

STUDY OF EQUILIBRIA IN CADMIUM BROMIDE COMPLEXES SOLUTIONS FROM THE ASPECT OF THEIR QUANTITATIVE DETERMINATION

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Abstract: The study of equilibria established in cadmium bromide complexes solutions was performed voltammetrically, by applying the linear sweep technique on the hanging mercury drop electrode, HMDE. In the studied systems the initial cadmium-ion concentration was equal, and the concentration of ligands, bromide ion, was gradually increased along with maintaining the pH-value and ion force of the solution at the constant values. The resulting shifts of the voltammogram peak reduction potential, which come as a result of the change in the electroactive species concentration due to the increase of the ligand concentration, were treated by the method of DeFord-Hume. In this manner four cadmium bromide complexes species were detected and their stability constants were determined. All obtained stability constants matched the literature data in a satisfactory manner.

Key words: cadmium, bromide-complexes, stability constants, voltammetry.

Introduction

Cadmium is one of the most toxic metals in our environment. That is why cadmium was and still is a subject of intensive studies. There is a particular interest in studying the influence of its presence in a solution, both in the form of a “free ion”, but also in the form of a complex.

In the natural liquid media, like natural waters, rivers and lakes, sea waters and body fluids, due to the conditions present there, cadmium is more often found in the form of complex compounds, and therefore the interest in studying complex species is much bigger (Raspor, 1980). The distribution of individual complex species and free metal ion will depend on the equilibrium established in the system, and its position is determined by the conditions under which the system is placed. The mentioned studies were conducted with constant parameters: temperature, pressure, ion force, pH-value of the solution and overall concentration of the metal ion. The position of equilibrium in the system, in which there exist the conditions for complex formation, will depend on the concentration of the creator of a complex or ligand, i.e. ion or dipole molecule that coordinates the metal ion.

In the complexation reactions, ligands bind to a central metal ion gradually, building different complex species. In the solution an equilibrium state gets established comprising all complex forms that exist in the given moment. Each complex species has its own, specific chemical and toxicological characteristics, so that each species by its presence in an adequate quantity and in its own manner contributes to the reactions that can take place in the given media. Therefore, the knowledge of the concentrations of individual complex species in liquid media is significant for understanding and assessing their effect on pollution and biotoxicological characteristics (Bernhard, Brinckman & Sadler, 1986).

Since it is still not possible by direct measuring to determine the concentrations of individual complex species, the information on this can be obtained only based on the knowledge of the total concentration of metal ion, total concentration of ligands and knowledge of adequate stability constants that quantify each individual equilibrium reaction of forming an adequate complex form. By knowing the mentioned values

it is possible by the calculations to obtain the information on how the metal ion is distributed among the individual complex forms. This manner of determining the concentration of individual complex species of metals requires the knowledge of exact numerical values of the adequate stability constants.

The stability constants of metal complexes can be determined by various methods, like: spectroscopy, i.e. atomic absorption spectroscopy, AAS, atomic emission spectroscopy, AES, inductively coupled plasma mass spectroscopy, ICP-MS, X-ray fluorescence, XRF, potentiometry and voltammetry. The spectroscopic techniques are long-lasting, they require complicated procedures, sophisticated instrumentation and cannot be used for the routine study of a big number of samples (Yanping, Wanzhi, Xiaohua, Jinxiang & Jian, 2007). For that reason, voltammetric methods and techniques are widely applied in the study of complexation of metal ions with different ligands and speciation of complex forms, because they are characterized by attractive variants, like: susceptibility, selectivity, simplicity of operational procedures and mobility (Grabaric, B., Grabaric, Z., Diaz-Cruz, Esteban & Casassas, 1998). They are also very much suitable for the studies in model-systems and for determining stability constants (DeFord & Hume, 1951).

Materials and Methods

All used chemicals: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Carlo Erba Reagenti, Italy), NaBr (Kemika, Croatia), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Semikem, Bosnia and Herzegovina), HClO_4 , 70 % (Lachema, Czech Republic), were of a high degree purity. The solutions were prepared by using redistilled water.

