https://doi.org/10.15407/ujpe70.9.598

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SINGLY CHARGED IONS AND MOLECULAR MOBILITY IN FORMIC ACID AT 298.15 K

The diffusion coefficients D_i^0 and the diffusion displacement lengths $\overline{d}$ have been calculated for 16 singly charged ions H^+, Li^+, Na^+, K^+, NH_4^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, $Pent_4N^+$, Cl^-, Br^-, I^-, ClO_4^-, BPh_4^-, and $HCOO^-$ from literature data on their limiting molar electrical conductivity at 298.15 K in formic acid. Based on the justified parameter $\overline{d}-r_i$, where r_i is the ion radius, the negative (at $\overline{d}-r_i < 0$) or positive (at $\overline{d}-r_i > 0$) solvation is determined for each ion. Most ions, except H^+ and $HCOO^-$, are solvated positively. Unlike other ions, the negative solvation of the formate ion occurs due to the domination of intermolecular interactions over the ion-molecule interactions. For a proton, the negative solvation is caused by the prototropic transfer mechanism.

Keywords: formic acid, singly charged ions, diffusion, electrical conductivity, short-range solvation, negative solvation.

1. Introduction

This work continues our systematic studies of the influence of singly charged ions on the translational mobility of the nearest solvent molecules, which are of different nature and have different physicochemical parameters (density, viscosity, dielectric constant, and so forth), such as water [1], heavy water [2], ethylene glycol [3–5], saturated alcohols [6], and amides [7]. The main scientific achievement of those studies was not only the establishment of the fact that the length of the translational motion of ions in those solvents deviates from the Stokes–Einstein law (SEL), but also the proposition and the mathematical justification of the difference $\overline{d} - r_i$, where $\overline{d}$ is the translational displacement length of the ion, and r_i is its structural radius, as a measure of the ion influence on the immediate environment of solvent molecules.

As is known, the SE-based description of the ion mobility in solutions is associated with a substantial influence of the medium viscosity. Although the mobility of ions is considered as a motion of a solid sphere in a viscous medium (continuum)–i.e., this is an approximation–this model can bring about correct conclusions. According to the criterion proposed by us, the Stokes–Einstein law is satisfied if $\overline{d} - r_i = 0$, i.e., if the solvation is absent altogether. In this case, an ion is subjected to a force that slows down its motion. This force arises due to the solvent viscosity, and the length of the translational ion displacement is equal to the ion radius, $\overline{d} = r_i$.

In previous works [1–7], we found that the Stokes–Einstein law is not obeyed in most cases, neither at $\overline{d} - r_i > 0$ nor at $\overline{d} - r_i < 0$. Therefore, the difference $\overline{d} - r_i$ was not considered as the thickness of the solvation shell [8], but as a measure of a deviation from this law. In addition, in view of the critical approach made in work [8] concerning the physical meaning of the Stokes radius, the concept of the latter was replaced by the length of the translational ion displacement $\overline{d}$ [3]. By the way, in work [9], the ratio $\overline{d}/\tau$ was considered as the average velocity, and the value $\overline{d}$ as the average length of the ion displacement or the ion jump in the diffusion mode during the time τ.

Citation: V'yunyk I.M., Bulavin V.I., Kramarenko A.V. Singly charged ions and molecular mobility in formic acid at 298.15 K. *Ukr. J. Phys.* **70**, No. 9, 598 (2025). https://doi.org/10.15407/ujpe70.9.598.

A mathematical justification of choosing the difference $\overline{d}-r_i$ as a measure of the near-field ion solvation was made in work [4] using the friction coefficient (FC) concept. The value of the latter does not depend on the nature of the force acting on the particle [9]. According to works [10, 11], the total FC ζ can be represented as the sum of two components,

$$\zeta = \zeta_{\text{at}} + \zeta_{\nu}, \tag{1}$$

where ζ_{at} is the attraction FC, and $\zeta_{\nu} = f r_i \eta_0$ is the viscous FC.

