# Cadmium complexes of trans-crotonic acid in aqueous solutions

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By using cadmium ion-selective electrode, the existence of complexes consisting of cadmium cation and anion of *trans*-crotonic acid in mole ratio 1:1 and 1:2 (CdL<sup>+</sup>, CdL<sub>2</sub>) has been disclosed in aqueous solution of *trans*-crotonic acid in the pH region 3—5.45. The voltage of a cell comprising a cadmium ion-selective electrode and silver chloride electrode is governed by the equation

$$E = E' - \frac{\vartheta}{2} \log \left\{ 1 + \frac{K_{1100}c_{a}K_{a}}{c_{H_{3}0^{+}} + K_{a}} + \frac{K_{1200}c_{a}^{2}K_{a}^{2}}{(c_{H_{3}0^{+}} + K_{a})^{2}} \right\}$$

The equilibrium constants of formation of complexes  $CdL^+$  and  $CdL_2$  were calculated by the method of successive approximation;  $\log \{K_{1100}\} = 1.97 \pm 0.07$ ,  $\log \{K_{1200}\} = 2.33 \pm 0.03$ .

С помощью ион-селективного кадмиевого электрода в водном растворе *транс*-кротоновой кислоты в интервале pH = 3—5,45 было потенциометрически доказано присутствие комплексов, содержащих катион кадмия (II) и анион *транс*-кротоновой кислоты в молярном соотношении 1:1 или 1:2 (CdL<sup>+</sup>, CdL<sub>2</sub>). Напряжение гальванического элемента, состоящего из кадмиевого ион-селективного и хлористосеребрянного электродов в данных растворах подчиняется уравнению

$$E = E' - \frac{\vartheta}{2} \log \left\{ 1 + \frac{K_{1100}c_{a}K_{a}}{c_{H_{3}0^{+}} + K_{a}} + \frac{K_{1200}c_{a}^{2}K_{a}^{2}}{(c_{H_{3}0^{+}} + K_{a})^{2}} \right\}$$

Методом последовательной аппроксимации были рассчитаны равновесные константы образования комплексов  $CdL^+$  и  $CdL_2$ ; log  $\{K_{1100}\} = = 1,97 \pm 0,07$ ; log  $\{K_{1200}\} = 2,33 \pm 0,03$ .

The use of ion-selective electrodes enables us to determine potentiometrically the composition of complexes and calculate thermodynamic parameters for complex-forming reactions [1, 2]. The topic of this study is potentiometric exploration of complex-forming equilibria in the system  $Cd^{2+}$ —trans-crotonic acid—water.

The complexes of general formula  $[Cd_qH_kL_x(OH)_y(H_2O)_z]^{(2q-x-y)^+}$  may arise by replacement of the molecules of water in the hydrated cation of cadmium by the molecules of *trans*-crotonic acid and dissociation of this complex or by interaction between the cadmium ion and the anion of *trans*-crotonic acid produced by dissociation. For simplification, we are not going to state in the text the number of water molecules in the hydrated cation.

The cadmium complexes formed in aqueous solution of *trans*-crotonic acid have influence on the voltage of a cell comprising a cadmium ion-selective electrode and reference electrode. The general equation expressing this influence [1, 2] has the form

$$E = E_0 + \frac{RT}{zF} \ln c_M - \frac{RT}{zF} \ln \left\{ \sum_{q=1}^{O} \sum_{x=0}^{X} \sum_{k=0}^{K} \sum_{y=0}^{Y} q \right. \\ \left. \cdot \frac{(K_{qxyk})^{1/q} (c_{qxyk})^{q-1/q} K_a^{x/q} c_a^{x/q} c_{H_3O}^{k-y/q}}{(c_{H_3O}^+ + K_a)^{x/q}} \right\}$$
(1)

The analysis of the dependence of voltage of a given cell on individual parameters ( $pc_M$ ,  $pc_a$ , pH) enables us to determine the composition of predominant complexes in the investigated system [1, 2].

