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1963

SovietRxiv

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PHYSICAL CHEMISTRY

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SOLVATION AND RESOLVATION ENERGY (VALUES OF $\lg \gamma_0$) OF INDIVIDUAL IONS IN NONAQUEOUS SOLUTIONS

(Presented by Academician M. I. Kabachnik, 24 XI 1962)

On the basis of the closeness of the solvation energies of isoelectronic cations and anions and their further convergence with increasing principal quantum number n of the vacant orbitals ([1]), we developed a new method for separating the total solvation energies into the energies of individual ions ([2]). With the aid of this method, solvation energies were determined in water, methanol, ethanol and butanol, isoamyl alcohol, ammonia, hydrazine, acetonitrile, acetone, and formic acid ([2],[3]).

The initial total energies were obtained:

1) For water, methanol, ethanol, and ammonia–almost exclusively from emf chains without transport (total energies) and with transport (differences of energies). These are the most reliable data, since they are based only on normal potentials and, consequently, refer to the state of ions at infinite dilution.
2) For hydrazine, acetonitrile, and formic acid–from emf chains with transport (differences) and from solubility data (sums of energies). Although in these media, with comparatively high dielectric constants, only ionic solubility takes place, these data are nevertheless somewhat less reliable than the preceding ones.
3) For butanol, isoamyl alcohol, and acetone the data were obtained almost entirely from solubilities. Only for finding the energy of the H^+ ion were data from an emf chain reversible to HCl ions used. These data are less reliable both because of the limited nature of the initial data and because in these media, with comparatively low dielectric constants, ion association arises, which leads to an increase in solubility compared with the purely ionic one and to an overestimation

Table 1

Solvation energy of ions (kcal/g-ion)

Ions	NH_3	N_2H_4	H_2O	CH_3OH	C_2H_5OH	C_4H_9OH	$C_5H_{11}OH$	CH_3COCH_3	CH_3CN	HCOOH
Ions	19.0	51.7	79.0	31.5	24.0	17.8	15.8	19.0	36.7	57.0
H^+	278.0	274.5	256.5	252.5	251.5	251.5	252.0	252.0	249.0	243.0
Cl^-	68.0	73.5	74.5	73.0	72.5	71.5	70.5	70.0	64.0	79.0
Br^-	65.5	71.0	69.0	67.5	67.0	68.5	64.8	68.0	62.5	71.0
J^-	59.5	59.5	60.5	60.5	58.5	58.0	59.0	57.0	57.5	61.5
Li^+	121.0	113.5	117.0	115.0	113.0	114.5	115.5	115.0	114.5	113.5
Na^+	96.5	92.0	94.0	92.0	89.0	88.5	85.0	80.0	90.5	91.5
K^+	77.0	75.0	77.0	75.0	72.5	69.0	69.5	68.0	75.0	73.0
Rb^+	71.0	70.0	72.5	69.0	66.5	60.0	65.0	62.0	70.5	70.0
Cs^+	63.0	61.5	63.0	59.5	58.5	57.0	57.0	57.0	61.5	61.0
Ca^{++}	355.5	363.0	371.0	–	–	–	–	–	350.0	358.0
Ag^+	131.5	128.5	110.5	106.0	106.0	–	–	–	115.0	111.0
Zn^{++}	530.0	508.5	492.5	479.0	472.0	–	–	–	472.0	474.0
Cd^{++}	457.0	446.5	428.0	415.0	413.5	–	–	–	412.0	413.0

of total energies. We decided to use these data as well, since they nevertheless characterize the dependence between the solvation energy and the properties of the solvents.

