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Hydration Processes in HCl and Aqueous Salt Solutions

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Abstract: In this work, the number of hydration of ions (K^+ and Cl^-, K^+ and Br^-, K^+ and I^-, H^+ and Cl^-, Li^+ and Cl^-, Cs^+ and Cl^-, Na^+ and Cl^-) in dilute aqueous solutions of some electrolytes of KCl, KBr, KI, HCl, LiCl, CsCl, and NaCl was studied by the proposed refractometric method. Further, the effect of polyethylene glycol (PEG-6000) on the hydration processes for ions in aqueous solutions of KCl and KBr was studied. It turned out that when the polymer is introduced into the solution, the hydration numbers of ions decrease, which is apparently due to the role of the PEG oxygen atom competing with ions in interaction with water molecules.

Keywords: Hydration, hydration number, solution, salts, polyethylene glycol

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1 INTRODUCTION

As is known, all the properties of substances, including solutions, are related to their energy state and structure. Therefore, studying the interaction between all components of the solution leading to the formation of a certain structure is important. One of the important processes occurring in the solution is solvation (hydration, if the solvent is water).

When salts are dissolved in water, the salt dissociates into ions, and these ions do not interact with each other in dilute solutions. The hydration number of a compound is defined as the average number of molecules bound to the compound more strongly than they are bound to other water molecules (1).

As is known, hydration is the process of interaction of water molecules with ions, atoms, and molecules introduced into it. The process of hydration characterizes practically all structural and energetic changes occurring in the solution. The degree of hydration is characterized by the number of hydrates (h) and the thickness of the hydrate shell of the particles of the dissolved substance.

There are multiple methods of determining the number of hydrations based on the differences in the properties of water in the general and hydrated shell (NMR, IK) (2-7). Therefore, the obtained values of the hydration number, determined by different methods, do not, as a rule, coincide (8). In the present research paper, hydration numbers of ions were found by the refractometric method described in the work (9-11).

2 EXPERIMENTAL SECTION

In the work, we used PEG with a molecular weight of Mn=6000 produced by the company "Panreac" (Spain), as well as salts of the "chemically clean" type, KCl, KBr, KI, HCl, LiCl, CsCl, and NaCl. All experiments were carried out using bidistilled water.

As known, polyethylene glycol (PEG) of different molecular masses is widely used in various biotechnological processes.

Mixtures of aqueous solutions of PEG and various polymers and a number of organic and inorganic salts form two-phase systems that are widely used for the separation and purification of biological materials (proteins, viruses, cells, etc.), for the fractionation of some high-molecular-weight compounds, for the early diagnosis of some diseases, etc. Therefore, the study of the effect of polyethylene glycol on the process of hydration of ions is important when studying the mechanisms of phase formation in water two-phase systems.

It is known that the formation of water-two-phase systems is connected with the interactions of phase-forming components (hydrophobic and hydrophilic hydration) with water. Different local microstructures arise around each component, and upon reaching a certain size, each of these structures turns into a separate stable thermodynamic phase, and the system becomes two-phase.

With the aim of achieving this goal, we conducted a study on the process of hydration of salts used to obtain different two-phase systems in diluted aqueous solutions. Additionally, we investigated the impact of PEG on this process. PEG serves as a polymer component of the two-phase system PEG-sodium citrate-water.

3. RESULTS AND DISCUSSION

A very simple and experimentally convenient method for determining the hydration number of salts was proposed based on the study of the concentration dependence of the refractive index of a salt solution.

In the works indicated in the introduction, an analytical formula was obtained that relates the slope of the concentration dependence of the refractive index of the solution to the number of hydrations (9-11):

$$h_1+h_2=\frac{3\,Mtg\,\Phi}{\rho N_A\,\alpha_{H_2O}}-i\frac{r_{K^{+j}}}{r^3_{H_2O}}-j\frac{r_R^{-i}}{r^3_{H_2O}} \quad (1)$$

where ρ is the density of the solution; N_A — Avogadro's number; M – molar mass KR; h_1, h_2 – number of hydration ions K^+ and R^-; and c – mass concentration of KR in the solution.

We applied this method to determine the hydration number of ions in dilute aqueous solutions of HCl and the salts NaCl, CsCl, LiCl, KCl, KBr, and KI. The concentration dependence of the refractive index of dilute aqueous solutions of salts was carried out on a refractometer FR0429.

In dilute solutions, when the ions do not interact with each other, the value $(n^2-1) / (n^2+2)$ depends linearly on the concentration. When reaching certain threshold concentrations, the linear dependence is broken $(n^2-1) / (n^2+2)$ - c. We worked in areas of such concentrations where this dependence does not deviate from linearity.

The obtained data in coordinates $(n^2-1)/(n^2+2)$ – c for various salts are presented in Figures 1 and 2.

