ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 1, pp. 47–51. © Pleiades Publishing, Ltd., 2009.
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Thermochemical Study of the Complex Formation of Mercury(II) with Nitrilotriacetic Acid in an Aqueous Solution

D. F. Pyreu* and E. V. Kozlovskii
Ivanovo State University, Ivanovo, Russia
** E-mail: pyreu@ivanovo.ac.ru*

Received January 5, 2008

Abstract—The formation constant of the $Hg(Nta)_2^{4-}$ complex, where Nta^{3-} is the nitrilotriacetate ion, is determined by pH-metric titration at 298.15 K and ionic strength $I = 0.5$ (KNO_3) ($\log\beta = 21.49 \pm 0.10$). The thermal effects for the formation of the $Hg(NTa)_{i2-3i}$ complexes ($i = 1, 2$) are determined by a direct calorimetric method (–56.69 ± 1.04 and –85.88 ± 1.32 kJ/mol for $i = 1$ and 2, respectively).

DOI: 10.1134/S1070328409010102

INTRODUCTION

Only few works [1–6] devoted to the study of the complex formation of mercury(II) with nitrilotriacetic acid (NTA) in aqueous solutions can be found in the literature [1–6]. In our opinion, the most reliable values for the stability constant of the Hg(II) mononitrilotriacetate complex were obtained [1, 2] using the potentiometric and spectrophotometric methods. The most full IUPAC database [7] contains only six publications concerning the $HgNta^-$ complex, while $Hg(Nta)_2^{4-}$ is discussed in none of the works, although the $HgNta^-$ complex is coordinately unsaturated. Data on thermochemistry are also lacking. As shown in the review [8], the constant values obtained in the most part of the above works should be considered carefully. Therefore, it was of interest to determine the stability constant of the Hg(II) bis-complex and the thermal effects for the formation of the Hg(II) complexes with HTA from direct calorimetric measurements.

EXPERIMENTAL

Synthesis of $Na_4Hg(Nta)_2 \cdot 5H_2O$ (I), where Nta^{3-} is the nitrilotriacetate ion, was carried out by the dissolution of freshly prepared mercury(II) oxide in a solution containing the stoichiometric amount of H_3Nta (analytical grade) and Na_2CO_3 (reagent grade) according to the equation

$$\begin{aligned} &HgO + 2H_3Nta + 2Na_2CO_3 \\ &= \underset{(I)}{Na_4Hg(Nta)_2} + 2CO_2 + 3H_2O. \qquad (1) \end{aligned}$$

The solution containing a minor excess of HgO was filtered through a glass filter, and salt **I** was precipitated by the addition of an equal volume of ethanol. The crystalline precipitate that formed was dried at ~40°C. The composition of compound **I** was determined by elemental analysis and thermogravimetry.

For $C_{12}H_{12}O_{12}N_2Na_4Hg \cdot 5H_2O$			
anal. calcd. %:	C, 18.99;	N, 3.69;	H, 1.59.
Found (%):	C, 18.93;	N, 3.46;	H, 2.57.

Compound **I** was analyzed by thermogravimetry on a Q-Derivatograph instrument (Paulik-Paulik-Erdey) in the temperature interval from 15 to 250°C with heating rates of 2.5 and 5 K/min. The weight of a sample was 575 g. The heating of the Hg(II) complexonate to 180°C was accompanied by a weight loss (68 mg) corresponding to the loss of five molecules of water of crystallization without thermal destruction. The maximum rate of water removal was observed at 150°C.

Mercury nitrate $Hg(NO_3)_2 \cdot H_2O$ (reagent grade) was used. A working solution of $Hg(NO_3)_2 + HNO_3$ was standardized complexonometrically using the Xylenol Orange indicator [9]. A carbonate-free solution of NaOH was prepared using a standard procedure [10]. Potassium nitrate (analytical grade) used to create the ionic strength was doubly recrystallized.

The complex formation in the Hg(II)–HTA system is described by the stepped addition of the nitrilotriacetate ion to the Hg^{2+} cation

$$Hg^{2+} + Nta^{3-} = HgNta^-, \qquad (2)$$

$$HgNta^- + Nta^{3-} = Hg(Nta)_2^{4-}. \qquad (3)$$

Since no literature data on the second step of complex formation of Hg(II) with HTA are available, we had to study additionally the Hg^{2+}–Nta^{3-}–H^+ system by potentiometry.

