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DETERMINATION OF THE DEGREE OF IONS HYDRATION BY THE ELECTRICAL CONDUCTIVITY OF THEIR AQUEOUS SOLUTIONS

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It is shown that the changes in local viscosity of water around ions can be revealed by the data on ions electrical mobility in their aqueous solutions. On the basis of these changes, an approach is suggested which involves the evaluation of the water structure in the nearest surroundings of these ions. The degree of hydration of ions can be quantified by the number of molecules retained near ions in the case of positive hydration and the number of molecules, which are repelled from ions in the case of negative hydration. The number of water molecules is calculated from the effective radius of the moving object (ion and associated water molecules, ion and repelled water molecules) provided the local viscosity of water around the ions is equal to the viscosity in the bulk water. It is confirmed that positive hydration is observed for Li^+ and Na^+ cations and F^- anion, while negative hydration is typical of K^+, Rb^+, and Cs^+ cations and Cl^-, Br^-, and I^- anions. The obtained results are in a good agreement with the changes of entropy which are associated with the structural changes of water in surroundings of singly charged ions owing to their hydration, as well as with the formation of crystalline hydrates for these ions salts.

Keywords: aqueous solutions, water structure, ions hydration, ions electrical mobility, local viscosity of water.

Introduction

The researches on water properties and aqueous solutions are still of great interest, and among the newest results of these researches, the data on modeling by molecular dynamics method can be highlighted, those are related to the analyses of balance between hydrated ions and hydrated clusters [1], the interaction of water molecules with other molecules, ions and surface [2,3], the influence of ions on water structure [4–7], the evaluation of hydration energy and entropy [8,9], and the orientation and mobility of water molecules [10–12]. An influence of ions hydration type on the crystalline hydrates of salts formation from their aqueous solutions is analyzed in paper [13].

The purpose of this study is to quantify the degree of hydration of monovalent ions. The task of the work is to determine the amount of water molecules in the vicinity of hydrated ions, which affects their mobility in comparison with the volume of solution. To this end, the measurements of the conductivity of aqueous solutions were performed.

Methods

Recently, an approach was proposed to evaluate the local viscosity of water around hydrated ions using the data on electrical mobility of ions in aqueous solutions [14]. It is known that the electrical mobility of ions in aqueous solutions is determined by the following equation:

$$U = \frac{ze}{6\pi r\eta}, \quad (1)$$

where ze is the ion's electric charge (z is the ion's valence and e is the elementary charge), r is the ion's radius and η is the solvent's viscosity.

There is the following relation between the electrical mobility U and the limiting equivalent conductivity of ions λ in the Faraday constant F:

$$\lambda = FU. \quad (2)$$

Taking into account Eq. (2), the values of the boundary equivalent electrical conductivity will be further used, which can be easily determined experimentally.

Combining Eqs. (1) and (2) and knowing the magnitude of the boundary equivalent conductivity and crystallographic radii of ions, one can calculate the local viscosity of water around the hydrated ions moving in the electric field by the following equation:

$$\eta = \frac{zeF}{6\pi r\lambda}. \qquad (3)$$

Results and discussion

The proposed method for determining the local viscosity of water around the hydrated ions can be used to quantify the degree of hydration of ions assuming that an increase of local viscosity around the ions compared with the bulk water viscosity is due to positive hydration, for which, by definition, the ordering of water molecules in the immediate environment of ions is distinctive, and the reduction of local viscosity around the ions in comparison to the viscosity of bulk water is caused by negative hydration, which results in disordering the water molecules in the nearest surround of ions. The ordering of water molecules around the ion will contribute to an increase in their number compared with the structure of bulk water, and on the contrary disordering will result to a decrease in their number around the ion (Fig. 1).

