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**REDAKCIJA GLASNIKA HEMIČARA I TEHNOLOGA  
BOSNE I HERCEGOVINE**

Hemijski institut Prirodno-matematičkog fakulteta Sarajevo,  
Vojvode Putnika 43

### The Thermal Analysis of Formamide Complexes of some Zinc and Cadmium Salts

M. Glavaš

Laboratory of Inorganic Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

Several formamide complexes of zinc and cadmium salts:  $ZnCl_2 \cdot 3FA$ ,  $ZnBr_2 \cdot 3FA$ ,  $ZnJ_2 \cdot 2FA$ ,  $Zn(NO_3)_2 \cdot 4FA$ ,  $Zn(Ac)_2 \cdot 2FA$ ,  $ZnSO_4 \cdot 6FA$ ,  $CdCl_2 \cdot 4FA$ ,  $CdBr_2 \cdot 4FA$ ,  $CdJ_2 \cdot 4FA$ ,  $Cd(NO_3)_2 \cdot 4FA$  and  $Cd(Ac)_2 \cdot 2FA$  ( $FA = HCONH_2$ ) were prepared and their thermal decomposition was studied.  
(1 table, 3 figure, 9 references, original in German)

V. MILIĆEVIĆ

### Application of Silver Electrode in Dimethylsulphoxide II (Solubility Products of Silver Halides)

V. Milićević and D. Vasiljević

Laboratory of Physical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

The values of the solubility products in DMSO were determined potentiometrically, conductometrically and by the Ag-110 isotope activity measurements. The following results have been obtained:

	Potentiom. method	Ag-110 isotope measur.	Conductome- tric measurements
AgCl	9,2	9,1	9,2
AgBr	9,8	9,7	9,8
AgJ	10,8	—	—

All of the measurements have been done at 25,00 0,02°C.

Furthermore, mobility of the Ag ion in DMSO has been estimated to be 13,8 0,2  $\text{ohm}^{-1} \text{cm}^2$  at 25°C.  
(10 reference, original in English)

F KRLEŽA



<p>Thermal decomposition of Zinc Formamide Complexes Cadmium Formamide Complexes</p> <p>545.8:541.486</p>	<p>GHTBH — 1</p> <p>I. The Thermal Analysis of Formamide Complexes of Some Zinc and Cadmium Salts</p> <p>I. M. Glavag II. Laboratory of Inorganic Chemistry, Institute of Chemistry, Faculty of Sa- cience, University of Sa- rajevo, Sarajevo, Bosnia and Herzegovina, Yugo- slavia</p>	
<p>Demethylsulphoxide as solvent Silver electrode application of Silver halides Solubility products of</p> <p>547.269:545.3:546.57</p>	<p>GHTBH — 2</p> <p>I. Application of Silver Ele- ctrode in Dimethylsulpho- xide II (Solubility Products of Silver Halides)</p> <p>I. Mileevic V. II. Vasiljevic D. III. Laboratory of Physical Chemistry, Institute of Chemistry, Faculty of Sa- cience, University of Sa- rajevo, Sarajevo, Bosnia and Herzegovina, Yugo- slavia</p>	



GHTBH — 3

545.82:541.122

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 11—18 (1971/72)

**Spectrophotometric Determination of Stability Constants of Methoxyacetato Complexes of Cobalt, Nickel, and Copper**

*D. Tuhtar, J. Savić and M. Savić*

*Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

Stoichiometric stability constants of Co(II), Ni(II), and Cu(II) methoxyacetato complexes were determined spectrophotometrically at 25°C in 2M NaClO<sub>4</sub>, using Bjerrum's method of corresponding solutions. Stability constants were evaluated graphically and then refined using a non-linear least-square («Gauss») treatment. (3 figures, 6 tables, 10 references, original in English)

F. KRLEŽA

GHTBH — 4

545.82:541.122

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 19—24 (1971/72)

**Spectrophotometric Determination of Stability Constants of Ethoxyacetato Complexes of Cobalt, Nickel, and Copper**

*D. Tuhtar, M. Savić and J. Savić*

*Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

Stoichiometric stability constants of Co(II), Ni(II), and Cu(II) ethoxyacetato complexes were determined spectrophotometrically at 25°C in 2M NaClO<sub>4</sub>, using Bjerrum's method of corresponding solutions. Graphically estimated values of stability constants were refined using a non-linear least-square («Gauss») procedure. 6 tables, 3 figures, 5 references, original in English)

F. KRLEŽA

GHTB — 5

545.82:546.621

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 25—29 (1971/72)

**Spectrophotometric Determination of Aluminium in Steel**

*V. Đurkin, F. Krlježa and V. Vatreňjak*

*Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

A simple and rapid method for the spectrophotometric determination of aluminium in steel, without preliminary separation of iron and other elements, is described.

The sample (0,5—1 g) is dissolved in conc. hydrochloric acid, iron and copper are reduced to Fe(II) and Cu(I) by ascorbic acid and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, respectively. The pH of the solution is adjusted to 4, 5 and the optical density of the red aluminium-aluminon complex is measured directly at 520 nm, 30 minutes after. The amount of aluminium present in the steel is obtained from the calibration curve.

(3 tables, 19 references, original in German)

M. SAVIC

<p>545.82:546.621 Aluminum in Steel Spectrophotometric detn. of Aluminum as complexing agent</p>	<p>GHTB — 5</p> <p>1. Spectrophotometric Determination of Aluminum in Steel</p> <p>I. V. Durkin II. F. Križka III. V. Vatreňjak IV. Laboratory of Analytical Chemistry, Institute of Science, University of Sa- rajevo, Sarajevo, Bosnia and Herzegovina, Yugo- slavia</p>	
<p>545.82:541.122 Cobalt(II) complexes of Ethoxyacetic acid, complexes of Nickel(II), complexes of</p>	<p>GHTB — 4</p> <p>1. Spectrophotometric De- termination of Stability Constants of Ethoxyace- tato Complexes of Co- balt(II), Nickel(II), and Copper(II)</p> <p>I. Tuhtar D. II. Savic M. III. Savic J. IV. Laboratory of Analytical Chemistry, Institute of Science, University of Sa- rajevo, Sarajevo, Bosnia and Herzegovina, Yugo- slavia</p>	
<p>545.82:541.122 Cobalt(II), complexes of Copper(II), complexes of Methoxyacetic acid, complexes of Nickel(II), complexes of</p>	<p>GHTB — 3</p> <p>1. Spectrophotometric De- termination of Stability Constants of Methoxya- cetato Complexes of Co- balt, Nickel, and Copper.</p> <p>I. Tuhtar D. II. Savic J. III. Savic M. IV. Laboratory of Analytical Chemistry, Institute of Science, University of Sa- rajevo, Sarajevo, Bosnia and Herzegovina, Yugo- slavia</p>	



GHTBH — 6

545 82:541.122

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 31—41 (1971/72)

**Potentiometric Determination of Stability Constants of Lactato and  $\beta$ -Hydroxypropionato Complexes of Indium(III)**

*J. Savić and M. Savić*

*Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

Stoichiometric stability constants of In(III) lactato and  $\beta$ -hydroxypropionato complexes were detd. potentiometrically at 25°C in 2M NaClO<sub>4</sub> by Fronaeus titration technique. Graphically estimated values of stability constns. were refined using a non-linear least-square («Gauss») procedure.

(5 tables, 8 references, original in English)

F. KRLEZA

GHTBH — 7

541.486:541.123:547.63

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 43—48 (1971/72)

**The Influence of Glycerol and of Formamide on the Extraction Equilibria of the Complexes of Alkali Metals and Ammonium-ion with the Indicator Bromthymol Blue, in systems water — chloroform**

*M. Savić and J. Savić*

*Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

The pK values of the extraction equilibria of the complexes of alkali metals with univalent anion (HBTB<sup>-</sup>) of the indicator bromthymol blue, have been studied as a function of the dielectric constant and of the logarithm of the atomic number of alkali metals in systems water + glycerol — chloroform and water + formamide — chloroform.

(1 table, 2 figures, 2 references, original in French)

V. DURKIN



<p>545.82:541.122</p> <p><math>\beta</math>-hydroxypropionic acid, complexes of Indium(III), complexes of Lactic acid, complexes of</p>	<p>6 — GHTBH</p> <p>I. Potentiometric Determination of Lactate and <math>\beta</math>-Hydroxypropionate Complexes of Indium(III)</p> <p>I. Savic J. II. Savic M. III. Laboratory of Analytical Chemistry, Institute of Science, Faculty of Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	
<p>541.486:541.123:547.63</p> <p>Alkali metals complexes, extraction equilibria of Ammonium-ion complexes, extraction equilibria of Bromthymol Blue complexes, extraction equilibria of</p>	<p>7 — GHTBH</p> <p>I. The Influence of Glycol and of Formamide on the Extraction Equilibria of the Complexes of Alkali Metals and Ammonium-ion with the Indicator Bromthymol Blue in systems water — chloroform.</p> <p>I. Savic M. II. Savic J. III. Laboratory of Analytical Chemistry, Institute of Science, Faculty of Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	

**Complexometric Determination of Divalent Cations of Second, Fourth and Fifth Analytic Groups in the Systems with Aluminium which is previously Masking with Glycerol**

F. Krlježa and N. Vuletić

Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

The Determination of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  in the presence of  $\text{Al}^{3+}$  was investigated by means of complexometric titration. The influence of  $\text{Al}^{3+}$  was eliminated by masking with glycerol. pH-range and indicators applied are described for each particular determination. The investigations were carried out in the concentration range of  $\text{Me}^{2+}$   $5 \cdot 10^{-4}$  to  $2.7 \cdot 10^{-3}$  M and for  $\text{Al}^{3+}$   $7.5 \cdot 10^{-3}$  to  $2.8 \cdot 10^{-2}$  M. Relative standard errors and variations coefficient was found. Relations of relative constants of stability  $\text{Me}^{2+}$  — KIII,  $\text{Al}^{3+}$  — KIII,  $\text{Me}^{2+}$  — glycerol, and  $\text{Al}^{3+}$  — glycerol is discussed.

(1 table, 6 references, original in German)

V. ĐURKIN

**Analytical Studies of the Iron(II)-Iron(III) and Chromium (III)-Chromium(VI) Systems and the Investigation of Two-, Three-, and Four-component Combinations of the Cation Using Radioactive Tracers**

S. Kozomara and F. Krlježa

Institute for the Nuclear Science »Boris Kidrič«, Vinča — Beograd, Serbia, Yugoslavia

Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

Using the method of radioactive tracers the system of iron(II)-iron(III) and chromium(III)-chromium(VI) were studied, and those methods on the two-, three-, and four-component systems of the cations mentioned above were applied.

(11 tables, 6 references, original in German)

V. MILIČEVIĆ

<p>Aluminum, masking of Complexometric titrn. Divalent Cations, detn. of Glycerol as masking agent Stability Constants, discussed</p> <p>545.2:546.4:546.7</p>	<p>1. Complexometric Determination of Divalent Cations of Second Fourth and Fifth Analytic Groups in the Systeme with Aluminum.</p> <p>I. F. Križka II. N. Vuletic III. Laboratory of Analytical Chemistry, Institute of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	<p>GHTB — 8</p>
<p>Combination Two-, Three-, Four-Component: Fe(II), Fe(III), Cr(VI) of Analytical studies of Radioactive Tracers, using</p> <p>546.72:546.76:541.15</p>	<p>1. Analytical Studies of the Iron(II)-Iron(III) and Chromium(III)-Chromium(VI) and the Investigation of Two-, Three- and Four-component Combinations of the same Cation using Radioactive Tracers</p> <p>I. S. Kozomora II. F. Križka III. Institute for the Nuclear Science »B. Kidrič« Vinča — Beograd, Serbia, Yugoslavia IV. Laboratory for Analytical Chemistry, Institute of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	<p>GHTB — 9</p>



### Adducts of some Alkali and Alkaline-earth Salts with N, N-Dimethylacetamide

M. Glavaš and T. Ribar

Laboratory of Inorganic Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

A series of N, N-Dimethylacetamide adducts of some alkali and alkaline-earth salts was prepared and characterized. Thermogravimetric and differential thermal analysis were used to investigate the thermal dissociation of these adducts.

(2 tables, 4 figures, 7 references, original in Serbo-Croatian-Croato-Serbian)

V. MILIČEVIĆ

### Base Catalysed Hydrolysis of o-Nitrophenylacetate in a Mixed Dimethylsulfoxid — Water System

V. Sišlov, D. Sutić, P. Ilić

Laboratory of Physical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

Change of the rates of base catalysed o-nitrophenylacetate hydrolysis has been investigated in a mixed DMSO-water solvent system of 0,0 to 0,7 mole fraction of DMSO. Catalysts under the investigation have been: NaOH (0,01M), imidazole (0,008 — 0,2M) and glycine anion (0,04 — 0,08M).

Large increase in the rates of the reaction has been observed under the catalytic action of OH<sup>-</sup> ion or glycine anion, while the rates of the reaction decrease under the catalytic influence of imidazole.

(5 tables, 3 figures, 20 references, original in Serbo-Croatian-Croato-Serbian)

V. MILIČEVIĆ

### Dissociation Constants of Acetic Acid in the Mixed Solvents

T. Ribar, B. Skundrić

Laboratory of Physical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

Dissociation constants of acetic acid in mixed solvents, dimethylsulphoxide — water and dimethylformamide — water have been determined by conductometric method.

(1 table, 4 references, original in Serbo-Croatian-Croato-Serbian)

V. MILIČEVIĆ

<p>Thermogravimetric and differential thermal analysis of Alkaline Salts-Adducts of Alkaline-Earth Salts-Adducts of N,N-Dimethylacetamide Ad-ducts</p> <p>545.8:541.486</p>	<p>GHTBH — 10</p> <p>I. Adducts of Some Alkali and Alkaline-Earth Salts with N,N-Dimethylacetamide I. M. Glavas II. T. Ribar III. Laboratory of Inorganic Chemistry, Institute of Science, University of Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	
<p>Base catalysis in a mixed dimethylsulfoxide-water system Change of the catalytic efficiency in the mixed solvents OH<sup>-</sup>, glycine anion and imidazole catalysis of o-nitrophenylacetate in aqueous dimethylsulfoxide.</p> <p>541.128:541.122:547.269</p>	<p>GHTBH — 11</p> <p>I. Base Catalysed Hydrolysis of o-Nitrophenylacetate in a Mixed Dimethylsulfoxid — Water System I. V. Sislav II. D. Sutić III. P. Ilić IV. Laboratory of Physical Chemistry, Institute of Science, University of Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	
<p>Conductometric determination of Dissolution constants of Acetic acid in Mixed solvents</p> <p>545.37:541.122</p>	<p>GHTBH — 12</p> <p>I. Dissociation Constants of Acetic Acid in the Mixed Solvents I. T. Ribar II. B. Skundrić III. Laboratory of Physical Chemistry, Institute of Science, University of Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	



GHTBH — 13

546.621:545.2

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 91—93 (1971/72)

**The Complexometric Determination of Aluminium in Presence of Iron(III) Using Calcein as Indicator**

V. Đurkin

Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

The procedure for the complexometric determination of aluminium in presence of iron using calcein as fluorescent indicator, was performed.

We found the ratio between Al and Fe that enables the determination of Al in presence of Fe. This ratio must not be smaller than 1:4, otherwise the error in determination of Al is greater than 6%.

(1 table, 4 references, original in Serbo-Croatian-Croato-Serbian)

F. KRLEŽA

GHTBH — 14

541.486:541.132.3

Original Scientific Paper

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 95—97 (1971/72)

**Influence of pH on the Complex Formation Between Cr(III) and Glycerol**

V. Đurkin

Laboratory of Analytical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

The influence of pH on the complex formation between Cr(III) and glycerol was investigated spectrophotometrically. Molar ratio Cr — glycerol was 1:3500 and the pH of the systems varied from pH 2 to 13, using different buffers. It was found that the most optimal pH range for the Cr-glycerol complex formation was over pH 9.

(1 figure, 4 references, original in Serbo-Croatian-Croato-Serbian)

F. KRLEŽA

GHTBH — 15

541.123.547.26

Note

Glasnik hem. i teh. BiH

GHTBAB 19/20 (1) 99—101 (1971/72)

**Decarbonilation of Ethyl Formate in H<sub>2</sub>SO<sub>4</sub> of High Concentration**

T. Ribar, M. Glavaš, A. Papo

Laboratory of Physical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia

The first order rate constants of decarbonilation of ethyl formate in H<sub>2</sub>SO<sub>4</sub> (concentration range: 88,5 — 98,2 wt.%) have been determined. The rate of the reaction reaches a maximum value at 93,5 wt. % H<sub>2</sub>SO<sub>4</sub>.

(2 tables, 7 references, original in Serbo-Croatian-Croato-Serbian)

V. MILIĆEVIĆ



<p>541.123.547.26</p> <p>The first order rate constants of Decarboxylation of Ethyl formate in <math>H_2SO_4</math> (88.5—98.2 wt.%)</p>	<p>GHTBH — 15</p> <p>I. Decarboxilation of Ethyl Formate in <math>H_2SO_4</math> of high Concentration I. T. Ribar II. M. Glavas III. A. Papo IV. Laboratory of Physical Chemistry, Institute of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	
<p>541.486:541.132.3</p> <p>Chromium(III)-Glycerol Complex Formation, pH Influence on</p>	<p>GHTBH — 14</p> <p>I. Influence of pH on the Complex Formation between Cr(III) and Glycerol I. V. Durkin II. Laboratory of Analytical Chemistry, Institute of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	
<p>546.621:545.2</p> <p>Aluminium in Presence of Iron Calcein as Indicator-Complexometric Determination of</p>	<p>GHTBH — 13</p> <p>I. The Complexometric Determination of Aluminium in Presence of Iron (III) Using Calcein as Indicator I. V. Durkin II. Laboratory of Analytical Chemistry, Institute of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia</p>	

## The Hydrolysis of Chlorodimethyl Ether and Related Compounds II

T. Ribar, M. Glavaš, B. Skundrić

*Laboratory of Physical Chemistry, Institute of Chemistry Faculty of Science, University of Sarajevo, Sarajevo, Bosnia and Herzegovina, Yugoslavia*

The energy and entropy of activation of the hydrolysis of chlorodimethyl ether and its homologues have been determined. The influence of the change of solvent composition of the rate of these reactions has been examined. Our results suggest that the two mechanism,  $S_N1$  and  $S_N2$ , operate simultaneously.

(2 tables, 6 references, original in Serbo-Croatian-Croato-Serbian)

V. MILICEVIC

1. The Hydrolysis of Chlorodimethyl Ether and Related Compounds II

I. T. Ribar

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and Herzegovina, Yugo-

slavia

The energy and entropy of  
activation of the hydrolysis of  
Chlorodimethyl ether and  
its homologues  
Mechanism S<sub>1</sub> and S<sub>2</sub> ope-  
rate simultaneously



GHTBH 1

545.8:541.486  
Original Scientific Paper

## DIE THERMOLYSE VON FORMAMID-KOMPLEXEN EINIGER ZINK- UND KADMIMUMSALZE

M. Glavaš

*Institut für Chemie, Naturwissenschaftliche Fakultät, Universität Sarajevo, Sarajevo,  
Bosnien und Herzegowina, Jugoslawien*

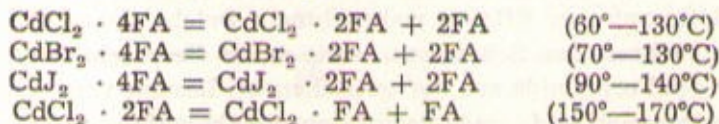
Die folgenden Formamidkomplexe wurden synthetisch dargestellt und deren Thermolyse untersucht:  $ZnCl_2 \cdot 3FA$ ,  $ZnBr_2 \cdot 3FA$ ,  $ZnJ_2 \cdot 2FA$ ,  $Zn(NO_3)_2 \cdot 4FA$ ,  $Zn(Ac)_2 \cdot 2FA$ ,  $ZnSO_4 \cdot 6FA$ ,  $CdCl_2 \cdot 4FA$ ,  $CdBr_2 \cdot 4FA$ ,  $CdJ_2 \cdot 4FA$ ,  $Cd(NO_3)_2 \cdot 4FA$  und  $Cd(Ac)_2 \cdot 2FA$  ( $FA = HCONH_2$ ).

Formamid hat sich als ein geeignetes Lösungsmittel bei Erforschung gewisser chemischer Reaktionen erwiesen. Der polare Charakter, die hohe Dielektrizitätskonstante und das günstig gelegene »Arbeitsgebiet« dieses Lösungsmittels bewirken gute Auflösung vieler anorganischer Salze<sup>1-3</sup>. Wenn Formamidsolvate verschiedener Lewis-Säuren isoliert werden,<sup>4,5</sup> können die wohl ausgeprägten Donator-Eigenschaften des Formamids erkannt werden.

In Fortsetzung unserer Untersuchungen über die thermische Dissoziation von Metallsalzkomplexen mit verschiedenen Amiden<sup>6-8</sup> haben wir nun eine Reihe von Zink- und Kadmiumsolvaten dargestellt und diese durch thermogravimetrische (TG) und differentielle thermale Analyse (DTA) charakterisiert. Die hierbei verwendete experimentelle Technik ist in einer früher veröffentlichten Arbeit<sup>9</sup> beschrieben worden.

In der Tabelle I sind analytische Daten über die synthetisch bereiteten Komplexe zusammengestellt.

Der Verlauf der thermischen Zersetzung wird durch die Kurven in Abb. 1 und Abb. 2 veranschaulicht. Zum Unterschied von Zinkhalogenid-Komplexen, deren thermische Dissoziation kontinuierlich verläuft (Kurven 1 bis 3, Abb. 1), werden die Kadmiumhalogenidsolvate stufenweise desolvatisiert (Kurven 1 bis 3, Abb. 2). Es werden hierbei zunächst Disolvate als Zwischenprodukte gebildet:



Bei der thermogravimetrischen Analyse von  $CdCl_2 \cdot 4FA$  tritt außerdem noch ein Monosolvat auf:

Diese Arbeit wurde mit finanzieller Beihilfe vom Fond für wissenschaftliche Arbeit der Sozialistischen Republik Bosnien-Herzegowina durchgeführt.

TABELLE I

Analyseergebnisse mit Formamid-Komplexen

Komplex	Gehalt an				Thermogravimetrische Analyse			
	Kation		Anion		Formamid		Oxid	
	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.
ZnCl <sub>2</sub> · 3FA	24,09	24,04	26,09	26,06	49,77	50,2	.....	.....
ZnBr <sub>2</sub> · 3FA	18,14	17,98	44,36	44,32	37,50	36,9	.....	.....
ZnJ <sub>2</sub> · 2FA	15,96	15,97	62,01	61,96	22,00	22,3	.....	.....
Zn(NO <sub>3</sub> ) <sub>2</sub> · 4FA	17,70	17,18	33,60	33,00	.....	.....	22,02	21,5
ZnSO <sub>4</sub> · 6FA	15,15	15,19	22,26	21,87	62,76	62,3	.....	.....
Zn(Ac) <sub>2</sub> · 2FA	23,91	23,85	43,15	42,98	.....	.....	29,76	30,5
CdCl <sub>2</sub> · 4FA	30,93	31,21	19,51	19,39	49,86	49,4	.....	.....
CdBr <sub>2</sub> · 4FA	24,85	24,76	35,33	35,30	40,06	39,3	.....	.....
CdJ <sub>2</sub> · 4FA	20,57	20,49	46,46	46,32	33,16	33,0	.....	.....
Cd(NO <sub>3</sub> ) <sub>2</sub> · 4FA	26,99	26,87	29,77	29,48	.....	.....	30,82	31,5
Cd(Ac) <sub>2</sub> · 2FA	35,08	35,36	36,82	36,56	28,04	29,2	40,07	40,8

Die äusserste Desolvationsstufe ist bei 200°, bzw. bei 230°C abgeschlossen, anschliessend folgt ein relativ breites Gebiet, in welchem die desolvatisierten Kadmiumhalogenide beständig sind. Bei den Thermolyseverläufen von Zinkhalogenidkomplexen sind die Temperaturintervalle mit abgeflachten Kurvenverlauf nicht aufgezeichnet.

Die nitrat- und azetathältigen Zink- und Kadmiumkomplexe und das ZnSO<sub>4</sub> · 6FA zersetzen sich einstufig und die Desolvation ist meistens mit Zersetzung des Salzes verbunden (Kurven 4 bis 6, Abb. 1 und Kurven 4,5 in Abb. 2). In letzterer Hinsicht bildet jedoch der Zinksulfatkomplex eine Ausnahme, da dessen Thermolyseverlauf auf eine Beständigkeit des desolvatisierten Sulfats bis in den Bereich hoher Temperaturen hinweist.

Auf den DTA-Kurven der Komplexe (Abb. 3) kann man Aufzeichnungen endothermischer Effekte wahrnehmen, welche durch die Zersetzung unter gleichzeitigem Schmelzen, sowie durch die anschliessende Verflüchtigung des Formamids aus der entstehenden Lösung verursacht sind. Nur die Kadmiumchlorid- und Kadmiumbromidkomplexe zersetzen sich ohne zu schmelzen. Der während der Zersetzung stattfindende Oxydationsprozess bedingt exothermische Spitzen.



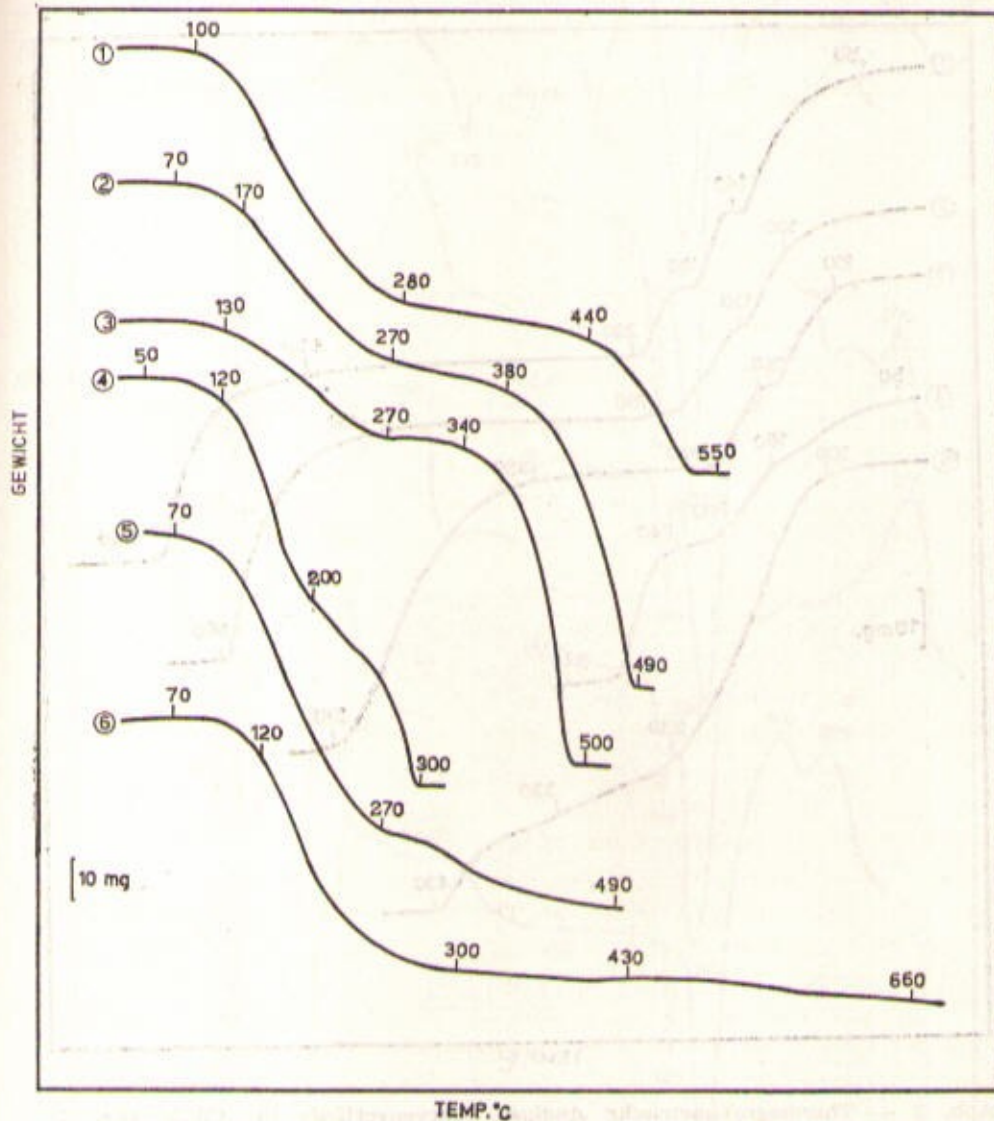


Abb. 1 — Thermogravimetrische Analyse: Kurvenverläufe für  $\text{ZnCl}_2 \cdot 3\text{FA}$  (1),  $\text{ZnBr}_2 \cdot 3\text{FA}$  (2),  $\text{ZnJ}_2 \cdot 2\text{FA}$  (3),  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{FA}$  (4),  $\text{Zn}(\text{Ac})_2 \cdot 2\text{FA}$  (5) und  $\text{ZnSO}_4 \cdot 6\text{FA}$  (6)