The electrochemical measurements were conducted by using the voltammetric technique with the linear change of potential on the stationary electrode, i.e. linear sweep voltammetry, LSV, on the hanging mercury drop electrode, HMDE. For generating the impulse voltage and for observing the course of voltammetric functions of current-voltage, the apparatus used consisted of three-electrode electrochemical cell, Princeton Applied Research, model 303A, with the working, referential and auxiliary electrode, potentiostat/galvanostat PAR, model 263A and the computer with the installed program, model 270/250 Research Electrochemistry Software, version 4.3. Ag/AgCl electrode ($E = 0.222 \text{ V}$) was used as a referential electrode, and Pt-wire was used as an auxiliary electrode. The pH meter, pH Meter HANNA pH 21, was used for measuring pH-value of the solution. The voltammetric measurements were conducted in the electrochemical cell of small volume of only 10 cm^3 . Before the beginning of the voltammogram registration, the working solution was deaerated by transmitting a slow current of inert gas. For that purpose here we used nitrogen that had been previously cleaned from the potential traces of the leftover oxygen by filtering through a wash bottle with the solution of ammonium metavanadate, and then washed by filtering through a wash bottle with the redistilled water. The samples were not thermostated due to the usage of the electrochemical cell of small volume, but all experiments were conducted at $25 \pm 2^\circ \text{C}$.

The concentration of cadmium(II)-ions was in all samples equal and amounted to $5 \cdot 10^{-5} \text{ moldm}^{-3}$. The solution ion force in all samples was maintained constant and amounted to $\mu = 4 \text{ moldm}^{-3}$. The pH-value of all samples was also maintained constant and amounted to $\text{pH} = 2$, and it was adjusted by using perchloric acid with the concentration of $0,01 \text{ moldm}^{-3}$. The concentration of ligand, bromide ion, was gradually increased in the scope from 0 to 4 moldm^{-3} , but in such a way that the ion force of the solution was maintained constant: $(4 - x) \text{ moldm}^{-3} \text{ NaClO}_4 + x \text{ moldm}^{-3} \text{ NaBr}$.

The instrumental parameters defining the conditions under which voltammetric scanning of samples was conducted, were as follows: period of deaeration 240 s, period of establishing equilibrium 30 s, initial potential, $E_{\text{init}} = -0,350 \text{ V}$, final potential, $E_{\text{fin}} = -1,000 \text{ V}$. Measurements were conducted at the speed of potential change of 20 mVs^{-1} .

In voltammetry, the characterization of kinetically labile complexes (ML_n) is usually based on ob-

serving the shift of the reduction signal due to the increase of ligand concentration with the constant concentration of metal ion and fixed ion force (DeFord & Hume, 1951) (Crow, 1969). The source of this procedure lies in Nernst equation, i.e. change of the ratio of the concentrations of oxidized and reduced form of the studied redox couple. The oxidized or reduced potential of the metal ion is significantly affected by the presence of the substances that build complex compounds with that ion. Since the redox-potential of the system M^{n+}/M is proportional to the concentration of the M^{n+} -ion in the solution, it is obvious that the redox-potential of the system will be significantly changed if we add to the solution the substances that complexly bind the metal ion and so result in decreasing its concentration of a free metal ion.

By complexitating the metal ion the redox potential of the system M^{n+}/M is shifted towards more negative values up to the value that depends on the complex stability constant and concentration of the complexitating agents (Bard & Faulkner, 2000). That potential shift enables determination of the existing complex species, as well as its formation constant under the condition that the reaction on the electrode is reversible.

The calculation of the complex stability constants by the method of DeFord-Hume (DeFord & Hume, 1951) is based on the relation:

$$F_0 = \exp \left[\frac{nF}{RT} \Delta E_p + \ln \frac{(I_p)_s}{(I_p)_k} \right] = 1 + \sum_{i=1}^n \beta_n [L]^n$$

where:

F_0 - equals the function that was introduced for the suitability of representing the experimentally measured values, ΔE_p , $(I_p)_s$, $(I_p)_k$;

ΔE_p - peak potential shift, $\Delta E_p = (E_p)_s - (E_p)_k$;

$(E_p)_s$ - peak potential in the solution without the presence of ligands, i.e. peak potential of "free" metal ion;

$(E_p)_k$ - peak potential in the solution with the present ligand;

$(I_p)_s$ - peak current in the solution of "free" metal ion, i.e. without the presence of ligand in the solution;

$(I_p)_k$ - peak current in the solution with the present ligand;

β_n - cumulative stability constant; $[L]$ - ligand concentration. F , n , R and T have their usual meaning just like in Nernst equation.

