

[CONTRIBUTION FROM THE JAMES BRYANT CONANT LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

On the Relation between H_0 and Water Activity

BY CHARLES PERRIN*

RECEIVED JUNE 4, 1963

The "excess acidity," $-H_0 - \log [H^+]$, of hyperacid solutions may be understood in terms of the average hydration change accompanying protonation of a Hammett base. Subject to an assumption concerning activity coefficients, the slope of the curve of $H_0 + \log [H^+]$ against the logarithm of the water activity is identified with the average number of water molecules liberated on protonating a Hammett base. The hydration model is applied to estimating H_0 values in sodium perchlorate-perchloric acid mixtures, with the use of tables of H_0 values and water activities in perchloric acid solutions and of water activities in sodium perchlorate solutions. The estimated values of H_0 in the mixed solutions are in good agreement with experimental values, except in very concentrated salt solutions.

Bascombe and Bell¹ proposed that the difference between pH and Hammett's acidity function² H_0 may be understood in terms of hydration changes. They proposed that protonation of a Hammett base is to be represented by the reaction



where n is the number of water molecules liberated upon protonation of the base, but not necessarily the hydration number of the proton. On the basis of this model, they derived the equation

$$-H_0 - \log [H(OH_2)_n^+] + n \log a_w = \log \frac{f_B f_{H(OH_2)_n^+}}{f_{BH^+}} \quad (1)$$

They assumed that $f_{BH^+} \cong f_{H(OH_2)_n^+}$, since both of these species are hydrated cations. They then identified $[H(OH_2)_n^+]$ with $[H^+]$, the total hydrogen ion concentration, and plotted the left side of the equation, with $n = 4$, against molarity of sulfuric, perchloric, or hydrochloric acid, to obtain a straight line whose slope is small, as would be expected from the behavior of the $\log f_B$ term which remains on the right side of the equation. (A line so obtained, plotted against the negative logarithm of the water activity in perchloric acid, is shown as the curve labeled 4 in Fig. 1.) They therefore concluded that four water molecules are liberated on protonating a Hammett base, and that the excess acidity of hyperacid solutions is, indeed, due to a diminished water activity.

Bunnett^{3a} has objected to this simple model. He pointed out that in 8 M perchloric acid the ratio $(H_0 + \log [H^+])/\log a_w$ is greater than the average number of water molecules available to each proton. He concluded that it is not possible to ascribe hyperacidity solely to hydration changes, but that part of the effect must arise from a not inconsiderable variation of $f_{H(OH_2)_n^+}/f_{BH^+}$ with medium.

It is the purpose of this paper to show that hyperacidity may still be understood in terms of hydration changes. However, the approach of Bascombe and Bell must be modified to allow for a variable hydration change.

Before discussing the effect of a variable hydration change on H_0 values, it is instructive to consider the effects of variable order in a simpler case. Several researchers⁴ have observed reactions involving the appearance of a reactant with a variable order in their kinetic rate expressions. Each of these researchers

has identified the reaction order, *in a given medium*, as the slope of the tangent of the curve of the logarithm of the observed first-order rate constant against the logarithm of the concentration of the reactant whose kinetic order is to be determined, without justifying this procedure. For generality, let the reaction be

written as $A + nB \xrightarrow{k} \text{products}$, with B present in large excess, and with a corresponding rate law (where k_{obsd} , the observed first-order rate constant for disappearance of A, is a function of the concentration of reactant B)

$$v = -d[A]/dt = k_{\text{obsd}}[A] = k[A][B]^n, \text{ or } k_{\text{obsd}} = k[B]^n$$

Taking logarithms leads to $\log k_{\text{obsd}}/k = n \log [B]$, which implies that the order, n , is to be determined from the ratio of $\log k_{\text{obsd}}/k$ to $\log [B]$. Nevertheless, it seems intuitively obvious, on chemical grounds, that the order should be determined from the slope of $\log k_{\text{obsd}}$ vs. $\log [B]$. Certainly, the order of the reaction in a given solution is a "local" phenomenon, depending only upon conditions in that solution, and ought not to depend upon the rate of the reaction in other solutions, or upon the value of k (which is equal to the value of k_{obsd} observed at unit concentration of B and therefore depends upon the units chosen for [B]).

