, cr, 298.15 K)= –4653.0±2.5 kJ mol^{-1}; $\Delta_c H^0$(*L*-HPhe$^{\pm}$, cr, 298.15 K)= –4646.8±0.8 kJ mol^{-1}; $\Delta_f H^0$(CO_2, gas, 298.15 K) and $\Delta_f H^0$(H_2O, liq, 298.15 K) are the standard enthalpies of formation of CO_2 and H_2O, which recommended by [13]. The substitution of numerical values in Eq. (4) gives possibility to obtained following values: $\Delta_f H^0$(*D,L*-HPhe$^{\pm}$, cr., 298.15 K)= –460.3±2.5 kJ mol^{-1} and $\Delta_f H^0$(*L*-HPhe$^{\pm}$, cr., 298.15 K)= –466.5±0.8 kJ mol^{-1}.

The standard enthalpies of formation of phenylalanine solutions at various degrees of dilution were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln.}, \mathrm{nH_2O}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{cr.}, 298.15\ \mathrm{K}) &+ \\ + \Delta_{sol} H(\mathrm{HPhe}^{\pm}, \mathrm{cr.}, 298.15\ \mathrm{K})&\end{aligned} \quad (5)$$

where $\Delta_f H^0$(HPhe$^{\pm}$, cr., 298.15 K) is the standard enthalpy of formation of crystalline amino acid; $\Delta_{sol} H$(HPhe$^{\pm}$, cr., 298.15 K) is the heat of dissolution of crystalline amino acid in water.

As can be seen from Table 1, the heat effects of formation of *L*-phenylalanine and *D,L*-phenylalanine in aqueous solutions over the concentration range covered is almost independent of the degree of dilution, a quite natural behavior at such high dilution.

The standard enthalpies of formation of the phenylalanine zwitterions in a hypothetically nondissociated states at infinite dilution in an aqueous solution were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln}, \mathrm{nH_2O}, \mathrm{hyp.nondiss.}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln}, \mathrm{nH_2O}, 298.15\ \mathrm{K}) &- \\ \alpha(\mathrm{H_2Phe}^{+})\Delta_{ass} H^0(\mathrm{HPhe}^{\pm}) + \alpha(\mathrm{Phe}^{-})\Delta_{ass} H^0(\mathrm{Phe}^{-})&\end{aligned} \quad (6)$$

where $\alpha(\mathrm{H_2Phe}^+)$ and $\alpha(\mathrm{Phe}^-)$ are fractions of the $\mathrm{H_2Phe}^+$ and Phe^- species, respectively; $\Delta_{ass} H^0$(HPhe$^{\pm}$) and $\Delta_{ass} H^0$(Phe$^-$) are the heat effects of stepwise association of the Phe$^-$. The values of $\Delta_{ass} H^0$(HPhe$^{\pm}$, 298.15 K) and $\Delta_{ass} H^0$(Phe$^-$, 298.15 K) were determined in [14]. The total contribution of the second and third terms on the right-hand side of Eq. (6) does not exceed 0.1 kJ mol^{-1}, being nearly constant over the concentration range covered.

The standard enthalpies of formation of the phenylalanine isomers in a hypothetically nondissociated state at infinite dilution were determined by extrapolation of the values calculated by Eq. (6) to zero molality *m* of the solution (Fig. 1). As a result, the least-squares method yielded:

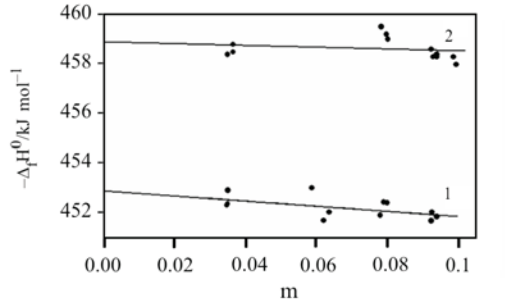

Fig. 1 Graphical determination of the standard enthalpy of formation of 1 – *D,L*-phenylalanine and 2 – *L*-phenylalanine in a hypothetical nondissociated condition at a nonzero dilution ($\Delta_f H^0$(HPhe$^{\pm}$, sln, nH_2O, stand. cond., hyp.undiss., 298.15 K))

(*L*-isomer) $\Delta_f H^0$(HPhe$^{\pm}$, sln, nH_2O, hyp.nondiss., 298.15 K) = –458.8±0.8 kJ mol^{-1};

(*D,L*- isomer) $\Delta_f H^0$(HPhe$^{\pm}$, sln, nH_2O, hyp.nondiss., 298.15 K) = –452.9±2.5 kJ mol^{-1}.

It should be mentioned that value of the enthalpy of dissolution of crystalline *D,L*- phenylalanine in water at infinite dilution $\Delta_{sol}H_{\infty}$(HPhe$^{\pm}$)=7.67±0.22 kJ mol^{-1} was determined in this work; it is well agreed with data [8].

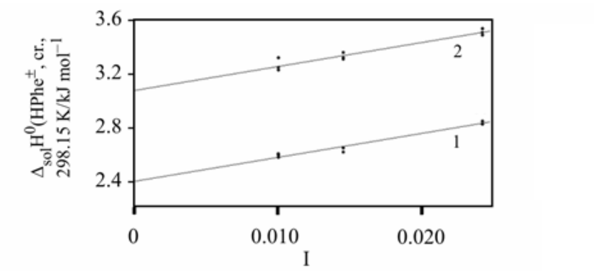

Fig. 2 Graphical determination of the heat of dissolution of 1 – *L*-phenylalanine and 2 – *D,L*-phenylalanine in a KOH solution at infinite dilution ($\Delta_{sol}H^0$(HPhe$^{\pm}$, cr. 298.15 K))

The standard enthalpies of formation of the L$^-$ species in aqueous solutions were determined from the heat of solution of the phenylalanine isomers in alkaline solutions at equivalent rations not lesser than 1:2 (Table 2). The process of dissolution of amino acids in a KOH solution can be represented as:

$$\text{HPhe}^{\pm}_{(cr)} + \text{OH}^-(\text{sln}, nH_2O) = \\ = \text{Phe}^-(\text{sln}, nH_2O) + H_2O_{(liq)} \qquad (7)$$

Calculations showed that the extent of reaction (7) was not less than 99.9%.