Let us express the total FC via the ion diffusion coefficient,

$$\zeta = \frac{kT}{D_i^0} = f\overline{d}\eta_0. \tag{2}$$

With regard for this relation, let us rewrite Eq. (1) in the form

$$\zeta_{\text{at}} = \zeta - f r_i \eta_0 = \frac{kT}{D_i^0} - f r_i \eta_0. \tag{3}$$

Replacing $\frac{kT}{D_i^0}$ by the equivalent quantity $f\overline{d}\eta_0$, we can write that

$$\zeta_{\text{at}} = f\overline{d}\eta_0 - f r_i \eta_0 = f\eta_0\left(\overline{d} - r_i\right). \tag{4}$$

Thus, the parameter $\overline{d}-r_i$ follows from the difference between the total and viscous friction coefficients, which are characterized by the $\overline{d}$- and r_i-values, respectively.

The coefficient ζ_{at} contains all information about the ion's influence on the mobility of solvent molecules that are closest to the ion, except for information that is taken into account in the Stokes–Einstein law. This law is fulfilled, if $\overline{d} = r_i$, or $\overline{d} - r_i = 0$. Different signs of the deviation of this difference from zero allowed us to classify ions into structure destroyers (chaotropes, at $\overline{d}-r_i < 0$) and structure strengtheners (kosmotropes, at $\overline{d} - r_i > 0$).

In work [6], the components of ζ_{at} were also determined,

$$\zeta_{\text{at}} = \zeta_{\text{at}}^{\text{IM}} + \zeta_{\text{at}}^{\text{MM}}. \tag{5}$$

The estimation of the component $\zeta_{\text{at}}^{\text{MM}}$ was carried out according to the equation [6]

$$\zeta_{\text{at}}^{\text{MM}} = \frac{\Delta G_{\text{MM}}^{*}}{D_{\text{S}} N_{\text{A}}}, \tag{6}$$

where D_{S} is the solvent self-diffusion coefficient, ΔG_{MM}^{*} is the change in the Gibbs energy of the short-range interaction between the solvent molecules located near ions and their neighbors, when they are moved to a certain distance from the ion, and N_{A} is Avogadro's number.

Among the most important results obtained while analyzing the components of the attraction friction coefficient was the establishment of their opposite signs ($\zeta_{\text{at}}^{\text{IM}} > 0$, $\zeta_{\text{at}}^{\text{MM}} < 0$) for singly charged ions in water and n-alcohols [6]. The intermolecular component $\zeta_{\text{at}}^{\text{MM}}$ has a negative value regardless of the ion solvation type and the solvent. The opposite signs of the ζ_{at}-components probably correspond to different-sign energy effects of the processes of water molecule exchange between the primary solvation shell (PSS) of ions and pure water associates.

It is from such positions that the influence of singly charged ions on formic acid was considered in the previous study [12], and they were classified into chaotropes and kosmotropes. In this work, unlike work [12], the behavior of singly charged ions in formic acid solutions was studied in more details. Formic acid is an interesting substance in physical, chemical, and biological aspects. It has a rather large dielectric constant ($\varepsilon = 57.0$ at 293.15 K) and is used as a solvent for many organic and inorganic substances. It is the simplest among carboxylic acids, thus being a model for permanent fundamental experimental and theoretical studies due to a good many areas of its application. It has again attracted interest as a potential material for hydrogen storage [13], in simulating the process of atmospheric aerosol formation and nucleation, which significantly affect climate changes and the air quality [14], and in other theoretical aspects, which are discussed below.

