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## Potentiometric Determination of Stability Constants of Cobalt(II), Nickel(II), and Cadmium(II) Phenylacetate Complexes Using Computer Controlled Electrometric System

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The stability constants of cobalt(II), nickel(II) and cadmium(II) phenylacetate complexes were obtained by potentiometric titration in a buffer solution of constant ionic strength  $2 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ).

A computer controlled semiautomatic potentiometric titration system has been constructed in order to obtain high reproducible experimental data by different types of potentiometric titration.

### INTRODUCTION

Determination of composition and stability of metal ion phenylacetate complexes represents a continuation of systematic investigation of unsubstituted and substituted monocarboxylate complexes performed in our laboratory (see e. g. refs 1 and 2), with the intention to give some insight into the factors influencing their stability. This paper describes a potentiometric titration system built around a PDP-8/E minicomputer (OS-8/10 system) and its application to study the potentiometric equilibrium of metal ion complexes specified in the title.

So far only a few papers have dealt with equilibrium study of phenylacetate complexes<sup>3</sup>. Only indium(III)<sup>4</sup> and copper(II)<sup>5,6</sup> phenylacetate complexes have been investigated, while no stability data have been reported for cobalt(II), nickel(II) and cadmium(II) complexes with the same ligand. The stability of zinc(II), copper(II) and lead(II) phenylacetate complexes could not be determined by potentiometric titration due to the low solubility of complex species (Zn(II), Cu(II) and Pb(II) monocarboxylate complexes have been included in all our previous investigations).

Laboratory minicomputers and microprocessors are used more and more frequently in the automation of laboratory measurement. This is dictated by specific application problem, instrument availability, prices and other factors. Automatic potentiometric titration systems based on electronic modules<sup>8</sup>, minicomputers<sup>9,10</sup> and recently microprocessors<sup>11,12</sup> have been reported. Our system is based on a PDP-8/E minicomputer (OS-8/10 system), which is also used for on line measurements in DC<sup>13</sup> and AC polarography, cyclic voltammetry and pulse polarography.

The potentiometric titrations were performed with a selfconstructed semi-automatic titrator. Preparation of stock solutions, burette filling, cleaning of the electrodes and temperature control were the only steps of the experiment which were not computer controlled. Volume addition of buffer solutions, potential sampling and numerical and statistical data handling were performed under computer control. This automation in potentiometric titrations made possible a more accurate titrant volume delivery and potential sampling, shortening at the same time the complete titration procedure, compared with that used previously<sup>7</sup>.

#### EXPERIMENTAL

##### *Apparatus and System Description*

The main components of the titration system have been summarized in Table I. The electromechanical burette was constructed in our laboratory. Essentially it was a motor driven piston burette made from calibrated glass tubing (Schott, Mainz) and thermostated with a water jacket. The driving motor can be activated either by computer or manually, and once started the piston driving motor generates through a mechanical gear and a coupled microswitch electrical pulses, corresponding to the volume delivered. These pulses are counted by the computer.

A block diagram of the complete titration system is shown in Figure 1. Sub-routines for the control of burette, digital voltmeter and scanner were written in symbolic assembler (SABR), while programs for experimental data handling were written in Fortran. Various initial parameters necessary for the titration were input to the computer either from DECwriter or from the magnetic tape(disk). Input parameters are given in Table II. In the absence of metal ion, the initial metal parameters were input via the DC writer, while, in the presence of a constant metal ion concentration the required parameters were taken from a magnetic tape(disk). A block diagram of the computer program is shown in Figure 2, for the titration in absence (1) and in presence (2) of metal ions in buffer solutions.

