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Abstract

Full Text

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

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Recently we proposed a new method for separating the total solvation energy [(1)] into the solvation energy of individual ions, according to which the solvation energy of an individual ion is found by extrapolating the dependence of the quantities

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

from $\frac{1}{n^2}$ to $\frac{1}{n^2} = 0$.

The present communication is devoted to the application of this method for finding A_x of ions in a series of nonaqueous solvents for which solvation energies had not previously been established from e.m.f. data (with the exception of formic acid [(2)]). For hydrazine and acetonitrile, and for formic acid itself, only data on the e.m.f. of cells with transference [(3)] are known, from which differences in solvation energies can be calculated.

In connection with the absence of data on the e.m.f. of cells without transference in these and other solvents, we calculated data on the total solvation energies, based on the values of the mean zero activity coefficients of salts $\gamma_{0\pm}$ (the primary medium effect [(4)]), using their relation to the hydration and solvation energies

$$2.3\nu RT \lg \gamma_{0\pm} = \sum A_{x\mathrm{H_2O}} - \sum A_{x\mathrm{Me}^+}. \qquad (1)$$

The quantities $\lg \gamma_{0\pm}$ were calculated from solubility data by the equation

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

In work carried out jointly with V. S. Chernyi [(5)], we showed that the ratio of the mean concentration activity coefficients $\gamma^*_\pm$ of saturated solutions is close to unity,

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

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

and, consequently,

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

The calculation of the total energies was carried out by equation (1). In doing so we used the values of $\sum A_{x\mathrm{H_2O}}$ in water, calculated by us earlier from e.m.f. values [(1)].

This method of calculation is applicable only in those cases where the same solid phase is in equilibrium with aqueous and nonaqueous solutions, i.e., when the salt does not form crystalline solvates. If this condition is met, the $\sum A_x$ values calculated from e.m.f. data and from solubility agree. As an example we cite the values of $\sum A_x$ in methanol, calculated from e.m.f. data and from solubility according to Strelov' s data [(6)]. These data differ by no more than 1 kcal/g-ion. In connection with the above, this

method cannot be used to calculate the energy for lithium salts, sodium bromide and iodide, and some other salts.

Data on the solvation energies of hydrohalic-acid ions were calculated from the total solvation energy of ions of alkali-halide salts that do not form crystal solvates, and from the difference in solvation energies calculated from e.m.f.:

$$\sum A_{x\mathrm{HG}} = \sum A_{x\mathrm{MeG}} + \left(A_{x\mathrm{H}^+} - A_{x\mathrm{Me}^+}\right).$$

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

From the data for the hydrohalides and the values of the energy differences calculated from e.m.f., the total solvation energies of any salts can be calculated, including those for which they cannot be determined directly from solubility.

Table 1

Comparison of the values $\sum A_x$ from e.m.f. data and from solubility in methanol

Salt	From e.m.f.	From solubility [6]	Salt	From e.m.f.	From solubility [6]
NaCl	162.0	164.2	RbJ	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	CsJ	119.7	120.0
RbBr	138.0	137.1			

In the calculations for acetonitrile and formic acid we used the solubility data of Shtrelov [6], and for hydrazine, the data compiled in the book by Audrieth and Ogg [7]. To calculate the energy differences in these solvents we used the data on e.m.f. of transfer chains collected by V. Pleskov [3].

From the solubility data given in Seidell' s handbook [8], we also calculated the total chemical solvation energies of ions in n-butanol, isoamyl alcohol, and acetone. For these solvents no data are known on cells with transference, and only the values of the e.m.f. of the cells [9] $Pt(H_2)$ HCl/AgCl, Ag, from which $\sum A_x$ of HCl ions were calculated, are known. In addition, from known e.m.f. data for cells reversible to KJ in acetone [10] and NaJ [11] in n-butanol, the values $\sum A_x$ of these salts, needed for further calculations, were computed. The values $\sum A_{x\mathrm{HI}}$ in these solvents were obtained from data on $\sum A_{x\mathrm{HCl}}$, $\sum A_{x\mathrm{MeI}}$, and $\sum A_{x\mathrm{MeCl}}$. The results obtained in this way for these solvents are, of course, less reliable than for solvents for which the e.m.f. of cells with transference are known, not only because of the limited initial data, but also because in these solvents with low dielectric constants salts can dissolve not only in the form of ions, but also in the form of ionic associates, which leads to increased solubility and to overestimated total solvation energies.

On the basis of these data, the solvation energies of individual ions were calculated by extrapolation to $1/n^2 \to 0$. From the data of Table 2 and Fig. 1 it follows that extrapolation in these solvents is no less reliable than for water, ammonia, methanol, and ethanol. As a rule, the extrapolated quantities differ from one another and from the limiting value by no more than 1–2 kcal/g-ion. From the values found for $A_{x\mathrm{H}+}$, $A_{x\mathrm{Li}+}$, and $A_{x\mathrm{Ag}+}$, we found the values A_x of halide ions, which were used as the basis for calculating the energies of the remaining ions [1] (see Table 3).

