Four Methods for Estimating the Concentration of Ions in Electrolyte Solutions

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Abstract The results of measuring the volt-ampere characteristics of a 1% aqueous solution of KCl at room temperature are presented. The question of the parameters determined from the dependence I(U) is discussed. A hypothesis about the electrical shielding of the electrode potential by ions is proposed. Based on the information about electrochemical functions, a method for determining the concentration of ions from the experimental curve is developed and shown.

Keywords KCl solution · Volt-Ampere characteristic · Electric field · Ion Mobility · Solubility · Modelling

1 Introduction

Many applied problems concerning the physicochemical properties of electrolyte solutions require the determination of electrolyte parameters, such as solubility, density, electrical conductivity, concentration of charged particles, and the like. In this paper, an overview of the main methods for measuring the concentration of ions is carried out and an attempt is made to determine this concentration by electrical measurements of the volt-ampere characteristic in the interelectrode space of 1% KCl solution.

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1.1 The First Method

The substance is weighed and dissolved in an electrolyte solution. In the case when the solution is far from saturation, it is believed that the substance completely dissociates into ions. Otherwise, salt solubility tables are used.

1.2 The Second Method

In it, the concentration of ions in solution is determined by the method of appendages [1]. The volt-ampere characteristic (VAC, I(U)) of the electrolyte is measured, then the corresponding substance is dissolved in it and the VAC is measured again. From the proportion, the initial concentration is found by increasing the electric current. It is assumed that the concentration of ions and, respectively, I(U) are linearly related.

1.3 The Third Method

Allows us to determine the ion density from the experimental dependence I(U). To measure the VAC, an electrolytic cell with a size of 0.05 × 0.05 m2 was made, the electric current through which was measured using operational amplifiers [5]. To prepare the electrolyte, 6.6 × 10–5 kg of potassium bromide was weighed, which was dissolved in 0.1 kg of distilled water. Niobium plates with areas of 5.6×10^{-5} and 5.27×10^{-4} m^2, respectively, were used as electrodes. Figures 1 and 2 show the dependencies I(U) and E(U). Here we give the dependence I(U) with the opposite sign, as is customary in probe diagnostics. In this case, it becomes obvious that the curve I(U) is a hyperbolic sine [8]. As can be seen from Fig. 1, the low current region is in the range of ± 0.2 V. Outside of this segment, the electric current increases sharply. The electric field repeats the dependence I(U) in a similar way (see Fig. 2).

The method of determining the concentration from the VAC graph is borrowed from the theory of plasma. A pulse is passed through the conductive medium. In this case, the electric current in the circuit and the electric field are measured. In our case, taking into account the diffusion motion of charged particles and the ion distribution function in the electrolyte solution, the current to the electrode is described by the formula

$$I(U) = C \cdot qnbES \cdot sh(f[qU_0/kT]) \tag{1}$$

where q is the electric charge of the ion, n is concentration of ions in solution, b is mobility of ions in a liquid medium, E is electric field, U0 is the potential that is applied to the electrode, kT is thermal energy of the particle, f is a number of electrochemical functions, C is some constant associated with the ion energy distribution

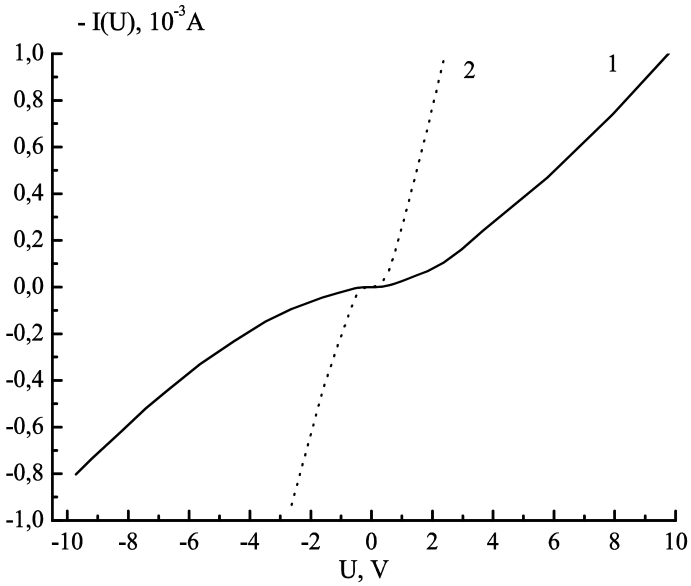

Fig. 1 VAC in KBr solution: 1—on the usual scale, 2—the dependence of I(U) is increased by 10 times

