Reports of the Academy of Sciences of the USSR

N. A. IZMAILOV

1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 150, No. 1

PHYSICAL CHEMISTRY

N. A. IZMAILOV

PROTON AFFINITY AND THE ACIDITY AND BASICITY OF NONAQUEOUS SOLVENTS

(Presented by Academician M. I. Kabachnik on 24 XI 1961)

The solvation energies of protons, determined by the method of extrapolation to $\frac{1}{n^2} = 0$ ((1), Table 1), are in all solvents considerably higher than the solvation energies of the other monovalent cations. For example, in water the hydration energy of the proton is 256.5 kcal/g-ion, whereas the hydration energy of the lithium ion is only 117 kcal/g-ion.

The high solvation energy of protons is a consequence of the fact that the proton attaches to the first solvent molecule by means of a covalent bond, forming a lyonium ion MH^+. Further solvation of the lyonium ion, in mechanism and in energy, is similar to the solvation of the other cations. The primary solvation of the lyonium ion occurs through the formation of molecular orbitals, with the lyonium ion serving as an acceptor of lone electron pairs supplied by the central atoms of the solvent molecules (2). Lyonium ions solvated by the primary shell interact with solvent molecules through electrostatic forces, forming a secondary solvation shell. In connection with the special mechanism of proton solvation, their solvation energy varies from solvent to solvent to the greatest extent, namely, from 278.0 kcal/g-ion in ammonia to 243.0 kcal/g-ion in formic acid (3). According to the magnitude of the proton affinity in the liquid state (solvation energy), the solvents are arranged by basicity in the following order:

$$NH_3 > N_2H_4 > H_2O > CH_3OH > C_2H_5OH > n\text{-}C_4H_9OH =$$

$$= i\text{-}C_5H_{11}OH \geq CH_3COOH_3 > CH_3CN > HCOOH.$$

Data on the ionic product of the medium make it possible to find the energy of affinity of solvated lyate ions for protons in solutions. Indeed,

$$\mathrm{M + H^+ + solv. = MH_c^+ + A_{XH^+}}$$

$$\frac{\mathrm{MH_c^+ + (M-H)_c^- = 2M + solv. + A_{neutr}}}{\mathrm{H^+ + (M-H)_c^- \rightleftarrows M + solv. + A_{XH^+} + A_{neutr}}}\,.$$

The value A_{neutr} is equal, with the opposite sign, to the change in the isobaric potential of the neutralization reaction, $A_{\text{neutr}} = -\Delta Z_{\text{neutr}}$, and can be calculated from the ionic product of the solvent: $A_{\text{neutr}} = -RT \ln K$.

Table 1 gives the values of A_{neutr} and the values of the proton affinity of lyate ions $(\mathrm{M-H})_c^-$. If the magnitudes of proton solvation energy characterize the proton-acceptor—basic—properties of solvents, then the energies of affinity for protons of solvated lyate ions characterize the proton-donor properties of solvents, i.e., their acidity. Although, as a rule, an increase in the basicity of a solvent is accompanied by a decrease in acidity (an increase in the affinity of the ions $(\mathrm{M-H})_c^-$), these quantities change nonproportionally. Thus, the basicity of ammonia

greater than that of water by 21.5 kcal/g-ion, while its acidity is less by 45.0 kcal/g-ion; the basicity of formic acid is less than that of water by 13.5 kcal/g-ion, while its acidity is greater by 24.0 kcal/g-ion (see Table 1). Although the energies of proton solvation in hydrazine and in ammonia are close, hydrazine is nevertheless a considerably more acidic solvent than ammonia, since the affinity of its lyate ions for the proton is already 12.5 kcal/g-ion lower than that of ammonia.

Table 1

Energy of the processes accompanying proton addition in various solvents

Solvent	$A^+_{XH} = -\Delta Z_X$	$-\Delta Z = A_{MH^+} + (M-H)^-_c \uparrow\downarrow\leftarrow 2M + C$	$-\Delta Z = A_{HH^+} + (M-H)^-_c \uparrow\downarrow\leftarrow M + C$	A^+_{XMH}	$A_X(M-H)^-$	$-\Delta Z = \pi^{\tau}_{H^+\to M}\ MH^+$	π by (4)	π by (6)	π by (5)	$\pi\,\frac{\Delta^3}{H^+ + (M-H)^- \uparrow\downarrow\leftarrow M}$	Literature data (7)
NH_3	278.0	42.6	320.6	88.0	101.0	190.0	–	211.3	200.0	421.5	419.0 ÷ 380
N_2H_4	274.5	33.6	308.1	86.0	103.5	188.5	–	–	–	411.6	–
H_2O	256.5	19.0	275.5	85.0	107.5	171.5	169.0	186.6	170.0	383.0	383.0 ÷ 386.0
CH_3OH	252.5	23.0	275.5	83.0	106.0	169.5	180.0	209.0	–	381.5	–
C_2H_5OH	251.5	26.5	278.0	82.0	105.5	169.5	193.0	216.0	–	383.5	–