2. Calculation Part

According to literature data on the limiting molar electrical conductivity λ_0 for 16 singly charged ions – H^+, Li^+, Na^+, K^+, NH_4^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, Pent_4N^+, Cl^-, Br^-, I^-, ClO_4^-, HCOO^-, and BPh_4^- – in formic acid [15, 16], we calculated the diffusion coefficients D_i^0 of those ions at 298.15 K using the Nernst–Einstein equation

$$D_i^0 = \frac{RT}{|z_i|F^2}\lambda_0. \tag{7}$$

Characteristics of singly charged ions in formic acid at 298.15 K ($\zeta_{\text{at}}^{\text{MM}} = -46.355 \times 10^{12}$ kg/s)

Ion	$r_i \times 10^{10}$, m	$\lambda_i^0 \times 10^4$, $\text{cm} \cdot \text{m}^2/\text{mol}$	D_i^0, $\text{m}^2 \cdot \text{s}^{-1}$	$\overline{d} \times 10^{10}$, m	$(\overline{d} - r_i) \times 10^{10}$, m	$\zeta_{\text{at}} \times 10^{12}$, $\text{kg} \cdot \text{s}^{-1}$	$\zeta_{\text{at}}^{\text{IM}} \times 10^{12}$, $\text{kg} \cdot \text{s}^{-1}$
H^+	2.47	79.8	2.125	0.95	–1.53	–3.117	43.238
Li^+	0.69	19.5	0.519	3.89	3.20	6.518	52.873
Na^+	1.02	21.0	0.559	3.62	2.60	5.296	51.651
K^+	1.38	24.0	0.639	3.17	1.79	3.646	50.001
NH_4^+	1.48	27.1	0.722	2.81	1.33	2.709	49.064
Me_4N^+	2.80	23.2	0.618	3.27	0.47	0.957	47.312
Et_4N^+	3.37	19.2	0.511	3.95	0.58	1.181	47.536
Pr_4N^+	3.79	14.6	0.389	5.20	1.41	2.872	49.227
Bu_4N^+	4.13	13.8	0.367	5.50	1.37	2.791	49.146
$Pent_4N^+$	4.43	11.4	0.304	6.66	2.23	4.543	50.898
Cl^-	1.81	26.4	0.703	2.88	1.07	2.180	48.535
Br^-	1.96	28.2	0.751	2.69	0.73	1.487	47.842
I^-	2.20	32.9	0.875	2.31	0.11	0.224	46.579
ClO_4^-	2.40	29.2	0.778	2.60	0.19	0.387	46.742
$HCOO^-$	2.04	50.0	1.339	1.52	–0.53	–1.080	45.275
BPh_4^-	4.21	12.3	0.328	6.17	1.96	3.993	50.348

On the basis of available data for D_i^0 of ions and the viscosity of pure solvent, η_0 [16], the length of the translational ion displacement $\overline{d}$ is calculated using the Stokes–Einstein equation

$$\overline{d} = \frac{kT}{f D_i^0 \eta_0}. \tag{8}$$

In Eqs. (7) and (8), T is the absolute temperature, R is the universal gas constant, k is the Boltzmann constant, z_i is the ion charge, and F is the Faraday constant. The multiplier f was taken equal to 6π for the "sticking" condition and to 4π for the "slipping" one. The results of calculations of the D_i^0- and $\overline{d}$-values for examined ions are quoted in Table. The structural radii of ions taken from work [17] are also given.

By analyzing the results of calculations of the quantities D_i^0, $\overline{d}$, and $\overline{d} - r_i$ for the studied ions in formic acid (Table), the following regularities were found.

1. The quantities D_i^0 and $\overline{d}$ depend on the structural radius of the ion and on the sign of its charge. As the radius increases along the series of ions of the same type:

a) Li^+–Na^+–K^+–NH_4^+: D_i^0 increases, and $\overline{d}$ decreases;

b) NH_4^+–Me_4N^+–Et_4N^+–Pr_4N^+–Bu_4N^+–$Pent_4N^+$: D_i^0 decreases, and $\overline{d}$ increases;

c) Cl^-–Br^-–I^-: D_i^0 increases, and $\overline{d}$ decreases.

