On the Relationship between the Dissociation of Indicators in Non-Ideal Acid Solution and the Dissociation of the Acid itself

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The study of the equilibria of weak bases in concentrated solutions of univalent acids has brought to light that, within experimental uncertainties, the M_c function is able to describe the dissociation of the acid itself; this allows the confident evaluation of thermodynamic equilibrium constants and leads to a new point of view in the field of concentrated ionic solutions.

Acidity functions (H_x) are extensively adopted as a useful tool for probing concentrated acid solutions and describing the behaviour of solutes.[1—3] However they have been found to be affected by several inconsistencies[1,2] and in particular they fail in reproducing the dissociation of the acid itself.[1,4]

Bunnett and Olsen[5] have suggested a different approach based on an empirical linear free energy relationship (2) between each pair of weak bases (B',B'') involved in equilibrium (1). The general validity of equation (2) allowed

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

$$\log [B'H^+]/[B'][H^+] = a + b \log[B''H^+]/[B''][H^+] \tag{2}$$

the construction of the M_C activity coefficient function[6] which accounts for the equilibria of a large number of indicators, even of different structure, in concentrated sulphuric and perchloric acid. Subsequently, the M_C function has been derived by more refined mathematical methods[7—9] and

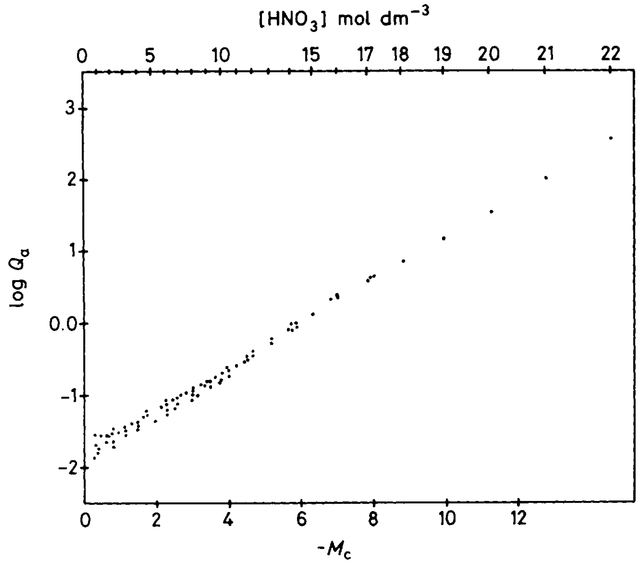

Figure 1.

extended to other solvents.[10] (Some authors refer to M_C as the excess acidity function [3,9,11].)

In the M_C treatment equilibrium (1) is described by two independent parameters, namely pK_B and n_B appearing in equation (3). This implies that the natural pH scale cannot be

$$\log [BH^+]/[B][H^+] = pK_B + n_B M_C \qquad (3)$$

extended from dilute to concentrated solutions in a consistent and general manner.[12]

The aim of the present work is to give new and very promising evidence for the development of the M_C treatment.

Very recently we suggested[13] that M_C could describe the dissociation (4) of the acid itself. This has been tested in

$$AH \rightleftarrows A^- + H^+ \qquad (4)$$

aqueous nitric acid solutions for which accurate dissociation α values are available in the whole acidity range.[14] In Figure 1 log Q_a, defined by equation (5), is plotted against M_C. The M_C

$$\log Q_a = \log [AH]/[A^-][H^+] \qquad (5)$$

values have been taken from ref. 15. As is evident, a good linear relationship is obtained above 1 mol dm^{-3} and equation (6) is valid with 'pK_a' = -1.9 and $n_a = -0.3$ in the reported

$$\log Q_a = \text{'}pK_a\text{'} + n_a M_C \qquad (6)$$

range. The value of 'pK_a' appears not to be very different from the pK_a data of the literature.[14,16] It is worth noting that all previous attempts using acidity functions have failed in reproducing the dissociation (4) over a wide acidity range.[1,4]

The validity of equation (6) in practically the whole acidity range, strongly supports the fact that equation (3) holds even outside the range where it has been tested and that the corresponding pK_B can be regarded as a unbiased estimate of the 'true thermodynamic equilibrium constant' of the weak bases used as indicators. Preliminary results confirm the general applicability of equation (6) to other concentrated aqueous solutions of univalent acids. We can assume that the validity of equation (6) in concentrated acid solutions is related to a pair distribution function of ions which is little affected by charge interactions at short distances.[17] Indeed, at very low concentration, where charge interactions are predominant, equation (6) would fail as it disagrees with Debye–Hückel theory and the experimental mean ionic activity coefficient.[16] Thus 'pK_a'cannot be regarded as a true thermodynamic constant for the dissociation (4). However previous arguments do not invalidate equation (3).

It is noteworthy that the validity of equation (6) implies that the M_C description of equilibria, in concentrated solutions, is independent of the formal species we are using for it.[13] It is natural to define, through equation (7), a new function (M)

$$M = \log Q_a - \text{'}pK_a\text{'} = n_a M_C \qquad (7)$$

which is independent of the choice of a particular scale or reference indicator and solely related to the solvent. The M function, a factor apart, is the 'excess free energy variation function' [namely $(\Delta R_{\text{real}} - \Delta F_{\text{ideal}})/RT$] for the dissociation equilibrium of the solvent. So the terminology 'excess acidity function' seems to be not quite suitable, also because it is not possible to construct a real acidity function from M_C or M.

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