THE ENERGY OF SOLVATION AND RESOLVATION (VALUES OF log γ_0) FOR INDIVIDUAL IONS IN NONAQUEOUS SOLUTIONS

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On the basis of the similarity in the energies of solvation of isoelectronic cations and anions and their further approach with increase in the principal quantum number n of the vacant orbitals [1], we have developed a new method for dividing the total energies of solvation into the energies of the individual ions [2]. This method has been used to determine the energies of solvation in water, methanol, ethanol, butanol, isoamyl alcohol, ammonia, hydrazine, acetonitrile, acetone, and formic acid [2, 3].

TABLE 1. Energy of Solvation 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_3COOH_3	CH_3CN	HCOOH
	Dielectric constants (dc)									
	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
I^-	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

The initial over-all energies were obtained as follows:

1) For water, ethanol, methanol, and ammonia they were obtained almost exclusively from the emf of cells without transfer (over-all energies) and with transfer (energy differences). These are the most reliable data since they are based only on normal potentials and hence relate to the state of the ions at infinite dilution.

2) For hydrazine, acetonitrile, and formic acid they were obtained from the emf of cells with transfer (differences) and from solubility data (energy sums). Although in these media, which have comparatively high dielectric constants, only ionic solubility takes place, these data are nevertheless less reliable than the previous data.

3) For butanol, isoamyl alcohol, and acetone the data were obtained almost exclusively from the solubility. Data on the emf of a cell reversible with respect to HCl ions were used only to find the energy of the H^+ ion. These data are less reliable, both as a result of the restricted character of the initial data and also in connection with the fact that in these media, which have comparatively low dielectric constants, association of the ions takes place, leading to an increase in the solubility compared with the purely ionic solubility and to an increase in the over-all energies. Nevertheless, we decided to use these data since they characterize the relationship between the solvation energy and the properties of the solvent.

Table 1 compares the energies of solvation of the individual ions, obtained for all the above solvents from the over-all energies found by extrapolation to $1/n^2 \to 0$. The solvents are arranged in Table 1 in decreasing order of the

energy of solvation of protons: From 278 kcal/g-ion for ammonia to 243 for formic acid, i.e., by 35.0 kcal/g-ion. The magnitude of the solvation energy of the proton is independent of the dielectric constant and depends only on the chemical nature of the solvent. The solvents can be divided into four groups depending on the nature of the solvation energy of ions:

1. Water and alcohols. In this group of hydroxyl-containing leveling solvents, the solvation energy of both cations and anions in general decreases with decrease in the dielectric constants (dc). The decrease in the solvation energy of anions is less, however, than that of cations. In the case of anions, the energy decreases to isoamyl alcohol by 3-4 kcal/mole and in the case of cations by 7-8 kcal/mole. At the same time the change in the energy for both cations and anions decreases with increase in the radius of the ions, or in the principal quantum number n of the vacant orbitals. Unlike the case of other cations the solvation energy of the proton decreases considerably on going from water to methanol and then remains almost unchanged. The solvation energy for divalent ions is much lower.

2. The characteristic features of basic solvents are: 1) A marked increase in the solvation energy of protons compared with that for water—by 20-25 kcal/mole. Despite the lower dielectric constant, the solvation energy of ammonia is greater than that for hydrazine. Unlike the case of alcohols, in the case of basic solvents the ratio of the solvation energy of cations to the solvation energy of anions increases with decrease in the dc. The energy of solvation of certain cations in ammonia is even higher than that in water. A characteristic feature of nitrogen-containing solvents is their high affinity for ions which do not have the electronic structure of an inert gas, such as silver, zinc, and cadmium; this is due to the tendency of these ions to undergo complex formation.

3. In acidic solvents which have a low affinity for protons, the change in the solvation energies shows the opposite relationships. Thus in formic acid, which has a low affinity for protons ($A_{XH^+} = 243.0$) there is a marked decrease in the solvation energy of cations and a simultaneous marked increase in the solvation energy of anions, in spite of the comparatively high dc = 57. As a result of this, 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 due to the formation of hydrogen bonds between the solvated ion and solvent molecules.

