

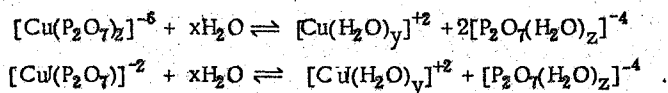
ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH

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The solution of the problem of the mechanism of electrode processes during the electroprecipitation of metals from solutions of their complex salts can not be accomplished without detailed study of the composition and properties of the complex ions which are found in the electrolyte. This situation is of a general character and, consequently in studying the possibility of the galvanic precipitation of copper from pyrophosphate bath we encountered the necessity of specially considering the question of its composition.

It is necessary to note that in the last few years a number of investigations of the composition and stability of complex ions of copper pyrophosphate have appeared. The analysis of the available data permits the following conclusions to be made.

Depending on the pH and concentration of the components, when solutions of copper sulfate and sodium pyrophosphate were mixed the following ions were detected: $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$; $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$; $[\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)]^{-5}$; $[\text{Cu}(\text{HP}_2\text{O}_7)_2]^{-4}$; $[\text{Cu}(\text{P}_2\text{O}_7)(\text{OH})]^{-3}$. The first two complexes appeared as a result of the general complex formation reaction and naturally participate in solvation equilibria of the type [1]:

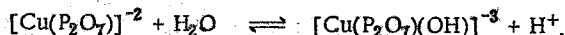


The instability constant of the $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ion has been determined by many investigators: Stabrovsky [2] cited the value $K_{\text{inst.}} = 3.1 \cdot 10^{-10}$, Rogers and Reynolds [3] $K_{\text{inst.}} = 2 \cdot 10^{-11}$ and, finally Waters and Aaron [4] $K_{\text{inst.}} = 2 \cdot 10^{-9}$. There are many contradictory data for the instability constants of the $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ ion.

As is well known from the literature data, both complexes under consideration can exist in the pH range approximately from 7 to 10 [4]. In addition, there is an indication [4] of the existence of the complexes $[\text{Cu}_2\text{P}_2\text{O}_7]^0$ and $[\text{Cu}_4(\text{P}_2\text{O}_7)]^{+4}$, but these ions, apparently, are only formed in very dilute solutions.

In a number of cases the solvation equilibria in copper-pyrophosphate solutions can be complicated by side reactions of the acid-base type.

Thus, at pH > 10 the following equilibrium takes place:



Similar complex cuprate-pyrophosphate anion was detected by a number of authors [5,6] and its instability constant was equal, according to their data, to $6 \cdot 10^{-14}$ or $2 \cdot 10^{-16}$.

At pH > 11 the copper-pyrophosphate complex is destroyed and a precipitate of cupric oxide hydrate settles out.

In acidic solutions equilibria are possible which lead to the formation of complex copper-pyrophosphate ions containing the $(\text{HP}_2\text{O}_7)^{-3}$ group. At pH 5.3-7.0 the formation of the ion $[\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)]^{-5}$ with an instability constant of 10^{-10} [6] was noted, while at pH < 5.3 the ion $[\text{Cu}(\text{HP}_2\text{O}_7)_2]^{-4}$ with an instability constant close to $4 \cdot 10^{-7}$ [6] was noted. The study of the latter complexes was complicated in connection with the fact that in acid solutions a precipitate of the hypothetical composition $\text{Na}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$ settled out [6].

As is evident from the information set forth on the stability of copper pyrophosphate complexes, there is one very substantial hiatus in them — this is the sharp discrepancy of the available data on the instability constant of the $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ complex. At the same time, the precise knowledge of this quantity is necessary to elucidate the concrete picture of the composition of the copper-pyrophosphate solutions of varying concentration. Its knowledge is also important for the solution of the question of the mechanism of electrode reactions in a copper-pyrophosphate bath.

To fill this gap we calculated the instability constants of the complex ions $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ and $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ on the basis of analysis of the data on the measurement of the potentials of a copper electrode in the corresponding solutions.

