

## APPLICABILITY OF EXCESS ACIDITY FUNCTIONS IN LOW-ACIDITY MEDIA

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**It is demonstrated that excess acidity functions do not correspond well to the pH scale in dilute solutions. Acidity constants,  $pK_{BH^+}$ , of seven moderately weak bases were determined; they were calculated by means of excess acidity functions, since the corresponding ionizations occur at acidity levels where the pH scale is partly used. The excess acidity method permitted extrapolation of measurements made in concentrated acids down to dilute solutions only up to about 5% (w/w) perchloric acid.**

### INTRODUCTION

Several decades ago, Hammett and Deyrup<sup>1</sup> established a method of measuring the acidity constants,  $pK_{BH^+}$ , of weak bases: using nitro-substituted primary amines, they defined the acidity function  $H_0$ , which would allow access to an acidity range where the pH could not be used. Later, it was realized that some of the assumptions, particularly the Hammett cancellation assumption (or zeroth-order approximation), were valid only for weak bases of similar structure. In a previous paper<sup>2</sup> we discussed the validity of the Hammett cancellation assumption and suggested a corrected version of Hammett's equation, which provides better results for acidity constants of weak bases.

In order to investigate series of compounds other than primary amines, the need for other scales different from  $H_0$  soon became evident; of importance here is underlying the review on acidity functions by Cox and Yates,<sup>3</sup> who outlined the approaches to developing universal functions that could be valid for studying equilibria or reaction rates. The excess acidity functions are constructed using a wide variety of compounds and for this reason they are currently preferred and extensively used, in general with very good results.<sup>4,5</sup> Nevertheless, we verified that they do not manifest the predicted behaviour if the excess acidity method is applied to dilute perchloric acid solutions. This is a drawback in the study of bases susceptible to being protonated at acidities ranging from (i) dilute aqueous acidic solutions to (ii) moderately strong acidic solutions; in such cases the pH scale becomes useful only in the vicinity of limit

(i), whereas other acidity scales need to be used near limit (ii). Fortunately, the number of this sort of moderately weak (or strong) base is relatively small, since most bases behave either as strong bases, in which case the pH scale is adequate as a measure of acidity, or as weak bases, for which enough sufficient thermodynamic equations exist for a proper evaluation of  $pK_{BH^+}$  and/or the correct interpretation of acid-catalysed reactions.

In order to obtain further insight into the correlation between acidity functions and the pH scale, seven bases that protonate between the limits (i) and (ii) above were investigated in this work, using aqueous perchloric acid media: *p*-nitroaniline, *o*-nitroaniline, *o*-phenylenediamine, *o*-aminobenzonitrile, 2-chloro-4-nitroaniline, 4-chloro-2-nitroaniline and 2-chloro-5-nitroaniline.

### EXPERIMENTAL

The seven bases were commercially available, and were further purified by sublimation in a vacuum line, using a cold-finger apparatus and oil-bath; melting points were in agreement with literature values. Doubly distilled, deionized water was used throughout for preparing solutions; before use nitrogen was bubbled through it. In all instances the solutions used were freshly prepared and kept in the dark.

The acid solutions were made up to a constant total volume and a constant total base concentration, always using the same pipette and volumetric flask. Stock solutions of the bases were prepared using aqueous perchloric acid of an intermediate acidity within the set of solutions utilized for each indicator. Perchloric acid

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molarities were calculated directly from molar concentrations of perchloric acid, since this species is fully ionized up to at least 60% (w/w).<sup>5</sup>

Extents of protonation of these bases were determined spectrophotometrically by measuring ionization ratios; they showed fixed isosbestic points and no medium effects. Absorbance readings were measured in duplicate at three different wavelengths, at the absorption maxima and on both sides. The procedure followed in obtaining ionization ratios was applied with good results, as described in detail earlier.<sup>3,6</sup>

Spectral curves and absorbance measurements were made with a Milton-Roy Model 3000 spectrophotometer with a diode-array detection system; this permits standard and multiple expansion scales in absorbances ( $\pm 0.0001$ ) and wavelengths ( $\pm 0.1$ ), and also differential modes for measurements. It is furnished with a temperature cell-holder adapter for 1-nm cells, electrically regulated and controlled by computer; the cell compartments were maintained at  $25 \pm 0.01$  °C. Volumetric manipulations were made with solutions thermostated at  $25 \pm 0.01$  °C with a Grant LTD 6 circulator. The reference cell contained

the same solvent as the sample under measurement. The stability of the solutions utilized for measurements was assessed by recording UV-visible spectral curves after several days and comparing them with the original curves. Control of ionic strength was not necessary, since this factor is included in the excess acidity function method;<sup>7</sup> acidity constants were calculated by extrapolation to infinite dilution.