The degree of ions hydration can be estimated by the number of molecules retained near the ions in the case of positive hydration, and the number of molecules repelled from the ions in the case of negative hydration. Such a number of water molecules can be determined by changing the effective radius of the moving object (ion and associated water molecules, ion and missing water molecules) using the following equation:

$$N = \frac{4\pi(R_o^3 - R_i^3)}{3V_o}, \qquad (4)$$

where R_o is the calculated radius of moving object, R_i is the ion's radius, V_o is the volume of water molecule.

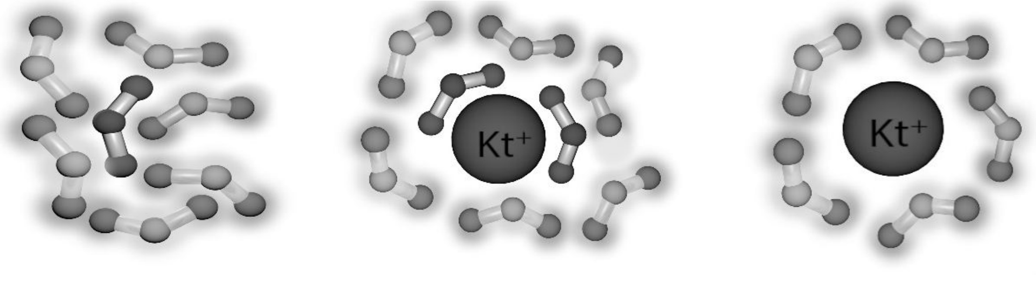
If N accepts positive values, then there is a positive hydration; this indicates the number of excessively retained water molecules near the ion that move along with it. If N takes negative values, then there is a negative hydration; this indicates the number of excessively repelled water molecules around the ion. The radius of a moving object is determined from the condition of equality of local viscosity of water around the ions of bulk water viscosity by the following equation:

$$R_o = \frac{zeF}{6\pi\lambda\eta_o}, \qquad (5)$$

where ze is the electric charge of the ion (z is the valence of the ion and e is the elementary charge), F is the Faraday constant, η_0 is the bulk viscosity of water and λ is the boundary equivalent of the electrical conductivity of the ions.

The numbers of water molecules around the singly charged ions according to the equivalent electrical conductivity data of their aqueous solutions for a temperature of 25^0C are given in Table 1. As can be seen from the results for the temperature of 25^0C, N has positive values for lithium, sodium and fluorine ions. This means that there are, on average, constantly 5–6 water molecules as a single unit with it in the dynamic equilibrium around the lithium ion, 1–2 water molecules around the sodium ion, and about 1 water molecule around the fluorine ion. For other ions, N takes a negative value which indicates a certain number of repelled individual water molecules near these ions compared with the volume structure of water. For example, in the case of potassium ions, one molecule of water is repelled for about half of the ions, for one ion a water molecule is repelled for about near every ion of rubidium and chlorine, from one to two molecules of water are repelled for cesium and bromine ions, and from 2 to 3 water molecules are repelled for iodine ions.

The obtained results are in good agreement with the changes in entropy that are related to the



a b c

Fig. 1. Structure of bulk water (a) caused by positive (b) and negative (c) ions hydration

structural changes in water during the hydration of singly charged ions, according to which the ions studied by the type of hydration are distributed equally (Table 2) [15].

Table 1

Average amount of water molecules around the singly charged ions

Ions	Average amount of water molecules around the ions	Hydration type	Structural effect
Li^+	5.97	Positive	Ordering
Na^+	1.75	Positive	Ordering
K^+	–0.59	Negative	Disordering
Rb^+	–1.11	Negative	Disordering
Cs^+	–1.62	Negative	Disordering
F^-	1.08	Positive	Ordering
Cl^-	–0.98	Negative	Disordering
Br^-	–1.68	Negative	Disordering
I^-	–2.68	Negative	Disordering

Table 2

Changes in entropy associated with structural changes in the water around the singly charged ions due to their hydration [15]