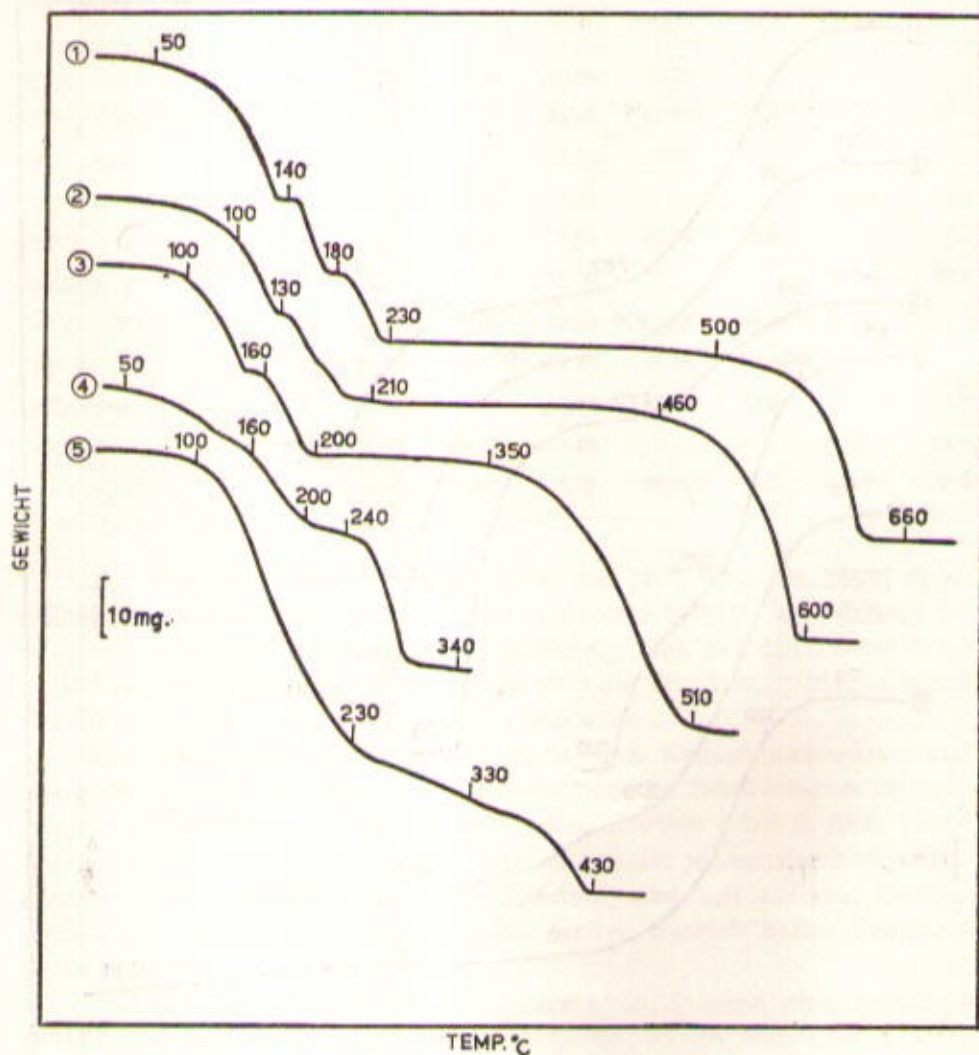


Abb. 2 — Thermogravimetrische Analyse: Kurvenverläufe für  $\text{CdCl}_2 \cdot 4\text{FA}$  (1),  $\text{CdBr}_2 \cdot 4\text{FA}$  (2),  $\text{CdJ}_2 \cdot 4\text{FA}$  (3),  $\text{Cd}(\text{Ac})_2 \cdot 2\text{FA}$  (4) und  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{FA}$  (5)



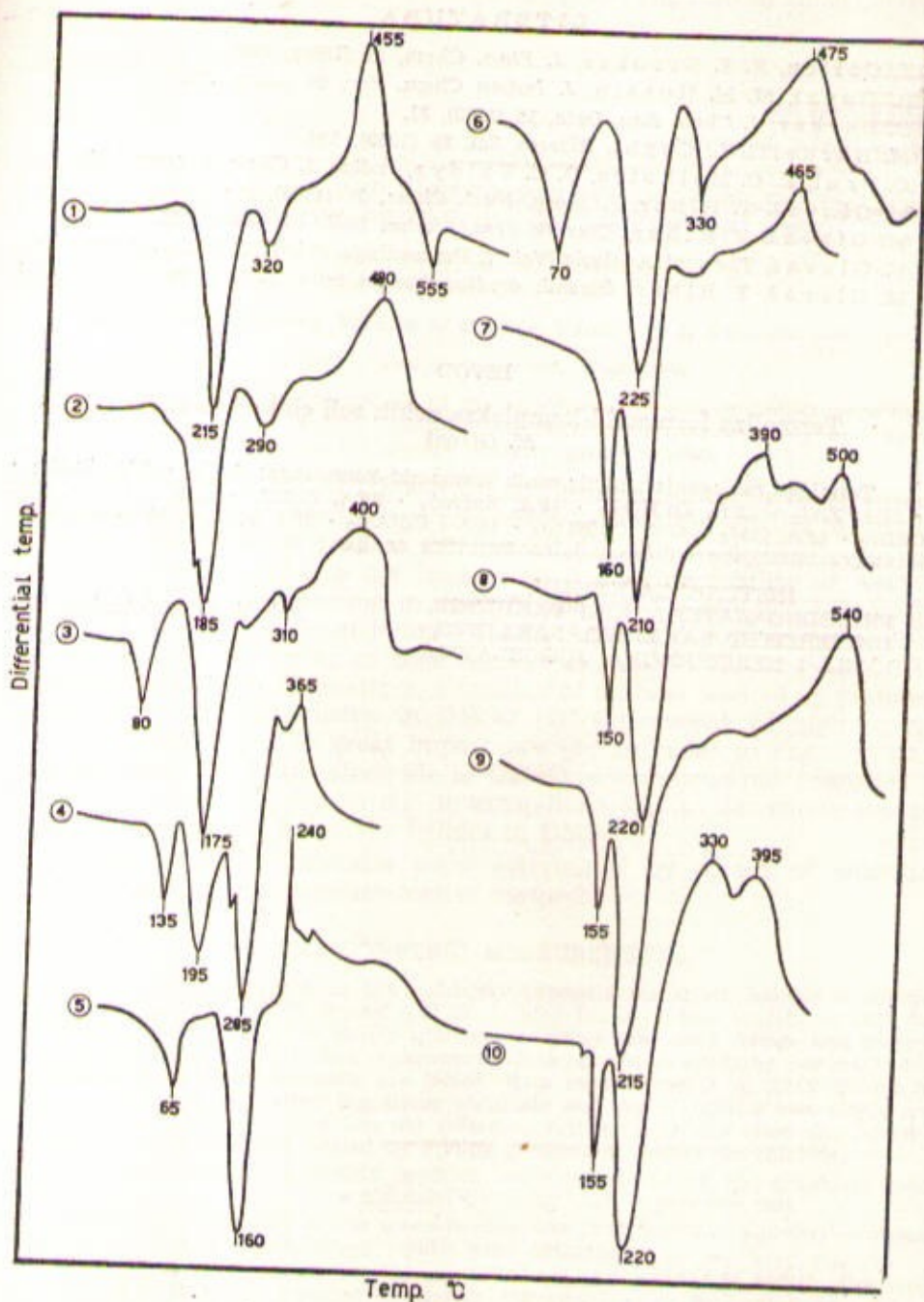


Abb. 3 — Differentielle Thermalanalyse: Kurvenverläufe für  $\text{CdCl}_2 \cdot 4\text{FA}$  (1),  $\text{CdBr}_2 \cdot 4\text{FA}$  (2),  $\text{CdJ}_2 \cdot 4\text{FA}$  (3),  $\text{Cd}(\text{Ac})_2 \cdot 2\text{FA}$  (4),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{FA}$  (5),  $\text{ZnCl}_2 \cdot 3\text{FA}$  (6),  $\text{ZnBr}_2 \cdot 3\text{FA}$  (7),  $\text{ZnJ}_2 \cdot 2\text{FA}$  (8),  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{FA}$  (9) und  $\text{Zn}(\text{Ac})_2 \cdot 2\text{FA}$  (10)

## LITERATURA

1. E. Colten, R. E. Brooker, *J. Phys. Chem.*, **62** (1958), 1959.
2. R. Gopal, M. M. Husain, *J. Indian Chem. Soc.*, **40** (1963), 272.
3. B. Becker, *J. Chem Eng. Data*, **15** (1970), 31.
4. M. Nardelli, L. Coghi, *Ricerca Sci.*, **29** (1959), 134.
5. C. Paul, K. C. Malhotra, O. C. Vaidya, *Indian J. Chem.*, **4**, (1966), 198.
6. M. Glavaš, T. Ribar, *J. Inorg. Nucl. Chem.*, **31** (1969), 291
7. M. Glavaš, T. Ribar, *Glasnik hem. i tehn. BiH*, **16** (1968), 123.
8. M. Glavaš, *Thermal Analysis*, Vol. 7, Proceedings Third ICTA Davos, 1971, 341.
9. M. Glavaš, T. Ribar, *Glasnik društva hem. i tehn. BiH*, **19/20** (1971—72) 69.

## IZVOD

**Termoliza formamid-kompleksa nekih soli cinka i kadmiuma**

M. Glavaš

Termičko razlaganje sintetiziranih formamid-kompleksa:  $ZnCl_2 \cdot 3FA$ ,  $ZnBr_2 \cdot 3FA$ ,  $ZnJ_2 \cdot 2FA$ ,  $Zn(NO_3)_2 \cdot 4FA$ ,  $Zn(Ac)_2 \cdot 2FA$ ,  $ZnSO_4 \cdot 6FA$ ,  $CdCl_2 \cdot 4FA$ ,  $CdBr_2 \cdot 4FA$ ,  $CdJ_2 \cdot 4FA$ ,  $Cd(NO_3)_2 \cdot 4FA$  i  $Cd(Ac)_2 \cdot 2FA$  ispitano je uz primjenu termogravimetrijske i diferencijalno termičke analize.

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Primljeno 12. oktobra 1972.



## APPLICATION OF SILVER ELECTRODE IN DIMETHYLSULPOXIDE II (SOLUBILITY PRODUCTS OF SILVER HALIDES)

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The values of the solubility products in DMSO were determined potentiometrically, conductometrically and by the Ag-110 isotope activity measurements.

We earlier reported (1), and as has been confirmed by other authors (2), that the  $\text{Ag}/\text{Ag}^+$  electrode is reversible in dimethylsulphoxide (DMSO) solution. The same is true of the reference electrode  $\text{Ag}/\text{AgCl}$ , but this system is troublesome to use because of the high solubility of  $\text{AgCl}$  in excess chloride ion resulting in the formation of the complex ion  $\text{AgCl}_2^-$  (1, 2, 3). It has also been found (1) that  $\text{AgBr}$  and  $\text{AgI}$  are soluble in excess anions, i. e. complex ions  $\text{AgBr}_2^-$  and  $\text{Ag}_2\text{I}_3^-$  are formed. After we performed these estimations, a number of authors worked on problems concerning electrochemistry in DMSO (4). Estimations of high energy battery systems are of great importance (5). In order to examine such system using the silver electrode in DMSO, a technique not described in literature, the first step in our investigations was to determine the solubility products of the silver halides in DMSO.

The solubility products were determined by means of potentiometric, isotopic and conductometric methods.

### POTENTIOMETRIC MEASUREMENTS

For the determination of the solubility products the silver halides in DMSO the apparatus which A. S. Brown and D. A. Mac Innes (6) had applied in 1935 for the determination of the solubility products in water was used. Lange and Swartz (7) reported theoretical data and experimental data obtained by applying this method of determination. The estimations are based upon measurements of EMF values of the concentration cell using the silver electrode and  $\text{AgCl}$ ,  $\text{AgNO}_3$  and  $\text{KNO}_3$  solutions. One of the half-cells was the reference cell while in the other the concentration of silver ions was varied by adding portions of potassium chloride.

The stoichiometric solubility products were calculated by the graphical method from the data which were obtained by using such a galvanic cell.

The method we used in our measurements was first tested in aqueous solutions of silver halides, and satisfactory results were obtained.

The measurements were carried out in 100 ml of  $1 \times 10^{-4}$  N  $\text{AgNO}_3$  dissolved in  $3 \times 10^{-2}$  N  $\text{KNO}_3$  solution in DMSO. Titrations were performed by adding aliquots of 0,1 ml  $\text{KCl}$ ,  $\text{KBr}$  or  $\text{KJ}$  solutions (that quantity containing  $1,7 \times 10^{-6}$  equivalents of the corresponding salt) to the above solution. We started by adding aliquots to both of the half-cells, after which the aliquots were added, one by one, to the measuring cell. After each addition the solution was stirred for half an hour



for it was found that in this period of time a constant EMF was established in the galvanic cell. All the measurements were carried out at a temperature of  $25 \pm 0,2^\circ\text{C}$ . The following solubility products, expressed as pL values, were obtained:

AgCl	AgBr	AgJ
9,2	9,8	10,8

These results are in the good agreement with the potential breaks obtained by potentiometric titrations. The potential breaks for formations AgCl and AgBr precipitates are of the same height, and the solubility products are of the same order of magnitude. The potential break for AgJ formation in DMSO is much greater than that of the chloride and bromide formation, and the solubility is lower. These results are in agreement with the theory of potentiometric titrations.

#### Ag-110 ISOTOPE MEASUREMENTS

In these measurements the method suggested by L. Gerford and G. Kof (8) was applied. Ag-110 in the form of silver nitrate solution was used as the radioactive indicator. Precipitates of silver chloride and bromide were obtained by mixing equimolar solutions of KCl and KBr with  $\text{AgNO}_3$ . In order to minimize the «salt effect» the precipitate was rinsed several times. The silver halide precipitates, which were heated during the precipitation in order to achieve faster formation of large crystals, were dissolved in DMSO and the activity of the solution above the precipitate was measured. A solution which was  $1 \times 10^{-4}$  M and had an activity of 2000 dpm was prepared for comparison with the saturated solutions in order to know the concentration of silver ions. The measurements were performed at the temperature of  $25 \pm 0,02^\circ\text{C}$ . The solubility products (pL) were found to be:

AgCl	AgBr
9,1	9,7

We were not able to estimate the AgJ solubility product because its solubility is low, and the specific activity of the silver ions we used was great enough to obtain reliable results.

#### CONDUCTOMETRIC MEASUREMENTS

The specific conductance of saturated halide solutions was experimentally evaluated and compared to the value of the limiting conductivity which was calculated from the equivalent ionic conductivity. From these two values, since the dilutions are high, the equivalent conductivity at concentration C can be taken as the equivalent conductivity at infinite dilution, and this allows us to calculate the equivalent concentration of electrolytes and also the solubility product (the solubility product for the binary electrolytes being equal to  $C^2$ ).

DMSO used in these estimations was obtained from the firm Rheinische Braunkohlen-Kraftstoff A. G. Wesseling as the commercial reagent grade material. It was purified by refluxing the material for several hours with CaO, followed by distillation. The DMSO so obtained was redistilled in a rectification column in a nitrogen atmosphere as described by Schäfer (9).

The melting point of DMSO thus purified was  $18,4^\circ\text{C}$  and the specific conductance was  $3,23 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

Using the  $\text{Cl}^-$  and  $\text{Br}^-$  equivalent conductivities at infinite dilution, reported by P. G. Sears et al. (10), and calculating the equivalent conductivity for  $\text{Ag}^-$  (which was not measured but obtained from the solubility product experimental data) as  $13,8 \pm 0,2$  at  $25^\circ\text{C}$ , the equivalent conductivity for silver chloride and bromide in DMSO were found to be:

$$\text{AgCl } 38,0 \text{ ohm}^{-1} \text{ cm}^2, \text{ AgBr } 38,2 \text{ ohm}^{-1} \text{ cm}^2$$

and pL values for AgCl and AgBr in DMSO are 9,2 and 9,8, respectively.

It is obvious that the results obtained by means of these three methods are in rather a good agreement.

## REFERENCES

1. T. Škerlaki i V. Milićević, *Glasnik društva hemičara NR BiH*, **11** (1962) 49.
2. D. C. Luehrs, R. T. Iwamoto and J. Kleinberg, *Inorg. Chem.*, **5** (1966) 201.
3. D. R. Cogley and J. N. Butler, *J. Electrochem. Soc.*, **113** (1966) 1074.
4. J. N. Butler, *J. Electroanal. Chem.*, **14** (1967) 89.
5. J. Farrar, R. Keller and M. M. Nicholson, High Energy Battery System Stadu. citat prema (4).
6. Brown S. A. and MacInnes D. A., *J. Am. Chem. Soc.*, **57** (1935) 459.
7. Lange and Schwartz, *Z. Physik. Chem.*, **129**, (1927) 111.
8. L. Gerfort, G. Koh. Praktikum po radiohimiji, Moskva 1963, str. 354.
9. Schläfer H. L. and Schafernicht K., *Angew. Chem.*, **72** (1960) 618.
10. P. G. Sears, G. R. Lester and L. R. Dawson, *J. Phys. Chem.*, **60** (1956) 1433.

## IZVOD

### Primjena srebrne elektrode u dimetilsulfoksidu II (Produkti topivosti srebrnih halogenida)

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Određeni su produkti topivosti srebrnih halogenida potenciometrijski, konduktometrijski i primjenom izotopa Ag-110. Za pL vrijednosti u dimetilsulfoksidu dobijeni su rezultati kako slijedi:

	Potenciometrijski	Izotopski	Konduktometrijski
AgCl	9,2	9,1	9,2
AgBr	9,8	9,7	9,8
AgJ	10,8	—	—

Sva mjerenja su vršena na  $25,00 \pm 0,02^\circ\text{C}$ .

Također je određena jonska pokretljivost Ag jona u DMSO koja iznosi  $13,8 \pm 0,2 \text{ ohm}^{-1} \text{ cm}^2$  na  $25^\circ\text{C}$ .

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Primljeno 20. decembra 1972.



GHTBH 3

545,82:541.122

Original Scientific Paper

## SPECTROPHOTOMETRIC DETERMINATION OF STABILITY CONSTANTS OF METHOXYACETATO COMPLEXES OF COBALT, NICKEL AND COPPER

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The stability constants of the mononuclear complexes formed by cobalt (II), nickel (II), and copper (II) ions in water solutions with methoxyacetate ions have been determined by spectrophotometric method, applying the method of corresponding solutions after J. Bjerrum. The investigations have been carried out at 25,0°C, in a perchlorate medium at ionic strength  $I = 2,0$ . The constants have been evaluated by Fronaeus' graphic method and then averaged with a digital computer program, according to R. S. Tobias (Gauss Z program).

The complex formation between cobalt (II), nickel (II) and copper (II) ions and methoxyacetate ions does not seem to have been investigated, except by A. Sandell (1). The investigations reported here have been carried out by the spectrophotometric method in the visible spectral region in Co(II), Ni(II), and Cu(II) perchlorate solutions.

The preliminary experiments indicated that the formed complexes were relatively weak, so we thought that Bjerrum's method (2) of corresponding solutions was the most convenient for their investigation.

### EXPERIMENTAL

All chemicals were analytically pure except methoxyacetic acid. Perchlorates of metals were prepared by adding excess perchloric acid to respective salts; thus copper (II) perchlorate was prepared from basic copper carbonate, and the perchlorates of cobalt (II) and nickel (II) from their nitrates. All nitric acid and most of the perchloric acid were removed by evaporation, and the residual perchlorates were recrystallized twice. Metal concentrations in stock solutions were determined by electrolysis (3), while the concentrations of free perchloric acid were estimated potentiometrically; free perchloric acid concentrations had to be allowed for when calculating total ligand concentrations in experimental solutions.

The methoxyacetic acid was purrum («Fluka»). Purification was made by vacuum distillation (1). The concentration of the acid was determined by potentiometric titration with standard sodium hydroxide solution. Sodium methoxyacetate was prepared from methoxyacetic acid and sodium hydroxide. In order to suppress the hydrolysis of the investigated metal ions, the measurements were carried out in buffer solutions of acid to salt ratio 1:1. Constant ionic strength  $I = 2,0$  was kept with sodium perchlorate.

The extinctionometric investigations were carried out with a UNICAM SP 500 spectrophotometer at a constant temperature of  $25.0 \pm 0.1^\circ\text{C}$ . All the investigated systems had a constant  $\text{pH} = 3.20 \pm 0.1$  with the exception of copper (II) where  $\text{pH} = 2.80 \pm 0.2$ . The reproducibility of the extinction measurement was  $\pm 0.001$  for the same solution, and  $\pm 0.003$  for repeatedly prepared solutions of the same kind.

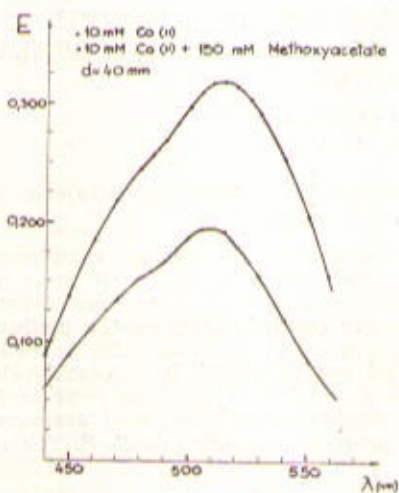


Fig 1. Light absorption curves of  $\text{Co(II)}$  solutions

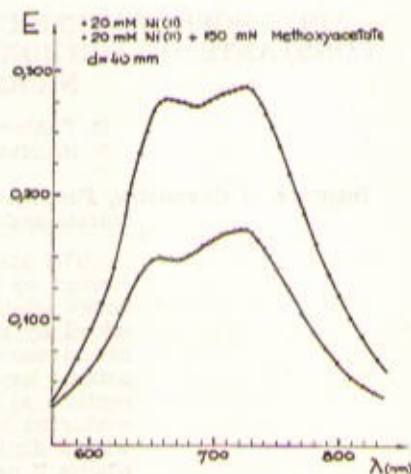


Fig 2. Light absorption curves of  $\text{Ni(II)}$  solutions

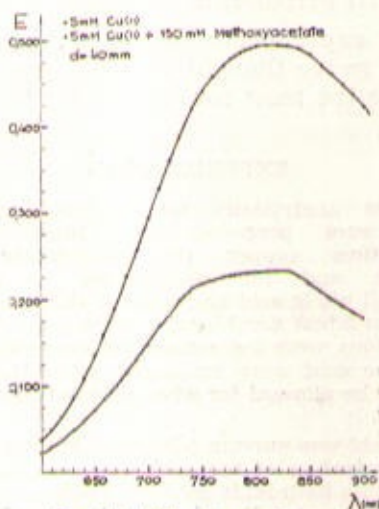


Fig 3. Light absorption curves of  $\text{Cu(II)}$  solutions



From the recorded light absorption curves in the visible spectral region (Figs. 1—3) the wavelengths were chosen so as to achieve the greatest possible separation of absorption curves with respect to the concentration change of ligand. The measurements of extinction were performed at the following wavelengths: for copper at 810 nm, for nickel at 665 nm, and for cobalt at 515 nm.

## RESULTS

The applied method after J. Bjerrum requires, in addition to high and constant ionic strength, negligibly small absorbance of free ligand  $L$ , absence of any association and dissociation of system components, so that the total absorbance of the solution ( $E$ ) is the sum of the individual absorbances of free metal ion and all complex species present in solution:

$$E = d(E_0[M] + E_1[ML] + E_2[ML_2] + \dots + E_N[ML_N]) = d \sum_{n=0}^N E_n \cdot [ML_n],$$

where are:

$d$  — the length of the optical path,

$E$  — molar extinction of metal ( $E_0$ ) and complex species ( $E_n$ ), respectively,  $[M]$  and  $[ML_n]$  — concentration of free metal ion and individual complex species, respectively.

Those solutions in which the total concentration of the metal ion ( $C_M$ ) and the ligand ( $C_L$ ) are different, but the free ligand concentrations and consequently the value of the average ligand number  $\bar{n}$  are the same, are termed corresponding solutions. Obviously, for two corresponding solutions the following relationship stands:

$$\bar{n} = \frac{C_L' - |L|}{C_M'} = \frac{C_L'' - |L|}{C_M''} \quad \text{or}$$

$$\bar{n} = \frac{C_M' - C_M''}{C_L' - C_L''}; \quad |L| = \frac{C_M' \cdot C_L'' - C_L' \cdot C_M''}{C_M' - C_M''}$$

Accordingly, for one series of solutions, maintaining a constant concentration of the metal ion  $C_M'$  and a constant optical path  $d'$ , extinctions  $E$  were recorded at the determined wavelength, for different ligand concentrations  $C_L$ . Therefore  $E = f'(C_L)$  curve was obtained. Then at another constant metal ion concentration  $C_M''$  and another thickness of the cells  $d''$ , satisfying the condition that  $C_M \cdot d' = C_M'' \cdot d''$ , extinctions for different concentrations of ligand  $C_L$  were recorded. Therefore the second  $E = f''(C_L)$  curve was obtained. Analogously, yet one or two curves  $E = f'''(C_L)$  and  $E = f''''(C_L)$  were obtained.

From these curves the corresponding solutions were determined, i. e. solutions having the same extinctions with different  $C_M'$ ,  $C_L'$ ;  $C_M''$ ,  $C_L''$  and so on. A plot of  $C_L$  against  $C_M$  should be a straight line of slope  $\bar{n}$  and intercept  $|L|$ , if there are no polynuclear complexes in the system. The values of  $\bar{n}$  and  $|L|$  were determined numerically using the method of least squares. Having obtained these values, the stability constants were graphically determined by applying the method of S. Fronaeus (4). The graphical stability constants with  $C_M$ ,  $\log |L|$  and  $\bar{n}$  values were treated

using the Gauss Z program devised by R. S. Tobias (5) for non-linear least squares refinement of equilibrium constants. The calculations were performed by a Gamma 30 digital computing unit in the Electronic Data Processing Center of the firm Energoinvest, Sarajevo. The computer performed, according to the program, 10 refinement cycles. Output data contained the stability constants, their standard errors, and calculated formation function.

Extinction curves  $E = f(C_L)$  were recorded for four [Cu(II)- and Co(II)-methoxyacetates] and for three [Ni(II)-methoxyacetates] different metal ion concentrations, with a constant product of the metal concentration and thickness of the cells in every series (6). (All ligand-free solutions of metal ions obeyed Beer's law.) Tables I-III contain results of these measurements. From the curves obtained the corresponding solutions were determined, having the same extinction for the different total metal ion and total ligand concentration. Data for such solutions is given in tables IV and V.

System Cobalt (II)-methoxyacetate

TABLE I

$C_M$ mM				$\lambda = 515 \text{ nm}$			
10		40		80		200	
$C_L$ mM	E d=40 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm	$C_L$ mM	E d=2 mm
4.2	0.198	2.1	0.187	4.0	0.190	5.5	0.194
9.2	0.202	7.1	0.191	14.0	0.192	25.5	0.202
19.2	0.217	17.1	0.202	34.0	0.207	45.5	0.210
39.2	0.242	37.1	0.221	54.0	0.222	65.5	0.220
59.2	0.261	57.1	0.240	74.0	0.237	85.5	0.229
79.2	0.276	77.1	0.243	94.0	0.257	135.5	0.250
99.2	0.289	97.1	0.272	144.0	0.279	185.5	0.270
149.2	0.322	147.1	0.301	194.0	0.300	235.5	0.291
199.2	0.349	197.1	0.323	244.0	0.322	285.5	0.309
249.2	0.368	247.1	0.347	294.0	0.340	335.5	0.324
299.2	0.381	297.1	0.362	344.0	0.356	385.5	0.338
349.2	0.391	347.1	0.378	394.0	0.370	435.5	0.356
399.2	0.400	397.1	0.388	444.0	0.381		
449.2	0.412	447.1	0.399	494.0	0.392		
499.2	0.421	497.1	0.408				



TABLE II  
System Nickel (II)-methoxyacetate

$C_M$ mM						$\lambda = 665$ nm									
20		80				160		20		80				160	
$C_L$ mM	E d=40 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm	$C_L$ mM	E d=40 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm
4.0	0.156	1.0	0.151	1.2	0.150	1.2	0.150	1.2	0.150	1.2	0.150	1.2	0.150	1.2	0.150
9.0	0.161	6.0	0.153	11.2	0.155	11.2	0.155	11.2	0.155	11.2	0.155	11.2	0.155	11.2	0.155
19.0	0.174	16.0	0.161	31.2	0.165	31.2	0.165	31.2	0.165	31.2	0.165	31.2	0.165	31.2	0.165
39.0	0.197	36.0	0.175	51.2	0.176	51.2	0.176	51.2	0.176	51.2	0.176	51.2	0.176	51.2	0.176
59.0	0.218	56.0	0.190	71.2	0.185	71.2	0.185	71.2	0.185	71.2	0.185	71.2	0.185	71.2	0.185
79.0	0.232	76.0	0.203	91.2	0.193	91.2	0.193	91.2	0.193	91.2	0.193	91.2	0.193	91.2	0.193
99.0	0.245	96.0	0.214	141.2	0.212	141.2	0.212	141.2	0.212	141.2	0.212	141.2	0.212	141.2	0.212
149.0	0.273	146.0	0.239	191.2	0.232	191.2	0.232	191.2	0.232	191.2	0.232	191.2	0.232	191.2	0.232
199.0	0.295	196.0	0.261	241.2	0.250	241.2	0.250	241.2	0.250	241.2	0.250	241.2	0.250	241.2	0.250
249.0	0.308	246.0	0.278	291.2	0.260	291.2	0.260	291.2	0.260	291.2	0.260	291.2	0.260	291.2	0.260
299.0	0.319	296.0	0.293	341.2	0.279	341.2	0.279	341.2	0.279	341.2	0.279	341.2	0.279	341.2	0.279
349.0	0.326	346.0	0.307	391.2	0.289	391.2	0.289	391.2	0.289	391.2	0.289	391.2	0.289	391.2	0.289
399.0	0.334	396.0	0.315	441.2	0.298	441.2	0.298	441.2	0.298	441.2	0.298	441.2	0.298	441.2	0.298
449.0	0.342	446.0	0.322	491.2	0.304	491.2	0.304	491.2	0.304	491.2	0.304	491.2	0.304	491.2	0.304
499.0	0.346	496.0	0.326												

TABLE III  
System Copper (II)-methoxyacetate

$C_M$ mM						$\lambda = 810$ nm																	
5		10				20		40		5		10				20		40					
$C_L$ mM	E d=40 mm	$C_L$ mM	E d=20 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm	$C_L$ mM	E d=40 mm	$C_L$ mM	E d=20 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm				
4.9	0.268	4.8	0.264	4.5	0.261	4.1	0.240	4.9	0.268	4.8	0.264	4.5	0.261	4.1	0.240	4.9	0.268	4.8	0.264	4.5	0.261	4.1	0.240
9.9	0.298	9.8	0.290	9.5	0.284	9.1	0.258	9.9	0.298	9.8	0.290	9.5	0.284	9.1	0.258	9.9	0.298	9.8	0.290	9.5	0.284	9.1	0.258
14.9	0.321	14.8	0.312	14.5	0.301	14.1	0.274	14.9	0.321	14.8	0.312	14.5	0.301	14.1	0.274	14.9	0.321	14.8	0.312	14.5	0.301	14.1	0.274
19.9	0.344	19.8	0.331	19.5	0.318	19.1	0.287	19.9	0.344	19.8	0.331	19.5	0.318	19.1	0.287	19.9	0.344	19.8	0.331	19.5	0.318	19.1	0.287
24.9	0.362	24.8	0.349	24.5	0.336	24.1	0.300	24.9	0.362	24.8	0.349	24.5	0.336	24.1	0.300	24.9	0.362	24.8	0.349	24.5	0.336	24.1	0.300
29.9	0.375	29.8	0.362	29.5	0.351	29.1	0.312	29.9	0.375	29.8	0.362	29.5	0.351	29.1	0.312	29.9	0.375	29.8	0.362	29.5	0.351	29.1	0.312
34.9	0.389	34.8	0.374	34.5	0.362	34.1	0.323	34.9	0.389	34.8	0.374	34.5	0.362	34.1	0.323	34.9	0.389	34.8	0.374	34.5	0.362	34.1	0.323
39.9	0.398	39.8	0.387	39.5	0.374	39.1	0.334	39.9	0.398	39.8	0.387	39.5	0.374	39.1	0.334	39.9	0.398	39.8	0.387	39.5	0.374	39.1	0.334
49.9	0.414	49.8	0.406	49.5	0.393	49.1	0.356	49.9	0.414	49.8	0.406	49.5	0.393	49.1	0.356	49.9	0.414	49.8	0.406	49.5	0.393	49.1	0.356
59.9	0.429	59.8	0.421	59.5	0.412	59.1	0.373	59.9	0.429	59.8	0.421	59.5	0.412	59.1	0.373	59.9	0.429	59.8	0.421	59.5	0.412	59.1	0.373
79.9	0.451	79.8	0.446	79.5	0.440	79.1	0.401	79.9	0.451	79.8	0.446	79.5	0.440	79.1	0.401	79.9	0.451	79.8	0.446	79.5	0.440	79.1	0.401
99.9	0.461	99.8	0.460	99.5	0.461	99.1	0.425	99.9	0.461	99.8	0.460	99.5	0.461	99.1	0.425	99.9	0.461	99.8	0.460	99.5	0.461	99.1	0.425

TABLE IV  
System

Cobalt (II)-methoxyacetate

Nickel (II)-methoxyacetate

E $\lambda = 515 \text{ nm}$	$C_M \text{ mM}$				E $\lambda = 665 \text{ nm}$	$C_M \text{ mM}$		
	10	40	80	200		20	80	160
	$C_L \text{ mM}$					$C_L \text{ mM}$		
0.200	7.6	17.3	29.0	45.0	0.170	17.0	31.6	48.2
0.210	14.9	27.0	42.0	62.0	0.180	25.0	45.4	69.0
0.220	22.1	37.8	55.5	80.6	0.190	33.5	60.0	91.2
0.230	30.0	48.4	69.4	101.7	0.200	41.0	72.8	110.0
0.240	38.6	60.0	84.0	124.5	0.210	51.0	89.2	134.1
0.250	48.5	71.4	99.8	147.9	0.220	62.1	107.0	159.0
0.260	59.8	83.2	116.0	172.0	0.230	76.0	125.4	188.5
0.270	72.0	97.0	133.0	198.3	0.240	91.2	146.0	215.0
0.280	85.1	113.0	152.0	224.0	0.250	108.0	174.0	247.9
0.290	99.1	130.0	172.0	252.5	0.260	125.0	198.2	278.0
0.300	113.8	149.0	193.5	280.8	0.270	145.5	220.0	304.2
0.310	129.0	169.0	217.7	309.9	0.280	168.0	249.0	343.0
0.320	145.1	190.0	242.0	338.0	0.290	193.5	282.0	388.5
0.330	162.4	211.0	269.0	368.0				
0.340	181.2	233.9	300.0	399.6				
0.350	203.0	258.9	329.0	431.0				
0.360	228.0	287.9	361.6	462.2				

TABLE V

System Copper (II)-methoxyacetate

E $\lambda = 810 \text{ nm}$	$C_M \text{ mM}$			
	5	10	20	40
	$C_L \text{ mM}$			
0.270	5.2	6.2	7.0	13.8
0.280	7.0	8.0	9.4	17.2
0.290	8.7	10.0	12.0	20.8
0.300	10.5	12.2	14.6	24.7
0.310	12.5	14.5	17.3	29.0
0.320	14.6	17.0	23.0	33.3
0.330	16.7	19.5	23.3	37.8
0.340	19.2	22.4	26.6	42.4
0.350	21.7	25.5	30.0	47.4
0.360	24.5	29.0	33.9	52.5
0.370	27.6	32.7	38.0	58.5
0.380	31.2	36.8	42.6	64.7
0.390	35.5	41.3	47.6	71.8
0.400	41.0	46.6	53.0	79.4
0.410	47.0	52.5	59.0	87.2
0.420	53.8	59.0	65.3	95.6
0.430	61.0	66.4	72.1	105.0
0.440	69.0	74.8	79.9	116.0



The measurements with copper(II) ion solutions in the presence of methoxyacetate could not be performed at higher methoxyacetate concentrations because of the intersection of extinctions curves. Therefore, the measurements in these systems could comprise only lower complex species present in solutions. The stability constants obtained by both the graphical and computational methods are shown in Table VI.