In reaction (7) Δz^2=0; therefore, the heat effects of dissolution of amino acids at a zero ionic strength were calculated by the equation [15]:

$$\Delta_r H = \Delta_r H^0 + \text{bI} \qquad (8)$$

where $\Delta_r H$ and $\Delta_r H^0$ are the heat effects of the reaction (7) at a certain and zero ionic strength.

Based on the $\Delta_r H$(7) values obtained and the values of $\Delta_f H^0$ (OH$^-$, sln, H_2O, 298.15 K) and $\Delta_f H^0$ (H_2O, liq, 298.15 K) from [15], the standard enthalpies of formation of deprotonate anions were calculated:

Table 2 Heat effects of dissolution of *L*-phenylalanine and *D,L*-phenylalanine in KOH solutions at 298.15 K (kJ mol^{-1})

Isomer	*q*/g	$\Delta_{sol}H$	Isomer	*q*/g	$\Delta_{sol}H$
L-Phe	C_{KOH}=0.01005 mol L^{-1}		*D,L*-Phe	C_{KOH}=0.01005 mol L^{-1}	
	0.03765	2.57		0.04100	3.22
	0.04001	2.60		0.03915	3.24
	0.03873	2.59		0.03845	3.31
	C_{KOH}=0.01455 mol L^{-1}			C_{KOH}=0.01455 mol L^{-1}	
	0.06225	2.64		0.06121	3.30
	0.06113	2.64		0.05913	3.35
	0.05590	2.61		0.05990	3.31
	C_{KOH}=0.02421 mol L^{-1}			C_{KOH}=0.02421 mol L^{-1}	
	0.0971	2.82		0.10035	3.48
	0.1012	2.84		0.09981	3.50
	0.1045	2.84		0.09963	3.53

Table 3 Standard enthalpies of formation of *L*-phenylalanine and *D,L*-phenylalanine and the products of their dissociation in aqueous solutions (kJ mol^{-1})

Isomer	Particle	Condition	$-\Delta_f H^0$ (298.15 K)
L-phenylalanine	$HPhe^{\pm}$	cr.	466.5±0.8
		sln, H_2O,stand.cond., hyp.undiss	458.3±0.8
	H_2Phe^+	sln, H_2O,stand.cond., hyp.undiss	459.7±0.9
	Phe^-	sln, H_2O,stand.cond.	413.1±0.8
D,L-phenylalanine	$HPhe^{\pm}$	cr.	460.3±2.5
		sln, H_2O,stand.cond., hyp.undiss.	452.7±2.5
	H_2Phe^+	sln, H_2O,stand.cond., hyp.undiss.	454.1±2.5
	Phe^-	sln, H_2O,stand.cond.	407.6±2.5

$$\begin{aligned}\Delta_f H^0 (\mathrm{Phe}^-, \mathrm{sln}, \mathrm{H_2O}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0 (\mathrm{HPhe}^{\pm}, \mathrm{cr}, 298.15\ \mathrm{K}) &+ \\ + \Delta_f H^0 (\mathrm{OH}^-, \mathrm{sln}, \mathrm{H_2O}, 298.15\ \mathrm{K}) + \Delta_r H^0 &+ \\ + \Delta_f H^0 (\mathrm{H_2O}, \mathrm{liq}, 298.15\ \mathrm{K})\end{aligned} \tag{9}$$

The standard enthalpies of formation of the $HPhe^{\pm}$ species were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln}, \mathrm{H_2O}, \mathrm{hyp.nondiss.}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0 (\mathrm{Phe}^-, \mathrm{sln}, \mathrm{H_2O}, \mathrm{stand.\ cond.}, 298.15\ \mathrm{K}) &- \\ - \Delta_{dis} H^0(\mathrm{HPhe}^{\pm}, 298.15\ \mathrm{K})\end{aligned} \tag{10}$$

The standard enthalpies of formation of the *L*-phenylalanine and *D,L*-phenylalanine zwitterions are in agreement with the values of $\Delta_f H^0(HPhe^{\pm}$, sln, H_2O, hyp.nondiss., 298.15 K) obtained previously. The weighted means of two independent calculations of $\Delta_f H^0(HPhe^{\pm}$, sln, H_2O, hyp.nondiss., 298.15 K) were accepted as the most probable values.

The standard enthalpies of formation of the H_2Phe^+ were calculated by equation:

$$\begin{aligned}\Delta_f H^0(\mathrm{H_2Phe}^+, \mathrm{sln}, \mathrm{H_2O}, \mathrm{hyp.nondiss.}, 298.15\ \mathrm{K}) &= \\ = \Delta_f H^0(\mathrm{HPhe}^{\pm}, \mathrm{sln}, \mathrm{H_2O}, \mathrm{hyp.nondiss.}, 298.15\ \mathrm{K}) &- \\ - \Delta_{dis} H^0(\mathrm{H_2Phe}^+, 298.15\ \mathrm{K})\end{aligned} \tag{11}$$

Calculated values of the standard enthalpies of formation the isomers of phenylalanine and the products of their dissociation in aqueous solutions were evaluated for the first time [Table 3]. This values are needed to perform exact thermodynamic calculations of equilibrium in solutions of *L*-phenylalanine and *D,L*-phenylalanine.

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