CONSTRUCTION OF INTERCONNECTED ACIDITY FUNCTIONS BASED ON *ortho* SUBSTITUTED ANILINES AND *N*-METHYLANILINES AS INDICATORS

Oldřich PYTELA[a1,]*, Jiří KULHÁNEK[a2], Eva JIRÁSKOVÁ[b1] and Taťjana NEVĚČNÁ[b2]

[a] *Department of Organic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: [1] oldrich.pytela@upce.cz, [2] jiri.kulhanek@upce.cz*

[b] *Department of Inorganic and Physical Chemistry, Palacký University Olomouc, 771 46 Olomouc, Czech Republic; e-mail: [1] jiraskova@prfnw.upol.cz, [2] nevecna@prfnw.upol.cz*

The log I values of 15 mainly *ortho* substituted derivatives of aniline and *N*-methylaniline have been measured spectrophotometrically in sulfuric, perchloric, and methanesulfonic acids. A new algorithm has been suggested for construction of acidity functions enabling simultaneous and independent construction of acidity functions in various media under the condition of equal values of pK_a of the same indicators in the given media. The so-called interconnected acidity functions have been constructed with using this algorithm and the log I values measured in the above media, and the pK_a values have been calculated. The resulting acidity functions and pK_a values agree well with the corresponding literature data.
Keywords: Acidity functions; Basicity; Amines; Anilines; *N*-Methylanilines; *ortho*-Effect; Substituent effects.

The determination of dissociation constants of weak bases by means of construction of acidity functions[1,2] is one of commonly adopted procedures. The formal definition of acidity function H as a difference between the pK_a value of an indicator (weak base) and logarithm of the concentration ratio of its protonated and nonprotonated forms, log I, at a given concentration of the protonating acid is quite simple (Eq. (*1*)).

$$H = pK_a - \log I \qquad (1)$$

The physico-chemical interpretation of acidity function as a function of concentration of the protonating acid (and/or its components[3]) and the indicator used is far more complicated[2,4–19]. Nevertheless, given a series of indicators fulfilling certain conditions (*e.g.* refs[2,4]), it is possible to experimentally obtain the I values of Eq. (*1*) and construct the acidity function as

a function of concentration of the respective acid (for a survey of algorithms, see, *e.g.*, ref.[20]). Subsequently, with help of Eq. (*1*), it is possible to calculate the pK_a values of the used indicators from the acidity function obtained and the experimental log *I* values. The pK_a values can also be determined, without constructing the acidity function, using the generalised acidity functions (excess acidity[6]) based on the similarity principle (Bunnett and Olsen[7], Marziano *et al.*[8–16], Cox *et al.*[17–19]). However, the pK_a values evaluated by various procedures differ, the differences being as high as in units[6,21–23]. The classic way of calculation of dissociation constants using of construction of the respective acidity function is probably more suitable for series of indicators of the same or similar chemical structures. This is particularly true with respect to a closer fit between the experimental log *I* values and the constructed acidity function in the respective concentration interval. The procedure has a drawback in the fact that the acidity function is constructed *per partes* with possible cumulated error for higher concentrations of acid. This drawback is not encountered in a procedure using the excess acidity functions[6,8–19], which is more general and easier for calculation. An advantage is the possibility of obtaining individual pK_a values of weak bases whereas a drawback is a potentially less close fit of the dependence of log *I* on the values of the generalised acidity function because of specific properties of the system measured.

Another complicating factor is the dependence of the pK_a values of weak bases on the protonating acid in the given medium. In spite of the fact that according to its thermodynamic definition the pK_a value should be independent of the acid used, the resulting values differ – sometimes even quite substantially – due to experimental method and the above-mentioned way of evaluation[8,11,13,16,22,24,25]. The correctness of the pK_a values obtained by means of various acidity functions can thus be hard to compare, and the process of taking the average value of data from different sources needs not always represent the best solution. The results obtained usually cannot be adopted in further interpretation, *e.g.*, in studies of effect of structure upon dissociation by means of correlation relationships. It can be expected that a pK_a value independent of the acid used will be accessible by measurements in a series of different acids with the presumption that suitable processing of experimental data will allow elimination of specific properties of the acids. The resulting acidity functions defined for a given series of indicators will then fulfil the above-given condition *viz.* they will provide the pK_a values independent of the acid used. Such presumption has not been formulated and the corresponding calculation procedure has not been suggested yet.

The aim of this paper is to suggest and verify the new calculation algorithm for the pK_a values independent of medium by means of constructing specific acidity functions referred to as "interconnected acidity functions". For verification of the procedure suggested, we have chosen suitable (predominantly *ortho*) substituted anilines and *N*-methylanilines and the media of sulfuric, perchloric and methanesulfonic acids. The calculation also includes the experimental values of log *I* obtained in the previous work[27] which only dealt with the dissociation constants of *ortho* substituted anilines in perchloric acid.

THEORETICAL AND CALCULATIONS

When evaluating pK_a values of weak bases in strongly acidic media, one always works with the same set of three quantities. The first is the pK_a value, which is a function of the indicator (weak base), temperature and medium. Both the indicator and temperature are defined unambiguously, while the properties of medium continuously change with changing concentration of the strong protonating acid. In order to approach the thermodynamic conception of dissociation constant as close as possible, it is advisable to define it in such a way as to depend on the solvent used (most often water) but not on the acid used and its concentration. This approach has been adopted in the present paper. The second quantity is the ratio of the protonated and nonprotonated forms of the indicator referred to as *I*. This quantity depends on the indicator, the protonating acid used and its concentration. The last quantity is a certain characteristic of acidity of medium (the acidity function *H* or the concentration of acid in combination with the excess acidity function): this quantity depends on the protonating acid and its concentration and (in the case of acidity function) also on the indicator. With regard to the above-mentioned requirement of independence of pK_a value upon the acid and its concentration, the characteristic of acidity of medium must include the activity coefficients of components of medium as well as those of both forms of the indicator. From among the quantities mentioned, experimentally accessible is the value of concentration ratio of protonated and nonprotonated forms of indicator (*I* or log *I*); also known are the type and concentration of the acid (or, as the case may be, the excess acidity function for the given acid too) and, of course, the indicator used.

If the log *I* values of the same indicators measured in various protonating acids are available, then it is possible – under the condition of medium-independence of dissociation constant – to construct simultaneously the

individual acidity functions in all the media by means of the iteration algorithm described elsewhere[20]. This algorithm was derived from Eq. (*1*) and is based on three operations in each iteration step In the first operation, the average of log I values of all the indicators is calculated for the same concentrations of acid. This provides an acidity function depending on concentration. The second operation consists in calculating (for each indicator) the average distances of log I values from the acidity function thus constructed, *i.e.* the pK_a values. In the last operation, the pK_a values of each indicator are changed (shifted) by the calculated pK_a value and used again in the first operation. The iteration calculation is finished if the maximum change is smaller than a chosen small number. The described algorithm[20] has been modified in the present work by including (into the second operation of each iteration step) the procedure of taking the average of pK_a values for the same indicator. Thereby the values of acidity functions in the individual acids are interconnected and the result is the "bound" acidity functions.

EXPERIMENTAL

Chemicals

The syntheses of 2,6-dichloroaniline, 2-nitroaniline, 2-methyl-6-nitroaniline, 4-chloro-2-nitroaniline, 2-chloro-6-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 2,6-dinitroaniline were described in an earlier paper[27]. 2-Methoxy-6-nitroaniline was synthesized[28] in 48% yield by 6-h heating of ethanolic solution of 1-methoxy-2,3-dinitrobenzene[28] with excess 20% aqueous ammonia in a sealed ampoule at 160 °C. A similar procedure was adopted for the *N*-methyl derivative by using aqueous methylamine (yield 32%). 2,5-Dichloro-4-nitroaniline was obtained[29] in 52% yield by nitration of 2,5-dichloroacetanilide and subsequent hydrolysis. *N*-Methyl-2-nitroaniline and *N*-methyl-4-nitroaniline were prepared[30] by 6-h heating of ethanolic 1-chloro-2-nitrobenzene and 1-chloro-4-nitrobenzene, respectively, with methylamine in a sealed ampoule at 130 °C (practical yields 60 and 79%, respectively). *N*-Methyl-2-chloro-6-nitroaniline was obtained[31] in 65% yield by 15-h heating ethanolic 1,2-dichloro-3-nitrobenzene[32] with methylamine in a sealed ampoule at 150 °C. *N*-Methyl-2,6-dinitroaniline was synthesised in 42% yield by heating 2-chloro-1,3-dinitrobenzene with methylamine[33].