Once the titration was started by the computer, an instruction to start the scanner was sent after a waiting time of  $T$  seconds and the emf of four indicator electrodes was measured by the digital voltmeter. The emf measurement after  $T$  seconds was repeated if the observed standard deviation was greater than the preset one ( $XVAR < SD$ ) for the maximum preset  $L$  times. The average value of the last measurement was used as the most probable one and the next dose of titrant was delivered. The volume of the titrant to be delivered was computer calculated in such

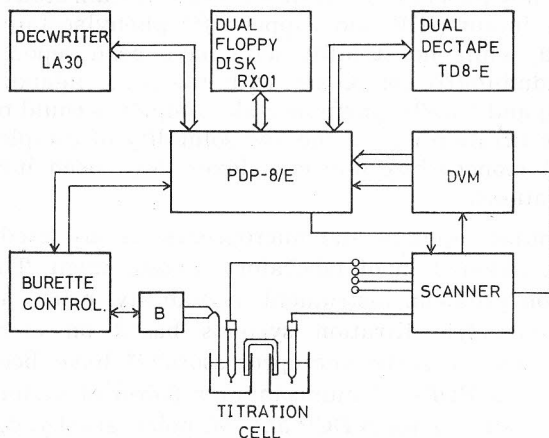


Figure 1. Block diagram of titration system.

TABLE I  
*The Components of Titration System*

Minicomputer	PDP-8/E (OS-8/10 system): DECwriter LA30, dual DECTape TD8E, dual floppy disk system RX8 and 8K of memory.
Digital voltmeter	HP 3480A with HP 3482A DC range unit. The specified accuracy is $\pm 0.01\%$ of the reading + $0.01\%$ of the range.
Scanner for electrode selection	Selfmade 4 channel scanner based on reed relay and computer controlled via interface.
Burette	Selfconstructed electromechanical motor driven piston burette.
Potentiometric cell	Metrohm EA 876.
Electrodes	Pt-electrodes (Metrohm EA 202).

TABLE II  
*Input Parameters for Computer Program*

Symbolic name	
<i>N</i>	Number of volume increments
<i>V<sub>0</sub></i>	Initial volume in the titration cell
<i>V<sub>1</sub></i>	Final volume at the end of titration
<i>C<sub>0</sub></i>	Ligand concentration in the titration cell
<i>C<sub>1</sub></i>	Ligand concentration in the burette
<i>T</i>	Waiting period after titrant addition to ensure chemical equilibrium
<i>B</i>	Number of indicator electrodes in the titration cell ( $\leq 4$ )
<i>L</i>	Maximal number of repeated electrode potential measurements
<i>XVAR</i>	Preset standard deviation of indicator electrode potential readings (typical value 0.1 mV)
<i>CKIS</i>	Concentration of HClO <sub>4</sub> in the reference solution
<i>HLNAL</i>	Acid-to-salt ratio in buffer solution
<i>CM</i>	Metal ion concentration

a way that the potential difference between two additions of the titrant remained approximately constant. Since the potential change during the titration of buffer solutions with metal ions was approximately logarithmic, the addition of the titrant was performed in a logarithmic mode, for  $C_0 < C_1$  and a linear one for  $C_0 > C_1$ . (symbols explained in Table II). At the end of the titration in the absence of complex formation, the number and volume of titrant increments and measured potentials for different ligand concentrations, as well as other initial parameters necessary for final concentration calculation, were recorded on the magnetic tape(disk). The same volume increments of the titrant were used as input parameters from the tape for titration of buffer solution in the presence of complex formation, ensuring the