The potentials were measured by the usual compensation method with the methodology not differing from that generally adopted [7].

The results of the indicated measurements are set forth in Table 1.

In the calculations of the instability constant we start from the equations:

$$K_1 = \frac{[P_2O_7^{-4}] [Cu^{+2}]}{[Cu(P_2O_7)^{-2}]} \quad \text{and} \quad K_2 = \frac{[P_2O_7^{-4}]^2 [Cu^{+2}]}{[Cu(P_2O_7)_2^{-6}]}$$

When the excess of $P_2O_7^{-4}$ ions is so great that one can assume the formation almost exclusively of $[Cu(P_2O_7)_2]^{-6}$ ions, the concentration of these ions is practically equal to the initial concentration of copper (C_{Cu}^0), while $[P_2O_7^{-4}]$ is respectively equal to the initial concentration of pyrophosphate after deducting $2C_{Cu}^0$. Thus $[Cu^{+2}] = \frac{K_2 C_{Cu}^0}{C_{P_2O_7}^0 - 2C_{Cu}^0}$

and therefore

$$E - E_{Cu}^0 = 0.03 \log \frac{K_2 C_{Cu}^0}{C_{P_2O_7}^0 - 2C_{Cu}^0} = 0.03 [\log K_2 + \log C_{Cu}^0 - \log (C_{P_2O_7}^0 - 2C_{Cu}^0)] \quad (1)$$

Evidently, when the initial concentration of pyrophosphate is close to the initial concentration of copper, the formation of the complex $[Cu(P_2O_7)_2]^{-6}$ is difficult to expect and then

$$E - E_{Cu}^0 = 0.03 [\log K_1 + \log C_{Cu}^0 - \log (C_{P_2O_7}^0 - C_{Cu}^0)] \quad (2)$$

It should be noted that the available literature data for K_1 are either such that K_1 is approximately equal to K_2 , or they correspond to the inequality $K_2 \ll K_1$. In the first case the conditions for fulfilling equation (1) are in general difficultly attainable. On the other hand, the conditions for fulfilling equation (2) can be obtained comparatively readily. They correspond to the first 5 systems set forth in Table 1.

TABLE 1

Potentials of a Copper Electrode in the System $CuSO_4 - Na_4P_2O_7 - H_2O$ and the Instability Constants of the Copper-Pyrophosphate Complexes at 25 °C

System no.	Concentration (in moles)		Assumed predominant form	E (in volts)	log $K_{inst.}$
	$CuSO_4$	$Na_4P_2O_7$			
1	0.0050	0.0050	$[Cu(P_2O_7)]^{-2}$	+0.198	-7.4
2	0.0100	0.0100		+0.219	-6.3
3	0.0200	0.0200		+0.222	-6.3
4	0.0200	0.0300		+0.172	-6.0
5	0.0300	0.0500		+0.162	-6.2
6	0.0050	0.0300	$[Cu(P_2O_7)_2]^{-6}$	+0.035	-9.8
7	0.0200	0.1000		+0.011	-10.6
8	0.040	0.100		+0.052	-10.2
9	0.040	0.200		-0.010	-10.5
10	0.20	0.500		+0.004	-11.5

The data of Waters and Aaron prove to correspond more with the actual conditions and therefore equation (1) can also be used in the determined limits.

Thus the obtained value for K_1 is $0.63 \cdot 10^{-6}$ and for K_2 is $0.5 \cdot 10^{-10}$. The values found for K_2 are found in agreement with the data of other authors [2,3] and the ratio of the constants satisfies the Babko-Khodakov condition [9]:

$$\frac{\log K_2 - \log K_1}{\log K_1} = \frac{P_2 - P_1}{-P_1} \quad (3)$$

where P_1 and P_2 are the energetic characteristics of the complexes, equal to -8 and -14 respectively [10].

