N. A. Izmailov and Yu. A. Kruglyak

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

N. A. Izmailov and Yu. A. Kruglyak

ON THE QUESTION OF ION SOLVATION

(Presented by Academician M. I. Kabachnik on 23 V 1960)

According to modern theories ([1]), the thermodynamic functions of ion hydration —the isobaric-isothermal potential ΔZ_h^i, enthalpy ΔH_h^i, and entropy ΔS_h^i—are calculated on the basis of purely electrostatic concepts. However, no evidence has so far been adduced confirming the electrostatic character of the interaction of ions with solvent molecules. As calculation shows ([1]), in view of the mutual compensation of certain energy effects, the principal contribution to the total hydration energy is made by the energy of ion–dipole interaction, usually written in the form

$$A = -nze\mu/r^2, \tag{1}$$

where n is the hydration number, z the charge of the ion, and μ the dipole moment of the water molecule.

Let us note that this formula is valid if $r \gg d$, where d is the size of the dipole, which is precisely not the case in solutions. Thus, according to the proposed theories, the thermodynamic functions of solvation should depend strongly on the chosen sizes of molecules and ions, dipole moments, and dielectric constants D. In their calculations, investigators used different values of n, μ, and r, and obtained agreement with experimental data within 10-15%.

Table 1

Solvent	D (at 25°C)	$\mu \cdot 10^{18}$	V_M	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Li^+	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Na^+	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) K^+	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Rb^+	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Cs^+	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Cl^-	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) Br^-	$-\Delta Z_s^i$ ([2]), kcal/g-ion (at 25°C) J^-
H_2O	78.25	1.84	18.07	117.0	96.0	78.0	74.4	64.0	74.0	68.0	59.4

Solvent	D (at 25°C)	$\mu \cdot 10^{18}$	V_M	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Li^+	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Na^+	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) K^+	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Rb^+	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Cs^+	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Cl^-	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) Br^-	$-\Delta Z_s^i$ (2), kcal/g-ion (at 25°C) J^-
H_2O (according to (3))	78.25	1.84	18.07	121	97	79	74	66	79	72	64
CH_3OH	32.63	1.66	40.71	116.0	93.0	76.0	—	60.4	71.0	67.0	59.6
C_2H_5OH	24.30	1.68	58.71	115.0	90.0	73.2	—	—	71.3	66.2	58.5
$HCOOH$	58.5 (16°)	1.19	37.93	116.0	99.5	73.9	73.2	65.0	78.3	—	—
NH_3	16	1.46	20.84	124.0	99.0	79.4	73.3	65.6	65.6	62.8	57.0

In Table 1, for a number of solvents, μ, D, molecular volumes V_M, and $-\Delta Z_s^i$ for several ions are given; these were calculated by one of us (2) by extrapolating sums and differences of the chemical solvation energies of one and the same ion with a series of other ions of ever increasing radii to the value $1/r_{\text{cryst}}$ of these ions equal to zero. As we see, the data of Table 1 indicate the practical independence of ΔZ_s^i from the named properties of the solvents. This is probably explained by the fact that the quantities ΔZ_s^i depend on more general causes than those taken into account when they are calculated on the basis of the electrostatic model.

N. A. Izmailov, together with E. F. Ivanova (3), attempted to calculate ΔH_s^i in alcohols by the method of K. P. Mishchenko and A. M. Sukhotin. Agreement with experimental data within 30% was obtained only when, as the radius of the alcohol molecules, the quantity

$$r_{\text{sp}} = r_{H_2O} \frac{M_{\text{sp}}}{M_{H_2O}}.$$

was adopted. This also testifies to the limited applicability of the electrostatic model only to aqueous solutions.

As A. F. Kapustinskii and K. B. Yatsimirskii showed, there is a monotonic dependence of $\frac{\Delta H_n^i}{z^2}$ on the ion radius, independently of its charge, whereas according to electrostatic theory one might expect a linear dependence of A on z according to (1).

According to the views developed by A. F. Kapustinskii, the correction to r_{cryst}, $b = \pm 0.28$ Å, necessary for establishing a single dependence of ΔH_n^i on r_{aq}, is readily explained if one abandons the electrostatic scheme of hydrate formation and assumes that, upon hydration, the cation surrounds itself with a "layer" of four pairs of electrons supplied by four water molecules. On the basis of the ideas he also developed concerning the droplet model of the atom ([4]), it was established that the average thickness of a layer of eight electrons is 0.26 Å.