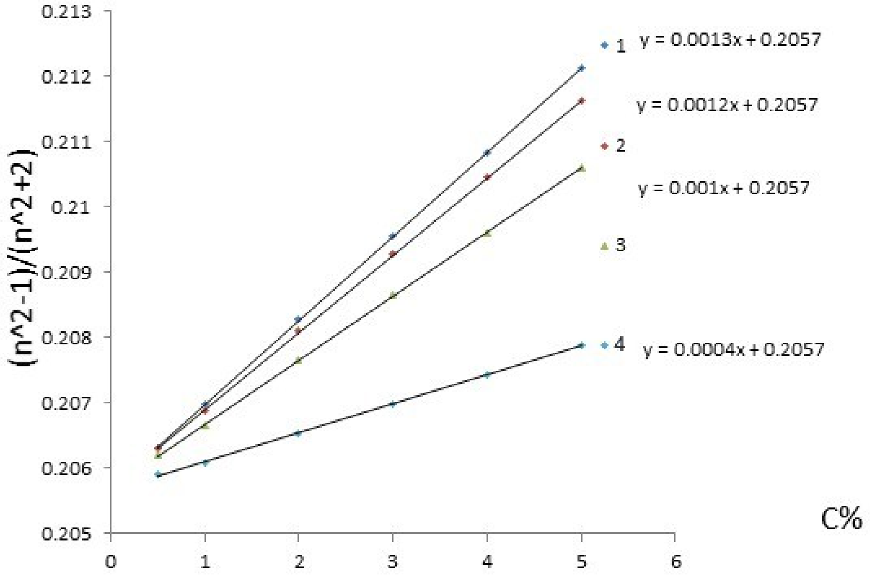

Figure. 1. Concentration relationship (n^2-1) / (n^2+2) for aqueous solutions 1.HCl, 2.LiCl, 3.NaCl, 4.CsCl

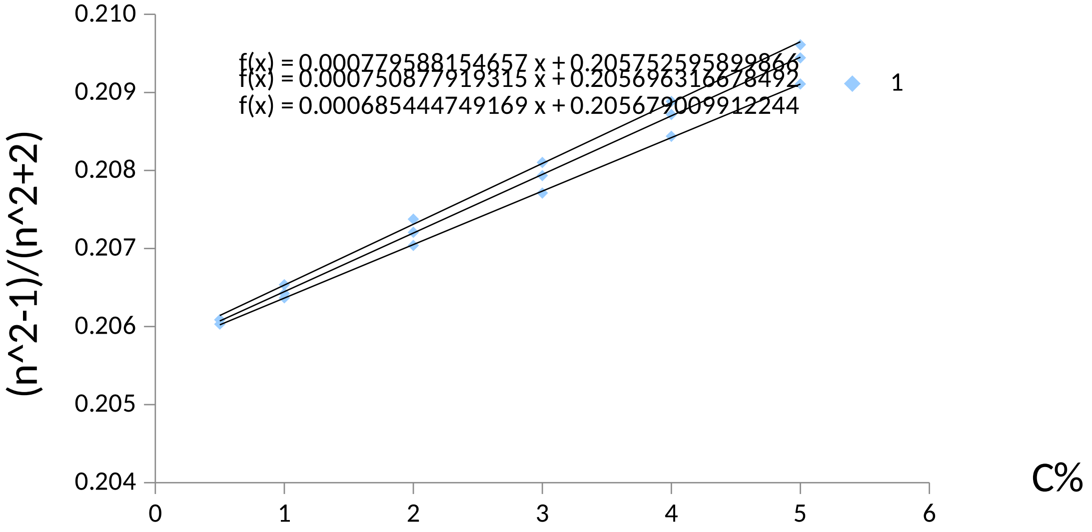

Figure.2. Dependence of the ratio on the concentration (n^2-1) / (n^2+2) of KCl, KBr, KI in the system 1. KCl+ water, 2. KBr+ water, 3. KI+ water

As follows from the figures, these dependences have a linear character. Substituting parameters taken from literature (12-14), ($r_{H^+}=33\ pm$, $r_{Cs}=167\ pm$, $r_{H_2O}=140\ pm$, $\alpha_{H_2O}=1.45\times10^{-30}\ m$, $\rho\approx10^3\ kg/m^3$, $r_{Cl^-}=200\ pm, r_{K^+}=138\ pm, r_{Er^-}=196\ pm$) included in formula [1], we determined the sum of the hydration numbers of H^+ and Cl^-, Li^+ and Cl^-, Na^+ and Cl^-, Cs^+ and Cl^-, K^+ and Cl^- ions based on the angular coefficient of the graph presented in Figures 1 and 2 , K^+ and Br^-, K^+ and I^-, in aqueous solutions of HCl, LiCl, NaCl, CsCl, KCl, KBr, and KI.

Refractive indices of dilute aqueous solutions of potassium salts KCl, KBr and KI were measured by the refractometric method in the concentration interval 0 ≤ c ≤ 5%. As can be seen from Table 1. the relationship is a linear function of salt concentration: The values of the parameters obtained from the experiment and for the aqueous solutions studied at a temperature of 25 °C were as follows: for all solutions, A=0.02057, and values for KCl B=0.001, for KBr B=0.0008, for KI B=0.0007, etc.