Actually, if K_1 is approximately equal to 10^{-6} , then according to equation (3)

$$\log K_2 = \frac{14 + 8}{8} (-6) = -1.75 \cdot 6 = -10.50.$$

On the basis of the obtained values of the instability constants a graph of the dependence of the contents of various complex forms in solution on the concentration of free pyrophosphate can be constructed.

The calculation was carried out according to the equations:

$$[Cu^{+2}] = \frac{100\%}{1 + \frac{[P_2O_7^{-4}]}{K_1} + \frac{[P_2O_7^{-4}]^2}{K_2}} \quad (4)$$

$$[Cu(P_2O_7)^{-2}] = [Cu^{+2}] \frac{[P_2O_7^{-4}]}{K_1}; \quad [Cu(P_2O_7)_2]^{-6} = [Cu^{+2}] \frac{[P_2O_7^{-4}]^2}{K_2}$$

The results of the calculation are presented in Fig. 1; it follows from its data that the concentration of the $[Cu(P_2O_7)]^{-2}$ anion is maximal only in a narrow interval of values for the concentration of $[P_2O_7^{-4}]$, and this form in the best case contains only 50% in all of copper and generally can not predominate; it is therefore clear that the calculated value of the instability constant K_1 is somewhat low, but this has no further theoretical significance and it can be confirmed that the ratio $\log K_2 : \log K_1$ is close to 2 in each case.

Such a conclusion is in complete agreement with the data of Waters and Aaron [4]. Its verification can be accomplished by means of the determination of the conductance of the system $CuSO_4 - Na_4P_2O_7 - H_2O$. The measurements were carried out by the usual method with the aid of a variable current bridge.

The temperature was held at $20 \pm 0.2^\circ$. The results of the measurements are presented in Table 2 and in Fig. 2 and bear witness to the existence of points of inflexion on the curves $\kappa = f(C)$, corresponding to the condition $[Na_4P_2O_7] : [CuSO_4] = 3 : 2$.

TABLE 2

Conductance of the System $CuSO_4 - Na_4P_2O_7 - H_2O$ at 20°

Concentration (in moles)		κ , ohms $^{-1}$ cm $^{-1}$	Concentration (in moles)		κ , ohms $^{-1}$ cm $^{-1}$
$CuSO_4$	$Na_4P_2O_7$		$CuSO_4$	$Na_4P_2O_7$	
0.020	0.020	0.0045	0.020	0.080	0.0134
0.020	0.025	0.0058	0.020	0.090	0.0242
0.020	0.030	0.0069	0.030	0.060	0.0094
0.020	0.035	0.0072	0.040	0.060	0.0083
0.020	0.040	0.0078	0.040	0.080	0.0123
0.020	0.045	0.0085	0.040	0.100	0.0160
0.020	0.050	0.0091	0.040	0.200	0.0240
0.020	0.060	0.0104	0.050	0.060	0.0111
0.020	0.070	0.0118	0.050	0.100	0.0153

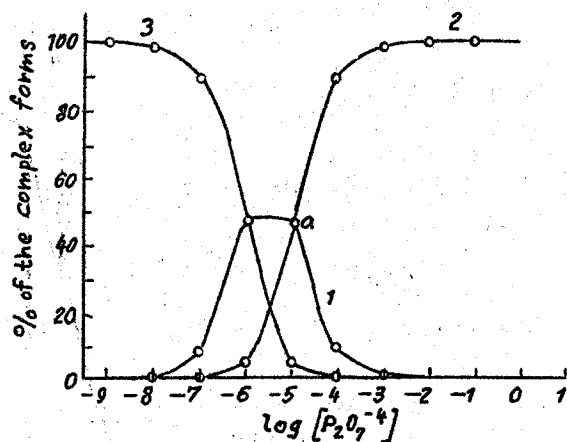


Fig. 1. Relative concentrations of the complex forms in the system $Cu^{+2} - P_2O_7^{-4}$
1) $[Cu(P_2O_7)]^{-2}$, 2) $[Cu(P_2O_7)_2]^{-6}$, 3) $Cu(H_2O)_n^{+2}$

