A NEW METHOD OF OBTAINING ENERGIES AND HEATS OF SOLVATION OF INDIVIDUAL IONS

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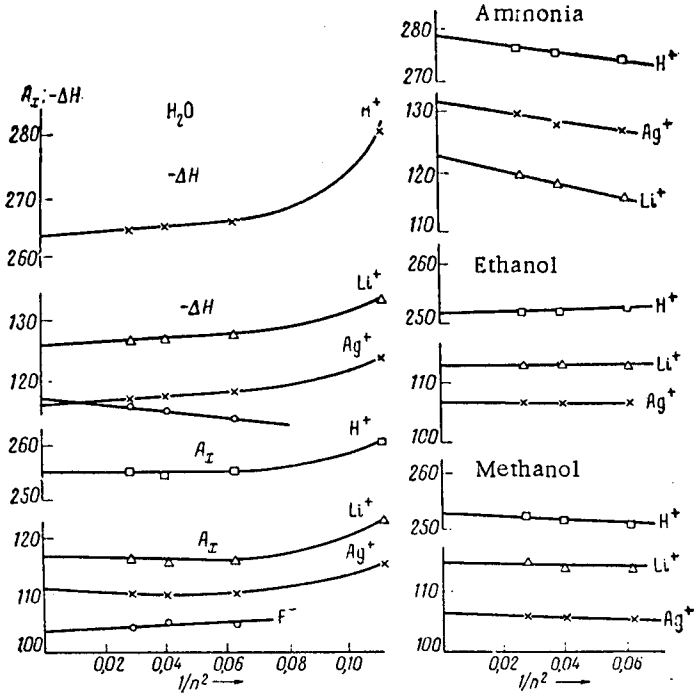
(Presented by Academician M. I. Kabachnik, November 24, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 149, No. 4,
pp. 884-887, April, 1963
Original article submitted November 22, 1961

New ideas concerning ion solvation and the process of complex formation have been developed in [1]. These suggest that the bonding of ions and solvent molecules results from formation of molecular orbitals. Here the central atom of the solvent molecules (oxygen, nitrogen) functions as the donor of an unshared pair of electrons while the ion with its vacant orbitals functions as an acceptor for these electrons. The solvation number is fixed by the coordination number, which is to say, by the number of vacant orbitals having approximately the same energy as the filled orbital. The primary solvation energy is therefore the energy of complex formation and the secondary energy, the energy of electrostatic interaction of the complex and the solvent molecules.



Extrapolation of the quantity $A_X + \left(\frac{A_{XMe^+} + A_{yHal^-}}{2}\right)_{n=3,4,5,6}$ for water, ammonia, ethanol, and methanol, and of the quantity $H_X + \left(\frac{H_{XMe^+} - H_{XHal^-}}{2}\right)_{n=3,4,5,6}$ for water. $H_X = -\Delta H_X$, $A_X = -\Delta Z_X$

The experimental data conform with this theory in showing the energies of solvation of isoelectronic ions to be approximately the same, not only in a single solvent, but in those various solvents where the electrons furnished by donor atoms come from the same electronic level [2].

The small differences in the heats of solvation ($-\Delta H$) are in the "secondary" energy and arise from differences in the dipole moments and dielectric constants of the solvents. Differences in the solvation energies ($-\Delta Z$) are also related to differences in solvation entropies which arise principally from structural differences in the solvents.

TABLE 1. Data for Extrapolation

Solvent	n	$1/n^2$	Ions (difference)	A	B	C	D
H_2O	3	0,11	Na+, F−	260,0	122,2	114,6	—
	4	0,0625	K+, Cl−	255,2	115,8	110,0	104,4
	5	0,04	Rb+, Br−	254,8	115,0	109,0	105,0
	6	0,028	Cs+, I−	255,3	116,0	109,4	104,0
NH_3		0,00		256,3	117,0	110,5	103,0
	4	0,0625	K+, Cl−	273,7	116,5	127,2	—
	5	0,04	Rb+, Br−	275,6	118,5	128,8	—
	6	0,028	Cs+, I−	276,2	119,7	129,5	—
CH_3OH		0,00		278,0	121,5	181,0	—
	4	0,0625	K+, Cl−	251,2	113,8	105,0	—
	5	0,04	Rb+, Br−	251,2	114,0	105,0	
	6	0,028	Cs+, I−	252,9	115,3	106,0	—
C_2H_5OH		0,00		252,5	115,0	106,0	—
	4	0,0625	K+, Cl−	252,2	112,5	106,2	—
	5	0,04	Rb+, Br−	252,0	113,2	107,2	—
	6	0,028	Cs+, I−	252,0	113,2	106,4	—
		0,00		251,7	113,0	106,0	=

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

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

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

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

TABLE 2. Comparison of A_X Values Obtained by Extrapolation to $1/r \to 0$ by Extrapolation to $1/n^2 \to 0$

Ion	H_2O		NH_3		CH_3OH		C_2H_5OH	
	$1/r$	$1/n^2$	$1/r$	$1/n^2$	$1/r$	$1/n^2$	$1/r$	$1/n^2$
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
	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
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

The experimental data indicate that there is a single, almost linear relation between the solvation energies of cations and anions and $1/n^2$, n being the principal quantum number of the vacant orbital. The solvation energies of cations and anions diminish with increasing n and approach a common value.

