ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 3, pp. 417–421. © Pleiades Publishing, Ltd., 2012.
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Effect of Background Electrolyte Concentration on the Heat Effects in the Processes of Formation of L-Asparagine Complexes with Cu^{2+} Ions in Aqueous Solution

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Received January 18, 2011

Abstract—A direct calorimetric method was used to measure the heat effects in the reactions of formation of Cu(II) complexes with L-asparagine in aqueous solutions at 298.15 K and ionic strength 0.5, 1.0, 1.5 (KNO_3). The standard thermodynamic characteristics ($\Delta_r H^0$, $\Delta_r G^0$, $\Delta_r S^0$) of the processes of complex formation in the system under study were calculated.

DOI: 10.1134/S1070363212030097

Numerous publications concern the determination of the constants of reactions of the copper(II) asparaginate complexes in aqueous solution. We recalculated the stability constants of CuL^+ and CuL_2, which were obtained by the different researchers in a variety of concentration conditions, to zero ionic strength according to Davis equation [1]. The most probable values of the thermodynamic stability constants of complexes of L-asparagine (L^-) with the ion Cu^{2+} were calculated as the mean values of those published in [2–5]: $\log \beta^0(CuL^+) = 8.29 \pm 0.01$, $\log \beta^0(CuL_2) = 15.09 \pm 0.05$. The recalculation of the constants to fixed values of ionic strength (I) was performed according to the equation proposed in [6].

Table 1 shows the thermodynamic characteristics of the formation of asparaginate Cu(II) complexes obtained by different researchers. It follows from Table 1 that the published data on the heat of complex formation in the system Cu^{2+}–L-asparagine are contradictory. The difference in the determined heat effects of the CuL_2 species amounts to 14 kJ mol^{-1}. Effect of background electrolyte concentration on the thermodynamic characteristics of complex formation was not studied.

The purpose of this paper is the determination by direct calorimetric method of the heat effects of the formation of copper(II) complexes with L-asparagine at 298.15 K and different values of ionic strength, as well as the calculation of standard thermodynamic characteristics of the complexation processes in the Cu^{2+}–L-asparagine system.

The heat effects of the interaction of solutions of copper(II) with solutions of L-asparagine accounting for all the processes occurring in the system can be calculated by formula (1).

$$\Delta_{mix}H - \Delta_{dil}H = \Delta_r H(CuL^+)\alpha(CuL^+) + \Delta_r H(CuL_2)\alpha(CuL_2) + \Delta_{dis}H(HL^{\pm})\alpha(HL^{\pm}) + \Delta_{dis}H(H_2L^+)\alpha(H_2L^+) + \Delta_r H(CuOH^+)\alpha(CuOH^+) + \Delta_r H_w\alpha(OH^-). \quad (1)$$

Here $\Delta_{mix}H$ is the heat effect of mixing the solutions of L-asparagine and $Cu(NO_3)_2$; $\Delta_{dil}H$ is the heat effect of dilution of $Cu(NO_3)_2$ solution in the background electrolyte solution; $\Delta_r H(CuL^+)$ and $\Delta_r H(CuL_2)$ are heat effects of reactions of complexation of CuL^+ and CuL_2 respectively; $\Delta_{dis}H(H_2L^+)$, $\Delta_{dis}H(HL^{\pm})$ are the enthalpies of the separate steps of L-asparagine dissociation [7]; $\Delta_r H$ ($CuOH^+$) is the heat of formation of 1:1 hydroxo complex of Cu^{2+}; $\Delta_r H_w$ is the heat of formation of water in a solution of KNO_3 [8]; $\alpha(CuL^+)$, $\alpha(CuL_2)$, $\alpha(H_2L^+)$, $\alpha(HL^{\pm})$, $\alpha(CuOH^+)$, and $\alpha(OH^-)$ are the degrees of the occurrence of the corresponding reactions.