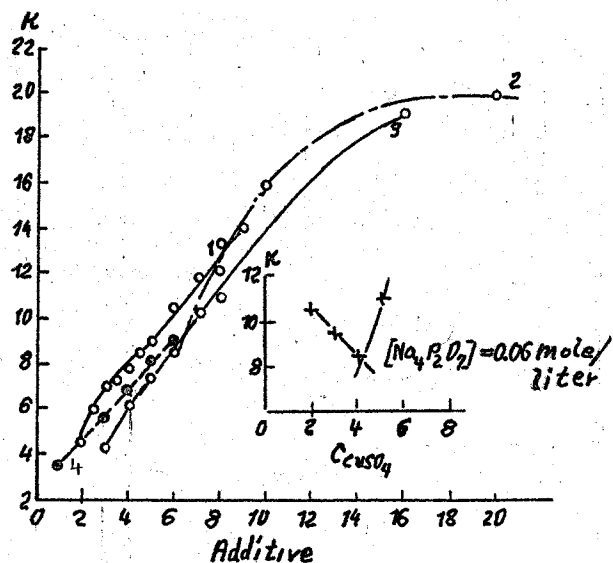


Fig. 2. Influence of complex formation on the conductance.
1) 0.02 m. $CuSO_4 + Na_4P_2O_7$, 2) 0.04 m. $CuSO_4 + Na_4P_2O_7$
3) 0.01 m. $CuSO_4 + Na_2C_2O_4$, 4) 0.02 m. $CuSO_4 + Na_3C_6H_5O_7$.

As can be concluded without difficulty, this point closely coincides with the point a on Fig. 1 and almost completely coincides with the transfer of copper into the $[Cu(P_2O_7)_2]^{-6}$ ion. The presence of such an inflexion is readily

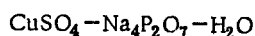
explained by the data obtained for the instability constant of the complex ions of copper pyrophosphate.

Thus, the results of the investigation show that under ordinary conditions the predominant ion in copper-pyrophosphate complex electrolyte is the $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ion. Inasmuch as the working conditions for a pyrophosphate bath are characterized by the following data: pH 7.5–9.0, $[\text{Na}_4\text{P}_2\text{O}_7] : [\text{CuSO}_4] \geq 2$, this ion is practically uniquely capable of participating in the cathode process since the concentration of all other forms of the complex compounds is extraordinarily small.

Another important conclusion from the data obtained consists in the fact that with further refinements in the pyrophosphate bath a ratio of concentrations $[\text{Na}_4\text{P}_2\text{O}_7] : [\text{CuSO}_4] \leq 2$, should be obtained, since under these conditions the nature of the stimulating ions is scarcely changed while the lowering of the concentration of free pyrophosphate presents a greater perspective, inasmuch as in this case the crystallization of the $\text{Na}_4\text{P}_2\text{O}_7$ salt at the surface of the cathode becomes scarcely probable [8]. The ensuring of a sufficiently satisfactory solubility of the anodes during the electrolysis can be achieved by addition to the electrolyte of sodium citrate and other side substances which form quite soluble but not very stable complexes with copper. A similar ratio of concentrations of CuSO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ with simultaneous introduction of substances which form collateral complexes in practice was accomplished by us and led to completely satisfactory results.

SUMMARY

1. The question of the composition of complex ions in a real pyrophosphate electrolyte, suitable for galvanic copper plating was considered.
2. The instability constants of complexes of copper pyrophosphate were measured potentiometrically. The values found for K_1 were $0.63 \cdot 10^{-6}$, and for K_2 , $0.5 \cdot 10^{-10}$.
3. The dependence of the conductance of the system



on the concentration of the components was studied. An inflexion point on the conductance curves, which corresponded to practically complete transfer of copper into the complex ion, was detected.

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