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### THE INFLUENCE OF SINGLY CHARGED IONS ON THE TRANSLATIONAL MOTION OF MOLECULES IN EXTREMELY DILUTE AMIDE SOLUTIONS

The type of short range solvation of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$  ions has been determined and analyzed in formamide (FA), N-methylformamide (MFA), N-dimethylformamide (DMF) at 298.15 K. In order to determine the type of ion solvation we used familiar-variable quantitative parameter  $(\bar{d} - r_i)$ , where  $\bar{d}$  is the translational displacement length of ion,  $r_i$  is its structural radius. It was found that the difference  $(\bar{d} - r_i)$  is equal to the coefficient of attraction friction (CAF) of ions normalized to the solvent viscosity and hydrodynamic coefficient. The sign of the CAF is determined by the sign of the algebraic sum of its ion-molecular and intermolecular components. In amide solutions the studied cations are cosmotropes (positively solvated ( $(\bar{d} - r_i) > 0$ ), structure-making ions) and anions are chaotropes (negatively solvated ( $(\bar{d} - r_i) < 0$ ), structure-breaking ions). In the amide series, regardless of the sign  $(\bar{d} - r_i)$ , the near-solvation enhances, which can be explained by the weakening of the specific interaction between the solvent molecules. The decrease of  $\bar{d}$  and respectively  $(\bar{d} - r_i)$  with increasing cation radius in a given solvent is the result of weakening of its coordinating force due to the decrease of charge density in the series  $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Rb}^+ - \text{Cs}^+$ . The increase of  $\bar{d}$  (and  $(\bar{d} - r_i)$ , correspondingly) for the ions studied in the series FA-MFA-DMF can be explained by the weakening of intermolecular interactions in this series, which leads to the strengthening of solvation. It was found that for the halide ions in the series FA-MFA-DMF the regular growth of  $\bar{d}$  parameter is explained by the weakening of the solvent structure. It was shown that  $\text{Li}^+$  ion with the lowest diffusion coefficient among cations and the highest  $\bar{d}$  value forms kinetically stable complexes in amide solutions.

**Keywords:** monatomic ions, diffusion, diffusion displacement length, positive and negative solvation, amides

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### ЗАКОНОМІРНОСТІ ВПЛИВУ ОДНОЗАРЯДНИХ ІОНІВ НА ПОСТУПАЛЬНУ РУХОМІСТЬ МОЛЕКУЛ В ГРАНИЧНО РОЗБАВЛЕНИХ АМІДНИХ РОЗЧИНАХ

Встановлено та проаналізовано тип ближньої сольватації іонів  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$  в формаміді (ФА), N-метилформаміді (МФА), N,N-діметилформаміді (ДМФА) при 298,15 К. Для визначення типу сольватації іонів використаний обґрунтований нами знакомісний кількісний параметр  $(\bar{d} - r_i)$ , де  $\bar{d}$  - довжина трансляційного зміщення іона,  $r_i$  - його структурний радіус. Встановлено, що різниця  $(\bar{d} - r_i)$  дорівнює коефіцієнту атракційного тертя (КАТ) іонів, нормованому на в'язкість розчинника і гідродинамічний коефіцієнт. Знак КАТ визначається знаком алгебраїчної суми його іон-молекулярної і міжмолекулярної складових. У амідних розчинах вивчені катіони-космотропи (сольватовані позитивно ( $(\bar{d} - r_i) > 0$ ), іони-структуроутворювачі), а аніони-хаотропи (негативно сольватовані ( $(\bar{d} - r_i) < 0$ )) іони - руйнівники структури). В ряду амідів незалежно від знака  $(\bar{d} - r_i)$  посилюється ближня сольватація, що пояснюється послабленням специфічної взаємодії між молекулами розчинника. Зменшення  $\bar{d}$  і відповідно  $(\bar{d} - r_i)$  зі зростанням радіуса катіона в окремо взятому розчиннику є результатом послаблення його координуючої сили внаслідок зменшення густини заряду в ряду  $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Rb}^+ - \text{Cs}^+$ . Збільшення  $\bar{d}$  (відповідно і  $(\bar{d} - r_i)$ ) для досліджених іонів в ряді амідів ФА-МФА-ДМФА можна пояснити послабленням в цьому ряді міжмолекулярних взаємодій, що зумовлює посилення сольватації. Установлене для галогенід-іонів в ряді ФА-МФА-ДМФА закономірне зростання параметра  $\bar{d}$  пояснюється зменшенням структурованості розчинника. Показано, що іон  $\text{Li}^+$  з найменшим коефіцієнтом дифузії і найбільшим значенням  $\bar{d}$  утворює кінетично стабільні комплекси в амідних розчинах.