#### **Experimental**

The hexahydrate of cadmium perchlorate was prepared by dissolving metallic anal. grade cadmium (Lachema, Brno) in chemically pure perchloric acid (VEB Apolda, GDR) at 433.15 K. Trans-crotonic acid (Lachema, Brno) was three times recrystallized (m.p. 344.65 K). It was used for preparing aqueous solutions in the concentration range  $0.8-0.1 \text{ mol } dm^{-3}$ . The ionic strength was held constant ( $I_c = 1.0 \text{ mol } dm^{-3}$ ) by means of sodium perchlorate, perchloric acid, and sodium hydroxide. All these chemicals were anal. grade reagents. Deionized water was used for the preparation of solutions. The voltage of the cell consisting of a cadmium ion-selective electrode Crytur 48-17 (Monocrystals, Turnov), reference silver chloride electrode OP-820 (Radelkis, Budapest), and salt bridge filled with 1.0 M-NaNO<sub>3</sub> was measured with a digital precision pH-meter OP-208 (Radelkis, Budapest) within accuracy  $\pm 1 \text{ mV}$ . The activity of hydrogen ions was determined with a glass electrode EA 107 (Metrohm, Switzerland). The measurements were carried out in a closed thermostated vessel EA 876-20T (Metrohm, Switzerland) at 298.15  $\pm 0.1 \text{ K}$ .

### **Results and discussion**

The slopes of the experimental dependence of the voltage of galvanic cell on individual parameters  $pc_M$ ,  $pc_a$ , and pH determine according to eqn (1) the

composition of complexes [1, 2]

$$\left(\frac{\partial E}{\partial pc_{\rm M}}\right)_{\rm pc_{\rm n}, pH} = -\frac{\vartheta}{zq} \tag{2}$$

$$\left(\frac{\partial E}{\partial pc_a}\right)_{pcm,pH} = \frac{\vartheta x}{zq}$$
(3)

$$\left(\frac{\partial E}{\partial pH}\right)_{pcM,pca} = \frac{\vartheta}{z} \left[\frac{k-y}{q} + \frac{x}{q} \frac{c_{H_3O^+}}{c_{H_3O^+} + K_a}\right]$$
(4)

We obtained these relationships so that we prepared solutions with two constant parameters (e.g. pH and  $pc_a$ ) while the third independent parameter (e.g.  $pc_M$ ) varied. For studying the dependence of the cell voltage on concentration of the cadmium ions two solutions were prepared and mixed. The concentration of the cadmium ions was  $10^{-2}$  mol dm<sup>-3</sup> in the first solution and  $10^{-4}$  mol dm<sup>-3</sup> in the second solution. The concentration of *trans*-crotonic acid and pH were constants. The pertinent relationship is represented in Fig. 1. We can see a linear course with the slope  $-\vartheta/2$  in the pH interval 3—5.45. The value of the slope gives evidence that the number of nuclei of the complex arising in solutions with concentration of the cadmium ions  $\leq 10^{-2}$  mol dm<sup>-3</sup> and ionic strength 1 mol dm<sup>-3</sup> in the pH interval 3—5.45 is equal to one.

The number of coordinated anions of acid may be determined from the dependence of the cell voltage on concentration of *trans*-crotonic acid  $(pc_a)$  at constant values of pH and  $p_{CM}$  and known number of nuclei of the complex (eqn (3)). The relationship between cell voltage and concentration  $c_a$  for  $c_M =$ 10<sup>-3</sup> mol dm<sup>-3</sup> and ionic strength 1 mol dm<sup>-3</sup> and constant value of pH (interval 3.4-5.45) is determined by the pH value of solution (Fig. 2). For low values of pH and low concentrations of trans-crotonic acid we may find out a section with zero slope. This slope increases with the value of pH and reaches the value  $\vartheta/2$  at pH = 4. The increase in pH value shifts the curves to lower values of the cell voltage. The curves in the pH region 5.0-5.45 show a linear section with the slope  $\vartheta$ . According to the authors of papers [1, 2], this fact may be interpreted as follows: The zero slope in the region pH < 4 indicates that no complex is formed in this case. In the pH region 4-5, a cation Cd<sup>2+</sup> coordinates one anion of trans-crotonic acid  $L^{-}$  to give the complex CdL<sup>+</sup>. Provided pH>5, the slope of the linear section of the curve has the value  $\vartheta$  and indicates coordination of two anions of *trans*-crotonic acid by one  $Cd^{2+}$  cation giving rise to the complex  $CdL_2$  as it follows from eqn (3). For monobasic acid, the protolytic constant of dissociation affects the slope of tangent of the graphical relationship between cell voltage and pH according to equ (4).