The synthesised derivatives were identified by means of NMR spectrometry (360 MHz, Bruker). Their purity was checked by GC/MS analysis (GCQ-tandem, Finnigan). The other anilines used were commercial products (Fluka Chemie AG). Before measurements, the anilines were purified by recrystallisation from ethanol (2-NO$_2$, 2-CH$_3$-6-NO$_2$, 2,4-diNO$_2$, 2,6-diNO$_2$, *N*-CH$_3$-4-NO$_2$) or aqueous ethanol (2-OCH$_3$-6-NO$_2$, *N*-CH$_3$-2-NO$_2$, *N*-CH$_3$-2,6-diNO$_2$). 2,5-Dichloro-4-nitroaniline was recrystallised from 50% acetic acid. The other anilines were recrystallised from hexane. Perchloric acid (Carlo Erba – Chímica Milano, pa.), sulfuric acid (Lachema Neratovice, pa.), methanesulfonic acid (Sigma–Aldrich), sodium hydroxide

(Lachema Neratovice, pa.), and methanol (Lachema Neratovice, for UV) were used without purification.

Measurement of Concentration Ratio of Protonated and Non-Protonated Forms of Indicators

The measurements were carried out spectrophotometrically using an SP 8-100 (Pye Unicam) and a DU 7500 (Beckman) apparatus. Exact concentrations of perchloric, sulfuric, and methanesulfonic acids were determined alkalimetrically. The concentrations of stock solutions of the individual substituted anilines in methanol were 10^{-1}–10^{-2} mol dm^{-3}. From the stock solutions, 0.05 cm^3 was pipetted in 25-ml calibrated flasks, they were filled up to the mark by adding the respective aqueous acid of suitable concentration, and the absorbance changes depending on concentration of protonating acid were read at the wavelength of the longest-wave maximum. Some measurements were repeated several times.

Construction of Acidity Function

The log I values were calculated from the spectral data in usual way[2]. For the construction of interconnected acidity functions using the above-described algorithm, the log I values of substituted anilines in perchloric acid were adapted given in a previous paper[27] along with the values of substituted anilines and N-methylanilines newly measured in sulfuric, perchloric and methanesulfonic acids (Tables I–III). As a standard indicator, to which the acidity functions were fixed during calculation, we adopted 2-nitroaniline with $pK_a = -0.300$ (ref.[27]). The suggested calculation algorithm was implemented by means of a program in Delphi language. The other calculations were carried out by standard statistical algorithms.

RESULTS AND DISCUSSION

Acidity Functions

The acidity functions H_0 in sulfuric, perchloric, and methanesulfonic acids constructed by the above-described algorithm from the data given in previous paper[20] and in Tables I–III are presented in Table IV. The graphical representation of dependence of H_0 on the acid concentration is in Fig. 1. The residual standard deviation $s = 0.064$ calculated from the difference between (pK_a – log I) values and H falls in a usual range[20].
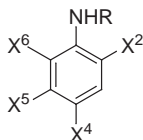
In order to verify the correctness of adjustment of values of the acidity functions and hence also the correctness of the suggested algorithm, the results were compared with the already published H_0 functions in sulfuric and perchloric acids[24,34] for the concentrations given in Table IV. The dependence obtained by regression for sulfuric acid[34] is given by Eq. (2).

$$H_0(H_2SO_4) = (0.028 \pm 0.022) + (0.985 \pm 0.006)\ H_0(H_2SO_4, \text{ref.}^{34})$$

$$s = 0.11,\ r = 0.999,\ n = 69 \tag{2}$$

T<small>ABLE</small> I
Values of log I depending on concentration of sulfuric acid in water for the studied substituted derivatives of aniline of the following general formula (the substituents not shown are hydrogens)

Substituents[a]	c (log I)
$X_2 = X_6 = Cl$	0.0470 (–1.08), 0.0789 (–0.881), 0.114 (–0.533), 0.149 (–0.464), 0.168 (–0.3), 0.195 (–0.168), 0.243 (–0.04), 0.271 (0.014), 0.289 (–0.016), 0.336 (0.061), 0.424 (0.182), 0.516 (0.229), 0.585 (0.316), 0.681 (0.474), 0.784 (0.507), 0.875 (0.602), 1.02 (0.682), 1.52 (0.989), 2.06 (1.312)
$X_2 = NO_2$ (1)	0.243 (–0.833), 0.321 (–0.632), 0.377 (–0.621), 0.424 (–0.562), 0.516 (–0.306), 0.633 (–0.212), 0.731 (–0.203), 0.828 (–0.145), 1.02 (–0.006), 1.21 (0.128), 1.36 (0.214), 1.45 (0.27), 1.52 (0.297), 1.63 (0.377), 1.77 (0.412), 1.91 (0.468), 2.06 (0.559), 2.24 (0.749), 2.42 (0.776), 2.60 (0.841), 2.83 (0.979), 2.93 (1.081), 3.22 (1.138), 4.07 (1.523), 5.22 (2.165)
$X_2 = NO_2$ (2)	0.336 (–0.716), 0.516 (–0.478), 0.633 (–0.376), 0.731 (–0.249), 0.875 (–0.106), 1.06 (–0.049), 1.14 (0.036), 1.41 (0.172), 1.52 (0.261), 1.63 (0.32), 1.84 (0.416), 1.91 (0.461), 2.06 (0.508), 2.24 (0.661), 2.42 (0.747), 2.60 (0.874), 2.93 (1.002), 5.00 (2.196)
$X_2 = NO_2$ (3)	0.219 (–0.843), 0.336 (–0.652), 0.516 (–0.374), 0.633 (–0.299), 0.731 (–0.245), 0.875 (–0.098), 1.06 (0.003), 1.14 (0.077), 1.41 (0.22), 1.52 (0.281), 1.63 (0.315), 1.84 (0.447), 1.91 (0.491), 2.06 (0.545), 2.24 (0.688), 2.42 (0.775), 2.60 (0.831), 2.93 (1.02), 5.00 (2.293)
$X_2 = CH_3O$, $X_6 = NO_2$ (1)	0.336 (–0.75), 0.424 (–0.709), 0.516 (–0.596), 0.681 (–0.453), 0.784 (–0.372), 0.875 (–0.261), 1.02 (–0.224), 1.12 (–0.187), 1.36 (–0.073), 1.52 (0.071), 1.63 (0.142), 1.73 (0.184), 1.84 (0.247), 1.91 (0.257), 2.06 (0.322), 2.24 (0.465), 2.55 (0.628), 2.93 (0.888)
$X_2 = CH_3O$, $X_6 = NO_2$ (2)	0.321 (–0.869), 0.424 (–0.745), 0.516 (–0.56), 0.585 (–0.525), 0.681 (–0.456), 0.784 (–0.342), 0.828 (–0.327), 0.875 (–0.293), 1.02 (–0.223), 1.12 (–0.133), 1.25 (–0.087), 1.36 (–0.022), 1.45 (0.061), 1.52 (0.093), 1.63 (0.118), 1.69 (0.17), 1.73 (0.176), 1.77 (0.213), 1.89 (0.29), 1.92 (0.304), 2.06 (0.319), 2.12 (0.447), 2.24 (0.479), 2.47 (0.582), 2.55 (0.642), 2.93 (0.845)

TABLE I
(*Continued*)