The calculation of equilibrium composition of solutions before and after the calorimetric experiment

Table 1. Published data on heat effects of formation of the L-asparagine complexes with the Cu^{2+} ion

References	Ionic strength, I	$-\Delta_r H(CuL^+)$, kJ mol^{-1}	$-\Delta_r H(CuL_2)$, kJ mol^{-1}	$\Delta_r S(CuL^+)$, J mol^{-1} K^{-1}	$\Delta_r S(CuL_2)$, J mol^{-1} K^{-1}
[2]	0.1 (KNO_3)		47.16		118
[3]	3.0 ($NaClO_4$)	27.5	61.5	73.9	97.7
[2]	0.2 (KCl)	26.3	53.9	60.6	92.4
[4]	0.1 (KNO_3)	22.3	47.4	73	112
[5]	0.1 (KNO_3)	22.54		78.49	

Table 2. Heat effects (J mol^{-1}) of the interaction of a Cu $(NO_3)_2$ solution (1.0437 mol kg^{-1}) with a solution of L-asparagine (0.02500 M)

Ionic strength (KNO_3)	$Cu(NO_3)_2$ solution sample, g	$-\Delta_{mix}H_1$	$Cu(NO_3)_2$ solution sample, g	$-\Delta_{dil}H_1$	$-\Delta_r H(CuL_2)$
0.5	0.29025	55220	0.29030	2520	52680
	0.28980	55240	0.29015	2520	52700
	0.28930	55400	0.29030	2590	52860
		$-\Delta_{mix}H_1$ 55290±180		$-\Delta_{dil}H_1$ 2540±100	$-\Delta_r H(CuL_2)$ 52740±220
1.0	0.28955	59180	0.29010	4180	55010
	0.29020	59300	0.28980	4190	55140
	0.28965	59400	0.29025	4150	55220
		$-\Delta_{mix}H_1$ 59290±200		$-\Delta_{dil}H_1$ 4170±100	$-\Delta_r H(CuL_2)$ 55120±200
1.5	0.29005	61500	0.29020	4280	57270
	0.29025	61520	0.29020	4200	57290
	0.28970	61220	0.28990	4200	57000
		$-\Delta_{mix}H_1$ 61410±300		$-\Delta_{dil}H_1$ 4230±110	$-\Delta_r H(CuL_2)$ 57180±320

with the RRSU software showed that in the chosen experimental conditions (c^0_{Me}:c^0_L = 1:3.3, pH 9.6–8.3) the yield of the complex CuL_2 was 99.9%. The completeness of the remaining reactions tends to zero. Therefore to find the heat of formation of CuL_2 species we used Eq. (2).

$$\Delta_r H(CuL_2) = (\Delta_{mix}H_1 - \Delta_{dil}H_1)/\alpha(CuL_2). \quad (2)$$

Here $\Delta_{mix}H_1$ is the heat effect of mixing the solutions of $Cu(NO_3)_2$ and L-asparagine; $\Delta_{dil}H_1$ is the heat effect of dilution of the $Cu(NO_3)_2$ solution with the background electrolyte solution. The heat effects of the CuL_2 complex formation are shown in Table 2.

At the interaction of solutions of $Cu(NO_3)_2$ with L-asparagine in the pH range 10.5–6.2 at a ratio of the reagents 1:1.2 the reactions of formation of the complexes CuL^+, CuL_2 and dissociation of the L-asparagine zwitter-ion occur. As showed the calculation of equilibrium composition of the solutions before and after the calorimetric experiment, the completeness of the reactions was 64, 26, and 2% respectively. The contribution of thermal effects of the other processes was negligible. Thus, the heat of formation of the complex CuL^+ was calculated according to Eq. (3).

$$\Delta_r H(CuL^+) = [\Delta_{mix}H_2 - \Delta_{dil}H_2 - \alpha(CuL_2)\Delta_r H(CuL_2) - \alpha(HL^{\pm})\Delta_{dis}H(HL^{\pm})]/\alpha(CuL^+). \quad (3)$$

Here $\Delta_{mix}H_2$ is the heat effect of mixing the solutions of $Cu(NO_3)_2$ and L-asparagine; $\Delta_{dil}H_2$ is the heat effect of dilution of the $Cu(NO_3)_2$ solution with the background electrolyte solution. Table 3 shows the experimental data and the calculation results.

