On complex formation in chemical copper plating processes from solutions with organophosphorus ligands

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Abstract. Nowadays the processes of chemical vapor deposition of metals are widely used in mechanical engineering, both for the production of materials with desired functional properties and for decorative purposes. One of the most widely used chemical vapor deposition processes is chemical copper plating. The paper aims to study the complexation of copper (II) with nitrilotrimethylene phosphonic acid and to identify the possibility of using nitrilotrimethylene phosphonic acid as ligands of copper (II) ions for obtaining stable solutions of chemical copper plating. The formation of copper (II) complexes with nitrilotrimethylene phosphonic acid has been studied by the electron paramagnetic resonance (EPR) method. The paper proposes a method for processing EPR data – measurements to calculate the distribution of complex forms in the form of dependence $= dP/dpH – f(pH)$, where $P$ – the EPR spectrum parameter, which seems promising for describing paramagnetic systems characterized by complex equilibria with small changes in the magnetic parameters relative to the line width. The significance of the results for the engineering industry is that the authors studied the new materials based on copper complexes with nitrilotrimethylene phosphonic acid. The article establishes compositions and calculates the stability constants of the complexes at various pH of the medium. The research also shows the possibility of obtaining high-quality metal coatings based on copper (II) complexes with nitrilotrimethylene phosphonic acid.

1. Introduction
It is hard to imagine modern development of the engineering industry without the use of the achievements of chemistry in the field of the synthesis of new chemicals and materials. In recent decades, metal-polymer materials formed by a chemical method have been widely used in mechanical engineering to produce a variety of protective and decorative coatings [1–4]. The advantages of chemical deposition, unlike other methods of coating (electroplating, cladding, thermal spraying, metallization in vacuum) are the possibility of obtaining a uniform coating on products of complex configuration, availability of materials, simplicity of equipment, low energy costs.

In solutions of chemical vapor deposition of metals, the nature of the complex-forming ligand plays an important role for ensuring the required stability of solutions. The stability of solutions is related to the strength of the formed complex ions and their spatial structure. In recent years, organophosphorus
complexones have attracted a lot of attention from researchers. They are widely used in various areas of the economy, including mechanical engineering [5,6].

The literature has information about the prospects for the use of organophosphorus ligands in the processes of chemical deposition of metals [7-10]. One of the most interesting representatives of complexing compounds with phosphonic groups is nitrilotrimethylene phosphonic acid (NTP). The combination of a high basicity nitrogen atom with phosphonic groups in a ligand molecule causes the formation of both stable mononuclear and strong polynuclear complexes with most metal ions. The availability of acid synthesis opens up wide possibilities for its practical use [11,12].

The existing solutions of chemical deposition of metals have insufficient stability and therefore the issues of increasing their stability and reusability remain highly relevant [13–15]. In this regard, the study of the complex formation processes in solutions of chemical copper plating based on nitrilotrimethylene phosphonic acid is becoming important in order to optimize the technological processes of metal plating and determine the methods of controlling these processes.

2. Methods
To study the complex formation of copper with nitrilotrimethylene phosphonic acid, we used the electron paramagnetic resonance (EPR) method [16–18]. The electron paramagnetic resonance method is one of the most sensitive to changes in the structure and composition of the first coordination sphere of the complexing metal. The main parameters of the EPR spectra are the intensity and width of the lines, the g-factor and the constant of the hyperfine interaction, which depend on the symmetry of the nearest surrounding of the central ion and on the nature of the ligand.

This paper, basing on the analysis and processing of the parameters of the EPR spectra of liquid and frozen solutions, discovers the probable structure of the resulting complex ions, and calculates the equilibrium constants of complex formation. The EPR spectra were recorded on an RE-1306 spectrometer equipped with a magnetic field calibrator assembled on the basis of a magnetic induction meter III-I-I. The samples were placed in calibrated capillaries of glass, which did not give an EPR signal in the working region of magnetic fields. The EPR spectra were recorded at 298 and 77 K in the three-centimeter wavelength range. In some cases, we took measurements at elevated temperatures (up to 390 K).