In further analysis we used Leden's graphical extrapolation method (Leden, 1941) based on which the cumulative stability constants are assessed by the polynomial function of zero order, F_0 , i.e. polynomial function of a higher order, F_1, F_2, \dots, F_n defined like:

$$F_1 = F_0 - 1/[L], F_2 = F_0 - \beta_1/[L], \dots, F_n = F_0 - \beta_{n-1}/[L].$$

From the consecutive diagrams of dependence of F -functions compared to the concentration of ligands, we can notice interesting specifics, which can be helpful in determining the number of formed complexes (Chekmeneva, Diaz-Cruz, Arino & Esteban, 2006). The last complex gives the line that is parallel with the concentration axis. The line with the positive gradient, rise, indicates further process of complexitation. Other diagrams result in curved lines.

Results and Discussion

By scanning samples with the speed of potential change of 20 mVs^{-1} we got the voltammograms from which their fundamental characteristics were read out, E_p and I_p with different concentrations of bromide. These values were tabled and presented in Table 1.

Table 1. Experimentally obtained values of potential and current of the cathode peak with varying concentrations of bromide. Total concentration of cadmium-ion $5 \cdot 10^{-5} \text{ moldm}^{-3}$, $\mu=4 \text{ moldm}^{-3}$ (NaClO_4), pH_2

$[\text{Br}^-]$ [moldm^{-3}]	$(E_p)_k$ [V]	$(I_p)_k$ [nA]			
-	-0,602	-357,9	0,6814	-0,692	-596,1
0,0010	-0,604	-504,0	0,7600	-0,694	-562,3
0,0042	-0,606	-583,2	0,8255	-0,696	-542,8
0,0075	-0,608	-595,1	1,0000	-0,700	-566,7
0,0148	-0,610	-587,6	1,1363	-0,701	-624,0
0,0215	-0,612	-595,3	1,2912	-0,702	-354,3
0,0468	-0,623	-602,8	1,4672	-0,706	-373,1
0,0681	-0,629	-608,2	1,6672	-0,710	-386,6
0,1334	-0,637	-590,3	1,8945	-0,714	-369,0
0,1778	-0,642	-525,4	2,1543	-0,719	-392,4
0,2443	-0,660	-516,0	2,4662	-0,731	-394,4
0,3162	-0,665	-503,8	2,7797	-0,739	-373,7
0,3833	-0,670	-501,2	3,1586	-0,749	-412,5
0,4643	-0,676	-473,0	3,3799	-0,752	-415,9
0,5625	-0,688	-534,5	3,5892	-0,754	-393,3
			3,9812	-0,761	-453,0

Table 2. presents derived values of the cathode peak potential shift ΔE_p and ratio between the current of “free” cadmium-ion cathode peak, $(I_p)_s$, and the current of cathode peak in the presence of complexing ion, $(I_p)_k$, for adequate concentrations of bromide.

Table 2. Derived values: shift of the cathode peak potential ΔE_p and ratio between the current of “free” cadmium-ion cathode peak, $(I_p)_s$ and the current of cathode peak in the presence of complexing ions, $(I_p)_k$. Total concentration of cadmium-ion $5 \cdot 10^{-5} \text{ moldm}^{-3}$, $\mu=4 \text{ moldm}^{-3}$ (NaClO_4), pH_2

$[\text{Br}^-]$ [moldm^{-3}]	ΔE_p [mV]	$(I_p)_s / (I_p)_k$			
0,0010	2,0	0,710	0,6814	90,0	0,600
0,0042	4,0	0,614	0,7600	92,0	0,637
0,0075	6,0	0,601	0,8255	94,0	0,659
0,0148	8,0	0,610	1,0000	98,0	0,632
0,0215	10,0	0,601	1,1363	99,0	0,574
0,0468	21,0	0,594	1,2912	99,9	1,010
0,0681	27,0	0,588	1,4672	104,2	0,959
0,1334	35,0	0,606	1,6672	108,6	0,926
0,1778	40,0	0,681	1,8945	112,9	0,970
0,2443	58,0	0,694	2,1543	117,6	0,912
0,3162	63,0	0,710	2,4662	129,6	0,907
0,3833	68,0	0,714	2,7797	137,8	0,958
0,4643	71,0	0,757	3,1586	147,4	0,867
0,5625	86,0	0,669	3,3799	150,1	0,860
			3,5892	151,6	0,910
			3,9812	159,2	0,790