This conflict may be resolved by rejecting the apparent simplicity of a rate constant, k , of variable order. Instead, we must allow for the simultaneous occurrence of reactions of different order, each with its own rate constant, k_n . Then

$$v = -\frac{d[A]}{dt} = k_{\text{obsd}}[A] = \sum_{n=0}^{\infty} k_n[A][B]^n$$

or

$$\log k_{\text{obsd}} = \log \sum k_n[B]^n$$

Differentiating with respect to $\log [B]$ leads to

$$\frac{d \log k_{\text{obsd}}}{d \log [B]} = \frac{d[B]}{d \ln [B]} \times \frac{d \ln \sum k_n[B]^n}{d[B]} = \frac{[B]}{\sum k_n[B]^n} \sum n k_n[B]^{n-1} = \frac{\sum n k_n[B]^n}{\sum k_n[B]^n} = \bar{n}$$

This derivative is an average value of n , where the averaging process is carried out with the quantity, $k_n[B]^n/\sum k_n[B]^n$, as weighting factor. This weighting factor is the fraction of the total reaction which proceeds specifically through n th-order kinetics. Thus, this derivation justifies the identification of the slope of the $\log k_{\text{obsd}} - \log [B]$ curve with the average order of the reaction with respect to the reactant B.

In the discussion of H_0 , the standard state for every proton hydrate⁵ is to be chosen so that in dilute solution $a_{H(OH_2)_n^+}$ approaches $[H^+]$, where $[H^+]$ is the

(5) Again, the species $H(OH_2)_n^+$ is not to be taken as a strict n -hydrate, but rather as a species with n more water molecules, in a thermodynamically meaningful sense, than the protonated Hammett base. It would be possible to allow for variable hydration of BH^+ , and even of B, but such an extension is no more general and only complicates the "bookkeeping."

* Department of Chemistry, University of California at San Diego, La Jolla, Calif.

(1) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

(3) (a) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4976 (1961); (b) **83**, 4967 (1961); (c) **83**, 4966 (1961).

(4) See, for example, E. Tommila, *Acta Chem. Scand.*, **9**, 975 (1955); E. Tommila and A. Nieminen, *ibid.*, **9**, 987 (1955); H. D. Zook and W. L. Cumby, *J. Am. Chem. Soc.*, **82**, 1386 (1960); D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *ibid.*, **83**, 3678 (1961).

stoichiometric hydrogen ion concentration. Although f_B , f_{BH^+} , and a_w approach unity in dilute solution, it should be noted that none of the $f_{H(OH_2)_n^+}$ does.⁶ Rather, $f_{H(OH_2)_n^+}$ approaches $[H^+]/[H(OH_2)_n^+]$, which is the reciprocal of the fraction of protons present as n -hydrates in dilute solution. This is the most convenient choice of standard state, since it permits the numerical specification of $a_{H(OH_2)_n^+}$, which is the thermodynamically significant quantity, rather than of $f_{H(OH_2)_n^+}$, which is not. At any event, our final result is independent of our choice of standard state.

Then $a_H \cdot a_w^n = a_{H(OH_2)_n^+}$, and

$$h_0 = \frac{a_H \cdot f_B}{f_{BH^+}} = \frac{a_{H(OH_2)_n^+} \cdot f_B}{a_w^n \cdot f_{BH^+}} = \frac{[H(OH_2)_n^+] f_{H(OH_2)_n^+} f_B}{a_w^n f_{BH^+}}$$

Taking logarithms and rearranging leads to the same equation (eq. 1) that Bascombe and Bell derived from their model.

However, this derivation relies upon thermodynamics alone and is valid for any integral value of n . Furthermore, when n can assume several values, it is no longer possible to identify $[H(OH_2)_n^+]$ with $[H^+]$, but the more general equation, $[H^+] = \sum_n [H(OH_2)_n^+]$,

must be used. When Bascombe and Bell plotted $-H_0 - \log [H^+] + n \log a_w$ against molarity of acid, they were examining the behavior of $-H_0 - \log ([H^+]/[H(OH_2)_n^+] + n \log a_w - \log [H(OH_2)_n^+]$ which is necessarily equal to

$$\log \frac{f_{H(OH_2)_n^+} f_B}{f_{BH^+}} + \log \frac{[H(OH_2)_n^+]}{[H^+]}$$

Figure 1 shows a plot of this quantity⁷ in perchloric acid for selected values of n against $-\log a_w$.