Similar changes of the D_i^0- and $\overline{d}$-values for the ions indicated above were found in our previous works [1–5]: the growth of D_i^0 and the reduction of $\overline{d}$ along cation series (a) and anion series (c) as the parameter r_i increases testifies to the electrostatic nature of solvation. In TAA ions (series (b)), the solvation nature is non-electrostatic, i.e., it is associated mainly with the non-electrostatic nature of interparticle interactions occurring in the solution [3, 4].

2. The stokes–Einstein law is not satisfied, neither under the hydrodynamic adhesion condition (6π), nor under the sliding one (4π).

3. All the researched ions (except for H^+ and $HCOO^-$) are kosmotropes in formic acid.

3. Results and Discussion

Formic acid belongs to solvents capable of solvating both cations and anions. The features of the electronic structure of its molecules were considered in works [13, 14, 18–20]. This acid exists mainly in the form of dimers in both the gaseous and liquid phases (see Fig. 1). These dimers are destroyed in highly dilute solutions or at high temperatures. In work [18], it was noted that, in liquid formic acid, hydrogen-bonded clusters mainly consist of short linear branched chains. Monomeric formic acid molecules exist as cis- and trans-isomers, with the trans conformers being more stable [18].

Formic acid can form hydrogen bonds of four different types [20] (Fig. 2). Both hydroxyl and carbonyl groups participate as proton donors and acceptors. Since each oxygen atom in the hydroxyl or carbonyl group has two bound-electron pairs, it can form two acceptor H-bonds, so, we obtain six H-bonds in total. The strongest are the donor H-bond formed by the hydroxyl (O–H) and the acceptor H-bonds with the participation of the hydroxyl and carbonyl groups.

As mentioned above, all examined ions, except for H^+ and $HCOO^-$, are solvent structure orderers (kosmotropes). The ability of cations (except for H^+) to strengthen the structure of formic acid can be explained by the presence of a carbonyl O atom with a high electron concentration in its molecule [20], through which the solvent molecules coordinate cations. Anions as electron pair donors can probably be coordinated by the acidic proton of formic acid; the latter is characterized by a somewhat lower affinity to the proton in comparison with other hydroxyl-containing solvents, e.g., water or saturated alcohols.

For a more detailed consideration of the features of the near-field solvation of ions, we used Eqs. (5) and (6) to calculate the components of the total attraction friction coefficient ζ_{at}. These equations take into account both intermolecular, the term $\zeta_{\mathrm{at}}^{\mathrm{MM}}$, and ion-molecular, the term $\zeta_{\mathrm{at}}^{\mathrm{IM}}$, interactions. The values of these components of ζ_{at} were taken from works [15,18] and are quoted in Table. According to Eq. (5), the sign of ζ_{at} (see Table) is determined by the sign of the dominant component and coincides with the sign of the difference $\bar{d} - r_i$, i.e., it indicates the type of near-field solvation. If $\zeta_{\mathrm{at}} < 0$, negative solvation is observed, i.e., the ion-molecule bonds are weaker than the intermolecular bonds, $\zeta_{\mathrm{at}}^{\mathrm{IM}} < \zeta_{\mathrm{at}}^{\mathrm{MM}}$. On the contrary, at positive solvation, ion-molecular interactions prevail over intermolecular ones, $\zeta_{\mathrm{at}}^{\mathrm{IM}} > \zeta_{\mathrm{at}}^{\mathrm{MM}}$. In addition, the value of ζ_{at} indirectly demonstrates the strengthening or weakening of the coordinating force of the solvent on a separate ion. The larger the value of ζ_{at} in the algebraic sense, the larger the tendency to form ion-molecular associates that strengthen and modify the solvent structure.