Table 1 compares the solvation energies of individual ions obtained for all the solvents listed, starting from the total energies found by the method of extrapolation to $1/n^2 \to 0$. In Table 1 the solvents are arranged in order of decreasing proton solvation energy: from 278 kcal/g-ion for ammonia to 243 for formic acid, i.e., by 35.0 kcal/g-ion. The magnitude of the proton solvation energy does not depend on the dielectric constant, but depends only on the chemical nature of the solvents. According to the character of the ion solvation energies, the solvents may be divided into 4 groups:

1. Water and alcohols. In this group of hydroxyl-containing, leveling solvents, as the dielectric constants (d.c.) decrease, the solvation energy of both cations and anions generally falls. However, the decrease in the solvation energy of anions is smaller than that of cations. For anions the energy decreases toward isoamyl alcohol by 3–4 kcal/g-ion, and for cations by 7–8 kcal/g-ion. At the same time, for both cations and anions the change in energy decreases with increasing ionic radius or with the principal quantum number n of the vacant orbitals. In contrast to the other cations, the solvation energy of the proton drops sharply in going from water to methanol, and then changes hardly at all. The solvation energy of divalent ions decreases considerably.
2. The characteristic features of basic solvents are: 1) a strong increase in the proton solvation energies in comparison with water—by 20–25 kcal/g-ion. Despite the lower dielectric constant, the solvation energies in ammonia are greater than in hydrazine. In contrast to alcohols, in basic solvents, as the d.c. decreases, the ratio of the solvation energy of cations to the

solvation energy of anions increases. In ammonia the solvation energy of some cations is even higher than in water. A special feature of nitrogen-containing solvents is their high affinity for ions that do not have noble-gas shells—such as silver, zinc, and cadmium—owing to the ability of these ions to form complexes.

3. In acidic solvents, which have a low affinity for the proton, inverse relationships occur in the changes of solvation energies. Thus, in formic acid, which is characterized by a low affinity for the proton ($A_{\mathrm{xH^+}} = 243.0$), despite a relatively high d.c. $= 57$, the solvation energy of cations decreases considerably and, at the same time, the solvation energy of anions increases considerably. As a result, the ratio of the solvation energies of anions to the solvation energies of cations increases to an even greater extent than in alcohols. This increase is probably a consequence of the formation of hydrogen bonds between the solvated ion and the solvent molecules.
4. Differentiating solvents—acetone and acetonitrile—occupy a special position; in them the relative strength of electrolytes changes greatly. As follows from the magnitude of the proton solvation energy, acetone is a more basic solvent than acetonitrile. However, the basicity of both solvents does not differ greatly from the basicity of the higher alcohols. Their characteristic feature is the low solvation energy of all the remaining ions. At the same time, in acetonitrile the solvation energy of anions decreases sharply (almost by 10 kcal/g-ion for Cl^-) and the solvation energy of cations decreases comparatively little. In this sense, despite its low affinity for the proton, acetonitrile behaves as a basic solvent. In acetone, on the contrary, the solvation energy of cations decreases sharply (14 kcal/g-ion for sodium and 9 kcal/g-ion for potassium), while the solvation energy of anions decreases comparatively little. In this sense acetone, having a greater affinity for the proton, behaves as an acidic solvent.

It should be noted that in all solvents, as the principal quan-

of the quantum number characterizing the vacant orbitals of the ions, the solvation energies of cations and anions decrease and approach one another. The solvation energy of cesium ions and especially of iodide ions changes least with the solvent.

From data on the magnitudes of the solvation energy of individual ions in various solvents, we calculated the values of $\lg \gamma_0$ for individual ions (^{4}).

The calculation was carried out according to the equation

$$\lg \gamma_0 = \frac{A_{x\,\mathrm{H_2O}} - A_{xM}}{2.3\nu RT}.$$

Since the values of A_x are determined with an accuracy of up to 0.5 kcal/g-ion, the errors in determining $\lg \gamma_0$ are comparatively large. Therefore we also took into account other possibilities for determining this quantity. We calculated $\lg \gamma_{0\mathrm{H}^+}$ from data on $\lg \gamma_0^{\mathrm{osn}}$ and $\lg \gamma_0^{\mathrm{el}}$ according to the equation $\lg \gamma_{0\mathrm{H}^+} = 2 \lg \gamma_0^{\mathrm{osn}} + \lg \gamma_0^{\mathrm{el}}$.