In what follows, we shall assume, in a manner similar to that of Bascombe and Bell, that $f_{H(OH_2)_n^+} f_B / f_{BH^+}$ is independent of medium for every n . (These activity coefficient ratios, in general, differ from unity, but the question of their medium dependence is independent of the actual values assigned to them as a result of the choice of standard state.) This assumption is not unreasonable, since both $H(OH_2)_n^+$ and BH^+ are hydrated cations, and both B and BH^+ contain organic moieties. It must be stressed that this assumption may not be valid, but the following discussion will derive a result which is consistent with this assumption, whereas Bunnett has pointed out that the treatment of Bascombe and Bell is not consistent with their assumption that $f_{H(OH_2)_n^+} \cong f_{BH^+}$. If the activity coefficients are medium independent, then the term, $\log f_{H(OH_2)_n^+} f_B / f_{BH^+}$, may be evaluated as the value of $\log [H^+]/[H(OH_2)_n^+]$ at infinite dilution. Thus, Fig. 1 is a plot of the fraction of protons present as the various hydrates, relative to the fraction of that hydrate present in dilute solution. As an example, we may consider the tetrahydrate, whose relative concentration reaches a maximum near 6.5 M perchloric acid ($\log a_w = -0.4$). Therefore, protonation of a Hammett base proceeds with liberation of four water molecules most often in the neighborhood of 6.5 M acid. In more dilute solutions, liberation of five waters is more important; in more concentrated solutions, liberation of three waters is more important. Moreover, the generality of maxima in these curves, and the above discussion of reactions with variable order, suggest the applicability of a derivative. The number of water molecules liberated in a given solution is again a "local" phenomenon, and ought not depend upon the behavior of the H_0 function in more dilute solutions. The curve labeled

(6) See, for example, G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., revised, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 272f.

(7) Data from M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957), and from J. F. Bunnett.^{8b}

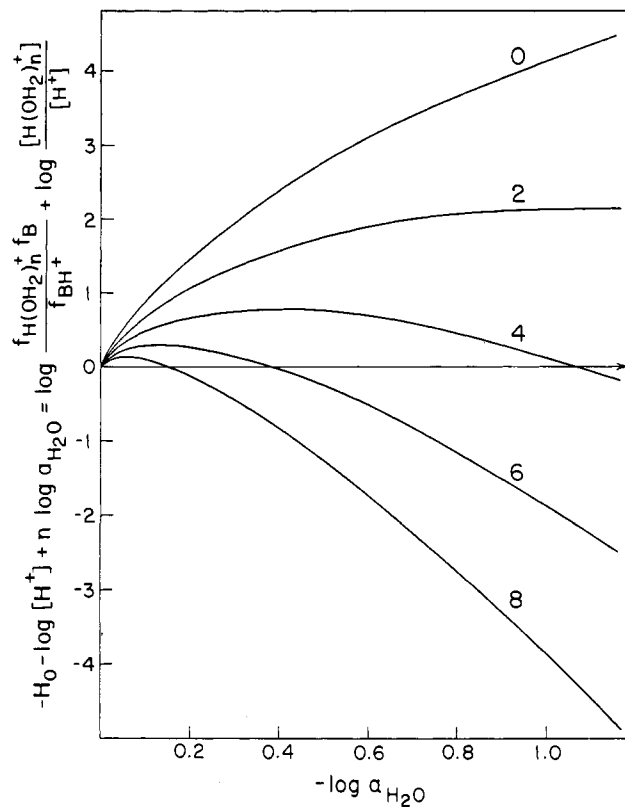


Figure 1.

"zero" in Fig. 1 is a plot of the "excess acidity," $-H_0 - \log [H^+]$ against $-\log a_w$. It therefore remains to justify, subject to the above assumption, the identification of the hydration change accompanying protonation of a Hammett base with the slope of the tangent to this curve, rather than with the ratio, $(H_0 + \log [H^+]) / \log a_w$, which is the slope of a chord drawn to the origin.

