Interaction of silver(I) ions with N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine (Quadrol)

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The compound N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine, Quadrol (abbreviated Q) reacts with silver(I) ions in aqueous solutions to form the complex ions $AgHQ^{2+}$, AgQ^+ and $AgQ(OH)$, their stability constant logarithms being 1.7 ± 0.2, 5.7 ± 0.1 and 6.3 ± 0.2, respectively.

**Key words:** silver(I), Quadrol, complex formation

INTRODUCTION

N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine (Scheme 1), which is also known as Quadrol (Q), due to its perfect chelating properties with regard to copper(II) ions is widely used as a ligand in electroless copper plating solutions [1–6]. Therefore, analysis of literature sources on the interaction of metal ions with Quadrol shows that the majority of publications deal with copper(II).

Spectrophotometric, conductometric and pH-metric titration methods were applied for investigation of Cu(II)-Q complex formation, showing that Quadrol forms a complex with Cu(II) ions in the molar ratio 1 : 1, the stability constant logarithm ($\log\beta_1$) being approximately 9 [7]. The complex of the same composition with the $\log\beta_1 = 8.45$ was identified when the pH-metric titration method was used [8]. The authors of Ref. [9] detected the presence of a diligand complex of CuQ_2^{2+} ($\log\beta_2 = 13.6$) besides CuQ^{2+} ($\log\beta_1 = 9.8$), and have investigated the crystal and molecular structure of the latter complex [10]. The presumption of the existence of more stable copper(II)-Quadrol complexes was stated in [11], and a detailed polarographic investigation of Cu(II) complex formation with Quadrol was carried out in a wide pH range. The authors observed formation of the above-mentioned com-

plexes of CuQ^{2+} and CuQ_2^{2+} ($\log\beta_1 = 10.6$ and $\log\beta_2 = 14.6$) within the pH range from 6 to 8, whereas a sharp increase in Cu(II) complexation was observed at pH over 10, showing formation of Cu(II)–Quadrol hydroxycomplexes $CuQ(OH)_2$ and $CuQ_2(OH)_2$.

According to the authors, the determined complex compounds are among the most stable Cu(II) complexes under these conditions ($\log\beta_{CuQ(OH)2} = 26.9 \pm 0.5$ and $\log\beta_{CuQ2(OH)2} = 29.1 \pm 0.3$. The pCu values are much higher than 20 at pH over 10, and this enables the existence of rather concentrated alkaline Cu(II) solutions in the presence of Quadrol [11]. Therefore, the use of Quadrol in electroless copper plating solutions is quite natural. The better technological parameters of these solutions compared with other commonly used
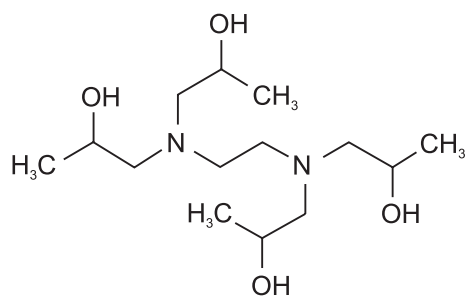
Scheme 1. Structural formula of N,N,N',N'-tetrakis-(2-hydroxypropyl)-ethylenediamine (Quadrol)

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electroless plating solutions containing tartrate or *EDTA* are apparently related to the higher stability of Cu(II) complexes with Quadrol.

Data on the interaction of other metal ions with Quadrol are not numerous. The authors of Ref. [9] have investigated Quadrol complex formation with cobalt(II), zinc(II) and lead(II), beside copper(II) (see above).

Differential pulse polarography has been used to determine the formation constants of Cd(II) and Pb(II) complexes with Quadrol. Both metal ions (M(II)) were found to form two kinds of complexes, MQ^{2+} and $MQ(OH)^+$, their stability constant logarithms being 7.98 and 11.75, and 11.3 and 13.00, respectively [12].

The same method of investigation was used to determine the composition and stability of Quadrol complexes with Bi(III). Two kinds of complexes (BiQ^{2+} and $BiQ(OH)^+$) with logarithms of stability constants equal to 12.0 and 24.0 were found [13].

The synthesis and X-ray structure of the seven-coordinate Ti(IV)(Quadrol) dimer was described. The structure was found dimeric, with each titanium atom chelating to an N_2O_5 donor set. One oxygen atom in each ligand is binucleating, thus forming a central Ti_2O_2 ring [14].