A series of pH-potentiometric titrations of solutions containing $Na_4Hg(Nta)_2$ and KNO_3 as a supporting elec-

Table 1. Thermodynamic parameters for the formation of the $HgNta_i^{2-3i}$ complexes (i = 1, 2) at 298.15 K and I = 0.5 (KNO_3)

Reaction	$\log K$	$-\Delta_rG^0$, kJ/mol	Δ_rH, kJ/mol	Δ_rS, J mol^{-1} K^{-1}
$Hg^{2+} + Nta^{3-} = HgNta^-$	13.48 ± 0.10 [1]	76.94 ± 0.57	–56.69 ± 1.04	67.9 ± 4.0
$Hg^{2+} + 2Nta^{3-} = Hg(Nta)_2^{4-}$	21.49 ± 0.10	122.66 ± 0.57	–85.88 ± 1.32	123.4 ± 4.8
$HgNta^- + Nta^{3-} = Hg(Nta)_2^{4-}$	8.01 ± 0.02	45.72 ± 0.11	–28.56 ± 0.14* –29.19 ± 1.68**	57.6 ± 0.6

Notes: * According to procedure 1.
** According to procedure 2.

trolyte with a solution of HNO_3 was carried out. The emf with the transfer including glassy and Ag/AgCl electrodes was measured by the compensation method. All measurements were carried out at 25°C and ionic strength $I = 0.5$ (KNO_3).

The stability constant (**$\log\beta_1$**) for $HgNta^-$ (13.48 ± 0.10) determined in [1] at 25°C and $I = 0.5$ ($NaClO_4$) using an ion-selective electrode agrees well with the published data [2] ($\log\beta_1$ = 13.51 was obtained using spectrophotometry in the UV region at 20°C and $I \approx 0.1$ ($NaClO_4$)). The $\log\beta_1$ value (13.30) obtained [3] by electrophoresis at 25°C and $I = 0.1$ ($NaClO_4$) is well consistent with the published data [1, 2]. This made it possible to use the $\log\beta_1$ value determined in [1] for the calculation of $\log\beta_2$ by the data of potentiometric titration. The $\log K$ value for reaction (3) calculated using the PHMETR program [11] is presented in Table 1.

The procedure of calorimetric measurements is similar to that described earlier [12]. The thermochemical study of the Hg^{2+}–Nta^{3-}–H^+ system was carried out using two procedures. According to the first one, the thermal effects of mixing of a solution of HNO_3, whose exact weighed sample was placed in an ampule, with a solution of $Na_4Hg(Nta)_2$ + KNO_3. This allowed us to calculate the thermal effect of the addition of the second HTA residue (**Δ_rH_3**).

The thermal effects of mixing (**$\Delta_{mix}H$**) of a solution of $Hg(NO_3)_2$ + HNO_3 with alkaline solutions of NTA containing approximately equal amounts of Na_3Nta and Na_2HNta and KNO_3 as a supporting electrolyte were measured using the second procedure. Under the same conditions, the heats of dilution (**$\Delta_{dil}H$**) of a solution of Hg(II) nitrate in an acidified solution of the supporting electrolyte were determined. The thermal effects of mixing in the Hg^{2+}–Nta^{3-}–H^+ (KNO_3) system are given in Table 2. The concentration ratios [Hg] : [HTA] provided the complex formation via two steps. The thermal effects for complex formation were calculated in combination using the HEAT program [13] taking into account the contributions of water ionization [14], the protonation of an additional ligand [15], and the hydrolysis of the Hg^{2+} cation to the overall thermal effect (the $\log\beta$ value for the $HgOH^+$ particle was taken from [16], and the thermal effect value was borrowed from [17]). The contribution of Hg^{2+} ion hydrolysis to the overall thermal effect was negligible. The results of calculation are presented in Table 1.

The good convergence of the Δ_rH_3 values calculated using two procedures (with their confidence intervals) indicates both the reliability of the Δ_rH_3 value and that the contribution to the observed thermal effect of other ionic forms ranged within the experimental error under the experimental conditions. The value obtained by the first procedure can be recommended as a more reliable Δ_rH_3 value. The diagram of the fractional partition of particles in the Hg^{2+}–Nta^{3-}–H^+ system is shown in the figure.