**Ключові слова:** одноатомні іони, дифузія, довжина дифузійного зміщення, негативна сольватація, амід.

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### ЗАКОНОМЕРНОСТИ ВЛИЯНИЯ ОДНОЗАРЯДНЫХ ИОНОВ НА ПОСТУПАТЕЛЬНОЕ ДВИЖЕНИЕ МОЛЕКУЛ В ПРЕДЕЛЬНО РАЗБАВЛЕННЫХ АМИДНЫХ РАСТВОРАХ

Установлен и проанализирован тип ближней сольватации ионов  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$  в формамиде (ФА), N-метилформамиде (МФА), N,N-диметилформамиде (ДМФА) при 298,15 К. Для определения типа сольватации ионов использован обоснованный нами знакопеременный количественный параметр  $(\bar{d} - r_i)$ , где  $\bar{d}$  - длина трансляционного смещения иона,  $r_i$  - его структурный ра-

диус. Установлено, что разность  $(\bar{d} - r_i)$  равна коэффициенту аттракционного трения (КАТ) ионов, нормированному на вязкость растворителя и гидродинамический коэффициент. Знак КАТ определяется знаком алгебраической суммы его ион-молекулярной и межмолекулярной составляющих. В амидных растворах изученные катионы – космотропы (сольватированы положительно  $((\bar{d} - r_i) > 0)$ , ионы-структурообразователи), а анионы – хаотропы (отрицательно сольватированные  $((\bar{d} - r_i) < 0)$  ионы – разрушители структуры). В ряду амидов независимо от знака  $(\bar{d} - r_i)$  усиливается ближняя сольватация, что объясняется ослаблением специфического взаимодействия между молекулами растворителя. Уменьшение  $\bar{d}$  и соответственно  $(\bar{d} - r_i)$  с ростом радиуса катиона в отдельно взятом растворителе является результатом ослабления его координирующей силы вследствие уменьшения плотности заряда в ряду  $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Rb}^+ - \text{Cs}^+$ . Увеличение  $\bar{d}$  (соответственно и  $(\bar{d} - r_i)$  для исследованных ионов в ряду амидов ФА – МФА – ДМФА можно объяснить ослаблением в этом ряду межмолекулярных взаимодействий, что приводит к усилению сольватации. Установлено для галогенид-ионов в ряду ФА – МФА – ДМФА закономерный рост параметра  $\bar{d}$  объясняется уменьшением структурированности растворителя. Показано, что ион  $\text{Li}^+$  с наименьшим среди катионов коэффициентом диффузии и наибольшим значением  $\bar{d}$  образует кинетически стабильные комплексы в амидных растворах.

**Ключевые слова:** одноатомные ионы, диффузия, длина диффузионного смещения, отрицательная сольватация, амиды.

## 1 Introduction.

In our study of the effect of single-charged ions of various nature on the mobility of the closest molecules of solvents with a spatial network of H-bonds ( $\text{H}_2\text{O}$ , ethylene glycol (EG), formamide (FA)) we have obtained a number of important regularities: 1) in solvents with homonuclear H-bonds ( $\text{H}_2\text{O}$ , EG) ( $\text{O} - \text{H} \cdots \text{O}$ ), a correlation between the sign of the deviation of the discrete diffusion displacement length  $(\bar{d})$  from the ion structural radius  $(r_i)$  as  $(\bar{d} - r_i)$  and its solvation according to Samoilov [4] was established; 2) as opposed to solvents with homonuclear H-bonds where  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$  ions behave as cosmotropes [5] and  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  ions behave as chaotropes [5], in formamide alkali metal cations are cosmotropes and  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  are chaotropes. Some specificity of the influence of single-atom uniquely charged ions on FA found experimentally was explained by qualitatively different structure of the molecule and fragment of the heteronuclear H-bond ( $\text{N} - \text{H} \cdots \text{O}$ ) as a structural element for building the spatial lattice. The established correlation was used to develop quantitative criteria for positive (1) and negative ion solvation:

$$(\bar{d} - r_i) > 0, \quad (1)$$

$$(\bar{d} - r_i) < 0 \quad (2)$$

The existence of this correlation allows the difference  $(\bar{d} - r_i)$  to be used as a measure of near-solvation and makes it possible to interpret the results obtained on the basis of the basic statements of the molecular-kinetic approach of Samoilov [4], successfully developed by Rodnikova [6] for solvents with a spatial H – H bond mesh. The  $(\bar{d} - r_i)$  difference was called in [1] as a deviation from the Stokes-Einstein law (SEL). This law is strictly satisfied for the model of a rigid spherical ion moving in a continuous fluid medium (continuum). The latter is characterized by a macroscopic viscosity value  $(\eta_0)$ . The criterion for the SEL is the following condition:

$(\bar{d} - r_i) = 0$ , i.e.  $\bar{d} = r_i$ . This condition characterizes the complete absence of ion solvation. Physically, the length of translational displacement of the ion is equal to its radius. Real cases of Stokes-Einstein law  $\Delta E_i = 0$  [4],  $(\bar{d} - r_i) = 0$  [1] correspond to the phenomenon of transition from negative to positive solvation and are explained by the compensation of opposite contributions from short-range ion-molecular (I – M) and intermolecular (M – M) interactions to the near-solvation characteristics.

The choice of the difference  $(\bar{d} - r_i)$  as a measure of the effect of the ion on the mobility of the solvent molecules closest to it was justified in [7] using the coefficient of friction, the value of which depends on the nature of the force acting on the ion. Following Wolynes [8], we represent the total coefficient of friction ( $\zeta$ ) in the form of viscous ( $\zeta_v$ ) and attraction ( $\zeta_{at}$ ) components:

$$\zeta = \zeta_v + \zeta_{at} \quad (3)$$

Then represent the total coefficient of friction through the diffusion coefficient of the ion ( $D_i^0$ ):

$$\zeta = \frac{kT}{D_i^0} = f \bar{d} \eta_0, \quad (4)$$

where  $\eta_0$  is the solvent viscosity.

The viscosity coefficient of friction ( $\zeta_v$ ) is described by the following equation:

$$\zeta_v = f r_i \eta_0 \quad (5)$$

In equations (3) and (4) the factor  $f$  was taken [7] to be  $6\pi$  for the hydrodynamic sticking condition and  $4\pi$  for the sliding condition. Taking into account (4) and (5) for  $\zeta_{at}$  we have:

$$\zeta_{at} = f \bar{d} \eta_0 - f r_i \eta_0 = f \eta_0 (\bar{d} - r_i) \quad (6)$$

The  $\zeta_{at}$  coefficient (the so-called coefficient of attraction friction, or CAF) contains all the information

about the effect of the ion on the mobility of the solvent molecules closest to it, except that described by Stokes' law (5)

Thus, the difference  $(\bar{d} - r_i)$  follows from the difference between the total and viscous friction coefficients, respectively characterised by the parameters  $\bar{d}$  and  $r_i$ . According to equation (6) the difference  $(\bar{d} - r_i)$  is actually equal to the attraction coefficient of friction normalized to  $f\eta_0$ . The mechanism of the effect of the ion on the translational motion of the solvent molecules nearest to it has not yet been known. However, it should be based on the phenomenon of near-solvation of ions, which is described by Samoilov [4] by values of  $\Delta E_i$  and  $\tau_i / \tau_0$  calculated from experiment.

Our proposed approach [1-3, 7] to study the influence of ions on near-solvation is not based on the Walden rule, but on a deviation from the Stokes-Einstein law.

In contrast to  $\bar{d}$ , the difference  $(\bar{d} - r_i)$  is a sign-variable quantity, consistent with experiment [1]. We consider the  $\bar{d}$  parameter [7] as a microscopic characteristic of the length of some discrete displacement that an ion passes between two equilibrium positions over a characteristic time ( $\tau$ ). It is a real and well reproducible value in experiment, quantitatively accounting for the macroscopic characteristics of the ion in solution ( $D_i^0$ ) and solvent ( $\eta_0$ ) [1].