Substituents[a]	c (log I)
$X_2 = CH_3$, $X_6 = NO_2$	0.424 (–1.088), 0.516 (–0.911), 0.585 (–0.781), 0.681 (–0.716), 0.784 (–0.606), 0.828 (–0.597), 0.875 (–0.559), 1.02 (–0.487), 1.12 (–0.418), 1.25 (–0.322), 1.36 (–0.27), 1.45 (–0.115), 1.52 (–0.157), 1.63 (–0.089), 1.69 (–0.038), 1.73 (–0.044), 1.77 (0.024), 1.89 (0.066), 1.92 (0.129), 2.06 (0.157), 2.12 (0.238), 2.24 (0.223), 2.47 (0.38), 2.55 (0.392), 2.93 (0.594)
$X_2 = NO_2$, $X_4 = Cl$ (1)	0.516 (–1.358), 0.784 (–0.979), 1.02 (–0.947), 1.21 (–0.646), 1.41 (–0.468), 1.58 (–0.398), 1.84 (–0.255), 2.06 (–0.146), 2.16 (–0.046), 2.39 (0.051), 2.53 (0.073), 2.72 (0.166), 2.88 (0.248), 2.93 (0.256), 3.22 (0.431), 3.44 (0.483)
$X_2 = NO_2$, $X_4 = Cl$ (2)	0.516 (–1.225), 0.784 (–0.967), 1.02 (–0.839), 1.21 (–0.547), 1.41 (–0.531), 1.58 (–0.376), 1.84 (–0.177), 2.06 (–0.131), 2.16 (–0.094), 2.39 (–0.007), 2.53 (0.084), 2.72 (0.221), 2.88 (0.241), 2.93 (0.296), 3.22 (0.378)
$X_2 = NO_2$, $X_4 = Cl$ (3)	1.02 (–0.82), 1.21 (–0.73), 1.41 (–0.65), 1.58 (–0.602), 1.73 (–0.521), 1.84 (–0.384), 2.06 (–0.312), 2.16 (–0.17), 2.39 (–0.087), 2.53 (–0.013), 2.72 (0.054), 2.88 (0.116), 2.93 (0.15), 3.22 (0.26), 3.44 (0.387)
$X_2 = NO_2$, $X_4 = Cl$ (4)	0.516 (–1.236), 1.02 (–0.783), 1.21 (–0.71), 1.41 (–0.6), 1.58 (–0.547), 1.73 (–0.467), 1.84 (–0.359), 2.06 (–0.294), 2.16 (–0.145), 2.39 (–0.063), 2.53 (–0.028), 2.72 (0.093), 2.88 (0.134), 2.93 (0.163), 3.22 (0.306), 3.44 (0.402)
$X_2 = X_5 = Cl$, $X_4 = NO_2$	2.24 (–0.778), 2.47 (–0.72), 2.55 (–0.628), 2.72 (–0.51), 2.83 (–0.461), 2.93 (–0.412), 3.44 (–0.15), 3.59 (–0.108), 3.80 (–0.035), 4.07 (0.058), 4.20 (0.164), 4.40 (0.214), 4.69 (0.329), 5.07 (0.528), 5.22 (0.572), 5.94 (0.919)
$X_2 = Cl$, $X_6 = NO_2$ (1)	3.59 (–0.733), 4.07 (–0.668), 4.20 (–0.554), 4.40 (–0.384), 4.69 (–0.206), 5.07 (–0.237), 5.22 (0.017), 5.46 (0.101), 5.64 (0.158), 5.94 (0.324), 6.13 (0.387), 6.36 (0.53), 6.74 (0.726), 7.42 (1.039)
$X_2 = Cl$, $X_6 = NO_2$ (2)	3.59 (–0.78), 4.07 (–0.686), 4.20 (–0.54), 4.40 (–0.394), 4.69 (–0.242), 5.07 (–0.106), 5.22 (–0.023), 5.46 (0.063), 5.64 (0.189), 5.94 (0.32), 6.13 (0.341), 6.36 (0.512), 6.74 (0.692), 7.42 (1.03)
$X_2 = X_4 = Cl$, $X_6 = NO_2$ (1)	4.20 (–1.225), 4.69 (–1.112), 5.00 (–0.749), 5.22 (–0.743), 5.46 (–0.652), 5.64 (–0.626), 5.94 (–0.5), 6.13 (–0.359), 6.36 (–0.267), 6.55 (–0.206), 6.74 (–0.078), 6.96 (–0.02), 7.19 (0.129), 7.42 (0.242), 7.57 (0.309), 7.72 (0.375), 8.13 (0.518), 8.48 (0.687), 9.15 (1.03)

TABLE I
(*Continued*)

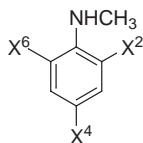| Substituents[a]	c (log I)
$X_2 = X_4 = Cl$, $X_6 = NO_2$ (2)	4.69 (–1), 5.00 (–0.99), 5.22 (–0.777), 5.46 (–0.665), 5.64 (–0.563), 5.94 (–0.43), 6.13 (–0.434), 6.36 (–0.265), 6.55 (–0.207), 6.74 (–0.052), 6.96 (–0.049), 7.19 (0.076), 7.42 (0.137), 7.57 (0.247), 7.72 (0.368), 8.13 (0.452), 8.48 (0.665), 9.15 (1.042)
$X_2 = X_4 = NO_2$ (1)	6.36 (–1.275), 6.74 (–1.133), 7.42 (–0.895), 7.77 (–0.688), 8.13 (–0.55), 8.48 (–0.355), 8.81 (–0.239), 8.92 (–0.156), 9.02 (–0.081), 9.15 (–0.113), 9.35 (0.065), 9.56 (0.209), 9.70 (0.267), 9.85 (0.349), 10.01 (0.397), 10.17 (0.472), 10.51 (0.7), 10.95 (1.045), 11.44 (1.161)
$X_2 = X_4 = NO_2$ (2)	7.77 (–0.831), 8.13 (–0.614), 8.48 (–0.398), 8.64 (–0.372), 8.81 (–0.37), 8.92 (–0.217), 9.02 (–0.123), 9.15 (–0.15), 9.35 (0.033), 9.56 (0.179), 9.70 (0.24), 9.85 (0.319), 10.01 (0.381), 10.17 (0.416), 10.51 (0.694), 10.95 (1.034), 11.44 (1.159)
$X_2 = X_6 = NO_2$ (1)	9.85 (–0.898), 10.17 (–0.714), 10.25 (–0.67), 10.32 (–0.423), 10.51 (–0.381), 10.69 (–0.212), 10.73 (–0.208), 10.95 (0.004), 11.19 (0.132), 11.44 (0.172), 11.63 (0.288), 11.73 (0.42), 11.93 (0.619), 12.38 (0.854), 12.60 (1.144)
$X_2 = X_6 = NO_2$ (2)	9.85 (–0.929), 10.17 (–0.785), 10.25 (–0.526), 10.32 (–0.431), 10.51 (–0.431), 10.69 (–0.236), 10.73 (–0.22), 10.95 (0.013), 11.19 (0.113), 11.44 (0.154), 11.63 (0.322), 11.73 (0.397), 11.93 (0.576), 12.38 (0.874), 12.60 (1.16)
$R = CH_3$, $X_2 = Cl$, $X_6 = NO_2$ (1)	0.0310 (–1.075), 0.0413 (–0.711), 0.0470 (–0.443), 0.0789 (–0.146), 0.0960 (–0.086), 0.149 (0.084), 0.195 (0.124), 0.243 (0.181), 0.289 (0.28), 0.424 (0.482), 0.516 (0.563), 1.02 (0.967)
$R = CH_3$, $X_2 = Cl$, $X_6 = NO_2$ (2)	0.0310 (–1.038), 0.0413 (–0.764), 0.0470 (–0.403), 0.0789 (–0.151), 0.0960 (–0.178), 0.149 (0.066), 0.195 (0.146), 0.243 (0.2), 0.289 (0.29), 0.424 (0.469), 0.516 (0.519), 1.02 (0.945)
$R = CH_3$, $X_2 = Cl$, $X_6 = NO_2$ (3)	0.0470 (–0.691), 0.0641 (–0.524), 0.0789 (–0.368), 0.0960 (–0.193), 0.149 (–0.041), 0.195 (0.029), 0.243 (0.14), 0.289 (0.265), 0.336 (0.313), 0.424 (0.465), 0.516 (0.552), 0.585 (0.67), 0.784 (0.84), 1.02 (1.094), 2.06 (1.636)
$R = CH_3$, $X_2 = Cl$, $X6 = NO_2$ (4)	0.0789 (–0.277), 0.0960 (–0.295), 0.149 (–0.102), 0.195 (0.026), 0.243 (0.126), 0.289 (0.23), 0.336 (0.432), 0.424 (0.397), 0.516 (0.605), 0.585 (0.65), 0.784 (0.798), 1.02 (1.021), 2.06 (1.588)

