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Abstract

Full Text

CHEMISTRY

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STUDY OF THE INTERACTION OF HYDROUS POTASSIUM METANIOBATE WITH OXALIC ACID

(Presented by Academician I. I. Chernyaev, 22 IV 1961)

Oxalic-acid solutions of niobium and tantalum are of considerable importance both in radiochemistry and in the analytical chemistry of these elements. Recently they have attracted the attention of researchers also from the standpoint of their use in the industrial separation of niobium from tantalum and other accompanying elements ([1–3]). However, until recently very little attention has been paid to the study of these solutions. The composition of the complexes formed in solution, their instability constants, and their limits of stability with respect to pH have not yet been precisely established. There is no experimental evidence for the sign of the charge of the complex particles formed, etc. All this served as the basis for carrying out the present work.

By methods of physicochemical analysis we studied the system $KNbO_3{-}H_2C_2O_4{-}H_2O$, examining both isomolar series and series with a constant concentration of potassium niobate. In the system studied we determined electrical conductivity, optical density, turbidity, depression of the freezing temperature of the solutions, their viscosity, pH, and also the diffusion coefficient. In measuring the diffusion coefficients we used niobium-95 as a tracer. As can be seen from Figs. 1, 2, and 3, when the methods listed above are used, the composition–property curves usually exhibit two extrema—one at the molar ratio $KNbO_3 : H_2C_2O_4$ equal to $1 : 0.5$, and the second at the ratio equal to $1 : 1$.

Fig. 1. Changes in electrical conductivity *(a)*, optical density *(b)*, and freezing

temperature of solutions *(c)* in the system $KNbO_3{-}H_2C_2O_4{-}H_2O$ in isomolar series.

The reaction of interaction of potassium metaniobate with oxalic acid at a molar ratio equal to $1:1$ can be represented in the form of the following equations:

$$KNbO_3 + H_2C_2O_4 = KHC_2O_4 + HNbO_3; \tag{1}$$

$$KNbO_3 + H_2C_2O_4 = K[NbO_2C_2O_4] + H_2O; \tag{2}$$

$$2KNbO_3 + 2H_2C_2O_4 = (NbO_2)_2C_2O_4 + K_2C_2O_4 + 2H_2O. \tag{3}$$

However, the data obtained allow us to dwell only on equation (2). Indeed, equation (1) is excluded because the precipitating ···

according to this equation, niobic acid is not capable of independent existence and should precipitate. However, as shown by the results of determining the turbidity and viscosity of the solutions, as well as by cryoscopy data and determination of diffusion coefficients, the maximum precipitation is observed at a molar ratio $\mathrm{KNbO_3 : H_2C_2O_4}$ equal to $1:0.5$. Hence it may be concluded that the first stage of the interaction of potassium metaniobate with oxalic acid proceeds according to the scheme:

$$\mathrm{2KNbO_3 + H_2C_2O_4 = K_2C_2O_4 + 2HNbO_3}.$$

This is also confirmed by the results of pH determination shown in Fig. 3. The solution in all series at the point $1:1$ remained transparent (Fig. 2b). Equation (3) should also be rejected on the basis of the data on pH determination of the series. At the point $1:1$, the pH of all the solutions studied was close to 4, i.e., it was weakly acidic, whereas according to equation (3) the pH at this point should be weakly alkaline. To confirm our assumptions, we carried out paper electrophoresis for solutions at the point $1:1$. It was found, in agreement with equation (1), that all the niobium moves toward the anode, i.e., it is part of negatively charged particles, whereas according to equation (3) it should have been part of positively charged particles or, if it forms a neutral complex, should not move at all. Since, however, the results of determining the diffusion coefficient in the system studied do not show interaction at the point $1:1$, but show interaction at approximately $1:2$, we decided to verify our results by calculation. For this purpose we additionally measured the self-diffusion coefficient of potassium metaniobate, which proved to be $1.478\cdot10^{-5}$ cm^2/sec at 25° and a concentration of about 0.03 mol/l. Since the self-diffusion coefficient of the complex formed was $1.238\cdot10^{-5}$ cm^2/sec under the same conditions, then, using the approximate Euler formula $D\sqrt{M} = D_1\sqrt{M_1}$, we attempted to estimate the molecular weight of the complex ion formed. The calculation

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

gave the value 199.7, which is quite close to the value 213, corresponding to the theoretical calculation for the ion $[NbO_2C_2O_4]^-$. Thus, the composition of the compound formed is also confirmed by measurement of the self-diffusion coefficients. It should be noted that the composition of the ion formed does not change up to the ratio $KNbO_3 : H_2C_2O_4$ equal to 1 : 10, as is evident from Fig. 2c.

Fig. 2. Change in electrical conductivity (a), transparency (b), and diffusion capacity (c) in the system $KNbO_3—H_2C_2O_4—H_2O$ in series with variable total concentration of the components

Fig. 3. Change in pH (a) and viscosity (b) in the system $KNbO_3—H_2C_2O_4—H_2O$ in equimolar series

Apparently, at pH below 2 the complex formed is present in solution in a strongly hydrolyzed state, which was reflected in the decrease in the values of the self-diffusion coefficients.

To test this assumption, we determined the self-diffusion coefficients in the system under study at a ratio of $KNbO_3 : H_2C_2O_4$ from 1 : 1 to 1 : 10 at a constant pH equal to 1.8. As the experiment showed, at all the studied ratios of potassium niobate to oxalic acid, the self-diffusion coefficient of the ion formed remains constant and close to the value given above. Thus, it may be considered proven that, at all the studied ratios of $KNbO_3 : H_2C_2O_4$, only one compound is formed, whose composition can be expressed by the formula $K[NbO_2C_2O_4]$.

Using the data we obtained from the study of the optical density of solutions of isomolar series, we estimated the value of the instability constant of the complex ion formed; it proved to be $8 \cdot 10^{-4}$. Finally, it should be noted that none of the methods used in our work showed the presence in solutions of a compound with an $Nb : H_2C_2O_4$ ratio equal to 1 : 3, which would correspond to the formation of the salts described by Russ (4).

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Note: Figure translations are in progress. See original paper for figures.