3. Results and discussion
Six-basic nitrilotrimethylene phosphonic acid has the following structure:

\[
\begin{align*}
&\text{H} - \text{N} - \text{CH}_2 - \text{P(O)(OH)}_2 \\
&\text{CH}_2 - \text{P(O)(OH)}_2 \\
&\text{CH}_2 - \text{P(O)(OH)O}^-
\end{align*}
\]

The study of complexation processes in the system Cu(II) – NTP – H₂O was carried out by the EPR method. Figure 1 shows the typical EPR spectra in different pH ranges, taken at room temperature in solutions with a metal ligand ratio of 1:2. In the pH range 0.5 - 13, copper ions form a series of coordination compounds with NTP. In the complexation processes, NTP exhibits the function of a polydentate ligand at the expense of the nitrogen atom and the oxygen atom of the phosphonic groups, which are able to coordinate with the metal ion. In a strongly acidic environment (pH <0.5), the EPR spectrum has one wide line with g-factor equal to 2.19, which is typical for the copper aquacomplex. With increasing pH, the shape and parameters of the spectra change, which is associated with changes in the composition and symmetry of the nearest coordination sphere of the central ion.
Figure 1. EPR spectra of copper (II) complexes with NTP in liquid solutions depending on pH: 1 – 2.09; 2 – 4.02; 3 – 5.47; 4 – 10.3; 5 – 12.48; 6 – 13.25; $C_{Cu(II)} = 0.02$ mol/l; $C_{NTP} = 0.04$ mol/l.

An increase in the pH of the environment of more than 0.5 causes a decrease in the g-factor value. This indicates the enhancement of the planar bond of the copper (II) ion with the ligand and the entry of the NTP molecule into the equatorial plane of copper. Depending on the pH of the solution, NTP, like other polybasic acids, could be in various dissociating forms. According to the literature data [1], the EPR spectrum observed up to a pH value of 3.5 should be attributed to the formation of a protonated complex $[\text{CuH}_2L]^-$ (Figure 1, 1), where NTP acts as a dual-ligand. The entry of the ligand into the equatorial plane of the central ion leads to a weakening of bonds with axial water molecules. In this regard, with a further increase in pH, the coordination of NTP occurs in the axial position of the complex and a spectrum is observed in the pH range 3.5–5.0 (Figure 1, cr. 2) can be attributed to the following protonated complex $[\text{CuH}_2L]^2^-$, where two coordination sites in the inner sphere of the central ion are occupied by the oxygen donor atoms of the double-deprotonated phosphonic NTP groups. The intensity of absorption of this type of complex is maximum at pH 4. At pH 4.5, the formation of a mono-impregnated complex $[\text{CuHL}]^3^-$ begins, which intensity increases as the pH rises and reaches its maximum value at pH 5.5 (Figure 1, 3). The character of the spectrum changes, a hyperfine structure appears from the nuclei $\text{Cu}^{63}/65$. During the transition to the fully deprotonated complex $[\text{CuL}]^4^-$
(Figure 1, 4), significant changes occur in the EPR spectrum, which may be caused by a strong distortion of the symmetry of the nearest coordination sphere of the central ion. The complex $[CuL]^4^{-}$ prevails in a wide range of pH 7.5 - 11.5. With further increase in pH, we detected a new type of spectrum (Figure 1, 5), which is basic in the pH range of 11.5 - 13. The appearance of this spectrum can be explained by the occurrence of a hydroxyl group in the inner sphere of the central ion. Thus, the EPR spectrum observed in the pH range > 11.5 should be attributed to the formation of a new complex particle - the mixed $[Cu(OH)L]^5^{-}$ hydro complex; the axial position is occupied by the nitrogen atom and the hydroxyl ion. An increase in pH more than 13 leads to a spectrum with a clearly defined ultrathin structure consisting of four components from copper nuclei. This is caused by the fact that at pH > 13 there is a transition of Cu (II) hydroxocomplexes in the $[Cu(OH)]_4^2^{-}$ complex. A similar type of spectrum with similar values of parameters was obtained in [19] in the study of copper (II) - tartrate complexes.