Ions	Changes in entropy ΔS_2, $J \cdot mol^{-1} \cdot K^{-1}$	Hydration type	Structural effect
Li^+	–55.6	Positive	Ordering
Na^+	–5.4	Positive	Ordering
K^+	34.3	Negative	Disordering
Rb^+	52.3	Negative	Disordering
Cs^+	59.0	Negative	Disordering
F^-	–70.0	Positive	Ordering
Cl^-	6.3	Negative	Disordering
Br^-	27.6	Negative	Disordering
I^-	54.8	Negative	Disordering

Good correlation was found between the type of hydration and the formation of crystalline hydrates for the salts of the studied singly charged ions (Table 3) [13]. As can be seen from these data, crystalline hydrates of their salts are not formed in the case when both ions have negative hydration. Obviously, they form a crystalline salt lattice without water molecules because of the high mobility of water molecules around them and the presence of a certain number of repelled water molecules.

Table 3

Correlation between the type of hydration and the formation of crystalline hydrates for salts of singly charged ions [13]

Hydration type	Salts	Availability of crystalline hydrate
Positive hydration of cation and anion	LiF	–
	NaF	–
Negative hydration of cation and anion	KCl	–
	KBr	–
	KI	–
	RbCl	–
	RbBr	–
	RbI	–
	CsCl	–
	CsBr	–
	CsI	–
Positive hydration of cation and negative hydration of anion	LiCl	$LiCl \cdot H_2O$
	LiBr	$LiBr \cdot 2H_2O$
	LiI	$LiI \cdot 3H_2O$
	NaCl	$NaCl \cdot 2H_2O$
	NaBr	$NaBr \cdot 2H_2O$
	NaI	$NaI \cdot 2H_2O$
Negative hydration of cation and positive hydration of anion	KF	$KF \cdot 2H_2O$
	RbF	$RbF \cdot 1.5H_2O$
	CsF	$CsF \cdot 1.5H_2O$

Such considerations lead to the conclusion that ions with positive hydration should easily form crystalline hydrates, but this fact is not confirmed experimentally. The absence of crystalline hydrates for salts with two ions with positive hydration is, obviously, due to the presence of a developed hydrated shell and the inadequacy of electrostatic attraction between these singly charged ions in these cases.

It is logical to assume that in the case when there are available ions in the solution with both types of hydration, the most favorable conditions of the introduction of water molecules into the crystalline structure of the salt are created: one ion is readily liberated from water molecules, while the other, on the contrary, holds the water molecules. This hypothesis is well confirmed by available experimental results (Table 3).

Temperature is an important factor affecting chemical processes. Figures 2 and 3 show the temperature dependences of the number of water molecules N (the degree of hydration of ions). As can be seen from these figures, the effect of temperature on the hydration of the studied ions is insignificant and the dependence of the degree of hydration on temperature passes through a minimum.

Conclusions

Thus the developed approach for estimating the degree of hydration of ions based on the data on equivalent electrical conductivity can reveal dynamic

