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Thermodynamic Characteristics of Formation Reactions of the Vanadium(V) Malonate Complex

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Abstract—The coordination equilibria in the vanadium(V)–malonic acid system were studied by calorimetry. The heats of formation reactions of the complex $VO_2CH_2(COO)_2^-$ at 298.15 K and I = 0.50, 0.75, and 1.00 ($NaC1O_4$) were determined. The standard thermodynamic characteristics of the studied equilibria were calculated.

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Vanadium(V) complexes with the malonic acid anion have been studied by the kinetic method [1]. The authors [1], who studied oxidation of iodide with bromate in the presence of vanadium and malonic acid in an acid medium (pH 2.7–2.9), arrived to the conclusion of existence of the complex $VO_2CH_2(COO)_2^-$ and calculated the stability constant of this complex to be equal to $(3.67 \pm 0.08) \times 10^4$ for a temperature of 298.15 K and $I = 0.2$ ($NaClO_4$). In another work [2], the stability constants of malonate complexes were determined by spectrophotometry at 293.15 K in sodium perchlorate ($I = 1.0$) at a total vanadium concentration of 4.8×10^{-4} mol/l in the pH range from 1.58 to 4.92 to be $\beta_1 = 3.6 \times 10^4$ and $\beta_2 = 3.35 \times 10^6$. At different ionic strengths of the solution and temperatures, the values found in the two studies [1, 2] are in good agreement with one another.

EXPERIMENTAL

The mixing enthalpy was determined using a precision isothermal-shell calorimeter [3]. All parts of the calorimeter contacting with corrosive medium were made of metallic tantalum and Teflon. The calorimeter operation was verified against the dissolution enthalpy of special purity grade potassium chloride in water. The results are in good agreement with the generally accepted values [4], which attests to the absence of noticeable systematic errors in the calorimeter operation.

Reagent grade perchloric acid, malonic acid, and sodium perchlorate were used as received. The concentrations of perchloric acid solutions were determined by titration. Solutions of $NaClO_4$ and H_2L were prepared from exact weighed portions. The reagent grade $VOCl_{3(liq)}$ was additionally purified by double distillation. The main difficulty in the preparation of a solution of $VOCl_3$ is due to the fact that vanadium oxytrichloride readily absorbs moisture from air and is hydrolyzed. Therefore, a solution of $VOCl_3$ was prepared by breaking the tube with liquid $VOCl_3$ on a specially designed setup [5]. The concentration of the vanadium oxytrichloride solution was determined by redox titration using diphenylamine as the indicator.

For determining the enthalpy of the formation reactions of the vanadium (V) malonate complex, the heats of mixing ($\Delta_{mix}\boldsymbol{H_1}$) of a solution of $VOCl_3$ (0.1908–0.2077 mol/l) and $HClO_4$ (0.8014 mol/l) with a 0.1001 M solution of malonic acid at 298.15 K and I = 0.50, 0.75, and 1.00 ($NaClO_4$) and the heats of dilution ($\Delta_{dil}\boldsymbol{H_1}$) of a solution of $VOCl_3$ and $HClO_4$ in a supporting electrolyte solution were measured. The ampoule was filled with a solution of vanadium oxytrichloride and perchloric acid using a precisely calibrated 0.75-ml capillary. The invariability of the solution volume was checked by weighing the ampoule before and after filling on a VLR-20 balance to an accuracy of $\pm 5 \times 10^{-5}$ g.

