

DISCUSSION

THE QUESTION OF THE COMPOSITION OF THE COPPER PYROPHOSPHATE BATH

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Papers by I. L. Agafonov [1] and V. P. Vasilyev and K. B. Yatsimirsky [2], containing a number of remarks pertaining to our study [3], were published in the Discussion Section of the Journal of General Chemistry.

Since most of these remarks deserve serious answer, and since the question raised in the cited studies relative to the real state of the copper-pyrophosphate electrolyte is of considerable interest in practice, we consider it obligatory to discuss the critical remarks made by I. L. Agafonov, V. P. Vasilyev and K. B. Yatsimirsky.

We will begin with the study of V. P. Vasilyev and K. B. Yatsimirsky. These authors correctly note the error, assumed by us in calculating the instability constant of the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$. Actually, the experimental data presented in our paper on the potential of the copper electrode led to a value of $1.3 \cdot 10^{-11}$ for the constant, as had been indicated in one of our other studies [4], and not to a value of $0.5 \cdot 10^{-10}$ [3]. This difference is practically without effect on the subsequent results.

The second remark of V. P. Vasilyev and K. B. Yatsimirsky reduces to the fact that the equation

$$E - E_{\text{Cu}}^0 = 0.03 [\log K_1 + \log C_{\text{Cu}}^0 - \log (C_{\text{P}_2\text{O}_7}^0 - C_{\text{Cu}}^0)] \quad (1)$$

is unsuitable for calculating the instability constant of the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{2-}$ in the case where $C_{\text{P}_2\text{O}_7}^0 = C_{\text{Cu}}^0$, i. e. where the initial concentrations of pyrophosphate and copper are equal. This comment is trivial, for it is evident that in the indicated case equation (1) should be replaced by:

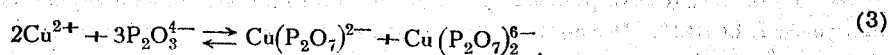
$$E - E_{\text{Cu}}^0 = \frac{0.03}{2} [\log K_1 + \log C_{\text{Cu}}^0]. \quad (2)$$

It is understood that we took this into consideration in our calculations of constant K_1 [3].

Further, V. P. Vasilyev and K. B. Yatsimirsky assert that our data on the instability constants of the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{2-}$ are unreliable for the reason that, based on our calculations, the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{2-}$ cannot compose more than 50% of the complex forms in solution, while in calculating the instability constants we assume that all of the free Cu^{2+} ions in solution are applied specifically to this complex, and not to $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$.

At first glance such an assumption can actually appear to be without basis. However, it is easily confirmed by simple calculation. As a matter of fact for system No. 5, for example, (Table 1 [3]), we have $C_{\text{Cu}}^0 = 0.03$, $C_{\text{P}_2\text{O}_7}^0 = 0.05$ m, $E = +0.162$ V.

If it is assumed that for this system 50% of the copper enters into the composition of $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$, and 50% into the composition of $\text{Cu}(\text{P}_2\text{O}_7)_2^{2-}$, we then obtain



and therefore $[\text{Cu}(\text{P}_2\text{O}_7)^{2-}] \cong [\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}] \cong 0.5 \cdot C_{\text{Cu}}^0 = 1.5 \cdot 10^{-2}$; $[\text{P}_2\text{O}_7^{4-}] \cong C_{\text{P}_2\text{O}_7}^0 - \frac{3}{2} C_{\text{Cu}}^0 = 5 \cdot 10^{-3}$;

while the reaction equilibrium constant is [3]:

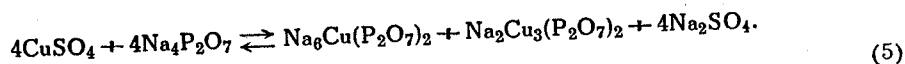
$$K = K_1 K_2 = \frac{[\text{Cu}^{2+}]^2 [\text{P}_2\text{O}_7^{4-}]^3}{[\text{Cu}(\text{P}_2\text{O}_7)^{2-}] [\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}]} \approx \frac{[\text{Cu}^{2+}] \left(C_{\text{P}_2\text{O}_7}^0 - \frac{3}{2} C_{\text{Cu}}^0 \right)^3}{0.25 (C_{\text{Cu}}^0)^2}, \quad (4)$$

when $K = 0.8 \cdot 10^{-17.2}$, and if $K_2 \cong 10^{-11}$, then $K_1 = 0.8 \cdot 10^{-6.2}$, which does not differ from the earlier obtained $K_1 = 10^{-6.2}$. A similar calculation for the remaining systems is even more complicated, since we do not know beforehand in which proportions the complexes $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ and $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ are formed, if their instability constants are not known. Incidentally, we will mention here an error by I. L. Agafonov, who postulates [1] that the solution to the last problem reduces to writing the equation for a reaction of the (3) type with the stoichiometric coefficients before the Cu^{2+} and $\text{P}_2\text{O}_7^{4-}$, determining their ratio $C_{\text{Cu}}^0 : C_{\text{P}_2\text{O}_7}^0$. In treating this problem in our paper [3] we postulated that when $C_{\text{Cu}}^0 : C_{\text{P}_2\text{O}_7}^0 = 2/3$ it is possible for the copper to migrate completely into the $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ ion. As a matter of fact, with the indicated ratio the concentration ratio $[\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}] : [\text{Cu}(\text{P}_2\text{O}_7)^{2-}]$ evidently becomes even less than 1.