The calculated values of $\Delta_r H(CuL^+)$ and $\Delta_r H(CuL_2)$ were extrapolated to zero ionic strength of the solution with the Eq. (4) [6].

$$\Delta H - \Delta Z^2\Psi(I) = \Delta H^0 + bI. \quad (4)$$

Here ΔH, ΔH^0 are the enthalpy changes at a finite value of ionic strength and at I = 0, respectively; $\Psi(I)$ is a function of ionic strength, calculated theoretically; ΔZ^2 is the difference between the squares of the charges of the reaction products and the initial components; b is an empirical coefficient.

Table 3. Heat effects (J mol^{-1}) of the interaction of Cu $(NO_3)_2$ solution (1.0437 mol kg^{-1}) with a solution of L-asparagine (0.01200 M)

Ionic strength (KNO_3)	$Cu(NO_3)_2$ solution sample, g	$-\Delta_{mix}H_2$	$Cu(NO_3)_2$ solution sample, g	$-\Delta_{dil}H_2$	$\alpha(CuL^+)$	$-\Delta_rH(CuL^+)$
0.5	0.39045	33800	0.39000	2700	0.6388	28870
	0.39030	33720	0.39045	2680	0.6388	28660
	0.38965	33780	0.39005	2690	0.6381	28830
		$-\Delta_{mix}H_2$ 33770±100		$-\Delta_{dil}H_2$ 2690±100		$-\Delta_rH(CuL^+)$ 28790±230
	0.39040	35910	0.39050	4150	0.6314	28990
	0.38995	35830	0.39030	4160	0.6311	28840
1.0	0.39000	35840	0.39025	4060	0.6311	28860
		$-\Delta_{mix}H_2$ 35860±100		$-\Delta_{dil}H_2$ 4120±140		$-\Delta_rH(CuL^+)$ 28900±210
	0.38975	37010	0.39050	4220	0.6312	29570
	0.39025	37000	0.39035	4300	0.6315	29600
1.5	0.38985	36970	0.39050	4380	0.6312	29490
		$-\Delta_{mix}H_2$ 36990±100		$-\Delta_{dil}H_2$ 4300±200		$-\Delta_rH(CuL^+)$ 29550±220

Graphical extrapolation of the heat effects of complex formation to zero ionic strength is shown in Fig. 1. The values of the heat effects of formation of the complexes CuL^+ and CuL_2 obtained in this work agree satisfactorily with the data of [2, 3] [$\Delta_rH(CuL^+)$] and [2, 4] [$\Delta_rH(CuL_2)$], respectively.

The calculated values of the thermodynamic characteristics of complexation in the system of Cu^{2+}–L-asparagine are shown in Table 4. The process of complex formation in the Cu^{2+}–L-asparagine system is accompanied by a positive change in entropy.

It follows from Fig. 1 that the exothermicity of the process of the complex CuL_2 formation increases with increasing ionic strength of the solution, since upon increase in the background electrolyte concentration the amount of free water molecules in solution decreases, which leads to a decrease in the contribution of the endothermic process of desolvation to the value of Δ_rH. However, the heat effect of the formation of species CuL^+ is almost independent of the ionic strength. Evidently in the case of the formation of this complex the coordination of water molecules in the inner coordination sphere of the metal is impeded by the growing concentration of KNO_3. A similar effect of potassium nitrate was noted in the study of the Cu^{2+} complexing with L-glutamine and L-valine [9, 10].