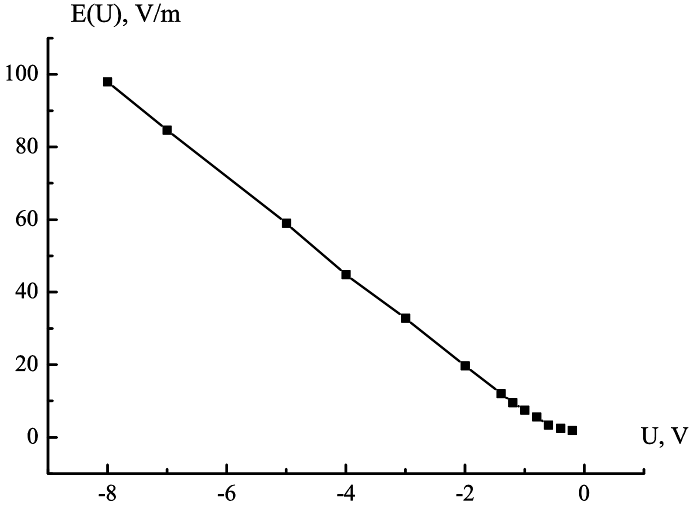

Fig. 2 Dependence of E(U) in KBr solution

function. In the case of electrolytic VAC, the ion density can be determined from the expression

$$n = \frac{I(U)}{q \cdot b \cdot S \cdot E} \tag{2}$$

Here we assume that sh[f(qU/kT))] = 1. The ion concentration value calculated by Eq. (2) is.

$$n = \frac{7.8 \times 10^{-6}}{1.6 \times 10^{-19} \times 6.8 \times 10^{-8} \times 0.56 \times 10^{-4} \times 3.8 \times 1} = 3.37 \times 10^{24} \mathrm{m}^{-3}$$

The ion concentration calculated by weight KBr is 3,765·1024 m^{-3}. As can be seen from the calculations, the error of the method is no more than 10–12%. In our model, we assume that C = 0.5. In fact, behind this coefficient there is a very complex series of hypotheses about the distribution of ions by energy, the discussion of which we would like to postpone for some time. This issue is not a matter of principle, but requires a large volume of in-depth discussions.

The fourth method is also related to the measurement of VAC. An algorithm for determining the ion concentration was proposed in [7]. Let's look at it in more detail. The charge that accumulates in the POPS from the beginning of the experiment to time t is equal to.

$$Q = \int_0^t I(U(t))dt$$

We transform the integrand as follows

$$Q = \int_0^t I(U(t))\frac{dU}{dU}dt = \int_0^t I(U(t))\frac{dt}{dU}dU = \int_0^t I(U(t))\frac{1}{V_p}dU \tag{3}$$

where Vp is the scanning speed when measuring VAC, and the integral (3) itself is the hysteresis area I(U(t))dU. In our experiment, the scanning speed is a strictly linear function, since an integrator based on an operational amplifier serves as a linearly varying signal generator. However, we are not interested in the charge itself, but in the density of ions in close proximity to the smaller electrode. Then

$$n(r,t) = \frac{Q}{q \cdot S \cdot h(U)} \tag{4}$$

therefore, the left and right sides of Eq. (4) must be divided by the volume surrounding the electrode. Then

$$n(r.t) = \frac{1}{q \cdot S \cdot h(U)} \int_0^t I(U(t)) \frac{1}{V_p} dU = \frac{1}{q \cdot S \cdot h(U)} \cdot \frac{S_{I(U(T))}}{V_p} \tag{5}$$

As can be seen, to determine the ion concentration in this technique, it is necessary to know the thickness of the bulk charge layer, the area of the electrodes, the magnitude of the hysteresis of the VAC and the scanning speed I(U). Since we have the opportunity to determine the concentration of charged particles by method 1 and 3, we will solve the inverse problem: using Eq. (5), we estimate the thickness of the POPS.

In an electrolytic cell with a size of 5 × 5 sm, the VAC of a KCl solution was measured (KCl is chemically pure, the molar concentration was 0.01). The ions of this substance have mobility close in absolute value and, accordingly, drift velocity. This circumstance makes it possible to obtain an almost symmetrical VAC. This is important for modeling the kinetic processes accompanying the passage of electric current through the solution. Niobium plates with areas of $1.34{\cdot}10^{-4}$ and $5.27{\cdot}10^{-4}$, respectively, were used as electrodes. The measurement of the I(U) curves was carried out in a pulsed mode, since this method minimizes the influence of electrochemical processes [5]. In the center of the cell, at a distance of 0.01 m from each other, two auxiliary niobium electrodes with an area of $0.4\ 10^{-4}$ were located. The difference of their potentials was recorded on a digital oscilloscope.