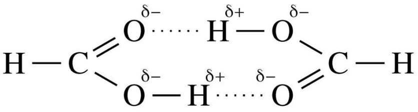

Fig. 1. Formic acid dimer

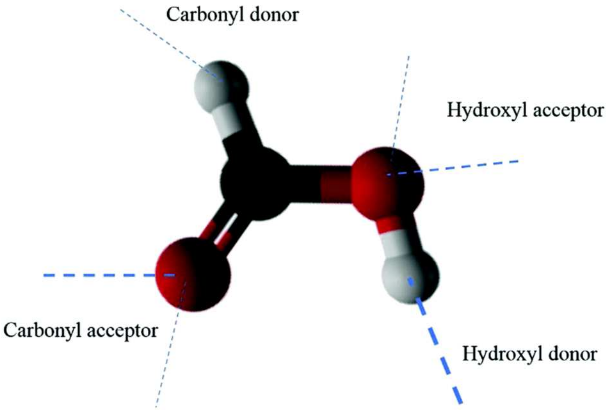

Fig. 2. Types of hydrogen bonds in formic acid. The strongest H-bonds are marked as thick lines [20]

The opposite signs of the component contributions to ζ_{at}, namely, $\zeta_{\mathrm{at}}^{\mathrm{MM}} < 0$ and $\zeta_{\mathrm{at}}^{\mathrm{IM}} > 0$, are associated with different energy effects of the exchange processes of solvent molecules in the PSS of ion and in the pure solvent. The exit of a solvent molecule from the PSS of ion requires some energy expenditure, which slows down its diffusion and leads to a positive contribution to ζ_{at}. On the other hand, the reduced diffusion of a solvent molecule from the PSS of ion is compensated by the interaction of this molecule with solvent molecules in the solvent bulk.

In the case of positive solvation, for a solvent molecule to exit from the PSS, it must overcome a potential barrier; the higher the ordering of molecules in the solution as compared to the pure solvent, the larger the magnitude of the barrier, i.e., $\zeta_{\mathrm{at}} > 0$ at $\zeta_{\mathrm{at}}^{\mathrm{MM}} < 0$, $\zeta_{\mathrm{at}}^{\mathrm{IM}} > \left|\zeta_{\mathrm{at}}^{\mathrm{MM}}\right|$, and $\zeta_{\mathrm{at}} = \zeta_{\mathrm{at}}^{\mathrm{MM}} + \zeta_{\mathrm{at}}^{\mathrm{IM}} > 0$. If an ion is negatively solvated ($\zeta_{\mathrm{at}} < 0$), then the potential barrier value is smaller than in the pure solvent: $\zeta_{\mathrm{at}} < 0$ at $\zeta_{\mathrm{at}}^{\mathrm{MM}} < 0$, $\zeta_{\mathrm{at}}^{\mathrm{IM}} < |\zeta_{\mathrm{at}}^{\mathrm{MM}}|$, and $\zeta_{\mathrm{at}} = \zeta_{\mathrm{at}}^{\mathrm{MM}} + \zeta_{\mathrm{at}}^{\mathrm{IM}} < 0$. In other words, the positive ion solvation is characterized by the dominant influence of the absolute values of the component associated with desolvation, $\zeta_{\mathrm{at}}^{\mathrm{IM}} > |\zeta_{\mathrm{at}}^{\mathrm{MM}}|$. In the case of negative solvation, on the contrary, the contribution from $\left|\zeta_{\mathrm{at}}^{\mathrm{MM}}\right|$ dominates, which testifies to a strengthening of the bond between the solvent molecule that has left the ion solvation shell and the molecule in the solvent bulk, $\left|\zeta_{\mathrm{at}}^{\mathrm{MM}}\right| > \zeta_{\mathrm{at}}^{\mathrm{IM}}$ [3].

The reduction of $\overline{d}$ and, accordingly, $\overline{d} - r_i$ and ζ_{at}, as the radius of the alkali metal cation increases (see Table) is a result of weakening of the ion coordinating force due to a reduction of the ion charge density in the series $\mathrm{Li^+}$–$\mathrm{Na^+}$–$\mathrm{K^+}$.