The standard heat effect of formation of monocoordinated asparaginate copper(II) complex corresponds to the greater exothermicity [$\Delta_rH^0(CuL^+)$ = –27450 J mol^{-1}] than in the formation of glutamine, $\Delta_rH^0(CuGlu^+)$ = –21110 J mol^{-1} [9], and valine, $\Delta_rH^0(CuVal^+)$ = –22 350 J mol^{-1} [10] complexes, because the side chain of L-asparagine is more hydrophilic than the side chain of L-glutamine and L-valine. In the interaction of aqua complexes of copper(II) with Asn^- ion in the complex far less extensive destruction of hydration shells of the reacting species occurs than in the interaction of Cu^{2+} ions with Glu^- and Val^-. The magnitude of the change in entropy in the case of complex formation $CuAsn^+$ [$\Delta_rS^0(CuAsn^+)$ 66.7 J mol^{-1} K^{-1}] is less than $\Delta_rS^0(CuGlu^+)$ 86.0 J mol^{-1} K^{-1} [9] and $\Delta_rS^0(CuVal^+)$ 88.1 J mol^{-1} K^{-1} [10], which confirms the validity of the above assumptions. The endothermic contribution of the desolvation to the heat effect at the formation of asparaginate copper(II) complex is smaller than at the formation of glutaminate and valinate complexes.

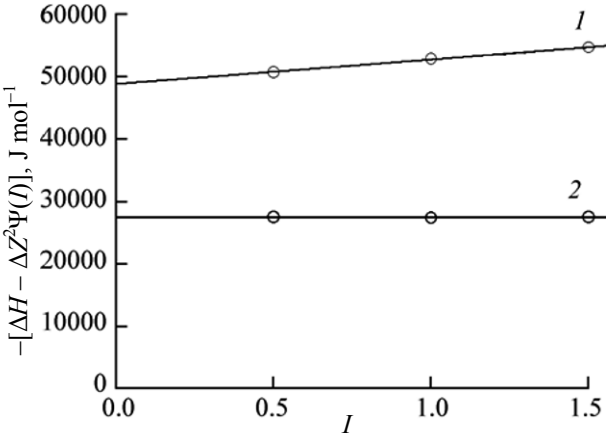

Fig. 1. Determination of standard heat effects of complex formation of CuL_2 (*1*) and CuL (*2*) at 298.15 K (background electrolyte KNO_3).

Table 4. Standard thermodynamic characteristics of the formation of Cu^{2+} complexes with L-asparagine

Process	log β^0	$-\Delta_r H^0$, J mol^{-1}	$-\Delta_r G^0$, J mol^{-1}	$\Delta_r S^0$, J mol^{-1} K^{-1}
		I 0		
$Cu^{2+} + L^- \leftrightarrow CuL^+$	8.29±0.01	27450±220	47320±60	66.7±0.5
$Cu^{2+} + 2L^- \leftrightarrow CuL_2$	15.09±0.05	48860±320	86130±290	125.1±0.6
		I 0.5		
$Cu^{2+} + L^- \leftrightarrow CuL^+$	7.65±0.01	28790±210	43670±60	49.9±0.5
$Cu^{2+} + 2L^- \leftrightarrow CuL_2$	14.12±0.05	52740±220	80600±290	93.4±0.3
		I 1.0		
$Cu^{2+} + L^- \leftrightarrow CuL^+$	7.57±0.01	28900±210	43210±60	48.0±0.5
$Cu^{2+} + 2L^- \leftrightarrow CuL_2$	13.99±0.05	55120±200	79860±290	83.0±0.3
		I 1.5		
$Cu^{2+} + L^- \leftrightarrow CuL^+$	7.54±0.01	29550±220	43040±60	45.2±0.5
$Cu^{2+} + 2L^- \leftrightarrow CuL_2$	13.93±0.05	57180±320	79510±290	74.9±0.5

EXPERIMENTAL

Measurements of thermal effects of mixing ($\Delta_{mix}H$) and diluting ($\Delta_{dil}H$) were performed in a calorimeter with isothermal shell and automatic recording the curve of calorimetric experiment [11]. We used crystalline L-asparagine of chemically pure grade. Before weighing the substance was dried to constant weight at 343 K. A solution of alkali KOH free of carbonate, of the chemically pure grade, was prepared by the method of [12]. The specified ionic strength value was reached by adding potassium nitrate recrystallized from distilled water. The concentration of the $Cu(NO_3)_2$ solution prepared from the reagent of chemically pure grade was determined iodometrically and complexometrically. Experiments were carried out at 298.15 K and ionic strengths 0.5, 1.0, and 1.5. The medium pH was monitored using a pH meter. The solution samples were weighed with an accuracy of ±1.10^{-5}, the equilibrium composition of a solution in each experiment was calculated with the RRSU software [13]. To calculate the confidence interval of the average ΔH value obtained in three parallel experiments the Student's test was used with a confidence level of 0.95.