The data from Table 2. are used in DeFord-Hume’s expression for calculating polynomial function of the zero order, $F_0(X)$. Based on the obtained values of the functions $F_0([\text{Br}^-])$, in accordance with DeFord-Hume, other functions were also calculated: $F_1([\text{Br}^-])$, $F_2([\text{Br}^-])$, $F_3([\text{Br}^-])$ and $F_4([\text{Br}^-])$. Each function was presented in the corresponding $F([\text{Br}^-]) - [\text{Br}^-]$ diagram, and the diagrams from $F_0([\text{Br}^-]) - [\text{Br}^-]$ to $F_4([\text{Br}^-]) - [\text{Br}^-]$ are presented in figures, Fig.1., Fig.2., Fig.3., Fig.4. and Fig.5. As the final result of pro-

cessing results we obtained numerical values of the corresponding stability constants of cadmium bromide complexes: $\beta_1, \beta_2, \beta_3, \beta_4$.

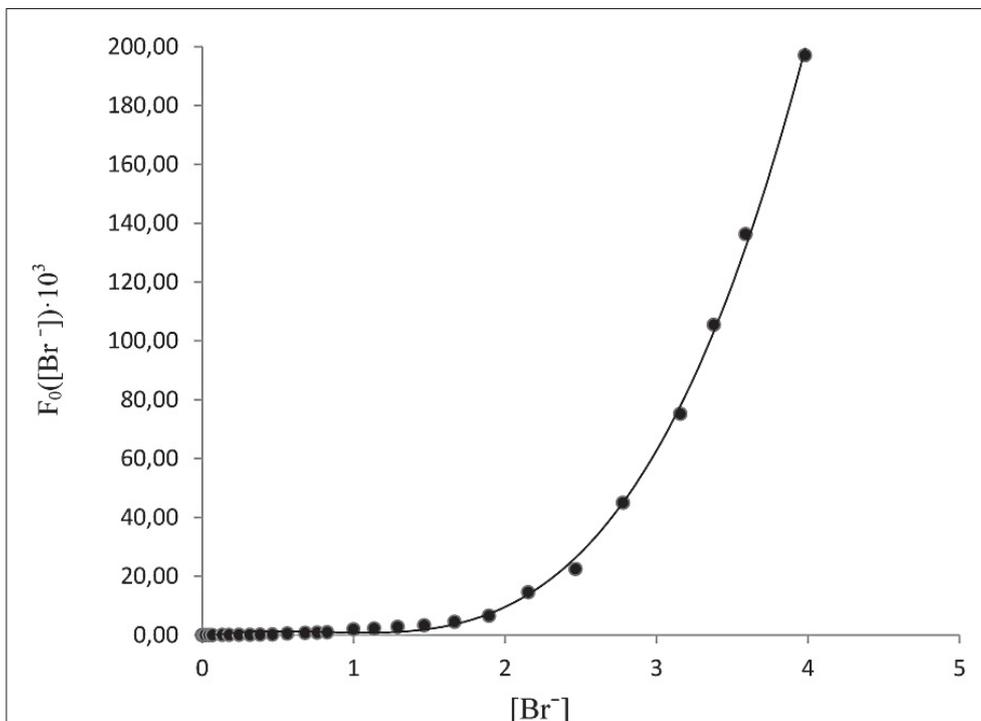


Figure 1. Dependence of function $F_0([\text{Br}^-])$ on the concentration of bromide