## RESULTS AND DISCUSSION

Attempts have been made to solve the problem concerning the use of acidity functions in the calculation of the acidity constants of weak bases, whose ionization equilibria may be expressed as



and the corresponding acidity constants as

$$pK_{BH^+} = \log I - \log C_{H^+} - \log f_{B}f_{H^+}/f_{BH^+} \quad (2)$$

Values of ionization ratios  $I = C_{BH^+}/C_B$  of the seven moderately weak bases were measured at different perchloric acid concentrations, as already described<sup>3</sup>

Table 1. Absorbances ( $A$ ) measured and values of excess acidity functions ( $X$ ,  $X_0$ ,  $M_c$ ) and ionization ratios ( $\log I$ ) calculated in media of increasing perchloric acid concentration ( $C_{H^+}$  and %, w/w)

Base <sup>a</sup>	$A$	$C_{H^+}$ (M)	$C_{H^+}$ (%, w/w)	Log $I$	$X$	$X_0$	$-M_c$
<i>p</i> -Nitroaniline (378 nm)	2.275	0.011	0.099	-1.089	0.0019	0.0033	-0.0019
	2.208	0.014	0.129	-0.943	0.0026	0.0043	-0.0006
	2.102	0.020	0.190	-0.769	0.0036	0.0063	0.0020
	2.006	0.025	0.241	-0.645	0.0046	0.0080	0.0042
	1.847	0.035	0.343	-0.479	0.0064	0.0114	0.0086
	1.382	0.080	0.798	-0.108	0.0145	0.0263	0.0285
	1.118	0.116	1.161	0.079	0.0209	0.0379	0.0444
	0.973	0.143	1.432	0.184	0.0260	0.0465	0.0563
	0.796	0.187	1.872	0.320	0.0340	0.0603	0.0757
	0.674	0.232	2.320	0.423	0.0420	0.0740	0.0956
	0.437	0.365	3.631	0.655	0.0658	0.1129	0.1545
	0.281	0.544	5.365	0.890	0.0991	0.1618	0.2340
	0.159	0.856	8.305	1.161	0.1740	0.2396	0.3739
	0.078	1.346	12.721	1.484	0.2970	0.3515	0.5983
	0.057	1.614	15.036	1.623	0.3713	0.4110	0.7274
	0.046	1.792	16.536	1.720	0.4246	0.4509	0.8097
	<i>o</i> -Nitroaniline (410 nm)	0.459	0.064	0.637	-1.936	0.0178	0.0210
0.455		0.082	0.818	-1.677	0.0204	0.0269	0.0294
0.442		0.118	1.181	-1.276	0.0255	0.0386	0.0453
0.433		0.148	1.482	-1.117	0.0299	0.0481	0.0585
0.407		0.234	2.340	-0.824	0.0432	0.0746	0.0965
0.377		0.368	3.660	-0.604	0.0659	0.1137	0.1558
0.333		0.546	5.384	-0.368	0.0995	0.1623	0.2349
0.268		0.858	8.323	-0.090	0.1689	0.2401	0.3749
0.195		1.349	12.747	0.204	0.3098	0.3521	0.5997
0.154		1.616	15.053	0.387	0.4068	0.4114	0.7253
0.132		1.795	16.561	0.500	0.4818	0.4516	0.8112
0.112	2.018	18.399	0.617	0.5883	0.5028	0.9203	

Table 1. (Continued)