As it follows from experimental measurements, two kinds of complexes, *i.e.*  $CdL^+$  and  $CdL_2$ , were revealed in the investigated system. The general equation



a) pH = 3.00; b) pH = 3.25; c) pH = 3.40; d) pH = 4.00; e) pH = 4.80; f) pH = 5.00; g) pH = 5.45.



describing the relationship between cell voltage and composition for our system and conditions may be expressed as follows

$$E = E' - \frac{\vartheta}{2} \log \left\{ 1 + \frac{K_{1100} c_{a} K_{a}}{c_{H_{3}O^{+}} + K_{a}} + \frac{K_{1200} c_{a}^{2} K_{a}^{2}}{(c_{H_{3}O^{+}} + K_{a})^{2}} \right\}$$
(5)

The equilibrium constants of formation of the complexes  $K_{1100}$  and  $K_{1200}$  were calculated from eqn (5) by the method of successive approximation; log  $\{K_{1100}\} = 1.97 \pm 0.07$  and log  $\{K_{1200}\} = 2.33 \pm 0.03$ .

The correctness of the calculated equilibrium constants was verified by comparing the relationship between cell voltage and pH determined experimentally and calculated according to eqn (5) (Fig. 3).

The composition of the cadmium complexes in aqueous solutions of *trans*-crotonic acid as a function of pH is characterized by the distribution diagram (Fig. 4) which was constructed by the use of general equation

$$\alpha_{qxyk} = \frac{qc_{qxyk}}{c_{\mathsf{M}}} \cdot 100 \tag{6}$$









This equation assumes the following form for mononuclear complexes of bivalent cadmium [3]

$$\alpha_{1x00} = K_{1x00} c_{a}^{x} \cdot 10^{2E/\theta} \quad 100$$
<sup>(7)</sup>

The complex CdL<sup>+</sup> exhibiting the maximum at pH = 3.9 (Fig. 4, curve *a*) predominates at low pH in the solution of *trans*-crotonic acid ( $c_a = 0.5 \text{ mol dm}^{-3}$ ,  $I_c = 1 \text{ mol dm}^{-3}$ ) and cadmium perchlorate ( $c_M = 10^{-3} \text{ mol dm}^{-3}$ ). With increasing pH value the concentration of this complex decreases and the complex CdL<sub>2</sub> gradually appears (Fig. 4, curve *b*). The concentration of the free aquo complex Cd<sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub> also decreases with increasing pH value (Fig. 4, curve *c*).

The complex-forming processes in aqueous solution of *trans*-crotonic acid are dependent on pH of medium. The concentration of the anions of acid, which replace the molecules of water in the aquo complex, increases with pH. The arising complexes  $CdL^+$  and  $CdL_2$  are analogous to the complexes of crotonic acid with  $UO_2^{2^+}$  [4].

## **Symbols**

E	electromotive force of a cell with complex-forming agent	[mV]
E'	electromotive force of a cell without complex-forming agent	[mV]
$\vartheta = \frac{RT}{F}$	factor in the Nernst equation	[mV]
z	charge number of cation	

q	number of nuclei in complex	
x	number of ligands	
k	number of protolytic groups	
у	number of hydroxide groups	
Kqxyk	stability constant of complex	[mol <sup>-1</sup> dm <sup>3</sup> ]
Cqxyk	concentration of complex	[mol dm <sup>-3</sup> ]
Ka	protolytic constant of trans-crotonic acid $K_a = 2.00 \times 10^{-5}$ [5]	$[mol dm^{-3}]$
Ca	concentration of trans-crotonic acid	$[mol dm^{-3}]$
См	concentration of cadmium ions	[mol dm <sup>-3</sup> ]
C <sub>H3O</sub> +	concentration of hydrogen ions	[mol dm <sup>-3</sup> ]
$\alpha_{qxyk}$	percentage of a given complex	

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