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Determination of the hydration numbers of several organic salts by the refractometric method

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Abstract

Hydration is a fundamental process that governs the structural and energetic properties of aqueous electrolyte solutions. In this study, a refractometric method based on the Lorentz–Lorenz equation was employed to determine the total hydration numbers of sodium acetate, zinc acetate, and sodium citrate. The analysis yielded hydration numbers of 6.3, 10.5, and 20.3, respectively. These results confirm that ion charge, ionic size, and molecular architecture significantly influence hydration behavior. Specifically, the higher hydration number of zinc acetate is attributed to the strong electric field of the divalent Zn^{2+} ion, while sodium citrate's high value highlights the collective impact of multiple functional groups. Ultimately, this work demonstrates that refractometry is an effective tool for investigating the complex interplay of electrostatic and structural factors in hydration phenomena.

Keywords: Hydration number, refractometry, organic salts, ion hydration, water structure.
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1. Introduction

Hydration is the fundamental process underlying the structural and energetic changes occurring in aqueous solutions. Hydration refers to the process by which ions formed during the dissociation of electrolytes in water attract surrounding water molecules and form hydration shells. The determination of hydration numbers is of considerable theoretical and practical importance and plays a significant role

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in biology, medicine, and various industrial processes. The hydration number, which represents the number of water molecules associated with an ion, provides valuable insight into the behavior of ions in solution.

As is well known [1-5], ions in electrolyte solutions influence both the mobility of surrounding water molecules and the overall structure of water through their electric fields. Ions with small radii and high surface charge densities strongly bind water molecules, forming hydration shells that reduce molecular exchange rates and promote water structuring. In contrast, ions characterized by large radii and low charge densities increase the mobility and exchange rate of water molecules, thereby disrupting the water structure. Consequently, changes in the structure of water are largely determined by the physical characteristics of the ions, particularly their charge and radius.

However, hydration is not limited solely to the binding of water molecules located in the immediate vicinity of an ion. It also includes both “near” and “far” hydration regions, in which the electric field of the ion influences water molecules beyond the first hydration shell. This influence alters macroscopic properties of the solution, such as viscosity, diffusion, and electrical conductivity, and has led to the introduction of the concept of the “structural temperature” of water [2-11]. Recent studies have demonstrated that ion–water interactions are not confined to the primary hydration shell; rather, they can induce more extensive modifications in the hydrogen-bond network of water [3, 4]. Since different experimental techniques exhibit different sensitivities to the ionic field, it is natural that different hydration numbers (e.g., 2, 7, 15, 22, etc. for the Na^+ ion) are reported for the same ion. Therefore, hydration should be considered not merely in terms of the number of bound water molecules, but rather as a process involving changes in the overall structure of water and its hydrogen-bonding network.

For many years, ion hydration has been studied primarily for inorganic salts. The hydration of inorganic ions is predominantly hydrophilic in nature and is largely determined by ionic radii and surface charge densities. In contrast, the hydration mechanism of organic salts is more complex. Owing to the structural complexity of organic ions, hydration results from the competitive interplay between hydrophilic and hydrophobic effects, leading to different degrees of modification of the internal structure of water. Consequently, a comparative investigation of the hydration properties of inorganic and organic salts remains an important and relevant research topic.

2. Refractometric Method for Hydration Number Determination

The aim of the present study is to determine the total hydration number ($h_1 + h_2$) of ions in aqueous solutions of several organic salts using a refractometric method, to investigate the relationship between the obtained results and the ionic radii and charge densities, and to perform a comparative analysis of the structural changes induced by these salts in the aqueous medium.

The determination of hydration numbers can be carried out using a number of complex, labor-intensive, and economically inefficient methods. In contrast to these approaches, the refractometric method based on the refractive index of light is characterized by experimental simplicity, rapid response, and sufficient accuracy. At the same time, the refractometric approach allows the hydration process to be considered not merely as the number of water molecules bound to an ion, but as a collective structural reorganization of the entire system, enabling the hydration number to be evaluated with high precision [5].

For this purpose, by applying the Lorentz–Lorenz equation and performing a series of mathematical transformations, the following expression was derived for determining the total hydration number of the cation and anion ($h_1 + h_2$):

$$h_{K^+} + h_{A^-} = \frac{3M_{KA}}{\rho N_A \cdot \alpha_{H_2O}} tg\varphi - i\left(\frac{r_{K^+}}{r_{H_2O}}\right)^3 - j\left(\frac{r_{A^-}}{r_{H_2O}}\right)^3 \quad (1)$$

In Equation (1), M_{KA} is the molecular mass of the dissolved salt, ρ is the density of the solution, N_A is Avogadro's constant, α_{H_2O} is the polarizability of a water molecule, and r_{K^+}, r_{A^-}, and r_{H_2O} are the radius of the cation, anion, and water molecule, respectively. The parameters i and j denote the ionic charges. The value of the parameter $tg\varphi$ is determined experimentally from the slope of the concentration dependence of the function $(n^2 - 1)/(n^2 + 2)$ (Figure 1), where n is the refractive index of the solution.