CAF was used in [9] as a quantitative measure of the effect of an ion on the dynamics of nearby water molecules due to ion-molecular and intermolecular interactions according to Samoilov's views [4]. Later [10] the constituents of CAF were also defined:

$$\zeta_{at} = \zeta_{at}^{MM} + \zeta_{at}^{IM} \quad (7)$$

Among the most important results of the analysis of the components of the attraction friction coefficient was the establishment [10] of their opposite signs ( $\zeta_{at}^{IM} > 0$ ,  $\zeta_{at}^{MM} < 0$ ) for single charge ions in water and  $n$ -alcohols. The intermolecular component of the CAF ( $\zeta_{at}^{MM}$ ) has a negative value independently of the solvation of the ion and of the solvent. The opposite signs of the  $\zeta_{at}$  components probably correspond to different sign energy effects of the exchange processes of water molecules between the primary solvation shell (PSS) of ions and pure water associates.

It was interesting to use the approach we developed to investigate the influence of single-charged ions of different nature on the mobility of molecules in the series of

amides: FA – MFA – DMFA, solvents of the same class but with different degrees of structuring. The latter in amides is determined by the structure of the reactive fragments of the molecule: the carbonyl and amino groups bonded together. All of the amides named have a carbonyl group. So, acceptors (cations, molecules with acceptor groups) will be coordinated through the oxygen atom of the carbonyl group in all solvents. However, the molecules of these solvents differ in the substituents at the nitrogen atom. In the series under consideration, the number of hydrogen atoms in the amino group and therefore in the molecule decreases (respectively, 2, 1, 0). The gradual introduction of methyl groups instead of H atoms into the H–N–H group of formamide leads to a significant change in the amide properties in the FA – MFA – DMF series (see Table 1).

Unsubstituted primary formamide is a solvent with a spatial network of H-bonds capable of solvation of both cations and anions. Unlike FA monomethylamide MFA does not form a spatial network of H-bonds. However, there are H-bonds between its molecules. Average number of H-bonds per molecule of MFA is 1.79; 1.89, and for FA 3.43 [11]. The H-bond system in MFA consists of weakly branched chains which, in fact, leads to the decrease of its viscosity by half in comparison with FA (Table 1).

A relative permittivity growth ( $\epsilon$ ) at the introduction of one methyl group into a formamide molecule instead of H atom is explained both by the absence of spatial network of H-bonds in MFA, and causes an increase of molecules rotational mobility and formation of cyclic dimers with antiparallel orientations of dipole moments. The latter causes a decrease in the Kirkwood correlation factor.

DMF is a typical aprotic solvent. According to several authors [12,13] liquid DMF has no associations formed due to specific interactions (donor-acceptor and H-bonds) between the molecules. DMF molecules form linear associations due to Van der Waals forces which are more stable than cyclic dipole-dipole ones.

## 2. Calculations

The methodology for calculating the length of the discrete ion translational displacement has been described earlier [1]. The calculation was carried out for  $T = 298.15$  K using equation (9):

$$\bar{d} = \frac{kT}{6\pi D_i^0 \eta_0}, \quad (8)$$

where  $k$  is Boltzmann constant. The ion diffusion coefficient  $D_i^0$  in amide solutions was calculated from equation

(9), using experimental data on the limiting molar electric conductivity of ions ( $\lambda_i^0$ ) [11]:

$$D_i^0 = \frac{RT}{|z_i|F^2} \lambda_i^0, \quad (9)$$

where  $R$  is the gas constant,  $z_i$  is the ion charge,  $F$  is Faraday number.

Values of viscosity of solvents are taken from [11] (Table 1). Values of  $\bar{d}$  and  $D_i^0$  calculated from equations (8) and (9) for singly charged ions under consideration are given in Tables 2-4. There are also presented values of  $\lambda_i^0$  and the structural radius of ions ( $r_i$ ), the parameter ( $\bar{d} - r_i$ ), and the value of the generalized momentum of ions  $m_i^{ob}$  [7].

The value of  $\zeta_{at}$  was calculated from equation (6) using the obtained values of the parameter ( $\bar{d} - r_i$ ) for single-charged ions in amide solutions (FA, MFA and DMF).