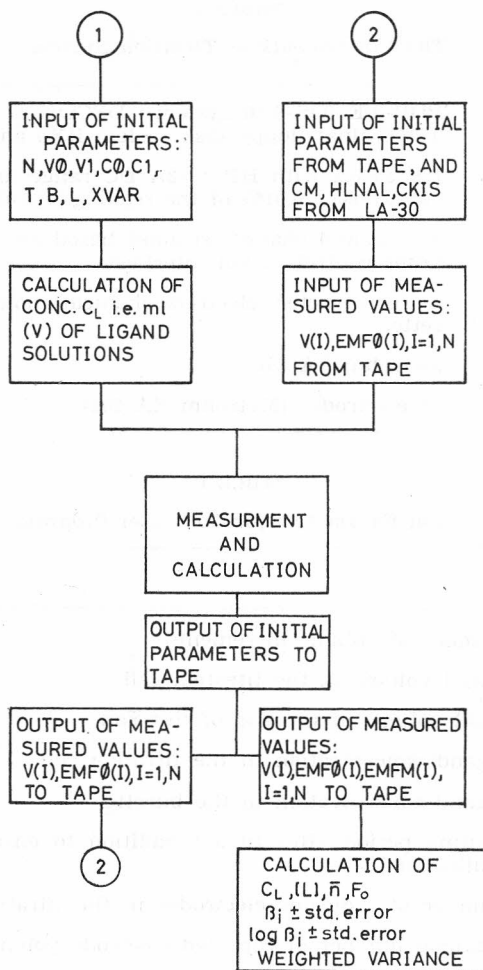


Figure 2. Program sequence for measurements and data handling.

potential measurements to be performed at same total ligand concentration as in the absence of complex formation.

From initial parameters, delivered volume increments and potential measured at different ligand concentrations (corresponding to monocarboxylic acid dissociation in the presence and absence of complex formation), total and free ligand concentration and the average number of ligand bound per one metal ion,  $\bar{n}$ , were calculated. From these secondary parameters, using Fronaeus' method<sup>14</sup>, the well known polynomial  $F_0 = 1 + \sum \beta_i [L]^i$  was calculated. The stability constants and their 95 per cent confidence intervals were obtained by the least squares fitting of the  $F_0$  polynomial using an algorithm described elsewhere<sup>7</sup>.

### Reagents and Solutions

Commercially available phenylacetic acid (Merck) was recrystallized twice from aqueous solution. Buffer solutions were prepared by neutralization with sodium hydroxide solution. The concentration of sodium phenylacetate in buffer solutions

was determined by potentiometric titration in glacial acetic acid medium<sup>15</sup>. The concentration of metal ions in perchlorate medium was determined by potentiometric chelatometric titration. Sodium perchlorate was recrystallized twice from water and the metal perchlorates were prepared by the procedure described earlier<sup>15</sup>.

The composition of starting solutions and the titration procedure were the same as described previously<sup>7</sup>, except that with the present system the titrant was added discontinuously. Each investigated system was measured at two metal ion concentrations, each at two acid-to-salt ratio, 1 : 1 and 1 : 0.5. Concentrations of cobalt(II) and nickel(II) were 45 mmol dm<sup>-3</sup> and 90 mmol dm<sup>-3</sup>, while those of cadmium(II) were 20 mmol dm<sup>-3</sup> and 40 mmol dm<sup>-3</sup>. Due to the low solubility of phenylacetic acid and of its sodium salt, the investigations were performed up to only 100 mmol dm<sup>-3</sup> of ligand concentration.

In all buffer solutions the ionic strength was kept constant at 2 mol dm<sup>-3</sup> by the addition of sodium perchlorate.

All potentiometric titrations were performed at (298.2 ± 0.1) K with quinhydrone electrodes vs. a reference solution containing 19.12 mmol dm<sup>-3</sup> of perchloric acid plus sodium perchlorate to give the ionic strength of 2 mol dm<sup>-3</sup>.

## RESULTS AND DISCUSSION

The selfmade burette was calibrated by weighing the volumes of water delivered for determined piston displacement. These volumes were registered by computer as the corresponding number of generated pulses. The results of two independent calibration are presented in Table III. From these results it can be seen that the burette is precise and linear over its entire range of operation within the weighing error of delivered water.

TABLE III

No. of volume increments*	Weight of volume increments	
	X <sub>1</sub> /mg	X <sub>2</sub> /mg
1	358.1	358.4
2	358.0	358.2
3	358.6	358.5
4	358.7	358.2
5	358.6	358.6
6	358.7	358.5
7	358.6	358.2
8	358.6	358.0
9	358.8	358.6
10	357.9	357.9
11	358.0	357.9
12	357.9	358.2
13	357.9	358.0
14	357.9	358.0
15	358.2	358.1
16	358.0	358.2
17	358.1	358.3
18	358.4	358.1
19	358.5	357.8
20	358.0	
21	358.1	

$\bar{X}_1 = (358.3 \pm 0.3) \text{ mg}$      $\bar{X}_2 = (358.2 \pm 0.2) \text{ mg}$

\* One volume increment corresponds to 500 burette counts i. e. electrical pulses.

