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SHORT COMMUNICATIONS

Proc. Estonian Acad. Sci. Chem., 1990, 39, N 3, 185—186
https://doi.org/10.3176/chem.1990.3.11

УДК 541.452

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PROTONATION OF A WEAK BASE FORMING TWO CONJUGATED ACIDS

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(*Presented by J. Kann*)

Protonation of a weak base according to

$$B+H^+ \rightleftarrows BH^+ \tag{1}$$

yields only one BH^+-form. In aqueous strong acid solutions equilibrium (1) is characterized by two parameters, i. e. by its pK_{BH^+} and solvation parameter (m^*) values [1]. The mathematical procedures used for the estimation of pK_{BH^+} and m^* values [1, 2] are based on the assumption that the dependence of the measured parameter (ε) on the protonation ratio $I=c_{BH^+}/c_B$ may be given by the equation

$$\varepsilon=\frac{1}{1+I}\varepsilon_B+\frac{I}{1+I}\varepsilon_{BH^+}, \tag{2}$$

where ε_B and ε_{BH^+} are the ε values for B- and BH^+-forms respectively.

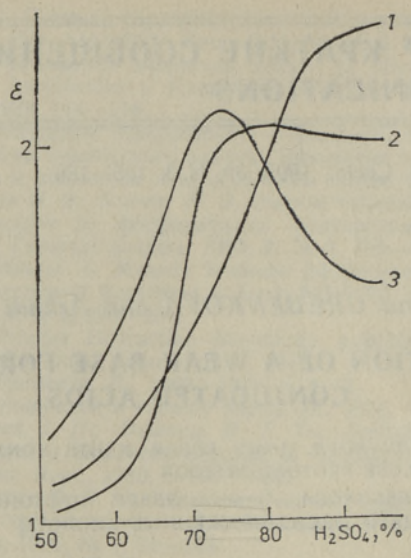
The protonation of some weak bases seems to be more complex: there is good reason to believe that in strongly acidic media monoprotonation of some weak bases (hydroxybenzenes and their alkyl esters [3], for instance) may occur yielding the O-protonated ($_1BH^+$) and/or C-protonated ($_2BH^+$) form. The species $_1BH^+$ and $_2BH^+$ are both monoprotonated differing in chemical structure only. Accordingly, we can write

$$\begin{aligned} B+H^+ &\rightleftarrows {}_1BH^+, \\ B+H^+ &\rightleftarrows {}_2BH^+. \end{aligned} \tag{3}$$

The ratio $c_{_1BH^+}/c_{_2BH^+}$ depends on the medium used. As a rule, in a system containing little or no water the C-protonation ($_2BH^+$) dominates. On the other hand, in strong acid-water mixtures with moderate acid concentrations the O-protonation ($_1BH^+$) prevails. In acidic solutions between these two extremes both the monoprotonated forms, $_1BH^+$ and $_2BH^+$, may coexist in rather comparable concentrations. If so, the measurable parameter is given by

$$\varepsilon=\frac{1}{1+I_1+I_2}\varepsilon_B+\frac{I_1}{1+I_1+I_2}\varepsilon_{_1BH^+}+\frac{I_2}{1+I_1+I_2}\varepsilon_{_2BH^+}, \tag{4}$$

where $I_1=c_{_1BH^+}/c_B$ and $I_2=c_{_2BH^+}/c_B$. Because of their different chemical structure, the species $_1BH^+$ and $_2BH^+$ have different ε values ($\varepsilon_{_1BH^+}$ and $\varepsilon_{_2BH^+}$, respectively). In this situation (Eq. (4)) there is no possibility of characterizing the basicity of the base studied by a single basicity constant (K_{BH^+}) and a single solvation parameter (m^*). Instead of



Simulated dependences $\varepsilon=\varphi$ (% acid) according to Eq. (4); the respective I_1 and I_2 values were obtained by Eq. (5). The following parameters were used:

1 — $pK_{1\,BH^+}=-3.00$, $pK_{2\,BH^+}=-7.00$, $m_1^*=0.55$, $m_2^*=1.20$, $\varepsilon_B=1.00$, $\varepsilon_{1\,BH^+}=1.60$, $\varepsilon_{2\,BH^+}=2.30$;

2 — $pK_{1\,BH^+}=-4.50$, $pK_{2\,BH^+}=-6.00$, $m_1^*=0.70$, $m_2^*=1.10$, $\varepsilon_B=1.00$, $\varepsilon_{1\,BH^+}=2.50$, $\varepsilon_{2\,BH^+}=2.00$;

3 — $pK_{1\,BH^+}=-3.00$, $pK_{2\,BH^+}=-7.00$, $m_1^*=0.55$, $m_2^*=1.20$, $\varepsilon_B=1.00$, $\varepsilon_{1\,BH^+}=2.30$, $\varepsilon_{2\,BH^+}=1.60$.

that two basicity constants, K_{1BH^+}, K_{2BH^+}, and two solvation parameter (m^*) values, m_1^*, m_2^*, should be used. Assuming that the Cox-Yates method [1] is applicable to Eq. (3), the indicator ratios I_1 and I_2 may be obtained from equations

$$\log I_1=\log c_{H^+}+m_1^*X+pK_{1\,BH^+},$$
$$\log I_2=\log c_{H^+}+m_2^*X+pK_{2\,BH^+}. \qquad (5)$$

It is obvious that in the case of two protonated forms (Eq. (3)), the calculation of pK_{1BH^+}, pK_{2BH^+}, m_1^* and m_2^* values is more complicated than in a simple case (Eqs. (1) and (2)). The values of pK_{1BH^+}, pK_{2BH^+}, m_1^*, and m_2^* may be obtained from Eqs. (4) and (5), applying nonlinear regression methods to them (minimizing differences between the measured and calculated ε values in Eq. (4)).

The flexibility of Eq. (4) is shown in Figure: the "nonideal" behaviour of dependences $\varepsilon=\varphi$ (% acid), not well understood in terms of Eq. (2), is now quite a rule and may easily be explained by assuming that Eq. (3) represents the process studied.

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Received
Jan. 18, 1990