The magnetic parameters obtained from the spectra of liquid solutions (Table 1) show an initial increase in the hyperfine interaction with the Cu (II) nucleus and a decrease in $g_{iso}$ in the series $[CuH_2L]^3^{-}$, $[CuH_2(L)_2]^{2^{-}}$, $[CuHL]^3^{-}$ followed by a sharp drop in the hyperfine interaction (HFI) with the nucleus Cu(II) for $[CuL]^4^{-}$ and complete disappearance for $[Cu(OH)L]^5^{-}$. This can be explained by the initial control of the complex with the formation of a structure that is maximally close to a tetragonal elongated octahedral for $[CuHL]^3{-}$ with the subsequent transition to the structure of a trigonal bipyramid, which is accompanied by a sharp decrease in HFI with the Cu (II) nucleus. The formation of $[CuL]^4^{-}$ causes a change in the geometry of the complex and a strong mixing of $d_{x^2-y^2}$ and $d_{z^2}$ conditions. The formation of the $[Cu(OH)L]^5^{-}$ complex with an even stronger ligand $OH^-$ compared to $H_2O$ leads to a trigonal compression along the $N \to Cu \to OH^-$ axis and an additional decrease in HFI with the nucleus Cu (II). Removing the degeneracy of the electronic levels by the mechanism of the dynamic Jahn-Teller effect leads to a complete averaging of the hyperfine structure from Cu (II) and the spectrum represents a single structureless line with a width of ~ 45 Oe.

Table 1. The isotropic ($g_{iso}, A_{iso}$) and anisotropic ($g_{||}, g_{\perp}, A_{||}, A_{\perp}$) parameters of the EPR spectra in the system Cu(II) – NTP – H_2O, $C_{Cu(II)} = 0.02$ mol / l; $C_{NTP} = 0.04$ mol / l.

| Complex ion                  | $g_{iso}$ | $A_{iso}$, [Oe] | $g_{||}$ | $g_{\perp}$ | $<g>$ | $A_{||}$, [Oe] | $A_{\perp}$, [Oe] | $\alpha^2$ |
|-----------------------------|-----------|-----------------|---------|-------------|-------|----------------|-----------------|------------|
| $[Cu(H_2O)_6]^{2+}$         | 2,19      | -               | 2,044   | 2,08        | 2,19  | 133            | -               | 0,84       |
| $[Cu(H_2L)(H_2O)]^{4^{-}}$  | 2,18      | 45              | -       | -           | -     | -              | -               | -          |
| $[CuH_2L(H_2O)_3]^{2^{-}}$  | 2,17      | -               | -       | -           | -     | -              | -               | -          |
| $[CuHL(H_2O)_2]^{3^{-}}$    | 2,17      | 55              | -       | -           | -     | -              | -               | -          |
| $[CuL(H_2O)]^{4^{-}}$       | 2,18      | 50              | $g_x = 2.329$ | $g_y = 2.14$ | $g_z = 2.05$ | 130            | -               | 0,79       |
| $[CuL(OH)]^{5^{-}}$         | 2,165     | 45              | -       | -           | -     | -              | -               | -          |
| $[Cu(OH)_2]^{2^{-}}$        | 2,134     | 78,3            | 2,272   | 2,061       | 2,131 | 190            | 32              | 0,86       |

In the research of complexation reactions, the spectra of frozen solutions (when there is an anisotropy of the $g$-factor and the HFI constants) are of particular interest, since the anisotropic components are more sensitive to the environment of the paramagnetic ion than their average values. An analysis of the EPR spectra taken in the Cu(II) – NTP – H_2O system at 77 K allowed us to determine their parameters, which are listed in Table 1. Lowering the temperature of the solution and freezing at 77 K leads to stability in the entire pH range of four kinds of complexes. Magnetic parameters obtained from the spectra of frozen solutions confirm the conclusions of the analysis of the isotropic parameters of the EPR. In the acidic pH range, the EPR spectra of copper (II) complexes in frozen solutions are anisotropic lines with resolved components of the hyperfine structure in a parallel orientation. At low pH values, the aquacomplex $[Cu(H_2O)_6]^{2+}$ is thermodynamically stable. The range of its existence in vitrified...
solutions expands to pH 3.5. At pH 4, we observe the formation of the \([CuL]^{4-}\) complex; it is stable in the pH 4–11 range and is characterized by a strong rhombic nature of the magnetic parameters (Table 1), which is also typical for trigonal bipyramidal complexes. The maximum dentate equals to four is easily realized at low temperatures, as evidenced by the presence of the complex form \([CuL]^{4-}\) at sufficiently low pH values of the solution. The \([CuH_2L]^-, [CuH_2L]^{2-}, [CuHL]^{3-}\) complexes are probably characterized by a rapid proton exchange, which is indirectly confirmed by the absence of these forms in the EPR spectra of frozen solutions. The broadening of the lines leads to a weak distinguishability of these forms in the EPR spectra. In the pH range above 11, the EPR spectra of copper (II) complexes have a complex shape with poorly resolved components of the hyperfine structure. In the pH range of 11.5 - 12.75, the \([CuL(OH)]^{5-}\) complex accumulates, and at pH 12.75, along with this complex, the \([Cu(OH)_{4}]^{2-}\) axial symmetry complex begins to accumulate as well, which spectrum has a well-resolved hyperfine structure in the region of parallel and perpendicular orientation.