RESULTS AND DISCUSSION

A comparative analysis of the thermodynamic characteristics of the formation of the nitrilotriacetate complexes and glycinate complex $Hg(Gly)_2$ calculated by the published data [18, 19] ($Hg^{2+} + 2Gly^- = Hg(Gly)_2$, $\log\beta = 20.03 \pm 0.07$; $\Delta_rH = -88.24 \pm 0.62$ kJ/mol; $\Delta_rS = 87.5 \pm 2.5$ J mol^{-1} K^{-1} at 25°C and $I = 0$) showed that the main contribution to the change in the enthalpy was made by the coordination of the donor N atom. At the same time, the change in the entropy of the reaction involving Nta^{3-} is appreciably greater than that with Gly^-, which is due to the replacement of all inner-sphere water molecules by the donor atoms of the nitrilotriacetate ion. Somewhat lower thermal effect of the reaction for Nta^{3-} as compared to Gly^- can be explained by a decrease in the basicity of the N atom on going from Gly^- to Nta^{3-}.

The structural features of the seven-vertex complexes of EDTA with the Fe^{3+}, Mn^{2+}, and Cd^{2+} ions are described in detail in the review [20] devoted to the stereochemistry of metal complexonates. According to [20], the appearance of a coordination number of seven is favored by an increase in the cation size, a higher affinity to coordination by the cation of oxygen atoms compared to nitrogen atoms, and no stabilization

Table 2. Thermal effects for mixing of a solution of $Hg(NO_3)_2$ (0.2828 mol/kg) + HNO_3 (0.09377 mol/kg) with solutions of $H_3Nta + NaOH + KNO_3$ at 298.15 K and $I = 0.5$ (KNO_3)

Weighed sample of solution ($Hg(NO_3)_2 + HNO_3$), g	Concentration of solution after mixing ×10^3, mol/l		$\Delta_{mix}H$, kJ/(mole of Hg^{2+})	$\Delta_{mix}H - \Delta_{dil}H$, kJ/(mole of Hg^{2+})
	Hg^{2+}	H^+		
$Ò_{Nta} = 0$				
0.57460	3.250	10.0	–1.893	$\Delta_{dil}H = -1.824$
0.62035	3.509	10.0	–1.754	
$c_{Nta} = 0.008060$ mol/l; $c_H = 0.004260$ mol/l				
0.61040	3.447	5.403	–63.02	–61.19
0.61080	3.449	5.404	–62.78	–60.95
0.64165	3.623	5.461	–59.41	–57.59
0.72535	4.096	5.618	–55.78	–53.96
0.64075	3.624	5.462	–59.88	–58.06
$c_{Nta} = 0.008007$ mol/l; $c_H = 0.004101$ mol/l				
0.64855	3.662	5.315	–60.31	–58.48
0.66120	3.734	5.339	–60.49	–58.67
0.61725	3.486	5.257	–62.00	–60.17
0.57330	3.237	5.174	–66.33	–64.51
0.58730	3.322	6.202	–64.16	–62.33
$c_{Nta} = 0.008043$ mol/l; $c_H = 0.004209$ mol/l				
0.50025	2.825	5.146	–71.21	–69.38
0.47625	2.689	5.101	–73.00	–71.18
0.39940	2.255	4.957	–81.49	–79.66
0.41135	2.323	4.979	–79.55	–77.73
0.46760	2.645	5.086	–72.71	–70.88
$c_{Nta} = 0.008039$ mol/l; $c_H = 0.004197$ mol/l				
0.29050	1.640	4.741	–94.11	–92.29
0.29805	1.683	4.755	–95.24	–93.42
0.28495	1.609	4.731	–97.62	–95.80
0.27750	1.567	4.717	–96.40	–94.57
0.29415	1.664	4.749	–94.73	–92.90

energy in the octahedral symmetry field at the configurationd^0, d^5, d^{10}. One more water molecule, along with the complexone that retains its hexadentate number, is in the composition of the internal coordination sphere of the complexonate. In the most part of the structurally studied zinc complexonates, the central ion has a coordination number of six, whereas Cd^{2+} is characterized by seven-vertex coordination, in particular, in the $MgCdEdta \cdot 10H_2O$ composition. The Hg(II) complexonates are much less structurally studied [21]. Taking into account that the structural type (coordination polyhedron) of the complexonates is retained in the most part of cases on going from the solid phase to solution, the appearance of the coordination number seven or eight can reasonably be expected for the Hg^{2+} cation, whose ion radius is much larger than that of Cd^{2+}.

The thermodynamic parameters for reactions (2) and (3) involving Zn(II), Cd(II), and Hg(II) are given in Table 3. The formation of the Hg(II) nitrilotriacetate complexes is accompanied by much higher thermal effects compared to Zn and Cd, which is caused, first, by the strong affinity of the Hg^{2+} cation to the donor atoms of the amine nitrogen. The exotherm sharply increases upon the coordination of the first Nta^{3-} ion in the series of metals with the d^{10} coordination, and $-\Delta_r H$ increases rather weakly during the second coordination step. This can be due to the weakening of the desolvation of the central ion upon the addition of the second Nta^{3-} ion.

