THE SOLVATION ENERGY OF IONS IN FORMIC ACID, HYDRAZINE, ACETONITRILE, n-BUTYL AND iso-AMYL ALCOHOLS AND ACETONE

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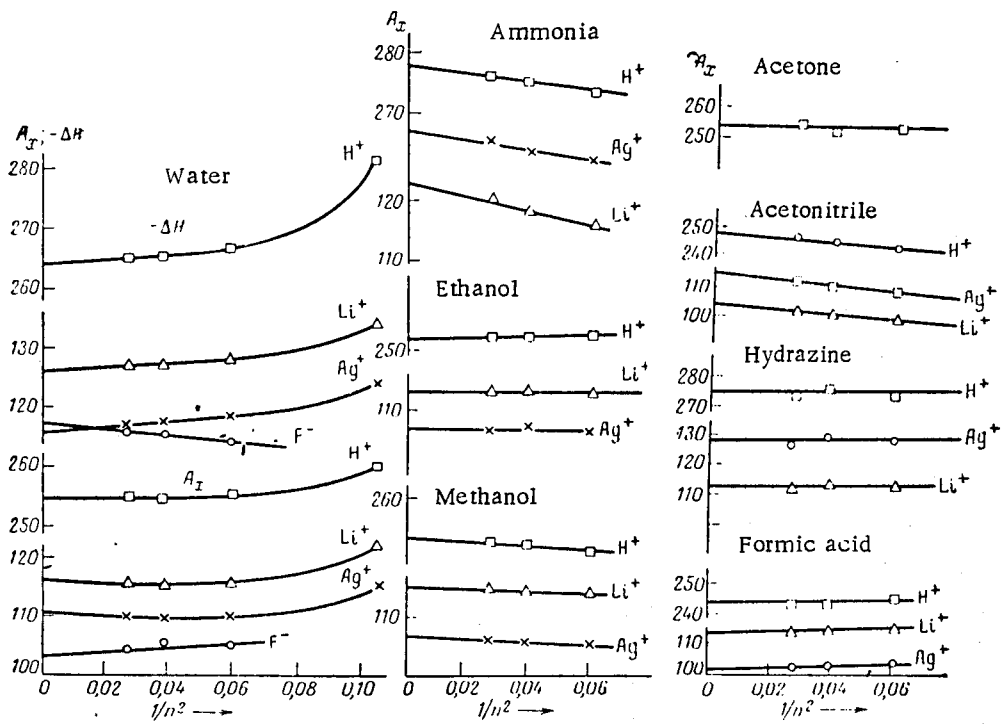
We have recently presented a new method of dividing the total energy of solvation [1] into the energy of solvation of the separate ions, according to which the solvation energy of the individual ion is found by extrapolation of the quantity $A_{X\,ion} + \frac{A_{XX^{-*}} - A_{XMe^+}}{2}$ $(n = 3, 4, 5, 6)$ from $\frac{1}{n^2}$ to $\frac{1}{n^2} = 0$.



Dependence of the solvation energy of individual ions on the value of $1/n^2$ in various solvents.

The present communication is devoted to an application of this method to the determination of A_X of ions in a number of nonaqueous solvents for which the solvation energy, starting from the emf, has not been obtained (apart from formic acid [2]). For hydrazine and acetonitrile, and strictly speaking for formic acid itself, the only data known are those which concern the emf of cells with transport [3], from which it is possible to calculate the solvation energy.

In connection with the absence of data concerning the emf of cells without transport in these and other solvents, we have calculated data about the total solvation energy, basing these upon the values of the mean zero activity coefficients of the salts [$\gamma_{0\pm}$ (primary salt effect [4])] using their connection with the energies of hydration and solvation:

*In this article, X^- is used to represent a halide ion [Publisher's note].

$$2{,}3\nu RT \lg \gamma_{0\pm} = \sum A_{x\mathrm{H_2O}} - \sum A_{x\mathrm{Me}^+}. \quad (1)$$

TABLE 1. Comparison of the Values of ΣA_X From emf Data and From the Solubility in Methanol

Salt	From emf	From solubility [6]	Salt	From emf	From solubility [6]
NaCl	162,0	164,2	RbI⁻	130,2	129,5
KCl	146,5	147,4	CsCl	132,5	131,4
KBr	142,3	143,1	CsBr	127,6	127,1
RbCl	142,6	141,9	CsI⁻	119,7	120,0
RbBr	138,0	137,1			