The data presented indicate the inadequacy of the electrostatic model of solvation and of the scheme, based on this model, for calculating solvation energy. In view of this, it seems expedient to us to try to move to other concepts and to consider ion solvation as a process of complex formation. Until recently, the calculation of the energy of formation of complexes, as of solvates, was based on the electrostatic model of interaction. In recent years, however, it has been abandoned in favor of the molecular-orbital method ([5]), which has the advantage that it encompasses all types of bonds, from covalent to ionic. In particular, to explain the nature of the bonds in solvates, concepts of donor–acceptor bonds within the framework of the molecular-orbital theory may be invoked.

One may imagine that, in hydrates, the electron donors are the oxygen atoms present in water molecules, which have free unshared electron pairs in the state with $n = 2$, while the electron acceptors are elementary ions providing vacant orbitals. By vacant orbitals we mean free orbitals closest in energy to the filled ones, in accordance with the order of arrangement of electron levels in atoms. Proceeding from the energetic equivalence of the bonds in solvates, it is necessary to admit hybridization of the vacant orbitals of ions. In such a case, the choice of orbitals immediately indicates to us the solvation number and the geometrical arrangement of the addends in solvates. In Table 2, for ions of alkali and halide elements, the probable vacant orbitals, the type of their hybridization ([6]), the geometric—

Table 2

Ion	Vacant orbitals	Type of their hybridization	Hydrate structure	n according to our data	n according to K. P. Mishchenko	n according to A. F. Kapustinskii	$-\Delta H_i$, kcal/g-ion
Li^+	$2s$, $2p$	sp^3	Tetrahedral	4	4	4	124
Na^+	$3s$, $3p$	sp^3	Tetrahedral	4	6	4	100}
F^-	$3s$, $3p$	sp^3	Tetrahedral	4	6	4	109}
K^+	$4s$, $3d$	sd^5	Mixed	6	8	4	80}
Cl^-	$4s$, $3d$	sd^5	Mixed	6	8	4	79}
Rb^+	$5s$, $4d$	sd^5	Mixed	6	8	4	75}
Br^-	$5s$, $4d$	sd^5	Mixed	6	8	4	72}
Cs^+	$6s$, $4f$	sf^7	—	8	8	4	65}

Fig. 1

Figure 1: Fig. 1

Ion	Vacant orbitals	Type of their hybridization	Hydrate structure	n according to our data	n according to K. P. Mishchenko	n according to A. F. Kapustinskii	$-\Delta H_i$, kcal/g-ion
J^-	$6s$, $4f$	sf^7	–	8	8	4	62}

arrangement of water molecules in hydrates, the hydration numbers, and the values of ΔH_h^i, calculated from the data of N. A. Izmailov ([3]). For comparison, the hydration numbers adopted by K. P. Mishchenko and A. F. Kapustinskii are also given. Isoelectronic ions are joined by braces. As is seen from the data of Table 2, the arrangement of water molecules in the hydrates of Li^+, Na^+, and F^- must be tetrahedral, which corresponds to present-day ideas about the small influence of these ions on the structure of water, and their hydration can in fact be regarded as the substitution of molecules by ions in tetrahedral cells of water. For the remaining ions one may assume hybridization of the sd^5 and sf^7 types with solvation numbers 6 and 8, respectively. In this case there is a greater disturbance of the structure of water, which also explains the differences in the hydration phenomena of the ions K^+ and Cl^-, Rb^+ and Br^-, Cs^+ and J^-, as compared with the ions Li^+, Na^+, F^-.

In solvates, as in complex compounds, the covalency of the bonds decreases with increasing ionic radius; therefore, in a first approximation, solvation of large ions may be regarded as ion–dipole interaction.

According to the electrostatic theory, all terms in the equation for ΔZ_h^i depend on $1/r$. Therefore a functional dependence between them has repeatedly been established. At the same time, a different character of the dependence was found for cations and anions. Proceeding from the concepts developed here, it is more correct to seek the dependence of ΔZ_h^i or ΔH_h^i on the energy characteristic of the vacant orbitals of the ions, which is the principal quantum number n. From the simplest considerations one may expect that the energy of chemical interaction of an ion with the solvent should be inversely proportional to n^2. With increasing n, the solvation energy should decrease. The difference in the solvation energies of neighboring ions in a group should also fall with increasing n. This follows from the fact that, with increasing n, the terms of the ions approach one another more and more closely. The indicated regularities are confirmed by the data of Table 2.