Substituents[a]	c (log I)
$R = CH_3$, $X_4 = NO_2$ (1)	0.0470 (–0.617), 0.0960 (–0.341), 0.131 (–0.228), 0.168 (–0.133), 0.219 (–0.002), 0.271 (0.151), 0.321 (0.249), 0.377 (0.281), 0.424 (0.366), 0.516 (0.471), 0.585 (0.519), 0.681 (0.647), 0.784 (0.728), 0.875 (0.821), 1.02 (0.894), 1.06 (0.912), 1.12 (0.949), 1.14 (0.959)
$R = CH_3$, $X_4 = NO_2$ (2)	0.0470 (–0.566), 0.0960 (–0.317), 0.131 (–0.222), 0.168 (–0.091), 0.219 (0.064), 0.271 (0.19), 0.321 (0.265), 0.377 (0.314), 0.424 (0.36), 0.516 (0.523), 0.585 (0.571), 0.681 (0.673), 0.784 (0.721), 0.875 (0.79), 1.02 (0.905), 1.06 (0.918), 1.12 (0.964), 1.14 (0.983)
$R = CH_3$, $X_2 = NO_2$ (1)	0.219 (–1.148), 0.516 (–0.738), 0.731 (–0.546), 0.828 (–0.413), 1.02 (–0.32), 1.12 (–0.247), 1.21 (–0.187), 1.36 (–0.062), 1.45 (–0.004), 1.52 (0.022), 1.63 (0.115), 1.77 (0.202), 1.91 (0.256), 2.06 (0.348), 2.24 (0.48), 2.42 (0.62), 2.60 (0.727), 2.83 (0.827), 2.93 (0.876), 3.22 (1.062), 4.07 (1.578)
$R = CH_3$, $X_2 = NO_2$ (2)	0.336 (–1.034), 0.424 (–0.881), 0.585 (–0.706), 0.784 (–0.465), 1.02 (–0.292), 1.12 (–0.242), 1.31 (–0.103), 1.58 (0.062), 1.77 (0.187), 1.92 (0.324), 2.24 (0.536), 2.60 (0.713), 2.83 (0.868), 2.93 (0.868), 3.22 (0.985), 3.44 (1.26), 3.59 (1.26), 3.80 (1.371), 4.07 (1.532)
$R = CH_3$, $X_2 = NO_2$ (3)	0.336 (–0.782), 0.424 (–0.686), 0.784 (–0.394), 1.02 (–0.218), 1.12 (–0.112), 1.31 (–0.034), 1.58 (0.085), 1.77 (0.213), 1.92 (0.348), 2.24 (0.548), 2.60 (0.725), 2.83 (0.878), 2.93 (0.933), 3.22 (1.094), 3.44 (1.228), 3.59 (1.301), 3.80 (1.376), 4.07 (1.525)
$R = CH_3$, $X_2 = NO_2$ (4)	0.336 (–0.729), 0.424 (–0.746), 0.784 (–0.383), 1.02 (–0.249), 1.12 (–0.15), 1.31 (–0.042), 1.58 (0.087), 1.77 (0.216), 1.92 (0.372), 2.24 (0.566), 2.60 (0.757), 2.83 (0.888), 2.93 (0.949), 3.22 (1.104), 3.44 (1.242), 3.59 (1.318), 3.80 (1.397), 4.07 (1.507)
$R = CH_3$, $X_2 = X_6 = NO_2$	2.24 (–1.162), 2.60 (–0.796), 2.83 (–0.695), 2.93 (–0.681), 3.22 (–0.536), 3.44 (–0.525), 3.59 (–0.554), 3.80 (–0.404), 4.07 (–0.257), 4.20 (–0.235), 4.40 (–0.197), 4.69 (0.022), 5.07 (0.324)

[a] The numbers in brackets denote the order of repeated measurements, if any.

Values of log I depending on concentration of perchloric acid in water for the studied substituted derivatives of aniline of the following general formula (the substituents not shown are hydrogens)
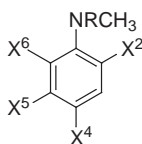

Substituents[a]	c (log I)
X_2 = Cl, X_6 = NO_2 (1)	0.0483 (–0.397), 0.0748 (–0.175), 0.0972 (–0.113), 0.120 (0.038), 0.148 (0.185), 0.181 (0.26), 0.214 (0.387), 0.250 (0.414), 0.280 (0.476), 0.328 (0.522), 0.369 (0.655), 0.412 (0.697), 0.566 (0.904), 0.723 (1.056)
X_2 = Cl, X_6 = NO_2 (2)	0.0483 (–0.317), 0.0748 (–0.168), 0.0972 (–0.062), 0.120 (0.01), 0.148 (0.17), 0.181 (0.252), 0.214 (0.362), 0.250 (0.424), 0.280 (0.517), 0.328 (0.568), 0.369 (0.644), 0.412 (0.726), 0.566 (0.939)
X_4 = NO_2 (1)	0.0154 (–1.223), 0.0337 (–0.833), 0.0748 (–0.523), 0.120 (–0.312), 0.148 (–0.161), 0.181 (–0.081), 0.214 (0.008), 0.250 (0.098), 0.280 (0.191), 0.328 (0.271), 0.412 (0.373), 0.475 (0.513), 0.606 (0.602)
X_4 = NO_2 (2)	0.0154 (–1.22), 0.0337 (–0.837), 0.0748 (–0.504), 0.120 (–0.317), 0.148 (–0.193), 0.181 (–0.065), 0.214 (0.029), 0.250 (0.094), 0.280 (0.19), 0.328 (0.263), 0.412 (0.379), 0.475 (0.494), 0.606 (0.612)
X_2 = NO_2 (1)	0.369 (–0.88), 0.566 (–0.649), 0.723 (–0.502), 0.896 (–0.302), 1.06 (–0.247), 1.2 (–0.117), 1.31 (–0.04), 1.39 (0.03), 1.55 (0.089), 1.65 (0.197), 1.76 (0.265), 1.88 (0.31), 2.04 (0.354), 2.15 (0.417), 2.42 (0.553)
X_2 = NO_2 (2)	0.214 (–1.055), 0.566 (–0.59), 0.723 (–0.494), 0.896 (–0.281), 1.06 (–0.201), 1.2 (–0.069), 1.31 (–0.004), 1.39 (0.069), 1.55 (0.132), 1.65 (0.209), 1.76 (0.275), 1.88 (0.348), 2.04 (0.38), 2.15 (0.471)

[a] The numbers in brackets denote the order of repeated measurements, if any.