Table 1. The sum of numbers of hydration of potassium ions K^+ and anions Cl^-, Br^-, I^- at temperature 25 °C

	r_1+r_2	h_1+h_2
KCl	319	23.7
KBr	334	24.2
KI	358	37.3

Through h_1, the number of hydration of potassium ions is indicated, and through h_2 - the number of hydration of Cl^-, Br^-, and I^- anions, respectively. It can be seen that with the growth of the radii of the anions, the sum of the hydration numbers of the ions increases. If the number of hydrations of cation (anion) ions is assumed to be the same in all cases, then the increase in the amount can be explained by the growth of the surface area of anions (cations) with the growth of their radii.

Despite the identical charges of all anions (cations) in this case, the main role is played by the steric factor: with the growth of the radii of anions (cations), new positions for the placement of water molecules on the surface of the anion (cation) arise, and the number of hydration of anions (cations) increases in the following sequence: Cl^-, Br^- and I^-. (H^+, Li^+, Na^+, Cs^+, Table 2.)

Table 2. The sum of the numbers of hydration ions Cl^- and cations H^+, Li^+, Na^+, K^+, Cs^+ at temperature 25ºC

	r_1+r_2	**h_1+h_2**
HCl	233	13.3
LiCl	276	14
NaCl	295	16.3
CsCl	348	20

Figure 3 shows the graph of the dependence of the sum of the hydration numbers of the cations H^+, Li^+, Na^+, Cs^+, and anion Cl^- on the sum of the radii of the Cl^- and the corresponding cations constructed according to Table 2.

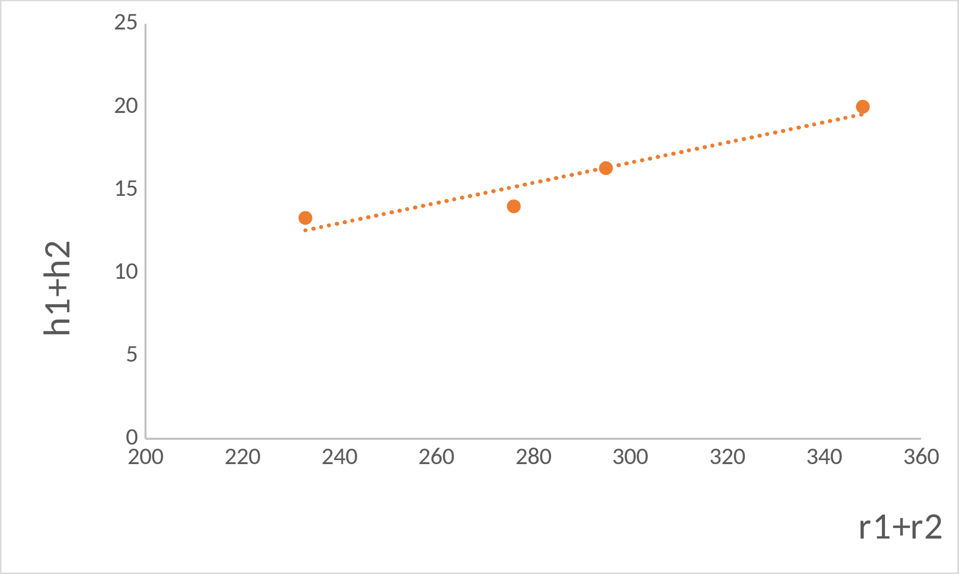

Figure. 3. Dependence of the hydration numbers of anion Cl^- and cations H^+, Li^+, Na^+, Cs^+ on the radius of the corresponding ions

The influence of polyethylene glycol (PEG-6000) on the value (h_1+h_2) for ions K^+ and Cl^-, K^+ and Br^- is studied further. The obtained results are shown in tables 3 and 4.

Table 3. The sum of the numbers of hydration of anion Cl^- and cation K^+ at temperature 25ºC

Solvents	**h_1+h_2**
$KCl+H_2O$	23.7
KCl+PEG(0.04 g 39%)+ H_2O	13.5
KCl+PEG(1.1g 39%) + H_2O	5.8

Table 4. The sum of the hydration numbers of anion Br^- and cation K^+ at temperature 25^0C

Solvents	**h_1+h_2**
$KBr+H_2O$	24.2
$KBr+PEG(0.3g)+H_2O$	16.7
$KBr+PEG(0.5g)+H_2O$	12.6

As follows from the table, when the polymer is introduced into the solution, the number of hydration ions decreases, which is apparently connected with the competing role of the PEG oxygen atom in the interaction with water molecules.

4. CONCLUSION

In this work, we studied the number of hydration of ions (K^+ and Cl^-, K^+ and Br^-, K^+ and I^- H^+ and Cl^-, Li^+ and Cl^-, Cs^+ and Cl^-, Na^+ and Cl^-) in aqueous solutions of HCl, KCl, KBr, KI, HCl, LiCl, CsCl, and NaCl. An analysis of the hydration numbers of ions suggests that the hydration number increases with increasing ion radius. This result can be explained by the increase in the surface area of the ions as their radii increases**.**

As it follows from the obtained data, when polyethylene glycol is introduced into the studied solution due to the structuring of water under the influence of PEG, the number of free water molecules and the possibility of salt ion hydration decrease, which is accompanied by a decrease in the number of hydration of ions.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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