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Fig. 1

Figure 1: Fig. 1

Abstract

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A NEW METHOD FOR FINDING THE ENERGIES AND HEATS OF SOLVATION OF INDIVIDUAL IONS

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In work (^{1}) new ideas were developed concerning the solvation of ions as a process of complex formation. According to these ideas, the bond between solvent molecules and ions is effected as a result of the formation of molecular orbitals. In this case the central atoms of solvent molecules

Fig. 1. Extrapolation of the quantities

$$A_x + \left(\frac{A_{x\mathrm{Me}^+} + A_{y\Gamma^-}}{2} \right)_{n=3,\,4,\,5,\,6}$$

for water, ammonia, ethanol, and methanol, and of the quantities

$$H_x + \left(\frac{H_{x\mathrm{Me}^+} - H_{x\Gamma^-}}{2} \right)_{n=3,\,4,\,5,\,6}$$

for water.

$$H_x = -\Delta H_x$$

$$A_x = -\Delta Z_x$$

of the solvents (oxygen, nitrogen) are donors of unshared electron pairs, while the ions are their acceptors, presenting to them their vacant orbitals. The solvation number is determined by the coordination number, i.e., by the number of filled vacant orbitals with the nearest energy levels. The primary solvation energy therefore represents the energy of complex formation, and the secondary energy represents the energy of electrostatic interaction of the complex with solvent molecules.

In accordance with the developed concepts, the experimental data indicate that the solvation energies of isoelectronic ions are close to one another not only in a single solvent, but also in different ones, if the solvent molecules contain atoms that are electron donors situated at the same electronic levels (^{2}).

Small differences in the heats ($-\Delta H$) of solvation depend on differences in the "secondary" energy and are due to different dipole moments and dielectric constants of the solvents. Differences in the energies ($-\Delta Z$) of solvation are also connected with differences in the entropies of solvation and are caused mainly by differences in the structure of the solvents.

From the experimental data it follows that the magnitudes of the solvation energies of cations and anions give a single dependence, close to linear, on n^2 of the vacant orbitals, where n is the principal quantum number. As n decreases, the energy values for cations and anions fall and approach one another.

This dependence was used by us to develop a new method for finding the solvation energies of individual ions. The method is based on the fact that the difference between the solvation energies of isoelectronic halide and alkali-metal ions ($A_{x\Gamma^-} - A_{x\mathrm{Me}^+}$), with decreasing $1/n^2$, tends to zero. Determination of the solvation energy of an individual ion, for example the hydrogen ion, is based on extrapolation to $1/n^2 = 0$ of the dependence of the quantities

$$A_{x\ \mathrm{ion}} + \left(\frac{A_{x\Gamma^-} - A_{x\mathrm{Me}^+}}{2}\right)_{n=3,4,5,6},$$

found for different values of n, on the value $1/n^2$. The extrapolated quantity is found as the half-sum of the sums of the solvation energies of the hydrogen ion and the halide ions and of the differences between the solvation energies of the hydrogen ion and the alkali-metal ions. The sums and differences of the energies are found from emf chains without transference and with transference. The corresponding data for heats of solvation are found from heats of dissolution.

Table 1

Data for extrapolation

Solvent	n	$1/n^2$	Ions (differences)	A	B	C	D
H_2O	3	0.11	Na^+, F^-	260.0	122.2	114.6	–
H_2O	4	0.0625	K^+, Cl^-	255.2	115.8	110.0	104.4

Solvent	n	$1/n^2$	Ions (differences)	A	B	C	D
H_2O	5	0.04	Rb^+, Br^-	254.8	115.0	109.0	105.0
H_2O	6	0.028	Cs^+, J^-	255.3	116.0	109.4	104.0
NH_3		0.00		256.3	117.0	110.5	103.0
NH_3	4	0.0625	K^+, Cl^-	273.7	116.5	127.2	–
NH_3	5	0.04	Rb^+, Br^-	275.6	118.5	128.8	–
NH_3	6	0.028	Cs^+, J^-	276.2	119.7	129.5	–
CH_3OH		0.00		278.0	121.5	181.0	–
CH_3OH	4	0.0625	K^+, Cl^-	251.2	113.8	105.0	–
CH_3OH	5	0.04	Rb^+, Br^-	251.2	114.0	105.0	–
CH_3OH	6	0.028	Cs^+, J^-	252.9	115.3	106.0	–
C_2H_5OH		0.00		252.5	115.0	106.0	–
C_2H_5OH	4	0.0625	K^+, Cl^-	252.2	112.5	106.2	–
C_2H_5OH	5	0.04	Rb^+, Br^-	252.0	113.2	107.2	–
C_2H_5OH	6	0.028	Cs^+, J^-	252.0	113.2	106.4	–
		0.00		251.7	113.0	106.0	–