### DISCUSSION

The comparison of the obtained values of stability constants for the copper (II)-methoxyacetate system with potentiometric literature data (1) shows quite a good agreement, although there are some differences in the applied method, different ionic strength, and different temperature. So A. Sandell reported for copper (II)-methoxyacetate  $\beta_1 = 66$ , while our value is  $\beta_1 = 65,3$ .

From the values of the first stability constants,  $\beta_1$ , it can be seen (Table VI) that the stability of the monoligand complex increases for all investigated systems in the series:  $\text{Co} < \text{Ni} < \text{Cu}$ , which is in agreement with the natural order established by Irwing and Williams (7).

TABLE VI  
Stability Constants ( $\pm$  standard errors)

	Metal ion	$\beta_1$		$\beta_2$	
		graph.	comp.	graph.	comp.
Methoxyacetate	$\text{Co}^{2+}$	14.4	$14.3 \pm 0.2$	40.3	$42.2 \pm 0.8$
	$\text{Ni}^{2+}$	18.7	$18.0 \pm 0.8$	115	$124.4 \pm 3.7$
	$\text{Cu}^{2+}$	67.7	$65.3 \pm 1.1$	1034	$1109 \pm 25$

It would be interesting to compare the obtained values of stability constants of methoxyacetate  $\text{Co(II)}$ ,  $\text{Ni(II)}$ , and  $\text{Cu(II)}$  with the corresponding values of the metal complexes with acetate ion to see if methoxy group has any specific influence on the complex stability. On the basis of basicity of ligand itself the corresponding acetate complexes are expected to be more stable. Unfortunately, the published values of stability constants for the acetate complexes of these metals differ greatly (8,9) so that it is even difficult to say which complexes are more stable. In any case, judging from most of the literary data, acetate and methoxyacetate complexes of investigated metals have sufficiently similar stability, so that there is no question of any chelate effect of methoxy group in methoxyacetate complexes. This is supported by the fact that no shift of the absorption maximum occurs in the presence of methoxyacetate ions but only the increase of light absorption as in the case of acetate complexes (10).

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## REFERENCES

1. Sandell, A., *Acta Chem. Scand.*, **15** (1961) 190.
2. Bjerrum, J., »Metal Ammine Formation in Aqueous Solution« (Diss.), P. Haase, Copenhagen, 1941.
3. Vogel, A. I., »Quantitative Inorganic Analysis«, Third Edition, Longmans, London, 1966, p. 608, 613.
4. Fronaeus, S., *Acta Chem. Scand.* **4** (1950) 72.
5. Tobias, R. S. and Yasuda, M., *J. Inorg. Chem.*, **2** (1963) 1307.
6. Fronaeus, S., *Acta Chem. Scand.*, **5** (1951) 139.
7. Irwing, H. and Williams, R. J. P., *J. Chem. Soc.*, (1953) 3192
8. Sillén, L. G. and Martell, A. E., »Stability Constants of Metal-ion Complexes«, Special Publication No. 17, The Chemical Society, London, 1964, Tables No. 114, 150 and 212.
9. Sillén, L. G. and Martell, A. E., »Stability Constants of Metal-ion Complexes«, Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971, Tables No. 114, 150 and 212.
10. Grabarić, B. and Filipović, I., *Croat. Chem. Acta*, **42** (1970) 479.

## IZVOD

### Spektrofotometrijsko određivanje konstanti stabilnosti metoksiacetato kompleksa kobalta, nikla i bakra

D. Tuhtar, J. Savić and M. Savić

Određene su konstante stabilnosti metoksiacetato kompleksa Co(II), Ni(II) i Cu(II), primjenom spektrofotometrijske metode korespondentnih rastvora prema Bjerrum-u. Mjerenja su vršena u vidljivom području spektra. Odnos koncentracija metoksiacetatne kiseline i metoksiacetata u tamponskim rastvorima bio je 1:1. Jonska jakost rastvora bila je 2,0 (NaClO<sub>4</sub>), t = 25 ± 0,1°C. Konstante stabilnosti su najprije određene grafičkom metodom prema Fronaeus-u, a zatim su ovako grafički dobijene vrijednosti rafinirane kompjuterski primjenom Gauss Z programa prema R. S. Tobias-u.

Dobijene su ove kumulativne konstante stabilnosti (± standardna greška).

Kobalt:	$\beta_1 = 14,3 \pm 0,2;$	$\beta_2 = 42,2 \pm 0,8$
Nikl:	$\beta_1 = 18,0 \pm 0,8;$	$\beta_2 = 124,4 \pm 3,7$
Bakar:	$\beta_1 = 65,3 \pm 1,1;$	$\beta_2 = 1109 \pm 25$

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## SPECTROPHOTOMETRIC DETERMINATION OF STABILITY CONSTANTS OF ETHOXYACETATO COMPLEXES OF COBALT, NICKEL, AND COPPER

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The complex formation between Co(II), Ni (II), and Cu(II) ions and ethoxyacetate ions in aqueous solutions was studied by the spectrophotometric method, applying the method of corresponding solutions after J. Bjerrum. Stability constants of present complexes were determined both by Fronaeus' graphic method and a computer method, applying the Gauss Z program after R. S. Tobias.

Just as for the methoxyacetate ions, literature data about the spectrophotometric determination of stability constants of ethoxyacetato complexes are very scarce (1).

In the previous paper (2), the complex formation between Co(II), Ni(II), and Cu(II) ions and methoxyacetate ions in aqueous solutions was studied, and stability constants of corresponding mononuclear complexes were determined.

In the present paper, the investigations were carried out by the same metallic ions [i. e. Co(II), Ni(II), and Cu(II)], with ethoxyacetate ion as ligand. J. Bjerrum's method (3) of corresponding solutions was applied, and it proved to be a suitable one for the investigated systems in the visible spectral region (2).

### EXPERIMENTAL

Ethoxyacetic acid was purrum (»Fluka«). Purification was carried out by vacuum distillation (1). Concentration of the acid was determined potentiometrically with standard sodium hydroxide solution. Buffer solution of the constant acid to salt ratio (1:1) were prepared from the ethoxyacetic acid and its sodium salt. The other chemicals were the same as before (2). Optical densities were recorded on spectrophotometer UNICAM SP 500, at  $25.0 \pm 0.1^\circ\text{C}$ . Ionic strength ( $I=2.0$ ) was kept constant in all investigated systems by adding sodium perchlorate.

From the recorded light absorption curves (Figs. I—III), the following wavelengths were selected for subsequent measurements: for cobalt 515 nm, for nickel 665 nm, and for copper 800 nm.

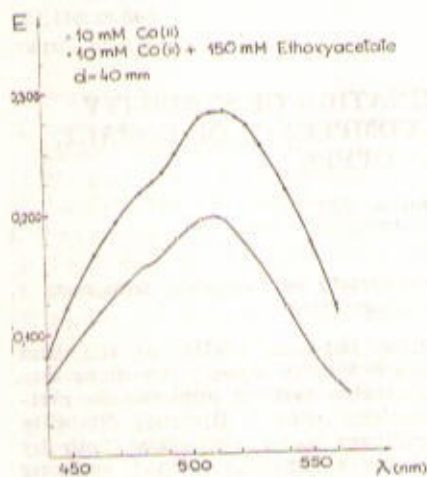


Fig 1 Light absorption curves of Co(II) solutions

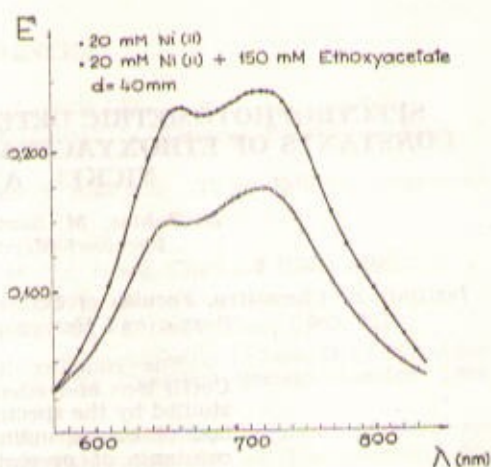


Fig 2. Light absorption curves of Ni(II) solutions

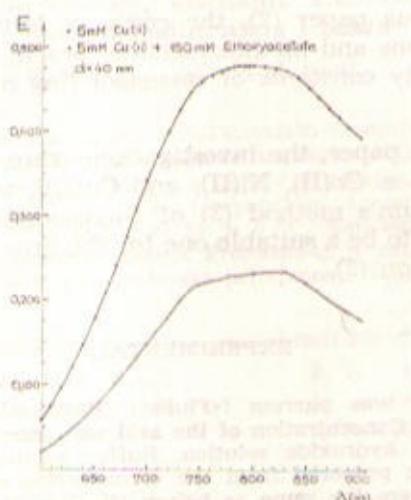


Fig 3 Light absorption curves of Cu(II) solutions



## RESULTS AND DISCUSSION

The corresponding solutions, the average number of ligands bound to one central group,  $\bar{n}$ , and the free ligand concentration  $[L]$ , were determined by applying J. Bjerrum's method as before (2).

The experimental data needed for the absorbance vs. total ligand concentration curves are given in table I—III. From these curves corresponding solutions were determined (Table IV and V).

$\bar{n}$  and  $[L]$  values were evaluated numerically by the least squares method. From these values stability constants were graphically determined by applying the method of S. Fronaeus (4). These graphical constants, together with  $C_M$ ,  $\log [L]$ , and  $\bar{n}$  values, were treated by using the Gauss. Z program devised by R. S. Tobias for non-linear least squares refinements of equilibrium constants (5). Calculations were carried out with a Gamma 30 digital computer as before. The graphical and calculated stability constants are given in Table VI. The obtained values of stability constants of ethoxyacetate Co(II), Ni(II), and Cu(II) are very similar to the values obtained for methoxyacetates of these metals. This could be expected from the very similar basicity of both ligands (1). A slight tendency of somewhat greater stability of methoxyacetate was visible.

TABLE I  
System Cobalt (II)-ethoxyacetate

$C_M$ mM				$\lambda = 515 \text{ nm}$			
10		20		40		80	
$C_L$ mM	E d=40 mm	$C_L$ mM	E d=20 mm	$C_L$ mM	E d=10 mm	$C_L$ mM	E d=5 mm
4.2	0.189	2.1	0.188	4.0	0.192	5.5	0.189
9.2	0.196	7.1	0.191	14.0	0.196	25.5	0.197
19.2	0.203	17.1	0.200	34.0	0.210	45.5	0.207
39.2	0.217	37.1	0.214	54.0	0.220	65.5	0.218
59.2	0.231	57.1	0.227	74.0	0.234	85.5	0.225
79.2	0.241	77.1	0.237	94.0	0.245	110.5	0.240
99.2	0.253	97.1	0.249	119.0	0.256	135.5	0.248
124.2	0.263	122.1	0.260	144.0	0.268	160.5	0.257
149.2	0.277	147.1	0.272	169.0	0.278	185.0	0.264
174.2	0.284	172.1	0.281	194.0	0.285	235.5	0.279
199.2	0.293	197.1	0.291	244.0	0.300	285.5	0.294
249.2	0.311	247.1	0.305	294.0	0.310	335.5	0.305
299.2	0.324	297.1	0.318	344.0	0.322	385.5	0.314
349.2	0.334	347.1	0.328	394.0	0.333	435.5	0.320
399.2	0.342	397.1	0.335	444.0	0.348		
449.2	0.351	447.1	0.342				

TABLE II  
System Nickel (II)-ethoxyacetate

C <sub>M</sub> mM						λ = 665 nm			
20		40		80		160			
C <sub>L</sub> mM	E d=40 mm	C <sub>L</sub> mM	E d=20 mm	C <sub>L</sub> mM	E d=10 mm	C <sub>L</sub> mM	E d=5 mm		
4.0	0.152	3.0	0.148	1.0	0.148	1.2	0.147		
9.0	0.156	8.0	0.153	6.0	0.152	11.2	0.148		
19.0	0.161	18.0	0.157	18.0	0.156	31.2	0.155		
39.0	0.188	38.0	0.169	36.0	0.166	51.2	0.162		
59.0	0.192	58.0	0.181	56.0	0.175	71.2	0.170		
79.0	0.202	78.0	0.191	76.0	0.186	91.2	0.173		
99.0	0.214	98.0	0.202	96.0	0.195	116.2	0.189		
124.0	0.220	123.0	0.210	121.0	0.202	141.2	0.198		
149.0	0.231	148.0	0.220	146.0	0.212	166.2	0.201		
174.0	0.239	173.0	0.228	171.0	0.219	191.2	0.204		
199.0	0.246	198.0	0.236	196.0	0.229	241.2	0.219		
249.0	0.258	248.0	0.247	246.0	0.240	291.2	0.227		
299.0	0.268	298.0	0.257	296.0	0.251	341.2	0.238		
349.0	0.273	348.0	0.265	346.0	0.262	391.2	0.247		
399.0	0.281	398.0	0.273	396.0	0.270				
449.0	0.289			446.0	0.280				

TABLE III  
System Copper (II)-ethoxyacetate

C <sub>M</sub> mM						λ = 800 nm			
5		10		20		40			
C <sub>L</sub> mM	E d=40 mm	C <sub>L</sub> mM	E d=20 mm	C <sub>L</sub> mM	E d=10 mm	C <sub>L</sub> mM	E d=5 mm		
4.9	0.269	4.8	0.262	4.5	0.255	4.1	0.244		
9.9	0.295	9.8	0.289	9.5	0.275	9.1	0.259		
14.9	0.323	14.8	0.308	14.5	0.291	14.1	0.273		
19.9	0.340	19.8	0.327	19.5	0.308	19.1	0.286		
24.9	0.358	24.8	0.342	24.5	0.322	24.1	0.295		
29.9	0.370	29.8	0.361	29.5	0.338	29.1	0.306		
34.9	0.386	34.8	0.375	34.5	0.349	34.1	0.316		
39.9	0.393	39.8	0.383	39.5	0.359	39.1	0.328		
44.9	0.400	44.8	0.391	44.5	0.365	44.1	0.338		
49.9	0.409	49.8	0.399	49.5	0.378	49.1	0.346		
59.9	0.417	59.8	0.410	59.5	0.392	59.1	0.358		
69.9	0.428	69.8	0.424	69.5	0.405	69.1	0.378		
79.9	0.437	79.8	0.427	79.5	0.420	79.1	0.391		
89.9	0.445	89.8	0.439	89.5	0.425	89.1	0.401		
99.9	0.451	99.8	0.448	99.5	0.431	99.1	0.402		



TABLE IV

System

Cobalt (II)-ethoxyacetate

Nickel (II)-ethoxyacetate

E $\lambda = 515$ nm	$C_M$ mM				E $\lambda = 665$ nm	$C_M$ mM			
	10	20	40	80		20	40	80	160
	$C_L$ mM					$C_L$ mM			
0.200	14.0	18.0	21.0	32.0	0.160	14.0	20.0	24.0	47.0
0.210	27.0	33.0	36.5	55.5	0.170	26.5	37.0	44.0	73.0
0.220	41.5	48.0	52.5	80.0	0.180	41.0	58.0	64.0	103.0
0.230	58.0	64.0	70.0	105.0	0.190	57.0	75.0	86.0	136.0
0.240	75.0	82.5	88.0	131.0	0.200	76.0	98.0	110.0	173.0
0.250	94.0	101.0	108.0	157.0	0.210	96.0	121.0	137.0	211.0
0.260	114.5	121.5	128.0	184.0	0.220	120.0	148.0	166.0	250.0
0.270	136.0	143.5	152.0	212.0	0.230	147.0	178.0	200.0	302.0
0.280	159.0	168.0	179.0	242.0	0.240	177.0	215.0	237.0	354.0
0.290	184.5	196.0	211.0	275.0	0.250	212.0	265.0	287.0	406.0
0.300	212.6	228.0	250.0	314.0					

TABLE V

System Copper (II)-ethoxyacetate

E $\lambda = 800$ nm	$C_M$ mM			
	5	10	20	40
	$C_L$ mM			
0.290	8.6	10.6	13.6	21.2
0.300	10.5	12.9	16.8	25.7
0.310	12.7	15.4	20.0	30.2
0.320	14.9	18.0	23.6	35.0
0.330	17.2	20.6	27.0	40.0
0.340	20.0	23.4	31.0	45.5
0.350	22.6	26.8	35.2	51.7
0.360	25.8	30.0	39.0	57.8
0.370	29.0	33.9	44.0	64.0
0.380	33.0	39.0	52.0	71.0
0.390	38.0	44.0	58.0	78.5
0.400	44.0	51.3	65.0	87.0
0.410	51.8	59.0	73.0	98.0

TABLE VI  
Stability Constants ( $\pm$  standard errors)

	Metal ion	$\beta_2$		$\beta_1$	
		graph.	comp.	graph.	comp.
Ethoxyacetate	Co(II)	12.4	$11.5 \pm 0.5$	58.4	$68.9 \pm 2.0$
	Ni(II)	15.2	$14.9 \pm 1.6$	59.2	$81.2 \pm 6.9$
	Cu(II)	57.5	$54.6 \pm 2.0$	1627	$1694 \pm 41$

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## REFERENCES

- Sandell, A., *Acta Chem. Scand.*, **15** (1961) 190.
- Tuhtar, D., Savić, J., and Savić, M., *Glasnik Druš. hem. i tehn. BiH*, **19** (1971) (in press).
- Bjerrum, J., »Metal Ammine Formation in Aqueous Solution« (Diss.), P. Haase, Copenhagen, 1941.
- Fronaeus, S., *Acta Chem. Scand.*, **4** (1950) 72.
- Tobias, R. S. and Yasuda, M., *J. Inorg. Chem.* **2** (1963) 1307.

## IZVOD

Spektrofotometrijsko određivanje konstanti stabilnosti etoksiacetato kompleksa kobalta, nikla i bakra

D. Tuhtar, M. Savić and J. Savić

Primjenom spektrofotometrijske metode korespondentnih rastvora prema Bjerum-u, određene su konstante stabilnosti etoksiacetato kompleksa Co(II), Ni(II) i Cu(II). Mjerenja su vršena u vidljivom području spektra. Odnos koncentracija kiseline i soli u rastvorima bio je 1:1, jonska jakost rastvora 2,00 (NaClO<sub>4</sub>),  $t = 25 \pm 0,1^\circ\text{C}$ .

Konstante stabilnosti su najprije određene Fronaeus-ovom grafičkom metodom, a zatim rafinirane kompjuterski, primjenom Gauss Z programa prema R. S. Tobias-u.

Dobijene su slijedeće kumulativne konstante stabilnosti ( $\pm$  standardna greška):

Kobalt:	$\beta_1 = 11,5 \pm 0,5;$	$\beta_2 = 68,9 \pm 2,0$
Nikl:	$\beta_1 = 14,9 \pm 1,6;$	$\beta_2 = 81,2 \pm 6,9$
Bakar:	$\beta_1 = 54,6 \pm 2,0;$	$\beta_2 = 1694 \pm 41$

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## SPEKTROPHOTOMETRISCHE ALUMINIUMBESTIMMUNG IM STAHL

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Eine spektrophotometrische Schnellmethode für die Aluminiumbestimmung in Stählen mit weniger als 1% Aluminiumgehalt wird beschrieben. Diese Methode erfordert nicht die vorherige Abtrennung von Eisen und begleitenden Elementen. Stahlproben werden in konz. HCl aufgelöst, Fe(III) und Cu(II) mit Ascorbinsäure, bzw.  $\text{Na}_2\text{S}_2\text{O}_3$  zu Fe(II) und Cu(I) reduziert, die Lösung mit Azetatpuffer auf pH 4,5 eingestellt und frisch bereitete 0,1%-ige Aluminonlösung wird zugesetzt. Aluminium verbindet sich in schwach saurer Lösung mit Aluminon zu einem rotgefärbten Lack, welcher 30 Minuten nach der Aluminonzugabe maximale Lichtabsorption bei 520 nm aufweist.

Sowohl hoch-, als auch niedriglegierte Stahllarten enthalten einen hohen Prozentsatz an Eisen und anderen Elementen, die bei Aluminiumbestimmungen störend wirken. Diese Elemente muss man also vor der Bestimmung entweder entfernen (wofür am häufigsten die Elektrolyse an einer Quecksilberkathode<sup>1-7</sup>), bzw. die Extraktion mit organischen Lösungsmitteln<sup>8-16</sup> verwendet wird), oder man muss sie maskieren.

Die Erfahrung lehrt, dass allen Methoden, die auf einer Abtrennung von Eisen und anderen Elementen vom Aluminium beruhen, sei es ob durch Elektrolyse, oder durch Extraktion, gewisse Nachteile innewohnen, indem solche Methoden zu vollständiger Abtrennung geraume Zeit beanspruchen, oder mehrfache Extraktionen erfordern und dadurch zu häufigeren Fehlern Anlass geben.

Da bei der Durchführung von Analysen, ausser Präzision und Selektivität, auch die benötigte Zeit einen wichtigen Faktor ausmacht, stellen wir uns die Aufgabe, eine schnelle und einfache Methode für die Aluminiumbestimmung in Stählen ohne vorherige Abtrennung von störenden Elementen zu entwickeln.

### EXPERIMENTALLER TEIL

#### Apparatur

Optische Messungen wurden mit einem Unicam SP 500 Spektrophotometer, unter Verwendung von Glaszellen mit 1 cm optischer Weglänge, durchgeführt.

#### Lösungen

Die Lösungen folgender Stoffe wurden aus analysenreinen Salzen hergestellt: Al, Fe(III), Cu(II), Cr(III), Mn(II), Ni(II), V(v), Sn(II) und W. Pro Milliliter enthielten diese Lösungen je 10  $\mu\text{g}$  Al, 10 mg Fe, 3,25 mg Cu, 29,50 mg Cr, 12,65

*Anmerkung:* Dieser Artikel beschreibt einen Teil der Arbeit die mit finanzieller Beihilfe des Fonds für wissenschaftliche Arbeit der sozialistischen Republik Bosnien-Herzegowina durchgeführt wurde.

mg Mn, 0,99 mg Ni, 22,50 mg V, 2,20  $\mu\text{g}$  Sn und 2,00  $\mu\text{g}$  W. Azetatpuffer pH 4,50 wurde durch Auflösen von 137 g  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$  in 60 ml Eisessig und auffüllen mit Wasser auf 1 Liter bereitet. Täglich frisch wurde 2%-ige Ascorbinsäurelösung bereitet, während sich 0,1%-ige wässrige Aluminonlösung ein bis zwei Tage hält. In den Versuchen wurde auch 1%-ige  $\text{Na}_2\text{S}_2\text{O}_3$  - Lösung verwendet.

*Prüfung des Verhaltens von Metallionen gegenüber Aluminon*

Die Reaktion von Aluminon mit einer grösseren Anzahl von Metallionen, die in verschiedenen Stahllarten als Legierungszusätze vorkommen, wurden unter jenen Bedingungen geprüft, die in Gegenwart von Aluminium zur Bildung des gefärbten Komplexes führen. Die verwendeten Konzentrationen dieser Ionen entsprachen ungefähr jenen im Stahl; diese Konzentrationen sind im vorherigen Abschnitt angegeben worden. Durch diese Versuche wurde festgestellt, dass keines der untersuchten Ionen, mit Ausnahme von Fe(II) und Cu(II), mit Aluminon reagiert; die nichtreagierenden Ionen vermögen daher die Aluminiumbestimmung nicht zu stören.

*Reduktion von Fe(III) mit Ascorbinsäure*

Die 10 mg Fe/ml enthaltende Fe(III)-Lösung wurde mit frischer Ascorbinsäurelösung zu Fe(II) reduziert, indem letztere tropfenweise zur ersteren hinzugefügt wurde, bis die gelbe Farbe des Fe(III)-Ions verschwand. Daraufhin wurden weitere 0,5 ml Ascorbinsäurelösung und 2 ml 0,1%-iger Aluminonlösung zugesetzt und der Ansatz mit Azetatpuffer auf 50 ml aufgefüllt. Nach halbstündigen Stehen wurde die optische Dichte der Lösung bei 520 nm gegen eine Blindprobe ohne Fe gemessen.

TABELLE I

*Reduktion von Fe(III) mit Ascorbinsäure*

Probe No.	mg Fe(III)	ml Ascorbinsäurelg.	ml 0,1% Aluminonlg.	Azetatpuffer	$D_{520 \text{ nm}}$
1	10,0	1,50	2,00	auf 50 ml	0,000
2	10,0	1,50	2,00	„	0,001
3	10,0	1,50	2,00	„	0,000
4	10,0	1,50	2,00	„	0,002

*Reduktion von Cu(II) mit  $\text{Na}_2\text{S}_2\text{O}_3$*

Cu(II) ergibt mit Aluminon einen roten Komplex, während Cu(I) nicht reagiert. Die Reduktion von Cu(II) zu Cu(I) wird am leichtesten mit  $\text{Na}_2\text{S}_2\text{O}_3$  bewirkt,<sup>17, 18</sup> wobei das entstandene Cu(I) zugleich mit  $\text{S}_2\text{O}_3^{2-}$  eine beständige Komplexverbindung bildet. Ein grossen Überschuss von  $\text{Na}_2\text{S}_2\text{O}_3$  darf nicht anwesend sein, weil dan in sauren Medium zum Ausfällung von elementarem Schwefel kommt. 1%-ige  $\text{Na}_2\text{S}_2\text{O}_3$ -Lösung wird allmählich bis zur Entfärbung der Cu(II)-Lösung zugesetzt. Proben mit 4,87  $\mu\text{g}$  Cu(II)-Gehalt wurden mit verschiedenen Mengen  $\text{Na}_2\text{S}_2\text{O}_3$  behandelt, daraufhin wurden je 2 ml 0,1%-ige Aluminonlösung zugefügt, das Gesamtvolumen mit Azetatpuffer auf 50 ml gebracht und die optische Dichte bei 520 nm gegen eine Blindprobe ohne Cu gemessen.