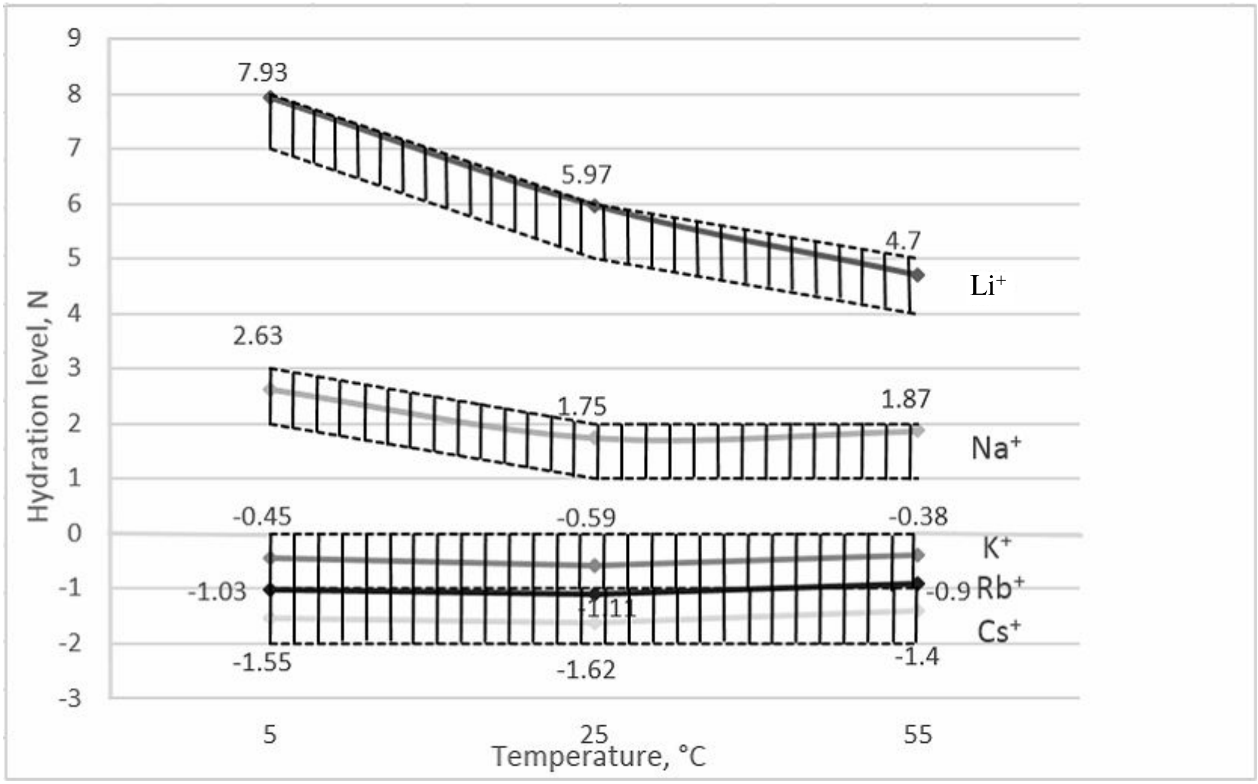


Fig. 2. Temperature dependences of the degree of hydration of cations from the main subgroup of the first group

