Reports of the Academy of Sciences of the USSR

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 118, No. 4

PHYSICAL CHEMISTRY

Yu. P. SYRNIKOV

ON THE NATURE OF THE INTERACTION OF ANIONS WITH WATER MOLECULES IN SOLUTION

(Presented by Academician I. I. Chernyaev on 17 VI 1957)

In considering the hydration of ions, no fundamental distinction is usually made between the hydration of an anion and that of a cation; the water molecule is treated here as a rigid dipole. Such a simplified model is to some extent acceptable for calculating thermochemical quantities; however, in a number of cases—for example, in studying the acoustic properties of solutions of strong electrolytes—it is insufficient. At present, at the Physical Faculty of Leningrad State University, the acoustic properties of electrolyte solutions are being studied ($^{1-3}$). The purpose of the present work was to obtain additional information necessary for explaining some of these properties.

As is known, the water molecule consists of an electronegative oxygen atom and two protons, possesses sharply expressed electropolar properties, and can form hydrogen bonds. In liquid water the molecules are connected with one another precisely by such bonds. At present (^{4}), the hydrogen bond is considered to be, by its nature, close to a donor-acceptor bond. When a hydrogen bond arises in the complex A—H···. B—R, a redistribution of the density of the electron shell occurs chiefly in atom B; the H atom acts as the "acceptor," atom B as the electron "donor," and the electron of atom B becomes shared between the proton and atom B. This is the most characteristic feature of the hydrogen bond, which gives it a special place among other types of intermolecular interaction.

When a strong electrolyte is dissolved in water, the latter dissociates into an anion and a cation. The anion and the cation enter into interaction with water molecules, and this interaction is called hydration. It should be noted that different authors assign a somewhat different meaning to the concept of hydration. By hydration we shall understand the interaction of an ion with the water molecules nearest to it.

In the hydration of a cation, the water molecule approaches the cation with its

Fig. 1

Figure 1: Fig. 1

electronegative part, oxygen, and the interaction of the cation with the water molecules is, in its nature, sharply different from the bonding of water molecules with one another. Correspondingly, the structure of the hydration shell of the cation must differ from the structure of pure water.

In the case of anion hydration, the situation is different. An anion is an electronegative atom (or group of atoms), and the water molecule approaches it with its electropositive part—the proton; moreover, several water molecules approach the anion at once, and several protons become associated with it. The excess electrons of the anion prove to be shared among several protons, and the interaction of the anion with the water molecules entering into its hydration shell has a donor-acceptor character. For each "acceptor" —proton—there is a part of an electron (at least in the case of monovalent and divalent anions). But such a bond is, by its nature, very close, if not identical, to the bond existing between molecules in pure water, i.e., to the hydrogen bond.

A quantitative calculation of interactions of this kind presents very great difficulties, since it requires the solution of quantum-mechanical

many-body problem. An experimental verification of this assumption is of interest. It is known that the most direct way of detecting and investigating the hydrogen bond is provided by spectroscopic studies and, above all, by infrared absorption spectra. A number of studies have been carried out on the infrared absorption spectra of ionic solutions (5,6); however, no special investigations of the absorption bands of the O–H group in solutions of strong electrolytes, with the aim of studying the interaction of water molecules with an anion, have been performed.

We undertook measurements of the infrared absorption of ionic solutions in the region 1.35-1.60 μ (the first overtone of the O–H group).

Fig. 1. Dependence of the absorption coefficient on wavelength for solutions of nitrate salts.
1 –absorption in pure water; **2** –absorption in a $NaNO_3$ solution (13.7 moles H_2O per 1 mole $NaNO_3$); **3** –absorption in a $NaNO_3$ solution (31.6 moles H_2O per 1 mole $NaNO_3$); **4** –absorption in a KNO_3 solution (31.6 moles H_2O per 1 mole KNO_3)

It is known that if the O–H group enters into a hydrogen bond, then instead of a narrow band in the region 1.36 μ, corresponding to the free O–H group of the water molecule, a broad band appears, shifted into the region of longer wavelengths, and this shift is approximately proportional to the energy of the hydrogen bond. Thus, from infrared absorption spectra one can judge whether free O–H groups and O–H groups that have entered into a hydrogen bond are

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

present in the system, and approximately estimate the energy of the hydrogen bond.