The ammonium cation $\mathrm{NH_4^+}$ has the highest electrical conductivity λ_0 and the shortest diffusion displacement length $\overline{d}$ among the alkali metal cations and the TA ions (Table). However, by its coordination ability, this ion differs from the alkali metal cations and approaches the TAA ions. In our opinion, the coordination of an $\mathrm{NH_4^+}$ ion by HCOOH molecules may occur due to the H-bond between the H atom of the $\mathrm{NH_4^+}$ ion and the carbonyl O atom of the solvent. This leads to the formation of a kinetically stable complex with the cation $\mathrm{NH_4^+}$, which diffuses as a single unit.

The apolar groups of the TAA ions (as well as $\mathrm{BPh_4^-}$) cannot interact strongly with formic acid molecules and form clathrate structures, which inhibit their diffusion. This leads to an increase of $\overline{d}$, $\overline{d} - r_i$, and ζ_{at} and, consequently, to the growth of their positive solvation. Thus, in this case, the short-range solvation of the TAA and $\mathrm{BPh_4^-}$ ions is not a result of the strong ion-molecular (I-M) interaction, but a result of the interaction between the solvent molecules surrounding the apolar groups of the TAA and $\mathrm{BPh_4^-}$ ions. Accordingly, the interaction between the solvent molecules in the primary solvation shell becomes stronger, and stronger bonds are formed between them in comparison with the bonds in the pure solvent.

The halide ions and the perchlorate ion are coordinated by the hydrogen of the hydroxyl group. Unlike $\mathrm{BPh_4^-}$, these ions have a higher charge density and reveal the dominant electrostatic nature of solvation. In the series $\mathrm{Cl^-}$–$\mathrm{Br^-}$–$\mathrm{I^-}$, the anion radius increases monotonously, which leads to a weakening of the ion-solvent molecule interaction in this series, i.e., to short-range solvation. This change is also reflected in the values of $\zeta_{\mathrm{at}}^{\mathrm{IM}}$ of these ions, which decreases when transiting from $\mathrm{Cl^-}$ to $\mathrm{I^-}$, i.e., its value is largest for the chloride ion. Just this ion forms the strongest bond with the solvent molecule. At the same time, with the increase of the anion radius, the translational motion of the solvent molecules increases.

The anion $\mathrm{HCOO^-}$ is negatively solvated. The negative value of ζ_{at} is a conditional quantity that characterizes the destruction degree of intermolecular bonds in the solvent under the ionic influence [3]. Physically, this corresponds to an enhancement of the translational motion of solvent molecules under the influence of this anion, an increase in the frequency of exchange of the solvent molecules closest to the ion and in the solvent bulk, which leads to a reduction of the local viscosity in comparison with the macroscopic value, which is taken into account when calculating the friction viscosity coefficient (Eq. (1)) [3]. As is known [13, 18], the formate ion is stable in the form of the cluster diformate hydrogenate ion $\mathrm{HCOOH \cdots OOCH^-}$, which is formed during the interaction of an HCOOH molecule with its anion. The latter does not belong to rigid systems. This fact probably explains an anomalously high mobility of the $\mathrm{HCOO^-}$ ion in HCOOH. Thus, the mobility of the $\mathrm{HCOO^-}$ ion in formic acid is favored by its weak interaction with the solvent molecule, i.e., weak solvation. As a result, the mobility of the formate ion is slightly inhibited by the solvent. But the origin of the weak solvation of formate ion is a stronger interaction between the solvent molecules. This conclusion is confirmed by both an abnormally high ion mobility in anhydrous formic acid and the negative value of ζ_{at} of this ion (see Table).

Ion mobility and solvation are two interrelated processes that largely depend on the solvent molecular structure.

Protonated formic acid has two tautomers: $\mathrm{H{-}C(OH)_2^+}$ and $\mathrm{H{-}CO{-}OH_2^+}$; the former, the protonated carbonyl, is more stable. The latter tautomer in the hydroxyl protonated form has a significantly higher (by 209 kJ/mol) activation energy [21]. Therefore, we believe that the excess proton is mainly coordinated by the carbonyl oxygen atom of the methanoic acid molecule by means of the donor-acceptor mechanism.