There are no quantitative data on complex formation between silver(I) and Quadrol, except the reference in a patent that the mixture of Quadrol and citric acid was used as a complexing agent for silver(I) ions in the solutions of immersion silver plating of copper [15]. Therefore, the aim of the work presented herein was to investigate silver(I) complex formation equilibria in Quadrol solutions, using the direct potentiometry technique with a silver indicator electrode.

EXPERIMENTAL

Reagents and solutions
Quadrol (98%) was obtained from Fluka. Other chemicals were obtained from Sigma-Aldrich and were either analytical or reagent grade. All chemicals were used as received.

Instrumentation
The potential of the indicator electrode (Ag) was measured by using a universal V7-16 voltmeter (Belarus) at 20 °C. The reference electrode was an Ag / AgCl electrode with a saturated KCl solution. All potentials are presented in reference to SHE. The solutions were deaerated by bubbling Ar. Measurements of pH were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode.

Calculations
The activity of free (uncomplexed) silver(I) ions (a_{Ag}) was calculated from the following equation:

$$\log a_{Ag} = (E - E_0) / 0.058, \qquad (1)$$

where E_0 is the standard redox potential of the Ag^+/Ag couple, equal to 0.799 V, and E is the measured potential of the Ag electrode.

The values of a_{Ag^+} were used to calculate the parameters of silver(I) complexes according to equation:

$$[Ag^+]_0 / a_{Ag^+} = \sum_{x_i, y_i, z_i = 0}^{N} \beta_{x_i y_i z_i} [HL]^{x_i} [L]^{y_i} a_{OH^-}^{z_i}, \qquad (2)$$

where $[Ag^+]_0$ is the total concentration of Ag(I) ions, $[HL]$ is an equilibrium concentration of monoprotonated Quadrol, $[L]$ is an equilibrium concentration of unprotonated Quadrol and a_{OH^-} stands for activity of OH^- ions.

The composition and stability constants of Ag(I) complexes was obtained during iterative approximation by minimizing the least-squares (LS) functional obtained from Eq. (2). To estimate the accuracy of the stability constants, we assumed that the potential of the silver electrode was within ±0.1 mV. If the accuracy of any stability constant diverges to infinity in the next iteration, then the deletion of such complex from the functional has no influence on the sum of least squares. In this case, we assume that such complex does not exist under these conditions.

RESULTS AND DISCUSSION

We carried out several series of experiments with different concentrations of Ag(I) and Quadrol at different pH values in solutions with pH 2–14. As can be seen from the results (Fig. 1), no changes in the Ag electrode potential are observed at pH from 2 to ca. 4, showing an absence of Ag(I) complex formation with Quadrol. With the further increase in solution pH, the potential of the Ag electrode shifts to more negative values, demonstrating a decrease in the concentration of free, i. e. uncomplexed, Ag(I) ions due to the formation of complexes. A sharp decrease in Ag(I) concentration was observed at pH over 4, i. e. when increasing the pH of solutions from
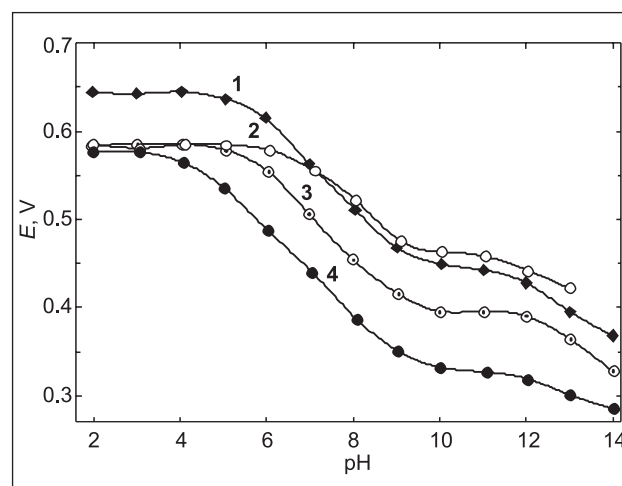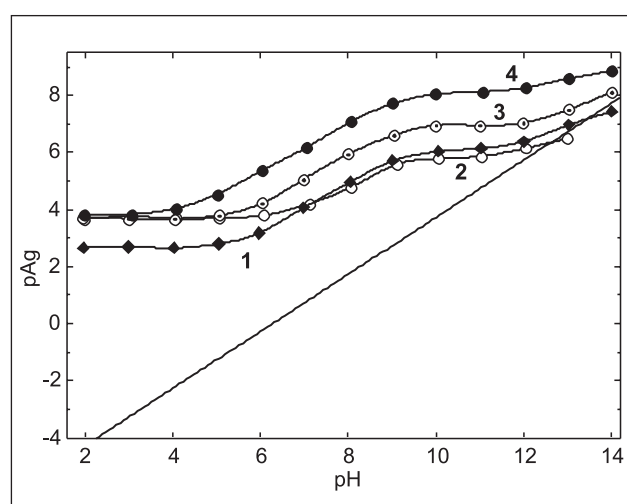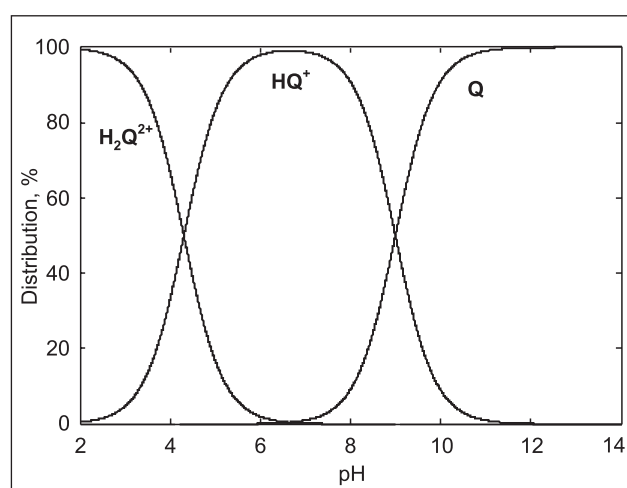