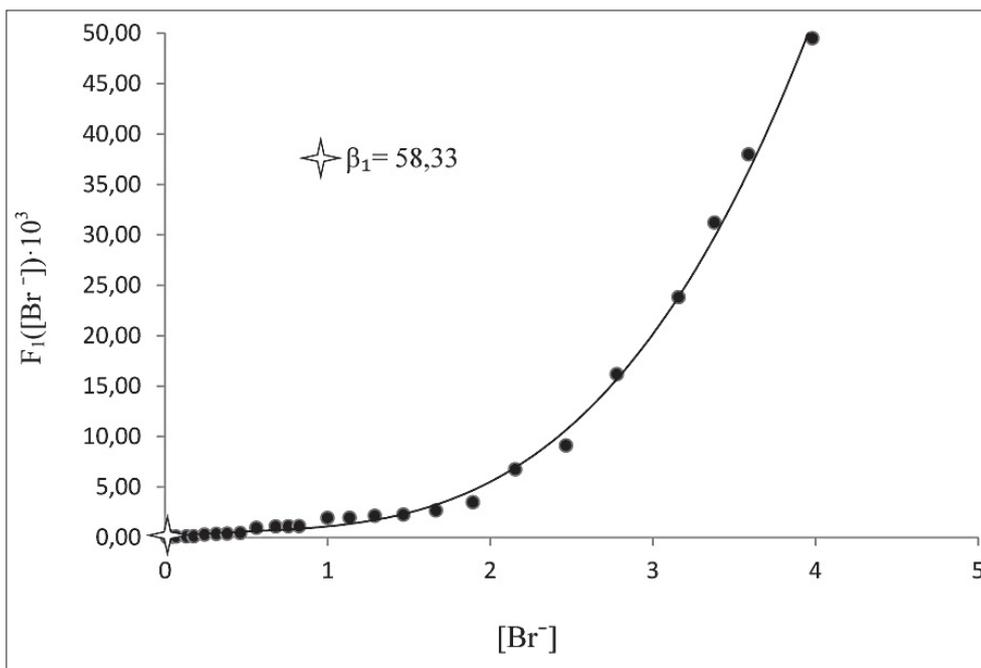


Figure 2. Dependence of function $F_1([\text{Br}^-])$ on the concentration of bromide

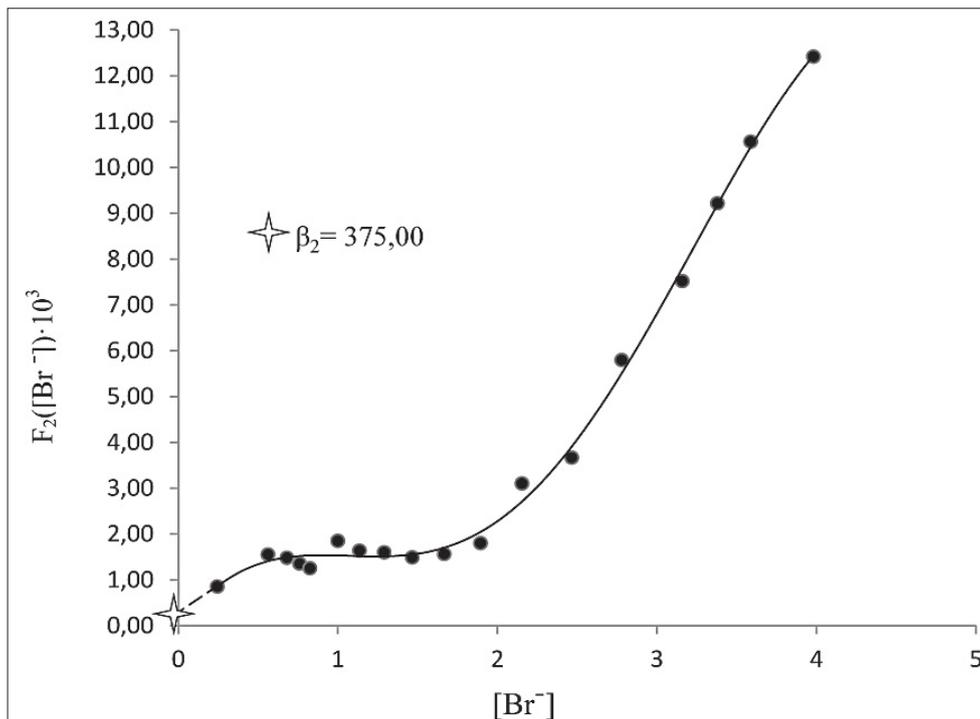


Figure 3. Dependence of function $F_2([\text{Br}^-])$ on the concentration of bromide