TABELLE II

*Reduktion von Cu(II) mit  $\text{Na}_2\text{S}_2\text{O}_3$*

Probe	$\mu\text{g}$ Cu(II)	ml $\text{Na}_2\text{S}_2\text{O}_3$	ml Aluminonlg.	$D_{520 \text{ nm}}$
1	4,87	1,80	2,00	0,000
2	4,87	2,00	2,00	0,000
3	4,87	2,00	2,00	0,000



*Aufstellung einer Kalibrationskurve zur Aluminiumbestimmung*

Je 1, 2, 3, 4 und 5 ml Aluminiumlösung (10  $\mu\text{g}$  Al/ml) wurden genau in 50-ml Messkolben hineinpipettiert, jede der Proben mit 1.00  $\mu\text{ml}$  Fe(III)-Lösung (10 mg Fe/ml), 2 ml 2%-iger Ascorbinsäurelösung und 2 ml 0.1%-iger Aluminonlösung versetzt und mit Azetatpuffer pH 4,5 zur Marke aufgefüllt. Die Ansätze wurden 30 Minuten stehengelassen, worauf deren optische Dichten bei 520 nm gegen eine Blindprobe ohne Aluminon gemessen wurden.

*Auflösen der Stahlproben*

Stahlproben werden in konzentrierter Chlorwasserstoffsäure aufgelöst. Die Einwage soll sich nach dem vermutlichen Aluminiumgehalt richten und kann von 0,5 bis 1 g betragen. Die abgewogene Probe wird in einem hohen Becherglas von 150 ml mit 2 ml konzentrierter Chlorwasserstoffsäure übergossen und bei mässiger Temperatur kurz erwärmt. Dann werden 20 ml destillierten Wassers hinzugefügt und anschliessend auf 2 ml eingedampft. Eine neue Portion HCl wird zugesetzt, nach kurzem Erwärmen wird mit Wasser verdünnt und durch abermaliges Eindampfen auf das ursprüngliche Volumen gebracht. Dieses Verfahren wird so oft wiederholt, bzw. dreimal bis sich der Stahl aufgelöst hat. Schliesslich wird die Lösung in einen Messkolben filtriert, dessen Inhalt nach dem erwarteten Aluminiumgehalt gewählt wird, und zwar (a) bei 0,8 bis 1% Al 200 ml, (b) bei 0,02 bis 0,8% 100 ml und (c) unter 0,02% Al 50 ml. Das Filterpapier wird anschliessend bis zur neutralen Reaktion mit destilliertem Wasser nachgewaschen und — falls ein ungelöster Rückstand bemerkbar ist — im Platintiegel verascht. Auf die Asche lässt man einige Tropfen konz.  $\text{H}_2\text{SO}_4$  und 40%-iger HF-Lösung fliessen und erhitzt so lange bis sich etwa vorhandenes  $\text{SiO}_2$  als  $\text{SiF}_4$  verflüchtigt. Der Abdampfrückstand wird mit etwas  $\text{KHSO}_4$  geschmolzen, in wenig konz. HCl aufgenommen und mit dem Filtrat vereinigt. Der pH-Wert dieser Stahlösung sollte zwischen 1 und 2 liegen; liegt er unter 1, muss man die Lösung entsprechen entsäuern. Schliesslich füllt man mit destilliertem Wasser zur Marke auf.

*Gehaltbestimmung von Aluminium in Stahl*

1,5 bis 3 ml Stahlösung werden in einen 50-ml Messkolben hineingemessen, so dass die zu bestimmende Aluminiummenge zwischen 10 und 40  $\mu\text{g}$  liegt. Dazu werden 1,5 ml 2%-ige Ascorbinsäurelösung, 2 ml 1%-ige  $\text{Na}_2\text{S}_2\text{O}_3$ -Lösung und 2 ml 0,1%-ige Aluminonlösung zugegeben und mit Azetatpuffer bis zur Marke aufgefüllt. Nach 30 Minuten wird die optische Dichte bei 520 nm gegen eine Blindprobe abgelesen, die alle Bestandteile der Probe ausser Aluminon enthält. Die Aluminiumkonzentration wird mit Hilfe der Kalibrationskurve gefunden.

**ERGEBNISSE DER SPEKTROPHOTOMETRISCHEN  
GEHALTSBESTIMMUNG VON ALUMINIUM IN STAHL**

Die untersuchten Stahllarten wiesen einen Aluminiumgehalt zwischen 0,008 und 1,07% auf. Einzelergebnisse sind in Tabelle III wiedergegeben.

Ein Vergleich der gefundenen (Kolonne II) mit den Standardwerten (Kolonne I) zeigt sehr gute Übereinstimmung, obwohl der Aluminiumgehalt an sich sehr niedrig ist; das dreiwertige Eisen musste jedoch bei der Bestimmung zu zweiwertigem reduziert und Cu(II) mit  $\text{Na}_2\text{S}_2\text{O}_3$  maskiert sein.

TABELLE III  
 Aluminiumgehalt verschiedener Stahlarten

Stahlprobe	Al in %	
	Standardgehalt (I)	Gefunden (II)
NBS 106 B	1,07	1,12
1 Cr Al 1a	0,873	0,885
ČKD 161 A	0,48	0,50
ČKD Praha	0,26	0,267
Normal	0,064	0,066
Normal	0,031	0,033
Normal	0,029	0,030
Normal	0,020	0,022
Normal	0,008	0,010

## LITERATUR

1. Kar, H. A., *Metals and Alloys* 6, (1935), 156, Zit. nach 19 S. 282.
2. Peters, F., *Chem Analyst* 24, 1955), 4.
3. Morsing, J., *Jernkontorets Ann.* 121 (1937), 143, Zit. nach 19 S. 282.
4. Klinger, P., *Arch. Eisenhüttenw.* 13, (1939/40), 21, Zit. nach 19 S. 282.
5. Pavlish, A. E., and J. D. Sullivan, *Metals and Alloys* 11, (1940) 56.
6. Weissler, A., and C. E. White, *Ind. Eng. Chem. Anal. Ed.* 18, (1946) 530.
7. Blair, D., K. Pover, D. L. Griffiths, and J. H. Wood, *Talanta* 7, (1960) 80.
8. Rothe, J. W., *Stahl u. Eisen* 12, (1892) 1062, Zit. nach 19 S. 280.
9. Dodson, R. W., G. J. Forney, and E. H. Swift, *J. Am. Chem. Soc.* 46, (1926) 668.
10. Elliott, C., and J. W. Robinson, *Analyt. Chim. Acta* 13, (1955) 235.
11. Elliott, C., and J. W. Robinson, *Analyt. Chim. Acta* 13, (1955) 309.
12. Wells, J. E., and D. P. Hunter, *Analyst* 73, (1948) 671.
13. Dagnall, R. M., T. S. West, and P. Young, *Analyst* 90 (1965) 13.
14. Kuznetsov, V. I., *Z. Allgem. Chem. (USSR)* 17, (1947) 175.
15. Bankmann, E. und Specker, *Angew. Chem.* 69 (1957) 733.
16. Bankmann, E. und Specker, *Z. anal. Chem.* 162 (1958) 18.
17. Kaliničenko, J. J., *Zav. lab.* 24, (1958) 266.
18. Cheng, L. K., *Anal. Chem.* 30, (1958) 243.
19. Koch, O. G. und G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, Springer-Verlag Berlin—Heidelberg—New York, 1964.



## IZVOD

## Spektrofotometrijsko određivanje aluminijuma u čeliku

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Opisana je brza metoda za spektrofotometrijsko određivanje aluminijuma u čelicima sa sadržajem aluminijuma ispod 1%, bez predhodnog odvajanja Fe i praćećih elemenata ekstrakcijom ili elektrolizom na Hg-katodi. Uzorak čelika rastvoren je u konc. HCl. Fe(III) i Cu(II) redukovani su do Fe(II) i Cu(I) sa askorbinskom kiselinom, odnosno  $\text{Na}_2\text{S}_2\text{O}_3$ . Sistem je tamponiran acetatnim tamponom pH 4,5, a zatim je dodana svježe priređena otopina 0,1% aluminona. Aluminium sa aluminonom gradi, u slabo kiseloid sredini, crveno obojeni lak koji maksimalno apsorbuje na 520 nm, 30 minuta nakon dodataka aluminona.

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**POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS OF  
LACTATO AND  $\beta$ -HYDROXYPROPIONATO COMPLEXES OF  
INDIUM(III)**

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Stability constants for lactato and  $\beta$ -hydroxypropionato complexes of indium were obtained potentiometrically. Measurements were carried out at a constant ionic strength  $2(\text{NaClO}_4)$  and a constant temperature of  $25 \pm 0.1^\circ\text{C}$ , and the results plotted for evaluation of stability constants by Fronaeus' graphical method. These values were used for averaging by least-square error calculations with a digital computer program, according to R. S. Tobias ( $\sigma$ -Gauss Z $\sigma$  program). The following values of cumulative constants were obtained:

Lactates:  $\log \beta_1 = 3.26$ ;  $\log \beta_2 = 6.05$ ;  $\log \beta_3 = 7.44$ ;  
 $\log \beta_4 \approx 8.5$ .

$\beta$ -Hydroxypropionates:  $\log \beta_1 = 3.48$ ;  $\log \beta_2 = 6.09$ ;  
 $\log \beta_3 = 7.64$ ;  $\log \beta_4 \approx 8.5$ .

Indium(III) complexes have been the subject of many investigations, but the literature data about its lactato and  $\beta$ -hydroxypropionato complexes are very scarce. Only we could find some data about indium lactato complexes (1,2). By liquid ion-exchanger method (1) it was found that  $\log \beta_1 = 3.0$  and  $\log \beta_2 = 5.6$ . The calculation of the stability constants from the polarographic data (2) was not possible, since the half-wave potential of the free indium ion could not be obtained experimentally because of irreversibility of the electrode process in the absence of the lactate.

In the present paper, the stability constants were determined potentiometrically using quinhydrone electrodes. The applicability of the quinhydrone electrodes to measurements in solutions containing indium ions was previously established (3).



## EXPERIMENTAL

*Reagents*

All chemicals were of analytical grade, except sodium- $\beta$ -hydroxypropionate (a product from »Fluka«, Buchs, Switzerland), which had the grade »purum«. This salt was recrystallised from water. Its concentration was ascertained by potentiometric titration with standard sodium hydroxide solution and checked with a cation exchanger.

The lactate solution was prepared by the addition of a known excess of sodium hydroxide solution to the solution of lactic acid. In this way the condensation products of the lactic acid were converted to the lactate.

Buffer solutions with a constant acid-to-salt ratio were prepared on the day of use or every second day, adding a sufficient and known amount of perchloric acid to the solution of sodium lactate or sodium  $\beta$ -hydroxypropionate.

Indium perchlorate was prepared by dissolving pure indium ( $> 99,99\%$ ) in nitric acid. The solution was evaporated with an excess of perchloric acid until the negative test for nitric acid. The salt obtained was recrystallised from water. The concentration of indium in the stock solution was determined by gravimetric analysis as  $In_2O_3$ . The remaining amount of perchloric acid was determined titrimetrically in the presence of sodium chloride (3).

Sodium perchlorate, Fluka, puriss p. a. was used just as obtained in adjusting the ionic strength of various solutions up to 2.

The quinhydrone was a product of »Merck« (Germany).

*Equipment*

The electrodes were pure gold wires freshly ignited in alcohol flame.

The salt bridges used had a very simple U construction, with a three-way stopcock between the two arms dipping into the two half-cells. Electrical contact between the half-cells and the bridge solution (2 M  $NaClO_4$ ) was made by the capillary tips at the ends of the bridge. The electrical resistances of the bridges were between 50.000 — 100.000 Ohms.

A »Dynamco« digital voltmeter which was used, provided a measurement of direct current voltages with a high degree of accuracy ( $\pm 0,01$  mV). Potentials were measured to 0,1 mV.

For delivery the titrant micropipetes »Metrohm« E 457 were used.

*Procedure*

In order to determine stability constants, it is necessary to know the average number of ligands bound to a metal ion ( $\bar{n}$ ) in an equilibrium complexes mixture, and the equilibrium concentration of the anionic ligand ( $[L]$ ) over a sufficiently large range of ligand concentration.

These values are correlated with the stability constants by the expression for the formation function:

$$\bar{n} = \frac{\beta_1 [L] + \beta_2 [L]^2 + \dots + n \beta_n [L]^n}{1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n}$$

Therefore, if some pairs of  $\bar{n}$  and  $[L]$  are known, it is possible to evaluate stability constants with a graphical or computation method.

In this work, the values of  $[L]$  and  $\bar{n}$  were calculated from EMF measurements.

The titrations were made using Fronaeus (4) titration technique with 2 half-cell compartments, and partly using Fronaeus-Chopin (4, 5) arrangement with 3 half-cell compartments in series.

A	B	C
Au — quinhydrone	Au — quinhydrone	Au — quinhydrone
$[H]_A$ mM $HClO_4$	$C_M^0$ mM $In(ClO_4)_3$	$NaClO_4$ 2 M
$NaClO_4$ up to $I = 2$	$C_H^0$ mM $HClO_4$	
	$NaClO_4$ us to $I = 2$	

Compartment A contained a reference solution of a known and constant perchloric acid concentration. Compartment B contained indium perchlorate with a known initial concentration of indium and perchloric acid, while compartment C contained 2 M  $NaClO_4$ . Each compartment having 10 ml (v<sub>0</sub>) of initial solution of a constant ionic strength 2 ( $NaClO_4$ ), was thermostated at  $25 \pm 0,1^\circ C$ .

Compartments B and C were titrated with the same buffer solution, and the resulting electromotive forces  $E_{AB}$  and  $E_{AC}$  were measured. Every titration series was repeated at least three times and the potentials were reproducible within 0,2 mV, and only some times within 0,3 mV.

In the further calculations the average values of  $E_{AB}$  and  $E_{AC}$  were used. The potentials became stable almost immediately after addition of the ligand solution.

The buffer solutions used had constant ratios of the stoichiometric concentrations of organic acid and its sodium salt ( $\delta = C_M^0/C^0$ ), and a constant ionic strength 2 ( $NaClO_4$ ).

The difference in hydrogen ion concentration between the compartment B and C during the titration, resulted from the complex formation in the compartment B. Since the hydrogen concentration in the compartment A was known and constant, different concentrations of hydrogen ion in compartment B ( $[H]_B$ ) and C ( $[H]_C$ ) were easily calculated from electromotive forces. The total equilibrium concentration of anionic ligand and the average number of ligand bound per metal ion were calculated by a digital computer PDP 8/E, from the equations:

$$[L] = - \frac{[H]_C}{[H]_B} \left[ \frac{\delta C_L + C_H - [H]_B + [H]_C \cdot \left( \delta + \frac{C_M - [H]_B}{C_L} \right)}{\delta - \frac{[H]_C}{C_L}} \right]$$

and

$$\bar{n} = \frac{C_L + [H]_B - C_H - [L]}{C_M}$$

## RESULTS AND DISCUSSION

When examining complexes of indium with different monocarboxylate ions, N. Sunden (3) found no hydrolysis of indium ion in buffer solutions even with acid to salt ratio of 1,31:1 in acetate and 1:1 in glycolate buffers. Although both lactic and  $\beta$ -hydroxypropionic acids are stronger than acetic acid (6), we took special care to avoid the hydrolytic rea



tions of indium. The concentration of the organic acid in the buffer solutions used has been varied widely. The titrations were made with two different buffers of a high acid-to-salt ratios of 4:1 and 5,5:1 for lactates, and 5,5:1 and 10;1 for less acidic  $\beta$ -hydroxypropionates.

Furthermore, titrations were performed at two different indium ion concentrations (0,01 M and 0,02 M) with both lactate and  $\beta$ -hydroxypropionate solutions, in order to judge whether the polynuclear complexes are formed. Some experimentally obtained values of  $E_{AB}$ ,  $E_{AC}$ ,  $[L]$  and  $\bar{n}$  are collected in Tables 1—4.

Table I. Titration of  $In^{3+}$  with lactate

$[H]_A = 20,19 \text{ mM}$ ;  $C_M^0 = 10,121 \text{ mM}$ ;  $C_H^0 = 1,915 \text{ mM}$ ;  $C_L^0 = 301,4 \text{ mM}$ ;  $\delta = 5,5$ ;  
 $v_0 = 10,00 \text{ ml}$

Volume (ml)	$E_{AB}$ (mV)	$E_{AC}$ (mV)	$[L]$ mM	$\bar{n}$
0,10	36,70	88,13	0,412	0,556
0,20	33,13	85,80	0,772	0,886
0,30	32,90	84,83	1,180	1,155
0,40	34,43	84,30	1,695	1,370
0,50	37,40	83,97	2,397	1,539
0,60	41,07	83,77	3,379	1,700
0,70	45,03	83,57	4,591	1,809
0,80	48,70	83,40	5,958	1,881
0,90	51,93	83,30	7,557	1,965
1,00	54,70	83,20	9,267	2,039
1,20	59,00	83,10	12,975	2,173
1,40	62,03	82,93	16,807	2,290
1,60	64,37	82,80	20,742	2,387
1,80	66,20	82,77	24,619	2,479
2,00	67,60	82,70	28,441	2,567
2,50	70,27	82,57	37,952	2,730
3,00	72,03	82,42	47,059	2,857
3,50	73,33	82,33	55,748	2,952
4,00	74,33	82,27	63,950	3,031
4,50	75,10	82,20	71,708	3,093
5,00	75,70	82,13	78,996	3,150
6,00	76,60	82,03	93,820	3,306

Table II. Titration of  $In^{3+}$  with lactate

$[H]_A = 20,19 \text{ mM}$ ;  $C^o_M = 20,242 \text{ mM}$ ;  $C^o_H = 3,830 \text{ mM}$ ;  $C^o_L = 301,4 \text{ mM}$ ;  $\delta = 5,5$ ;  
 $v_0 = 10,00 \text{ ml}$

Volume (ml)	$E_{AB}$ (mV)	$E_{AC}$ (mV)	[L] mM	$\bar{n}$
0,20	19,38	85,80	0,420	0,566
0,30	17,28	84,83	0,601	0,751
0,40	16,28	84,28	0,787	0,916
0,50	16,12	83,92	0,990	1,063
0,60	16,58	83,70	1,239	1,208
0,70	17,58	83,50	1,509	1,326
0,80	19,05	83,38	1,804	1,419
0,90	20,85	83,25	2,181	1,516
1,00	23,00	83,18	2,632	1,605
1,20	28,28	83,00	3,871	1,755
1,40	33,98	82,88	5,595	1,883
1,60	39,20	82,80	7,744	2,001
1,80	43,82	82,72	10,295	2,104
2,00	47,58	82,70	13,034	2,204
2,50	54,42	82,52	20,535	2,415
3,00	58,90	82,40	28,299	2,591
3,50	62,02	82,28	36,019	2,740
4,00	64,50	82,20	43,804	2,850
4,50	66,38	82,12	51,304	2,945
5,00	67,90	82,03	58,623	3,018
6,00	70,13	81,93	73,310	3,203
7,00	71,77	81,87	84,529	3,238
8,00	72,97	81,77	95,903	3,299
9,00	73,90	81,70	106,210	3,349
10,00	74,60	81,60	115,604	3,388



Table III. Titration of  $In^{3+}$  with  $\beta$ -hydroxypropionate

$[H]_A = 20,19$  mM;  $C^o_M = 10,121$  mM;  $C^o_H = 1,915$  mM;  $C^o_L = 307,69$  mM;  $\delta = 5,5$ ;  
 $v_0 = 10,00$  ml

Volume ( $\mu$ nl)	$E_{AB}$ (mV)	$E_{AC}$ (mV)	[L] mM	$\bar{n}$
0,10	48,90	126,17	0,148	0,400
0,20	52,70	125,60	0,355	0,644
0,30	58,03	125,33	0,661	0,870
0,40	64,30	125,17	1,125	1,081
0,50	70,53	125,07	1,784	1,280
0,60	76,43	124,97	2,678	1,462
0,70	81,77	124,93	3,813	1,624
0,80	86,33	124,90	5,158	1,767
0,90	90,27	124,83	6,714	1,888
1,00	93,53	124,77	8,404	1,995
1,20	98,67	124,70	12,112	2,166
1,40	102,37	124,67	16,029	2,304
1,60	105,17	124,57	20,133	2,406
1,80	107,27	124,47	24,236	2,493
2,00	108,97	124,43	28,314	2,568
2,50	111,90	124,33	38,178	2,728
3,00	113,87	124,23	47,703	2,835
3,50	115,27	124,10	56,842	2,899
4,00	116,20	124,03	65,095	2,997
4,50	117,00	123,93	73,199	3,035
5,00	117,53	123,87	80,420	3,123
6,00	118,43	123,70	94,275	3,179
7,00	119,03	123,60	106,339	3,263
8,00	119,53	123,50	117,459	3,276
9,00	119,83	123,40	127,125	3,342

Table IV. Titration of  $\text{In}^{3+}$  with  $\beta$ -hydroxypropionate

$[\text{H}]_{\text{A}} = 20,19 \text{ mM}$ ;  $\text{C}_{\text{M}}^{\circ} = 10,121 \text{ mM}$ ;  $\text{C}_{\text{H}}^{\circ} = 1,915 \text{ mM}$ ;  $\text{C}_{\text{I}}^{\circ} = 181,82 \text{ mM}$ ;  $\delta = 10$ ;  
 $v_{\text{e}} = 10,00 \text{ ml}$

Volume (ml)	$E_{\text{AB}}$ (mV)	$E_{\text{AC}}$ (mV)	[L] mM	$\bar{n}$
0,20	43,55	111,20	0,263	0,517
0,30	44,90	110,70	0,418	0,665
0,40	47,05	110,40	0,606	0,799
0,50	49,75	110,15	0,842	0,923
0,60	52,75	110,05	1,129	1,041
0,70	55,85	109,95	1,477	1,154
0,80	59,05	109,85	1,901	1,261
0,90	62,15	109,80	2,394	1,363
1,00	65,10	109,75	2,960	1,459
1,20	70,45	109,45	4,341	1,630
1,40	75,05	109,55	5,921	1,781
1,60	78,90	109,45	7,746	1,904
1,80	82,05	109,30	9,731	2,006
2,00	84,65	109,25	11,777	2,096
2,50	89,40	109,10	17,071	2,270
3,00	92,60	108,95	22,411	2,392
3,50	94,80	108,85	27,508	2,496
4,00	96,45	108,70	32,491	2,568
4,50	97,75	108,60	37,246	2,623
5,00	98,70	108,50	41,653	2,684
6,00	100,15	108,30	49,931	2,760
7,00	101,15	108,15	57,305	2,826
8,00	101,85	108,05	63,783	2,907
9,00	102,45	107,90	69,970	2,913
10,00	102,90	107,80	75,437	2,941



The curves representing  $\frac{\bar{n}}{[L]}$  as a function of  $[L]$  (Fig. 1 and 2) for different buffers and different indium ion concentrations, coincide within the limits of accidental errors, and it may be allowed to neglect both the hydrolytic reactions and formation of polynuclear complexes in the investigated systems.

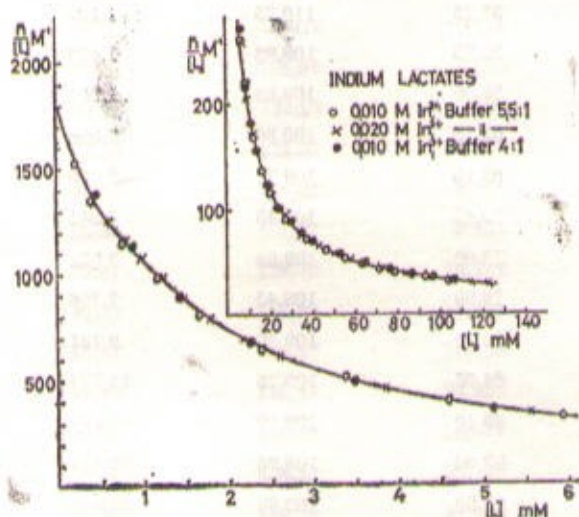


Fig. 1.  $\frac{\bar{n}}{[L]}$  as a function of  $[L]$  for the lactate system.

The calculated values of  $\bar{n}$  and  $[L]$  could be then utilized for graphical determination of stability constants by Fronæus' (7) method. These graphically determined constants with  $\log [L]$ ,  $\bar{n}$  and  $C_M$  values were used as input data for executing the Gauss Z program for non-linear least square refinement calculation according to R. S. Tobias (8).

Calculations were carried out with a Gamma 30 digital computer. The program provided for ten refinement cycles of the stability constants. Output data contained the stability constants, their standard errors, and calculated formation function.

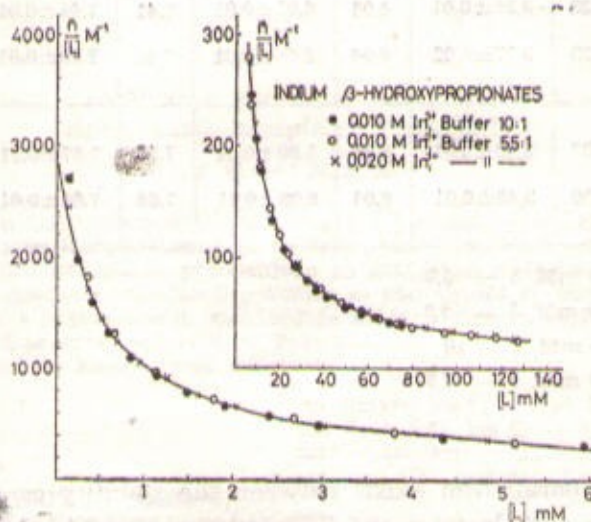


Fig. 2.  $\frac{\bar{n}}{[L]}$  as a function of  $[L]$  for the  $\beta$ -hydroxypropionate system.

The values of stability constants obtained by both the graphical and digital methods are presented in Table V.

Indium forms 4 complexes with both lactate and  $\beta$ -hydroxypropionate, in the concentration range of ligand investigated, up to 200 mM. The agreement between the stability constants calculated separately for different  $C_M$  and  $\delta$  values confirmed the statement that the formation of polynuclear complexes and the hydrolysis were negligible.

However, the authors prefer the values of stability constants obtained at the lower indium ion concentrations and buffer solutions with high acid concentration (the values under a and d).

Judging by the value of the first stability constants, it seemed that the complexes of indium with  $\beta$ -hydroxypropionic acid are somewhat more stable than the corresponding lactate complexes. This is in agreement with the fact, that the stability of complexes of a metal with different ligands depends on the ligand basicity.



Table V. Indium solutions

Ligand	log $\beta_1$		log $\beta_2$		log $\beta_3$		log $\beta_4$	
	graph.	comp.	graph.	comp.	graph.	comp.	graph.	comp.
Lactate a	3,23	3,26 ± 0,01	6,06	6,05 ± 0,01	7,41	7,44 ± 0,01	8,52	~ 8,5
b	3,23	3,27 ± 0,02	6,06	6,08 ± 0,01	7,41	7,50 ± 0,01	8,52	~ 8,5
$\beta$ -hydroxypropionate c	3,57	3,49 ± 0,01	5,98	5,99 ± 0,01	7,58	7,57 ± 0,01	8,19	~ 8,2
d	3,59	3,48 ± 0,01	6,04	6,09 ± 0,01	7,68	7,64 ± 0,01	8,52	~ 8,5

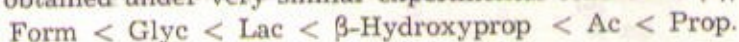
a  $C_M$  — 10 mM,  $\delta$  — 5,5

b  $C_M$  — 20 mM,  $\delta$  — 5,5

c  $C_M$  — 10 mM,  $\delta$  — 10

d  $C_M$  — 10 mM,  $\delta$  — 5,5

The same parallelism exists between the stability constants of indium complexes with lactates and  $\beta$ -hydroxypropionates obtained in this work, and the constants with propionates, acetates, glycolates and formiates, obtained under very similar experimental conditions (3), i. e.:



However, inspecting the higher stability constants of indium lactato and  $\beta$ -hydroxypropionato complexes, it looks as if the complexity of both ligands with indium is nearly the same. This could be, probably, due to the presence of the hydroxyl group in the  $\alpha$  — position in the lactate ion.

The complexity of indium with both ligands is rather strong, but it is not sufficient to mask the precipitation of indium hydroxide, although the precipitation of hydroxide from lactate solutions is very slow.

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## LITERATURA

1. Toko, Janos, Magy, *Kem. Foly.* 74 (12) (1968) 590-5.
2. J. S. Savić and I. Filipović, *Croat. Chem. Acta* 37 (1965) 91.
3. N. Sundén, *Svens. Kem. Tidskr.*, 65 (1953) 257-274.
4. S. Fronaeus, *Acta Chem. Scand.*, 6 (1952) 100.
5. G. Chopin and J. Choporian, *J. Inorg. Nucl. Chem.*, 22 (1961) 97.
6. Spravochnik himika, III, Izz. »Hemiya«, Moskva, 1965, p. 85-98.
7. S. Fronaeus, *Acta Chem. Scand.*, 4 (1950) 72.
8. R. S. Tobias and M. Jasuda, *Inorg. Chem.*, 2 (1963) 1307.

## IZVOD

**Potenciometrijsko određivanje konstanti stabilnosti laktato- i  $\beta$ -hidroksipropionato-kompleksa indiuma(III)**

J. Savić i M. Savić

Određene su konstante stabilnosti laktatnih i  $\beta$ -hidroksipropionatnih kompleksa In(III) potenciometrijskom metodom uz upotrebu hinhidronskih elektroda. Konstante stabilnosti prisutnih kompleksa procijenjene su grafičkom metodom prema S. Fronaeus-u. Ovakvo dobijene vrijednosti poslužile su kao osnova za izračunavanje konstanti stabilnosti i odgovarajućih standardnih grešaka komoću digitalnog računara, koristeći Gauss Z program prema R. S. Tobias-u.

Dobijene su ove kumulativne konstante:

za laktate:  $\log \beta_1 = 3,26$ ;  $\log \beta_2 = 6,05$ ;  
 $\log \beta_3 = 7,44$ ;  $\log \beta_4 \approx 8,5$ .  
 za  $\beta$ -hidroksipropionate:  $\log \beta_1 = 3,48$ ;  
 $\log \beta_2 = 6,09$ ;  $\log \beta_3 = 7,64$ ;  $\log \beta_4 \approx 8,5$ .

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Prilmljeno 19. decembra 1972.