4. A unique position is occupied by the differentiating solvents, acetone and acetonitrile, in which the ratio of the strengths of the electrolytes changes considerably. It follows from the magnitude of the energy of solvation of the proton that acetone is a more basic solvent than acetonitrile. The basic strength of both solvents, however, does not differ considerably from that of the higher alcohols. Their unique feature is the low energy of solvation of all other ions. At the same time, in the case of acetonitrile there is a marked decrease in the solvation energy of anions (by almost 10 kcal/mole for Cl^-) and a comparatively low decrease in the energy of solvation of cations. In this case, in spite of the low affinity for protons, acetonitrile behaves as a basic solvent. In the case of acetone on the other hand, there is a sharp decrease in the energy of solvation of cations (14 kcal/g-ion for sodium and 9 kcal per g-ion for potassium) and a comparatively low decrease in the energy of solvation of anions. In this sense acetone, which has a high affinity for protons, behaves as an acidic solvent.

It should be noted that in all the solvents, with increase in the principal quantum number characterizing the vacant orbitals of the ions, the energies of solvation of the cations and anions decrease and approach one another. The change in the solvation energy of ions with change in the solvent is least for cesium ions and iodide ions.

Data on the values of the solvation energies of individual ions in different solvents were used to calculate the values of log γ_0 for the individual ions [4]. The calculation was carried out from the equation

$$\lg \gamma_0 = \frac{A_{x\,H_2O} - A_{x\,M}}{2{,}3\nu RT} \cdot$$

Since the values of A_X were determined with an accuracy of 0.5 kcal/g-ion, the errors in the determination of log γ_0 are comparatively high. We therefore took account of other possibilities in the determination of this quantity. The value of log γ_{OH^+} was calculated from data on log γ_0^{bas}, and log γ_0^{el} was calculated from the equation log γ_{OH^+} = = 2 log γ_0^{bas} + log γ_0^{el}.

The data obtained by the two methods show comparatively good agreement. The activity coefficients of the other ions were calculated as follows: log γ_0 for the halide ions was found from data on the value of ΔA_X for these ions and log $\gamma_{0\pm}$, obtained from the equation

$$\lg \gamma_{0\pm} = \frac{\Sigma A_{x\,H_2O} - \Sigma A_{x\,M}}{2{,}3\nu RT}$$

and the accepted values of log γ_{OH^+}. The value of log γ_0 for the individual cations was calaculated from data on ΔA_X and $\Delta\Sigma A_X$, obtained from the emf values, the solubility, and log $\gamma_{0\pm}$ for halide ions. Table 2 summarizes the averaged values of log γ_0 for the individual ions in all the above solvents.

TABLE 2. Activity Coefficients of the Individual Ions

Ions	NH_3	N_2H_4	CH_3OH	C_2H_5OH	n-C_4H_9OH	i-$C_5H_{11}OH$	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	0,1
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 even more clearly the energy change on going from one solvent to another, i.e., the resolvation energies. In the water—alcohol series, the values of log γ_0 increase linearly with decrease in the dc, the increase being greater for cations and less for anions. In all cases log γ_0 decreases with increase in the principal quantum number n. In basic solvents, log γ_0 for anions is greater than that for cations and log γ_0 for cations with low values of n has a negative value, i.e., $A_{XM} > A_{XH_2O}$. In acidic solvents the opposite relationship is observed: Anions have negative values of log γ_0. Acetone is characterized by high positive values of log γ_0 for cations and acetonitrile by high values for anions.

Thus on going from one solvent to another there is a change in the relationship between the energies of solvation of cations and anions. As a rule, solvents with a high affinity for protons (ammonia and hydrazine) are cation-active, or "cationophilic" and solvents with a low affinity for protons are anion-active, or "anionophilic". An intermediate position is occupied by acetonitrile, which is a cation-active solvent but has a low affinity for protons, and also by acetone which is anionophilic in spite of its comparatively high affinity for protons.

The data obtained for the energies of solvation and resolvation of individual ions in different solvents makes it possible to solve a number of important problems: To create a single scale of potentials and a single scale of acidity and to determine the magnitude of the boundary potentials of nonaqueous solutions. Moreover, like the values of the total energies and mean zero activity coefficients, they make it possible to estimate the changes in the thermodynamic properties of electrolytes: Solubilities, strengths, the emf of cells with and without transfer, and other properties.

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