TABLE 2. Data for Extrapolation

Solvent	n	$1/n^2$	Ions (difference)	A	B	C
HCOOH	4	0,0625	K+ Cl⁻	246,0	117,0	114,3
	5	0,04	Rb+ Br⁻	243,6	114,2	111,5
	6	0,028	Cs+ I⁻	243,4	113,9	111,4
N_2H_4		0,00		243,2	113,5	111,0
	4	0,0625	K+ Cl⁻	274,0	112,7	128,0
	5	0,04	Rb+ Br⁻	276,1	114,7	129,7
	6	0,028	Cs+ I⁻	274,0	112,4	127,6
CH_3CN		0,00		274,7	113,3	128,4
	4	0,0625	K+ Cl⁻	243,5	109,6	109,6
	5	0,04	Rb+ Br⁻	244,9	110,5	111,0
	6	0,0528	Cs+ I⁻	246,7	112,5	112,8
C_4H_9OH		0,00		248,5	114,5	115,5
	4	0,0625	K+ Cl⁻	251,8	—	—
	5	0,04	Rb+ Br⁻	251,4	—	—
	6	0,028	Cs+ I⁻	252,1	—	—
$C_5H_{11}OH$ *		0,0		251,7		
	4	0,625	K+ Cl⁻	252,8	—	—
	$\lg \gamma_{0H^+}$ from			252,0		
CH_3COCH_3	Mean			252,4		
	4	0,0615	K+ Cl⁻	253,6		
	5	0,04	Rb+ Br⁻	252,3		
	6	0,073	Cs+ I⁻	264,4		
	$\lg \gamma_{0H^+}$ from	0,0		254,0 250,0		
				252,0		

Notes.

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

$$B = A_{x\mathrm{Li}^+} + \left(\frac{A_x X^- - A_{x\mathrm{Me}^+}}{2}\right)_{n=\mathrm{const}};$$

$$C = A_{x\mathrm{Ag}^+} + \left(\frac{A_x X^- - A_{x\mathrm{Me}^+}}{2}\right)_{n=\mathrm{const}}.$$

* In connection with the absence of data for other values of n, the magnitude of A_{xH^+} in $C_5H_{11}OH$ was calculated as a mean value from A_{xH^+} with n = 4, and A_{xH^+}, obtained from log γ_{OH^+} from the equation $\log \gamma_{OH^+} = 2 \log \gamma_0^{osn} + \log \gamma_0^{el}$ (4)

The value of log $\gamma_{0\pm}$ was calculated from data on the solubility, from the equation:

$$\lg \gamma_{0\pm} = \lg \frac{a_{\mathrm{H_2O}}}{a_{\mathrm{Me}}} = \lg \frac{m_{\mathrm{H_2O}}}{m_{\mathrm{Me}}} + \lg \frac{\gamma^*_{\pm \mathrm{H_2O}}}{\gamma^*_{\pm \mathrm{Me}}}. \quad (2)$$

In investigations carried out together with V. F. Chernyi [5] we have shown that the ratio of the mean concentration activity coefficient, $\gamma^*_\pm$ of saturated solutions is close to unity,

$$\frac{\gamma^*_{\pm \mathrm{H_2O}}}{\gamma^*_{\pm \mathrm{Me}}} \approx 1,$$

and therefore,

$$\lg \gamma_{0\pm} \approx \lg \frac{m_{\mathrm{H_2O}}}{m_{\mathrm{Me}}}. \quad (3)$$

Calculation of the total energy was carried out using Eq. (1). For this purpose we used the value of ΣA_{xH_2O} in water, calculated by ourselves earlier from the emf values [1].

We use this method of calculation only in those cases for which one and the same solid phase is found in equilibrium with aqueous and nonaqueous solutions, that is, when the salt does not form crystalline solvates. If this condition is satisfied, ΣA_X, calculated from the emf and from the conductivity gives component values. As an example, we give the values of ΣA_X in methanol, calculated from the emf, and from the solubility as given in the data of Strehlow [6]. These data do not diverge by more than 1 kcal/g-ion. In connection with what has been said above, it is not possible by this means to calculate the energy for lithium salts, sodium bromide, sodium iodide, and some other salts.

Data concerning the energy of solvation of the ions of hydrogen halides have been calculated from the total energy of solvation of the ions of the alkali halides which do not form crystalline solvates, and the difference in the solvation energy, obtained from the emf: $\Sigma A_{xHX} = \Sigma A_{xMeX} + (A_{xH^+} - A_{xMe^+})$.

From the data for the hydrogen halides and the magnitude of the energy calculated from the emf, it is possible

to obtain the total solvation energy of any salts, including those cases for which it is not possible to obtain these values directly from the solubility.

In the calculations for acetonitrile and formic acid we made use of data on solubility given by Strehlow [6], while for hydrazine we use the data collected in the book by Odrin and Odt [7]. To obtain the energy difference in these solvents we made use of data on the emf of cells with transport collected by V. Pleskod [3].