Fig. 1. Dependence of silver electrode potencial on pH. Solution composition (M): $[Ag(I)]_0 - 0.005$ (1) and 0.0005 (2–4); $[Q]_0 - 0.05$ (1 and 3), 0.005 (2) and 0.5 (4)

ca. 4 up to ca. 10. Later, at pH 10–12, the potential of the Ag electrode remained practically constant and shifted to more negative values with a further increase in solution alkalinity (Fig. 1).

One can see that the complexing ability of Quadrol depends on solution pH (Fig. 2). Therefore, we have calculated the pH-dependence of Quadrol distribution among the forms (protonated and unprotonated), using the following deprotonation values of Quadrol: pK_{a1} = 4.30 and pK_{a2} = 8.99 [17]. The results presented in Fig. 3 show that the deprotonated form of Quadrol (H_2Q^{2+}) prevails in acid solutions up to pH ca. 4.3; with the further increase in solution pH, the deprotonation of this form occurs, and the monoprotonated form of Quadrol (HQ^+) prevails in the pH region 4.4–8.9. At higher pH values, the deprotonation of the monoprotonated form

of Quadrol proceeds, and at pH over 9 the predomination of the unprotonated form of Quadrol (Q) begins and simultaneously the monoprotonated form at pH over 12 disappears (Fig. 3).

Knowing the equilibria of different forms of Quadrol and having data of measurements of the potential of the Ag electrode in solutions with different Quadrol concentrations and pH, preliminary assumptions on the composition of Ag(I)-Quadrol complexes can be made.

It is clear that the diprotonated form of Quadrol (H_2Q^{2+}) does not form complexes with silver(I) ions, since no complexation was observed in the pH region from 2 to ca. 4 where H_2Q^{2+} predominates (Fig. 3). The further increase in solution pH results in deprotonation of H_2Q^{2+} and formation of the monoprotonated form of HQ^+, which takes part in complex formation with Ag(I), since the potential of the Ag electrode shifts to more negative values (Fig. 1). At pH over 7, the share of the monoprotonated form of HQ^+ begins to decrease with an increase in the unprotonated form of Q (Fig. 3). At the same time, the potential of the Ag electrode shifts onward to more negative values, showing participation of the unprotonated form of Quadrol (Q) in the complexation of Ag(I) ions (Fig. 1). At pH over 11, Quadrol exists practically fully in the form of Q (Fig. 3), and the further increase in solution pH does not influence Quadrol equilibria. No changes in the potential of Ag(I) electrode are observed at pH 11–12 (Fig. 1). The rise in the complexation degree of Ag(I) ions at pH over 12 (Fig. 2) can be accounted for the formation of Ag(I)–Quadrol hydroxycomplex as well as with formation of the known soluble Ag(OH) and Ag(OH)$_2^-$ hydroxycomplexes [18], since the concentration of OH⁻ ions rises with an increase in pH.