Fig. 2. Dependence of the absorption coefficient on wavelength for solutions of chloride salts.
1 –absorption in pure water; **2** –absorption in a NaCl solution (10.7 moles H_2O per 1 mole NaCl); **3** –absorption in a KCl solution (16.5 moles H_2O per 1 mole KCl)

The measurements were carried out at the Forestry Engineering Academy on a nonrecording spectrophotometer with glass optics. The spectrophotometer had high resolving power (4 Å per division of the counting drum), since an echelette with 600 lines per 1 mm was used as the spectral analyzer. Solutions of 8 salts with 4 different anions were measured. The results of the measurements are shown in Figs. 1–4. In calculating the absorption coefficient of the solutions, the optical density of the solution was divided by the concentration of water in the solution. As can be seen from the data presented, in ionic solutions, even at saturation concentrations, the absorption bands in the first approximation lie in the same region as in pure water, i.e., water molecules bound to an anion interact with it approximately in the same way as water molecules interact with one another. The energy of this interaction for some anions differs somewhat from the energy of bonding between water molecules themselves. Thus, for a saturated $NaNO_3$ solution the maximum of the absorption band lies at λ 1.4346 μ, while the maximum of absorption of pure water lies at 1.4518 μ. For a KNO_3 solution, where the salt concentration is lower, the absorption band has two maxima: one corresponds to the maximum in the saturated $NaNO_3$ solution, the other to the maximum in pure water.

water. A similar picture is observed for the $NaNO_3$ solution at a molar concentration equal to the molar concentration of the KNO_3 solution.

Fig. 3. Dependence of the absorption coefficient on wavelength for solutions of iodide salts.
1 –absorption in pure water; 2 –absorption in a CdJ_2 solution (29.1 moles of H_2O per 1 mole of CdJ_2); 3 –absorption in a KJ solution (9 moles of H_2O per 1 mole of KJ)

Thus, it may be considered that the maximum at λ 1.4346 μ corresponds to the vibration frequency of the O–H group interacting with the anion NO_3^-. For chloride and sulfate salts, the maximum of the absorption band falls at the

Fig. 4

Figure 4: Fig. 4

same wavelength as in pure water. The absorption band of the KJ solution has a maximum at λ 1.4350 μ. The absorption band of CdJ_2 is also shifted into the region of shorter wavelengths; however, the salt concentration in this solution is noticeably lower than in the KJ solution, and the band corresponding to pure water predominates.

On the basis of the foregoing, it may be said that the assumption advanced here regarding the nature of the interaction of the anion with water molecules is in agreement with spectroscopic data. It may further be assumed that, since the water molecules interacting with the anion are, from the side of the anion, under conditions similar to those existing in pure water (i.e., they are also bound to the anion by a hydrogen bond), the structure of the hydration shell of the anion is similar to the structure of water itself.

From this point of view, the results of A. Pasynskii' s work (^{7}) are understandable: he determined hydration numbers acoustically from the decrease in the compressibility of the solution in comparison with pure water and obtained much lower values of the hydration numbers than those following from thermochemical data. This result is explained by the fact that water molecules are bound to the anion by hydrogen bonds; the compressibility of the hydration shell of the anion is approximately the same as the compressibility of water itself, and hydration of the anion does not reduce the compressibility of the solution.

Fig. 4. Dependence of the absorption coefficient on wavelength for solutions of sulfate salts.
1 –absorption in pure water; 2 –absorption in an $MgSO_4$ solution (34.4 moles of H_2O per 1 mole of $MgSO_4$); 3 –absorption in a $CdSO_4$ solution (25 moles of H_2O per 1 mole of $CdSO_4$)

I express my deep gratitude to I. G. Mikhailov, V. P. Karelova, and V. V. Bazilevich for valuable advice and guidance.

Leningrad State University
named after A. A. Zhdanov

Leningrad Forestry Academy

Received
10 VI 1957

CITED LITERATURE

1. I. G. Mikhailov, *ZhFKh*, **30**, issue 2, 466 (1956).

2. I. G. Mikhailov, V. A. Shutov, *Vestn. Leningr. Univ.*, ser. phys. and chem., No. 16, issue 3, 16 (1956).

3. I. G. Mikhailov, Yu. P. Syrnikov, in: *Collection. Application of Ultrasound to Investigations of Matter*, issue VI, Moscow Regional Pedagogical Institute, 1958.

4. N. D. Sokolov, *Uspekhi Fizicheskikh Nauk*, **57**, 205 (1955).

5. R. B. Barnes, R. C. Gore, U. Liddel, V. Z. Williams, *Infra-red Spectroscopy*, N. Y., 1944.

6. L. Kellner, *Reports on Progress in Physics*, **15**, 1952.

7. A. Pasynskii, *ZhFKh*, **11**, 606 (1938).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.