We estimated the covalence parameter \(\alpha^2\) (the density of the unpaired electron on the central atom), which makes it possible to qualitatively estimate the degree of covalence of the metal – ligand bond (Table 1). The value \(\alpha^2\) is calculated by the formula [20]:

\[
\alpha^2 = \frac{A_\parallel}{P} + (g_\parallel - 2.0023) + \frac{2}{7}(g_\perp - 2.0023) + 0.04,
\]

where \(P\) - constant characterizing the hyperfine interaction in a free uncomplexed central atom, \(P = 0.036\) cm\(^{-1}\) for copper (II) complexes. The values \(g_\parallel, g_\perp, A_\parallel\) and \(A_\perp\) determined from spectra taken at liquid nitrogen temperature.

It turned out that in the deprotonated complex the bond of copper (II) with the ligand is the most covalent. NTP, acting as a tetradentate ligand in a deprotonated complex, leads to a stronger bond in the equatorial plane, which is reflected in a decrease in the parameter \(\alpha^2\). Values of \(g\) - factors \(< g_\parallel >\) calculated by the equation:

\[
< g > = \frac{g_\parallel + 2g_\perp}{3}
\]

slightly differ from the \(g\) - factors determined from the EPR spectra of liquid solutions (Table 1). This suggests that the symmetry of the nearest environment of copper (II) is preserved in the solution.

Thus, based on the data obtained, the following equilibria can be used as the basis for the mathematical model of equilibrium processes in the system Cu (II) - nitrilotrimethylene phosphonic acid:

\[
\begin{align*}
Cu^{2+} + H_6L \rightleftharpoons & [CuH_3L]^+ + 3H^+ \quad (3) \\
Cu^{2+} + H_6L \rightleftharpoons & [CuH_2L]^{2-} + 4H^+ \quad (4) \\
Cu^{2+} + H_6L \rightleftharpoons & [CuHL]^{3-} + 5H^+ \quad (5) \\
Cu^{2+} + H_6L \rightleftharpoons & [CuL]^{4-} + 6H^+ \quad (6) \\
Cu^{2+} + H_6L + H_2O \rightleftharpoons & [Cu(OH)L]^{5-} + 7H^+ \quad (7) \\
Cu^{2+} + 4H_2O \rightleftharpoons & [Cu(OH)_4]^{2-} + 4H^+ \quad (8)
\end{align*}
\]

Basing on the EPR data and using \(CPRESSP\) (Chemical Parametres of Equilibria in Solutions with Solid Phases) [21] software, we determined the equilibria constants complex stability constants (Table 2).

**Table 2.** Equilibrium and stability constants of copper (II) complexes with nitrilotrimethylene phosphonic acid.

| Complex                  | \(\lg K_p\) | \(\lg \beta\) |
|-------------------------|-------------|---------------|
| \([CuH_3L]^-\)          | -1.61       | 5.25          |
| \([CuH_2L]^{2-}\)      | -4.92       | 8.08          |
| \([CuHL]^{3-}\)        | -9.59       | 10.86         |
| \([CuL]^{4-}\)         | -16.27      | 16.07         |
| \([Cu(OH)L]^{5-}\)     | -28.08      | 18.26         |
| \([Cu(OH)_4]^{2-}\)    | -37.11      | 18.90         |
In the pH range of 0 - 10, we used the experimental dependence $<H>=f(pH)$ (figure 2) for calculations, where H is the magnetic field strength corresponding to the position of the inflection point for the high-field component of the EPR spectrum. In the case when changes in the magnetic parameters of the spectra occur within the width of the line, it can be assumed that $<H>$ of the selected point of the spectrum is determined by a linear combination of characteristic values for the particles present in equilibrium with a weight proportional to their concentration. An increase in pH more than 11 leads to a dramatic change in the shape of the spectrum associated with the formation of the complex form $[Cu(OH)L]^3^−$ and the value of the $<H>$ parameter at the same time ceases to be a linear combination of the value of $H_i$ of individual complexes. However, the difference in the widths of the lines leads to the fact that the overlay of the lines does not significantly affect the amplitude of the line related to $[CuL(OH)]^5^−$, which made it possible to use the dependence $I=f(pH)$ in the pH 10 region - 13.5 (Figure 3), where I is the intensity of the EPR signal, for the processing.