Values of log I quantity depending on concentration of methanesulfonic acid in water for the studied substituted derivatives of aniline of the following general formula (the substituents not shown are hydrogens)

Substituents[a]	c (log I)
$X_2 = X_6 = Cl$ (1)	0.0303 (–1.265), 0.0633 (–0.893), 0.0919 (–0.716), 0.151 (–0.577), 0.249 (–0.281), 0.293 (–0.166), 0.394 (–0.035), 0.508 (0.116), 0.687 (0.254), 0.863 (0.379), 1.37 (0.649), 1.89 (0.832), 2.00 (0.853)
$X_2 = X_6 = Cl$ (2)	0.0303 (–1.222), 0.0633 (–0.766), 0.0919 (–0.487), 0.151 (–0.417), 0.249 (–0.224), 0.293 (–0.09), 0.394 (0.04), 0.508 (0.169), 0.687 (0.344), 0.863 (0.449), 1.10 (0.556), 1.37 (0.69), 1.89 (0.867), 2.00 (0.891)
$X_2 = NO_2$ (1)	0.115 (–0.943), 0.170 (–0.9), 0.249 (–0.75), 0.508 (–0.401), 0.652 (–0.329), 0.721 (–0.292), 0.833 (–0.225), 0.863 (–0.206), 1.03 (–0.113), 1.14 (–0.052), 1.30 (0.035), 1.39 (0.086), 1.54 (0.123), 1.79 (0.245), 2.00 (0.292), 2.29 (0.4), 2.47 (0.45), 2.68 (0.555), 3.02 (0.605), 3.88 (0.922), 4.87 (1.191)
$X_2 = NO_2$ (2)	0.249 (–0.98), 0.334 (–0.844), 0.508 (–0.595), 0.652 (–0.38), 0.721 (–0.275), 0.833 (–0.267), 1.03 (–0.173), 1.14 (–0.102), 1.30 (–0.023), 1.39 (0.042), 1.54 (0.096), 1.79 (0.194), 2.00 (0.254), 2.29 (0.36), 2.47 (0.436), 2.68 (0.52), 3.02 (0.583), 3.88 (0.854), 4.87 (1.15)
$X_2 = CH_3O$, $X_6 = NO_2$	0.550 (–0.746), 1.03 (–0.376), 1.30 (–0.2), 2.29 (0.123), 4.21 (0.721), 5.19 (1.03), 6.16 (1.405)
$X_2 = CH_3$, $X_6 = NO_2$ (1)	0.356 (–1.128), 0.550 (–0.896), 0.687 (–0.734), 0.863 (–0.669), 1.05 (–0.544), 1.26 (–0.439), 1.47 (–0.385), 1.64 (–0.27), 1.89 (–0.187), 2.08 (–0.127), 2.29 (–0.042), 2.47 (0.027), 2.68 (0.132), 2.86 (0.16), 3.02 (0.202), 3.33 (0.292), 3.62 (0.404), 3.88 (0.474), 4.36 (0.614), 4.87 (0.767), 5.19 (0.867), 6.16 (1.184)
$X_2 = CH_3$, $X_6 = NO_2$ (2)	0.201 (–1.408), 0.356 (–1.204), 0.550 (–0.872), 0.687 (–0.771), 0.863 (–0.696), 1.05 (–0.507), 1.26 (–0.424), 1.47 (–0.377), 1.64 (–0.279), 1.89 (–0.143), 2.08 (–0.075), 2.29 (–0.037), 2.47 (0.05), 2.68 (0.142), 2.86 (0.166), 3.02 (0.193), 3.33 (0.286), 3.62 (0.402), 3.88 (0.478), 4.36 (0.603), 4.87 (0.761), 5.19 (0.883), 6.16 (1.198)

TABLE III
(*Continued*)

Substituents[a]	c (log I)
$X_2 = NO_2$, $X_4 = Cl$ (1)	0.652 (–1.291), 1.14 (–0.93), 1.39 (–0.758), 2.00 (–0.435), 2.29 (–0.438), 2.86 (–0.235), 3.33 (–0.098), 3.62 (0.02), 3.88 (0.066), 4.21 (0.151), 4.87 (0.387), 4.97 (0.413), 5.19 (0.468), 5.58 (0.578), 5.80 (0.758), 6.51 (0.936), 7.17 (1.197), 7.72 (1.329), 8.04 (1.571)
$X_2 = NO_2$, $X_4 = Cl$ (2)	0.652 (–1.249), 1.14 (–0.823), 1.39 (–0.763), 2.00 (–0.512), 2.29 (–0.41), 2.86 (–0.232), 3.33 (–0.104), 3.62 (0.027), 3.88 (0.057), 4.21 (0.169), 4.87 (0.364), 4.97 (0.416), 5.19 (0.488), 5.58 (0.551), 5.80 (0.74), 6.51 (0.907), 7.17 (1.18), 7.72 (1.316), 8.04 (1.487)
$X_2 = X_5 = Cl$, $X_4 = NO_2$ (1)	3.49 (–1.03), 4.21 (–0.784), 4.97 (–0.549), 5.42 (–0.386), 5.58 (–0.318), 5.80 (–0.245), 6.00 (–0.16), 6.29 (–0.074), 6.51 (0.016), 6.68 (0.18), 6.96 (0.169), 7.17 (0.266), 7.55 (0.411), 8.04 (0.585), 8.46 (0.727), 8.65 (0.843), 8.90 (1.063), 9.19 (1.231), 9.86 (1.326)
$X_2 = X_5 = Cl$, $X_4 = NO_2$ (2)	2.68 (–1.194), 3.49 (–0.999), 4.21 (–0.704), 4.97 (–0.539), 5.42 (–0.362), 5.58 (–0.307), 5.80 (–0.207), 6.00 (–0.133), 6.29 (–0.067), 6.51 (0.008), 6.68 (0.172), 6.96 (0.146), 7.17 (0.26), 7.55 (0.398), 8.04 (0.499), 8.90 (1.056), 9.86 (1.33)
$X_2 = Cl$, $X_6 = NO_2$ (1)	5.58 (–0.858), 6.05 (–0.785), 6.51 (–0.566), 6.96 (–0.524), 7.17 (–0.406), 7.39 (–0.272), 7.55 (–0.226), 7.72 (–0.13), 8.04 (–0.055), 8.25 (–0.028), 8.46 (0.069), 8.65 (0.247), 8.83 (0.246), 9.00 (0.335), 9.19 (0.444), 9.43 (0.535), 9.77 (0.697), 10.08 (0.92), 10.36 (1.159)
$X_2 = Cl$, $X_6 = NO_2$ (2)	5.58 (–1.012), 6.05 (–0.772), 6.51 (–0.61), 6.96 (–0.434), 7.17 (–0.435), 7.39 (–0.322), 7.55 (–0.244), 7.72 (–0.146), 8.04 (–0.096), 8.25 (–0.024), 8.46 (0.091), 8.65 (0.226), 8.83 (0.255), 9.00 (0.327), 9.19 (0.452), 9.43 (0.56), 9.77 (0.755), 10.08 (0.965), 10.36 (1.188)
$X_2 = X_4 = Cl$, $X_6 = NO_2$ (1)	6.16 (–1.345), 7.39 (–1.137), 8.13 (–0.896), 8.46 (–0.764), 8.65 (–0.583), 8.90 (–0.504), 9.19 (–0.358), 9.35 (–0.264), 9.43 (–0.202), 9.68 (–0.14), 9.86 (–0.024), 9.97 (0.056), 10.08 (0.105), 10.17 (0.219), 10.36 (0.342), 10.61 (0.368), 11.00 (0.767), 11.91 (1.105)