GHTBH 7

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Original Scientific Paper

**L'INFLUENCE DU GLYCEROL ET DU FORMAMIDE SUR LES EQUILIBRES D'EXTRACTION DES COMPLEXES DES METAUX ALCALINS AVEC L'INDICATEUR BLEU DE BROMOTHYMOLO, AUX SYSTEMES L'EAU — CHLOROFORME**

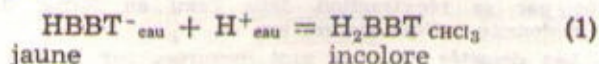
M. Savić — J. Savić

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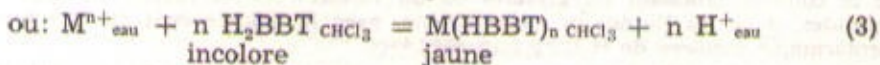
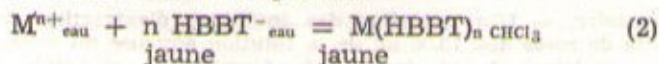
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L'anion HBBT<sup>-</sup>, coloré en jaune, de l'indicateur bleu de bromothymol (H<sub>2</sub>BBT), forme les complexes extractibles, MHHBT, avec les métaux alcalins et l'ion d'ammonium, NH<sub>4</sub><sup>+</sup>. On a étudié l'influence du contenu croissant du glycérol ou du formamide dans la phase aqueuse sur les équilibres d'extraction de ces complexes. On a déterminée la dépendance du pK des équilibres d'extraction des complexes de la constante diélectrique de la phase aqueuse, et, aussi, des logarithmes des nombres ordinaux (log N) des alcalins au système périodique des éléments.

Au cours des études des équilibres acide-base de l'indicateur bleu de bromothymol aux systèmes l'eau-chloroforme, on a constaté que, dans les milieux faiblement acides ou neutres, à côté de l'équilibre d'extraction acide-base:



(avec  $\text{pK}'_{\text{H}_2\text{BBT}} = 5,53 \pm 0,08$ ,  $t = 20^\circ\text{C}$ ,  $I = 0,001$ ), est possible, aussi, l'équilibre d'extraction des complexes:



Ici, M<sup>n+</sup> représente un uni- ou deux-valent cation métallique, y compris et les métaux alcalins et l'ion d'ammonium, NH<sub>4</sub><sup>+</sup>.

La détermination des constantes des équilibres d'extraction:

$$K' = \frac{[\text{M}^{n+}]_{\text{eau}} \cdot [\text{HBBT}^-]_{\text{eau}}}{[\text{M}(\text{HBBT})_n]_{\text{CHCl}_3}} \quad (4)$$

pour les complexes des alcalins a montré qu'il s'agit ici des complexes relativement peu stable. On a démontré, aussi, que les pK' des complexes



des alcalins sont la fonction linéaire du logarithme du nombre ordinal ( $\log N$ ) de l'élément dans le système périodique des éléments.(1)

Puisque il s'agit ici de l'extraction des complexes des métaux alcalins dans un solvant inerte, de type de chloroforme, nous avons considéré comme intéressant d'étudier l'influence de la présence de certains solvants, autres que l'eau et chloroforme, sur la position des équilibres d'extraction de ces complexes.

On a étudié seulement la direction de l'influence du contenu croissant du glycérol ou de formamide dans la phase aqueuse, donc deux solvants lesquels sont bien mixibles avec l'eau, mais insoluble au chloroforme. Glycérol a la constante diélectrique un peu inférieure (41,1), et formamide un peu supérieure (109,5) de celle de l'eau pure (80,4).

Les valeurs des constantes diélectriques des mélanges glycérol-l'eau on a prise de (2), et pour les mélanges de formamide-l'eau, les valeurs appliquées représentent une estimation faite sur la base de type de la variation de la constante diélectrique pour les mélanges de certains autres solvant et de l'eau.

#### PARTIE EXPERIMENTALE

**Réactifs.** — On a appliqué les réactifs de la pureté garantie (p. a.). Le bleu de bromothymol était un produit de MERCK.

Les solutions des chlorures des alcalins sont préparées par le pesage exact des sels, préalablement séchés à la température de 500 à 550°C. La concentration de la solution de chlorure d'ammonium est vérifiée par l'échangeur des ions.

L'indicateur bleu de bromothymol a été directement introduit au système en forme de la solution chloroformique incolore  $2,0 \cdot 10^{-4} M$  de  $H_2BBT$ . Cette solution, au cours de la préparation, a été décolorée par le rincage avec une solution 1 M de  $HClO_4$ , et, ensuite, par l'eau redistillée jusqu'à une réaction neutre de la couche aqueuse. La concentration de  $H_2BBT$  dans la solution chloroformique est vérifiée par sa réextraction dans l'eau en forme du  $BBT^{2-}$  et par la mesure de la densité optique de cet ion.

**Appareils.** — Les densités optiques sont mesurées par le spectrophotomètre UNICAM SP 500, avec les cuves de silice, et le pH par le pH-mètre Radiometer M 22. L'agitation des solutions pour l'extraction est effectuée par l'agitateur horizontal Labor.

**Mode opératoire.** — L'investigation des équilibres d'extraction des complexes MHBTT est faite de sorte que 10,00 ml de la solution aqueuse du cation métallique, avec le contenu croissant du glycérol ou du formamide, est agitée, au cours de 40 minutes, dans les flacons de polyéthylène, avec le volume égal de la solution chloroformique incolore de  $H_2BBT$   $2,10^{-4} M$ .

Le contenu du glycérol dans la phase aqueuse a été varié de 0 à 80% (en poids), et la teneur de formamide de 0 à 80% (en volume).

Après la séparation des couches on a mesuré la densité optique de la phase aqueuse sur 435 et 620 nm, de la couche chloroformique sur 420 nm, comme et le pH de la couche aqueuse.

Les essais blancs ont eu la même composition des solvants comme et les essais étudiés.

Toutes les déterminations sont effectuées à la force ionique constante et égale à 0,4, ce qui a été assuré par la concentration du sel métallique. Grâce à l'extraction faible du complexe MHBTT, cela a fait que la concentration du métal soit constante dans l'équilibre.



La détermination des concentrations d'équilibre du HBBT<sup>-</sup> et du BBT<sup>-2</sup> dans l'eau, et MBBT dans chloroforme est faite comme précédemment (1).

Tous les essais sont effectués à la température ambiante (environ 20°C).

Les essais sont effectués dans les milieux non-tamponnés, et les pH des solutions ont été étalés de pH 4 à 8.

## RESULTATS

Les résultats obtenus sont présentés dans le tableau suivant.

TABLEAU

LES VALEURS DES CONSTANTES D'EQUILIBRE D'EXTRACTION DES COMPLEXES MBBT EN FONCTION DE LA CONSTANTE DIELECTRIQUE (CD) DE LA PHASE AQUEUSE

La composition de la phase aqueuse			Les pK' des complexes		
% (w/w) du glycérol	% (v/v) du formamide	CD	LiHBBT	NaHBBT	KHBBT
80	0	52,3	-0,80 ± 0,01	-0,60 ± 0,02	-0,66 ± 0,11
60	0	62,0	-0,63 ± 0,06	-0,39 ± 0,03	-0,32 ± 0,04
40	0	68,8	-0,51 ± 0,01	-0,19 ± 0,02	-0,07 ± 0,07
20	0	74,7	-0,50 ± 0,03	-0,16 ± 0,25	0,00 ± 0,01
0	0	80,4	-0,28 ± 0,06	+ 0,08 ± 0,03	+ 0,24 ± 0,05
0	20	85,3	-0,45 ± 0,03	-0,09 ± 0,02	-0,12 ± 0,11
0	40	91,7	-1,02 ± 0,04	-0,52 ± 0,14	-0,48 ± 0,12
0	60	98,3	-1,16 ± 0,03	-0,76 ± 0,02	-1,02 ± 0,25
0	80	103,9	-1,60 ± 0,04	-1,15 ± 0,14	-1,41 ± 0,12
			NH <sub>4</sub> HBBT	RbHBBT	CsHBBT
80	0	52,3	-0,70 ± 0,08	-0,70 ± 0,02	-0,61 ± 0,07
60	0	62,0	-0,41 ± 0,06	-0,30 ± 0,02	-0,20 ± 0,18
40	0	68,8	-0,06 ± 0,12	-0,02 ± 0,02	+ 0,09 ± 0,21
20	0	74,7	+ 0,16 ± 0,06	+ 0,21 ± 0,15	+ 0,30 ± 0,05
0	0	80,4	+ 0,39 ± 0,06	+ 0,40 ± 0,11	+ 0,56 ± 0,04
0	20	85,3	+ 0,09 ± 0,14	-0,51 ± 0,03	+ 0,13 ± 0,02
0	40	91,7	-0,43 ± 0,20	-0,76 ± 0,05	-0,50 ± 0,14
0	60	98,3	-0,85 ± 0,04	-1,19 ± 0,06	-1,06 ± 0,08
0	80	103,9	-1,17 ± 0,07	-1,65 ± 0,04	-1,46 ± 0,03

## DISCUSSION

Les résultats montrent que l'augmentation de la teneur soit du glycérol, soit du formamide, dans la phase aqueuse, mène à la diminution des valeurs des pK', comme c'est démontré sur la figure 1A pour le complexe de césium. Ça signifie que l'augmentation de la teneur de l'une ou de l'autre de ces deux substances mène à la diminution de l'extractibilité des complexes étudiés.

Puisque nous supposons que dans ces complexes il s'agit des paires de ions, exprimé plus ou moins, c'est alors que l'effet de l'addition du formamide, en tenant comptes de l'augmentation de la constante diéle-

ctrique de la phase aqueuse, est en général logique. Cependant, l'influence du glycérol est contraire, puisque ici la diminution de la constante diélectrique mène à la diminution de l'extractibilité des complexes.

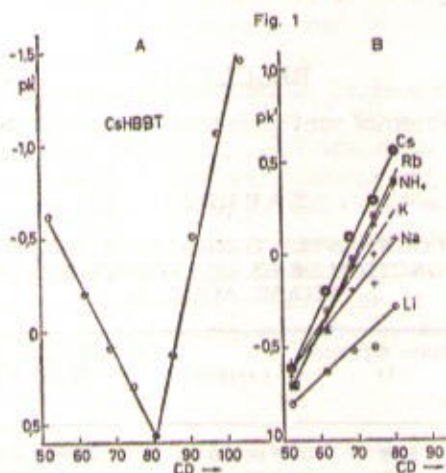


Fig. 1 — La dépendance du  $pK'$  de la constante diélectrique (CD) de la phase aqueuse

1A — La courbe  $pK' = f(CD)$ . La partie à gauche, le système: l'eau + glycérol, la partie à droite, le système: l'eau + formamide

1B — Les courbes  $pK' = f(CD)$  pour la phase aqueuse avec le glycérol pour les complexes de tous métaux alcalins et d'ammonium

Par conséquent, outre que la variation de la constante diélectrique, on doit supposer l'influence et des autres facteurs, par exemple de la solvation des ions métalliques par le glycérol ou formamide, et que tels solvats réagissent avec  $HBBT^-$  et s'extraient plus difficilement.

À savoir, comme c'est visible de la figure 1B et 2AB, les variations de l'extractibilité des complexes des métaux individuels sous les conditions étudiées ne sont pas égales pour tous les métaux, et qu'on peut remarquer une différence distincte dans le comportement des complexes de lithium et de sodium et des complexes de potassium, ammonium, rubidium et de césium.

Puisque les ions de  $Li^+$  et  $Na^+$  sont hydratés les plus forts, c'est, alors, logique, que ces deux ions soumettent les moins à l'influence du contenu croissant du glycérol ou du formamide.

De toute façon qu'une certaine influence doit attribuer et à la différence individuelle dans les caractères chimiques, comme on peut voir dans l'influence inégale de l'addition du glycérol et du formamide sur les complexes métalliques individuels.



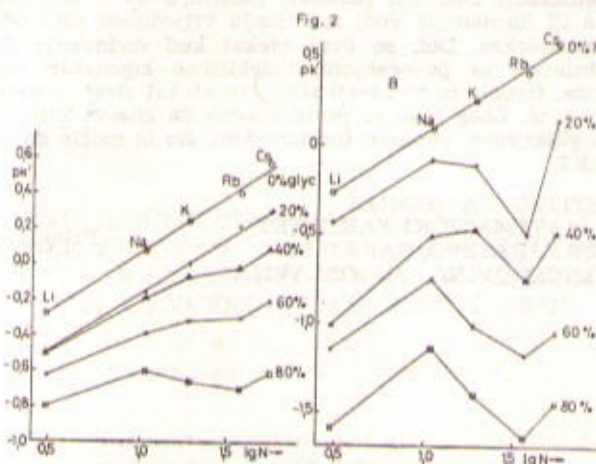


Fig. 2 — La dépendance du  $pK'$  du logarithme du nombre ordinals du métal alcalin ( $\log N$ ) dans le système périodique des éléments

1A — Les courbes  $pK' = f(\log N)$  pour les phases aqueuses avec le contenu croissant du glycérol (Glyc.)

1B — Les courbes  $pK' = f(\log N)$  pour les phases aqueuses avec le contenu croissant du formamide (FA)

Enfin, on ne peut pas exclure et les autres effets, par exemple la variation des coefficients de la répartition des complexes étudiés entre les phase aqueuses avec une teneur différente du glycérol ou du formamide et le chloroforme.

#### BIBLIOGRAPHIE

1. M. Savić, *Glasnik hem. i tehn. BiH*, 17 (1969) 13.
2. G. Charlot et B. Trémillon, *Les réactions chimiques dans les solvants et les sels fondus*, Gauthier-Villars Ed., Paris, 1963, p. 304.

#### IZVOD

**Uticaj glicerina i formamida na ekstrakcione ravnoteže kompleksa alkalnih metala sa indikatorom bromtimol-plavim, u sistemima voda-hloroform**

M. Savić — J. Savić

Žuti anjon HBBT- indikatora bromtimol-plavo ( $H_2BBT$ ) u sistemima voda-hloroform gradi ekstraktivne komplekse MHBBT sa alkalnim metalima i amonijum-jonom. Ispitivan je uticaj rastućeg sadržaja glicerina ili formamida u vodenoj fazi, na položaj ekstrakcionih ravnoteža ovih kompleksa.

Sadržaj glicerina variran je od 0 do 80% (težinski), a sadržaj formamida od 0 do 80% (zapreminski). Dobijeni rezultati pokazuju da u oba slučaja povećanje sadržaja glicerina ili formamida vodi smanjenju vrijednosti  $pK'$ , odnosno opadanju ekstraktivnosti kompleksa. Dok se ovaj efekat kod dodavanja formamida može djelimično objašnjavati sa povećanjem dielektrične konstante vodene faze, kod dodavanja glicerina, trebalo bi očekivati suprotan efekat zbog smanjenja dielektrične konstante vodene faze. Zbog toga se pretpostavlja da znatan uticaj ima solvatacija metalnih jona sa glicerinom, odnosno formamidom, što bi moglo da oteža ekstrakciju kompleksa MHHBT.

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Primljeno 16. juna 1972.



## KOMPLEXOMETRISCHE BESTIMMUNGEN VON ZWEIWERTIGEN KATIONEN DER ZWEITEN, VIERTEN, UND FÜNFTEN ANALYTI- SCHEN GRUPPE IN SYSTEMEN MIT ALUMINIUM, DAS VORHER MIT GLYCEROL MASKIERT WURDE

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Eingegangen am 14. December 1972.

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Die Möglichkeit der komplexometrischen Bestimmungen von  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  und  $\text{Ba}^{2+}$  in Anwesenheit von  $\text{Al}^{3+}$  wurde untersucht und entsprechende Verfahren wurden ausgearbeitet, bei denen Aluminium mit Glycerol maskiert ist. Die zweiwertigen Kationen werden dann gegen geeigneten Metallindikatoren und pH-Werte komplexometrisch bestimmt. Die Konzentrationen der zweiwertigen Kationen liegen zwischen  $5 \cdot 10^{-4}$  und  $2,7 \cdot 10^{-3}$  M. Die obere Konzentrationsgrenze des Aluminiums, bei welcher die Methode für die Bestimmung von  $\text{Me}^{2+}$  noch anwendbar sind, liegt zwischen  $7,5 \cdot 10^{-3}$  und  $2,8 \cdot 10^{-2}$  M. Der Standardfehler und der Variationskoeffizient wurden berechnet und sie zeigen die Brauchbarkeit der vorgeschlagenen Verfahren. Ferner wurde das für die Maskierung von Aluminium notwendige Molverhältnis  $\text{Al}^{3+}$ : Glycerol festgestellt. Die Verhältnisse zwischen den relativen Grössen der Stabilitätskonstanten der Komplexe  $\text{Al}^{3+}$ -Glycerol,  $\text{Me}^{2+}$ -Glycerol sowie  $\text{Al}^{3+}$ -KIII und  $\text{Me}^{2+}$ -KIII werden diskutiert.

### EINLEITUNG

Nachdem entsprechende Verfahren für komplexometrische Bestimmungen von zweiwertigen Kationen in Systemen mit Eisen bzw Chrom vorgeschlagen worden sind,<sup>1, 2, 3, 4, 5, 6</sup> bei denen das dreiwertige Kation mit Glycerol maskiert ist, untersuchten wir die Möglichkeit der komplexometrischen Bestimmungen von Kupfer, Blei, Quecksilber, Cadmium, Zinn,

Diese Arbeit wurde mit finanzieller Beihilfe vom Fonds für wissenschaftliche Arbeit der Sozialistischen Republik Bosnien-Herzegowina durchgeführt.

Kobalt, Nickel, Mangan, Zink, Calcium, Strontium und Barium in Systemen mit Aluminium bei denen Aluminium ebenfalls mit Glycerol maskiert ist. Diese Bestimmungen wurden in Systemen mit Gesamtvolumen von 100 ml durchgeführt.

#### EXPERIMENTELLES

1. Komplexometrische Bestimmung des Kupfers, cca 10 mg  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$  10–30 mg, Glycerol 30–50 ml, pH-Wert 3,5 mit 1 bis 5 g  $\text{NH}_4\text{NO}_3$ , direkte Titration, Indikator Murexid von Gelb auf Violett.

2. Komplexometrische Bestimmung des Bleis, cca 10 mg  $\text{Pb}^{2+}$ , 10–30 mg,  $\text{Al}^{3+}$ , Glycerol 20–35 ml, pH-Wert 10,4–10,7 mit 4 N  $\text{NH}_3$ , direkte Titration, Indikator Methylthymolblau: von Blau auf Rosa bzw Grau.

3. Komplexometrische Bestimmung des Quecksilbers, 20 mg  $\text{Hg}^{2+}$ , 10–20 mg  $\text{Al}^{3+}$ , Glycerol 15–20 ml, pH-Wert 10,3–10,7 mit 6–10 4 N  $\text{NH}_3$ , direkte Titration, Indikator Thymolphthalein-komplexon: von Blau auf Blassrosa, mehr Violett.

4. Komplexometrische Bestimmung des Cadmiums cca 10 mg  $\text{Cd}^{2+}$ , 10–40 mg  $\text{Al}^{3+}$ , Glycerol 15–35 ml, pH-Wert 10,5 mit 5–15 ml  $\text{NH}_3$ , direkte Titration, Indikator Methylthymolblau: von Blau auf Grau oder schwach Rosa.

#### 5. Komplexometrische Bestimmung des Zinns

Die starksaure Lösung, die etwa 6 mg  $\text{Sn}^{2+}$  und 10 bis 40 mg  $\text{Al}^{3+}$  enthält, versetzt man mit 10–40 ml Glycerol und dann mit Wasser bis 100 ml. Nach kräftigen Durchmischen setzt man Methylthymolblau zu und dann unter ständigen Mischen 20 ml 1 N NaOH, erwärmt auf 50° bis 60°C bis zur Bildung einer violettblauen Färbung, pH-Wert 2,5, und titriert dann warm mit KIII auf Orange.

6. Komplexometrische Bestimmung des Kobalts, cca 10 mg  $\text{Co}^{2+}$ , 10–70 mg  $\text{Al}^{3+}$ , Glycerol 3–70 ml, pH-Wert 12,5 mit 20 ml 5 N KOH, Indikator Fluorexon, Rücktitration mit  $\text{CaCl}_2$  bis zu grünliche Fluoreszenz.

7. Komplexometrische Bestimmung des Nickels, cca 10 mg  $\text{Ni}^{2+}$ , 10–70 mg  $\text{Al}^{3+}$ , Glycerol 30–70 ml, pH-Wert 10,5 mit conc  $\text{NH}_3$ , Indikator Murexid. Bei 20 ml conc  $\text{NH}_3$  ändert sich die Farbe des Systems von Gelb auf Weinrot. Direkte Titration von Weinrot auf Violett. In der Nähe des Äquivalenzpunktes ist der Farbumschlag ausserordentlich schnell.

8. Komplexometrische Bestimmung des Mangans, cca 10 mg  $\text{Mn}^{2+}$ , 10–30 mg  $\text{Al}^{3+}$ , Glycerol 10–30 ml, etwas Ascorbinsäure, pH-Wert 10,5 mit 5 N  $\text{NH}_3$ , direkte Titration, Indikator Methylthymolblau von Grünlich auf Rosa.

9. Komplexometrische Bestimmung des Zinks, cca 10 mg  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  von 10–30 mg, Glycerol 10–30 ml, pH-Wert 10,5 mit 10 ml 5 N  $\text{NH}_3$ , es wird auf 30°C erwärmt und dann gegen Methylthymolblau von Blau auf Weinrot titriert.

10., 11., 12. Komplexometrische Bestimmungen des Calciums, Strontiums und Bariums, cca 10 mg  $\text{Me}^{2+}$ ,  $\text{Al}^{3+}$  10–50 mg, Glycerol 15–50 ml, pH-Wert 11, 9–12,2 mit 3–6 ml 5 N KOH und 5–7 ml 2 N  $\text{NH}_4\text{Cl}$ . Direkte Titration, Indikator Thymolphthaleinkomplexon: von Blau auf Blassgrau.

Die Standardabweichungen der einzelnen Messungen, die Standardabweichungen des Mittelwertes und die Variationskoeffizienten sind in der Tabelle 1 zusammengefasst,

In der Tabelle sind die Resultate von 10 Parallelbestimmungen für jedes Kation und das für die Fälle wo  $\text{Al}^{3+}$  in obere Konzentrationsmenge anwesend ist.



TABELLE 1

Me <sup>2+</sup>	Verfahren	GENOMMEN IN 100 ml			pH	Indikator	Abweichung 1 2 3
		mg		ml Glycerol			
		Me <sup>2+</sup>	Al <sup>3+</sup>				
Cu <sup>2+</sup>	1	10,00	30	50	3,5	MUREXID	0,102 0,036 1,005
Pb <sup>2+</sup>	2	10,34	30	35	10,4—10,7	MTB	0,060 0,021 0,594
Hg <sup>2+</sup>	3	19,03	20	20	10,3—10,7	THPHX	0,090 0,032 0,473
Cd <sup>2+</sup>	4	9,71	40	35	10,5	MTB	0,025 0,009 0,252
Sn <sup>2+</sup>	5	6,14	40	40	1,5	MTB	0,114 0,036 1,062
Co <sup>2+</sup>	6	10,28	40	45	12,5	FLUOREXON	0,149 0,042 1,435
Ni <sup>2+</sup>	7	9,68	30,20	50	10,5	MUREXID	0,120 0,038 1,224
Mn <sup>2+</sup>	8	10,96	30,17	30	10,18	MTB	0,112 0,039 1,024
Zn <sup>2+</sup>	9	10,85	30,17	30	10,30	MTB	0,030 0,011 0,028
Ca <sup>2+</sup>	10	<b>10,00</b>	52,00	40	11,9—12,2	THPHX	0,115 0,041 1,106
Cr <sup>2+</sup>	11	10,12	52,80	40	11,9—12,2	THPHX	0,143 0,055 1,413
Ba <sup>2+</sup>	12	10,60	52,80	40	11,9—12,2	THPHX	0,153 0,054 1,420

Legende:

Indikatoren:

MTB: METHYLTHYMOLBLAU  
 THPHX: THYMOLPHTHALEINKOMPLEXON

Abweichungen:

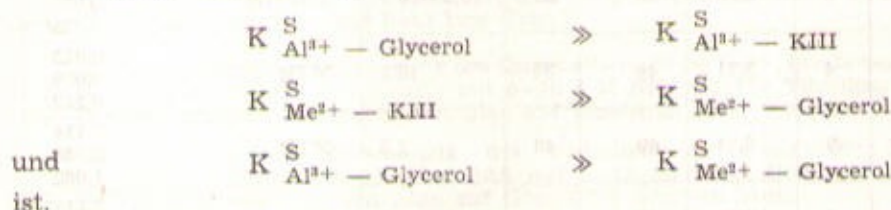
1. STANDARDABWEICHUNG DER EINZELEN MESSUNGEN %
2. STANDARDABWEICHUNG DES MITTELWERTES %
3. VARIATIONSKOEFFIZIENT %

## SCHLUSSFOLGERUNG UND DISKUSSION

Die Konzentrationsgrenzen zwischen der zweiwertigen Kationen liegen zwischen  $5 \cdot 10^{-4}$  und  $2,7 \cdot 10^{-3}$  M. Die obere Konzentrationsgrenze des Aluminiums, bei welcher die Methode für die Bestimmung von zweiwertigen Kationen noch anwendbar ist, beträgt  $7,5 \cdot 10^{-3}$  bis  $2,68 \cdot 10^{-2}$  M.

Um das Gleichgewicht der Reaktion zwischen  $Al^{3+}$  und Glycerol im Sinne des Komplexes  $Al^{3+}$  — Glycerol zu verschieben, gibt man Glycerol im Überschuss zu. Das Molverhältnis  $Al^{3+}$ : Glycerol ist 1:276 bis 1:608 und das Molverhältnis Glycerol: Wasser 1:1,75 bis 1:16; wir haben es mithin mit Mischsystemen Wasser-Glycerol zu tun. Die angewendeten pH-Werte ermöglichen die Maskierung von  $Al^{3+}$  mit Glycerol.

Aus der Bestimmungen geht hervor, dass:



Eben, diese Verhältnisse ermöglichen die Bestimmung zweiwertiger Kationen in Mischsystemen Wasser-Glycerol in Anwesenheit von Aluminium.

## LITERATURA

1. F. Krleža, *Mikrochim. Acta*, 1966, 785.
2. F. Krleža, *Glasnik hem i teh. BiH* 15 (1966—67) 19.
3. F. Krleža, *Croat. Chem. Acta*, 39 (1967) 47.
4. F. Krleža, *Glasnik hem. i teh. BiH*, 16 (1968) 37.
5. F. Krleža, *Croat. Chem. Acta*, 41 (1969) 9.
6. F. Krleža, N. Vuletić, *Croat. Chem. Acta*, 42 (1970) 75.

## IZVOD

**Kompleksometrijsko određivanje dvovalentnih kationa druge, četvrte i pete analitičke grupe u sistemima, koji sadrže aluminium, koji se maskira glicerolom**

F. Krleža i N. Vuletić

Ispitana je mogućnost određivanja  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Sn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  i  $Ba^{2+}$  kompleksometrijskom titracijom u sistemima, koji sadrže aluminium, koji se maskira glicerolom. Izrađeni su odgovarajući postupci, određene prikladne pH-vrijednosti i indikatori za ova određivanja. Koncentracije dvovalentnih kationa leže između  $5 \cdot 10^{-4}$  i  $2,7 \cdot 10^{-3}$  M, dok je granična koncentracija za  $Al^{3+}$  uz koju su ova određivanja moguće između  $7,5 \cdot 10^{-3}$  M i  $2,8 \cdot 10^{-2}$  M.

Određene su standardna odstupanja pojedinih mjerenja, standardna odstupanja od srednje vrijednosti i varijacioni koeficijenti. Diskutirani su odnosi relativnih konstanti stabilneta kompleksa:  $Me^{2+}$ -KIII,  $Al^{3+}$ -KIII,  $Me^{2+}$ -Glicerol,  $Al^{3+}$ -Glicerol.

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**EINE ANALYTISCHE UNTERSUCHUNG DER SYSTEME EISEN (II) —  
EISEN (III) CHROM (III) — CHROM (VI) UND DER ZWEI-, DREI- UND  
VIERKOMONENTIGEN KOMBINATIONEN DEREN IONEN MIT  
RADIOAKTIVEN INDIKATOREN**

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Eingegangen am 23. October 1972.

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Nach Voruntersuchungen an radioaktiv markierten Redoxsystemen, Eisen(II)-Eisen(III) und Chrom(III)-Chrom(VI), wurden analytische Verfahren ausgearbeitet, die zum Studium von zwei-, drei-, und vierkomponentigen Systemen deren Ionen verwertet wurden.

Wenn ein Gemisch von Eisen- und Chromsalzen in einem Nuklearreaktor bestrahlt wird, entstehen infolge von Chalmers-Szillard-Reaktionen beide Valenzstufen des Eisens und des Chroms. Um die Wechselwirkungen derselben zu verfolgen und die Einflüsse von Bestrahlungsdauer und Retention studieren zu können, muss die bestrahlte Probe aufgelöst und deren Gehalt an Eisen (II) und (III), sowie Chrom (III) und (VI) radiometrisch bestimmt werden. Nun wird aber der durch Auflösen bedingte Zusammenbruch der Kristallgitter sowohl den Isotopenaustausch verschiedenartigen Ionen desselben Elements, als auch die gegenseitige Redoxreaktion von Eisen (II) und Chrom (VI) begünstigen. Vor den Bestimmungen sind daher die einzelnen Valenzstufen beider Elemente zu trennen, und wenn der Isotopenaustausch sehr rasch verläuft, muss er vor dem Trennungsversuch aufgehalten werden; es muss auch die Redoxreaktion zwischen Eisen (II) und Chrom (VI) verhindert werden.

Wir haben zunächst das Verhalten der Systeme Eisen (II) — Eisen (III) und Chrom (III) — Chrom (VI) bei Zusatz von radioaktiven Indikatoren untersucht; die hierbei entwickelten Verfahren benützten wir dann bei der Erforschung von mehrkomponentigen Systemen dieser Kationen.

**EXPERIMENTELLER TEIL**

*Lösungen*

Die Standardlösung von  $^{59}\text{FeCl}_3$  wurde aus einem trägerfreien, in 0.1 N Chlorwasserstoffsäure gelösten  $^{59}\text{FeCl}_3$ -Präparat (Herstellerfirma: Amersham) durch Trägerzusatz bereitet, so dass ein Eisengehalt von 200  $\mu\text{g}$  pro ml erhalten wurde. Die spezifische Aktivität dieser Lösung war 308 416 Imp/Min pro ml.  $^{59}\text{FeCl}_3$ -Standard-



lösung wurde jeweils frisch, durch Reduktion von  $^{59}\text{FeCl}_3$  mit Hydroxylamin in heisser saurer Lösung gewonnen.<sup>1</sup> Der Eisengehalt dieser Lösung wurde durch Permanganattitration nach Zimmermann und Reinhard bestimmt und durch Verdünnen auf 200  $\mu\text{g/ml}$  gebracht. Die fertige Standardlösung besass eine spezifische Aktivität von 158.490 Imp/Min pro ml.

