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Definition of the Protonation Equilibria of Weak Organic Bases

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Abstract: The Bunnett and Olsen treatment of equilibria in moderately concentrated acids has been compared with the "excess acidity function" procedure recently described by Cox and Yates. The two treatments, although using a different approach to building a reference acidity scale, reach the same results and conclusions. The importance of describing the protonation equilibria of weak bases with two parameters, pK_{XH^+} and the solvation parameter (ϕ_e or m^*), is also emphasized.

The problem of defining the basicity of weak organic bases was solved in a practical sense in 1966 when Bunnett and Olsen[2] reported the linear free-energy relationships which exist between pairs of bases A and B, where B is a reference base (fs are molar activity coefficients, ϕ_e is a slope parameter):

$$\log (f_A f_{H^+}/f_{AH^+}) = (1 - \phi_e) \log (f_B f_{H^+}/f_{BH^+}) \qquad (1)$$

In subsequent years this type of relationship has been tested and used by many authors in aqueous solution[2-7] as well as in mixed solvents.[8] In some cases, approaches have been used which were somewhat different from the original one, but in every case the relationships given by eq 1 were found to be valid. The only major question still open lies in the choice of the reference scale, i.e., the values to be used for the $\log (f_B f_{H^+}/f_{BH^+})$ term.

According to one view, the best choice would be to take (H_0 + $\log C_{H^+}$) as the value for the activity coefficient term on the right-hand side of eq 1.[2,3,6,8] Another school of thought,[4,5,7] due mainly to Marziano and co-workers, maintains that this term can be evaluated without the use of any Hammett type acidity function at all (such as H_0), thus avoiding the problems of finding a particular set of bases for which the more stringent Hammett relationship (eq 2) still holds and of anchoring the scales to the ideal dilute solution region. The first of these approaches is

$$f_{B_1}/f_{B_1H^+} = f_{B_2}/f_{B_2H^+} \qquad (2)$$

essentially the original Bunnett–Olsen treatment,[2] while the second is the excess acidity or X-function method.[7] The term "excess acidity" is used becausen X represents the difference between the observed acidity and that which the system would have if it were ideal (i.e., with all activity coefficients equal to unity).[7] We now have compared the two treatments using the same extensive set of data and the previously reported defining equation for the X function[7] to assess the advantages and limitations of each method.

Results and Discussion

The H_0 values used were interpolated from the data carefully obtained in aqueous sulfuric acid by Johnson, Katritzky, and Shapiro,[9] who studied the protonation behavior of a well-behaved set of nitroaniline bases. The values for the X function were evaluated as follows.[7] From the definition of the equilibrium constant K_{SH^+} for protonation and deprotonation of a general base X, usually expressed as

$$XH^+ \rightleftharpoons X + H^+$$

$$K_{SH^+} = a_X a_{H^+}/a_{XH^+}$$

we may write

$$pK_{XH^+} = \log (C_{XH^+}/C_X C_{H^+}) + \log (f_{XH^+}/f_X f_{H^+}) \qquad (3)$$

where C is molar concentration and a is molar activity. If there can be shown to be a linear relationship between activity coefficient terms such as that in eq 1 we may now write

$$\log (f_X f_{H^+}/f_{XH^+}) = m^* \log (f_{Ref} f_{H^+}/f_{RefH^+}) = m^* X \qquad (4)$$

where the activity coefficient quotient for the reference base is expressed by the function X and the slope parameter by m^*. Such linear relationships can be shown to be valid empirically for large numbers of pairs of typical weak organic bases.[4,5,7] Combining eq 3 and 4 and rearranging, we obtain

$$X = (\log (C_{XH^+}/C_X) - \log C_{H^+} - pK_{XH^+})/m^* \qquad (5)$$

With the use of a set of initial trial pK_{XH^+} and m^* values, a set of estimated X values is computed from eq 5. X values pertaining to a small (a fraction of a percent) interval of acid concentration are averaged and all average values are fitted into a polynominal in percent of sulfuric acid. X values from the polynomial are then used to compute new trial values of pK_{XH^+} and m^* as the intercepts and slopes of linear plots of $\log (C_{XH^+}/C_X) - \log C_{H^+}$ vs. X. The procedure is repeated until convergence to the final pK_{XH^+} and m^* values and X function is achieved and the sum of the standard deviations from the entire set of plots reaches a minimum.

