# DIFFERENTIAL KINETIC ANALYSIS
# OF ALKALINE-EARTH IONS USING SQUARE WAVE POLAROGRAPHY

M.KOPANICA and V.STARÁ

*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
*Czechoslovak Academy of Sciences, 110 00 Prague 1*

Linear extrapolation method was applied to the differential kinetic analysis of binary mixtures of alkaline-earth ions. The method is based on the square wave polarographic measurement of the changes of nonreacted cadmium(II) ions concentration in the course of the substitution reaction between the alkaline-earth–DCTA (1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid) complexes and identical concentration of cadmium(II) ions. The necessary amount of cadmium(II) ions is determined by square wave polarographic measurement of the amount of cadmium(II) ions released from the Cd-EDTA complex by the reaction with the alkalineearth ions from the sample solution which proceeds in ammoniacal medium. The determination is obstructed only by ions interfering with square wave polarographic determination of cadmium(II) in the pH range 7—9.

Metal substitution reactions of the EDTA-type complexes have been thoroughly studied[1,2] and the possible analytical application of the phenomena observed were described. In the course of metal–metal substitution reactions of EDTA type complexes the formation of unstable intermediates takes place as a result of direct reaction of the original complex with another metal ion. Only the substitution reactions of DCTA (1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid, $H_4L$) differ in their mechanism[3-5], which in this case consists of two following steps

$$M - DCTA + H \rightarrow H - DCTA + M, \qquad (A)$$

$$H - DCTA + M' \rightarrow M' - DCTA + H^+, \qquad (B)$$
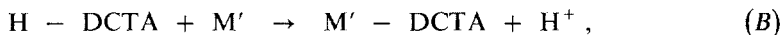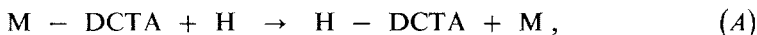
where M and M′ are different metal ions, the charges of which are omitted here. Reaction (A) is the rate-determining step and its rate which depends solely on the hydrogen ions concentration, is specific for each metal ion. Differences in the dissociation rates of various DCTA complexes are very large and thus these substitution reactions can be applied to differential kinetic analysis of various metals[6]. The dissociation rates of the alkaline-earth–DCTA complexes are relatively high (corresponding dissociation constants are $10^4-10^8$ $mol^{-1}$ $s^{-1}$ (ref.[6]) and therefore for the differential kinetic determination of these ions, the application of stopped-flow mixing is necessary[7].

In the present work is described the application of the linear extrapolation method[8] for the differential kinetic analysis of the mixtures of alkaline-earth ions based

on square wave polarographic measurements of the changes of $Cd^{2+}$ concentration in the course of the substitution reactions

$$CaL^{2-} + Cd^{2+} \rightarrow Ca^{2+} + CdL^{2-}, \qquad (C)$$

$$MgL^{2-} + Cd^{2+} \rightarrow Mg^{2+} + CdL^{2-}. \qquad (C1)$$
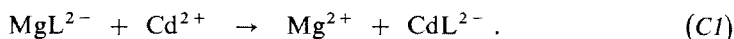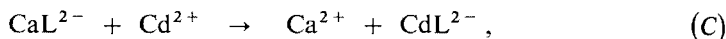
## EXPERIMENTAL

### Reagents and Apparatus

All solutions were prepared from a.g. chemicals. 0·01M solutions of the DCTA reagent, cadmium(II) and alkaline-earth salts were standardized using recommended procedures. Before the measurement these solutions were diluted to the concentration $5 . 10^{-4}$M. Mixtures of boric acid and sodium borate were used as buffer solutions. Twice distilled water was used for all measurements. Sodium perchlorate was used to adjust the ionic strength 0·1.

Square-wave polarographic curves were recorded using the polarograph OH-104 (Radelkis, Hungary). The temperature of the solutions was maintained at 22°C by means of a thermostat (Ministat 607, MTA, Hungary). The pH values were measured with a glass electrode using the pH meter PHM-25 (Radiometer, Denmark).

### Procedure

The extent of the reactions $(C)$ and $(C1)$ was measured by the recording of the square wave polarographic curves of cadmium(II) ions at given time intervals after mixing the reactants. The reaction mixture containing the alkaline-earth–DCTA complexes, buffer solution and sodium perchlorate was placed into the thermostated cell with electrodes and dissolved oxygen was removed by nitrogen. The cadmium(II) solution was added to the reaction mixture using a syringe, passage of nitrogen was stopped and the square wave polarographic curves were recorded in the dependence of time.

