

# Proton Conductivity and Phase Transition in Potassium Hydroxide Monohydrate

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**Abstract**—The ionic conductivity of a proton conductor, namely, potassium hydroxide monohydrate, has been studied in the temperature range of 200–410 K. It has been established that the temperature dependence of the conductivity has the Arrhenius form with an activation enthalpy of  $\sim 0.4$  eV. The pre-exponential factors for the intervals above and below room temperatures differ by a factor  $\sim 2.5$ . The anomalous temperature behavior observed in the range of 285–345 K indicates a phase transition with  $T_c \sim 295$  K. The mechanism of proton transport has been discussed.

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## 1. INTRODUCTION

Hydrogen-containing solid compounds (salts, acids and hydroxides) have been attracting attention for more than half a century as promising proton-conducting materials. Inorganic proton conductors meet presently with strong competition with polymer materials in the field of applications, if not as subjects for use in basic research centered on the investigation of charge and mass transport processes. Proton conductors are unique in this respect, because they occupy an intermediate position between the “conventional” electronic and ionic conductors. Leaving aside the historic aspect, we note that hydroxides of metals (including the alkali ones) have become subjects of intense investigation in the recent decade (see review in [1]). It turned out that derivatives of individual compounds in the form of solid eutectics and crystalline hydrates exhibit high proton conductivity at temperatures below 370 K (and even below room temperatures). Significantly, they feature electrochemical activity when used in assemblies with cheaper, other than noble metals. KOH monohydrate, the subject of investigation in the present paper, is one of several hydrate compounds in the KOH–H<sub>2</sub>O system. The phase diagram of this system was studied in detail long ago. But the data on the ionic conductivity of KOH · H<sub>2</sub>O presented in [1–3] are the only ones available.

It appeared of interest to continue investigation of this proton conductor below the room temperature region.

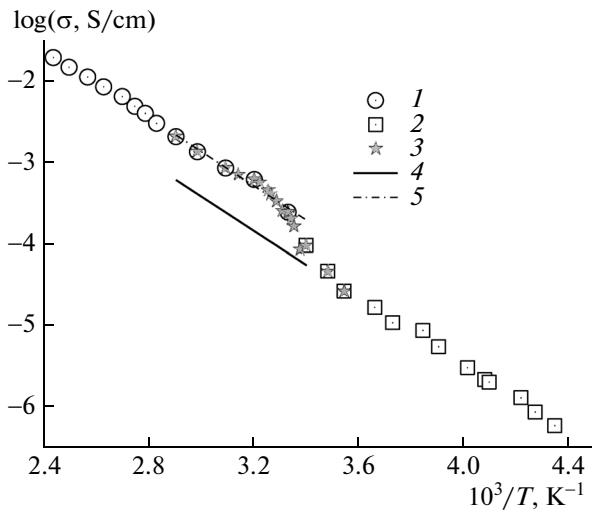
## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Electrical measurements were performed in the standard four-point arrangement, with Pt contacts used as electrodes. The monohydrate was plugged in a Teflon tube with an inner diameter of 10 mm and 5 cm long.

The preparation of samples from melt ( $T_{\text{melt}} = 416$  K) was run under strict monitoring of the liquid phase composition, taking into account possible losses of water in the form of vapor, whose equilibrium pressure is  $\sim 0.6$  Pa at 420 K. Formation of samples by filling Teflon tubes was performed in a nitrogen atmosphere with the corresponding water vapor pressure. The absence of published data on the solidus line in solid monohydrate at temperatures below the room level (up to 200 K) is a basic challenge. This is particularly true for deuterated compounds. We spared us these difficulties by dropping the measurements of the isotopic conductivity effects below room temperatures, which were performed earlier above them [1–3].

Low-temperature measurements were performed with the Dewar housing the samples placed into a vessel filled with liquid nitrogen. The temperature of the samples fell off very slowly (with a rate of 10–12 K/h) from the room level to 200 K. The temperature was measured with a copper–constantan thermocouple.