The search for satisfied convergence of experimental and calculated data was carried out during the search for the minimum of the functional:

$$F_{max} = \sum_{n=1}^{N} (x_{exp} - x_{calc})^2,$$

where $x_{exp}$ – experimental value of properties – $H$ or $I$; $x_{calc}$ – its calculated version.

For the system Cu(II) – NTP in the range of pH 0 - 13.5, in the presence of a twofold excess of the ligand with respect to the metal ion in the region of pH> 11, deprotonation of the complex form $[CuL]^4^−$ takes place with the formation of the hydroxocomplex $[Cu(OH)L]^5^−$, which with a further increase in the alkalinity of the environment (pH> 13.1) decomposes with the formation of a copper complex $[Cu(OH)_4]^2^−$. During the calculation procedures, we obtained the following values of the stability constants: for $[Cu(OH)L]^5^−$ $= 18,25 \pm 0,04$ and $[Cu(OH)_4]^2^− = 18,9 \pm 0,08$. The latter constant has good convergence with the literature data [1].
Figure 2. The change in the magnitude of the magnetic field (H) of the high-field component of the EPR spectrum depending on pH: \( C_{\text{Cu(II)}} = 0.02 \text{ mol} / \text{l}; \ C_{\text{NTP}} = 0.04 \text{ mol} / \text{l} \).

Figure 3. The change in the intensity of the EPR signal depending on the pH in solutions containing 0.02 mol/l Cu(II) and 0.04 mol/l NTP.

Figure 4 shows the magnetic resonance data as a differential dependence representing the ratio of the change in the position of the characteristic point of the EPR spectrum to the change in the pH of the solution.

Figure 4. Change in \( \frac{dp}{d\text{pH}} \) and \( \frac{dJ}{d\text{pH}} \) depending on pH; \( C_{\text{Cu(II)}} = 0.02 \text{ mol/l}; \ C_{\text{NTP}} = 0.04 \text{ mol/l} \).

Comparison of the obtained dependence with the distribution of complex forms showed that the areas of maximum accumulation of individual complexes correspond to minimal changes in the position of the high-field component of the spectrum, and sharp maxima correspond to the boundaries of the existence of the complexes. The region of existence of \([CuH_2L]^{2-}\) and the boundary of the forms \([CuH_2L]^{2-}\) and \([CuHL]^{3-}\) are poorly expressed due to the proximity of the formation constants of these complexes. The regions of existence of \([Cu(H_2O)_6]^{2+}, [CuH_3L]^+, [CuHL]^{3-}, [CuL]^{4-}\) and \([Cu(OH)L]^{5-}\) on the differential diagram are clearly shown. It seems to us that this type of dependence, namely \( \frac{dp}{d\text{pH}} \sim f(\text{pH}) \), where P is a parameter of the EPR spectrum, is promising for describing paramagnetic systems characterized by complex equilibria with relatively small changes in the magnetic parameters relative to the width of the line.
4. Conclusion

The electron paramagnetic resonance technique was studied using copper (II) complexes with nitrilotrimethylene phosphonic acid. The study of complexing properties suggests that stable complex compounds in a wide range of pH values. Based on the cumulative study of liquid and frozen solutions with a consistent change in pH (pH change step of 0.25), we obtained data on the composition and stability of copper (II) complexes with NTP formed in the pH range 0 - 13 established in the region of their existence and structure. The obtained information is of significant interest in regard with the practical effects of solutions, copper (II) complexes and NTP for chemical deposition without the use of toxic electrolytes.

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