Assume that $[H^+]/h_0$ may be expanded in a power series in water activity: $[H^+]/h_0 = \sum_n q_n a_w^n$. To find

the coefficients q_n we write

$$\frac{[H^+]}{h_0} = \sum \frac{[H(OH_2)_n^+]}{h_0} = \sum \frac{a_H \cdot a_w^n}{f_{H(OH_2)_n^+}} \times \frac{f_{BH^+}}{a_H \cdot f_B} = \sum \frac{f_{BH^+}}{f_{H(OH_2)_n^+} f_B} a_w^n$$

from which it is apparent that

$$q_n = \frac{[H(OH_2)_n^+]}{h_0 a_w^n} = \frac{f_{BH^+}}{f_{H(OH_2)_n^+} f_B}$$

Notice that the assumption that q_n is medium independent is equivalent to assuming that an aggregate of n water molecules protonates as a Hammett base, i.e., that the concentration of proton n -hydrates is proportional to h_0 (the effective protonating power of the solution) times a_w^n (roughly speaking, the concentration of n -fold water aggregates), with a proportionality constant independent of medium. Consider the derivative

$$\begin{aligned} \frac{d(-H_0 - \log [H^+])}{d(-\log a_w)} &= \frac{d \log [H^+]/h_0}{d \log a_w} = \frac{da_w}{d \ln a_w} \times \\ &= \frac{d \ln \sum q_n a_w^n}{da_w} = \frac{a_w}{\sum q_n a_w^n} \sum n q_n a_w^{n-1} = \frac{\sum n q_n a_w^n}{\sum q_n a_w^n} = \\ &= \frac{\sum n [H(OH_2)_n^+]}{\sum [H(OH_2)_n^+]} = \bar{n} \quad (2) \end{aligned}$$

Therefore, this derivative is an average value of n , weighted by $[H(OH_2)_n^+]/[H^+]$, which is the fraction of protons which liberate n water molecules on protonating a Hammett base.

Experimentally, it is found^{8c} that the slope is initially *ca.* 10 and drops gradually to 2 near 10 *M* perchloric or sulfuric acid, although it is not entirely independent of the actual acid investigated. However, these slopes represent average hydration changes not at all inconsistent with the composition of the solutions, and there are no empirical grounds for discarding the above assumptions. That is to say, this derivation indicates the consistency of an interpretation of hyperacidity based upon hydration changes, without requiring consideration of variations in activity coefficients.

In perchloric acid-sodium perchlorate mixtures, the quantity $-H_0 - \log [H^+] + 4 \log a_w$ is not constant, but increases from 0.04 in dilute acid to 0.96 in 8 *M* salt solutions.⁸ The variation may be understood by integrating the extremities of eq. 2 to obtain

$$-H_0 - \log [H^+] = \int_0^{-\log a_w} \bar{n} d(-\log a_w)$$

It is not justifiable to set $\bar{n} = 4$, but explicit account must be taken of its variation with medium. The above assumption, that $[H^+]/h_0$ may be expressed as a power series in a_w , implies, as a corollary, that \bar{n} is a function of water activity alone, and, if so, the value of the integral, as a function of water activity, may be calculated from H_0 values and water activities in perchloric acid alone⁷ and used to estimate H_0 in mixed perchlorate solutions, whose vapor pressures may be estimated by Zdanowski's rule.⁹

Table I lists calculated and observed H_0 values in the 23 solutions investigated. The standard deviation of the error is 0.11, but part of the discrepancy may arise from the fact that the experimental values are for 40°, whereas the calculations are made for 25°, from H_0 and ΔpK values in the literature. The error so induced is such as to increase the discrepancy between calculated and observed H_0 values in high salt-low acid solutions, and to decrease the discrepancy in high acid-low salt solutions. In short, in the former solutions, the acidity is greater than would be expected on the basis of this simple hydration model, suggesting that one of the above assumptions is only an approximation. Insofar as Bascombe and Bell have shown that the "excess acidity," $-H_0 - \log [H^+]$, is only approximately a unique function of the activity of water, it should not have been expected that specific anion effects might not enter in these mixed solutions to invalidate the expansion of $[H^+]/h_0$ as a power series in a_w . But the approximate nature of this assumption means only that the actual number of water molecules liberated on protonating a Hammett base depends slightly upon the anion present, and upon the concentration of the anion, and in no way invalidates the attribution of hyperacidity to hydration changes. Notice also that the results of Taft¹⁰ do not invalidate the treatment based upon hydration changes, but only warn that the average hydration change accompanying protonation of an indicator base depends upon the structure of the base. Thus, the various acidity functions, and even nonunique values of an acidity function determined with related indicators,^{10,11} may

(8) C. Perrin, Ph.D. Thesis, Harvard University, 1963; C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2773 (1963).