Substituents[a]	c (log I)
$X_2 = X_4 = Cl$, $X_6 = NO_2$ (2)	7.39 (–1.235), 8.13 (–0.916), 8.46 (–0.789), 8.65 (–0.582), 8.90 (–0.467), 9.19 (–0.392), 9.35 (–0.281), 9.43 (–0.226), 9.68 (–0.152), 9.86 (–0.016), 9.97 (0.05), 10.08 (0.105), 10.17 (0.198), 10.36 (0.33), 10.61 (0.336), 11.00 (0.767), 11.91 (1.084)
$X_2 = X_4 = NO_2$ (1)	9.86 (–0.822), 10.08 (–0.739), 10.36 (–0.426), 10.48 (–0.474), 10.61 (–0.42), 10.72 (–0.32), 10.83 (–0.126), 11.00 (–0.065), 11.26 (–0.013), 11.58 (0.143), 11.64 (0.233), 11.80 (0.189), 11.91 (0.249), 12.25 (0.592), 12.41 (0.595)
$X_2 = X_4 = NO_2$ (2)	9.43 (–1.195), 9.86 (–0.976), 10.08 (–0.712), 10.48 (–0.526), 10.61 (–0.491), 10.72 (–0.347), 10.83 (–0.186), 11.00 (–0.014), 11.26 (0.053), 11.58 (0.142), 11.64 (0.206), 11.80 (0.214), 11.91 (0.23), 12.10 (0.47), 12.25 (0.576), 12.41 (0.697), 13.00 (0.934), 13.28 (1.37)
$X_2 = X_4 = NO_2$ (3)	9.43 (–1.321), 10.08 (–0.752), 10.36 (–0.49), 10.83 (–0.11), 11.00 (–0.05), 11.26 (0), 11.80 (0.195), 11.91 (0.263), 12.41 (0.702), 13.00 (0.944)
$X_2 = X_6 = NO_2$ (1)	11.91 (–0.692), 12.25 (–0.427), 12.41 (–0.364), 12.51 (–0.362), 12.61 (–0.272), 12.80 (–0.059), 13.00 (0.055), 13.06 (0.146), 13.14 (0.141), 13.20 (0.227), 13.28 (0.671), 13.59 (0.809), 13.90 (0.949), 14.20 (1.231)
$X_2 = X_6 = NO_2$ (2)	11.91 (–0.72), 12.25 (–0.592), 12.41 (–0.301), 12.51 (–0.322), 12.61 (–0.222), 12.80 (–0.082), 13.00 (0.068), 13.06 (0.058), 13.14 (0.139), 13.20 (0.183), 13.28 (0.636), 13.59 (0.776), 13.90 (0.936), 14.20 (1.16)
$X_2 = X_6 = NO_2$ (3)	10.36 (–1.787), 10.83 (–1.26), 11.00 (–1.085), 11.26 (–1.046), 11.64 (–0.84), 11.91 (–0.797), 12.25 (–0.315), 13.00 (0.069), 13.28 (0.596)
$R = CH_3$, $X_2 = CH_3O$, $X_6 = NO_2$	0.0210 (0.428), 0.0303 (0.673), 0.0633 (1.02), 0.151 (1.544)
$R = CH_3$, $X_2 = Cl$, $X_6 = NO_2$ (1)	0.0210 (–0.892), 0.0303 (–0.659), 0.0409 (–0.557), 0.0491 (–0.451), 0.0633 (–0.339), 0.0767 (–0.22), 0.0919 (–0.157), 0.115 (–0.046), 0.151 (0.077), 0.201 (0.241), 0.249 (0.304), 0.293 (0.377), 0.394 (0.53), 0.508 (0.685), 0.687 (0.823), 0.863 (0.933), 1.37 (1.265), 1.89 (1.407)

TABLE III
(*Continued*)

Substituents[a]	c (log I)
R = CH$_3$, X$_2$ = Cl, X$_6$ = NO$_2$ (2)	0.0210 (–0.868), 0.0303 (–0.648), 0.0409 (–0.627), 0.0491 (–0.393), 0.0633 (–0.269), 0.0767 (–0.167), 0.0919 (–0.054), 0.115 (0.073), 0.201 (0.192), 0.249 (0.318), 0.293 (0.384), 0.394 (0.542), 0.508 (0.677), 0.687 (0.834), 0.863 (0.941), 1.37 (1.136), 1.89 (1.382)
R = CH$_3$, X$_4$ = NO$_2$	0.863 (0.554), 1.89 (1.08), 2.86 (1.528), 3.88 (1.792)
R = CH$_3$, X$_2$ = NO$_2$	0.863 (–0.642), 1.89 (–0.091), 2.86 (0.196), 3.88 (0.594), 5.19 (1.024), 6.16 (1.445)
R = CH$_3$, X$_2$ = X$_6$ = NO$_2$ (1)	6.00 (–0.582), 6.51 (–0.361), 6.68 (–0.172), 6.82 (–0.125), 6.96 (–0.145), 7.17 (–0.088), 7.39 (0.037), 7.72 (0.272), 8.04 (0.398), 8.13 (0.419), 8.39 (0.575), 8.46 (0.541), 8.65 (0.731), 8.90 (0.955), 9.05 (0.953), 9.19 (0.946), 9.86 (1.327)
R = CH$_3$, X$_2$ = X$_6$ = NO$_2$ (2)	4.21 (–1.048), 4.87 (–0.86), 5.42 (–0.619), 5.58 (–0.562), 5.80 (–0.549), 6.00 (–0.438), 6.29 (–0.372), 6.51 (–0.237), 6.68 (–0.069), 6.82 (–0.044), 6.96 (–0.054), 7.17 (0.026), 7.39 (0.121), 7.72 (0.343), 8.04 (0.43), 8.13 (0.481), 8.39 (0.608), 8.46 (0.604), 8.65 (0.774), 8.90 (1.003), 9.05 (0.963), 9.19 (0.955), 9.86 (1.418)

[a] The numbers in brackets denote the order of repeated measurements, if any.

The statistical hypotheses of intercept equal zero (t_{test} = 1.264, $t_{0.95}$(67) = 1.996) and unit slope (t_{test} = 1.963, $t_{0.95}$(67) = 1.996) in Eq. (*1*) were not rejected. Therefrom it follows that the acidity function obtained by us and those given in literature are identical within experimental error. The relationship between our acidity function and that of ref.[24] for perchloric acid is given by Eq. (*3*).

$$H_0(\text{HClO}_4) = (0.116 \pm 0.031) + (0.955 \pm 0.009) \, H_0(\text{HClO}_4, \text{ref.}^{24})$$

$$s = 0.75, \; r = 0.998, \; n = 52 \tag{3}$$

In this case, the statistical hypotheses of intercept equal zero (t_{test} = 4.82, $t_{0.95}$(50) = 2.009) and unit slope (t_{test} = 38.1, $t_{0.95}$(50) = 2.009) were rejected. The agreement between the two functions is worse in this case, the differences being caused by small deviations in the course of the two acidity functions, particularly those in the middle of the concentration interval.

Values of acidity functions H_0 depending on concentration c (in mol dm^{-3}) of sulfuric, perchloric, and methanesulfonic acid in water

c	$H_0(H_2SO_4)$	$H_0(HClO_4)$	$H_0(CH_3SO_3H)$	c	$H_0(H_2SO_4)$	$H_0(HClO_4)$	$H_0(CH_3SO_3H)$
0.02		1.690		3.4	−1.607	−1.590	−0.964
0.04	1.494	1.324	1.456	3.6	−1.743	−1.690	−1.071
0.06	1.264	1.173	1.179	3.8	−1.856	−1.832	−1.142
0.08	1.083	1.066	1.036	4.0	−1.936	−1.938	−1.161
0.10	1.012	0.966	0.885	4.2	−2.006	−2.071	−1.192
0.15	0.811	0.765	0.762	4.4	−2.129	−2.188	−1.279
0.20	0.672	0.599	0.616	4.6	−2.242	−2.308	−1.353
0.25	0.561	0.508	0.557	4.8	−2.349	−2.410	−1.412
0.30	0.448	0.387	0.511	5.0	−2.448	−2.483	−1.462
0.35	0.351	0.326	0.448	5.2	−2.528	−2.589	−1.522
0.40	0.302	0.257	0.316	5.4	−2.622	−2.695	−1.569
0.45	0.247	0.173	0.247	5.6	−2.733	−2.789	−1.633
0.50	0.206	0.096	0.214	5.8	−2.820	−2.913	−1.686
0.60	0.098	0.023	0.146	6.0	−2.900	−3.008	−1.726
0.70	−0.045	−0.053	0.038	6.2	−2.989	−3.113	−1.894
0.80	−0.096	−0.116	−0.023	6.4	−3.083	−3.234	−1.916
0.90	−0.209	−0.211	−0.040	6.6	−3.194	−3.342	−1.978
1.00	−0.229	−0.280	−0.097	6.8	−3.273	−3.433	−2.055
1.2	−0.384	−0.415	−0.238	7.0	−3.343	−3.526	−2.112
1.4	−0.496	−0.530	−0.340	7.2	−3.475	−3.643	−2.169
1.6	−0.600	−0.647	−0.417	7.4	−3.545	−3.796	−2.233
1.8	−0.721	−0.767	−0.501	7.6	−3.621	−3.971	−2.355
2.0	−0.840	−0.837	−0.549	7.8	−3.682	−4.156	−2.462
2.2	−1.007	−0.949	−0.641	8.0	−3.766	−4.245	−2.510
2.4	−1.059	−1.059	−0.702	8.2	−3.861	−4.358	−2.546
2.6	−1.202	−1.178	−0.776	8.4	−3.933	−4.456	−2.665
2.8	−1.318	−1.260	−0.829	8.6	−3.998	−4.568	−2.741
3.0	−1.377	−1.364	−0.875	8.8	−4.082	−4.798	−2.882
3.2	−1.470	−1.484	−0.917	9.0	−4.239	−4.963	−2.983