Equation (7) was used to separate CAF as a measure of the effect of ions on solvent molecules. The CAF component  $\zeta_{at}^{MM}$  was estimated using equation [10]:

$$\zeta_{at}^{MM} = \frac{\Delta G_{MM}^*}{D_S N_A}, \quad (10)$$

where  $D_S$  is the self-diffusion coefficient of the solvent,  $\Delta G_{MM}^*$  is the change of Gibbs energy of short-range interaction of solvent molecules, which are close to ions, with their neighbours at some distance from the ion,  $N_A$  is the Avogadro number.

The calculated by equation (7) values of CAF  $\zeta_{at}^{IM}$  component for singly charged ions in amide solutions (FA, MFA, DMF) at 298.15 K are given in Tables 2-4. Table 1 shows the values of the CAT component for the solvents mentioned above.

### 3. Analysis of calculation results

The following regularities and facts are established analyzing the results of the calculation:

1. The value of  $\bar{d}$  for singly charged ions in FA, MFA, DMF depends on the structural radius of the ion (except negatively solvated ions), on its charge sign and on the solvent.

2. In investigated amides as well as in water [1] and ethylene glycol [2]  $\bar{d}$  parameter decreases with increasing structural radius of ion in series of  $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Rb}^+ - \text{Cs}^+$  cations, what witnesses the electrostatic component of solvate ion shells formation nature. At the same time in the series of  $\text{Cl}^- - \text{Br}^- - \text{I}^-$  anions the  $\bar{d}$  value

practically remains constant.

3. The detected increase of  $\bar{d}$  for cations in series FA – MFA – DMF shows the weakening of structural influence of ion on solvent in contrast to anions whose influence on solvent does not depend on the size of  $\text{Cl}^- - \text{Br}^- - \text{I}^-$  anion.

4. For the considered ions in FA, MFA and DMF at 298.15 K the Stokes-Einstein law is not satisfied:  $(\bar{d} - r_i) \neq 0$ . By the sign of the criterion  $(\bar{d} - r_i)$  the ions can be classified into cosmotropes  $(\bar{d} - r_i) > 0$  and chaotropes  $(\bar{d} - r_i) < 0$ . In the amides studied, the cations behave as cosmotropes. Their structure-making effect in the  $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Rb}^+ - \text{Cs}^+$  series decreases. Structure-breaking ability of anions increases with the increase of their radius.

5. In the series FA – MFA – DMF regardless of the sign of the solvent effect criterion  $(\bar{d} - r_i)$  the near solvation increases, which can be explained by the weakening of specific interaction between the solvent molecules.

6. The revealed negative values  $(\bar{d} - r_i) < 0$  and  $\zeta_{am} < 0$  for the anions ( $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ) in aprotic DMF can be explained in the framework of Samoilov's concept [4] taking into account not only the specificity of the interaction between the solvent molecules but also the specificity of these ions influence on the solvent. The fact of the influence of these anions on the solvent is still remarkable.

7. The contributions to CAF regardless of the type of solvation of ions  $((\bar{d} - r_i) > 0, (\bar{d} - r_i) < 0)$  in FA, MFA and DMFA have opposite signs:  $\zeta_{am}^{MM} > 0, \zeta_{am}^{IM} > 0$  The sign of CAF (see Tables 2-4) according to equation (7) is determined by the sign of the prevailing component and according to equation (7) coincides with the  $(\bar{d} - r_i)$  sign. The small negative value of the contribution  $\zeta_{am}^{MM} = -20.204 \text{ kg}\cdot\text{s}^{-1}$  in DMF is probably due to low dielectric constant (Table 1). By the way, the dependence of the CAT component on the value of the inverse dielectric constant of the studied amides ( $1/\epsilon$ ) is described by a straight line with a correlation coefficient of 0.9957.

### 4. Discussion

At explaining the results of investigation the solvation of uniquely charged ions in amides with different degree of structure was considered in accordance with the views of Samoilov [4] not as binding of any quantity of solvent molecules, but as their influence on translational mobility of the latter. As a measure of the effect of the ion on the solvent the value  $(\bar{d} - r_i)$  was used [7].