Base <sup>a</sup>	A	CH <sup>+</sup> (M)	CH <sup>+</sup> (%, w/w)	Log I	X	X <sub>0</sub>	-M <sub>c</sub>
<i>o</i> -Aminebenzotrile (208 nm)	0.075	2.463	21.936	0.909	0.8536	0.6113	1.1459
	0.055	2.798	24.490	1.164	1.1114	0.7004	1.3239
	2.484	0.013	0.119	-1.493	0.0023	0.0040	-0.0011
	2.457	0.018	0.170	-1.338	0.0033	0.0057	0.0011
	2.379	0.028	0.272	-1.056	0.0051	0.0091	0.0055
	2.222	0.038	0.373	-0.738	0.0068	0.0134	0.0100
	2.074	0.056	0.556	-0.538	0.0101	0.0184	0.0179
	1.922	0.074	0.738	-0.376	0.0134	0.0243	0.0259
	1.706	0.110	1.101	-0.180	0.0200	0.0360	0.0417
	1.579	0.138	1.382	-0.073	0.0249	0.0449	0.0541
	1.372	0.183	1.832	0.097	0.0332	0.0590	0.0740
	1.272	0.229	2.290	0.181	0.0414	0.0731	0.0943
	0.994	0.365	3.631	0.441	0.0657	0.1129	0.1545
	0.796	0.547	5.393	0.680	0.0998	0.1625	0.2354
	0.637	0.865	8.388	0.965	0.1723	0.2418	0.3779
	0.513	1.365	12.887	1.390	0.3030	0.3557	0.6071
	0.483	1.638	15.240	1.588	0.3781	0.4164	0.7358
<i>o</i> -Phenylenediamine (280 nm)	0.211	0.056	0.556	-0.963	0.0167	0.0184	0.0179
	0.181	0.111	1.111	-0.519	0.0245	0.0363	0.0422
	0.173	0.129	1.292	-0.437	0.0271	0.0421	0.0501
	0.156	0.156	1.562	-0.281	0.0311	0.0506	0.0620
	0.127	0.202	2.022	-0.046	0.0382	0.0649	0.0824
	0.111	0.248	2.479	0.078	0.0455	0.0788	0.1027
	0.085	0.385	3.826	0.289	0.0689	0.1185	0.1634
	0.071	0.476	4.710	0.417	0.0858	0.1436	0.2038
	0.058	0.568	5.594	0.553	0.1039	0.1680	0.2447
	0.048	0.705	6.895	0.676	0.1331	0.2029	0.3060
	0.032	0.887	8.592	0.941	0.1760	0.2470	0.3879
	0.024	1.161	11.082	1.144	0.2507	0.3101	0.5127
	0.384	0.499	4.932	-1.369	0.089	0.1498	0.2140
	0.342	1.001	9.637	-0.758	0.201	0.2736	0.4396
	0.292	1.500	14.060	-0.417	0.339	0.3857	0.6704
	0.238	1.999	18.245	-0.148	0.496	0.4984	0.9109
	0.182	2.495	22.184	0.103	0.674	0.6195	1.1626
0.130	3.001	25.994	0.352	0.875	0.7582	1.4356	
0.090	3.500	29.559	0.588	1.089	0.9139	1.7240	
0.054	3.999	32.945	0.896	1.318	1.0905	2.0346	
0.030	4.505	36.208	1.267	1.564	1.2992	2.3753	
4-Chloro-2-nitroaniline (420 nm)	0.315	0.499	4.932	-1.483	0.089	0.1498	0.2140
	0.284	1.001	9.637	-0.823	0.201	0.2736	0.4396
	0.251	1.500	14.060	-0.511	0.339	0.3857	0.6704
	0.209	1.999	18.245	-0.232	0.496	0.4984	0.9109
	0.182	2.299	20.653	-0.078	0.602	0.5702	1.0604
	0.155	2.599	22.984	0.072	0.714	0.6466	1.2172
	0.129	2.899	25.242	0.220	0.833	0.7288	1.3791
	0.091	3.299	28.144	0.466	1.001	0.8487	1.6053
	0.077	3.499	29.552	0.575	1.089	0.9136	1.7234
	0.045	3.999	32.945	0.916	1.318	1.0905	2.0346
2-Chloro-5-nitroaniline (272 nm)	0.149	0.060	0.596	-1.267	0.009	0.0197	0.0197
	0.201	0.200	2.002	-0.204	0.033	0.0643	0.0815
	0.233	0.400	3.973	0.158	0.070	0.1228	0.1700
	0.252	0.601	5.909	0.392	0.111	0.1766	0.2594
	0.261	0.749	7.308	0.523	0.142	0.2138	0.3257
	0.267	0.849	8.240	0.623	0.164	0.2380	0.3707
	0.275	1.001	9.637	0.784	0.201	0.2736	0.4396
	0.287	1.500	14.060	1.164	0.339	0.3857	0.6704

<sup>a</sup> The absorption maxima for readings are given in parentheses.