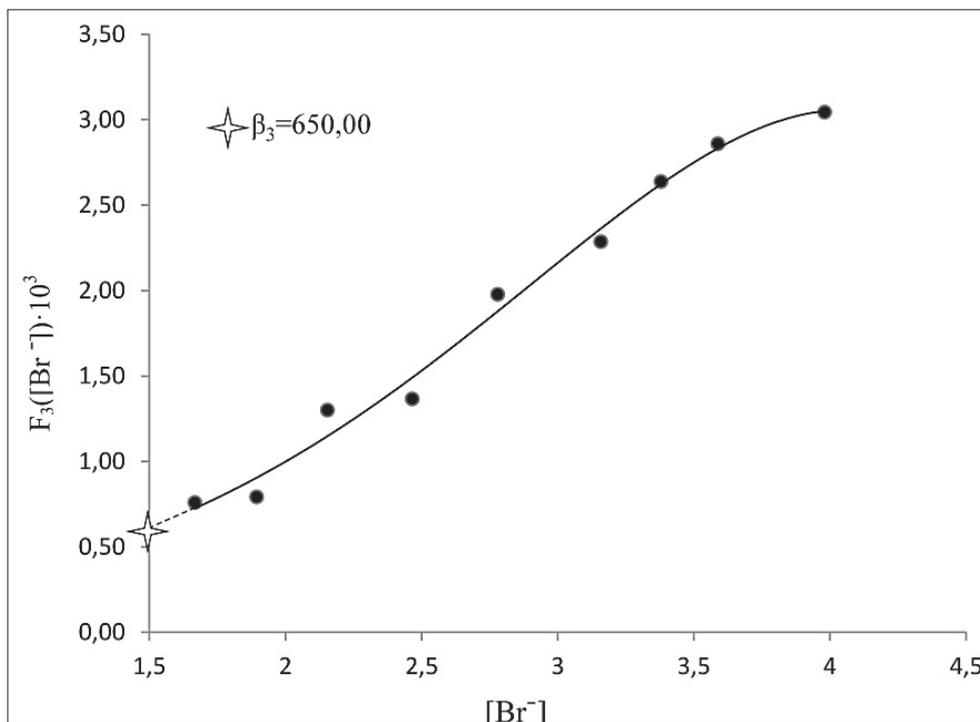


Figure 4. Dependence of function $F_3([\text{Br}^-])$ on the concentration of bromide