Fig. 2. Relationships of pH to pAg in Quadrol-containing solutions. Solution composition (M): [Ag(I)]$_0$ – 0.005 (1) and 0.0005 (2–4); [Q]$_0$ – 0.05 (1 and 3), 0.005 (2) and 0.5 (4). The straight line represents pAg values calculated from AgOH solubility product, equal to $10^{-7.8}$ [16]

On the grounds of experimental dependencies of the silver electrode potential on pH and total Quadrol concentration and equilibria of Quadrol forms, we assumed that the silver(I) complexes containing monoprotonated or unprotonated forms of Quadrol could be formed, whereas incorporation of OH⁻ group into the composition of Ag(I)–Quadrol complex takes place in strongly alkaline solutions. As can be seen from the results obtained (Fig. 1), with an increase by one pH unit (6 < pH < 9) and a tenfold increase in the total concentration of Quadrol (at a constant pH value), the potential of the silver electrode is shifted approximately by 60 mV, showing participation of one Quadrol molecule (monoprotonated or unprotonated) in Ag(I) complex formation. Additionally, formation of dinuclear complexes was excluded, since the silver electrode potential changes by ca. 60 mV on a 10-fold decrease of the total Ag(I) concentration at constant pH (cf. curves 1 and 3 in Fig. 1), showing participation of one Ag(I) ion in complex formation.

Calculations using the least-squares technique indicated the presence of three kinds of Ag(I)–Quadrol complexes in solutions, namely $AgHQ^{2+}$, AgQ^+ and AgQ(OH), with their stability constant logarithm values equal to 1.7 ± 0.2, 5.7 ± 0.1 and 6.3 ± 0.2, respectively. It is worth noting that the

Fig 3. Dependence of distribution of Quadrol among the forms on solution pH (pK_{a1} = 4.30 and pK_{a2} = 8.99)
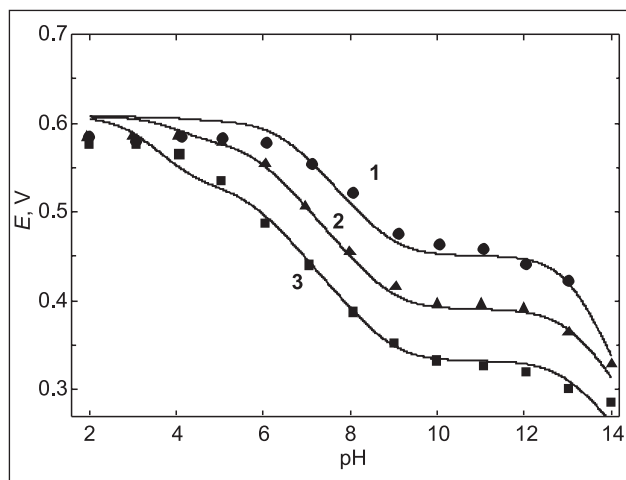
Fig. 4. Dependence of silver electrode potencial on pH. Solution composition (M): [Ag(I)]$_0$ − 0.005, [Q]$_0$ − 0.005 (1), 0.05 (2) and 0.5 (3). The symbols represent experimental values, the solid lines–values calculated from stability constants

possible existence of Ag(I) complexes containing two Quadrol species (protonated or unprotonated) or soluble silver(I) hydroxycomplexes of Ag(OH) and Ag(OH)$_2^-$ (logβ_1 = 3.02 and logβ_2 = 4.69 [18]) was also considered in the calculations.

Comparison of the experimentally determined potential values of the silver electrode with that calculated on the grounds of the determined stability constants of Ag(I)–Quadrol complexes (AgHQ^{2+}, AgQ$^+$ and AgQ(OH)) and soluble silver(I) hydroxycomplexes (Ag(OH) and Ag(OH)$_2^-$) shows a rather good agreement and confirms propriety of the characteristics of Ag(I)–Quadrol complexes (Fig. 4).

The characteristics of Ag(I) complexes obtained from experimental data are in accordance with the general behaviour of these Ag(I)–Quadrol solutions. The solutions become turbid, and AgOH precipitates as the pH increases to over 13, the Ag(I) and Quadrol concentrations being 0.0005 and 0.005 M, respectively. The calculations using Ag(I)–Quadrol complex stability constants have shown that the concentration of free silver ions at pH over 13 indeed exceeds the value allowed by the Ag(OH) solubility product.

Calculations of silver ion distribution among the complexes (Fig. 5) under conditions of a ten-fold to thousand-fold excess of ligand (Quadrol) showed that in all cases the AgQ$^+$ complex predominates in solutions with pH 6–13. At higher pH values, it converts either to Ag(OH)$_2^-$ or to AgQ(OH). Domination of AgHQ^{2+} was observed in acidic solutions at pH 4–6 under conditions of a hundred-fold or higher excess of Quadrol.