The proton mobility in formic acid (see Table) is quite high. It is lower than that in water and methanol, but higher than in ethanol [3]. This fact gives reason to think that the proton transfer occurs in water and saturated alcohols through both the hydrodynamic and prototropic (relay) mechanisms [3]. The authors of work [22] came to the same conclusion.

As was shown in our work [3], the essence of the prototropic mechanism governing the proton transfer in hydroxyl-containing solvents consists in that a proton transfer from one solvent molecule to another occurs in the "free solvent" bulk. The "free solvent" molecules exchange with the same molecules in the primary solvation shell of the proton. That is, the resolvation of the negatively solvated carbonyl protonated cation $\mathrm{H{-}C(OH)_2^+}$ takes place. As was indicated above, negative solvation is associated with the enhancement of the translational motion of the solvent molecules in the PSS of ion (proton). Desolvation that occurs during resolvation leads to a restructuring of both the electronic structure and the system of chemical bonds in the $\mathrm{H{-}C(OH)_2^+}$ cluster.

We believe that the anomalous proton transfer is a result of short-range solvation, and the hydrogen-bonded solvent plays a key role in its realization. Under the proton influence, H-bonds in the solvent are easily broken and easily formed. This fact gives rise to the rearrangement of the dynamically changing proton states.

1. V. Bulavin, I. V'yunyk, Y. Lazareva. Diffusion and microscopic characteristics of singly charged ion transfer in extremely diluted aqueous solutions. *Ukr. J. Phys.* **62**, 769 (2017).
2. V. Bulavin, I. V'yunyk. Compensation of isotope effects at the near solvation of singly charged ions in light and heavy waters. *Ukr. J. Phys.* **67**, 527 (2022).
3. V.I. Bulavin, I.N. V'yunyk, A.V. Kramarenko, V.A. Minakov. Kinetic solvation of singly charged ions in infinitely dilute solutions in ethylene glycol: effect of temperature. *J. Solution Chem.* **51**, 1334 (2022).
4. V.I. Bulavin, I.M. V'yunyk, A.V. Kramarenko, O.I. Rusinov, V.A. Minakov. Near solvation of tetraalkylammon ions in ethylene glycol and in water. *Visn. Nats. Tekhn. Univ. KhPI Ser. Khim. Khim, Tekhnol. Ekol.* No. 2, 63 (2019) (in Ukrainian).
5. V.I. Bulavin, I.M. V'yunyk, A.V. Kramarenko, O.I. Rusinov. Specifics of establishing tetraalkylamonium ions near solvation' in solvents with a spatial network OF H-bonds. *Visn. Nats. Tekhn. Univ. KhPI Ser. Khim. Khim, Tekhnol. Ekol.* No. 1, 28 (2020) (in Ukrainian).
6. V.I. Bulavin, I.N. V'yunnik, A.V. Kramarenko. Kinetic solvation and electrical conductance of proton in infinitely diluted solutions of hydrogen halides in primary alcohols and in water: Influence of temperature and solvent *J. Mol. Liq.* **242**, 1296 (2017).
7. V.I. Bulavin, I.M. Vyunik, A.V. Kramarenko, O.I. Rusinov. The influence of singly charged ions on the translational motion of molecules in extremely dilute amide solutions. *Visn. Nats. Tekhn. Univ. KhPI Ser. Khim. Khim, Tekhnol. Ekol.* No. 2, 86 (2021) (in Ukrainian).
8. Y. Marcus. Are ionic stokes radii of any use? *J. Solution Chem.* **41**, 2082 (2012).
9. Yu.M. Kessler, A.L. Zaitsev. *Solvophobic Effects: Theory, Experiment, Practice* (Khimiya, 1989) (in Russian).
10. P.G. Wolynes. Molecular theory of solvated ion dynamics. *J. Chem. Phys.* **68**, 473 (1978).
11. D.F. Evans, T. Tominaga, J.B. Hubbard, P.G. Wolynes. Ionic mobility. Theory meets experiment. *J. Phys. Chem.* **83**, 2669 (1979) .
12. S. S. Inozemtsev, I.S. V'yunyk, S.I. Bulavin. In: *Abstracts of the 15th All-Ukrainian Scientific Conference of Students and Postgraduates "Karazin Chemical Readings", April 24–26, 2023* (Kharkiv National University, 2023), p. 187 (in Ukrainian).
13. M.A. Brown, F. Vila, M. Sterrer, S. Thürmer, B. Winter, M. Ammann, J.J. Rehr, J.A. van Bokhoven. Electronic structures of formic acid (HCOOH) and formate ($\mathrm{HCOO^-}$) in aqueous solutions. *J. Phys. Chem. Lett.* **3**, 1754 (2012).
14. B. Radola, S. Picaud, D. Vardanega, P. Jedlovszky. Analysis of mixed formic and acetic acid aggregates interacting with water: A molecular dynamics simulation study. *J. Phys. Chem. C* **121**, 13863 (2017).
15. Yu.A. Karapetyan, V.N. Eichis. *Physicochemical Properties of Electrolytic Non-aqueous Solutions* (Khimiya, 1989) (in Russian).
16. Yu.Ya. Fialkov, V.F. Grishchenko. *Electrolysis of Metals from Non-aqueous Solutions* (Naukova Dumka, 1985) (in Russian).
17. Y. Marcus. *Ions in Solution and Their Solvation* (John Wiley and Sons, 2015).
18. I. Bakó, J. Hutter, G. Pálinkás. Car-parrinello molecular dynamics simulation of liquid formic acid. *J. Phys. Chem. A* **110**, 2188 (2006).
19. K. Marushkevich, L. Khriachtchev, J. Lundell, M. Räsänen. cis-trans formic acid dimer: experimental observation and improved stability against proton tunneling. *J. Am. Chem. Soc.* **128**, 12060 (2006).
20. V. Hänninen, G. Murdachaew, G.M. Nathanson, R.B. Gerber, L. Halonen. *Ab initio* molecular dynamics studies of formic acid dimer colliding with liquid water. *Phys. Chem. Chem. Phys.* **20**, 23717 (2018).
21. O. Sekiguchi, V. Bakken, E. Uggerud. Decomposition of protonated formic acid: One transition state – Two product channels. *J. Am. Soc. Mass Spectr.* **15**, 982 (2004).
22. T.C. Wehman, A.I. Popov. Electrical conductance studies in anhydrous formic acid solutions. *J. Phys. Chem.* **72**, 4031 (1968).