However, here the bend, experimentally established in our study, on the electroconductivity-concentration curves, corresponding to $C_{\text{P}_2\text{O}_7}^0 : C_{\text{Cu}}^0 = 3/2$ becomes incomprehensible, although, contrary to the opinion of I. L. Agafonov [1], there is no reason to doubt the existence of such a bend. The analogous measurements of Rogers and Reynolds [5] also speak in support of its existence. As a result, an explanation of this effect is possible only after a more detailed study of the examined system has been made.

I. L. Agafonov further asserts that at a ratio $C_{\text{P}_2\text{O}_7}^0 : C_{\text{Cu}}^0 < 2$ a precipitate deposits in the solution only when the total copper concentration exceeds 10^{-4} M. This was not supported in our work, since the appearance of turbidity in dilute solutions ($C_{\text{Cu}}^0 \leq 10^{-2}$ M) was observed only at $C_{\text{P}_2\text{O}_7}^0 : C_{\text{Cu}}^0$ equal to 1.0-1.5, while according to the data of Rogers and Reynolds [9], a precipitate of $\text{Cu}_2\text{P}_2\text{O}_7$ deposits only at $C_{\text{P}_2\text{O}_7}^0 : C_{\text{Cu}}^0 = 0.5$.

It is also impossible to agree with the later statement of I. L. Agafonov that equilibrium is established in solution under the conditions $C_{\text{P}_2\text{O}_7}^0 : C_{\text{Cu}}^0 = 1$:



Any evidence in support of such a hypothesis is also absent in the earlier study of I. L. Agafonov, A. L. Agafonova and I. G. Shcherbakov [6]. The authors of the latter paper did not even attempt to experimentally determine the composition of the bottom phase under the conditions where a precipitate is actually formed, and instead invented reaction (5), probably from purely intuitive considerations.

Completely without basis is the statement made by I. L. Agafonov that "... at the concentrations, required in electroplating practice, the ionic composition of the solution is determined not as much by the excess $\text{P}_2\text{O}_7^{4-}$ ions, as by dilution of the solution or the formation of a precipitate with a deficiency of these ions ...". Here I. L. Agafonov confuses the meaning of the terms "ionic composition of the solution" and "concentration of ions in solution". The concentration of "free" pyrophosphate specifically determines (at constant pH) the solution composition. The formation of a precipitate influences only the concentration of the ions in solution (also at pH = const).

Also we cannot agree with statements like: "... without changing the nature of the discharging (emphasis is provided by us) ions, it is impossible to obtain the solution concentrations indicated by the authors (i. e. E. A. Ukshe and A. I. Levin)". "By adding sodium citrate, the authors in this manner anticipated the deposition of a precipitate, in which connection the composition of the discharging ions evidently changed partially".

These statements of I. L. Agafonov contradict both experiment and basic theoretical considerations [7]. Although the additions of foreign complex-formers do dissolve the precipitates, capable of being formed in the anolyte, they are practically without effect on the cathode process. As is known, such additions (seignette salt, sodium citrate, ammonia) have found wide use in electroplating practice [8, 9]. On the other hand, the copper-pyrophosphate electrolyte, devoid of SO_4^{2-} ions, as is known, was proposed by A. I. Gershevich and L. V. Gamburg [10, 12] in 1940, and was studied in detail in the work of I. S. Titov, M. E. Yanitskaya and E. A. Prandetskaya [11], and not by I. G. Shcherbakov, as stated by I. L. Agafonov.

In conclusion we will mention that in the paper under discussion [3] our goal was not to make a complete study of the composition of the copper-pyrophosphate electrolyte, but instead we set ourselves a much more modest goal, namely, to elucidate to what extent the instability constants of the ions $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ and $\text{Cu}(\text{P}_2\text{O}_7)^{2-}$ differ from each other. The potentiometric study method used by us is in itself extremely approximate for a number of reasons, the chief of which are the following: 1) ignorance as to the activity coefficients of the ions (working with a constant ionic strength could not save the situation here, but would only make the experimental error constant); 2) ignorance as to the diffusion potentials, which can apparently attain extremely high values at the boundary of solutions of the type of $\text{CuSO}_4\text{--Cu}(\text{P}_2\text{O}_7)_2^{6-}$; the use of a salt bridge cannot guarantee their elimination; 3) the lack of precision for the standard electrode potential of copper, which is known only with an accuracy of a hundredth of a volt [13].

This approximate nature of the potentiometric method used in itself does not permit the expectation of obtaining "exact" results by its use. It is known that its accuracy fails to exceed a log K unit. On the other hand, the system $\text{CuSO}_4\text{--Na}_4\text{P}_2\text{O}_7$ is made very complicated by the formation of various precipitates or complexes of the type of $\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)^{5-}$ and $\text{Cu}(\text{P}_2\text{O}_7)\text{OH}^{3-}$. Up to now the influence of these impediments has not been studied sufficiently even for dilute solutions [14, 15]. It is natural that a further study of copper-pyrophosphate electrolytes is completely essential, and a discussion of the difficulties that arise here is of great interest.

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