## RESULTS

### Substitution Reaction between Alkaline-Earth–DCTA Complexes and Cadmium(II) Ions

Using the square wave polarographic measurement it was found that the rates of the reactions between an alkaline-earth–DCTA complex and an excess of cadmium(II) ions (approx. a 10-fold excess) are too fast to be measured with a convenient mixing technique. This finding is in an agreement with the results connected with the study of the reactions of DCTA complexes with lead(II) or copper(II) ions[7]. On the other hand the course of the studied reactions can be followed using the described technique under the conditions when the concentration of the complex was identical with that of cadmium(II) ions. The rates of studied reactions were found to depend on the hydrogen ions concentration; the rate of the reactions of calcium, magnesium

and strontium DCTA complexes decreased with decreasing concentration of hydrogen ions.

The kinetics of the reactions between calcium, magnesium, and strontium DCTA complexes and identical concentrations of cadmium(II) ions $(10^{-5}-10^{-6}\text{M})$ was measured in the pH interval $7-8$. It was found that the plot of the reciprocal of the nonreacted cadmium(II) ions concentration $vs$ time was linear over 90% of the reactions completion, indicating thus the second order of the reactions studied. At higher pH values (pH $8-9$), the second order dependence was found linear only up to approx. 70% of the reaction completion; this phenomenon is probably due to the formation of hydroxo complexes which influence the reaction mechanism.

Kinetic measurements showed that the rates of the reactions of the individual DCTA complexes differed considerably. Under identical conditions the rates of the studied reactions increased in the sequence: Mg–DCTA < Ca–DCTA < Sr–DCTA. Dissociation rate constants of the magnesium, calcium, and strontium DCTA complexes have the values[6] $5\cdot6 . 10^4$, $4\cdot1 . 10^5$ and $6\cdot1 . 10^6$ $\text{mol}^{-1} \text{s}^{-1}$, resp.; these values predict that the rates of the substitution reactions involving the mentioned complexes should increase according to the sequence given above.

The experimental results described verified that the reactions of the alkaline-earth––DCTA complexes with cadmium(II) ions under the conditions of identical reactants concentrations proceed as the irreversible reactions of the second order. The rates of these reactions depend solely on the concentration of hydrogen ions and the reaction mechanism can be expressed by the reaction steps $(A)$ and $(B)$ similarly as in the case of other metal–metal substitution reactions of DCTA complexes[6]. In the pH interval $7-9$ and under the second order conditions, the extent of the reaction can be followed by square wave polarographic measurement of the concentration of the nonreacted cadmium(II) ions in the dependence on time without application of any special mixing technique. The differences of the rates of the reactions of the individual alkaline-earth–DCTA complexes with cadmium(II) ions can be expressed by the ratio of the experimental rate constants corresponding to the reaction of an individual alkaline-earth–DCTA complex. These rate constants were determined from the slopes of the linear dependence $1/[\text{Cd}^{2+}]$ $vs$ time for each DCTA complex. The ratio of the rate constants of the reactions of the calcium and magnesium complexes $k_{\text{CaL}}/k_{\text{MgL}}$ was found $6\cdot8$ at pH $7\cdot4$, that of the calcium and strontium complexes, $k_{\text{SrL}}/k_{\text{CaL}}$, $12\cdot5$ at pH $8\cdot2$. These findings lead to the conclusion that the binary mixtures of alkaline-earths can be simply analyzed using the linear extrapolation method[8] based on the square wave polarographic measurement.

*Determination of the Sum of Alkaline-Earth Ions*

For the differential kinetic analysis of a mixture using the linear extrapolation method[8], following conditions should be fulfilled: an irreversible second order reaction

of each component of a mixture with a common reagent and different rates of these reactions; suitable method for the determination of the total composition of a mixture, and suitable experimental technique for the determination of the concentration changes in the dependence on time.

In the studied case two of the mentioned conditions are satisfactorily fulfilled: character of the reaction kinetics and the experimental technique — square wave polarography. On the other hand the determination of the sum of alkaline-earth ions can be carried out by the titration with *e.g.* EDTA, but only at moderate concentrations of these ions. The square wave polarographic measurement enables, however, to follow the changes of the cadmium(II) ions in the concentration range $10^{-4}-10^{-6}$M; this means that the substitution reaction between alkaline-earth––DCTA complex and cadmium(II) ions can be followed in the given concentration range. Therefore an attempt was made to find a mode for the determination of the sum of alkaline earth ions present in minor concentrations.