The entire reproducibility of the computerized measuring system for two independent measurements can be assessed from the results given in Table IV. In this table the stability constants and their 95 per cent confidence intervals for cadmium(II) phenylacetate complexes are given. The obtained confidence intervals reflect the precision of volume addition and potential measurements, and are for almost an order of magnitude improved compared to the procedure used earlier<sup>7</sup>.

TABLE IV

*Two Independent Determinations of the Stability Constants of Cadmium Phenylacetate Complexes*

Independent measurement no.	$\lg \frac{K_1}{\text{dm}^3 \text{ mol}^{-1}}$	$\lg \frac{\beta_2}{\text{dm}^6 \text{ mol}^{-2}}$
I	1.151 $\pm$ 0.001	1.880 $\pm$ 0.003
II	1.146 $\pm$ 0.001	1.890 $\pm$ 0.003

Under  $\pm$  sign 95 per cent confidence limits are given.

The stability constants of cobalt(II), nickel(II) and cadmium(II) phenylacetate complexes together with their 95 per cent confidence intervals are given in Table V, for two metal ion concentrations and acid-to-salt ratio 1:1 in buffer solutions. A good agreement between formation curves obtained for different metal ion concentrations and acid-to-salt ratios suggests the absence of polynuclear and/or hydroxy complexes. Comparing the value of stability constants of monoligand phenylacetate complexes with the average values of

TABLE V

*Stability Constants of Phenylacetate Complexes with Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup>; T = 298.2 K, I = 2 mol dm<sup>-3</sup> (NaClO<sub>4</sub>)*

Metal ion	$\lg \frac{K_1}{\text{dm}^3 \text{ mol}^{-1}}$	$\lg \frac{\beta_2}{\text{dm}^6 \text{ mol}^{-2}}$
Cd <sup>2+</sup>	1.150 $\pm$ 0.001	1.917 $\pm$ 0.01
Ni <sup>2+</sup>	0.653 $\pm$ 0.001	0.986 $\pm$ 0.01
Co <sup>2+</sup>	0.623 $\pm$ 0.001	0.522 $\pm$ 0.01

pK<sub>A</sub> = 4.34 (Our measurement value)

Under  $\pm$  sign 95 per cent confidence limits are given.

corresponding acetate complexes obtained in this laboratory using different methods<sup>16-18</sup>, it can be concluded that the stability of acetate complexes of the investigated metal ions is higher than the stability of phenyl substituted acetate complexes. This is in accordance with the higher basicity of acetate ligand estimated by pK<sub>A</sub> values (pK<sub>A</sub> = 4.74 for acetic acid and 4.34 for phenylacetic acid).

At the end it can be mentioned that the semiautomatic titration system makes possible to obtain high quality results for different types of potentiometric

metric titrations (e. g. different potentiometric titrations using two computer controlled burettes and using different types of indicator electrodes), shortening the time for the experiment and simplifying the experimental procedure.

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## SAŽETAK

**Potenciometrijsko određivanje konstanti stabilnosti fenilacetato-kompleksa kobalta(II), nikla(II) i kadmija(II) s pomoću elektrometrijskog sustava upravljanoga elektroničkim računalom**

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Konstante stabilnosti fenilacetato-kompleksa kobalta(II), nikla(II) i kadmija(II) određene su potenciometrijskom titracijom u tamponskim otopinama stalne ionske jakosti  $2 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ). Izgrađen je poluautomatski potenciometrijski titracijski uređaj upravljan elektroničkim miniračunalom kako bi se dobili visoko precizni eksperimentalni podaci u potenciometrijskim titracijama različite vrsti.

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