(Table 1). Although distinct thermodynamic equations can be used at present to calculate  $pK_{BH^+}$  of weak bases outside the pH scale, those pioneered by Marziano and co-workers<sup>4</sup> [equation (3)] and Cox and Yates<sup>5</sup> [equation (4)] are the most commonly used in non-ideal media and constitute the excess acidity method:

$$\log I - \log C_{H^+} = -n_{ij}M_c + pK_{BH^+} \quad (3)$$

$$\log I - \log C_{H^+} = m^*X + pK_{BH^+} \quad (4)$$

where  $n_{ij}$  and  $m^*$ , the slope parameters, represent the sensitivity of the bases to the changing acidity.

Equations (3) and (4) are basically the same, although the functions  $X$  and  $M_c$ , termed excess acidity functions, have different values at the same acid concentration; they represent the difference between the observed acidity and that which the system would have if it were ideal,<sup>5</sup> and are defined as the activity coefficient ratio term for a hypothetical standard base  $B^*$ :

$$\log f_{B^*}f_{H^+}/f_{BH^+} = k \log f_{B^*}f_{H^+}/f_{B^*H^+} \quad (5)$$

where  $k = -n_{ij}$  in equation (3) and  $k = m^*$  in equation (4). Values for  $\log f_{B^*}f_{H^+}/f_{B^*H^+} = X$  (or  $M_c$ ) as functions of perchloric acid concentration were reported by both groups at different levels of refinement.<sup>4,5a</sup> Subsequently, Cox and Yates calculated an improved function,  $X_0$  for perchloric acid,<sup>5b</sup> the behaviour of which with equation (4) is also discussed in this work.

Table 1 contains all the values  $X$ ,  $X_0$  and  $M_c$  necessary for  $pK_{BH^+}$  calculation. Despite the fact that these values differ at the same mineral acid concentration, they lead to very close final results; thus,

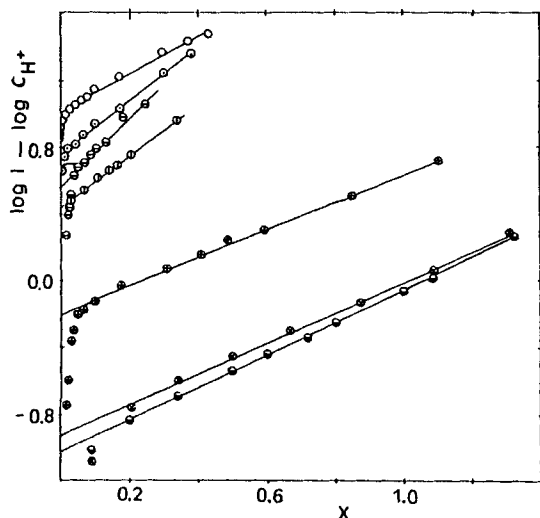


Figure 1. Plots of  $\log I - \log C_{H^+}$ , against  $X$  for (○) *p*-nitroaniline, (⊕) *o*-nitroaniline, (○) *o*-phenylenediamine, (⊙) *o*-aminobenzonitrile, (⊗) 2-chloro-4-nitroaniline, (○) 4-chloro-2-nitroaniline and (○) 2-chloro-5-nitroaniline

Figure 1 shows plots of  $\log I - \log C_{H^+}$  against  $X$  for the set of bases studied, but similar results would have been attained by plotting against  $X_0$  or  $M_c$ .

Noticeable deviations with respect to ideal behaviour were observed at the lowest acidities; deviations from the linearities predicted by equations (3) and (4) begin at acidities within the range 0.25–5% (w/w) perchloric acid, depending on the structure of the base. Bases such as *p*-nitroaniline, *o*-nitroaniline, *p*-aminobenzonitrile and *o*-phenylenediamine become considerably protonated at acidities below 5%, as can be inferred from the corresponding ionization ratios. Figure 2 shows the spectral curves for *p*-nitroaniline from which ionization ratios were measured. Extrapolation of the straight portions at the highest acidities of each curve (Figure 1) yielded intercepts coincident with the  $pK_{BH^+}$  of the bases, regardless of what acidity function was used; therefore equations (3) and (4) apply fairly well within these portions. On the other hand,  $\log I - \log C_{H^+}$  is also linearly related to molar acid concentrations within the same portions of the curves, which implies the fulfilment of the relationship

$$\log f_{B^*}f_{H^+}/f_{BH^+} = bC_{H^+} \quad (6)$$

and hence

$$\log I - \log C_{H^+} = pK_{BH^+} + bC_{H^+} \quad (7)$$

where  $pK_{BH^+}$  is extracted directly from the intercept of equation (7). Table 2 (top) lists the values of  $pK_{BH^+}$  calculated according to equations (3), (4) and (7).

