FURTHER DISCUSSION ON THE POLAROGRAPHIC DETERMINATION OF THE COMPOSITION AND STABILITY OF COMPLEX IONS IN SOLUTION IN STEPWISE COMPLEX FORMATION

Ya. I. Turyan

As is known, in stepwise complex formation the graphical relationship between the half-wave potential $(E_{\frac{1}{2}})_c$ and the logarithm of the addend concentration ($\log C_X$) is expressed by a curve (in contrast to the corresponding straight line when only one complex ion is present [1]), and this complicates a quantitative treatment of the results.

K. B. Yatsimirsky [2,3] proposed a comparatively simple method of finding the consecutive instability constants with the aid of the curve $(E_{\frac{1}{2}})_c - \log C_X$, under the conditions that in solution complex ions exist with coordination numbers (p): 1,2,3,4, etc.

L. P. Adamovich and M. S. Novakovsky [4] raised the point that the complexes with certain coordination numbers in the 1,2,3,4, etc. series cannot be formed due to steric hindrance or some other difficulties. On this basis the authors [4] conclude that the K. B. Yatsimirsky method makes it impossible to accurately establish the composition of the intermediate complex ions, and only indicates the minimum and maximum coordination numbers, corresponding to a given addend concentration interval. Being in complete agreement with the argument of L. P. Adamovich and M. S. Novakovsky, we believe, for the case where the condition p = 1,2,3,4, etc. is disturbed, that also the minimum and maximum coordination numbers cannot be determined by the K. B. Yatsimirsky method, since for a different addend concentration interval these coordination numbers become intermediate.

The remarks made by L. P. Adamovich and M. S. Novakovsky undoubtedly deserve consideration. Nevertheless, the voluminous experimental material on stepwise complex formation in solutions shows that the condition p = 1,2,3,4, etc. is observed most frequently.

At the same time there are other difficulties associated with the use of the K. B. Yatsimirsky method. This caused us to reexamine the problem of the polarographic study of stepwise complex formation.

In addition to the indicated condition, in deriving the relationship between $(E_{\frac{1}{2}})_c$ and C_X, K. B. Yatsimirsky [2,3] makes use of still another condition: the domination of only two forms of the complex ions MX_p and MX_{p+1} (we neglect the charges on the ions) when the concentrations $C_{MXp} = C_{MXp+1}$ are equal. This condition, when compared with the first, should apparently be much less frequently observed experimentally. As a matter of fact, there may even be cases where some pairs of complexes MX_p and MX_{p+1} fail to dominate at all addend concentrations. On the other hand, it may be observed that there is domination of MX_p and MX_{p+1}, but not at $C_{MXp} = C_{MXp+1}$. Strictly speaking, the K. B. Yatsimirsky method is inapplicable in both examples. It is evident that fulfillment or nonfulfillment of the examined condition depends on the ratio values of the instability constants of different complex ions, and since the instability constants are the values being sought, then the validity of the condition that the forms MX_p and MX_{p+1}, dominate cannot be verified on the basis of the constants found in this manner.

As a result, in using the K. B. Yatsimirsky method it is necessary to keep a number of limitations in mind. This is understandable if it is considered that the K. B. Yatsimirsky equation is an approximate solution of the general relationship between $(E_{\frac{1}{2}})_c$ and C_X that was obtained by DeFord and Hume [5]. In connection with this, for a more complete examination of the problem it is expedient to also turn to the exact solution of this equation, given in the same study [5].

For this we will first assume that in solution at addend concentration C_X there exist complex ions with random coordination numbers in the interval 1–J: 1,2,3...p, p + 1, ... J and corresponding instability constants K_1, K_2, K_3 ... Kp, Kp+1... K_J. In addition, the simple ions of the metal are also present in the solution. If it is assumed as a first approximation that the diffusion current constants of the indicated ions are the same, and, for simplicity, assume that the activity coefficients are equal to unity, then it is possible to derive, in accord with the work of DeFord and Hume [5], the following general relationship between $(E_{\frac{1}{2}})_c$ and C_X:

$$(E_{1/2})_c = (E_{1/2})_s - \frac{RT}{nF} \ln\left(1 + \frac{C_x}{K_1} + \frac{C_x^2}{K_2} + \cdots + \frac{C_x^p}{K_p} + \frac{C_x^{p+1}}{K_{p+1}} + \cdots + \frac{C_x^J}{K_J}\right), \quad (1)$$

where $(E_{\frac{1}{2}})_s$ is the half-wave potential of the simple metal ion. From this equation it is easy to obtain the K. B. Yatsimirsky equation, if it is assumed that in solution only two forms of the complex ions MX_p and MX_{p+1} dominate. Actually, in this case all of the terms in parentheses, can be neglected with the exception of C_X^p/K_p and C_X^{p+1}/K_{p+1}, which leads to the K. B. Yatsimirsky equation:

$$(E_{1/2})_c = (E_{1/2})_s - \frac{RT}{nF} \ln\left(\frac{C_x^p}{K_p} + \frac{C_x^{p+1}}{K_{p+1}}\right). \quad (2)$$

The given equation, under the conditions p = 1,2,3,4, etc. and domination MX_p and MX_{p+1} at C_{MXp+1}, K. B. Yatsimirsky solves by the method of tangents to the curve $(E_{\frac{1}{2}})_c - \log C_X$.

The essence of an exact solution of equation (1), where fulfillment of the indicated conditions is not required, reduces to a use of the graphical method of Leden [6], already examined in our literature [3]. It is necessary to mention that DeFord and Hume [5] fail to consider that although at first in the derivation of equation (1) random coordination numbers are assigned in the interval 1-J, nevertheless the use of the Leden method permits them to solve the problem of actually existing coordination numbers. As a matter of fact, if the Leden function [6] F(X) at $C_X = 0$ is obtained, differing from zero by a value greater than experimental error, then this means that the corresponding complex ion actually exists. F(X) can have only a positive value or zero. If at $C_X = 0$, F(X) is equal to zero or differs from zero by a value less than experimental error, then it is impossible to solve the problem of whether in general the given complex ion is formed, or whether being formed, it possesses very small stability. From the practical viewpoint both of these conclusions are identical.

In conclusion we will compare the instability constants, obtained with the aid of the exact method of DeFord and Hume, with the corresponding constants obtained on the basis of the approximate, but simpler method of K. B.

Complex	Method	K'_1	K'_2	K'_3	K'_4
Thiocyanate complexes of cadmium [7]	DeFord and Hume	11	56	6*	60
	Yatsimirsky	18	62	87	49
Thiocyanate complexes of zinc [8]	DeFord and Hume	3	7	1	20
	Yatsimirsky	5	10	14	9
Pyridine complexes of zinc [9] **	DeFord and Hume	26	13	–	–
	Yatsimirsky	18	68	–	–

* As indicated in study [7], this value had been obtained more accurately earlier by Leden [6].

** We do not present the constants K'_3 and K'_4, since only the order of their values was obtained in study [9].

Yatsimirsky. For this we made use of the data from the studies of Hume, DeFord and Cave [7], Frank and Hume [8], and Nyman [9], and determined the instability constants with the aid of the K. B. Yatsimirsky method. The indicated authors used the DeFord and Hume method. A comparison of the formation constants, $K' = 1/K$, found with the aid of the

two methods, is given in the Table. From this Table it can be seen that a number of the constants, obtained by the two methods, show quite good agreement. However, there are also considerable differences (for example, K_3' for Cd + CNS and Zn + CNS, and K_2' for Zn + Py), conditioned by the approximate nature of the K. B. Yatsimirsky method. In particular, this approximate nature is explained by the fact that in the systems Cd + CNS and Zn + CNS the complex ion MX_3, either in pair with MX_2 or in pair with MX_4, fails to dominate at all values of C_X. In addition, the condition of the complexes MX_p and MX_{p+1} showing domination at the point of equal concentrations $C_{MX_p} = C_{MX_{p+1}}$ is also not always fulfilled in the examined systems. Thus, at $C_{ZnCNS} = C_{Zn(CNS)_2}$ the C_{Zn} concentration still constitutes $\cong$ 30 %. This also could have introduced some error in finding the constants with the aid of the K. B. Yatsimirsky method.

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Kishinev State University

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