Such determination is based on the fact, that the apparent formation constant of the Cd–EDTA complex is less than that of the calcium, magnesium and strontium EDTA complexes in strongly ammoniacal solutions[9]. In ammoniacal media cadmium(II) ions are released from their EDTA complex in the presence of calcium and/or magnesium, as expressed by the reaction

$$2\,CdY^{2-} + Mg^{2+} + Ca^{2+} + 8\,NH_3 \rightarrow$$

$$\rightarrow\ CaY^{2-} + MgY^{2-} + 2\,Cd(NH_3)_4^{2+}\,. \qquad (D)$$
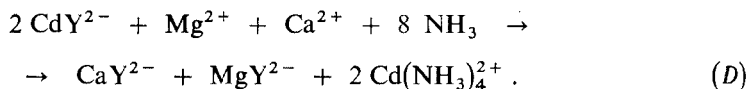
where $CdY^{2-}$, $CaY^{2-}$ and $MgY^{2-}$ are the corresponding EDTA complexes ($H_4Y =$ = EDTA). The release of $Cd(NH_3)_4^{2+}$ ions, as expressed by reaction $(D)$, is quantitative and fast in 5M ammonia solution and when an excess of Cd–EDTA complex is present in the analyzed solution (approx. 30-fold excess of Cd–EDTA compared with the total concentration of alkaline-earth ions). The release of cadmium(II) ions occurs also in the presence of strontium(II) or calcium(II) ions, similarly as indicated by reaction $(D)$ with the exception that the sufficient concentration of ammonia is 1M. According to these findings, the determination of the sum of calcium and magnesium or the sum of calcium and strontium, based on the reaction $(D)$ is carried out in 5M and 1M ammonia solution, respectively, by the measurements of the square wave polarographic peaks of the released cadmium(II) ions. These results are in a good agreement with the study published by Hagiwara[8] and represent a simple way for the determination of the sum of alkaline earth ions necessary for the application of the linear extrapolation method.

The described indirect determination of the sum of the alkaline-earth ions is convenient for the purposes of the differential kinetic analysis of the alkaline-earth mixtures because: *a*) the molar amount of released cadmium(II) ions found (reac-

tion $(D)$) is equal to the amount of DCTA reagent which is to be added to the analyzed solution to form quantitatively the alkaline-earth–DCTA complexes, and b) simultaneously the found amount of cadmium(II) ions (reaction $(D)$) is equal to the amount of cadmium(II) ions which is to be added to the analyzed mixture of alkaline-earth–DCTA complexes to initiate the reaction $(C)$ and $(CI)$.

### Analysis of Alkaline-Earth Mixtures Using Linear Extrapolation Method

The different rates of the reactions between the mentioned alkaline-earth–DCTA complexes and cadmium(II) ions under the second order conditions enable the differential kinetic analysis of the alkaline-earth mixtures using the linear extrapolation method.

Under the conditions when

$$[Cd^{2+}]_0 = [CaL^{2-}]_0 + [MgL^{2-}]_0, \tag{E}$$

where the indexes correspond to the initial concentrations, the rate of the reaction

$$CaL^{2-} + MgL^{2-} + 2 Cd^{2+} \rightarrow 2 CdL^{2-} + Mg^{2+} + Ca^{2+} \tag{F}$$
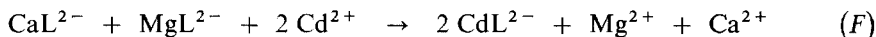
is expressed by the equation

$$- d[Cd^{2+}]/dt = dx/dt = k_{CaL}[Cd^{2+}][CaL^{2-}] + k_{MgL}[Cd^{2+}][MgL^{-2}], \tag{1}$$

where $x$ is the amount of $Cd^{2+}$ ions consumed at any time, $t$.