TABLE IV
(*Continued*)

c	$H_0(H_2SO_4)$	$H_0(HClO_4)$	$H_0(CH_3SO_3H)$	c	$H_0(H_2SO_4)$	$H_0(HClO_4)$	$H_0(CH_3SO_3H)$
9.2	−4.329	−5.073	−3.056	11.8	−5.849		−4.570
9.4	−4.431	−5.209	−3.104	12.0	−6.001		−4.643
9.6	−4.558	−5.447	−3.149	12.2	−6.146		−4.895
9.8	−4.602	−5.700	−3.354	12.4	−6.312		−5.008
10.0	−4.676	−5.955	−3.470	12.6	−6.528		−5.120
10.2	−4.748	−6.106	−3.624	12.8			−5.307
10.4	−4.983	−6.250	−3.764	13.0			−5.399
10.6	−5.058		−3.843	13.2			−5.693
10.8	−5.270		−4.139	13.4			−6.011
11.0	−5.396		−4.251	13.6			−6.115
11.2	−5.475		−4.310	13.8			−6.270
11.4	−5.538		−4.409	14.0			−6.422
11.6	−5.640		−4.527				
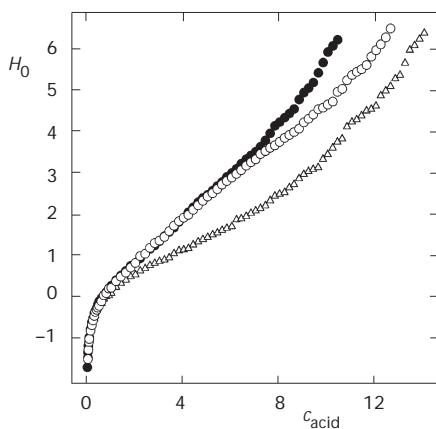
FIG. 1

Dependence of constructed acidity functions H_0 in sulfuric acid (○), perchloric acid (●), and methanesulfonic acid (△) on the concentration of acid c_{acid} in mol dm^{-3}

The agreement of the constructed acidity function in methanesulfonic acid cannot be verified because corresponding literature data are not available.

With regard to the fact that our acidity functions and those taken from literature were constructed on different experimental data, and the agreement with the more or less standard acidity function in sulfuric acid is very good, it is possible to claim that the suggested algorithm is correct.

The relationship between our acidity functions constructed in sulfuric and perchloric acids and the scale of the generalised function X (ref.[6]) is expressed by Eqs (*4*) and (*5*).

$$H_0(H_2SO_4) = (0.047 \pm 0.0118) + (1.136 \pm 0.034) \log c_{H^+} + (0.990 \pm 0.012) \, X$$

$$s = 0.06, \, r = 0.9997, \, n = 28 \tag{4}$$

$$H_0(HClO_4) = (0.123 \pm 0.026) + (0.970 \pm 0.052) \log c_{H^+} + (0.951 \pm 0.018) \, X$$

$$s = 0.08, \, r = 0.9993, \, n = 26 \tag{5}$$

In analogy to Eqs (*2*) and (*3*), also in this case the fit is very close (the residual standard deviation being comparable with the accuracy of measurements), which confirms both the correctness of the algorithm suggested and validity of the "excess acidity" principle as well as correctness of adjustment of the scale of X values.

In order to evaluate mutual similarity of the acidity function calculated, the values of Table IV were submitted to principal component analysis (PCA). The first latent variable characterising common properties of analysed acidity functions described 99.67% of their variability. This value is relatively high and indicates a high extent of mutual similarity of these acidity functions irrespective of different concentration scales and the fact that one of the acids is dibasic and the other two are monobasic. From Fig. 1 and from values of loading p in sulfuric acid ($p = 4.505$), perchloric acid ($p = 5.443$), and methanesulfonic acid ($p = 3.816$) obtained by PCA, it follows that (in accordance with ref.[2]) the steepness of the acidity function in perchloric acid is greater than that in sulfuric acid. The steepness of the acidity function in the weakest acid (methanesulfonic acid) is the lowest in this case.

pK_a Values of Indicators

The pK_a values calculated according to the above-given algorithm from the data published in a previous paper[27] and those given in Tables I–III, and the pK_a values taken from literature are summarised in Table V. The literature and the calculated values are compared graphically in Fig. 2. The points are fitted with a regression straight line, which documents both relations between the individual values and variance of the pK_a values published in literature. As it can be seen in Fig. 2, the agreement between the pK_a values calculated and those published in literature is very good.

Validity of the Algorithm Suggested

The validity of the algorithm suggested is considered to be verified by comparison of the acidity functions (Eqs (2)–(5)) and the pK_a values obtained by this algorithm with reliable literature data (Table V, Fig. 2). With respect to the fact that the calculations were based on different experimental data and different calculation procedures and the results agree well with literature, the algorithm suggested for calculating the bound acidity functions can be considered to be correct.
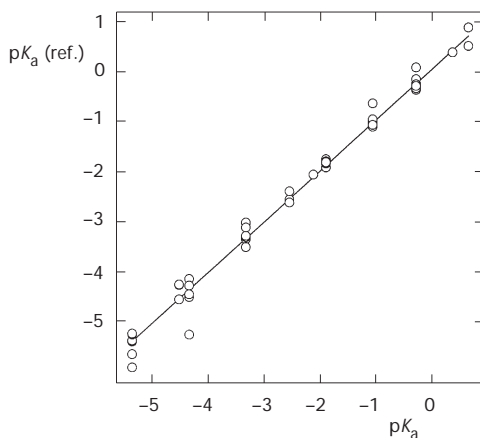
FIG. 2
Dependence of the pK_a values taken from literature and those calculated according to the suggested algorithm (Table V). The straight line was calculated by regression

Comparison of calculated pK_a values and their standard deviations s_{pK} of substituted anilines and *N*-methylanilines with corresponding literature data