Die Standardlösung von  $\text{K}_2^{51}\text{CrO}_4$  wurde ebenfalls aus einer trägerfrei  $\text{K}_2^{51}\text{CrO}_4$ -Lösung (hergestellt im Institut »Boris Kidrič«, Vinča) durch Hinzufügen von inaktivem Träger bereitet, so dass deren Gesamtchromgehalt 200  $\mu\text{g/ml}$  und die spezifische Aktivität 148.000 imp/Min je ml betrug.  $^{51}\text{CrCl}_3$ -Standardlösung wurde auf gleiche Art aus einem trägerlosen radioaktiven Präparat desselben Ursprungs hergestellt: Chromgehalt 200  $\mu\text{g/ml}$ , spezifische Aktivität 178.052 Imp/Min pro ml.

Gesättigte KCN und  $\text{BaCl}_2$ -Lösungen wurden aus entsprechenden analysenreinen Salzen der Fa. Merck, Darmstadt mit dreifach destilliertem Wasser bereitet.

Zum Einstellen der pH-Werte wurde eine Söresensche Glykokoll-Pufferlösung, pH 9, verwendet.

#### Apparatur

Radiometrische Messungen wurden mit einem Hohlkristall-Szintillationszähler, Modell DS 5 der Fa. Nuclear, Chicago, M-DS-5 durchgeführt. Die zu chromatographischen Trennungen verwendeten Kolonnen waren 10 cm lang, bei einem Durchmesser von 0.5 cm, und wurden mit einer Durchflussgeschwindigkeit von 4–5 Tropfen pro Minute betrieben.

#### Das System Eisen(II)-Eisen(III)

Enthält ein Redoxsystem Radioisotope, dann findet ein Isotopenaustausch zwischen den Oxydationsstufen statt und dieser muss vor Trennung der letzteren zum Stillstand gebracht werden. Dodson<sup>2</sup> und anderen Autoren<sup>3-5</sup> gelang die Unterbindung des Isotopenaustausches durch Überführen von Eisen(II) in einen  $\alpha$ ,  $\alpha'$ -Dipyridylkomplex. Wir versuchten hingegen die andere Valenzstufe auszuschalten und konnten in vorliegender Arbeit den Isotopenaustausch durch Überführen von Eisen(III) in einen Glycerolkomplex aufhalten.

Das jeweilige System wurde durch Abmessen bestimmter Mengen der Standardlösungen zusammengestellt, mit Glykokollpuffer pH 9 versetzt, und diesem Gemisch fügte man Glycerol [im Molverhältnis  $\text{Fe} : \text{C}_3\text{H}_5(\text{OH})_3 = 1 : 600^2$ ] und KCN-Lösung hinzu. Auf diese Weise wurde das Eisen(III) in den Glycerolkomplex, und das Eisen(II) in Hexacyanoferrat(II) überführt. Diese Komplexe wurden an einer aus basischem Aluminiumoxyd bestehenden Kolonne chromatographisch getrennt. Das Hexacyanoferrat wird von der Kolonne nicht zurückgehalten und lässt sich unmittelbar im Ausfluss radiometrisch bestimmen. Der Eisen(III)-Glycerolkomplex konnte darauf mit 0.1 N Chlorwasserstoffsäure eluiert und im Eluat bestimmt werden.

Dieses Verfahren wurde zunächst an Systemen geprüft, in welchen nur das Ion der einen oder der anderen Oxydationsstufe radioaktiv markiert war, dann aber auch an solchen wo beide Ionenarten mit radioaktiven Indikatoren versehen waren. Die bei diesen Prüfungen erhaltenen Ergebnisse sind in Tabelle I dargestellt.

#### Das System Chrom(III)-Chrom(VI)

Den in vorher beschriebener Weise bereiteten, [mit Glykokollpuffer pH 9 versetzten chromhaltigen Systemen wurden Glycerol [im Molverhältnis  $\text{Cr} : \text{C}_3\text{H}_5(\text{OH})_3 = 1 : 565$ ] und  $\text{BaCl}_2$ -Lösung hinzugefügt. Durch letztere Zugabe wird Chrom(VI) ausgefällt, so dass Chrom(III), welches in der Form des Glycerolkomplexes in Lösung verbleibt, unmittelbar nach Abtrennung der Flüssigkeit in ihr bestimmt werden konnte. Auch diesmal wurden sowohl die mit einer, als auch die mit beiden Ionenarten markierten Systeme untersucht. Die jeweiligen Ergebnisse sind in Tabelle II angeführt.



*Mehrkomponentensysteme*

Die in beiden vorhergehenden Abschnitten beschriebenen Verfahren wurden anschliessend auf solche Systeme angewendet, die Kombinationen von je zwei, drei, oder vier der genannten Ionenarten enthielten. In, allen diesen Systemen ist Glykolkopuffer zugefügt.

Die einzelnen Valenzstufen des Eisens und des Chroms wurden auf folgende Weise abgeschieden und bestimmt. Eisen(II) wurde stets mit KCN in Hexacyanoferrat(II) überführt, von den übrigen Valenzstufen adsorptionschromatographisch an einer Aluminiumoxydkolonnen abgetrennt und im wässrigen Ausfluss radiometrisch bestimmt. Da die Kolonne Eisen(III) und Chrom(III) zurückhält, trennt man diese Ionenarten so voneinander, dass man zuerst das Chrom(III) mit 0.1 N Essigsäure, die man mit Natriumazetat auf pH 4.3 bringt, und dann das Eisen(III) mit 0.1 N Chlorwasserstoffsäure eluiert. Eisen(III) und Chrom(III) werden vor der Trennung immer in Glycerolkomplexe überführt. Chrom(VI) wird zuerst abgetrennt, indem man es mit  $\text{BaCl}_2$  ausfällt, der  $\text{BaCrO}_4$ -Niederschlag wird dreimal mit dreifach destilliertem Wasser ausgewaschen und zur radiometrischen Bestimmung in 0.1 N Salpetersäure aufgelöst.

Alle Versuchsansätze wurden durch Abmessen von Standardlösungen zusammengestellt. Als Beispiel möge ein System dienen, das beide Valenzstufen sowohl des Eisens, als auch des Chroms enthält. Dieses wurde aus je 1 ml  $^{59}\text{FeCl}_2$ -Lösung, 1 ml  $^{59}\text{FeCl}_3$ -Lösung (mit Glycerol), 1 ml  $^{51}\text{CrCl}_3$ -Lösung (mit Glycerol), 1 ml  $\text{K}_2^{51}\text{CrO}_4$ -Lösung, 1 ml  $\text{BaCl}_2$ -Lösung, 1 ml KCN-Lösung und 4 ml Sörensen'sche Pufferlösung bereitet. Im weiteren Verfahren wurde das durch  $\text{BaCl}_2$  als  $\text{BaCrO}_4$  quantitativ ausgefällte sechswertige Chrom abzentrifugiert und weiterverarbeitet. In Lösung verblieben: Eisen(III) und Chrom(III) in Form von Glycerolkomplexen und Eisen(II) als Hexacyanoferrat(II). Zur Trennung dieser Bestandteile wurde eine aus basischem Aluminiumoxyd bestehende Kolonne verwendet. Eisen(II) wurde im Ausfluss, Chrom(III) und Eisen(III) nach der vorhin beschriebenen Elution in den entsprechenden Eluatn radiometrisch bestimmt.

## BESPRECHUNG DER ERGEBNISSE

Vorerst wurden die Systeme Eisen(II)-Eisen(III) und Chrom(III)-Chrom(VI) einzeln untersucht, wobei die radiometrischen Bestimmungen der Bestandteile in alkalischer Lösung durchgeführt wurden. Hierfür gab es mehrere Gründe. Wir gingen nämlich vom Grundgedanken aus, den Isotopenaustausch zwischen Eisen(II) und Eisen(III) dadurch zu verhindern, dass wir letzteres in den Glycerolkomplex, ersteres in Hexacyanoferrat(II) überführten. Das alkalische Milieu ermöglicht die Entstehung des Hexacyanoferrats und liefert eine Umgebung in der dieses beständig ist; überdies verhindert es eine etwaige Reaktion von Hexacyanoferrat(II) mit Eisen(III). Durch Bindung von Eisen(III) als Glycerolkomplex und die Überführung von Eisen(II) in Hexacyanoferrat(II) wurde aber nicht bloss der Isotopenaustausch unterbunden, es wurde auch das Redoxpotential der Valenzstufe Eisen(II) herabgesetzt. In Betreff auf die Abtrennungsmöglichkeit von Chrom(II) und Chrom(VI) und deren radiometrische Bestimmung in alkalischem Milieu konnte gezeigt werden, dass Chrom(VI) — nach Überführung von Chrom(III) in den Glycerolkomplex — bei pH 9 durch Bariumchlorid quantitativ gefällt wird; Auflösen des Niederschlags in 0.1 N Salpetersäure gestattet eine unmittelbare radiometrische Bestimmung von Chrom(VI). Eisen(II), Eisen(III) und Chrom(III), als Hexacyanoferrat(II), bzw. als



Glycerolkomplexe, lassen sich an basischem Aluminiumoxyd chromatographisch voneinander trennen, wobei die Eisen(III)- und Chrom(III)-Komplexe auf der Kolonne festgehalten werden, Hexacyanoferrat(II) hingegen mit dem Lösungsmittel ausfließt. Die in den Tabellen I und II zusammengestellten Ergebnisse zeigen, dass die radiometrische Bestimmung von Eisen(II) in Gegenwart von Eisen(III) in allen untersuchten Systemen, bei allen Verhältnissen dieser Valenzstufen von 1:99 bis 99:1 und einem Gesamtgehalt von 200 µg Fe, auch in Gegenwart von 200 µg Cr, durchführbar ist. Es sei an dieser Stelle noch hervorgehoben, dass unter den angegebenen Bedingungen kein Chrom(III) mit BaCrO<sub>4</sub> kopräzipitiert wurde.

Durch Kombinieren der beiden im experimentellen Teil beschriebenen Verfahren wurden folgende Systeme untersucht:

Eisen(II) -Chrom(III)	. . . . .	Tabelle III
Eisen(II)-Chrom(VI)	. . . . .	„ IV
Chrom(III)-Eisen(III)	. . . . .	„ V
Chrom(VI)-Eisen(III)	. . . . .	„ VI
Eisen(II)-Eisen(III)-Chrom(III)	. . . . .	„ VII
Eisen(II)-Eisen(III)-Chrom(VI)	. . . . .	„ VIII
Eisen(II)-Chrom(III)-Chrom(VI)	. . . . .	„ IX
Chrom(III)-Chrom(VI)-Eisen(III)	. . . . .	„ X
Eisen(II)-Eisen(III)-Chrom(III)-Chrom(VI)	. . . . .	„ XI

Nachweislich unterblieb in Systemen, die Eisen(II) und Chrom(VI) enthielten, die zwischen diesen Komponenten zu erwartende Redoxreaktion; diese wurde einerseits durch Ausfällen von Chrom(VI), andererseits durch Überführen von Eisen(II) in Hexacyanoferrat(II) verhindert. Die Trennung der dreiwertigen Kationenkomplexe Eisen(III)- und Chrom(III)-Glycerol wurde dadurch erreicht, dass zuerst der Chromkomplex 0.1 N Essigsäure-Natriumazetatgemisch pH 4.3 eluiert wurde, wonach der Eisenkomplex mit 0.1 N Chlorwasserstoffsäure eluiert werden konnte. Die in den Tabellen angegebenen Daten zeigen, dass sämtliche Fehler der radiometrischen Bestimmungen innerhalb der Standardabweichung des Zählwerks liegen.

Schliesslich kann gefolgert werden, dass es nach den in dieser Arbeit beschriebenen Verfahren möglich ist, Systeme von zwei- und dreiwertigem Eisen und drei- und sechswertigem Chrom, wie sie infolge von Bestrahlung eisen- und chromhaltiger Salze in Kernreaktoren entstehen, in deren Bestandteile aufzutrennen und diese einzeln radiometrisch zu bestimmen.



TABELLE I

Fe (II)			Fe (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
2	1,98	- 0,90	198	197,40	- 0,30
	2,00	-		197,90	- 0,05
10	9,94	- 0,60	190	188,00	- 0,10
	9,99	- 0,10		190,20	+ 0,10
25	25,00	-	175	175,18	+ 0,10
	24,91	- 0,36		175,08	+ 0,04
50	49,89	- 0,22	150	149,96	- 0,02
	49,82	- 0,36		150,00	-
75	74,85	- 0,20	100	124,85	- 0,11
	74,83	- 0,22		124,90	- 0,08
100	100,00	-	125	99,98	- 0,02
	100,09	+ 0,09		100,10	+ 0,10
125	125,00	-	75	75,00	-
	125,18	+ 0,18		74,99	- 0,01
150	149,00	- 0,66	50	49,82	- 0,36
	149,70	- 0,20		49,89	- 0,22
175	175,18	+ 0,48	25	24,83	- 0,68
	175,00	-		24,92	- 0,32
190	189,90	- 0,05	10	9,95	- 0,50
	189,70	- 0,68		9,99	- 0,10
198	198,30	+ 0,15	2	1,99	- 0,50
	198,73	+ 0,37		1,99	- 0,50

TABELLE II

Cr (III)			Cr (VI)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
20	20,13	+ 0,63	180	180,35	+ 0,19
	20,05	+ 0,25		180,00	—
60	59,89	— 0,18	140	140,17	+ 0,12
	59,99	— 0,02		140,07	+ 0,05
80	80,00	—	120	120,23	+ 0,19
	80,16	0,16		120,02	+ 0,01
100	100,12	+ 0,12	100	99,82	— 0,18
	100,09	+ 0,09		100,00	—
120	120,88	+ 0,56	80	80,28	+ 0,35
	120,00	—		80,32	+ 0,40
140	140,17	+ 0,12	60	60,12	+ 0,20
	140,00	—		59,88	— 0,20
160	160,00	—	40	40,08	+ 0,20
	160,00	—		39,82	— 0,45
180	178,91	— 0,60	20	20,04	+ 0,02
	179,05	— 0,52		20,10	+ 0,50



TABELLE III

Fe (II)			Cr (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
2	1,99	- 0,50	198	198,00	-
	1,98	- 0,90		198,10	+ 0,05
25	24,83	- 0,68	175	174,80	- 0,11
	24,86	- 0,56		174,90	- 0,06
50	50,05	+ 0,10	150	150,00	-
	49,89	- 0,22		150,11	+ 0,06
100	100,21	+ 0,21	100	99,99	- 0,01
	100,13	+ 0,13		100,00	-
175	175,18	+ 0,10	25	24,90	- 0,40
	175,21	+ 0,12		25,00	-
150	150,00	-	50	49,92	- 0,16
	149,95	- 0,03		50,00	-
175	174,80	- 0,11	25	24,90	- 0,40
	174,90	- 0,06		25,98	+ 0,32
198	198,40	+ 0,20	2	1,99	- 0,50
	198,19	+ 0,09		1,98	- 1,00

TABELLE IV

Fe (II)			Cr (VI)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
20	19,87	- 0,65	180	180,45	+ 0,25
	19,92	- 0,40		180,00	-
50	50,00	-	150	150,32	+ 0,21
	49,99	- 0,02		150,16	+ 0,10
70	70,20	+ 0,28	130	130,00	-
	70,08	+ 0,10		129,98	- 0,01
100	99,86	- 0,14	100	100,14	+ 0,14
	99,93	- 0,17		100,38	+ 0,38
130	130,00	-	70	70,00	-
	130,06	+ 0,04		69,43	- 0,81
150	150,23	+ 0,15	50	49,92	- 0,16
	150,09	+ 0,06		50,08	+ 0,16
180	179,24	- 0,42	20	20,00	-
	180,05	+ 0,02		20,00	-



TABELLE V

Cr (VI)			Fe (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
2	1,996	- 0,80	198	198,19	+ 0,19
	2,015	+ 0,75		198,40	+ 0,20
25	24,83	- 0,68	175	174,80	- 0,11
	24,87	- 0,52		175,18	+ 0,48
50	50,01	+ 0,02	150	150,11	+ 0,06
	50,00	-		149,95	- 0,03
75	74,93	- 0,09	125	125,00	-
	75,02	+ 0,02		125,60	+ 0,48
100	100,23	+ 0,23	100	100,00	-
	100,06	+ 0,06		99,98	- 0,02
125	124,19	- 0,64	75	74,93	- 0,09
	124,89	- 0,08		74,99	- 0,01
150	150,23	+ 0,25	50	49,80	- 0,40
	150,15	+ 0,10		49,89	- 0,22
175	175,00	-	25	25,00	-
	175,17	+ 0,09		24,98	- 0,08
198	198,00	-	2	1,990	- 0,10
	198,00	-		1,984	- 0,80

TABELLE VI

Cr (VI)			Fe (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
20	20,13	+ 0,65	180	180,55	+ 0,19
	20,05	+ 0,25		180,00	—
60	59,89	— 0,18	140	140,17	+ 0,12
	59,99	— 0,02		140,07	+ 0,05
80	80,00	—	120	120,23	+ 0,19
	80,16	0,16		120,02	+ 0,01
100	100,12	+ 0,12	100	99,82	— 0,18
	100,09	+ 0,09		100,00	—
120	120,88	+ 0,56	80	80,28	+ 0,35
	120,00	—		80,32	+ 0,40
140	140,17	+ 0,12	60	60,12	+ 0,20
	140,00	—		59,88	— 0,20
160	160,00	—	40	40,08	+ 0,20
	160,00	—		39,82	— 0,45
180	178,91	— 0,60	20	20,04	+ 0,02
	179,05	— 0,52		20,10	+ 0,50



TABELLE VII

Fe (II)			Fe (III)			Cr (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
5	4,86	- 2,80	5	5,00	-	190	190,00	-
	4,92	- 1,60		5,02	+ 0,40		190,00	-
20	20,05	+ 0,25	20	19,82	- 0,90	160	160,14	+ 0,08
	20,00	-		19,97	- 0,15		160,23	+ 0,14
50	50,08	+ 0,16	50	50,12	+ 0,24	100	99,86	- 0,14
	49,89	- 0,23		50,00	-		99,79	- 0,21
70	70,00	-	70	69,86	- 0,20	60	60,00	-
	70,23	+ 0,32		69,93	- 0,10		59,92	- 0,13
90	89,82	- 0,20	90	90,03	+ 0,03	20	19,86	- 0,70
	90,02	+ 0,02		90,00	-		20,03	+ 0,15
95	94,87	- 0,13	95	95,06	+ 0,06	10	9,93	- 0,70
	95,00	-		95,14	+ 0,14		9,98	- 0,20

TABELLE VIII

Fe (II)				Fe (III)				Cr (III)			
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)		genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)		genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	
5	4,93	-0,60		5	5,06	+1,20		190	189,63	-0,19	
	4,88	-2,40			5,00	-			189,71	-0,15	
20	20,13	+0,65		20	15,79	-1,05		160	160,00	-	
	20,08	+0,40			20,00	-			159,75	-0,15	
50	50,00	-		50	50,21	+0,42		100	99,65	-0,35	
	49,82	-0,36			50,01	+0,06			99,71	-0,29	
70	70,00	-		70	70,17	+0,24		60	60,00	-	
	69,83	-0,24			70,00	-			59,72	-0,46	
90	90,00	-		90	89,78	-0,24		20	19,73	-1,30	
	90,00	-			89,92	-0,08			19,82	-0,90	
95	95,13	+0,13		95	95,00	-		10	9,83	-1,70	
	95,08	+0,09			95,00	-			9,92	-0,80	



TABELLE IX

Fe (II)		Cr (III)			Cr (VI)			
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
190	190,00	—	5	4,89	-2,20	5	4,92	-1,80
	190,03	+0,01		5,02	+0,40		4,99	-0,20
160	159,83	-0,11	20	20,00	—	20	19,86	-0,70
	159,92	-0,05		20,13	+0,65		19,92	-0,40
100	99,79	-0,21	50	50,00	—	50	49,89	-0,22
	100,09	+0,09		50,00	—		49,92	-0,16
60	60,03	+0,05	70	69,99	-0,01	70	70,00	—
	60,08	+0,13		69,98	-0,03		69,86	-0,20
20	20,00	—	90	90,27	+0,30	90	89,68	-0,35
	20,00	—		89,98	-0,02		89,87	-0,14
10	9,76	-2,40	95	95,00	—	95	95,00	—
	9,83	-1,70		95,16	+0,16		94,82	+0,19

TABELLE X

Cr (III)			Cr (VI)			Fe (III)		
genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)	genommen ( $\mu\text{g}$ )	gefunden ( $\mu\text{g}$ )	Fehler (%)
5	4,96	-0,80	5	4,98	-0,40	190	190,00	-
	4,94	-1,20		4,92	-1,60		190,24	+0,12
20	20,00	-	20	19,86	-0,70	160	160,13	+0,08
	20,09	+0,45		19,94	-0,30		159,96	-0,02
50	50,13	+0,26	50	49,78	-0,44	100	100,32	+0,32
	49,89	-0,22		49,93	-0,14		100,00	-
70	70,00	-	70	69,69	-0,44	60	60,00	-
	70,09	+0,12		69,87	-0,18		60,09	+0,15
90	89,68	-0,35	90	89,92	-0,08	20	20,16	+0,80
	90,08	+0,08		89,64	-0,40		20,32	+1,60
95	95,00	-	95	94,83	-0,17	10	9,87	-1,30
	95,08	+0,08		94,91	-0,09		10,09	+0,90



TABELLE XI

Fe (II)			Fe (III)			Cr (III)			Cr (VI)			
Genommen (µg)	Getunden (µg)	Fehler (‰)	Genommen (µg)	Getunden (µg)	Fehler (‰)	Genommen (µg)	Getunden (µg)	Fehler (‰)	Getunden (µg)	Fehler (‰)	Genommen (µg)	Fehler (‰)
5	4,96	-0,80	5	4,97	-0,60	95	95,15	+0,15	95	95,00	95,00	-
	5,00	-		5,03	+0,60		94,88	-0,12		95,08	95,08	+0,08
20	20,05	+0,25	20	20,00	-	80	80,05	+0,06	80	79,78	79,78	-0,27
	20,00	-		19,76	+1,20		80,13	+0,26		80,09	80,09	-0,11
50	50,03	+0,06	50	50,00	-	50	50,16	+0,32	50	49,92	49,92	-0,16
	50,12	+0,24		49,73	-0,54		50,00	-		50,00	50,00	-
70	70,00	-	70	69,74	-0,31	30	30,25	+0,83	30	29,82	29,82	-0,60
	70,15	+0,21		70,09	+0,13		30,00	-		30,12	30,12	+0,40
95	94,89	-0,11	95	95,00	-	5	5,08	+0,16	5	4,87	4,87	-2,60
	94,83	-0,21		95,14	+0,14		4,92	-1,60		4,98	4,98	-0,50

## LITERATUR

1. Bray W. C., Simpson M. E., MacKenzie A. A. *J. Am. Chem. Soc.*, **41** (1919) 1363.
2. Dodson R. W., *J. Am. Chem. Soc.*, **72** (1950) 3315.
3. Adamson, *J. Phys. Chem.*, **56** (1952) 858.
4. Taube H., Myers H., Rish R. L., *J. Am. Chem. Soc.*, **75** (1953) 4153.
5. Siekierska K. E., Fenger J., Danish Atomic Energy Commission Research Establishment Riso Report No 183 (1968).
6. Krleža F., *Microchim. Acta*, **4-5** (1966) 785.

## IZVOD

**Analička studija sistema ferum(II)-ferum(III) i krom(III)-krom(VI) kao i dvokomponentnih, trokomponentnih i četverokomponentnih kombinacija navedenih kationa uz primjenu radioaktivnih obilježivača**

S. Kozomora, F. Krleža

U radu su studirani primjenom metode radiaktivnog obilježivača sistemi ferum(II)-ferum(III) i krom(III)-krom(VI), pa su nađeni postupci primjenjeni na dvokomponentne, trokomponentne i četverokomponentne sisteme navedenih kationa.

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## ADUKTI NEKIH ALKALNIH I ZEMNOALKALNIH SOLI SA N, N-DIMETILACETAMIDOM

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Pripremljeni su i okarakterisani adukti sa N, N-dimetilacetamidom (DMA):  $\text{LiCl} \cdot 1,5\text{DMA}$ ,  $\text{LiBr} \cdot 1,5\text{DMA}$ ,  $\text{LiJ} \cdot 4\text{DMA}$ ,  $\text{LiNO}_3 \cdot \text{DMA}$ ,  $\text{NaJ} \cdot 3\text{DMA}$ ,  $\text{KJ} \cdot 3\text{DMA}$ ,  $\text{KCNS} \cdot 3\text{DMA}$ ,  $\text{MgCl}_2 \cdot 4\text{DMA}$ ,  $\text{MgBr}_2 \cdot 4\text{DMA}$ ,  $\text{MgJ}_2 \cdot 4\text{DMA}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{DMA}$ ,  $\text{CaCl}_2 \cdot 4\text{DMA}$ ,  $\text{CaBr}_2 \cdot 5\text{DMA}$ ,  $\text{CaJ}_2 \cdot 5\text{DMA}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{DMA}$ ,  $\text{Ca}(\text{Ac})_2 \cdot 8\text{DMA}$ ,  $\text{SrCl}_2 \cdot 4\text{DMA}$ ,  $\text{SrBr}_2 \cdot 4\text{DMA}$ ,  $\text{SrJ}_2 \cdot 5\text{DMA}$ ,  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{DMA}$  i  $\text{BaBr}_2 \cdot 4\text{DMA}$ . Termogravimetrija i diferencijalno termička analiza su bile primjenjene za ispitivanje termičke disocijacije izoliranih adukata.

### UVOD

Ispitivanja u oblasti nevodениh rastvarača pokazala su da je N, N-dimetilacetamid (DMA) odličan jonizirajući rastvarač sa jako izraženim donorskim osobinama. Mnogobrojni kompleksi sa DMA kao ligandom<sup>1-6</sup> dobro ilustruju koordinirajuću sposobnost ovog amida. Međutim, od dimetilacetamidnih adukata alkalnih soli dosada je, koliko nam je poznato, izoliran samo  $\text{LiClO}_4 \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$ <sup>1</sup>, a o sintezi DMA-adukata elemenata IIa grupe nema podataka.

U ovom radu je opisano pripremanje većeg broja adukata alkalnih i zemnoalkalnih soli sa DMA. Izolirani adukti su okarakterisani kemijskim analizama, metodom termogravimetrije i diferencijalno termičke analize.

*Napomena:* Ovaj rad je izrađen uz materijalnu pomoć Fonda za naučni rad SRBiH u Sarajevu.

## EKSPERIMENTALNI DIO

**Kemikalije.** Sve upotrebljene anorganske soli bile su p.a. Hidratizirani magnezium bromid, te jodidid magneziuma, kalciuma i stronciuma bili su pripremljeni reakcijom odgovarajućeg karbonata sa konc. jodovodičnom kiselinom i uparivanjem dobijenog rastvora uz smanjen pritisak do kristalizacije. Za sintezu adukata je korišten N, N-dimetilacetamid firme Fluka, bez daljeg čišćenja.

**Pripremanje adukata.** Hidratizirana ili anhidrovana metalna sol bila je rastvorena u višku DMA uz zagrijavanje u evakuisanom sudu na vodenom kupatilu. Dobijeni rastvor je zatim destiliran uz smanjeni pritisak da bi se uklonila hidratna voda i višak rastvarača. Kristalizacija adukata iz ovako dobijenog zasićenog rastvora ponekad je nastupala već kod sobne temperature, ali je u većini slučajeva bilo potrebno hlađenje sa smjesom leda i soli ili u kriostatu do još niže temperature. Izlučeni adukti su ofiltrirani uz evakuisanje i čuvani u vakuumu iznad silikagela.

**Analitički postupak.** Identifikacija sintetiziranih adukata je izvršena kompleksometrijskim, argentometrijskim i acidometrijskim titracijama nakon propuštanja vodenog rastvora adukta kroz jako bazni odnosno jako kiseli jonski izmjenjivač firme Merck.

**Termogravimetrijska ispitivanja.** Ova ispitivanja su izvršena sa Chevenard-ovom termovagom (S. A. D. A. M. E. L.), tip TBM, uz atmosferski pritisak i brzinu grijanja od 5°C/min. Veličina uzorka je bila skoro konstantna i iznosila je oko 100 mg. Termoliza je vršena u otvorenom kvarnom lončiću.

**Diferencijalno termička analiza** je provedena u atmosferi vazduha uz istu brzinu grijanja kao i termogravimetrijska analiza, uz primjenu aparata firme Linseis. U cilindrične platinske sudove stavljano je 300 mg uzorka između dva jednaka sloja (od 200 mg) izžarenog  $\alpha$ -aluminijum oksida.

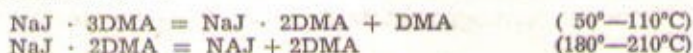
## REZULTATI

Sastav pripremljenih adukata vidi se iz tabele 1. Adukte ostalih halogenida natrijuma, kalijuma i barijuma nije bilo moguće sintetizirati zbog slabe rastvorljivosti ovih soli u DMA. Svi izolirani DMA adukti su bijele kristalne supstance. U vodi se lako rastvaraju uz otcjepljenje DMA.

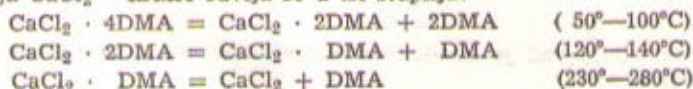
Ako se uporede izolirani DMA adukti sa dimetilformamidnim kompleksima odgovarajućih alkalnih i zemnoalkalnih soli,<sup>7</sup> onda se može konstatovati da jodidi litijuma, natrijuma i kalijuma, litium nitrat, magnezium klorid i magnezium nitrat grade sa oba ova amida adukate istog sastava.