In measurements performed in the range of 297–330 K, the thermal conditions were maintained by means of a water bath to within  $\pm 0.01$  K. Each temper-



**Fig. 1.** Ionic conductivity of the KOH monohydrate in the temperature range of 220–410 K according to (1) data obtained for the range of 300–410 K [1–3], (2) measurements performed below room temperature (220–300 K), and (3) special measurements performed in the region of the anomalous temperature behavior (296–325 K). (4, 5) Parts of the curves obtained by the linear interpolation of curves 2 and 1, respectively.

ature point was held for not less than three hours, with the temperature fluctuations monitored with a Beckman thermometer.

The behavior of conductivity with temperature in the range  $200 \text{ K} < T < 295 \text{ K}$  is described by the relation

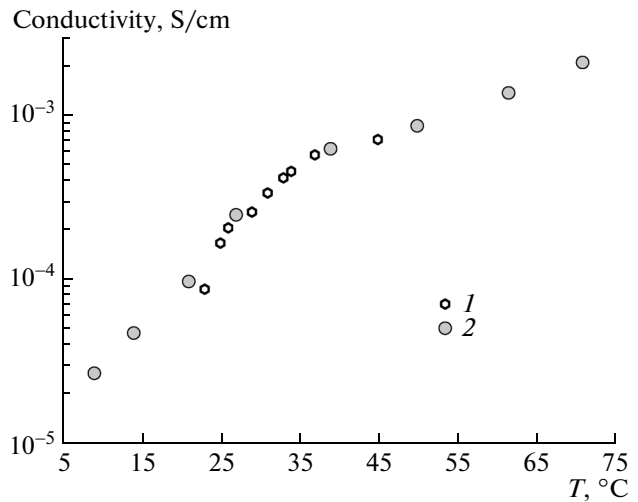
$$\sigma T = 6.22 \times 10^5 \exp(-0.39/kT),$$

whereas the conductivity above room temperature, in the range  $340 \text{ K} < T < 410 \text{ K}$  measured earlier is fitted by the relation

$$\sigma T = 3.02 \times 10^6 \exp(-0.41/kT).$$

Both these relations are displayed in Fig. 1 complete with the data obtained in a special experiment performed in the room-temperature region where the curve was found to be steeper. Measurements performed without careful maintenance of temperature revealed a strong scatter of data far beyond the error limits. The data obtained in this special experiment are plotted in Fig. 2.

Experiments aimed at measuring the room-temperature Hall effect were performed. As this should be expected for an ionic conductor, the galvanomagnetic effect turned out to be only slightly above the background level. Therefore one can present at this time only a preliminary estimate of the magnitude of the Hall effect:  $R = 4 \times 10^5 \text{ cm}^3/\text{C}$ , which yields for the carrier concentration  $n = 2 \times 10^{13} \text{ cm}^{-3}$ .

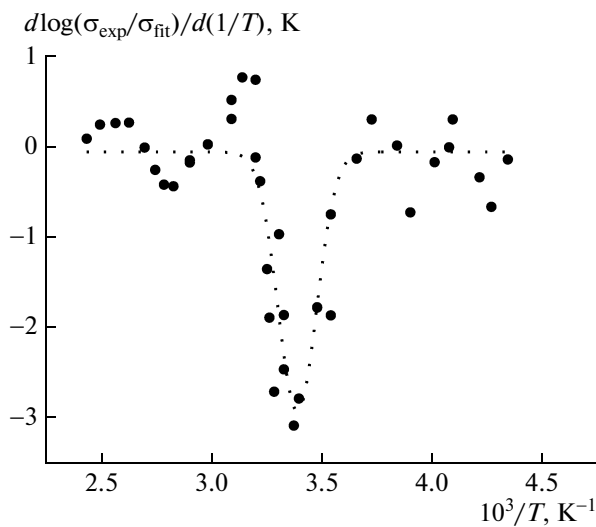


**Fig. 2.** Details of the anomalous temperature behavior of the conductivity of the KOH monohydrate in the range of 296–325 K according to (1) special measurements performed in steps of 1–3 K with each temperature point stabilized for no shorter than 3 h and (2) part of the data presented in Fig. 1 by curves 1 and 2.