As stated above, the calcium complex reacts with cadmium(II) ions faster than the magnesium complex. When the $CaL^{2-}$ complex reacted essentially to the completion, equation $(1)$ gives after integration

$$x = k_{MgL}[MgL^{2-}]([Cd^{2+}]_0 - x) t + [CaL^{2-}]_0. \tag{2}$$



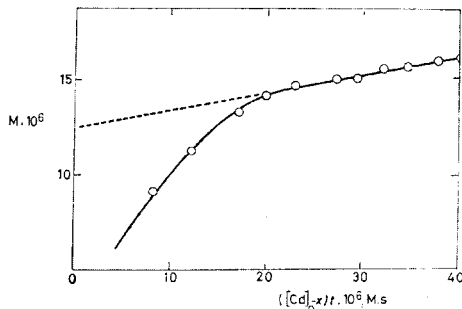Fig. 1

Analysis of the Calcium and Magnesium Mixture

$[Ca^{2+}]_0 = 1 \cdot 25 . 10^{-5} M$, $[Mg^{2+}]_0 = 4 \cdot 0 . 10^{-6} M$; measurement carried out in the interval 2–20 min.

The extrapolated intercept at $t = 0$ of the plot $x$ $vs$ $([Cd^{2+}]_0 - x) t$ determines the value $[CaL^{2-}]_0$ which is equal to the initial concentration of calcium(II) ions. A typical plot of this dependence is shown in Fig. 1.

*Analysis of the calcium and magnesium mixtures*: A portion of the sample solution ($10^{-4}$ to $10^{-6}$M alkaline-earth ions) is transferred into the polarographic cell containing 1M-$NH_3$ solution and approx. 50-fold excess of Cd-EDTA complex as compared with the concentration of calcium and magnesium. After removal of dissolved oxygen the square wave polarogram of released cadmium(II) ions is recorded. From the calibration graph (height of the cadmium peak $vs$ concentration of cadmium(II) ions) the concentration of released cadmium(II) ions is read. To the second portion of the sample solution (identical volume as in the previous case) is added DCTA reagent the concentration of which is exactly equal to that of the released cadmium(II) ions determined in the previous step. The resulting solution containing alkaline-earth--DCTA complexes is transferred into the polarographic cell containing borate buffer solution, pH 7·1—7·3. After removal of oxygen, standard solution of cadmium(II) ions (concentration equal to that as determined previously) is added into the cell and after a short mixing with nitrogen (30 s), the square wave polarograms of nonreacted cadmium(II) ions are recorded at measured time intervals ($\sim 20$ min). The calculation is carried out graphically by plotting $x$ $vs$ $([Cd^{2+}]_0 - x) t$, linear part of this plot is extrapolated and the intercept at $t = 0$ gives the concentration of $[CaL^{2-}]_0$ equal to the initial concentration of calcium. Concentration of magnesium is calculated from the sum calcium + magnesium determined by the measurement in ammoniacal solution. From the definitions given above it follows that $x = [Cd^{2+}]_0 - [Cd^{2+}]_t$ and $[Cd^{2+}]_0 - x = [Cd^{2+}]_t$; therefore the graph is obtained by plotting $([Cd^{2+}]_0 - [Cd^{2+}]_t)$ $vs$ $[Cd^{2+}]_t t$, where $[Cd^{2+}]_t$ is the concentration of nonreacted cadmium(II) ions determined at time $t$ and $[Cd^{2+}]_0$ is the initial concentration of cadmium(II) ions determined by the measurement in ammoniacal solution.

*Analysis of calcium and strontium mixtures*: This analysis is carried out identically as described above with the exception that the indirect determination of the sum calcium and strontium is carried out in 5M ammonia solution and the reaction of calcium and strontium DCTA complex with cadmium(II) ions is followed in borate buffer solution, pH 8·2—8·4. The faster reacting component in this case is the strontium complex.

Using the described procedures the mixtures of calcium and magnesium and mixtures of calcium and strontium were analyzed with an average error of $\pm 9·5\%$ (based on 25 determinations), the composition of the analyzed mixtures varied from 1·0 : 0·15 to 0·15 : 1·0, concentration of the alkaline-earth ions was in the range $10^{-5}—10^{-6}$M. Only the metal ions interfering with the square wave polarographic determination of cadmium (*e.g.* higher concentrations of indium(III)) interfere with the described determination; reactions of the DCTA complexes of other metal ions are too slow under the given conditions[6]. D.c. polarographic technique can also be applied for the proposed method, in this case the determination is, however, less sensitive. Compared with other kinetic methods[6,7] applicable for the analysis of alkaline earth mixtures, the described method is simple because no special mixing technique is necessary. Application of the square wave polarography enables to carry out analysis of the mixtures of alkaline earth ions of the concentrations as low as $10^{-6}$M.

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