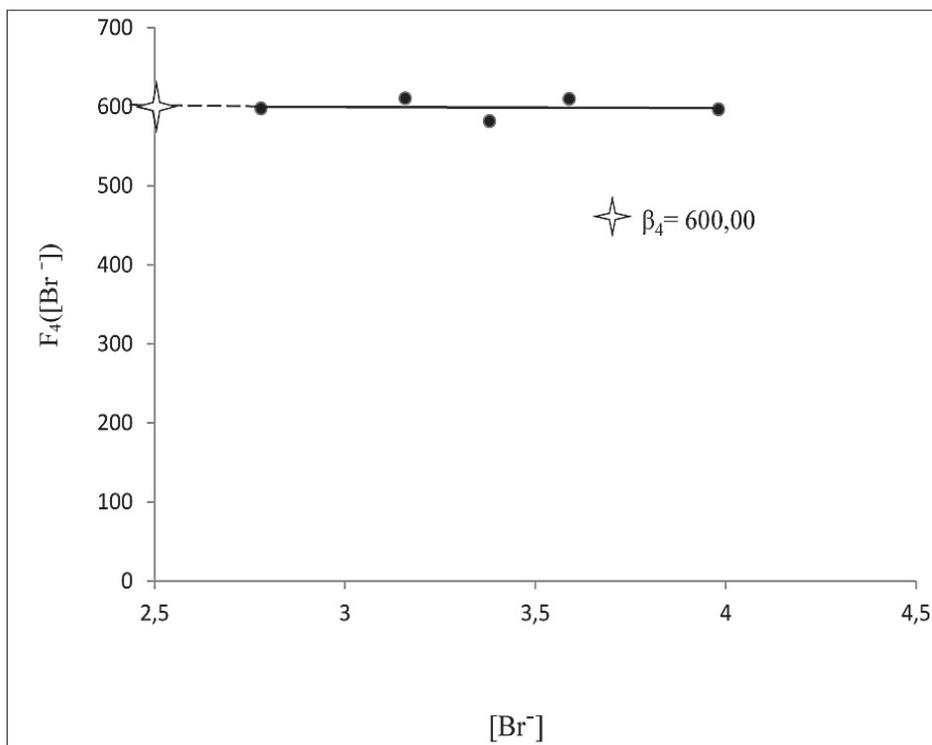


Figure 5. Dependence of function $F_4([\text{Br}^-])$ on the concentration of bromide

From the diagrams in Fig. 2., Fig.3., Fig. 4., and Fig. 5., graphically, by extrapolation of the curve on y-axis, the numerical values were determined of the cadmium bromide complex cumulative constants. For example, when the curve obtained in the in the diagram of function dependence $F_1([\text{Br}^-])$ on the bromide concentration (Figure 2.), is extrapolated on the value $[\text{Br}^-]=0$, the section on the ordinate provides the value of the constant β_1 . Accordingly, by processing diagrams in Figure 3. and Figure 4. the values of other two constants: β_2 and β_3 were also obtained.

In the diagram in Figure 5. presented values $F_4([\text{Br}^-])$ according to $[\text{Br}^-]$ give the direction parallel with the abscissa. The section of this horizontal line on the ordinate gives the value β_4 , which represents the stability constant of the complex form with the highest number of coordination.

The calculated cumulative stability constants of cadmium bromide complex and their logarithm values are as follows:

$$\begin{array}{ll} \beta_1=58,33; & \log \beta_1=1,77, \\ \beta_2=375,00; & \log \beta_2=2,57, \\ \beta_3=650,00; & \log \beta_3=2,81, \\ \beta_4=600,00; & \log \beta_4=2,78. \end{array}$$

By comparing the values of the stability constants obtained in this study with the literature values (Zelić & Branica, 1992)(Sillen & Martell, 1964)(Eriksson, 1953) we can conclude that we got a very good agreement for the values of the first two stability constants. However, the values for β_3 and β_4 , i.e. $\log \beta_3$ and $\log \beta_4$ are a little bit lower than the accessible values found in the literature. By working on the same systems different examiners found different number of complexes and adequate stability constants depending on the experimental conditions (Branica, Pižeta, Branica-Jurković & Zelić, 1989).

The cause of deviation could be in different methods for determining stability constants or different ion forces of the examined solutions.

The cumulative stability constants of different complex species of cadmium obtained by DeFord-Hume method, together with the fraction of each species in the solution calculated by Inczedy method (Inczedy, 1976), served for the construction of the diagram of distribution of cadmium-ion and its bromide complex in the examined area of bromide concentration from 0 to 3,9812 mol dm^{-3} . This diagram was presented in Figure 6. From the diagram we can see which complex species exist, i.e. dominate in the individual areas of bromide concentration.