Note.

$$A = A_{x\mathrm{H}^+} + \left(\frac{A_{x\Gamma^-} - A_{x\mathrm{Me}^+}}{2}\right)_{n=3,4,5,6};$$

$$B = A_{x\mathrm{Li}^+} + \left(\frac{A_{x\Gamma^-} - A_{x\mathrm{Me}^+}}{2}\right)_{n=3,4,5,6};$$

$$C = A_{x\mathrm{Ag}^+} + \left(\frac{A_{x\Gamma^-} - A_{x\mathrm{Me}^+}}{2}\right)_{n=3,4,5,6};$$

$$D = A_{x\mathrm{F}^-} + \left(\frac{A_{x\mathrm{Me}^+} - A_{x\Gamma^-}}{2}\right)_{n=3,4,5,6}.$$

As a rule, the quantities

$$A_{x\mathrm{H}^+} + \left(\frac{A_{x\Gamma^-} - A_{x\mathrm{Me}^+}}{2} \right)_{n=\mathrm{const}}$$

depend linearly on $1/n^2$, and for $n > 3$ differ from one another and from the limiting value by 1-2 kcal/g-ion; the differences are still smaller for the corresponding quantities of the heats of solvation (H_x) (Fig. 1).

By the same route, the solvation energies of any other cations and anions can be found. Of course, the determination is more reliable for the quantities A_x of such ions whose solvation energy is appreciably larger than that of the ions included in the difference; among monovalent cations these are H^+, Li^+, Ag^+, and among anions F^- (Fig. 1).

The data given in Table 1 for extrapolating the energy in water, methanol, ethanol, and ammonia were compiled from the same data that we previously used to find the solvation energy

by extrapolating the sums and differences of the energies to the value $1/r_{\mathrm{cr}} = 0$. The determination of the heats of solvation was based on the data of K. P. Mishchenko, A. F. Kapustinskii, and K. B. Yatsimirskii with co-workers (^{3}).

Subsequently, in the calculations we proceeded as follows: from the data on $A_{x\mathrm{H}^+}$, $A_{x\mathrm{Li}^+}$, and $A_{x\mathrm{Ag}^+}$, and from the data on $\sum A_{x\mathrm{Hg}}$, $\sum A_{x\mathrm{LiG}}$, $\sum A_{x\mathrm{AgG}}$, we found the mean values $A_{x\mathrm{F}^-}$, $A_{x\mathrm{Cl}^-}$, $A_{x\mathrm{Br}^-}$, $A_{x\mathrm{J}^-}$; these quantities were taken as the basis for the subsequent separation.

Table 2 compares data for A_x of ions in water, methanol, ethanol, and ammonia, obtained by extrapolation to $1/n^2$ and $1/r = 0$.

Table 2

Comparison of data on A_x-ions obtained by extrapolation to $1/r \to 0$ and $1/n^2 \to 0$

Ions	H_2O $1/r$	H_2O $1/n^2$	NH_3 $1/r$	NH_3 $1/n^2$	CH_3OH $1/r$	CH_3OH $1/n^2$	C_2H_5OH $1/r$	C_2H_5OH $1/n^2$
H^+	258.0	256.5	281.0	278.0	253.0	252.0	252.0	251.5
Cl^-	74.0	74.5	65.5	68.0	71.0	73.0	71.5	70.5
Br^-	68.0	69.5	62.8	65.5	67.0	67.5	66.0	67.0
J^-	59.0	60.5	57.0	59.5	59.5	60.5	58.5	58.5
Li^+	117.0	117.0	124.0	121.0	116.0	115.0	115.0	113.0
Na^+	96.0	94.0	99.0	96.4	93.0	92.0	90.0	89.0
K^+	78.0	77.0	79.4	77.0	76.0	75.0	73.0	72.5
Rb^+	75.4	73.0	73.3	71.0	–	69.0	–	66.5
Cs^+	64.0	63.0	65.5	63.0	60.5	59.5	–	58.0
Ag^+	112.0	110.5	132.0	131.5	108.0	106.0	108.0	106.0

Ions	H_2O $1/r$	H_2O $1/n^2$	NH_3 $1/r$	NH_3 $1/n^2$	CH_3OH $1/r$	CH_3OH $1/n^2$	C_2H_5OH $1/r$	C_2H_5OH $1/n^2$
Ca^{2+}	372.5	371.0	360.0	355.4	–	–	–	–
Zn^{2+}	492.0	492.5	536.0	530.0	481.0	479.0	473.0	472.0
Cd^{2+}	430.5	428.0	458.0	458.0	415.0	417.0	413.0	413.5

As can be seen, the quantities obtained by extrapolation to $1/n^2 = 0$ do not differ greatly from those obtained earlier (2) by extrapolation to $1/r = 0$. As a rule, in all solvents the solvation energies of cations are lower by 1.0–1.5 kcal/g-ion, and the corresponding quantities for anions are higher by the same amount. Accordingly, the heats of hydration proved to be lower by ∼ 1.0 kcal/g-ion for cations and higher for anions, in comparison with the data (3).

