Chemistry

ELECTRICAL CONDUCTIVITY OF POTASSIUM SALT––DIMETHYLSULFOXIDE–WATER SYSTEMS AT DIFFERENT TEMPERATURES

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Interactions of potassium salt–dimethylsulfoxide (DMSO)–water systems in 25–45^0C temperature range were studied using electrical conductivity method. The results show that the conductance of these solutions depends on anions salvation state and is reduced according to this row: $NO_3^- \succ Cl^- \succ I^- \succ Br^-$. Ion mobility increases with rising of temperature, which leads to an increase in the limiting conductance. With the addition of DMSO appears an extreme point on the dependence, which becomes more harshly when the temperature increases. At DMSO high concentrations (>1.60 *M*), K^+–DMSO interaction becomes more intensive, which leads to the formation of bulky solvate shell affecting negatively on the ion mobility.

Keywords: potassium salts, electrical conductivity, dimethylsulfoxide, interaction.

Introduction. Studies on electrical conductivity of an electrolyte in solution give many important qualitative insights of electrolyte solution properties [1]. Electrical conductance of an electrolyte in various aqueous, partial aqueous and non aqueous media has received considerable attention recently. Limiting ionic conductivities characterize the mobility of ions in the infinite-dilution limit. They provide a starting point for the computation of electrical conductivity at finite concentrations and are necessary as input for most theories of the concentration dependence of conductance [2, 3]. The presence of organic compounds in water solution can change water structure and affect the state of solvated ions. Some organic solvents can selectively solvate cations, but keep anions "free". Therefore, anion reactions are keenly accelerated in such solvents. DMSO is one of these solvents [4]. DMSO has been widely used in cell biology and DMSO–water mixtures as well [5]. Moreover, DMSO provides many other effects on living systems: protecting against damage by ionizing radiation [6, 7], inducing cellular fusion and increasing penetrability across biomembranes [8]. Due to the importantce, the aim of this article is to study electrical conductance of potassium salt ions (KCl, KBr, KI, KNO₃) in aqueous DMSO solution at different temperatures.

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Materials and Methods. KCl, KBr, KI and KNO$_3$ of chemically pure grade is purchased from "Reakhim". DMSO is from "Sigma Chemical Co" (USA). Bidistilled water is used for preparation of solutions. The DMSO concentration is varied within up to 3.53 *M*. Solution electrical conductivity is measured at different temperatures ($\pm 0.3^0 C$) on a Janway 4330 device (England). The mean value of 3 measurements is taken, the electrical conductivity measurement error is $\pm 2\%$. The presented graphs are constructed and analyzed using the ORIGIN 8.0 computer program.

Results and Discussion. The potassium salt (KCl, KBr, KI, KNO$_3$)–water––DMSO systems are chosen not only because of their important biological role, but also due to the fact that in these systems electrolyte resolution and DMSO competing interactions with water molecules and ions take place [9]. Potassium salt–water and potassium salt–water–DMSO systems can be studied by electrical conductivity method. The specific conductance (k) of salt solution is directly defined the instrumentally. Specific conductance is used for determining molar conductance (λ) of solutions at 25, 30, 35, 40 and $45^0 C$: $\lambda = k / 1000 \cdot C$, where *C* is concentration of salt. The limiting conductance (λ_0) of solutions is determined using Kohlraush relationship between conductance and concentration for strong electrolytes:

$$\lambda = \lambda_0 - B\sqrt{C} \, ,$$

where λ_0 is the conductance at infinite dilution, that is $\lambda \to \lambda_0$ as $C \to 0$, *B* is a positive constant for a given electrolyte and dependent on the electrochemical valence of the electrolyte, temperature and solvent. Thus, λ_0 can be readily obtained by plotting λ versus $\sqrt{C}$ and extrapolating to zero concentration [10].
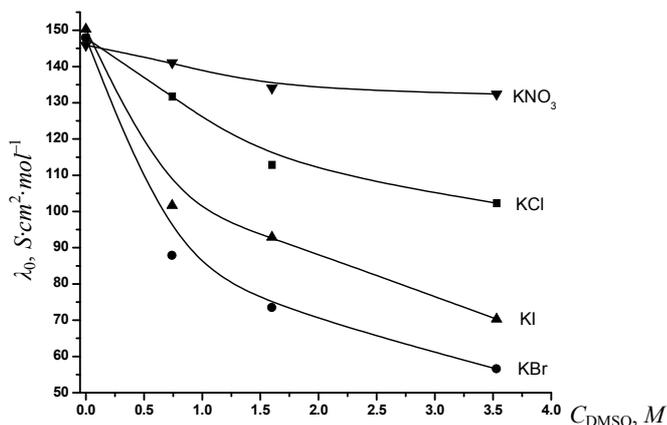
Fig. 1. Limiting conductance of potassium salts at different concentrations of DMSO, $t=25^0 C$.