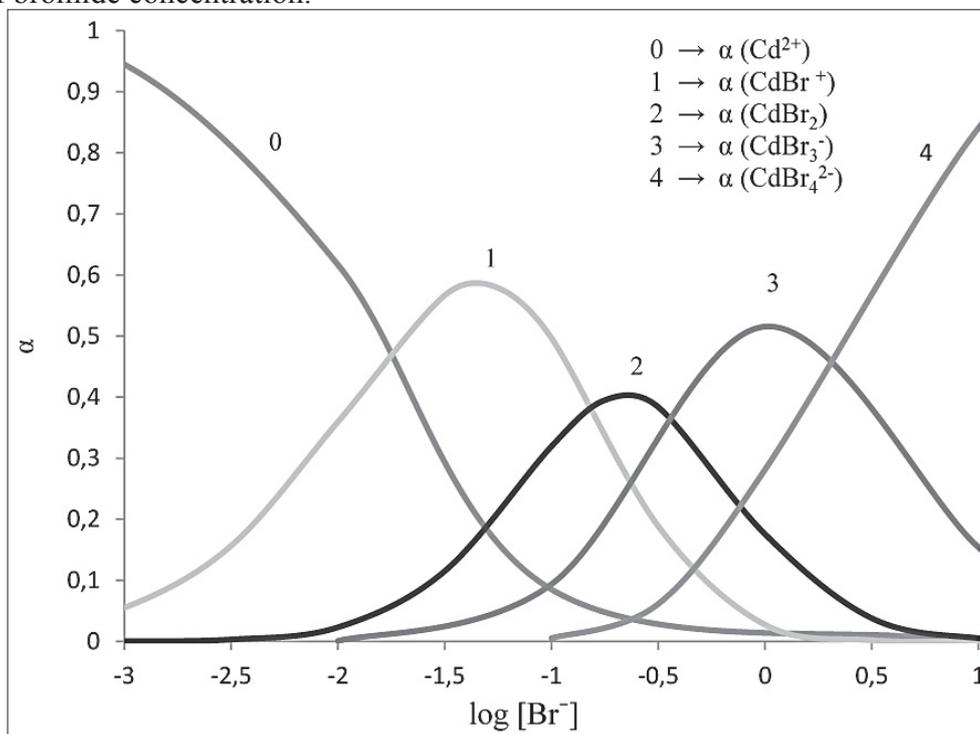


Figure 6. Distribution of cadmium-ion, free and tied in different complex species, depending on the bromide concentration. Diagram was constructed with the values obtained in this study

From the diagram in Figure 6. the values α were read out to show the distribution of Cd(II)-ions and existing complex species in the examined sample solutions. These values are presented in Table 3.

Table 3. Coefficients of distribution, α , complex species and Cd(II)-ions in the function of bromide concentration

[Br ⁻] [mol dm^{-3}]	log [Br ⁻]	$\alpha(\text{Cd}^{2+})$	$\alpha(\text{CdBr}^+)$	$\alpha(\text{CdBr}_2)$	$\alpha(\text{CdBr}_3^-)$	$\alpha(\text{CdBr}_4^{2-})$
0,0010	-3,0	0,94	0,06	0	0	0
0,0032	-2,5	0,82	0,17	0,01	0	0
0,0100	-2,0	0,62	0,36	0,02	0	0
0,0316	-1,5	0,30	0,56	0,11	0,03	0
0,1000	-1,0	0,09	0,49	0,32	0,10	0
0,3162	-0,5	0,03	0,19	0,39	0,33	0,06
1,0000	0	0,01	0,03	0,17	0,51	0,28
3,1623	0,5	0	0,01	0,04	0,38	0,57
3,9812	0,6	0	0	0,03	0,34	0,63

Based on the values α presented in Table 3. we can see that in the smallest bromide concentration of 0,0010 mol dm^{-3} there exists only complex CdBr⁺ with the portion $\alpha = 0,06$. In the concentration of bromide-ion of 0,3162 mol dm^{-3} there are present all species in the solution: from “free” Cd(II)-ion to the complex species with the highest number of coordination. In the bromide concentration of 3,1623 mol dm^{-3}

it is evident that almost entire Cd(II)-ion got tied in the complex species CdBr^+ , CdBr_2 , CdBr_3^- and CdBr_4^{2-} . Finally, based on Table 3. we can conclude that in the conditions of conducting our experiment the predominant species is CdBr^+ . This species also has the broadest area of the concentration domination.

Conclusions

This study examined the possibilities for using the linear sweep voltammetric technique, LSV in determining stability constants of cadmium bromide complexes. The experiment was conducted with the high ion force of the solution, i.e. high concentration of ligand for the purpose of obtaining complex species with the maximal number of coordination. It was proved that the methodology based on DeFord-Hume principle could be successfully applied for processing the data obtained from the voltammogram. In this manner four cadmium bromide complexes were detected with the corresponding stability constants: $\log \beta_1 = 1,77$; $\log \beta_2 = 2,57$; $\log \beta_3 = 2,81$; $\log \beta_4 = 2,78$. All obtained stability constants were in a satisfying agreement with the literature data. The measures obtained by using the voltammetric linear sweep technique can be used as an alternative for other more sophisticated techniques for quantifying the equilibria established in the solutions of the complex cadmium compounds.

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