(9) That isopiestic are straight lines in the $m M_1^+A^- - m M_2^+A^-$ plane; see L. S. Lilich, R. S. Smirnova, and A. I. Okatova, *Russ. J. Inorg. Chem.*, **7**, 191 (1962). For example, we have found⁸ that isopiestic are straight lines in the $M HClO_4 - M NaClO_4$ plane.

(10) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

(11) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962).

TABLE I

<i>M</i> HClO ₄	<i>M</i> NaClO ₄	$-\log a_w$	$-H_0$ (exptl.)	$-H_0$ (calcd.)	Error
0.435	..	0.007	-0.29	-0.27	0.02
0.880	..	.016	0.04	0.14	.10
3.045	..	.083	1.17	1.21	.04
3.38	..	.100	1.34	1.41	.07
4.29	..	.156	1.76	1.86	.10
0.0436	2.91	.056	-0.80	-0.79	.01
0.683	2.33	.061	.45	.44	-.01
1.29	1.73	.066	.73	.75	.02
2.17	0.86	.074	.99	1.04	.05
0.520	3.96	.105	.61	0.63	.02
1.62	2.92	.121	1.23	1.23	.00
2.52	2.03	.135	1.42	1.42	.00
0.0443	5.31	.130	0.02	-0.26	-.28
.436	5.57	.163	0.97	0.90	-.07
.760	5.25	.167	1.23	1.16	-.07
1.38	4.635	.183	1.50	1.48	-.02
1.99	4.04	.197	1.69	1.73	.04
3.18	2.86	.230	1.98	2.10	.12
4.38	1.675	.272	2.27	2.43	.16
0.082	7.78	.254	0.89	0.62	-.27
.331	7.61	.267	1.45	1.29	-.16
.583	7.35	.274	1.64	1.57	-.07
.97	6.965	.288	1.86	1.86	.00

be understood in terms of differing hydration and hydrogen-bonding requirements of the conjugate acid. However, the results of Boyd¹² indicate that in more acidic solutions (greater than 50% sulfuric acid), a hydration model would not be valid, since the activity coefficient ratios will change as a result of a decrease in f_B (salting-in of nitro compounds).

A similar treatment for H_R values in mixed perchlorate solutions is much less successful, with discrepancies between estimated and observed⁸ values as large as 1.5 H_R units. No good agreement should have been expected, in view of Högfeldt's finding¹³ that H_R is not a unique function of water activity in sulfuric, nitric, and perchloric acids. Although he has omitted consideration of the $\log [H^+]$ term, the effect of that term will be such as to increase the variation in $-H_R - \log [H^+]$ beyond what is shown in his graph. Thus, the actual number of water molecules liberated on ionizing a triaryl carbinol depends quite markedly on the anion. However, the poor result does not mean that the excess acidity, $-H_R - \log [H^+]$, of these solutions cannot be attributed to the liberation of water molecules on ionizing a triaryl carbinol.

The advantage of this formulation is that it provides an easily visualized explanation of hyperacidity, namely, liberation of water on protonation of a base. Furthermore, it provides a method of estimating H_0 values in moderately concentrated salt solutions containing a known concentration of acid, *without the necessity of making a single measurement in mixed acid-salt solutions*. All that is required is a table of H_0 values as a function of water activity in the acid solutions, and the values of the water activity in solutions of the pure salt.

Acknowledgments.—The author wishes to thank Prof. P. D. Bartlett and Prof. F. H. Westheimer for helpful discussions. This work was supported by a grant from the Chemistry Department of Harvard University.

(12) R. H. Boyd, *ibid.*, **85**, 1555 (1963).

(13) E. Högfeldt, *Acta Chem. Scand.*, **16**, 1054 (1962).