From the titration curve (Figure 1), the optimal molar ratio of the reacting components k (k=[Cu^{2+}]/[PVA]=0.50) was found. It means that one central metal atom bonds with two mono-links of polymer ligands.

3.2. Conductometric titration

In order to confirm the composition of the formed PVA-Cu^{2+} complex, the dependence of the conductivity corrected for the viscosity on the ratio of the initial component of the system was studied (Figure 2).

The increase in electrical conductivity is due to the released H^+ ions during the reaction between PVA and copper(II) ions. As can be seen from Figure 2, the electrical conductivity of the solution with an increase in the molar content of metal ions passes through the inflection point. Based on the data obtained as a result of conducted conductometric studies, it can be argued that the complexation process is accompanied by an increase in the electrical conductivity of the system at the ratios PVA-Cu^{2+}=2:1.

In the process of complexation of the PVA polymer ligand, their hydrodynamic dimensions decrease (chelate effect); protons are released, as evidenced by the experimental results. Thus, it can be assumed that the complex of the composition is formed in the PVA–Cu^{2+} system.

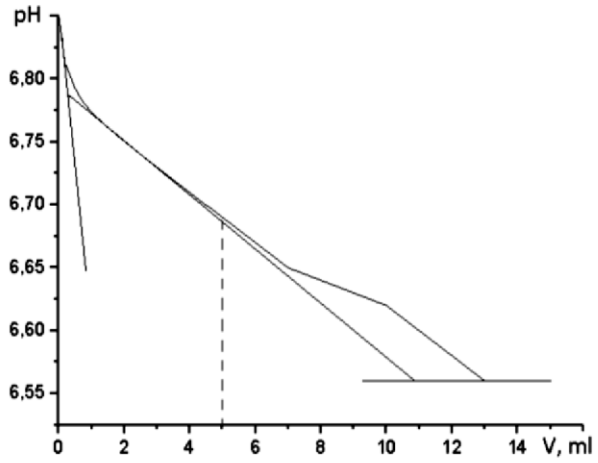

Figure 1 Curve of potentiometric titration of PVA (10^{-2} M) with copper salt $Cu(OAc)_2$ (10^{-2} M) (where V – titrant volume in mL, pH – pH of solution).

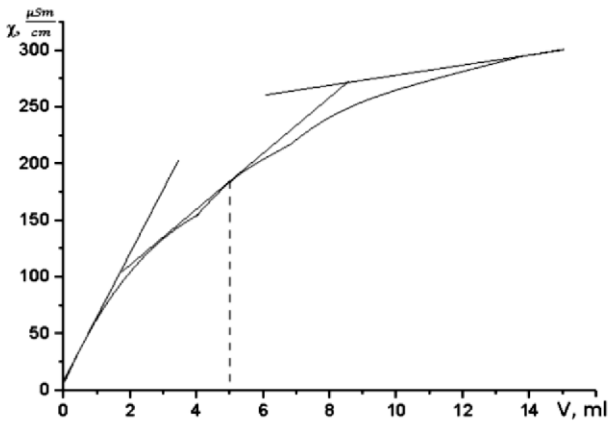

Figure 2 Curve of conductometric titration of PVA (10^{-2} M) with copper salt $Cu(OAc)_2$ (10^{-2} M) (where V – titrant volume in ml, χ – specific electrical conductivity of solution in μSm/cm).

3.3. Modified Bjerrum's method calculations

The stability constant of the resulting polymer complex and the coordination number of copper(II) were calculated using the modified Bjerrum's method. In accordance with the known method, the potentiometric study was carried out at three values of the ionic strength of the solution: 0.01, 0.05, and 0.1 mol/L, and the polymer ligand solution was titrated with hydrochloric acid (HCl), depending on the nature of the complexing metal salt, with a change in the pH of the medium in the absence and presence of metal ion, as well as at several temperatures (25, 45, 70 °C). Figure 3 shows the pH value change in the absence and presence of metal ions during the experiment. It is clearly seen that the pH value in the presence of metal ions is higher than in experiment without metal ions. It signifies the formation of the complex and means that the system reacts in the acidic medium.

Table 1 shows the values of the Bjerrum's formation functions (n) corresponding to the coordination number of the metal complexing agent at three ionic strengths and at 70 °C. The data obtained indicate the formation of a copper polymer complex in which the coordination number of the metal is equal to two.

3.4. Thermodynamic parameters of the process

The knowledge of the thermodynamic parameters (changes in Gibbs' energy ($\Delta_r G^\circ$), enthalpy ($\Delta_r H^\circ$) and entropy ($\Delta_r S^\circ$)) of the studied process is necessary for the scientifically based choice of the optimal conditions for its implementation in practice. Moreover, many researchers admit that the fundamental laws of thermodynamics, which were established for the systems consisting of low molecular weight compounds, can be applied to the systems involving macromolecules [23].

The PVA-$Cu(OAc)_2$ system is characterized with the negative Gibbs' energy, which indicates the spontaneous occurrence of the studied process in the direction of the compound formation (Table 2).

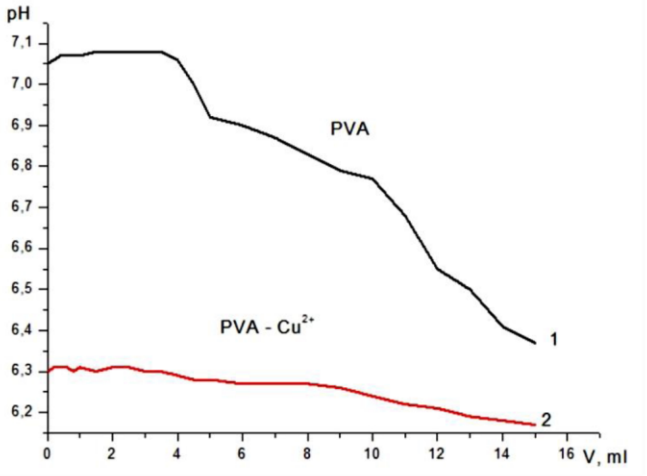

Figure 3 Curves of potentiometric titration of aqueous solutions of polyelectrolyte of PVA (10^{-2} M) (1) and PVA – Cu^{2+} (10^{-2} M) (2) by hydrochloric acid (10^{-2} M) and L_f=0.01, T = 25 °C.