None of the above-mentioned equations was fulfilled in dilute aqueous acid solutions, the behaviour being better described by second-order polynomials of the type

$$\log I - \log C_{H^+} = a_0 + a_1Y + a_2Y^2 \quad (8)$$

where  $Y = X, X_0$  or  $M_c$ . Table 2 (bottom) gives the coefficients and parameters calculated for the seven bases by least-squares fitting of equation (8).

A second-order approximation (where  $a_0 = pK_{BH^+}$ ,  $a_1 = m^*$  and  $a_2 = m^{**}$ ) requiring two main factors to explain the experimental data was suggested by Edward *et al.*,<sup>8</sup> who considered that first-order approximations were, in the limit, inaccurate. However, Traverso<sup>9</sup> pointed out that the second-order terms,  $m^{**}Y^2$ , were necessary, at least for sulphuric and perchloric acid media. Moreover, a simple interpretation of equation (8) cannot be made, since the parameters  $a_0$  should coincide with  $pK_{BH^+}$ , but they did not with the bases investigated in this work.

A plausible explanation of the deviations observed at the lowest acidities is difficult. The non-fulfilment of equations (3) and (4) could be first attributed to incorrect measurements of ionization ratios at the lowest acidities; nevertheless, this suggestion should be rejected, since the sets of spectral curves (Figure 2 is a representative example only, and is valid for all the other bases) upon which ionization ratios were measured displayed

Table 2. Acidity constants,  $pK_{BH^+}$ , and standard deviations calculated with different equations, and coefficients and statistical parameters of equation (8) calculated by the least squares method [ $N$  = number of data points,  $R$  = linear correlation coefficient;  $S(y)$  = standard deviation, % =  $HClO_4$  percentage (w/w) below which the fittings were made]

Equation/ parameter	<i>p</i> -Nitroaniline	<i>o</i> -Nitroaniline	<i>o</i> -Phenylene diamine	<i>o</i> -Aminobenzo nitrile	2-Chloro-4- nitroaniline	4-Chloro-2- nitroaniline	2-Chloro-5- nitroaniline
Equation (4) <sup>a</sup> :	1.012 ± 0.008	-0.200 ± 0.014	0.581 ± 0.011	0.736 ± 0.008	-0.942 ± 0.026	-1.121 ± 0.046	0.437 ± 0.009
Equation (4) <sup>b</sup> :	0.967 ± 0.003	-0.300 ± 0.030	0.510 ± 0.028	0.715 ± 0.014	-1.108 ± 0.019	-1.298 ± 0.037	0.360 ± 0.029
Equation (3) <sup>c</sup> :	0.991 ± 0.020	-0.239 ± 0.013	0.660 ± 0.014	0.744 ± 0.008	-1.073 ± 0.032	-1.239 ± 0.039	0.404 ± 0.017
Equation (7):	0.994 ± 0.002	-0.276 ± 0.016	0.581 ± 0.011	0.736 ± 0.008	-1.088 ± 0.030	-1.175 ± 0.026	0.412 ± 0.010
Ref. 3:	1.003 ± 0.020	-0.282 ± 0.018	0.581 ± 0.011	0.736 ± 0.008	-0.967 ± 0.032	-1.030 ± 0.042	0.446 ± 0.027
$a_0$	0.812	-2.940	-0.073	0.280			
$a_1$	36.08	173	24.79	44.60			
$a_2$	-1680	-2829	-181.6	-626.8			
$N$	6	4	4	5			
$R$	0.9981	0.9990	0.9947	0.9960			
$S(y)$	0.003	0.017	0.017	0.020			
$\%_0$	0.798	1.482	1.562	0.738			

<sup>a</sup> Using excess function  $X_1$ .

<sup>b</sup> Using excess function  $X_0$ .

<sup>c</sup> Using excess function  $-M_c$ .