CONCLUSIONS

The newly obtained data on the composition and stability of silver(I) and Quadrol complexes show that, depending on solution pH, Quadrol forms three different complexes. AgHQ^{2+} (logβ = 1.7 ± 0.2) predominates in acidic solutions, AgQ$^+$
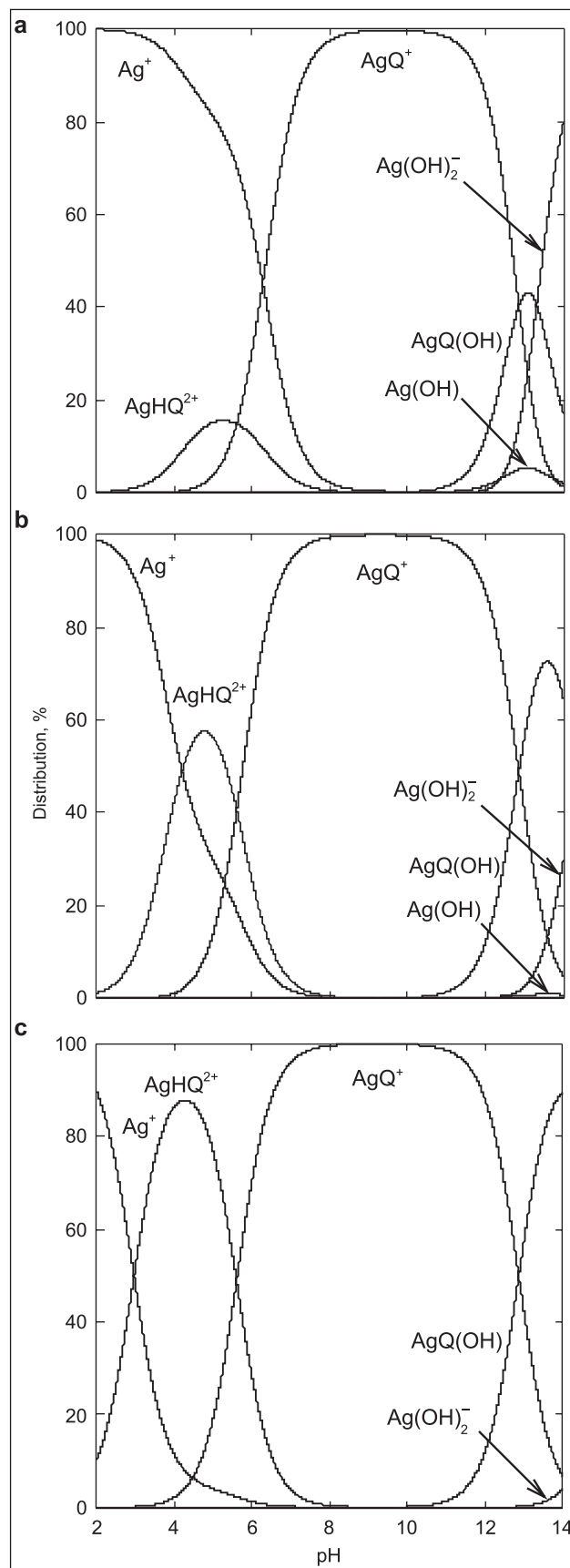

Fig. 5. Relationships between Ag(I) distribution and pH in Quadrol-containing solutions. Solution composition (M): [Ag(I)]$_0$ −0.0005; [Q]$_0$: a − 0.005, b − 0.05 and c − 0.5

(logβ = 5.7 ± 0.1) in weakly acidic, neutral and alkaline media, whereas AgQ(OH) (logβ = 6.3 ± 0.2) prevails in strongly alkaline solutions when the excess of Quadrol is hundredfold or higher.

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SIDABRO(I) SĄVEIKA SU N,N,N',N'-TETRAKIS-(2-HIDROKSIPROPIL)-ETILENDIAMINU (KVADROLU)

S a n t r a u k a

Nustatyta, kad N,N,N',N'-tetrakis-(2-hidroksipropil)-etilenediaminas (Q), pagal tirpalo pH, sudaro su sidabro(I) jonais šios sudėties kompleksinius junginius: AgHQ^{2+}, AgQ$^+$ ir AgQ(OH), kurių patvarumo konstantų logaritmai yra lygūs atitinkamai 1,7 ± 0,2, 5,7 ± 0,1 ir 6,3 ± 0,2.