Table 1 – Physico-chemical quantities of formamide (FA), N-methylformamide (MFA) and N,N-dimethylformamide (DMF) at 25 C [11]

Quantity	FA	MFA	DMF
Molar mass, g·mol <sup>-1</sup>	45.04	59.07	73.10
Melting point, °C	2.6	-3.8	-60.4
Boiling point, °C	210.5	182.4	153.0
Viscosity, mPa·s	3.302	1.65	0.802
Dipole moment, D	3.22	3.86	3.82
Relative permittivity	109.5	182.4	36.71
Self-diffusion coefficient, m <sup>2</sup> ·s <sup>-1</sup>	0.51·10 <sup>-9</sup>	0.847·10 <sup>-9</sup>	1.61·10 <sup>-9</sup>
Evaporation enthalpy, kJ·mol <sup>-1</sup>	60.57	56.25	47.57
Molecular connectivity index	3.42	1.79 <i>cis-isomer</i> 1.89 <i>trans-isomer</i>	—
*Intermolecular contribution to CAF ( $\zeta_{at}^{MM}$ ), kg·s <sup>-1</sup>	-162.20·10 <sup>-12</sup>	-204.91·10 <sup>-12</sup>	-20.204·10 <sup>-12</sup>

\*Our calculations

Table 2 – Singly charged ions quantities in formamide at 298.15 K

Ion	$r_i \cdot 10^{10}$ , m	$m_i^{o\sigma} \cdot 10^9$ , C/m	$\lambda_i^0 \cdot 10^4$ , Sm·m <sup>2</sup> /mol	$D_i^0 \cdot 10^9$ , m <sup>2</sup> ·s <sup>-1</sup>	$\bar{d}_i \cdot 10^{10}$ , m	$(\bar{d}_i - r_i) \cdot 10^{10}$ , m	$\zeta_{at} \cdot 10^{12}$ , kg·s <sup>-1</sup>
Li <sup>+</sup>	0.78	2.05	8.30	0.221	2.99	2.21	13.77
Na <sup>+</sup>	0.98	1.63	9.90	0.264	2.51	1.53	9.52
K <sup>+</sup>	1.33	1.20	12.40	0.330	2.00	0.67	4.19
Rb <sup>+</sup>	1.49	1.08	12.80	0.341	1.94	0.45	2.80
Cs <sup>+</sup>	1.65	0.97	13.40	0.357	1.85	0.20	1.27
NH <sub>4</sub> <sup>+</sup>	1.37	1.17	14.90	0.397	1.67	0.30	1.85
Cl <sup>-</sup>	1.81	0.89	17.50	0.466	1.42	-0.39	-2.43
Br <sup>-</sup>	1.96	0.82	17.50	0.466	1.42	-0.54	-3.37
I <sup>-</sup>	2.20	0.73	16.90	0.450	1.47	-0.73	-4.55
ClO <sub>4</sub> <sup>-</sup>	2.36	0.68	16.60	0.442	1.50	-0.86	-5.38

Table 3 – Singly charged ions quantities in N-methylformamide at 298.15 K

Ion	$r_i \cdot 10^{10}$ , m	$m_i^{o\sigma} \cdot 10^9$ , C/m	$\lambda_i^0 \cdot 10^4$ , Sm·m <sup>2</sup> /mol	$D_i^0 \cdot 10^9$ , m <sup>2</sup> ·s <sup>-1</sup>	$\bar{d}_i \cdot 10^{10}$ , m	$(\bar{d}_i - r_i) \cdot 10^{10}$ , m	$\zeta_{at} \cdot 10^{12}$ , kg·s <sup>-1</sup>
Li <sup>+</sup>	0.78	2.05	10.1	0.269	4.92	4.14	12.88
Na <sup>+</sup>	0.98	1.63	16.0	0.426	3.11	2.13	6.61
K <sup>+</sup>	1.33	1.20	16.5	0.439	3.01	1.68	5.23
Rb <sup>+</sup>	1.49	1.08	17.9	0.477	2.78	1.29	4.00
Cs <sup>+</sup>	1.65	0.97	18.5	0.493	2.69	1.04	3.22
NH <sub>4</sub> <sup>+</sup>	1.37	1.17	24.6	0.655	2.02	0.65	2.02
Cl <sup>-</sup>	1.81	0.89	25.6	0.682	1.94	0.13	0.41
Br <sup>-</sup>	1.96	0.82	28.2	0.751	1.76	-0.20	-0.61
I <sup>-</sup>	2.20	0.73	28.4	0.756	1.75	-0.45	-1.40
ClO <sub>4</sub> <sup>-</sup>	2.36	0.68	27.4	0.730	1.81	-0.55	-1.70