If the entropy change in the formation of $MNta^-$ for Zn and Cd is much higher than the $\Delta_r S$ value in the addition of the second Nta^{3-} ion, then the $\Delta_r S$ values for Hg

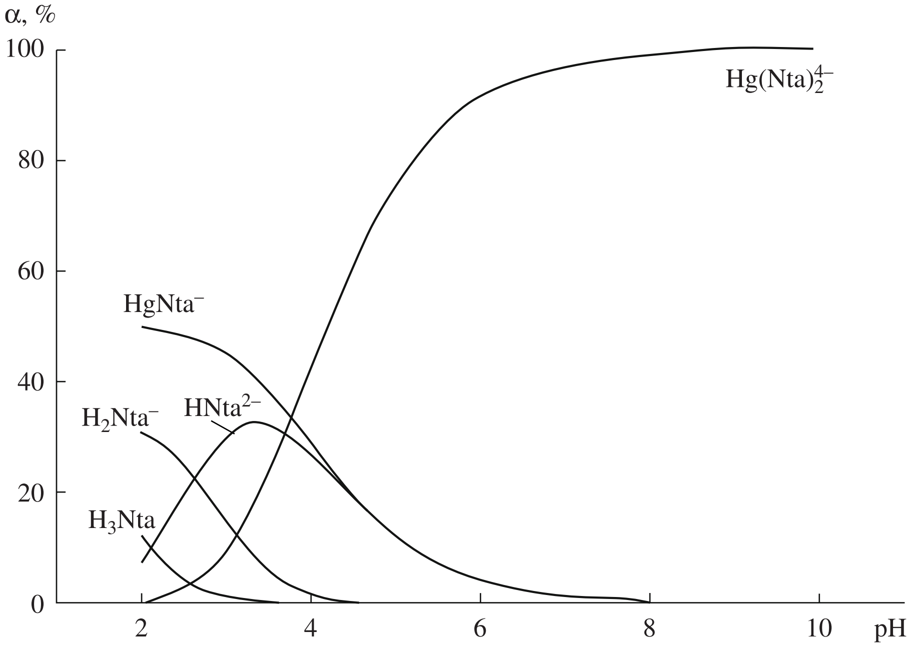

Diagram of the fractional partition of particles in theHg^{2+}–Nta^{3-}–H^+ system at 298.15 K and $I = 0.5$ (KNO_3) at the ratio Hg : Nta = 1 : 2 ($c_{Hg} = 0.005$ mol/l).

are approximately equal in these processes. This probably indicates an increase in the coordination capacity of the Hg^{2+} cation, resulting in the more complete accomplishment of the dentate number of Nta^{3-} in the $Hg(Nta)_2^{4-}$ complex compared to Zn and Cd. If the dentate nature of Nta^{3-} is not entirely accomplished in the Zn and Cd bisnitrilotriacetate complexes, then the possibility to increase the coordination capacity of Hg(II) [21] results in the situation that the average dentate number of nitrilotriacetate in the $Hg(Nta)_2^{4-}$ complex is higher than three.

Thus, the obtained thermochemical data indicate that the complex formation of Hg(II) with HTA via the second step differs noticeably from the processes involving Zn and Cd, which can be due to both the change in the coordination polyhedron on going from Zn and Cd to Hg and an increase in the coordination capacity of the mercury(II) cation compared to two other ions.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation in the

Table 3. Thermodynamic parameters of the reactions $M(Nta)_{n-1} + Nta = M(Nta)_n$ (charges are omitted), $n = 1, 2$ (M = Zn, Cd*, Hg) at 298.15 K and $I = 0.5$ ($\Delta_r H$ in kJ/mol, $\Delta_r S$ in J mol^{-1} K^{-1})

M^{2+}	$n = 1$			$n = 2$			Literature
	log *K*	$\Delta_r H$	$\Delta_r S$	log *K*	$\Delta_r H$	$\Delta_r S$	
Zn^{2+}	10.13	–5.19	176.5	3.82	–12.80	30.2	[22]
Cd^{2+}	9.20	–16.74	120.0	5.00	–21.33	24.2	[8]
Hg^{2+}	13.48	–56.69	67.9	8.01	–28.56	57.6	[1], this work

* At $I = 0.1$ (KNO_3).

framework of the project "Development of Mechanisms of Integration of the Ivanovo State University and the Institute of Problems of Chemical Physics of the Russian Academy of Sciences," grant no. 2.2.1.1.7181.

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