Solvent	$A^+_{XH} = -\Delta Z_X$	$-\Delta Z = A_{MH^+} + (M-H)^-_c \uparrow\downarrow\leftarrow 2M + C$	$-\Delta Z = A_{HH^+} + (M-H)^-_c \uparrow\downarrow\leftarrow M + C$	A^+_{XMH}	$A_X(M-H)^-$	$-\Delta Z = \pi^{\tau}_{H^+\to M} \leftrightarrow MH^+$	π by (4)	π by (6)	π by (5)	$\pi \frac{\Delta^3}{H^+ + (M-H)^- \uparrow\downarrow\leftarrow M}$	Literature data (7)
n-C_4H_9OH	251.5										
n-$C_5H_{11}OH$	252.0										
CH_3COCH_3	252.0										
CH_3CN	249.0	–	–	82.0	–	167.0	–	–	–	–	–
HCOOH	243.0	8.5	251.5	82.6	111.0	161.0	–	–	–	362.5	347.0 ÷ 382.0

Thus, a complete characterization of the acid-base properties of solvents must be based not only on quantitative data on the energies of formation of solvated lyonium ions, which characterize the basicity of solvents, but also on data on the energies of proton addition to solvated lyate ions, which characterize the acidity of solvents.

Table 1 also gives approximate data on the solvation energies of lyonium ions and lyate ions. The hydration energy of hydroxide ions was obtained on the basis of the notion that the solvation energies of isoelectronic ions are close and that they vary with the sizes of the ions (2). The hydration energy of the isoelectronic ion Na^+ is 94.0 kcal/g-ion, and the radius of the Na^+ ion, 0.95 Å, is considerably smaller than the radius of the H_3O^+ ion, 1.35 Å; on the other hand, the radius of the H_3O^+ ion is close to the radius of the K^+ ion, 1.33 Å (3), and the hydration energy of the potassium ion is 77.0 kcal/g-ion. Therefore it may be assumed that the hydration energy of the H_3O^+ ion should lie between 77 and 94 kcal/g-ion, on average 85.5 kcal/g-ion. This energy can also be estimated from the relationships in the energies and radii of the isoelectronic ions Na^+ and ammonium NH_4^+—the radius of the latter is 1.43 Å, and its energy is 75.0 kcal/g-ion. The hydration energy of the H_3O^+ ion should undoubtedly be higher than that of the NH_4^+ ion, owing to the smaller radius and the smaller number of protons in the ion. Its average value is close to the previously found 84.5 kcal/g-ion. Finally, for the hydration energy of the H_3O^+ ion we adopted 85.0 kcal/g-ion.

On the basis of the close correspondence in the change of the solvation energy of similar ions on going from one solvent to another, we assumed that the change in the solvation energy of lyonium ions is close to the change in the solvation energy of the isoelectronic ion Na^+. The energies found in this way are given in Table 1.

We found the solvation energy of lyate ions from the following considerations. According to the data of Mishchenko (^{4}) and co-workers, the solvation energy of the OH^- ion is 110 kcal/g-ion. Since our data for the isoelectronic ion F^- are 4.5 kcal less than the data of (^{4}) for this ion (107.0 and 102.5), we took A_{XOH^-} to be equal to 106.5. The solvation energy of other lyonium ions was calculated-

obtained from this value and from the change in the solvation energy of the nearest anion Cl^- with the change of solvent. From these data we calculated the affinity of lyate molecules and ions in vacuum for the proton (see Table 1).

We calculated the proton affinity of solvent molecules in vacuum as the difference between the solvation energies of protons and ly onium ions, and the proton affinity of lyate ions as the sum of the proton affinity of lyate ions in solution and their solvation energies.

Table 2

Change in proton affinity

Solvent	$\lg\gamma_0$, new values	$\lg\gamma_0$, former values	$2\lg\gamma_0$	$+\lg\gamma_0$	Literature data: Pleskov $^{(11)}$	Literature data: Grunwald $^{(12)}$	Literature data: Strehlow $^{(13)}$	Literature data: Hammett	Length of the pH_p scale	Position of the pA scale
NH_3	−15.8	−16.4	–		−16.7	–	–	–	0–32.7	15.8÷48.5
N_2H_4	−13.2	–	–		−15.5	–	–	–	0–24.7	13.2÷37.9
H_2O	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0–14.0	0÷14.0
CH_3OH	3.1	3.2	3.0		0.35	–	−0.35	0.35	0–16.9	−3.1÷13.8
C_2H_5OH	3.9	4.2	4.1		–	4.7	–	–	0–19.3	−3.9÷15.4
n-C_4H_9OH	4.2	4.7	4.7		–	–	–	–	–	–
n-$C_5H_{11}OH$	4.2	4.5	4.5		–	–	–	–	–	–
CH_3COCH_3	3.1	–	4.7		–	–	–	–	–	–
CH_3CN	5.5	–	–		4.2	–	2.4	1.9	–	–
$HCOOH$	10.0	8.6	–		8.8	–	8.0	4.7	0–6.1	−10÷−3.9

The proton affinity of water molecules in vacuum found by us is close to the value calculated by Latimer $^{(5)}$ and found experimentally by Tal' roze and Frankevich $^{(6)}$. The affinity energy of the hydroxyl ion (OH^-), the amide ion (NH_2^-) $^{(7)}$, and ammonia (5) is also close to the literature data. The energy of the $HCOO^-$ ion lies between the values available in the literature (7).