Received 27.05.25.
Translated from Ukrainian by O.I. Voitenko

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ОДНОЗАРЯДНІ ІОНИ І РУХЛИВІСТЬ МОЛЕКУЛ В МУРАШИНІЙ КИСЛОТІ ПРИ 298,15 K

Коефіцієнт дифузії (D_i^0) і довжину дифузійного зміщення ($\overline{d}$) 16 однозарядних іонів H^+, Li^+, Na^+, K^+, NH_4^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, $Pent_4N^+$, Cl^-, Br^-, I^-, ClO_4^-, BPh_4^-, $HCOO^-$ розраховано з літературних даних щодо їх граничної молярної електричної провідності при 298,15 K у мурашиній кислоті. На підставі обґрунтованого нами параметра ($(\overline{d} - r_i)$, де r_i – радіус іона) визначено негативну (при $(\overline{d} - r_i) < 0$) або позитивну ($(\overline{d} - r_i) > 0$) сольватацію йонів. Більшість йонів (крім H^+ і $HCOO^-$) сольватовані позитивно. Негативна сольватація форміат-іона, на відміну від інших йонів, зумовлена переважаючою міжмолекулярною взаємодією над іон-молекулярною. Для протона негативна сольватація викликана прототропним механізмом його переносу.

Ключові слова: мурашина кислота, однозарядні іони, дифузія, електрична провідність, ближня сольватація, негативна сольватація.