It was hoped that the algorithm would always give the same set of values for X, independent of the initially chosen set of trial pK_{XH^+} and m^* values. We have found, however, that this is not necessarily the case. For example, when the trial pK_{XH^+} and m^* values were chosen by a random number generator, the algorithm was unable to converge on an X function which was monotonic over the entire acidity range.

The problem lies with the definition of the reference base. Previously this was defined implicitly in the program to be a hypothetical base B^* with $m^* = 1.0$.[7] A more statistically rigorous program developed recently requires an explicit definition.[10] Rather than arbitrarily choosing the first base in the set (or any single compound) as the reference,[4] the definition used is that the average of *all* the m^* values for the entire set of bases used must be unity.[10] This is a limitation of the generality of X, since it will

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[2] Bunnett, J. F.; Olsen, F. P. *Can. J. Chem.* **1966**, *44*, 1899.

[3] Hammett, L. P., "Physical Organic Chemistry"; McGraw-Hill: New York, 1970.

[4] Marziano, N. C.; Cimino, G. M.; Passerini, R. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1915. Passerini, R.; Marziano, N. C.; Traverso, P. *Gazz. Chim. Ital.* **1975**, *105*, 901.

[5] Marziano, N. C.; Traverso, P. G.; Passerini, R. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 306. Marziano, N. C.; Traverso, P. G.; Tomasin, A.; Passerini, R. C. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 309.

[6] Arnett, E. M., Scorrano, G. *Adv. Phys. Org. Chem.* **1976**, *13*, 83.

[7] Cox, R. A.; Yates, K. *J. Am. Chem. Soc.* **1978**, *100*, 3861.

[8] Capobianco, C.; Magno, F.; Scorrano, G. *J. Org. Chem.* **1979**, *44*, 1654.

[9] Johnson, C. D.; Katritzky, A. R.; Shapiro, S. A. *J. Am. Chem. Soc.* **1969**, *91*, 6654.

[10] Cox, R. A.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116.

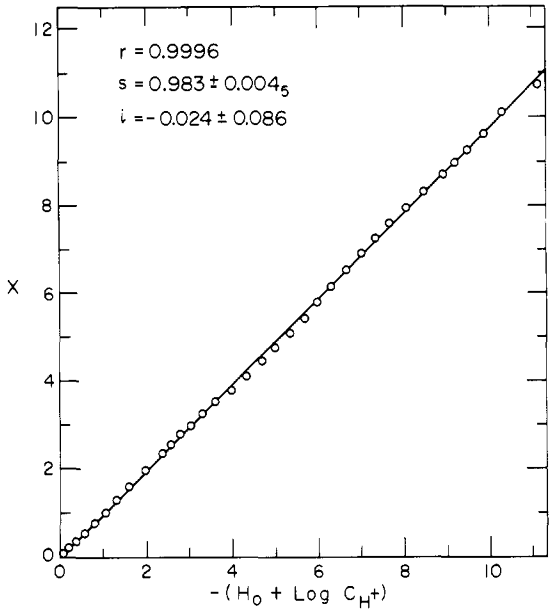

Figure 1. Comparison of X and $-(H_0 + \log C_H{}^+)$ for 0–99.5% (w/w) aqueous sulfuric acid.

only be a unique function of the medium if a large and representative set of bases is available (i.e., many with high m^* values and many with low values). Such a wide range of bases has been studied in aqueous sulfuric acid, but if such a representative set is not available in other media, it is better to rely on an H_0 scale and the original Bunnett–Olsen method, or else obtain pK_{XH^+} and m values from eq 6. Here the choice of H_0 (based on primary anilines) as a reference function for the activity coefficient behavior of all types of bases is arbitrary.

$$\log (C_{XH^+}/C_X) = -mH_0 + pK_{XH^+} \qquad (6)$$

However, it is very interesting that when X and $-(H_0 + \log C_{H^+})$ are compared for the entire range of aqueous sulfuric acid solutions the correlation between the two functions is very good, as shown in Figure 1,[11] with a slope close to unity. Recalling that the X function involves a wide range of bases, including anilines, carbonyls, thiocarbonyls, esters, amides, and indoles,[7] the close agreement with a measure of excess acidity based on anilines alone, such as H_0, is remarkable. The fact that X and $(H_0 + \log C_{H^+})$ are numerically practically equivalent supports the idea that either acidity scale may be used to interpret the basic properties of any type of weak organic base. The reasons why nitroanilines give such a reliable acidity scale as H_0 have been discussed elsewhere.[6]