The data obtained by both methods agree comparatively well. The activity coefficients of the remaining ions were calculated as follows: $\lg \gamma_0$ of the halide ions was found from data on the value ΔA_x of these ions and $\lg \gamma_{0\pm}$, obtained from the equation

$$\lg \gamma_{0\pm} = \frac{\Sigma A_{x\,\mathrm{H_2O}} - \Sigma A_{xM}}{2.3 \nu RT},$$

and from the adopted values of $\lg \gamma_{0\mathrm{H}^+}$. $\lg \gamma_0$ of individual cations was calculated from data on ΔA_x and $\Delta \Sigma A_x$, obtained from values of emf, solubility, and $\lg \gamma_{0\pm}$ of halide ions. Summary Table 2 gives the averaged values of $\lg \gamma_0$ for individual ions in all the solvents listed.

Table 2

Activity coefficients of individual ions

Ions	NH_3	N_2H_4	CH_3OH	C_2H_5OH	n-C_4H_9OH	n-$C_5H_{11}OH$	CH_3COCH_3	CH_3CN	$HCOOH$	H_2O
H^+	−15.8	−13.2	3.1	3.9	4.2	4.2	3.3	5.5	10.0	0.0
Cl^-	4.8	0.7	1.0	1.2	2.0	3.0	3.3	8.0	−3.3	0.0
Br^-	3.7	1.4	1.0	1.2	0.7	3.0	3.3	5.0	−1.3	0.0
I^-	0.6	0.7	0.0	0.8	1.4	1.1	2.6	2.3	−0.9	0.0
Li^+	−2.9	2.6	1.6	2.9	1.8	–	–	1.8	2.4	0.0
Na^+	−1.8	1.4	1.8	4.2	4.0	6.0	10.3	2.5	1.8	0.0
K^+	0.0	1.4	2.0	4.0	6.2	5.5	6.6	1.4	3.0	0.0
Rb^+	1.0	1.8	2.8	4.6	9.0	5.5	7.7	1.6	1.9	0.0
Cs^+	0.0	–	2.7	3.8	4.4	4.4	4.4	1.1	1.4	0.0
Ag^+	−15.6	−13.2	3.5	3.7	2.5	2.5	–	−3.0	−0.7	0.0
Ca^{++}	5.6	6.0						7.8	5.2	0.0
Zn^{++}	−13.8	−6.0	5.4	7.7	–	–	–	7.7	7.2	0.0
Cd^{++}	−10.9	−6.8	5.0	7.6	–	–	–	6.2	5.6	0.0

These data show still more clearly the change in energy on passing from solvent to solvent, i.e., the resolvation energies. In the series water—alcohols the values of $\lg \gamma_0$ increase linearly with decreasing dielectric constant, to a greater extent for cations and to a lesser extent for anions. With increasing principal quantum number n, $\lg \gamma_0$ decreases in all cases. In basic solvents, $\lg \gamma_0$ for anions is greater than for cations, while $\lg \gamma_0$ of cations with small n has a negative value, i.e. $A_{xM} > A_{x\,\mathrm{H_2O}}$. In acidic solvents the opposite relations occur: anions have negative values of $\lg \gamma_0$. Acetone is characterized by large positive values of $\lg \gamma_0$ for cations, and acetonitrile for anions.

Thus, on passing from solvent to solvent, the ratio in the solvation energy of cations and anions changes. As a rule, solvents with a high affinity for the proton (ammonia, hydrazine) are cation-active— “cationophilic,” whereas solvents with a low affinity for the proton are anion-active— “anionophilic.” An intermediate position is occupied by acetonitrile, a cation-active solvent but one with low affinity for the proton, and also by acetone, which, despite its comparatively high affinity for the proton, is anionophilic.

The data obtained on the energies of solvation and resolvation of individual ions in various solvents make it possible to solve a number of important problems: to create a unified scale of potentials and a unified scale of acidity, and to determine the values of boundary potentials of nonaqueous solutions. In addition, they, like the values of total energies and mean zero activity coefficients, make it possible to estimate changes in the thermodynamic properties of electrolytes: solubility, forces, e.m.f. of cells with and without transference, and other properties.

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Received
24 XII 1961

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