The proton affinity of alcohol molecules in vacuum is close to the affinity of water molecules and is considerably lower than the affinity values calculated by Kondrat' ev and Sokolov (8) and found by Tal' roze and Frankevich. The affinity values of the lyate ions of water and alcohols are close to one another.

The data obtained show that, just as in solution, the change in the proton affinity of molecules and lyate ions in vacuum does not proceed in parallel; in vacuum still greater differences are observed than in solutions and, consequently, the basicity and acidity of substances are different both in the liquid state and in vacuum.

The data on the solvation energy of protons given in Table 1 make it possible to find the values $\lg\gamma_{0H^+}$ of protons from equation (9)

$$\lg\gamma'_{0H^+} = \frac{A_{XH^+(H_2O)} - A_{XH^+(M)}}{2.3RT} = \frac{\Delta A_{XH^+}}{2.3RT}.$$

The values $\lg\gamma_{0H^+}$ found in this way, corrected with the aid of the values $\lg\gamma_{0H2}$ obtained from equation (9)

$$\lg\gamma_{0H^+} = 2\lg\gamma_0 \ + \lg\gamma_0 ,$$

are given in Table 2. The values of $\lg\gamma_0$ for ammonia, formic acid, and alcohols had already been calculated by us earlier from the values A_{XH^+}, found by extrapolating the sums and differences of the energies to $1/r \ \rightarrow 0$ (9,10). As is seen from Table 2, the data now obtained differ from those obtained earlier by 0.2-0.3 units of $\lg\gamma_0$. Comparison with the data of other authors (Table 2) shows that our data are close to those of Pleskov (11), obtained from e.m.f. values for solvents that differ strongly

···differing from water in their basicity, and to the value of $\lg\gamma_{0H^+}$ in ethanol obtained by Grunwald (12), and differ greatly from Shtrëlov' s data (13).

With the aid of the values found for $\lg\gamma_{0H^+}$, as we have already said, correlations can be obtained between the values of the specific acidities pH_p, defined by the logarithm of the activity of lyonium ions (14)

$$pH_p = -\lg a_{MHc^+} = -\lg m_{MHc^+}\gamma^*_{MHc^+}$$

(γ^* is the concentration activity coefficient of the lyonium ions), and the unified acidity pA, defined by the negative logarithm of the proton activity referred to an aqueous solution as standard (9,14).

$$pA = -\lg a_{H^+} = -\lg a_{MH^+} - \lg\gamma_{0H^+} = pH_p - \lg\gamma_{0H^+}.$$

Table 2 gives the lengths of the pH_p scales, i.e., the number of pH_p units between unit-activity solutions of lyonium and lyate ions, determined by the ionic product of the medium, and the position of the pH_p scale of the given solvent on the unified acidity scale pA.

Received
21 XI 1961

CITED LITERATURE

[1] N. A. Izmailov, DAN, **149**, No. 4 (1963).
[2] N. A. Izmailov, Yu. A. Kruglyak, DAN, **134**, 1390 (1960).
[3] N. A. Izmailov, DAN, **149**, No. 6 (1963).
[4] V. P. Vasil' ev, E. K. Zolotarev et al., ZhFKh, **34**, 1763 (1960).
[5] V. M. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, IL, 1954, p. 28.
[6] V. L. Tal' roze, E. L. Frankevich, DAN, **111**, 376 (1956); W. A. Severtson, T. J. Brice, J. Am. Chem. Soc., **80**, 2314 (1958); E. L. Frankevich, V. L. Tal' roze, DAN, **119**, 1174 (1958).
[7] K. B. Yatsimirskii, *Thermochemistry of Complex Compounds*, Academy of Sciences of the USSR Press, 1951.
[8] V. I. Kondrat' ev, N. D. Sokolov, ZhFKh, **29**, 1265 (1955).
[9] N. A. Izmailov, *Electrochemistry of Solutions*, Kharkov, 1959, pp. 353, 380.
[10] N. A. Izmailov, DAN, **126**, 1083 (1959); ZhFKh, **34**, 2414 (1960).
[11] V. A. Pleskov, *Advances in Chemistry*, **16**, 254 (1947).
[12] R. Gutbezahl, E. Grunwald, J. Am. Chem. Soc., **75**, 865 (1953).
[13] H. Strehlow, Zs. Electrochem., **56**, 827 (1952).
[14] N. A. Izmailov, DAN, **27**, 104 (1959).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.