THE PROTON AFFINITY, ACIDITY, AND BASICITY OF NONAQUEOUS SOLVENTS

N. A. Izmailov

(Presented by Academician M. I. Kabachnik, November 24, 1961)
Translated from Doklady Akademii Nauk SSSR, Vol. 150, No. 1,
pp. 120-123, May, 1963
Original article submitted November 21, 1961

When determined by the method of extrapolation to $1/n^2 = 0$ (see [1], Table 1), the energy of solvation of the proton proves to be considerably greater than the energy of solvation of any other univalent cation in the same solvent. Thus the energy of proton hydration in water is 256.5 kcal/g-ion, while the energy of lithium ion hydration is only 117 kcal/g-ion.

The high value of the energy of solvation of the proton results from the fact that the proton combines with the first solvent molecule covalently to form a lyonium ion MH^+. The mechanism of further solvation of this ion is analogous to the mechanism of solvation of any other cation and the energies of solvation are similar for the two cases. Primary solvation of the lyonium ion occurs through molecular orbital formation, the ion itself functioning as an acceptor for the unpaired electrons supplied by the central atom of the solvent molecule [2]. Lyonium ions which have been solvated in such a primary shell can interact electrostatically with the molecules of the solvent and thereby form a secondary solvation shell. The peculiarities of the solvation mechanism cause the solvation energy of the proton to vary radically in passing from one solvent to another, the range being from 278.0 kcal/g-ion in ammonia to 243.0 kcal/g-ion in formic acid [3]. Measured in terms of proton affinity in the liquid state (solvation energy), solvent basicity varies in the following order:

$$NH_3 > N_2H_4 > H_2O > CH_3OH > C_2H_5OH > n\text{-}C_4H_9OH = \\ = i\text{-}C_5H_{11}OH \geqslant CH_3COOH_3 > CH_3CN > HCOOH.$$

Values of the ion product for the medium can be used to find the proton affinity of the solvated lyate ion in solution. In fact, one has

$$M + H^+ + sol = MH_s^+ + A_{XH^+}$$
$$\frac{MH_s^+ + (M-H)_s^- = 2M + sol + A_{neut.}}{H^+ + (M-H)_s^- \rightleftarrows M + sol + A_{XH^+} + A_{neut.}}.$$

The value of A_{neut} is equal to the free energy change for the neutralization reaction but is of opposite sign, $A_{neut} = -\Delta Z_{neut}$, and can be determined from the ion product for the solvent through the relation $A_{neut} = -RT \ln K$.

Table 1 gives values of A_{neut} and the proton affinity for the lyate ion $(M-H)_s^-$. If the value of the proton solvation energy is assumed to measure the proton acceptor–basic character of the solvent, the proton affinity of the solvated lyate ion will measure its proton donor–acidic character. An increase in the basicity of the solvent is, as a rule, accompanied by a diminution in the acidity (by an increase in the affinity of the $(M-H)_s^-$ ion) but these variations are not mutually proportional. Thus the basicity of ammonia is greater than that of water by 21.5 kcal/g-ion and the acidity less by 45.0 kcal/g-ion, while the basicity of formic acid is less than that of water by 13.5 kcal/g-ion and the acidity greater by 24.0 kcal/g-ion (see Table 1). The energy of proton solvation is approximately the same in hydrazine and in ammonia but hydrazine is much the more acidic solvent, the proton affinity of its lyate ion being 12.5 kcal/g-ion lower than that of ammonia.

TABLE 1. The Energies of the Processes Involved in Proton Addition in Various Solvents

Solvent	$A_{XH^+} = -\Delta Z_X$	$-\Delta Z = A$ $MH^+_s + (M-H)^-_s \rightleftarrows 2M + S$	$-\Delta Z = A$ $H^+ + (M-H)^-_s \rightleftarrows M + S$	A_{XMH^+}	$A_{X(M-H)^-}$	$-\Delta Z = \pi$ $H^+ + M \rightleftarrows MH^+$	π according to [6]	π according to [8]	π according to [5]	$\pi = -\Delta 3$ $H^+ + (M-H)^- \rightleftarrows M$	Data of the literature [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	—
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

TABLE 2. Variation of the Proton Affinity

Solvent	log γ_0 new values	log γ_0 earlier values	$2 \log \gamma_0^{OCH} + \log \gamma_0^{el}$	Literature data: Pleskov [11]	Grundwald [12]	Strehlow [13]	Hammett	Range of pH_p scale	Position in 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	3,3	—	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

Thus a complete description of the acid—base properties of a solvent cannot be given solely in terms of the energy of formation of the solvated lyonium ion, a characteristic of solvent basicity, but requires knowledge of the energy of proton addition to the solvated lyate ion, a characteristic of solvent acidity.

Table 1 gives estimated values of the energies of solvation of lyonium and lyate ions. The energy of hydration of the hydroxonium ion was obtained on the basis of certain assumptions concerning the approximate equality of the solvation energies of isoelectronic ions and the variation of the solvation energy with the ionic radius [2]. The isoelectronic Na^+ ion has a hydration energy of 94.0 kcal/g-ion and a radius of 0.95 A, this being considerably less than the radius of the H_3O^+ ion which is 1.35 A [3]. On the other hand, the radius of the K^+ ion, 1.33 A [3], is approximately the same as that of the H_3O^+ ion while it hydration energy is 77.0 kcal/g-ion. Thus it can be assumed that the energy of hydration of the H_3O^+ ion lies between 77 and 94 kcal/g-ion with a mean at 85.5 kcal/g-ion. An estimate can also be made on the basis of the relation between the energies and radii of the isoelectronic Na^+ and NH_4^+ ions, the radius and energy of the latter being 1.43 A and 75.0 kcal/g-ion, respectively. The hydration energy of the H_3O^+ ion must certainly be higher than that of the NH_4 ion, since it is smaller and contains fewer protons. The mean value is close to that found earlier, 84.5 kcal/g-ion. The energy of hydration of the H_3O^+ ion was finally taken to be 85.0 kcal/g-ion.