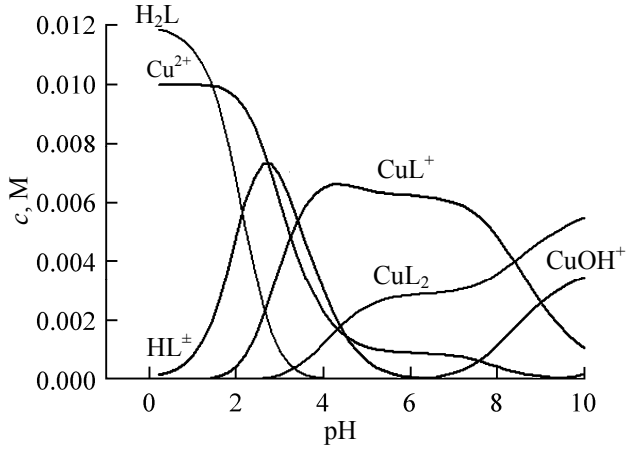

Fig. 2. Diagram of equilibria in the system of Cu^{2+}–L-asparagine (*T* 298.15 K, *I* 0.5) at a ratio of M:L = 1:1.2.

The conditions of the calorimetric experiments were selected and the experimental results were treated taking into account the following processes.

$$L^- + H^+ \leftrightarrow HL^{\pm},$$
$$L^- + 2H^+ \leftrightarrow H_2L^+,$$
$$Cu^{2+} + L^- \leftrightarrow CuL^+,$$
$$Cu^{2+} + 2L^- \leftrightarrow CuL_2,$$
$$H^+ + OH^- \leftrightarrow H_2O,$$
$$Cu^{2+} + HOH \leftrightarrow CuOH^+ + H^+.$$

Figure 2 shows a diagram of the distribution of species in aqueous solutions of Cu^{2+}–L-asparagine.

In order to determine the enthalpy of the complex CuL_2 formation the heat effects of the interaction of solutions of copper(II) nitrate with L-asparagine in the pH range 9.6 to 8.3 at the concentration ratio $c^0_{Me}:c^0_L$ = 1:3.3 were measured. The precisely weighed sample of Cu $(NO_3)_2$ solution (~0.29 g, concentration 1.0437 mol per 1 kg of the solution) was added to the L-asparagine solution of the concentration 0.025 M of 39.86 ml volume. The concentration of the Cu $(NO_3)_2$ solution in the calorimetric cell after cracking the ampule was ~7.5×10^{-3} M. Also, the heats of dilution of the solution of copper nitrate solution in the background electrolyte KNO_3 solutions were measured. The experimental data are listed in Table 2.

To determine the enthalpy of formation of CuL^+ species the heat effects of mixing $Cu(NO_3)_2$ and L-

asparagine solutions at a ratio of $c^0_{Me}:c^0_L \sim 1:1.2$ were measured. The ampule contained ~0.39 g samples of the copper nitrate solution of concentration 1.0437 mol kg^{-1}, the concentration of amino acid solution, taking into account the dilution to a final volume of the calorimetric liquid, was 0.012 M or less. In the calorimetric experiment the pH varied in the range from 10.5 to 6.2. We measured also the heat effects of dilution of the $Cu(NO_3)_2$ solutions in the solutions of various concentrations of potassium nitrate. The experimental data are listed in Table 3.

ACKNOWLEDGMENT

This work was supported by the Federal Target Program "Research and education personnel of innovative Russia" for years 2009–2013 (State contract no. 02.740.11.0253).

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