RESULTS AND DISCUSSION

The experimental data were processed taking into account the possibility of following acid–base and complex formation reactions:

$$VO_2^+ + L^{2-} = VO_2L^-, \quad (1)$$

$$VO_2^+ + 2L^{2-} = VO_2L_2^{3-}, \quad (2)$$

$$H^+ + L^{2-} = HL^-, \quad (3)$$

$$2H^+ + L^{2-} = H_2L, \quad (4)$$

$$VO_2^+ + H_2O = HVO_3 + H^+, \quad (5)$$

Thermodynamic characteristics of the coordination equilibria involving vanadium(V) and malonic acid at 298.15 K and I = 0.0–1.0

I ($NaClO_4$)	log K	$\Delta_r G$, J/mol	$-\Delta_r H$, J/mol	$\Delta_r S$, (J/(mol K)
		$VO_2^+ + HL^- = VO_2L^- + H^+$		
0	–0.50 ± 0.04	2854 ± 228	6505 ± 140	–31.4 ± 0.9
0.50	–0.49 ± 0.04	2797 ± 228	5430 ± 72	–27.6 ± 0.8
0.75	–0.50 ± 0.04	2854 ± 228	4860 ± 67	–25.9 ± 0.8
1.00	–0.50 ± 0.04	2854 ± 228	4346 ± 33	–24.1 ± 0.8
		$VO_2^+ + L^{2-} = VO_2L^-$		
0	5.19 ± 0.02	–29624 ± 114	798 ± 193	96.7 ± 0.8
0.50	4.59 ± 0.02	–26200 ± 114	2039 ± 100	81.0 ± 0.5
0.75	4.56 ± 0.02	–26028 ± 114	2155 ± 83	80.1 ± 0.5
1.00	4.56 ± 0.02	–26028 ± 114	2327 ± 94	79.5 ± 0.5

$$VO_2^+ + H_2O = VO_3^- + 2H^+, \quad (6)$$

$$VO_2^+ + 2H_2O = HVO_4^{2-} + 3H^+, \quad (7)$$

$$VO_2^+ + 2H_2O = VO_4^{3-} + 4H^+, \quad (8)$$

$$H^+ + OH^- = H_2O. \quad (9)$$

The equilibria were calculated according to the Brinkley method [6, 7] using RRSU software [7, 8]. The stability constants of vanadium(V) malonate complexes were taken from [2] and the constants of hydrolysis of vanadium(V) were taken from [9]. The calculation results indicate that under conditions chosen to study the complex formation equilibria, the following processes take place in the system:

$$HL^- + VO_2^+ = VO_2L^- + H^+, \quad \Delta_r H_{10}; \quad (10)$$

$$HL^- + H^+ = H_2L, \quad \Delta_r H_{11}. \quad (11)$$

The heat of reaction (10) can be calculated from the relation

$$\Delta_{min}H_1 - \Delta_{dil}H_1 = ([VO_2L^-]\Delta_r H_{10} + ([H_2L]_{fin} - [H_2L]_{init})\Delta_r H_{11})/c_V, \quad (12)$$

where $[VO_2L^-]$ is the equilibrium concentration of the VO_2L^- species in the final solution; c_V is the total vanadium concentration in the final solution; $[H_2L]_{init}$ and $[H_2L]_{fin}$ are the equilibrium concentrations of H_2L in the beginning and at the end of the calorimetric experiment. The heats of stepwise dissociation of malonic acid at the corresponding ionic strength and temperature were found in our previous study [10].

The known thermodynamic characteristics of processes (3) and (10) can be used to calculate the corresponding parameters for reaction (1) of formation of the vanadium(V) malonate complex

$$\Delta_r H_1 = \Delta_r H_3 + \Delta_r H_{10}. \quad (13)$$

The concentration heats were extrapolated to the zero ionic strength by using equation with one individual parameter [11]:

$$\Delta_r H - \Delta z^2 \Psi(I) = \Delta_r H^\circ + bI, \quad (14)$$

where $\Delta_r H$ and $\Delta_r H^\circ$ are enthalpy changes of the reaction for the final and zero ionic strength; b is an empirical coefficient; Δz^2 is the difference between the squared charges of the reaction products and the reactant species; $\Psi(I)$ is a function of the ionic strength calculated theoretically [11].

The thermodynamic characteristics (log1gK, $\Delta_r G$, $\Delta_r H$, and $\Delta_r S$) of the studied equilibria involving vanadium(V) and malonic acid determined on the basis of thermochemical measurements carried out in this work and using reported spectrophotometric data [2] are summarized in the table.

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