Table 2

Data for extrapolations

Solvent	n	$1/n^2$	Ions (difference)	A	B	C
HCOOH	4	0.0625	K^+ Cl^-	246.0	117.0	114.3
HCOOH	5	0.04	Rb^+ Br^-	243.6	114.2	111.5
HCOOH	6	0.028	Cs^+ J^-	243.4	113.9	111.4
N_2H_4		0.00		243.2	113.5	111.0
N_2H_4	4	0.0625	K^+ Cl^-	274.0	112.7	128.0
N_2H_4	5	0.04	Rb^+ Br^-	276.1	114.7	129.7
N_2H_4	6	0.028	Cs^+ J^-	274.0	112.4	127.6
CH_3CN		0.00		274.7	113.3	128.4
CH_3CN	4	0.0625	K^+ Cl^-	243.5	109.0	109.6
CH_3CN	5	0.04	Rb^+ Br^-	244.9	110.5	111.0
CH_3CN	6	0.0528	Cs^+ J^-	246.7	112.5	112.8
C_4H_9OH		0.00		248.5	114.5	115.5
C_4H_9OH	4	0.0625	K^+ Cl^-	251.8	–	–
C_4H_9OH	5	0.04	Rb^+ Br^-	251.4	–	–
C_4H_9OH	6	0.028	Cs^+ J^-	252.1	–	–
$C_5H_{11}OH$ *		0.0		251.7		
$C_5H_{11}OH$ *	4	0.625	K^+ Cl^-	252.8	–	–
from $\lg \gamma_{0H+}$				252.0		
CH_3COCH_3	Average			252.4		
CH_3COCH_3	4	0.0615	K^+ Cl^-	253.6		
CH_3COCH_3	5	0.04	Rb^+ Br^-	252.3		
CH_3COCH_3	6	0.073	Cs^+ J^-	264.4		
from $\lg \gamma_{0H+}$		0.0		254.0		
from $\lg \gamma_{0H+}$				250.0		
				252.0		

Note.

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

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

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

* Owing to the absence of data for other n, the value $A_{x\mathrm{H}+}$ in $C_5H_{11}OH$ was calculated as the mean value from $A_{x\mathrm{H}+}$ at $n = 4$ and $A_{x\mathrm{H}+}$, calculated from $\lg \gamma_{0\mathrm{H}+}$ by the equation

$$\lg \gamma_{0\mathrm{H}+} = 2 \lg \gamma_0^{\mathrm{osn}} + \lg \gamma_0^{\mathrm{el}}. \quad (4)$$

Earlier, by extrapolation to $1/r = 0$, only the energies for formic acid had been calculated. Comparison of the data now obtained with those obtained earlier shows that the solvation energy of cations, including hydrogen ions, is approximately 3.0 kcal/g-ion lower. The large differen-

is observed in the solvation energy of the ion Na^+ (91.5 instead of 99.5). This is due not so much to differences in the extrapolation methods as to the use of new data on $\sum A_x$, calculated from solubility.

Table 3

Solvation energies of ions (kcal/g-ion)

Ion	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
J^-	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	–	–

Solvation energies for the remaining solvents have been calculated for the first time. The solvation energies in hydrazine are similar to those in ammonia. In hydrazine the solvation energy of the proton is high: 274.5 kcal/g-ion (in ammonia, 278.0); the solvation energy of the other cations is somewhat lower than in ammonia and water. The solvation energies of anions are higher than in ammonia and close to those in water, which is a consequence of the high dielectric constant of hydrazine (51.7).

The solvation energies of cations and anions in *n*-butanol and isoamyl alcohol decrease in comparison with methanol and ethanol. The solvation energy of the proton practically does not change on going from ethanol to *n*-butyl and isoamyl alcohols. In general, the influence of all alcohols is similar. A special place is occupied by acetonitrile and acetone: both solvents have a close and comparatively high affinity for the proton: 252 kcal/g-ion for acetone and 249 kcal/g-ion for acetonitrile. However, despite the comparatively high affinity for the proton, the solvation energy of the other ions is considerably lower than in other solvents with the same or even lower affinity for the proton.

Compared with water, in acetone the solvation energy of cations is lower by 10–15 kcal/g-ion, and the solvation energy of anions is lower by only 3–4 kcal/g-ion.

In contrast to acetone, in acetonitrile the solvation energy of anions is greatly reduced (by 5–10 kcal/g-ion) and that of cations is reduced only slightly (by 2–3 kcal/g-ion). As a result, in both solvents the ratio between the solvation energies of cations and anions changes greatly in comparison with hydroxyl-containing and basic solvents, which probably explains to a significant extent their differentiating action.

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REFERENCES CITED

1. N. A. Izmailov, DAN, **149**, No. 4 (1963).
2. N. A. Izmailov, DAN, **126**, 1033 (1959); ZhFKh, **34**, 2414 (1960).
3. V. A. Pleskov, *Usp. khim.*, **16**, 254 (1947).
4. N. A. Izmailov, *Electrochemistry of Solutions*, Kharkov, 1959, p. 353.
5. N. A. Izmailov, V. S. Chernyi, ZhFKh, **34**, 319 (1960).
6. T. Pavlopoulos, H. Strehlow, *Zs. phys. Chem.*, **202**, 474 (1954).

7. L. Odrin, B. Odt, *Chemistry of Hydrazine*, IL, 1954.

8. A. Seidell, *Solubilities of Inorganic and Organic Substances*, N. Y., 1952.

9. N. A. Izmailov, V. V. Aleksandrov, E. F. Ivanova, *Tr. khim. fak. i inst. khim. KhGU*, **18**, 5 (1957).

10. V. V. Aleksandrov, Yu. A. Ershov, DAN, **132**, No. 6, 1327 (1960).

11. N. A. Izmailov, E. F. Ivanova, ZhFKh, **29**, 1614 (1955).

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