Indicator	pK_a (s_{pK})	pK_a, reference
2,6-Dichloroaniline	0.353 (0.068)	0.40^a (H_2SO_4)
2-Nitroaniline	–0.300 (0.053)	-0.25^b (H_2SO_4), -0.29^e (H_2SO_4), -0.33^f (H_2SO_4), -0.30^g (H_2SO_4), -0.35^h (H_2SO_4), 0.10^a ($HClO_4$), -0.31^b ($HClO_4$), -0.29^i ($HClO_4$), -0.28^j ($HClO_4$), -0.29^b (HCl), -0.31^k (HCl), $-0.32^{\mathbf{b}}$ (HNO_3), -0.22^b (H_3PO_4), -0.13^d (CF_3CO_2H), $-0,24^d$ (CCl_3CO_2H), -0.27^c (M_c)
2-Methoxy-6-nitroaniline	–0.481 (0.040)	
2-Methyl-6-nitroaniline	–0.694 (0.036)	
4-Chloro-2-nitroaniline	–1.076 (0.067)	-0.97^b (H_2SO_4), -1.02^e (H_2SO_4), -1.06^g (H_2SO_4), -0.97^h (H_2SO_4), -0.62^a ($HClO_4$), -1.03^b ($HClO_4$), -1.07^i ($HClO_4$), -1.03^b (HCl), -1.09^k (HCl), -1.09^b (HNO_3), -1.01^b (H_3PO_4), -0.94^d (CF_3CO_2H), -1.05^c (M_c)
2,5-Dichloro-4-nitroaniline	–1.913 (0.073)	-1.90^f (H_2SO_4), -1.75^g (H_2SO_4), -1.74^h (H_2SO_4), $-1.79i$ ($HClO_4$), $-1.78j$ ($HClO_4$), -1.82^k (HCl), -1.80^c (M_c)
2-Chloro-6-nitroaniline	–2.569 (0.047)	-2.54^f (H_2SO_4), -2.38^g (H_2SO_4), -2.60^c (M_c)

TABLE V
(*Continued*)

Indicator	pK_a (s_{pK})	pK_a, reference
2,4-Dichlor-6-nitroaniline	−3.347 (0.072)	−3.34[b] (H_2SO_4), −3.28[f] (H_2SO_4), −3.01[h] (H_2SO_4), −3.30[b] ($HClO_4$), −3.00[j] ($HClO_4$), −3.27[k] (HCl), −3.10[b] (H_3PO_4), −3.50[c] (M_c)
2,4-Dinitroaniline	−4.358 (0.064)	−4.14[a] (H_2SO_4), −4.50[b] (H_2SO_4), −4.45[f] (H_2SO_4), −4.27[g] (H_2SO_4), −4.27[h] (H_2SO_4), −4.55[b] ($HClO_4$), −4.26[i] ($HClO_4$), −4.25[j] ($HClO_4$), −5.25[c] (M_c)
2,6-Dinitroaniline	−5.375 (0.061)	−5.64[f] (H_2SO_4), −5.39[g] (H_2SO_4), −5.37[h] (H_2SO_4), −5.25[i] ($HClO_4$), −5.23[j] ($HClO_4$), −5.90[c] (M_c)
N-Methyl-2-methoxy-6-nitroaniline	2.227 (0.061)	
N-Methyl-2-chloro-6-nitroaniline	0.841 (0.084)	
N-Methyl-4-nitroaniline	0.633 (0.047)	0.90[l], 0.53[m]
N-Methyl-2-nitroaniline	−0.492 (0.060)	
N-Methyl-2,6-dinitroaniline	−2.141 (0.098)	−2.04[a] (H_2SO_4)

[a] Ref.[35], [b] ref.[4], [c] ref.[15], [d] ref.[36], [e] ref.[37], [f] ref.[38], [g] ref.[34], [h] ref.[25], [i] ref.[24], [j] ref.[39], [k] ref.[40], [l] ref.[41], [m] ref.[42], [n] ref.[43].

REFERENCES

1. Hammett L. P., Deyrup A. J.: *J. Am. Chem. Soc.* **1932**, *54*, 2721.
2. Rochester C. H.: *Acidity Functions*. Academic Press, London 1970.
3. Robertson E. B., DunFord H. B.: *J. Am. Chem. Soc.* **1964**, *86*, 5080.
4. Paul M. A., Long F. A.: *Chem. Rev. (Washington, D. C.)* **1957**, *57*, 1.
5. Cox R. A, Yates K.: *Can. J. Chem.* **1983**, *61*, 2225.
6. Cox R. A.: *Adv. Phys. Org. Chem.* **2000**, *35*, 1.
7. Bunnett J. F., Olsen F. P.: *Can. J. Chem.* **1966**, *44*, 1899.
8. Marziano N. C., Cimino G. M., Passerini R. C.: *J. Chem. Soc., Perkin Trans. 2* **1973**, 1915.
9. Marziano N. C., Traverso P. G., Passerini R. C.: *J. Chem. Soc., Perkin Trans. 2* **1977**, 306.
10. Marziano N. C., Traverso P. G., Tomasin A., Passerini R. C.: *J. Chem. Soc., Perkin Trans. 2* **1977**, 309.
11. Marziano N. C., Passerini R. C.: *J. Chem. Soc., Perkin Trans. 2* **1977**, 845.
12. Marziano N. C., Tomasin A., Tortato C.: *Org. React.* **1996**, *30*, 29.
13. Marziano N. C., Tomasin A., Tortato C.: *Org. React.* **1996**, *30*, 39.
14. Marziano N. C., Tortato C., Sheikh-Osman A. A., Riego J. M., Zaldivar J. M.: *Org. React.* **1997**, *31*, 87.
15. Marziano N. C., Tomasin A., Tortato C., Isandelli P.: *J. Chem. Soc., Perkin Trans. 2* **1998**, 2535.
16. Marziano N. C., Tortato C., Ronchin L., Bianchi C.: *Catal Lett.* **1998**, *56*, 159.
17. Cox R. A., Stewart R.: *J. Am. Chem. Soc.* **1976**, *98*, 488.
18. Cox R. A., Stewart R., Cook M. J., Katritzky A. R., Tack R. D.: *Can. J. Chem.* **1976**, *54*, 900.
19. Cox R. A., Yates K.: *J. Am. Chem. Soc.* **1978**, *100*, 3861.
20. Pytela O.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 645.
21. Traverso P. G.: *Can. J. Chem.* **1984**, *62*, 153.
22. Johnson C. D., Stratton B.: *J. Org. Chem.* **1986**, *51*, 4100.
23. Johnson C. D., Stratton B.: *J. Org. Chem.* **1987**, *52*, 4798.
24. Yates K., Wai H.: *J. Am. Chem. Soc.* **1964**, *86*, 5408.
25. Tickle P., Briggs A. G., Wilson J. M.: *J. Chem. Soc. B* **1970**, 65.
26. Yates K., Wai H., Welch G., McClelland R. A.: *J. Am. Chem. Soc.* **1973**, *95*, 418.
27. Jirásková E., Kulhánek J., Nevěčná T., Pytela O.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 1253.
28. Blanksma J. J.: *Rec. Trav. Chim. Pays-Bas* **1902**, *21*, 261.
29. Noelting E., Kopp E.: *Chem. Ber.* **1905**, *38*, 3506.
30. van Erp H.: *J. Prakt. Chem.* **1930**, *127*, 20.
31. van Duin C. F.: *Rec. Trav. Chim. Pays-Bas* **1932**, *51*, 878.
32. Kremer Ch. B., Bendich A.: *J. Am. Chem. Soc.* **1939**, *61*, 2658.
33. Auwers K., Frese E.: *Chem. Ber.* **1926**, *59*, 539.
34. Johnson C. D., Katritzky A. R., Shapiro S. A.: *J. Am. Chem. Soc.* **1969**, *91*, 6654.
35. Stewart R., Dolman D.: *Can. J. Chem.* **1967**, *45*, 925.
36. Randles J. E. B., Tedder J. M.: *J. Chem. Soc.* **1955**, 1218.
37. Bascombe K. N., Bell R. P.: *J. Chem. Soc.* **1959**, 1096.
38. Ryabova R. S., Medvetskaya I. M., Vinnik M. I.: *Zh. Fiz. Khim.* **1966**, *40*, 339.
39. Attiga S. A., Rochester C. H.: *J. Chem. Soc., Perkin Trans. 2* **1974**, 1624.
40. Arnett E. M., Mach G. W.: *J. Am. Chem. Soc.* **1966**, *88*, 1177.
41. Abrams W. R., Kallen R. G.: *J. Am. Chem. Soc.* **1976**, *98*, 7777.
42. Kershner L. D., Schowen R. L.: *J. Am. Chem. Soc.* **1971**, *93*, 2014.
43. Kuznetsov L. L., Gidaspov B. V.: *Zh. Org. Khim.* **1982**, *18*, 685.