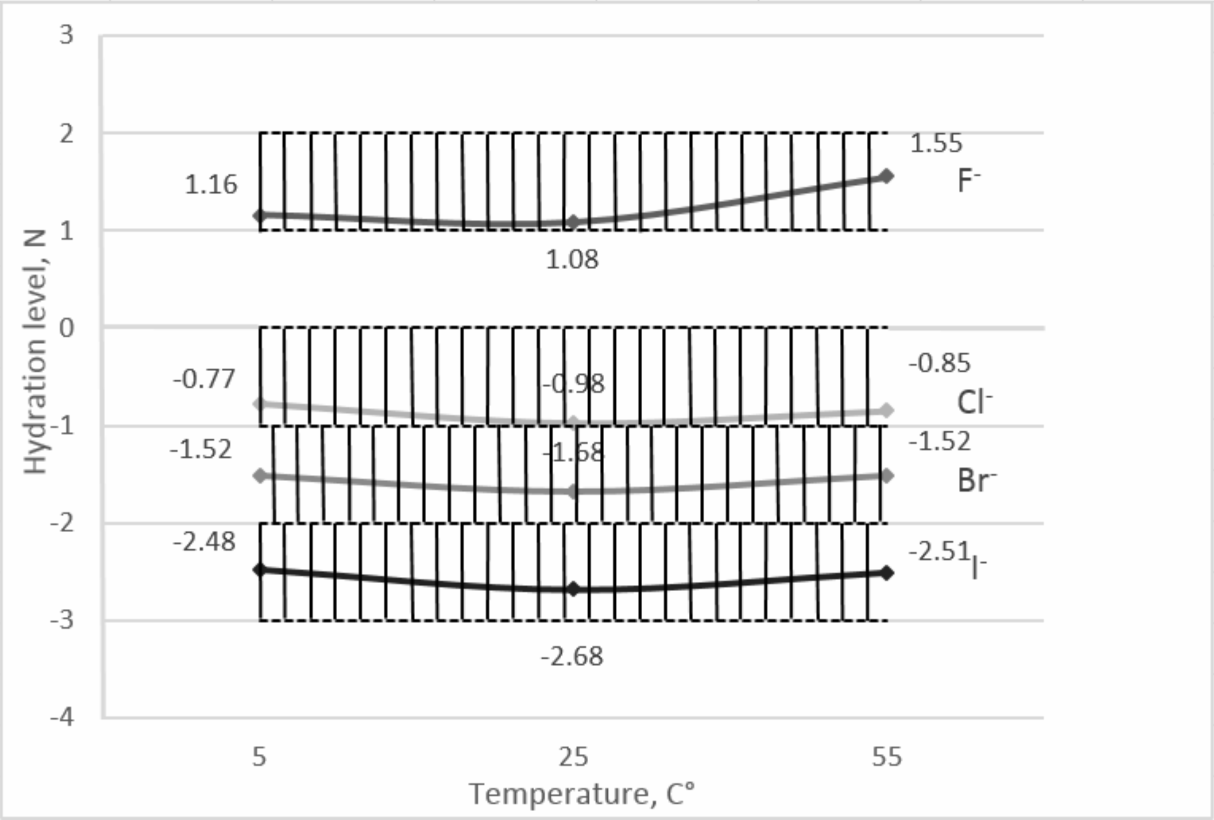


Fig. 3. Temperature dependences of the degree of hydration of anions from the main subgroup of the seventh group

changes in the structure of aqueous solutions. Positive hydration is typical of Li$^+$, Na$^+$ cations and F$^-$ anion, whereas negative hydration is observed for K$^+$, Rb$^+$, and Cs$^+$ cations and Cl$^-$, Br$^-$, and I$^-$ anions. The obtained results are in good agreement with the changes in entropy associated with the structural changes in the water around the singly charged ions due to their hydration and the formation of crystalline hydrates for the salts of these ions. It is established that the influence of temperature on the hydration of the investigated ions is insignificant and the temperature dependences of the degree of hydration of ions pass through a minimum.

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ВИЗНАЧЕННЯ СТУПЕНЯ ГІДРАТАЦІЇ ІОНІВ ЗА ЕЛЕКТРОПРОВІДНІСТЮ ЇХ ВОДНИХ РОЗЧИНІВ

З.М. Яремко, Р.Л. Буклів

Показано, що за даними про електрорухливість іонів у їх водних розчинах можна виявити зміни локальної в'язкості води в околі іонів. На основі цих змін локальної в'язкості води в околі іонів запропоновано підхід для оцінювання структури води в найближчому оточенні цих іонів. Ступінь гідратації іонів можна кількісно оцінити за кількістю молекул, що затримуються біля іонів у разі позитивної гідратації, та кількістю молекул, які виштовхуються від іонів у разі негативної гідратації. Таку кількість молекул води розраховують із ефективного радіуса рухомого об'єкта (іона і пов'язаних з ним молекул води, чи іона та виштовхнутих молекул води) за умови рівності локальної в'язкості води в околі іонів об'ємній в'язкості води. За одержаними результатами підтверджено, що для катіонів Li$^+$, Na$^+$ *та аніона* F$^-$ *характерна позитивна гідратація, а для катіонів* K$^+$, Rb$^+$, Cs$^+$ *та аніонів* Cl$^-$, Br$^-$, I$^-$ *– негативна гідратація. Одержані результати добре узгоджуються зі змінами ентропії, пов'язані із структурними змінами води в околі однозарядних іонів внаслідок їх гідратації, та утворенням кристалогідратів для солей цих іонів.*

Ключові слова: водні розчини, структура, гідратація іонів, електрорухливість іонів, локальна в'язкість води.

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Keywords: aqueous solutions; water structure; ions hydration; ions electrical mobility; local viscosity of water.

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