In the course of the research, a series of VAC was measured. The experimental curves I(U) are shown in Fig. 3. We present an image of the dependencies I(U) with the inverse sign. Before registering the curves, the electrodes were treated with an

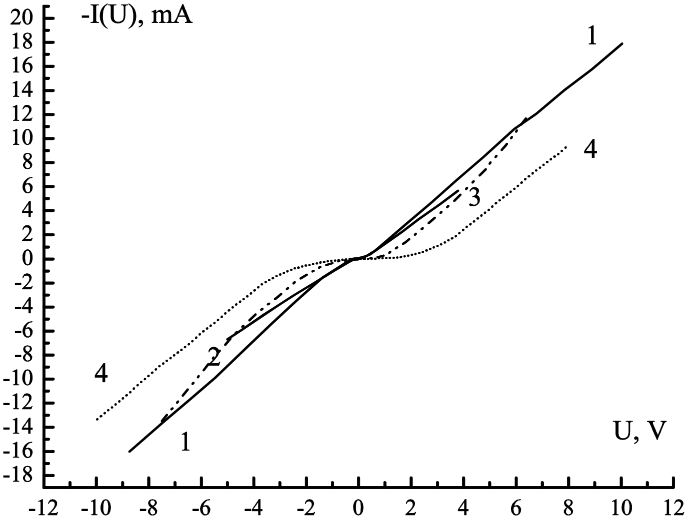

Fig. 3 VAC in 1% KCl solution: 1—first measurement I(U): 2,3, 4—VAC curves obtained after 10, 20 and 90 min of measurements

abrasive that removed the oxide layer of the electrode. Further measurements were carried out without processing the electrodes and mixing the electrolyte. The first curve I(U) was obtained immediately after processing the electrodes, the second and third—after 10 and 20 min of measurements, respectively. When registering the fourth curve, the electrolyte was replaced without processing the electrodes. The total time of the electrodes spent in the electrolyte solution during the experiment, we estimate about 90 min. To one degree or another, all VAC have hysteresis; with repeated scanning of the VAC, its manifestation becomes especially noticeable. For example, curves 2 and 3 in Fig. 3.

Figure 4 shows the first derivatives of the VAC according to the potential of the previous figure. As for the graphs, the "fast cosine" i.e. I'(U) is located on the interval of the slowly growing VAC, and the flat part is in the remaining part. This means that the cosine argument is a complex function. In other words, there is a screening effect in solutions: while the field in the solution and in the layer is small, we observe a "fast cosine", but as soon as the shielding takes effect, the cosine becomes "flat". Note that with a small electric field and the shielding is small in the entire volume: i.e. the sine argument is close to qU/kT ~ 1. The shielding of ions in this VAC interval is carried out by water molecules. With an increase in the field, its effect is weakened due to additional shielding by ions of opposite signs that are in POPS.

Figure 5 shows the dependence of the electric field (in absolute magnitude) on the voltage applied to the electrodes. The numbering of the curves corresponds to the notation in Fig. 3.

The evolution of curves over time, presented in Figs. 3, 4, 5, reveals several experimental facts. As a result of the experiment, symmetric curves I(U), I'(U),

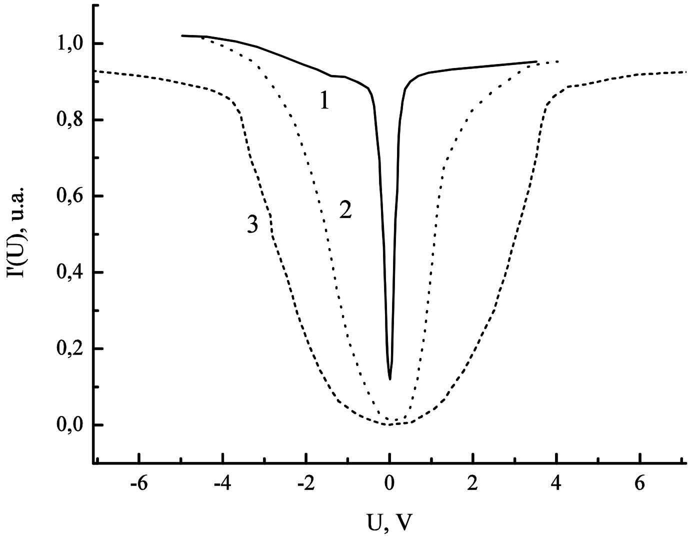

Fig. 4 I'(U) in 1% KCl solution:—first measurement I(U): 2—VAC curves obtained after 20 and 90 min of measurements