On the basis of the similarity in changes in the solvation energies of similar ions on passing from one solvent to another, the alteration of the solvation energy of the lyonium ion was assumed to be approximately the same as the alteration of the solvation energy of the isoelectronic Na^+ ion. Energies determined in this manner are shown in Table 1.

The solvation energy of the lyate ion was found in the following manner. The data of Mishchenko et al. [4] show the solvation energy of the OH^- ion to be 110 kcal/g-ion. Since our own value for the isoelectronic F^- ion was 4.5 kcal/g-ion less than that of [4] (107.0 and 102.5), A_{XOH^-} was assumed to be equal to 106.5. The solvation energies of the other lyonium ions were calculated from this value and from the alteration of the solvation energy of the Cl^- with change in volvent. These data were used to calculate vacuum proton affinities of molecules and lyate ions (see Table 1).

The vacuum proton affinity of the solvent molecule was calculated at the difference between the solvation energies of the proton and the lyonium ion, and the proton affinity of the lyate ion determined as the sum of the proton affinity of the ion in solution and the solvation energy.

Our calculated value for the vacuum proton affinity of the water molecule is close to that calculated by Latimer [5] and measured experimentally by Tal'roze and Frankevich [6]. The proton affinities of the hydroxyl ion (OH^-), the amide ion (NH_2^-) [7], and ammonia [5] are also close to the values of the literature. The energy of the $HCOO^-$ ion lies between the values found in the literature [7].

The vacuum proton affinities of the alcohol molecules are close to the proton affinity of water and considerably less than the values calculated by Kondrat'ev and Sokolov [8] and found experimentally by Tal'roze and Frankevich. The affinities of the lyate ions of water and the alcohols are approximately the same.

The data obtained here indicate that the vacuum proton affinities of molecules and lyate ions do not alter in parallel, the situation being the same as in solution. The difference in vacuum is even greater than in solution, and the basicity and acidity therefore differ in the liquid state and in vacuum.

The data on proton solvation energies of Table 1 can be used to determine the value of $\log \gamma_{0H^+}$ for the proton from the equation [9]:

$$\log \gamma_{0H^+} = \frac{A_{XH^+(H_2O)} - A_{XH^+(M)}}{2{,}3RT} = \frac{\Delta A_{XH^+}}{2{,}3RT} .$$

Values of $\log \gamma_{0H^+}$ determined in this manner were corrected with the aid of values of $\log \gamma_{0H^+}$ obtained from the equation [9]

$$\log \gamma_{0H^+} = 2 \log \gamma_0^{bas} + \log \gamma_0^{el},$$

to give the results presented in Table 2. Values of $\log \gamma_0$ for ammonia, formic acid, and alcohols had been calculated earlier on the basis of A_{XH^+} values obtained by extrapolating energy sums and differences to $1/r_{cr} \to 0$ [9, 10]. It is seen from the table that the present values differ from the previous ones by 0.2-0.3 $\log \gamma_0$ units. Comparison shows that our values are in good agreement with those obtained by Pleskov [11] from emf measurements on solvents which differ strongly from water in basicity and with the value of Grundwald [12] for ethanol, but depart markedly from the values of Strehlow [13].

It has already been pointed out that the values found for $\log \gamma_{0H^+}$ can be used to obtain a relation between the specific acidity, pH_p, defined as the logarithm of the activity of the lyonium ion [14]

$$pH_p = -\log a_{MH_s^+} = -\log m_{MH_s^+} \gamma^*_{MH_s^+}$$

(γ^* is the activity coefficient of the lyonium ion) and the ordinary acidity, pA, defined as the negative logarithim of the proton affinity referred to the aqueous solution as standard [9, 14].

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

Table 2 gives the range of the pH_p scales, i.e., the number of pH_p units between solutions of lyate and lyonium ions of unit activity, as determined by the ion product of the medium, and the positions of the solvent pH_p scales in terms of the pA scale of ordinary acidities.

LITERATURE CITED

1. N. A. Izmailov, DAN, 149, No. 4 (1963).

2. N. A. Izmailov and 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. W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solution [Russian translation], IL, 1954, p. 28.
6. V. L. Tal'roze and E. L. Frankevich, DAN, 111, 376 (1956); W. A. Severson and T. J. Brice, J. Am. Chem. Soc., 80, 2314 (1958); E. L. Frankevich and V. L. Tal'roze, DAN, 119, 1174 (1958).
7. K. B. Yatsimirskii, The Thermochemistry of Complex Compounds [in Russian], Izd. AN SSSR, 1951.
8. V. I. Kondrat'ev and N. S. Sokolov, ZhFKh, 29, 1265 (1955).
9. N. A. Izmailov, The Electrochemistry of Solutions [in Russian], Kharkov, 1959, pp. 353, 380.
10. N. A. Izmailov, DAN, 126, 1083 (1959); ZhFKh, 34, 2414 (1960).
11. V. A. Pleskov, Usp. khimii, 16, 254 (1947).
12. B. Gutbezal and E. Grundwald, J. Am. Chem. Soc., 75, 865 (1953).
13. H. Strehlow, Zs. Electrochem., 56, 827 (1952).
14. N. A. Izmailov, DAN, 127, 104 (1959).

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.