Protonation parameters may be evaluated from the two scales as follows. By substituting $(H_0 + \log C_{H^+})$ for $\log (f_{BH^+}/f_B f_{H^+})$ in eq 1 and combining eq 1 and 3 we obtain the Bunnett–Olsen equation

$$\log (C_{XH^+}/C_X) - \log C_{H^+} = (\phi_e - 1)(H_0 + \log X_{H^+}) + pK_{XH}{}^+ \qquad (7)$$

This may easily be rearranged to the more familiar[1] form

$$\log (C_{XH^+}/C_X) + H_0 = \phi_e(H_0 + \log C_{H^+}) + pH_{XH^+} \qquad (8)$$

At the same time eq 5 may be rewritten as

$$\log (C_{XH^+}/C_X) - \log C_{H^+} = m^*X + pK_{XH^+} \qquad (9)$$

Since X and $-(H_0 + \log C_{H^+})$ are for all practical purposes equivalent, the same pK value would be obtained from experimental ionization ratios with either eq 7 and 8 or eq 9.

We wish also to draw attention to the equivalent meaning of m^* and $(1 - \phi_e)$ which is evident from eq 7 and 9. These slope parameters are of paramount importance in defining the protonation behavior of weak bases. As discussed elsewhere, the protonation equilibria of weak bases must be expressed quantitatively by two parameters.[6,12] There is no way of obtaining important information such as the degree of protonation in a given concentration of acid from the thermodynamic pK_{XH^+} value alone, however accurately it may be known. The slope parameters m^* or ϕ_e are also essential for computing ionization ratios at any acid concentration outside of the ideal dilute region.[13]

Moreover, both ϕ_e and m^* have a similar kind of significance to that which can be attached to slope parameters in other linear free-energy relationships, such as Hammett ρ values or Brønsted α values. We have previously discussed how the slope parameter may be used to compare the solvation requirements of the protonation equilibria of a given structural class of base with those of the reference bases, which in the case of the ϕ_e parameter are the nitroanilines.[6,12] The comparison of these solvation properties has been of great importance in rationalizing the existence of several different acidity scales in aqueous media,[6] as well as in relating energies of solvation from gas phase to aqueous solutions.[14]

Experimental Section

All of the computations used the Fortran IV program previously described[7] and were performed on IBM System 370 or CDC CY 70 computers. The program, data, and results will appear in the microfilm edition.

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Supplementary Material Available: Program, input cards, and X functions from different m and pK_{XH^+} input data (14 pages). Ordering information is given on any current masthead page.

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(11) The data plotted in Figure 1 are from the following: X and C_{H^+}, ref 7; H_0, ref. 9. It must be noted that different X values can be obtained depending on the m and pK_{XH^+} input data. Moreover, we are currently investigating a different method to obtain the C_{H^+} values other than the function employed in ref 7.

(12) Bonvicini, P.; Levi, A.; Lucchini, V.; Modena, G.; Scorrano, G. *J. Am. Chem. Soc.* **1973**, *95*, 5960. Levi, A.; Modena, G.; Scorrano, G. *Ibid.* **1974**, *96*, 6585. Curci, R.; Di Furia, F.; Lucchini, V.; Levi, A.; Scorrano, G. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 341. Lucchini, V.; Modena, G.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3387. Perdoncin, G.; Scorrano, G. *Ibid.* **1977**, *99*, 6983.

(13) For example, the ionization ratios of *p*-nitrobenzamide (one of the 165 compounds used to define X) give, according to eq 8, $pK_{XH^+} = -1.95 \pm 0.05$ and $\phi_e = 0.58 \pm 0.02$, and, according to eq 9, $pK_{XH^+} = -1.99 \pm 0.03$ and $m = 0.47 \pm 0.02$. This compound is 5%, 50%, and 95% protonated in 19.1%, 51.0%, and 72.0% sulfuric acid, respectively.

(14) Taft, R. W.; Wolf, J. F., Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240.