### 3. DISCUSSION

In identification of the type and /or sign of carriers, the authors were guided by the data [1–3] amassed earlier on the mechanism mediating proton conductivity in hydroxide compounds, including the monohydrate. This conclusion was supported by the commonly accepted results of studies, among them EMF of the corresponding cell, and the H/D isotopic effect of the monohydrate conductivity for the temperature range of 410–320 K. Besides, it was established that the diffusion mobility of hydrogen particles in the monohydrate derived by the isotopic exchange method is fairly close to that calculated from the conductivity, allowing for the Nernst–Einstein relation. This aspect will be analyzed in more detail in our next paper.

Let us consider the anomalous behavior with temperature of conductivity in the range of 285–345 K. The “normal” temperature course of the conductivity exhibits practically the same activation enthalpy of 0.4 eV both above and below this interval. Staying within the frame of classical theory of ionic conductivity, this can be treated as the difference between the entropies of activation of both phases. The equality of activation energies suggests that we deal here with a difference between the initial states of the proton stemming from the different configuration (ordering) of hydrogen bonds in the monohydrate lattice. In this case, the experimental value of the difference between the activation enthalpies  $\Delta(\Delta S) = (1.16 \pm 0.4) \cdot 2 \text{ cal/mol K}$  is the difference between the configuration entropies. To a first approximation, this quantity corresponds to the ratio of the probabilities for a proton



**Fig. 3.** Temperature dependence of the conductivity of the KOH monohydrate in the form of the temperature derivative of the ratio of the data obtained experimentally and derived by the linear interpolation (see text for explanation). The dotted line is a Gaussian.

to occupy one of two states  $W_h/W_L = \exp((\Delta S)) = 10.2$ . This ratio can be obtained under the assumption that protons residing in a less ordered – high-temperature ( $h$ ) – phase move arbitrarily along all the six orbitals of oxygen ions ( $W_h = 60 = 6!/(2!4!)$ ), whereas in the ordered – low-temperature ( $L$ ) phase – they can move along five orbitals only ( $W_L = 10 = 5!/(2!3!)$ ). One of the orbitals is fixed rigidly by interaction with the  $K^+$  ion or by strong hydrogen bonding. In view of the fact that the pre-exponential factor is determined with a noticeable error ( $14.92 \pm 0.31$  and  $13.34 \pm 0.50$ ),

high-accuracy evaluation of  $\Delta S$  meets with difficulties and is offered here only as one of possible versions.

Staying within the limits of the concept of the part played by the factor of ordering, consider the course of conductivity in the region governed by anomalous behavior. To reveal more clearly the variation of the configuration entropy factor “confined” in the factor preceding the exponent, one had to separate out the strong temperature dependence of conductivity. This was reached by calculating the deviations of the experimental values of  $\sigma_{\text{exp}}$  from those obtained by linear interpolation ( $\sigma_{\text{fit}}$ ). The results are presented in Fig. 3 in  $\log(\sigma_{\text{exp}}/\sigma_{\text{fit}}) - 10^3/T$  coordinates. The anomaly is fitted satisfactorily with a Gaussian with the maximum in the region  $300 \pm 1$  K.

#### 4. CONCLUSIONS

The ionic conductivity of solid  $\text{KOH} \cdot \text{H}_2\text{O}$  in the temperature range of 200–410 K has been measured for the first time. Within this interval, the enthalpy of conduction is 0.4 eV. The phase transition in the range of 285–345 K is caused by a change in the ordering of protons, which are charge carriers in conduction. This is evidenced by the difference between the transport entropies above and below the phase transition.

#### REFERENCES

1. Yu. M. Baikov and V. M. Egorov, *Phys. Solid State* **51** (1), 33 (2009).
2. Yu. M. Baikov, *Solid State Ionics* **181**, 545 (2010).
3. Yu. M. Baikov, *Solid State Ionics* **208**, 17 (2012).

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