This relation has been used in developing a new method for obtaining the solvation energies of individual ions. This method is based on the fact that the difference in the solvation energies of isoelectronic halide and alkali metal ions ($A_{x\mathrm{Hal}^-} - A_{x\mathrm{Me}^+}$) tends to zero as $1/n^2$ diminishes. Determination of the solvation energy of the hydrogen ion, for example, involves extrapolation of the

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

$1/n^2$ relation, developed for various values of n, to $1/n^2 = 0$. The extrapolated quantity is found by adding to the sum of the solvation energies of the hydrogen and halide ions the difference of the solvation energies of the hydrogen and alkali metal ions and dividing the result by two. These energy sums and differences are obtained from the emf's of cells with and without transference. Values for the heats of solvation are found in a similar manner from heats of solution.

The quantities

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

are, in general, linear functions of $1/n^2$, values of such function for $n > 3$ differing from one another and from the limiting value by 1-2 kcal/g-ion. The corresponding values of the heat of solvation (H_X) differ by even less (figure).

Values of the solvation energy for other cations and anions can be obtained by exactly the same method. Naturally, the most trustworthy values of A_X are those for ions whose solvation energies are considerably greater than the solvation energies of the ions involved in the difference, e.g., H^+, Li^+, and Ag^+ among the monovalent cations, and F^- among the monovalent anions (figure).

The values of Table 1 have been used for energy extrapolations in water, methanol, ethanol, and ammonia; they have been compared with similar data which were employed earlier in obtaining solvation energies by extrapolating energy sums and differences to $1/r_{cr} = 0$. The data of K. P. Mishchenko, A. F. Kapustinskii, K. B. Yatsimirskii, et al [3] were used in determining the heats of solvation.

The calculations proceeded so that mean values of $A_{x\mathrm{F}^-}$, $A_{x\mathrm{Cl}^-}$, $A_{x\mathrm{Br}^-}$, and $A_{x\mathrm{I}^-}$, were obtained from data on $A_{x\mathrm{H}^+}$, $A_{x\mathrm{Li}^+}$, and $A_{x\mathrm{Ag}^+}$, and values of $\Sigma A_{x\mathrm{HHal}}$, $\Sigma A_{x\mathrm{LiHal}}$, $\Sigma A_{x\mathrm{AgHal}}$, and these, in turn, made the basis for further separations.

Table 2 gives a comparison of the A_X values for ions in water, methanol, ethanol, and ammonia as obtained by extrapolation to $1/n^2 = 0$ and by extrapolation to $1/r = 0$.

It is clear that the values obtained by extrapolation to $1/n^2 = 0$ are not essentially different from those obtained earlier [2] by extrapolation to $1/r = 0$. In general, the energy of cation solvation is 1.0-1.5 kcal/g-ion lower in each solvent and the energy of anion solvation higher by the same amount. Similarly, the heat of cation hydration proves to be ~1.0 kcal/g-ion lower than the value of [3], while the heat of anion hydration is higher by the same amount.

TABLE 3.

Ion	ΔH, from Miscenko, et al	ΔH, our extrap. in $1/n^2$	ΔZ, from Miscenko, et al	ΔZ, our values from emf's and extrap. in $1/n^2$	ΔS, from ΔH and ΔZ, from our data	ΔS, from Miscenko, allowing for 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+}	370,0	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
J^-	67,0	68,0	64,0	60,5	25,0	5,0

Table 3 gives our values for $-\Delta H_X$ and $-\Delta Z_X$ obtained by extrapolation in $1/n^2$ and values of $-\Delta S_h$ of hydration calculated from these. The values of ΔH_X and ΔS_X are compared with those of [3]. Our values of the entropy of solvation are close to those obtained from heat capacity measurements, at least to the extent of changing similarly in passing from one ion to another.

The methods which have been used so far in dividing the total energy into the individual ions fall into two groups. First, are those methods which are based on an assumedequality between the solvation energies of certain pairs of cations and anions. Bernal and Fowler [4] assumed equality of energy for the K^+ and F^- ions which have equal radii; MacInnes [5], determining activity coefficients, made a similar assumption concerning the K^+ and Cl^- ions, as did Lange and Miscenko [6], and Kapustinskii and Yatsimirskii [7] for the isoelectrons Cs^+ and I^- ions. Second, are those methods which draw on solvation energy, ionic radius relations [8-11] showing the energy diminishing as the radius of the ion increases. The earlier method of extrapolating sums and differences of solvation energies to $1/r_{cr} = 0$ [2] belongs to this group.

The method now proposed is a generalization of these two types of separation which makes use of the facts that: 1) The energies of solvation of isoelectronic ions are approximately the same, and 2) the energy of solvation diminishes as n^2 increases and the ionic radius rises according to $r = f(n^2)$. Moreover, the advantages of determining the limit by extrapolation of energy sums and differences are retained. It should be noted that extrapolation of half-sums of sums and differences of energies at fixed n to $1/n^2 = 0$ is more trustworthy than is extrapolation of similar quantities evaluated at fixed r_{cr} to $1/r_{cr} = 0$. This is due to the fact that the functional dependence of A_X on $1/n^2$ is the same for cations and anions whereas the same is not true of the functional dependence of A_X on $1/r_{cr}$. In principle, the method is based on the principle that the difference in solvation energies of isoelectronic cations and anions at fixed n tends to zero as n increases.

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