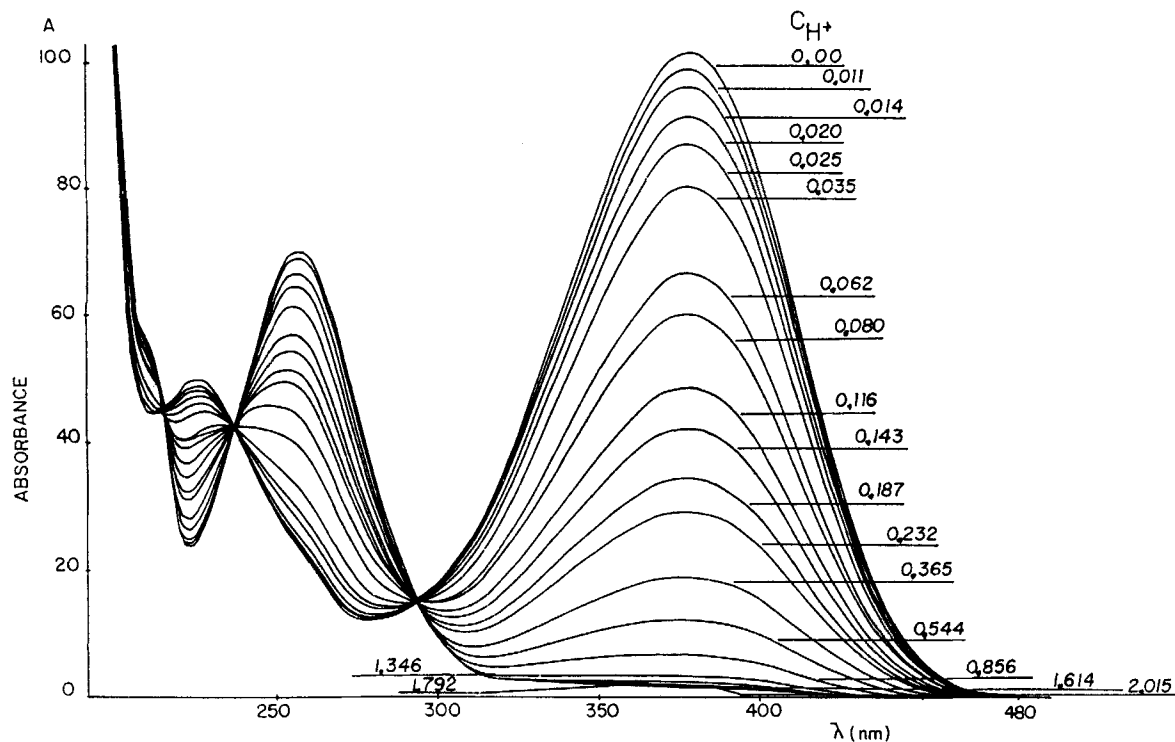


Figure 2. UV-visible absorption spectra of *p*-nitroaniline as a function of perchloric acid molarity,  $C_{H^+}$

clearly defined isosbestic points and, according to Arnett,<sup>10</sup> should lead to fairly good results. It could well happen, however, that the accuracy of the readings of absorbances was poorer at lower acidities, but this was not so, as is evident from Figure 2: at 378 nm the absorbance of *p*-nitroaniline became larger at low perchloric acid molarities (free base), being negligible at the highest concentrations (fully protonated base). Thus, the greatest deviations with respect to the predicted behaviour were found below 0.080 M perchloric acid just the acidity range where the accuracy and reproducibility of absorbance measurements were best.

It seems reasonable, therefore, to ascribe the origin of the anomalous behaviour of the bases investigated to a lack of continuity of the acidity functions utilized from high- and medium-acidity regions, where they apply successfully, to low-acidity regions, where they overlap with the pH scale. The point at which such a discontinuity occurs is dependent on the acidity function utilized and also on the structure of the base and/or on the protonation site. Kresge *et al.*<sup>11</sup> concluded that extrapolation of measurements made in concentrated acids down to dilute solutions yields best results with  $X_0$  up to 5%, whereas  $X$  and  $M_c$  displayed noticeable curvature, leading to incorrect results. Our own results support these observations, even though we found only

small differences among the behaviours of these excess functions.

All these findings are amenable to a qualitative interpretation in the light of the contributions of Buijs and Choppin<sup>12</sup> and Draeger and Williams,<sup>13</sup> who attribute to  $ClO_4^-$  ions the property of breaking the hydrogen bonds of water, since the number of hydrogen bonds existing in solution decreases with increasing acidity; this was not taken into account in the relationships that define  $X$ ,  $X_0$  and  $M_c$ . The parameters  $n_{ij}$  and  $m^*$ , characteristic of each base, have been interpreted in terms of solvation;<sup>14,15</sup> however, the variation in the degree of hydration starts to overlap at acidity levels of about 0.1 M perchloric acid (1%, w/w).<sup>16</sup>

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