## TG i DTA-ispitivanja.

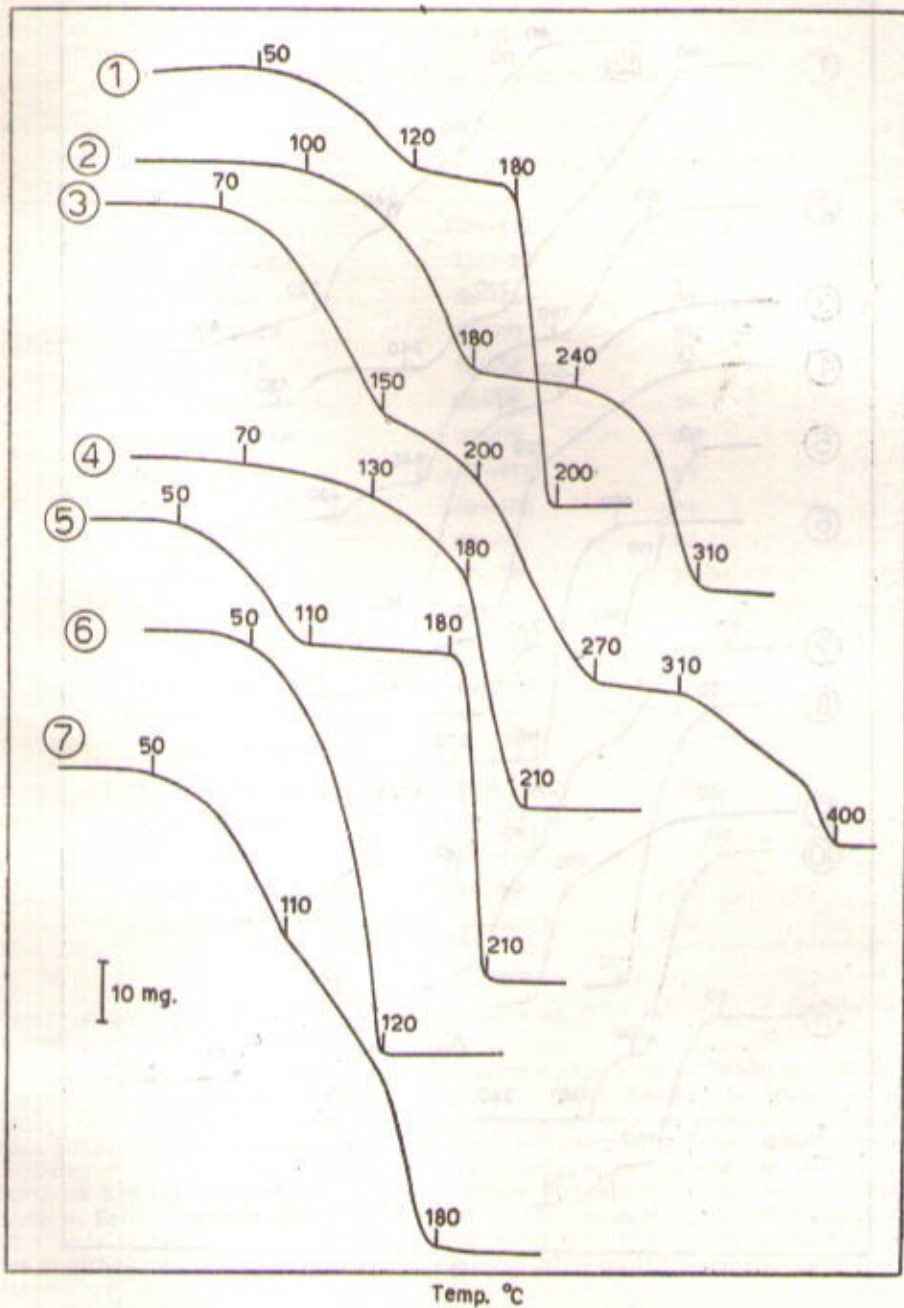
Rezultati dobijeni termogravimetrijskom analizom dati su u tabeli 2. TG krive ovih adukata (Sl. 1 i Sl. 2) pokazuju da se termoliza u većini slučajeva odvija uz oslobađanje DMA u stupnjevima. Kod LiCl · 1,5DMA, LiBr · 1,5DMA, NaJ · 3DMA (krive 1, 2 i 5 na Sl. 1), CaCl<sub>2</sub> · 4DMA, CaBr<sub>2</sub> · 5DMA, SrCl<sub>2</sub> · 4DMA, SrBr<sub>2</sub> · 4DMA i Sr(NO<sub>3</sub>)<sub>2</sub> · 4DMA (krive 5, 6, 10, 11 i 13 na Sl. 2) stupnjevit karakter desolvatacije je najbolje izražen. Termičko razlaganje ovih adukata dovodi do stvaranja dobro definisanih međuprodukata, što se na krivama termolize manifestira obično sa posve ravnim, relativno širokim platoima. Kod većine ovih adukata intermedijarno se stvaraju dosta stabilni di- odnosno mono-adukti, koje je obično bilo moguće izolirati. Tako termoliza LiCl · 1,5DMA dovodi do stvaranja monoadukta, sa područjem egzistencije od 120° do 170°C. TG kriva od LiBr · 1,5DMA pokazuje da se desolvatacija i ovog adukta odvija u dva stupnja. Međuprodukt, koji nastaje nakon eliminisanja polovine sadržanog DMA, razlaže se iznad 250°C. NaJ · 3DMA se termolizira uz primarno stvaranje diadukta:



Desolvatacija CaCl<sub>2</sub> · 4DMA odvija se u tri stupnja:

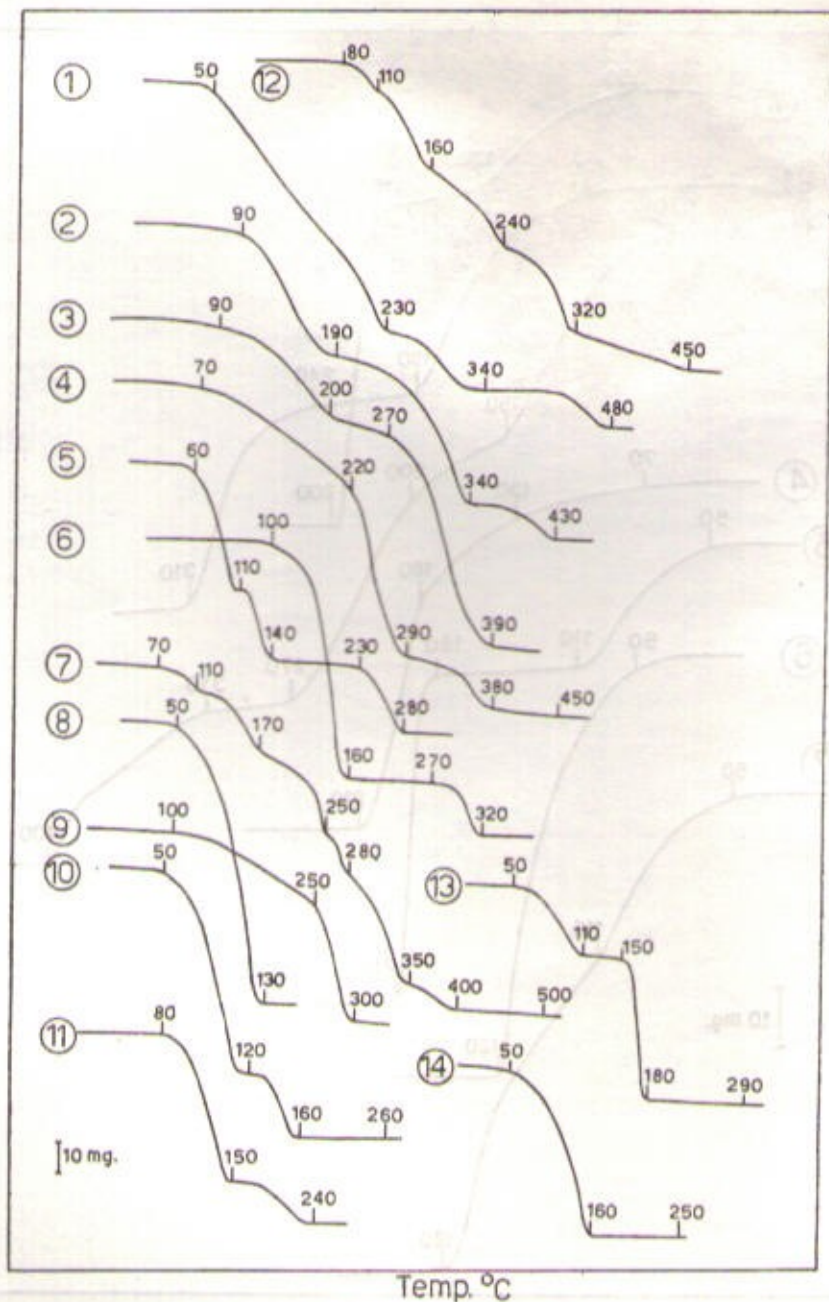






Sl. 1. TG krive DMA-adukata alkalnih soli

- 1) LiCl · 1,5DMA, 2) LiBr · 1,5DMA, 3) LiJ · 4DMA, 4) LiNO<sub>3</sub> · DMA, 5) NaJ · 3DMA, 6) KJ · 3DMA, 7) KCNS · 3DMA



Sl. 2. TG krive DMA-dukata zemnoalkalnih soli

- 1)  $MgCl_2 \cdot 4DMA$ , 2)  $MgBr_2 \cdot 4DMA$ , 3)  $MgJ_2 \cdot 4DMA$ , 4)  $Mg(NO_3)_2 \cdot 2DMA$ , 5)  $CaCl_2 \cdot 4DMA$ , 6)  $CaBr_2 \cdot 5DMA$ , 7)  $CaJ_2 \cdot 5DMA$ , 8)  $Ca(Ac)_2 \cdot 8DMA$ , 9)  $Ca(NO_3)_2 \cdot 2DMA$ , 10)  $SrCl_2 \cdot 4DMA$ , 11)  $SrBr_2 \cdot 4DMA$ , 12)  $SrJ_2 \cdot 5DMA$ , 13)  $Sr(NO_3)_2 \cdot 4DMA$ , 14)  $BaBr_2 \cdot 4DMA$



TABELA 1.

DMA-adukti alkalnih i zemnoalkalnih soli

Adukt	T. topljenja, °C	Higroskopan
LiCl · 1,5DMA	115—118	da
LiBr · 1,5DMA	71—73	da
LiJ · 4DMA	55—58	da
LiNO <sub>3</sub> · DMA	58—60	da
NaJ · 3DMA	55—58	da
KJ · 3DMA	92—95	ne
KCNS · 3DMA	75—78	da
MgCl <sub>2</sub> · 4DMA	110—113	ne
MgBr <sub>2</sub> · 4DMA	105—108	ne
MgJ <sub>2</sub> · 4DMA	66—69	da
Mg(NO <sub>3</sub> ) <sub>2</sub> · 2DMA	67—70	slabo
CaCl <sub>2</sub> · 4DMA	razl.*)	da
CaBr <sub>2</sub> · 5DMA	153—157**)	da
CaJ <sub>2</sub> · 5DMA	103—105	slabo
Ca(NO <sub>3</sub> ) <sub>2</sub> · 2DMA	46—48	slabo
Ca(Ac) <sub>2</sub> · 8DMA	razl.*)	da
SrCl <sub>2</sub> · 4DMA	razl.*)	da
SrBr <sub>2</sub> · 4DMA	141—145**)	da
SrJ <sub>2</sub> · 5DMA	111—113	slabo
Sr(NO <sub>3</sub> ) <sub>2</sub> · 4DMA	57—60	da
BaBr <sub>2</sub> · 4DMA	88—92**)	da

Svaka od ovih faza termolize registrirana je i na DTA-krivoj ovog adukta sa zasebnim pikovima (Sl. 4, kriva 5).

Monoadukt, koji se stvara u toku termolize CaBr<sub>2</sub> · 5DMA može se uporediti po temperaturnom intervalu stabilnosti sa CaCl<sub>2</sub> · DMA. Razlaganje SrCl<sub>2</sub> · 4DMA i SrBr<sub>2</sub> · 4DMA je dvostepen proces, u toku prvog stepena se eliminiše 3DMA molekule. Intermedijarno stvaranje monoadukta u toku termolize ovih adukata pokazuju i njihove DTA-krive. Endotermni pik sa temperaturom (minimuma kod 215°C odnosno 280°C na krivama 10 i 11 (Sl. 4) prouzrokavan je posljednjom fazom desolvatacije. Kada su SrCl<sub>2</sub> · DMA i SrBr<sub>2</sub> · DMA, koji su bili izolirani u toku TGA, podvrgnuti DTA onda je samo ovaj endotermni pik bio registriran. U toku prvog stupnja termolize Sr(NO<sub>3</sub>)<sub>2</sub> · 4DMA eliminiše se 1,5DMA molekule i od 180°C počinje plato desolvatazirane soli.

\*) Razlaže se bez topljenja.

\*\*\*) Omekšava u širem intervalu.

U tabeli 2. sumirani su rezultati analiza sintetiziranih adukata.

TABELA 2.

Analiza DMA-adukata alkalnih i zemnoalkalnih soli

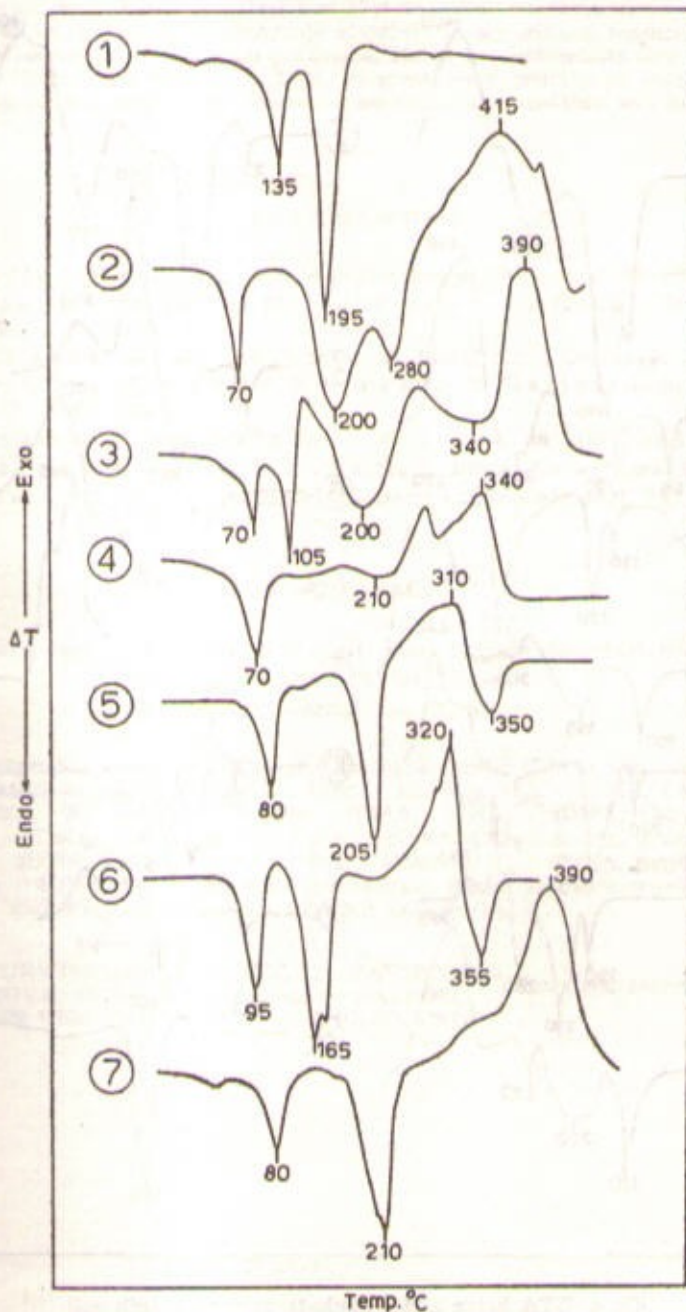
Adukt	Analiza				Termogravimetrijska analiza			
	kation teor. eksp.		anion teor. eksp.		DMA teor. eksp.		Ostatak eksp. za teor. oksid	
LiCl · 1,5DMA	4,01	3,96	20,49	19,98	75,50	75,8	....	....
LiBr · 1,5DMA	3,19	3,11	36,64	36,19	60,17	60,5	....	....
LiJ · 4DMA	1,44	1,41	26,33	26,41	72,23	71,7	....	....
LiNO <sub>3</sub> · DMA	4,45	4,42	39,72	39,70	55,81	55,5	....	....
NaJ · 3DMA	5,59	5,56	30,86	31,02	63,55	63,4	....	....
KJ · 3DMA	9,15	8,95	29,69	29,84	61,16	62,2	....	....
KCNS · 3DMA	10,87	10,94	16,20	16,08	72,93	72,4	....	....
MgCl <sub>2</sub> · 4DMA	5,48	5,50	16,02	16,04	78,50	79,2	9,02	9,6
MgBr <sub>2</sub> · 4DMA	4,54	4,46	29,83	29,41	....	....	8,54	9,0
MgJ <sub>2</sub> · 4DMA	3,88	3,76	40,52	39,96	....	....	6,41	6,7
Mg(NO <sub>3</sub> ) <sub>2</sub> · 2DMA	7,54	7,47	38,43	38,35	....	....	12,49	12,6
CaCl <sub>2</sub> · 4DMA	8,72	8,56	15,43	15,53	75,81	75,5	....	....
CaBr <sub>2</sub> · 5DMA	6,30	6,42	25,19	25,22	68,51	67,9	....	....
CaJ <sub>2</sub> · 5DMA	5,49	5,35	34,81	34,76	....	....	7,99	7,68
Ca(NO <sub>3</sub> ) <sub>2</sub> · 2DMA	11,84	11,65	36,66	36,58	51,50	52,1	....	....
Ca(Ac) <sub>2</sub> · 8DMA	4,69	4,63	13,82	13,77	81,40	81,1	....	....
SrCl <sub>2</sub> · 4DMA	17,27	17,22	14,03	14,04	68,70	68,9	....	....
SrBr <sub>2</sub> · 4DMA	14,60	14,71	26,98	26,93	58,42	57,8	....	....
SrJ <sub>2</sub> · 4DMA	11,27	10,95	32,68	32,33	....	....	13,33	13,9
Sr(NO <sub>3</sub> ) <sub>2</sub> · 4DMA	15,64	15,38	22,13	22,06	62,23	62,2	....	....
BaBr <sub>2</sub> · 4DMA	21,27	21,26	24,75	24,51	53,98	54,5	....	....

Na krivama termolize spomenutih adukata prikazan je samo proces desolvatacije. Oksidacija desolvatiziranih soli odvija se kod viših temperatura. Iz tabele 2. se vidi da se smanjenje mase, prouzrokovano eliminisanjem DMA u toku termolize, dobro slaže sa teorijskim vrednostima sadržaja DMA u ovim aduktima. Desolvatacija i oksidacija metalne soli odvijaju se zasebno i kod adukata litijum nitrata, jodida i tiocijanata kalijuma, nitrata i acetata kalcijuma te barijum bromida.

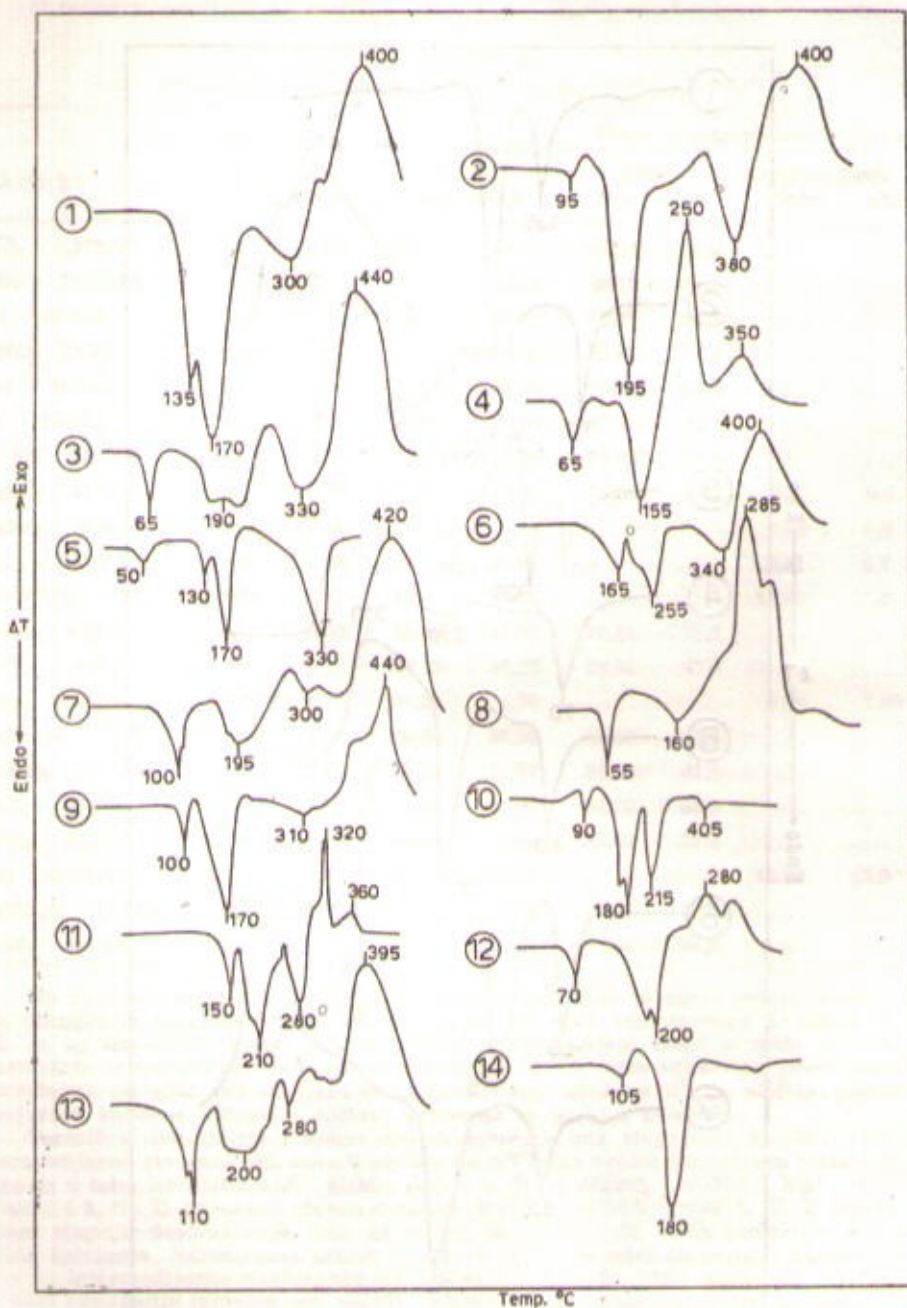
Termička disocijacija i nekih drugih adukata ima stupnjevit karakter, ali se intermedijarno stvoreni niži adukti obično ne odlikuju većom termičkom stabilnošću. Tako se u toku termolize LiJ · 4DMA (kriva 3, Sl. 1), MgBr<sub>2</sub> · 4DMA i MgJ · 4DMA (krive 2 i 3, Sl. 2) primarno stvara diadukt. MgCl<sub>2</sub> · 4DMA (kriva 1, Sl. 2) izgubi u prvom stupnju desolvatacije, koji se završi do 230°C, 3,25 DMA molekule. Adukt jodida kalcijuma stroncijuma (krive 7 i 12 na Sl. 2) također se razlaže diskontinuirano uz intermedijarno nastupanje adukta sa 4,5, 3, i 0,5 DMA molekule. Kod ovih adukata razlaganje metalne soli slijedi odmah nakon desolvatacionog procesa, ili se odvija paralelno sa oslobađanjem posljednjih molekula DMA. Zato u tim slučajevima nije bilo moguće odrediti sadržaj DMA na osnovu kriva termolize.

DTA krive (Sl. 3 i 4) pokazuju da razlaganje ovih adukata rezultira u endoternim pikovima. Sa izuzetkom CaCl<sub>2</sub> · 4DMA, Ca(Ac)<sub>2</sub> · 8DMA i SrCl<sub>2</sub> · 4DMA, ostali adukti se u toku termolize tope prouzrokujući na DTA krivama prvi endo-





Sl. 3. DTA krive DMA-adukata alkalinih soli  
 1)  $\text{LiCl} \cdot 1,5\text{DMA}$ , 2)  $\text{LiBr} \cdot 1,5\text{DMA}$ , 3)  $\text{LiJ} \cdot 4\text{DMA}$ , 4)  $\text{LiNO}_3 \cdot \text{DMA}$ , 5)  $\text{NaJ} \cdot 8\text{DMA}$ ,  
 6)  $\text{KJ} \cdot 3\text{DMA}$ , 7)  $\text{KCNS} \cdot 3\text{DMA}$



Sl. 4. DTA krive DMA-adjukata zemnoalkalnih soli

- 1)  $MgCl_2 \cdot 4DMA$ , 2)  $MgBr_2 \cdot 4DMA$ , 3)  $MgJ_2 \cdot 4DMA$ , 4)  $Mg(NO_3)_2 \cdot 2DMA$ , 5)  $CaCl_2 \cdot 4DMA$ , 6)  $CaBr_2 \cdot 5DMA$ , 7)  $CaJ_2 \cdot 5DMA$ , 8)  $Ca(NO_3)_2 \cdot 2DMA$ , 9)  $Ca(Ac)_2 \cdot 8DMA$ , 10)  $SrCl_2 \cdot 4DMA$ , 11)  $SrBr_2 \cdot 4DMA$ , 12)  $Sr(NO_3)_2 \cdot 4DMA$ , 13)  $SrJ_2 \cdot 5DMA$ , 14)  $BaBr_2 \cdot 4DMA$



termni efekt. Volatilizacija DMA u toku procesa ključanja registrirana je sa pikom, čija ekstremna tačka se nalazi kod 170° do 225°C. Na DTA krivama nekih adukata, koji se termoliziraju uz stvaranje stabilnih intermedijata, manifestiraju se pojedine faze termolize sa zasebnim pikovima, što je već spomenuto kod interpretacije TG kriva. Egzotermni pikovi na DTA krivama ovih jedinjenja prouzrokovani su oksidacijom oslobođenog DMA odnosno desolvatizirane metalne soli kod viših temperatura.

## LITERATURA

1. W. E. Bull, S. K. Madan, J. E. Willis, *Inorg. Chem.* **2**, (1963) 303.
2. R. S. Drago, D. W. Meek, M. D. Joesten, L. La Roche, *Inorg. Chem.* **2**, (1963) 124.
3. S. K. Madan, A. M. Donohue, *J. Inorg. Nucl. Chem.* **28**, (1966) 1617.
4. G. Vicentini, M. Perrier, J. C. Prado, R. Najjar, *Anais. Acad. Bras. Cienc.* **39**, (1967) 149.
5. G. Vicentini, R. Najjar, *J. Inorg. Nucl. Chem.* **30**, (1966) 2771.
6. G. Vicentini, M. Perrier, J. Prado, *J. Inorg. Nucl. Chem.* **31**, (1969) 825.
7. M. Glavaš i T. Ribar, *Glasnik hemičara i tehnologija BiH*, **16**, (1968) 123.

## ZUSAMMENFASSUNG

### Addukte von einigen Alkalimetall- und Erdalkalimetall-Salzen mit N, N-Dimethylacetamid

von M. Glavaš und T. Ribar

Die folgenden Addukte mit N, N-dimethylacetamid (DMA) wurden synthetisiert und charakterisiert: LiCl · 1,5DMA, LiBr · 1,5DMA, LiJ · 4DMA, LiNO<sub>3</sub> · DMA, NaJ · 3DMA, KJ · 3DMA, KCNS · 3DMA, MgCl<sub>2</sub> · 4DMA, MgBr<sub>2</sub> · 4DMA, Mg(NO<sub>3</sub>)<sub>2</sub> · 2DMA, CaCl<sub>2</sub> · 4DMA, CaBr<sub>2</sub> · 5DMA, CaJ<sub>2</sub> · 5DMA, (Ca(Ac)<sub>2</sub> · 8DMA, Ca(NO<sub>3</sub>)<sub>2</sub> · 2DMA, SrCl<sub>2</sub> · 4DMA, SrBr<sub>2</sub> · 4DMA, SrJ<sub>2</sub> · 5DMA, Sr(NO<sub>3</sub>)<sub>2</sub> · 4DMA und BaBr<sub>2</sub> · 4DMA. Die thermische Dissoziation dieser Addukte wurde thermogravimetrisch und differentialthermoanalytisch untersucht.

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## BAZNO KATALIZIRANA HIDROLIZA o-NITROFENILACETATA U SISTEMU DIMETILSULFOKSID — VODA

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Promjena specifične brzine hidrolize o-nitrofenilacetata u mješovitom rastvaraču DMSO-voda je praćena uz katalitičko djelovanje OH<sup>-</sup> iona, glicin aniona i imidazola. Efekat ubrzanja reakcije katalizirane OH<sup>-</sup> ionima je veoma velik i bitno ovisi od aktiviteta vode u rastvaračkom sistemu. Glicin je aktivniji kao katalizator u mješovitom rastvaraču nego u čistoj vodi, iako ovaj efekat dolazi do izražaja tek kod koncentracije DMSO veće od 60 vol %. Imidazol smanjuje svoju katalitičku efikasnost sa porastom koncentracije DMSO sve do  $X_{\text{DMSO}} = 0,3$ . Do tog sastava rastvarača log  $k_{11}$  prati smanjenje pK imidazola, a kod većih koncentracija DMSO, promjena sastava rastvarača praktično ne utiče na brzinu reakcije.

Porast specifične brzine bazno katalizirane hidrolize estera u mješovitom rastvaraču DMSO — voda, je praćena u nekoliko navrata.<sup>1, 2, 3, 4, 5, 6, 7</sup> Ubrzanje ove reakcije tumači se na dva načina: s jedne strane desolvatacijom hidroksilnog iona u rastvaraču koji sadrži dipolarno aprotionsku komponentu,<sup>4</sup> dok su većina autora skloni da ovom efektu dodaju i efekat dipolarno aprotionskih rastvarača da solvatacijom stabiliziraju aktivirani kompleks delokaliziranog naboja.<sup>1, 2, 3, 7, 8</sup> Ukoliko su ova dva efekta uzročnici porasta brzine hidrolize estera, moglo bi se očekivati da specifična brzina reakcije katalizirane hidroksilnim ionima prati promjenu bazičnosti sistema izraženu preko H-funkcije. Međutim, promjena bazičnosti 0,011 M (CH<sub>3</sub>)<sub>2</sub>NOH od vode do oko 1 M H<sub>2</sub>O u DMSO, iznosi oko 10<sup>10</sup> puta<sup>9</sup>, dok porast specifične brzine najreaktivnijih nitrofenilacetata u ovom istom području promjene sastava rastvarača, ide od 10<sup>3</sup> do 10<sup>6</sup> puta<sup>7</sup>. Kvantitativno praćenje promjene brzine hidrolize estera sa postepenim porastom dipolarno aprotionske komponente u rastvaraču, je praćeno za alkil estere benzoove kiseline<sup>1, 3</sup> odnosno, supstituirane benzoove kiseline,<sup>2</sup> te etilacetata.<sup>4</sup> Rezultati ukazuju da sterički faktor alkil ili acil grupe može da promjeni osjetljivost ove reakcije na dodatak dipolarno aprotionske komponente.<sup>1, 2, 3</sup>

Detaljnija ispitivanja sa stanovišta uloge vode u mješovitom rastvaraču i njenog uticaja na promjenu brzine hidrolize estera do sada nisu

Napomena: Ovaj rad je izrađen uz materijalnu pomoć Republičkog fonda za naučni rad SRBIH.



rađena. Posebno malo literaturnih podataka ima o generalno baznoj hidrolizi estera u mješovitom rastvaraču DMSO-voda.<sup>7</sup>

Ekperimenti obuhvaćeni ovim radom usmjereni su stoga u dva pravca:

1. Ispitivanje promjene brzine hidrolize jednog supstrata (o-nitrofenilacetata), katalizirane OH<sup>-</sup> ionima u području sastava rastvarača od čiste vode do 90 vol % DMSO ( $X_{\text{DMSO}} = 0,7$ ).