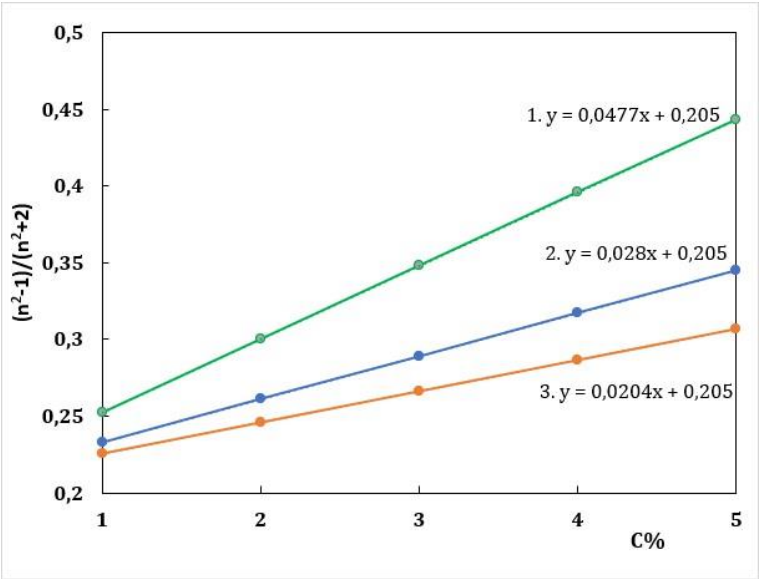

Figure 1. Concentration dependence of the $(n^2 - 1)/(n^2 + 2)$ ratio:
1. $NaCH_3COO$, 2. $Zn(CH_3COO)_2$, 3. $C_6H_5Na_3O_7$

As shown in the figures, these dependencies exhibit a linear character. By substituting the literature-derived parameters M_{NaCH_3COO}=82,03 g/mol, $M_{Zn(CH_3COO)_2}$= 183,48 g/mol, $M_{C_6H_5Na_3O_7}$=258,06 g/mol, α_{H_2O}=1,48*10^{-24} cm^3, r_{H_2O}=1,38Å, r_{Na^+}= 1,02Å, $r_{Zn^{2+}}$=0,74Å, $r_{CH_3COO^-}$=1,59Å, $r_{{C_6H_5O_7}^{3-}}$=2,6Å, into formula [1], we determined the sum of the hydration numbers.

The results obtained for the hydration numbers of a series of organic salts are presented in Table 1:

Table 1. Values of the h_1+h_2 parameters for a series of electrolytes

Solution	$r_1 + r_2$ **(pm)**	$h_1 + h_2$
$NaCH_3COO$	262	6.3
$Zn(CH_3COO)_2$	234	10.5
$C_6H_5Na_3O_7$	332	20.3

Analysis of Table 1 demonstrates that the nature of the electrolytes, as well as the charge and radii of the ions, exert a decisive influence on the hydration number.

3. Conclusion

Research findings indicate that in organic salts, the complex structures of both cations and organic anions, along with charge distribution and functional groups, lead to distinct hydration effects in an aqueous medium. When comparing $NaCH_3COO$ and $Zn(CH_3COO)_2$ systems, both of which contain the same acetate anion, the role of cationic properties in the hydration process becomes clearly evident. In zinc acetate solution, the smaller sum of ion radii (234 pm) and the divalent nature of the cation significantly increase the intensity of the electric field generated around the ion. Such high surface charge density ensures that zinc acetate binds a greater number of water molecules more strongly compared to sodium acetate and effectively restricts their translational mobility.

On the other hand, when examining the sodium citrate ($C_6H_5Na_3O_7$) salt, a distinct structural dependency is observed. Although this system exhibits the largest sum of ion radii (332 pm) among the organic salts investigated, its hydration number increases sharply to reach a maximum value of 20.3. Despite its larger geometric dimensions, this high hydration capacity is attributed to the unique internal configuration of the citrate anion. Specifically, the citrate anion is characterized by a trivalent negative charge, and its spatial structure encompasses numerous hydrophilic and hydrophobic centers. The simultaneous interaction of these centers with the aqueous environment significantly alters the macroscopic structure of the solvent. This process is characterized by a superposition effect, wherein local electrostatic and hydrophobic fields generated at various points of the citrate ion overlap

to induce more extensive structural ordering within the hydrogen-bond network of the water. Consequently, despite its large geometric size, sodium citrate exhibits a hydration effect significantly higher than that of salts containing the acetate group.

Thus, the formation of the hydration number in organic electrolytes is not solely dependent on the classical geometric radii of the ions; rather, it is directly influenced by the absolute value of the anion's charge and the collective (superposition) effect of intramolecular functional groups.

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