From the data on solubility contained in the handbook by Seidell [8] we have also calculated the total chemical energy of solvation of ions in n-butanol, in iso-amyl alcohol, and in acetone. For these solvents data have not been obtained using cells with transport, and the only known values relate to the emf of the cells [9] $Pt(H_2)/HCl/AgCl$, Ag, from which the values of ΣA_X have been calculated for the ions from hydrochloric acid. In addition, from the known emf of cells which are reversible with respect to potassium iodide in acetone [10] and to sodium iodide [11] in n-butanol, we have calculated values of ΣA_X for these salts, which are needed for further calculations. The values of ΣA_{XHX} in these solvents were obtained from data for ΣA_{XHCl}, ΣA_{XMeX} and ΣA_{XMeCl}. The results obtained in this way for these solvents, are certainly less reliable than those for solvents for which the emf of cells with transport are known, not only because of the limited nature of the initial data, but also because in these solvents, which have low dielectric constants, the salts may be dissolved both in the form of ions and also in the form of ionic associations, which will lead to an increase in the solubility, and so to increased total solvation energy.

TABLE 3. Solvation Energy of Ions (kcal/g-ion)

Ion	Solvent and dielectric constant				
	HCOOH (57,0)	N_2H_4 (51,7)	CH_3CN (36,7)	$C_5H_{11}OH$ (15,8)	CH_3COCH_3 (19,0)
H+	243,0	274,5	249,0	252,0	252,0
Cl−	79,0	73,5	64,0	70,5	70,0
Br−	71,0	71,0	62,5	64,5	68,0
I−	61,5	59,5	57,5	59,0	57,0
Li+	113,5	113,5	114,5	115,5	115,0
Na+	91,5	92,0	90,5	85,0	80,0
K+	73,0	75,0	75,0	69,5	68,0
Rb+	70,0	70,0	70,5	65,0	62,0
Cs+	61,0	61,5	61,5	57,0	57,0
Ca++	358,0	363,0	350,0	—	—
Ag+	111,0	128,5	115,0	—	—
Zn++	474,0	503,5	472,0	—	—
Cd++	413,0	446,5	412,0	—	—

Starting from these data, the energy of solvation of individual ions has been calculated by the method of extrapolation to $1/n^2 \to 0$. From the data given in Table 2 and the figure, it follows that the extrapolation in these solvents is no less reliable than that for water, ammonia, methanol and ethanol. As a rule, the extrapolated values differ amongst themselves, and from the limiting values, by no more than 1-2 kcal/g-ion. From the values found for A_{XH^+}, A_{XLi^+}, A_{XAg^+}, we have found the values of A_X for the halogen ions, which have also been used as the basis of the estimation of the solvation energy of the remaining ions [1] (see Table 3).

By means of extrapolation to $1/r = 0$, calculations have earlier been made of the energy only in the case of formic acid. Comparison of the data now obtained with those available formerly shows that the solvation energy of cations, including the hydrogen ion, is about 3.0 kcal/g-ion smaller. A large difference is observed in the case of the solvation energy of sodium ions (91.5 instead of 99.5). This is not wholly due to a difference in the extrapolation methods, but is also due to the use of new data on the values of ΣA_X, calculated from the solubility.

The solvation energy for the remaining solvents was calculated first. The solvation energies in hydrazine are similar to those in ammonia. In hydrazine, the energy of solvation of the proton is high: 274.5 kcal/g-ion (compared with 278.0 in ammonia); the solvation energy of the remaining cations is somewhat lower than in the ammonia and water. The solvation energy of ions is higher than in ammonia and close to that in water, which appears to be due to the high dielectric constant of hydrazine (51.7).

The solvation energy of cations and anions in n-butanol and iso-amyl alcohol is lower than in methanol and ethanol. The solvation energy of the proton is practically unchanged in moving from ethanol to n-butanol and iso-amyl alcohol. In the main, the effect of all the alcohols is the same. Acetonitrile and acteone have a special place: Both solvents have high and practically identical affinities with the proton: 252 kcal/g-ion for acetone, and 249 kcal/g-ion for acetonitrile. Nevertheless, in spite of the comparatively high affinity for the proton, the solvation energy of the remaining ions is appreciably lower than for the other solvents with the same or even lower affinity for the proton.

The energy of solvation of cations in acetone, compared with that in water, is lower by ca. 10-15 kcal/g-ion, while the solvation energy of anions is lower by 3-4 kcal/g-ion.

In contrast with acetone, the solvation energy of anions in acetonitrile is much lower (by 5-10 kcal/g-ion) and is also somewhat lower for cations (by 2-3 kcal/g-ion). In consequence of this, in these two solvents, the ratio

in the solvation energy of cations and ions is greatly altered in comparison with hydroxyl-compounds and basic solvents, which is presumably to a considerable extent due to their differentiating effect.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