Fig. 1 shows the dependence of potassium salts limiting electrical conductance from DMSO concentracion. In the presence of DMSO limiting conductance of all salts decreases. Conductivity decreases sharply at DMSO 0–1.15 *M* concentration range. As it was shown in [11], DMSO–water solutions are characterized by low electrical conductivity. Conductivity of DMSO–water systems are realized via prototropic mechanism, which is much lower than the ionic conductivity. That is why the conductivity of the solvent is not taken into

account. As it is known, various factors and effects (ion charge, solvated ions radiuses, counter ion interaction, etc.) can affect on electrical conductivity.

The diffusion coefficient of salt (D_{salt}) can be calculated from the D_+ and D_- values of the constituent ions by the relation:

$$D_{salt} = \frac{(z_+ + |z_-|)D_+ D_-}{z_+ D_+ + z_- D_-},$$

where z is the charge on the ion. The diffusion coefficient of the ion in dilute aqueous solution, which we have used for calculating D_{salt}, are taken from [12].

As it is shown in the Table, the λ_0 of salts is changed with the same regularities as the diffusion coefficient. Competing interactions of DMSO with water molecules can also affect on ion mobility. As it is shown in [9, 13], dialkylsulfoxide molecules displace water molecules in the primary hydrate shell of ions. At DMSO higher concentrations increasing effective interactions between DMSO and water molecules result is anions release from the hydrate shell. Conductance of these solutions is due to anions, which can be presented by following row: $NO_3^- \succ Cl^- \succ I^- \succ Br^-$ (see Table) [12].

Diffusion coefficients of ions, potassium salts and limiting conductance of these salts dilute aqueous solutions, $t=25^0C$

Ion	K^+	NO_3^-	Cl^-	I^-	Br^-
D_{ion}, $10^{-5}\,cm^2 \cdot s^{-1}$	1.957	1.902	2.032	2.045	2.080
Salt	–	KNO_3	KCl	KI	KBr
λ_0, $S \cdot cm^2 \cdot mol^{-1}$	–	145.25	147.74	150.83	152.16
D_{salt}, $10^{-5}\,cm^2 \cdot s^{-1}$	–	1.565	1.608	1.612	1.623

Fig. 2 shows the dependence of potassium chloride limiting conductance from DMSO concentration in 25–45^0C temperature range.
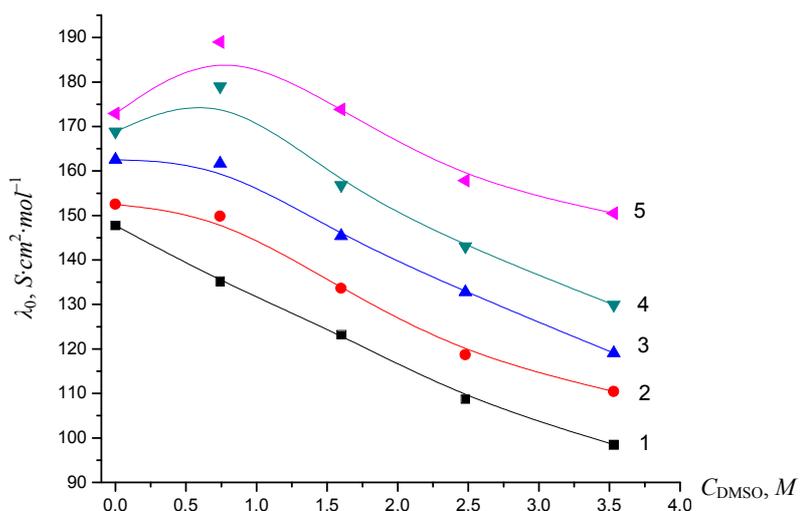
Fig. 2. Limiting conductance of potassium chloride in DMSO–water solution in different temperature, $t\,^0C$: 1 – 25; 2 – 30; 3 – 35; 4 – 40; 5 – 45.

Ion mobility increases with rising of temperature, which leads to an increase in the limiting conductance. With addition of DMSO, appears an extreme point on the dependence in $[DMSO] \approx 0.5-1$ *M*, which becomes more harshly, when the temperature increases. Appearance of the extreme point on these curves indicates the presence of competing interactions in the system. When a small amount of DMSO is added to the solution, the shielding of K^+ cation gets smaller, which leads to the increase of cation mobility. The further increase of DMSO concentration increases K^+–DMSO interaction, which leads to the formation of bulky solvate shell in DMSO 1.60–3.53 *M* concentration range. It affects negatively on the ion mobility.

Our studies of interactions in potassium salt–DMSO–water systems at $25-45^0C$ temperature range can be explained by ion mobility increases with rising the temperature, which can lead an increase in the limiting conductance. The conductance of these solutions depends on anions salvation state and is reduced according to this row: $NO_3^- \succ Cl^- \succ I^- \succ Br^-$. At DMSO high concentrations (>1.60 *M*) K^+–DMSO interaction becomes more intensive, which leads to the formation of bulky solvate shell affecting negatively on the ion mobility.

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