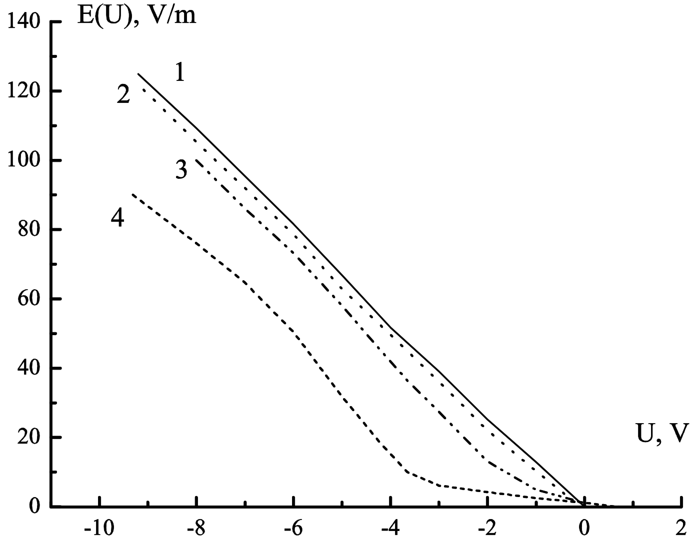

Fig. 5 Shows the dependences of the electric field in the middle of the cell: 1—the first measurement I(U): 2,3, 4—the VAC curves obtained after 10, 20 and 90 min of measurements

E(U) were indeed obtained. Further, the measured graphs show an expansion of the low current region. The third fact is that the shape of the VAC, its derivative and the corresponding dependence E(U) change. So, the non-current interval for curve 1 in Fig. 3 is several tenths of a volt, and for curve 4 this area expands to ± 3V. According to curve 4, shown in Fig. 1, at the inflection point of the graph, we take a current of 1.47 mA. This current value corresponds to a field of 13 V/m. Then, taking into account the mobility of potassium ions 6,8 10^{-8} $m^2/(V * s)$ and the area of the smaller electrode 1,34 * 10^{-4} m^2 for ion density, we obtain

$$n = \frac{I(U)}{qbS\Delta E \cdot sh(\varepsilon(U) \cdot qU_0/kT)} = \frac{0.00147}{1.6 \times 10^{-19} \times 6.8 \times 10^{-8} \times 1.34 \times 10^{-4} \times 13 \times 1} = 7.8 \times 10^{25} m^{-3}$$

The real density (1% KCl solution) is 8*1025 m^{-3}. The application of this technique to curve 3 in Fig. 1 at a current of 0.512 mA, an electric field of 81 V/m makes it possible to obtain an ion concentration of 8.1 1025 m^{-3}. Thus, we get a quantitative agreement with an error of 5%. Now we can estimate the thickness of the layer by the formula (5). We find the hysteresis area of curves 1 and 3 in Fig. 3 and determine the scanning speed of the potential (0.25 V/s). Then the value of the layer thickness is $2.67 \cdot 10^{-6}$ m.

It is usually assumed that the thickness of the bulk charge layer in a solution with ions having similar mobility values is 5–6 Debye radii From Fig. 3 it follows that changing the electrolyte portion does not change its resistance, since the slope of curve 4 remains the same as for the 1st curve. On the other hand, if we continued the measurement without changing the solution, we would get curves with increasing hysteresis. Then it should be recognized that the thickness of the layer at the electrodes increases significantly, since the other parameters included in formula (5) do not change. This is possible only under the assumption that the thickness of the layer depends on the concentration of hydrogen ions, the presence of which dramatically increases the thickness of POPS [8]. An increase in the thickness of POPS leads to a greater polarization of charged particles in the layer. As for curve 4 in Fig. 3, it is obvious the emission of hydrogen ions from the surface of the electrodes. Or in other words, during the passage of an electric current, the metal surface sorbs hydrogen atoms from water.

These methods may be of interest to specialists in physico-chemical, chemical-biological, geological-ecological and other related areas, where different approaches are required to determine the parameters of electrolyte solutions.

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