ELECTROTRANSPORT PROPERTIES OF IONS IN AQUEOUS SOLUTIONS OF H$_2$SeO$_4$ AND Na$_2$SeO$_4$


Coefficients of self-diffusion, absolute speeds of movement of ions and the activation energy of electrical conductivity are found from the conductance measurements of aqueous solutions of selenic acid and sodium selenate at different concentrations in a temperature range of 288-318 K. Both the Stokes and effective radii of ions and their hydrate numbers at 298 K are calculated. The obtained results are interpreted in the frames of Samoilov theory on positive and negative hydration of ions.

Keywords: selenic acid, sodium selenate, aqueous solutions, electrotransport properties of ions.

INTRODUCTION

Investigation of electrical conductivity of solutions is of great importance for studying the solvation and electrotransport properties of ions in electrolyte solutions. These properties depend both on the charges and radii of ions and on ion hydration degree [1-3]. According to Samoilov’s theory [1], positive and negative hydration of ions is defined depending on the mobility of water molecules in a hydrate environment of ions in comparison to pure water. Thus, the investigation of temperature dependence of electrotransport properties of ions in electrolyte solutions is of particular interest.

The value of $\Delta E_{\text{tr}}^0$ is the energy measure of hydrated ions. It represents a difference between heights of the potential barriers separating two neighboring equilibrium positions of water molecules in pure water, and on their transition from a hydrate shell into solution [4-11]. Acidic solutions are especially interesting, since hydrogen ions are moved there by the relay-race mechanism (in a go-ahead mode), while water molecules do not move. The H$^+$ ions migrate along hydrogen bonds between water molecules even without external electric field. On the contrary, the mechanism of movement of anions is not the go-ahead one. Their transfer energy depends on their charge, radius, and hydrate number. For the aqueous solutions of selenic acid and of sodium selenate there are no data on the temperature dependence of diffusion coefficient, $D^0$, and $\Delta E_{\text{tr}}^0$ for selenate anions in the literature.

The purpose of the present work is to obtain electrotransport characteristics of selenic acid and sodium selenate ions in aqueous solutions in a temperature range of 288-318 K.

EXPERIMENTAL PART

The initial solution of selenic acid is produced by dissolution of H$_2$SeO$_4$ (Fluka) in doubly distilled water ($\kappa = 8.9 \times 10^{-7}$ S cm$^{-1}$ at 25°C). The consequent series of nine solutions in a concentration range of 0.0204-0.0004 g-equiv dm$^{-3}$ is prepared by diluting aliquot parts. Exact concentration of solutions is defined gravimetrically by sedimentation of...
SeO$_4^{2-}$ ions with Pb(NO$_3$)$_2$ in the form of PbSeO$_4$ [12].

Na$_2$SeO$_4$ is prepared by mixing NaOH and H$_2$SeO$_4$ solutions taken in stoichiometric quantities. With this purpose, phenolphthalein is added to a solution of NaOH, and the solution of H$_2$SeO$_4$ is titling up to neutral reaction and discoloration of the indicator. Aqueous solution of Na$_2$SeO$_4$ obtained in such a way was subjected to concentration and crystallization. After two re-crystallizations at room temperature and drying in exsiccator over the concentrated sulfuric acid, we received Na$_2$SeO$_4$·10H$_2$O with purity of 99.9%. From this salt we have prepared nine solutions with concentration in a range of 0.0199-0.0004 g-equiv dm$^{-3}$.

Measurements of conductivity of solutions were made on a digital conductivity meter Inolab-WTW (Germany) with a conductimetric cell constant, $k = 0.4752$ cm$^{-1}$, in a temperature range of 288-318 K in one degree. Temperature was kept with accuracy of ±0.05 K by means of ultrathermostat U-1 (Germany). The solution in question was placed into a glass vessel (volume of 100 cm$^3$), supplied by a water jacket, and electromagnetically stirred. In order to prevent the dissolution of CO$_2$ and other atmospheric gases, a vessel was closed with a rubber cap through which the conductivity cell was inserted. The measurement error of the electrical conductivity of the solution did not exceed ±0.2% of the total measured value. All experimental data were processed by the least squares method.

**RESULTS AND DISCUSSION**

According to the procedure described in [13], with using the Fuoss–Onzager method, the values of equivalent conductivity of H$_2$SeO$_4$ and Na$_2$SeO$_4$ are found at infinite dilution and various temperatures. These values are calculated at infinite dilution of SeO$_2^{2-}$ ions for each temperature in the investigated interval using Kollrausch equation for independent movement of ions [3] and accounting for the literature data on the equivalent conductivity of cations [14]. The temperature dependence of the equivalent conductivity of H$_2$SeO$_4$, Na$_2$SeO$_4$ and their ions is presented in Fig. 1.

![Fig. 1](image.png)

Fig. 1. Temperature dependence of the equivalent conductivity at infinite dilution: $a$ — H$_2$SeO$_4$ (1), H$^+$ (2) and SeO$_4^{2-}$ (3); $b$ — Na$_2$SeO$_4$ (1), SeO$_4^{2-}$ (2) and Na$^+$ (3).