Fig. 1

As calculation ([1]) shows, the total hydration energy ΔZ_h^i differs from the energy of primary hydration ΔZ_{prim}^i by the presence of the terms nl, B, g, where l is the "internal" heat of evaporation of water, B is the energy of polarization of water by the field of the ion according to Born, and g is the energy of interaction of the molecules of the hydrate complex with the water surrounding it. But, as follows from the data of K. P. Mishchenko and A. M. Sukhotin, these terms mutually compensate one another ($nl + B + g \cong 0$), so that ΔZ_h^i actually characterizes ΔZ_{prim}^i. Further, part of the energy released in the formation of the hydrate is spent on ordering the water molecules around the ion, in accordance with which $\Delta S_h^i < 0$. The magnitude ΔS_h^i characterizes the change in the state of water in the field of the ion. Therefore, in order to characterize the dependence of ΔZ_{prim}^i on n, we used the quantities $\Delta H_h^i = \Delta Z_h^i + T\Delta S_h^i$. In Fig. 1, for ions of elements of the main subgroups of Groups I, II, and VII, the dependence

$$-\frac{\Delta H_h^i}{z^2}$$

on n^{-2} is represented graphically. As follows from Table 2 and Fig. 1, the quantities

ΔH_h^i of alkali-metal and halide ions with the same vacant levels coincide with one another within the limits of possible errors in the determination of ΔH_h^i. At the same time, the ions Cs^+, Rb^+, K^+, Na^+ and J^-, Br^-, Cl^- form one dependence (the straight solid line), while Li^+ and F^- deviate from this straight line. The dependence

$$-\frac{\Delta H_h^i}{z^2}$$

on n^{-2} for alkaline-earth metal ions has a similar character. Strictly speaking, the dependences presented split into three linear sections (dashed lines), which is explained by a change in the hydration numbers (see Table 2). The fact that singly charged cations and anions form one dependence indicates a common mechanism of their hydration (solvation). Analogous dependences for nonaqueous solutions lead to the same conclusions.

In accordance with the point of view being developed, the values of ΔH_{ih} for isoelectronic ions SH^-, Cl^-, K^+ (82, 84, and 81 kcal/g-ion, respectively), which have approximately identical vacant orbitals, are close. The values of ΔH_h^i are also close for such isoelectronic ions as OH^-, H_3O^+, F^-, and Na^+ ([3]).

The proposed concepts make it possible readily to justify the method, adopted by many investigators, of dividing the total hydration energy into ionic components by the pairs Cs^+ and J^-, or K^+ and Cl^-.

The point of view set forth explains the practical independence of ΔZ_s^i, especially ΔH_s^i, in solvents containing oxygen (water, alcohols, carboxylic acids) and

nitrogen (ammonia, amines). In the first group of these solvents the electron donors are oxygen atoms, in the second—nitrogen atoms, which provide, for the formation of molecular orbitals, electrons from one and the same state with the principal quantum number $n = 2$. It may be expected that close values of ΔH_s^i will be observed in all solvents containing atoms that supply electrons from one and the same level (for example, atoms of oxygen, nitrogen, fluorine).

As follows from Table 1, the differences in ΔZ_s^i for the ions cited amount to 5-10 kcal/g-ion. It may be assumed that these differences are a consequence of a change in the energy of secondary solvation, which depends strongly on the properties of the solvents (D, μ, V_m). Thus, the total solvation energy of ions in solvents whose molecules contain atoms with electrons located on close levels consists of a primary-solvation energy $\Delta Z^i_{\text{primary}}$, large in magnitude and only slightly dependent on the properties of the solvent, and a secondary-solvation energy $\Delta Z^i_{\text{secondary}}$, small but strongly dependent on the properties of the solvent. It also follows from what has been said that the $\Delta Z^i_{\text{primary}}$ values of different isoelectronic ions (having the same vacant orbitals) in a series of solvents whose molecules contain atoms that donate to the molecular orbitals electrons located on the same levels are close to one another.

Kharkov State University
named after A. M. Gorky

Received
12 V 1960

CITED LITERATURE

1. K. P. Mishchenko, A. M. Sukhotin, *ZhFKh*, **27**, No. 1, 26 (1953).
2. N. A. Izmailov, *DAN*, **126**, 1033 (1959).
3. N. A. Izmailov, *Electrochemistry of Solutions*, Kharkov, 1959, pp. 304, 343.
4. Program of the Work of the Scientific-Technical Conference of the MKhTI named after D. I. Mendeleev, Moscow, 1960, p. 4.
5. Ya. K. Syrkin, *Usp. khim.*, **8**, 903 (1959). G. Eyring, J. Walter, J. Kimball, *Quantum Chemistry*, IL, 1948, p. 306.

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