2. Ispitivanje promjene brzine hidrolize istog supstrata katalizirane aminskom bazom, od kojih je jedna neutralna baza (imidazol), a druga negativno naelektrisana (glicin anion).

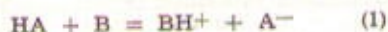
Brzina reakcije katalizirane ovim bazama praćena je u istom intervalu sastava rastvarača kao i kod katalize OH<sup>-</sup> ionima.

## EKSPERIMENTALNI DIO

### Aparati

Brzina hidrolize o-nitrofenilacetata praćena je spektrofotometrijski, na aparatima »Unicam«, SP-500 i »Durrum« Stopped — flow spektrofotometru.

pK vrijednost imidazola određena je takođe spektrofotometrijski. Mjerena je promjena ravnoteže



u ovisnosti od sastava rastvarača. Kao indikator korišten je o-nitrofenol, čiji se pK uslovno ne mjenja sa promjenom sastava rastvarača, pa je iz položaja ravnoteže 1. računata pK vrijednost puferskog sistema BH<sup>+</sup>/B.

$$\text{pK}_{\text{BH}^+/\text{B}} = \text{pK}_{\text{HA}/\text{A}^-} + \log \frac{(\text{BH}^+)}{(\text{B})} - \log \frac{(\text{HA})}{(\text{A}^-)} \quad (2)$$

Konstante su određene sa tačnošću od 3 do 4%.

Sva pH mjerenja u vodi napravljena su na pH metru firme »Radiometer« model 22 na 20°C.

### Hemikalije

Način pripravljanja i čišćenja o-nitrofenilacetata je opisan u literaturi<sup>10</sup>. Puferski sistem Im/ImH<sup>+</sup> je napravljen rastvaranjem čvrstog imidazola p. a. firme »Merck«, (koji je prethodno sušen), uz dodatak preraćunate količine HCl.

Glicin/glicin anion sistem je priređen takođe iz čvrstog glicina p. a. firme »Merck« uz dodatak preraćunate količine NaOH.

DMSO (purris B. D. H.) je čišćen vakuum destilacijom pod dušikom. Kontrola čistoće je vršena određivanjem tačke topljenja. Tačka topljenja je bila u granicama od 18,30 do 18,40°C.

Redestilisana prokuhana voda je bila upotrebljena za pravljenje svih rastvora.

### Kinetička mjerenja

Kinetički eksperimenti su vršeni na  $20 \pm 0,05^\circ\text{C}$  u svim kinetičkim mjerenjima. U eksperimentima sa imidazolom kao katalizatorom ukupna ionska sila je bila 0,2, a postizana je dodatkom preraćunate količine KNO<sub>3</sub>. pK mjerenja su takođe rađena uz konstantnu ionsku silu od 0,2. Brzina hidrolize estera praćena je spektrofotometrijski, mjerenjem brzine stvaranja o-nitrofenola na 372,5 nm, to jest na izobetičkoj tački za ravnotežu o-nitrofenola — o-nitrofenolata.

Reakcija je praćena od 1 do 3 poluvremena reakcije.

## REZULTATI I DISKUSIJA

Kinetička mjerenja reakcije hidrolize o-nitrofenilacetata katalizirane  $\text{OH}^-$  ionima, sumirana su u tabeli 1. Brzine ove reakcije su praćene uz uslove za reakciju pseudo prvog reda ( $k_{\text{eksp}}$ ), a katalitička konstanta ( $k_{\text{II}}$ ) je dobivena iz odnosa  $k_{\text{eksp}}/(\text{OH}^-)$ . Reakcija katalizirana molekulama rastvarača kod eksperimentalnih uslova navedenih u tabeli 1. je manja od prosječne eksperimentalne greške koja iznosi  $\pm 3\%$ . Specifična brzina ove reakcije u vodi uz ionsku silu  $I = 1,00$ , i na  $30^\circ\text{C}$  mjerena je ranije i iznosi  $k_{\text{II}} = 25,0 \text{ l mol}^{-1} \text{ s}^{-1}$ . Rezultati mjerenja na  $30^\circ\text{C}$  i bez prisustva stranog elektrolita daju vrijednost  $k_{\text{II}} = 12,1 \text{ mol}^{-1} \text{ sec}^{-1}$ .

TABELA 1

Promjena specifične brzine hidrolize o-nitrofenilacetata sa promjenom sastava rastvarača DMSO — voda

Katalizator: NaOH (0,01 — 0,005 M);  $t = 20,00 \pm 0,05^\circ\text{C}$

vol % DMSO	$X_{\text{DMSO}}$	NaOH mol/l	$k_{\text{eksp}}$ $\text{sec}^{-1}$	$k_{\text{II}}$ $\text{mol}^{-1} \text{ sec}^{-1}$	$\log k_{\text{II}}$
0,00	0,00	0,01	0,072	7,2	0,857
20	0,061	0,01	0,082	8,2	0,914
40	0,15	0,01	0,109	10,9	1,037
60	0,27	0,01	0,260	26,0	1,415
70	0,37	0,01	0,670	67,0	1,826
80	0,50	0,01	2,56	256	2,408
85	0,59	0,005	2,75	555	2,740
90	0,70	0,005	9,00	1800	3,256

Smatramo da se radi o sistematskoj grešci jednog od autora koja za praćenje relativne promjene brzine reakcije sa promjenom sastava rastvarača nije od velike važnosti.

Kinetička mjerenja hidrolize o-nitrofenilacetata katalizirane imidazolom sumirana su u tabeli 2. Vrijednosti  $k_{\text{II}}$  su dobivene iz nagiba pravca funkcionalne ovisnosti  $k_{\text{eksp}}$  od koncentracije imidazola [Im]. Odnos  $\text{ImH}^+/\text{Im}$  je variran od 3:1, 1:3 do 1:4. Vrijednosti  $k_{\text{II}}$  kod bilo kojeg od ovih odnosa se slažu unutar  $\pm 6\%$ . Kako se apsolutna vrijednost koncentracije katalizatora kreće od 0,008 do oko 0,2 M, smatramo da su slaganja u  $k_{\text{II}}$  zadovoljavajuća. Katalitički efekat imidazola u mješovitom rastvaraču DMSO-voda, praćen je kod konstantne ionske sile  $I = 0,2$  (uz dodatak  $\text{KNO}_3$  kao neutralne soli).

Rezultati mjerenja Brucie-a i saradnika<sup>11</sup> daju vrijednost specifične brzine u vodi za katalizator imidazol  $k_{\text{II}} = 1,07 \text{ l mol}^{-1} \text{ sec}^{-1}$  na  $30^\circ\text{C}$  i uz ionsku silu  $I = 1,0$ . Rezultati mjerenja brzine hidrolize o-nitrofenilacetata kod eksperimentalnih uslova navedenih u tabeli 2. i na  $30^\circ\text{C}$  daju  $k_{\text{II}} = 0,93 \text{ l mol}^{-1} \text{ sec}^{-1}$ . Razlika u vrijednosti  $k_{\text{II}}$  od  $14\%$  je nešto veća od eksperimentalne greške, što može da se pripíše razlici u ionskoj sili, koja nije zanemarujuća.



Rezultati mjerenja brzine hidrolize o-nitrofenilacetata u mješovitom rastvaraču DMSO-voda uz katalizator glicin anion, sumirani su u tabeli 3. Ionska sila je određena koncentracijom glicin aniona i kretala se u intervalu od 0,02 M do 0,04.

TABELA 2

Promjena specifične brzine hidrolize o-nitrofenilacetata sa promjenom sastava rastvarača DMSO — voda

Katalizator: Imidazol (0,008 do 0,2 M)

Odnos  $\text{ImH}^+$  prema  $\text{Im} = (3:1); (1:3); (1:4)$   $t = 20,0 \pm 0,1^\circ\text{C}$

$X_{\text{DMSO}}$	(Imidazola) ( $\text{mol} \cdot \text{l}^{-1}$ ) $\cdot 10^3$	$\text{ImH}^+ : \text{Im}$	$k_{\text{obs}} \cdot 10^3$ $\text{sec}^{-1}$	$k_{\text{II}}$ $\text{l mol}^{-1} \text{sec}^{-1}$	$2 + \log k_{\text{II}}$
0,00	3,0	3:1	2,13		
0,00	5,0	3:1	3,01		
0,00	7,0	3:1	4,21		
0,00	9,0	3:1	6,20	0,63	2,800
0,028	3,0	3:1	1,54		
0,028	5,0	3:1	2,67		
0,028	6,0	3:1	2,53		
0,028	7,0	3:1	2,97		
0,028	9,0	3:1	3,36	0,37	2,568
0,060	3,0	3:1	0,99		
0,060	5,0	3:1	1,48		
0,060	7,0	3:1	1,90		
0,060	9,0	3:1	2,48	0,25	2,398
0,10	3,0	3:1	0,56		
0,10	5,0	3:1	0,86		
0,10	7,0	3:1	1,17		
0,10	9,0	3:1	1,33	0,13	2,114
0,14	5,0	3:1	0,418		
0,14	8,0	3:1	0,726		
0,14	9,0	3:1	0,853		
0,14	11,0	3:1	1,06	0,095	1,980
0,27	8,0	3:1	0,330		
0,27	16,0	3:1	0,590		
0,27	24,0	3:1	0,820		
0,27	32,0	3:1	1,10	0,032	1,501
0,50	8,0	3:1	0,147		
0,50	12,0	3:1	0,216		
0,50	16,0	3:1	0,288		
0,50	20,0	3:1	0,388	0,018	1,256
0,50	60,0	1:3	0,97		
0,50	90,0	1:3	1,47		
0,50	120,0	1:3	1,92		
0,50	150,0	1:3	2,46	0,016	1,204
0,50	64,0	1:4	1,20		
0,50	128,0	1:4	2,15		
0,50	160,0	1:4	2,73		
0,50	192,0	1:4	3,18	0,017	1,230
0,71	64,0	1:4	1,07		
0,71	83,2	1:4	1,48		
0,71	96,0	1:4	1,59		
0,71	128,0	1:4	2,16	0,0171	1,232

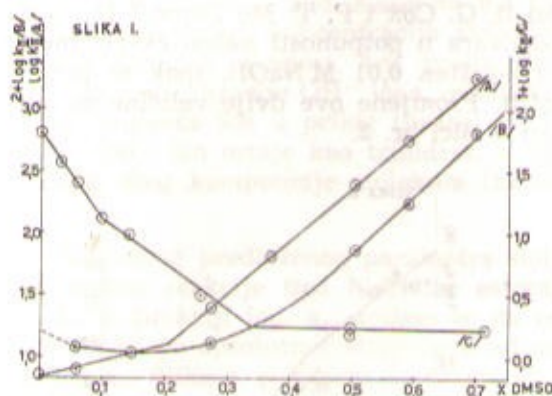
TABELA 3

Promjena specifične brzine hidrolize o-nitrofenilacetata sa promjenom sastava rastvarača DMSO — voda

Katalizator:  $\text{NH}_2\text{CH}_2\text{COO}^-$  (0,02 do 0,04 M); Odnos HA:A<sup>-</sup>=1:4 i 1:8; t=20.0±0,05°C

vol % DMSO	( $\text{NH}_2\text{CH}_2\text{COO}^-$ ) (mol·l <sup>-1</sup> )	Puferski odnos (gl:gl <sup>-</sup> )	$k_{\text{exp}}$ (sec <sup>-1</sup> )	$k_{\text{H}}$ l·mol <sup>-1</sup> sec <sup>-1</sup>	log $k_{\text{H}}$
20	0,04	1:4	0,048	1,20	0,080
40	0,04	1:4	0,044	1,10	0,042
60	0,04	1:4	0,054	1,35	0,130
80	0,02	1:8	0,156	7,80	0,892
85	0,02	1:8	0,360	18,0	1,256
90	0,02	1:8	1,34	67,0	1,826

U intervalu sastava rastvarača od 20 do 60 vol % DMSO vršena je kontrola doprinosa  $\text{OH}^-$  iona ukupnoj brzini reakcije<sup>12</sup>. Ekstrapolacija na koncentraciju katalizatora 0, daje odsječak čija je veličina unutar eksperimentalne greške (±3%). Kod većih koncentracija dipolarno aprotonske komponente, ekstrapolacija na nultu koncentraciju katalizatora nije vršena, te se vrijednosti  $k_{\text{H}}$  dobivene iz odnosa  $k_{\text{exp}}/(\text{gl}^-)$  mogu primiti sa izvjesnom rezervom.



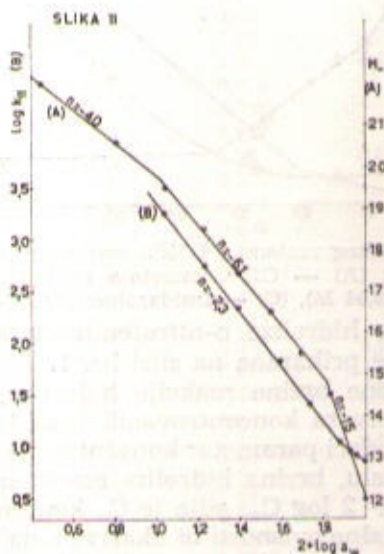
Slika br. 1 — Efekat molskog razlomka DMSO na brzinu reakcije hidrolize o-nitrorenilacetata katalizirane: (A) —  $\text{OH}^-$  ionovima (0,01 M), (B) — Glicin anionom (0,02 — 0,04 M), (C) — Imidazolom (0,008 — 0,2 M)

Promjene brzine hidrolize o-nitrofenilacetata sa molskim razlomkom DMSO grafički je prikazana na slici br. 1.

Ovisnost specifične brzine reakcije hidrolize estera sa promjenom bazičnosti vodenih rastvora koncentrovanih baza teoretski su obradili G. Yagil i M. Anbar<sup>13</sup>, uvodeći parametar koncentracije slobodne vode u izraze za brzinu. U tom smislu, brzina hidrolize estera treba da prati funkciju  $H_- + \log C_w$  ili  $H_- + 2 \log C_w$ , gdje je  $C_w$  koncentracija slobodne vode. Ova dva tipa funkcionalne ovisnosti bi ukazivala na to da li se tetraedarski međuproizvod spontano raspada na produkte, ili njegov raspad ide uz sudjelovanje vode kao reaktanta.



Promjena bazičnosti 0,011 M  $(\text{CH}_3)_4\text{NOH}$  u rastvaraču DMSO-voda je takođe obrađena sa stanovišta postojanja slobodne vode u mješovitom rastvaraču.<sup>14</sup> Ovo je, međutim, moguće samo do one granice sastava rastvarača dok slobodne vode još ima. Za sastav rastvarača  $X_{\text{DMSO}} > 0,5$ , račun pokazuje da je ova veličina zanemarljivo mala. Eksperiment s druge strane pokazuje veliki porast bazičnosti rastvaračkog sistema sa smanjenjem ukupne koncentracije vode u rastvaraču.<sup>9</sup> Isto tako se i hemijske reakcije odvijaju i preko molskog razlomka  $X_{\text{DMSO}} = 0,5$ , veoma često znatno brže nego kod manjih molskih razlomaka DMSO. Te činjenice govore u prilog pretpostavke da je energija hidratizirajućeg  $\text{OH}^-$  iona u koncentrovanim rastvorima DMSO bitno povećana, i da je voda u kompleksu sa DMSO hemijski aktivna. Kao doprinos ovoj tvrdnji, Bruice i saradnici daju mjerenja provodljivosti  $\text{OH}^-$  iona u 1 M  $\text{H}_2\text{O}$  u DMSO, koja je daleko bliža provodljivosti velikih aniona nego provodljivosti npr.  $\text{Cl}^-$  iona.<sup>15</sup> U principu se može očekivati da promjena specifične brzine hidrolize estera prati promjenu bazičnosti sistema, a da su obje ove veličine u uskoj ovisnosti ne od količine slobodne vode (tj. vode koja nije vezana niti za rastvarač niti kao hidratacijska voda), nego od aktiviteta ukupne vode u sistemu. Koeficijente aktiviteta vode u mješovitom rastvaraču DMSO-voda na 25°C izračunali su B. G. Cox i P. T. Mc Tigue.<sup>10</sup> H<sub>+</sub> funkcija za 0,011 M  $(\text{CH}_3)_4\text{HON}$  ne odgovara u potpunosti našim eksperimentalnim uslovima, gdje je kao baza korišten 0,01 M NaOH, ipak se polukvantitativna porađenja mogu vršiti. Promjene ove dvije veličine sa aktivitetom vode u rastvaraču date su u slici br. 2.



Slika br. 2 — (A) — Zavisnost H-funkcije od log (aktiviteta vode) u mješovitom rastvaraču DMSO — voda

(B) — Ovisnost log (katalitičke konstante hidrolize  $\text{OH}^-$  ionima) od log (aktiviteta vode) u mješovitom rastvaraču

Ako je  $H_-$  funkcija određena položajem ravnoteže reakcije<sup>14</sup>



njena vrijednost bi trebala da raste sa recipročnom vrijednošću četvrtog stepena aktiviteta vode u sistemu, tj.  $H_- = f(a_w)^{-4}$ . Slika br. 2 pokazuje da do molskog razlomka  $X_{DMSO} \approx 0,7$ , postoje dva nagiba: prvi ima vrijednost  $-15$ , a drugi  $-6,1$ . Tek poslije molskog razlomka DMSO od  $0,7$  nagib pravca postaje  $-4,0$ . Nagib veći (u apsolutnoj vrijednosti) od  $4$  mogli bi biti u vezi sa većom solvatacijom čestica lijeve strane jednačine  $3$ , a najvjerojatnije dodatnom solvatacijom osnovne specije  $OH^-(H_2O)_3$  od strane slobodne vode.

Ostaje problem, kako objasniti nagib pravca od  $-15$  u području od čiste vode do sastava rastvarača  $X_{DMSO} 0,2$ . Vrlo je vjerovatno da nagib pravca funkcionalne ovisnosti  $H_-$  od  $\log a_w$  predstavlja stvarnu razliku solvatacijskih brojeva čestica učesnika u ravnoteži (3) tek tada, kad koncentracija slobodne vode postaje dovoljno malena, da se razlika molskih volumena vode i DMSO može zanemariti<sup>14</sup> (kad  $X_{DMSO} = 0,2$   $C_{H_2O} \approx 28$  mol/l, a  $C_{DMSO} \approx 7$  mol/l. Ako svaka molekula DMSO veže 2 molekule vode, stehiometrijski slobodna voda bi bila  $28 - 14 = 14$  mol/l, dok kod  $X_{DMSO} = 0,3$   $C_{H_2O} \approx 21$  mol/l,  $C_{DMSO} \approx 9$  mol/l; stehiometrijski, koncentracija slobodne vode je  $21 - 18 = 3$  mola/l). Drugim riječima, tek poslije molskog razlomka  $X_{DMSO} = 0,7$  reakcijom neutralizacije  $OH^-$  iona, oslobađaju se samo četiri molekule vode. Ova činjenica ide u prilog tvrdnji da i u visokim koncentracijama DMSO,  $OH^-$  ion ostaje kao trihidrat, a da je energija ove specije jako povećana, zbog kompeticije molekula DMSO i  $OH^-$  iona za hidratnu vodu.<sup>15, 17</sup>

Ako umjesto Yagil-ovog predloženog parametra slobodne vode, uvedemo u izraze za brzinu reakcije tipa hidrolize estera, aktivitet vode, nagib pravca  $\log k_H$  u funkciji  $\log a_w$ , trebao bi da bude ili za jednu ili za dvije jedinice manji po apsolutnoj vrijednosti od nagiba  $H_-$  funkcije u zavisnosti od  $\log a_w$ . Slika 2. pokazuje da barem što se tiče hidrolize o-nitrofenilacetata nagib nije niti  $-5$  niti  $-4$ . Vrlo je vjerovatno da stvarni nagib funkcije  $\log k_H$  u ovisnosti od  $\log a_w$  predstavlja broj molekula vode koji se oslobađa na putu od reaktanata ka aktiviranom kompleksu. Razlika od eksperimentalnog i teoretskog nagiba u tom slučaju bi bio broj molekula vode, koja je ili zaostala kao hidratacijska voda  $OH^-$  iona, ili solvatacijska voda aktiviranog kompleksa.

Drugi dio rada odnosi se na ispitivanje promjene katalitičke efikasnosti nekih generalnih baza u sistemu DMSO-voda. Kao predstavnike odabrali smo imidazol i glicin anion. Oba suaminske baze, veoma dobri katalizatori u reakciji hidrolize nitrofenilacetata,<sup>11, 18, 19</sup> u vodenoj sredini. Kinetička mjerenja hidrolize o-nitrofenilacetata uz katalitičko djelovanje imidazola ističu dvije činjenice:

1. Brzina hidrolize opada sa dodatkom DMSO, do molskog razlomka  $X_{DMSO} \approx 0,33$ .



2. Poslije ovog molskog razlomka brzina reakcije se praktično ne mijenja sa promjenom sastava rastvarača. Molski razlomak  $X_{\text{DMSO}} = 0,33$  je veoma interesantan utoliko što je kod tog sastava stehiometrijski odnos vode i DMSO takav da je moguće kompletno ostvariti kompleks  $2\text{H}_2\text{O} \cdot \text{DMSO}$ . Ukoliko bi voda i mogla da bude aktivna komponenta u reakciji hidrolize, ona to u ovom slučaju i jeste samo dotle dok ima potpuno slobodne vode u rastvaraču. Kako je efikasnost katalizatora u uskoj vezi sa njegovom pK vrijednošću, objašnjenje smanjenja brzine reakcije pokušali smo naći u promjeni pK vrijednosti kiseline (protoniranog imidazola). Vrijednosti pK za  $\text{IMH}^+$  mjerene spektrofotometrijski uz indikator o-nitrofenol, date su u tabelama 4. i 5, a grafički su prikazane na slici br. 3, zajedno sa  $\log k_{\text{II}}$  u ovisnosti od aktiviteta vode u mješovitom rastvaraču.

TABELA 4

Indikatorski odnos o-nitrofenol — o-nitrofenolat u zavisnosti od sastava rastvarača  
DMSO — voda

Koncentracija:  $1,7 \cdot 10^{-3}$  M; Odnos  $\text{HA}:\text{A}^- = 1:1$  i  $1:2$

	vol % DMSO	HA/A <sup>-</sup>	1 + log HA/A <sup>-</sup>
420	0	1,21	1,0838
420	10	1,26	1,1037
420	20	1,19	1,0758
420	30	1,16	1,0645
430	40	1,12	1,0495
430	50	1,06	1,0262
430	60	1,16	1,0645
		sr. vrij. 1,16	sr. vrij. 1,0668
420	0	0,65	0,8153
420	10	0,61	0,7840
420	20	0,67	0,8250
420	30	0,64	0,8090
430	40	0,57	0,7579
430	50	0,56	0,7518
		sr. vrij. 0,62	sr. vrij. 0,7905

Praktično paralelno smanjenje pK vrijednosti i  $\log k_{\text{II}}$  sa  $\log a_w$  može da objasni promjenu katalitičke efikasnosti imidazola, barem u početnom intervalu ove funkcionalne ovisnosti.

Veoma važna razlika između imidazola i glicina je u tome, što je glicin anion negativno naelektrisana čestica, koja bi kao takva, mogla da se ponaša sasvim različito od imidazola u datom rastvaračkom sistemu.<sup>20</sup>

Kinetička mjerenja pokazuju veoma malu promjenu specifične brzine reakcije kod malih molskih razlomaka DMSO. Praktično, do znatnog ubrzanja reakcije dolazi tek kod  $X_{\text{DMSO}}$  većeg od 0,3. Znatna količina slobodne vode kod manjeg molskog razlomka od 0,3, ukazuje na mogućnost da energija glicin aniona ostaje praktično ista kao i u vodi, a

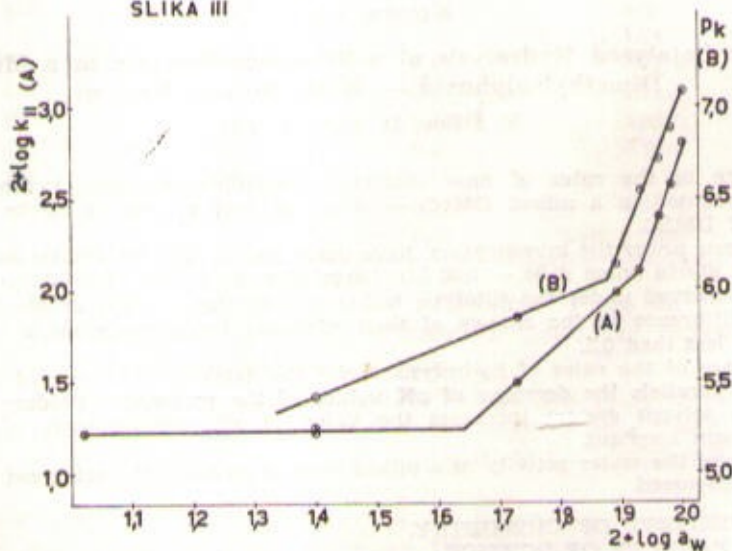
TABELA 5

Indikatorski odnos *o*-nitrofenol — *o*-nitrofenolat i  $pK_{\text{tit}}^{+}/m$  vrijednost u zavisnosti od sastava rastvarača DMSO — voda, uz 1m/1mH puferski sistem, koncentracije  $10^{-2}M$

Koncentracija: HA =  $3,6 \cdot 10^{-6}M$ ; Odnos 1:2 i 1:1

	B/BH <sup>+</sup>	vol % DMSO	HA/A <sup>-</sup>	log HA/A <sup>-</sup>	$pK_{\text{tit}}^{+}/m$
420	1,00	0	1,10	0,0420	7,08
420	1,00	10	1,73	0,2389	6,88
420	1,00	20	2,49	0,3966	6,72
420	1,00	30	3,84	0,5844	6,54
430	1,00	40	9,88	0,9946	6,13
430	1,00	50	18,60	1,2745	5,85
430	1,00	60	25,15	1,4005	5,42
420	0,50	0	0,56	0,7449—1	7,08
420	0,50	10	0,80	0,9043—1	6,92
420	0,50	20	1,18	0,0729	6,75
420	0,50	30	2,08	0,3192	6,50
430	0,50	40	4,32	0,6351	6,18
430	0,50	50	10,07	1,0032	5,82

SLIKA III



Slika br. 3 — (A) — Zavisnost log (katalitičke konstante) reakcije hidrolize katalizirane imidazolom; (B) —  $pK$ , protoniranog imidazola, od log (aktiviteta vode) u mješovitom rastvaraču DMSO — voda



kod većih koncentracija DMSO, može se bitno povećati uslijed smanjene solvatacije. Veoma bi interesantno bilo ispitati promjenu pK vrijednosti glicina i uporediti je sa promjenom specifične brzine ove reakcije.

## LITERATURA

1. D. D. Roberts, *L. Org. Chem.*, 29, (1964), 2039, 2714.
2. D. D. Roberts, *ibid.*, 30, (1965), 3516.
3. D. D. Roberts, *ibid.*, 31, (1966), 4037.
4. E. Tommila, M. L. Murto, *Acta Chem. Scand.*, 17, (1963), 1947.
5. G. V. Rao, N. Venkatasubramanion *Aust. J. Chem.*, 24, (1971), 201.
6. G. V. Rao, N. Venkatasubramanion, *Tetrahedron Lett.*, 52, (1967), 5275.
7. T. C. Bruice, A. Turner, *J. Am. Chem. Soc.*, 92, (1970), 3422.
8. A. J. Parker, *J. Chem. Soc.*, (1961), 1328.
9. D. Dolman, R. Stewara, *J. Can. Chem.*, 45, (1967), 911.
10. B. Holmquist, T. C. Bruice, *J. Amer. Chem. Soc.*, 91, (1969), 2982.
11. B. Holmquist, T. C. Bruice, *ibid.*, 91, (1969), 2985.
12. T. Škerlak, V. Šišlov, Elaborat ugov. teme br. 3367/1 sa Saveznim fondom za finansiranje naučnih djelatnosti SFRJ i Republičkim fondom za naučni rad SRBIH od 1. 10. 1970. god.
13. G. Yagil, M. Aibar, *J. Amer. Chem. Soc.*, 85 (1963), 2376.
14. G. Yagil, *J. Phys. Chem.*, 73, (1969) 1610.
15. R. Goitein, T. C. Bruice, *ibid.*, 76, (1972), 432.
16. B. G. Cox, P. T. M. Tuqie, *Austral. J. Chem.*, 20, (1967), 1815.
17. C. H. Rochester »Acidity Funkcions« Academic Press 1970. str. 232.
18. T. C. Bruice, G. L. Schmir, *J. Amer. Chem. Soc.*, 79, (1957), 1663.
19. M. L. Bender, B. W. Turnquest, *ibid.*, 79, (1952), 1652.
20. A. J. Parker, *Chem. Rev.*, 69, (1969), 1.

## SUMMARY

### Base Catalysed Hydrolysis of o-Nitrophenylacetate in a Mixed Dimethylsulphoxid — Water Solvent System

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Change of the rates of base catalysed o-nitrophenylacetate hydrolysis has been investigated in a mixed DMSO — water solvent system of 0,0 to 0,7 mole fraction of DMSO.

Catalysts under the investigation, have been: NaOH (0,01 M), Imidazole (0,008 — 0,2 M) and glycin anion (0,04 — 0,08 M). Large increase in the rates of the reaction has been observed under the catalytic action of OH<sup>-</sup> ion (5 · 10<sup>2</sup>) or glycine anion (60); the difference in the change of their efficiency being noticable in a solvent with X<sub>DMSO</sub> less than 0,3.

Decrease of the rates of hydrolysis under the catalytic influence of imidazole practically parallels the decrease of pK values of the protonated imidazole. When X<sub>DMSO</sub> in a solvent system increases the value of 0,3, specific rates of the reaction remain constant.

A role of the water activity in a mixed solvent on the OH<sup>-</sup> catalysed reaction, has been discussed.

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