Table 4 – Singly charged ions quantities in N,N-dimethylformamide at 298.15 K

Ion	$r_i \cdot 10^{10}$ , m	$m_i^{0\sigma} \cdot 10^9$ , C/m	$\lambda_i^0 \cdot 10^4$ , Sm·m <sup>2</sup> /mol	$D_i^0 \cdot 10^9$ , m <sup>2</sup> ·s <sup>-1</sup>	$\bar{d}_i \cdot 10^{10}$ , m	$(\bar{d}_i - r_i) \cdot 10^{10}$ , m	$\zeta_{at} \cdot 10^{12}$ , kg·s <sup>-1</sup>
Li <sup>+</sup>	0.78	2.05	26.1	0.695	3.92	3.14	4.74
Na <sup>+</sup>	0.98	1.63	30.0	0.799	3.41	2.43	3.67
K <sup>+</sup>	1.33	1.20	31.6	0.841	3.24	1.91	2.88
Rb <sup>+</sup>	1.49	1.08	33.2	0.884	3.08	1.59	2.40
Cs <sup>+</sup>	1.65	0.97	35.4	0.943	2.89	1.24	1.87
NH <sub>4</sub> <sup>+</sup>	1.37	1.17	39.4	1.049	2.60	1.23	1.85
Cl <sup>-</sup>	1.81	0.89	53.8	1.433	1.90	0.09	0.14
Br <sup>-</sup>	1.96	0.82	53.4	1.422	1.91	-0.05	-0.07
I <sup>-</sup>	2.20	0.73	51.1	1.361	2.00	-0.20	-0.30
ClO <sub>4</sub> <sup>-</sup>	2.36	0.68	51.6	1.374	1.98	-0.38	-0.57

For a long time, the equations of Stokes-Einstein law were used to estimate the size of particles in solutions, particularly charged ions. However, after the advent of more accurate methods based on X-ray diffraction or neutron diffraction, it became clear that the so-called Stokes radii ( $\bar{d}$ ) determined are not the real values of ions, especially those which in the terminology of Samoilov [4] (Collins [5]) are structure-breakers (chaotropes),  $\bar{d} < r_i$ . Marcus [11] has shown that this notion has no physical meaning or utility and should therefore be completely re-considered. Kuznetsova [14] came to the same conclusion when interpreting the Stokes ion radii.

On the other hand, the relative values of the Stokes radius as  $(\bar{d} - r_i)$  or  $\bar{d}/r_i$  undoubtedly reflect the real behaviour of ions in solutions [1, 15]. The correlation we found [1] between the solvation of ions and the sign of the difference between the Stokes «radius» and the structural radius  $(\bar{d} - r_i)$  was used to quantify the effect of the ion on the translational exchange of water molecules and allowed to replace the concept of Stokes «radius» to the length of the diffusion shift, which does not contradict the modern ideas about the behavior of ions in solutions [16].

By the way, Kessler [17] in well known formula  $\tau = \frac{\bar{d}^2}{6D_i^0}$

interprets  $\bar{d}/\tau$  as mean velocity and calls mean length of displacement or jump of ion in diffusion regime for time  $\tau$ . Undoubtedly the diffusion of the ion depends strongly on its state in the solution, i.e. on the solvation.

The length of a discrete forward displacement  $\bar{d}$  of the ion in the solution under the influence of thermal motion of molecules of the solvent is a positive value, which can be obtained from the experiment and which is not without the physical sense. Since the Stokes-Einstein law is not fulfilled for most real cases, the calculation of the

$\bar{d}$  parameter by equation (8) does not require any restrictions on the fairness of its application, except the fulfillment of hydrodynamic conditions [7]. It is also obvious that deviations from the Stokes-Einstein law for singly charged ions in structured solvents are due to their solvation, i.e., inhibition in addition to the viscous one. When interpreting the  $\bar{d}$  change under the influence of various factors, it is appropriate to use this term, which refers not to the change of ion size, but to the change of path length which an ion travels in diffusion mode between two equilibrium positions.