Table 3 gives the quantities $-\Delta H_x$ and $-\Delta Z_x$ obtained by us by extrapolation to $1/n^2$, and the values $-\Delta S_h$ of hydration calculated from them. The values ΔH_x and ΔS_x are compared with the data (3). The solvation entropy values we obtained are close to those obtained from heat capacities (in any case, the changes in entropy on going from ion to ion are analogous).

Table 3

Ion	$-\Delta H$ according to Mishchenko et al., $\Delta H_{\mathrm{KCl}} = \Delta H_{\mathrm{LiJ}}$	$-\Delta H$ our extrap. $1/n^2$	$-\Delta Z$ according to Mishchenko et al.	$-\Delta Z$ our calc. e.s., from extrap. $1/n^2$	$-\Delta S$ from ΔH and ΔZ according to our data	$-\Delta S$ according to Mishchenko, taking into account ΔS_{H^+}
H^+	265.0	264.0	–	256.5	25.0	3.4
Li^+	127.0	126.0	121.0	117.0	30.0	25.0
Na^+	101.0	100.0	92.0	94.0	20.0	18.0
K^+	81.0	80.0	78.0	77.0	10.0	10.0
Rb^+	75.0	74.0	74.0	72.5	5.0	7.0
Cs^+	67.0	66.0	66.0	63.0	10.0	6.0
Ag^+	117.0	116.0	113.0	110.5	18.0	19.0
Mg^{2+}	467.0	466.0	450.0	451.0	50.0	61.0
Ca^{2+}	386.0	385.0	373.0	371.0	47.0	46.0
Sr^{2+}	379.0	378.0	341.0	341.0	57.0	43.0
Ba^{2+}	320.0	319.0	310.0	320.0	−3.0	34.0
Zn^{2+}	496.0	495.0	479.0	492.5	8.0	61.0
Cd^{2+}	439.0	438.0	425.0	428.0	30.0	52.0
F^-	116.0	118.0	107.0	102.5	40.0	27.0
Cl^-	84.0	85.0	79.0	74.5	35.0	14.0
Br^-	76.0	77.0	72.0	69.5	25.0	10.0

Ion	$-\Delta H$ according to Mishchenko et al., $\Delta H_{\mathrm{KCl}} = \Delta H_{\mathrm{LiJ}}$	$-\Delta H$ our extrap. $1/n^2$	$-\Delta Z$ according to Mishchenko et al.	$-\Delta Z$ our calc. e.s., from extrap. $1/n^2$	$-\Delta S$ from ΔH and ΔZ according to our data	$-\Delta S$ according to Mishchenko, taking into account $\Delta S_{\mathrm{H^+}}$
J^-	67.0	68.0	64.0	60.5	25.0	5.0

The methods used up to the present for separating the total energy into the energies of individual ions can be divided into two groups: 1) methods based on accepting equality of the solvation energies of a definite pair of cations and anions. J. Bernal and R. Fowler (^{4}) assumed equality of the energies for the ions K^+ and F^- (equal radii), MacInnes (^{5}) in finding the activity coefficients of individual ions—K^+ and Cl^-, Lange and Mishchenko (^{6}), Kapustinskii and Yatsimirskii (^{7})—Cs^+ and J^- ions (isoelectronic ions); 2) methods using dependences of solvation energies on ionic radii ($^{8-11}$), based on the decrease in the solvation energy with increasing ionic radius. To this group of methods belongs the method of extrapolating sums and differences of solvation energies to $1/r_{\mathrm{cr}} = 0$, proposed by us earlier (^{2}).

The method now proposed generalizes both separation procedures, using: 1) the closeness of the solvation energies of isoelectronic ions and 2) the decrease of the solvation energy with increasing n^2, and consequently,

but of the radii of the ions, since $r = f(n^2)$. In addition, use is made of the advantages of the method we proposed earlier for finding the limiting value by extrapolating sums and differences of energies. It should be noted here that extrapolation of the half-sum from the sum and difference of energies at constant n to $1/n^2 = 0$ is more reliable than extrapolation of this quantity, obtained for constant r_{cr}, to $1/r_{\mathrm{cr}} = 0$, since the dependence of A_x for cations and anions on $1/n^2$, unlike their dependence on $1/r_{\mathrm{cr}}$, is identical. In essence, the method makes use of the circumstance that the difference in solvation energy of isoelectronic cations and anions with the same n tends to zero as n increases.

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