In terms of their influence on the translational mobility of FA, MFA and DMF molecules, the ions in question can be divided into structure-makers (cosmotropes [5]) and structure-breakers (chaotropes [5]). The first group includes alkali metal cations and NH<sub>4</sub><sup>+</sup> ion ( $(\bar{d} - r_i) > 0$ ,  $\zeta_{at} > 0$ ) and the second group includes Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup> anions ( $(\bar{d} - r_i) < 0$ ,  $\zeta_{at} < 0$ ).

The ability of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> cations to strengthen the amide structure can be explained by the presence of high electron density O atom in their molecules [18], through which solvent molecules are coordinated by these cations.

The Li<sup>+</sup> cation is a special one, whose influence on the molecules of polar solvents (FA, MFA and DMF) is due to its small size, and its highest polarizing effect among the alkali metal cations leads to high solvation energy and even to the formation of covalent bonds. Li<sup>+</sup> cation in solvents with spatial network of H-bonds (water, ethylene glycol, formamide) is dominated by I-M interaction over M-M interaction. According to [19], small-sized cations significantly modify the dynamic structure of their immediate environment, which is reflected in the experimentally determined quantitative characteristics. By the

way, among alkali metals  $\text{Li}^+$  cation in water, ethylene glycol and formamide has the lowest diffusion coefficient and its translational displacement length  $\bar{d}$  is the longest. The latter indicates the formation of kinetically stable complexes of  $\text{Li}^+$  cation, which diffuse as a unit.

At the same time, the coordination of the  $\text{NH}_4^+$  ion by the amide molecules probably occurs due to H-bonding between the H atom of the  $\text{NH}_4^+$  ion and the O atom of the amide molecule [20].

The decrease of  $\bar{d}$  and respectively  $(\bar{d} - r_i)$  with the increase of cation radius in a given solvent is the result of weakening of its coordinating force due to the decrease of charge density in the series  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ . The increase of  $\bar{d}$  (and  $(\bar{d} - r_i)$  as well) for the studied ions in the series FA – MFA – DMF can be explained by the weakening of intermolecular interactions in this series, which leads to the strengthening of solvation, i.e. ion-molecular interaction.

In the studied amides the anions are solvated weaker than the cations, which is an indication that the H-bond is less stable than the donor-acceptor one.

For the halide ions in the series FA – MFA – DMF the regular growth of  $\bar{d}$  parameter was found to correspond, according to Samoilov's ideas [4], to the reduction of the solvent structuring. In the structured formamide the investigated anions behave as chaotropes ( $(\bar{d} - r_i) < 0$ ). They coordinate FA molecules by type H-bond via H atoms of  $\text{NH}_2$  group.

As the ion size increases in the  $\text{Cl}^- - \text{Br}^- - \text{I}^-$  series the structure disorder of the formamide increases as evidenced by small and close values of  $\bar{d}$  and increasing negative values of the difference  $(\bar{d} - r_i) < 0$ , due to the growth of the structural radius of the ion. Earlier close  $\bar{d}$  values were found for negatively solvated single-atom ions in other solvents (water, ethylene glycol) [1,2], which probably results from the spherical shape of the anion. The disparity in the change in  $\bar{d}$  and  $r_i$  for a number of anions in the studied amides actually determines the sign of the difference  $(\bar{d} - r_i)$  and, therefore, the type of effect of the ion on the solvent. A negative value of  $(\bar{d} - r_i) < 0$  means that the FA –  $\text{Hal}^-$  interaction is weaker than the FA – FA interaction.

N-methylformamide with disrupted structure is more favourable to the action of the anion field on the solvent, the measure of which is  $d$ . The effect of the anions on the FA is an increase in  $d$ . Like in FA, the value of  $d$  in MFA is almost independent of the size of the anion.

In DMF there are no associations between molecules

due to specific interactions (donor-acceptor, H-bond). There are linear associations between highly polar DMF molecules due to Van der Waals forces which are more stable than cyclic dipole-dipole structures.

The obtained patterns of changing the influence of  $\text{Cl}^- - \text{Br}^- - \text{I}^-$  anions can be explained using one of the important statements of Samoilov about the influence of free solvent structuring on near-solvation, according to which the growth of solvent structure leads to weakening of solvation of ions and vice versa.

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