

CONSTRUCTION AND CHEMOMETRIC ANALYSIS OF ACIDITY FUNCTION IN PERCHLORIC ACIDEva JIRÁSKOVÁ^{a1}, Jiří KULHÁNEK^{b1}, Tatjana NEVĚČNÁ^{a2,*} and Oldřich PYTELA^{b2}^a Department of Inorganic and Physical Chemistry, Palacký University, 771 46 Olomouc, Czech Republic; e-mail: ¹ jiraskova@prfnw.upol.cz, ² nevecna@prfnw.upol.cz^b Department of Organic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: ¹ jiri.kulhanek@upce.cz, ² oldrich.pytela@upce.cz

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Four 2,6-disubstituted anilines with CH₃, Cl, and NO₂ substituents have been synthesized and, together with four commercial substances of the same type, subjected to spectrophotometry to find the concentration ratios of the protonated and non-protonated forms in aqueous perchloric acid of 0.02–10.55 mol dm⁻³ concentration. By a procedure devised earlier, the acidity function has been constructed and the pK_a values calculated. The Principal Component Analysis was applied to the acidity function obtained and on other eight acidity functions of perchloric acid were taken from literature. It was found that the first principal component explained 99.78% of variability, which indicated high degree of similarity of the said functions irrespective of the indicator type and solvent used. The regression dependences acidity function values on the first principle component are very close, the regression coefficient expressing the measure of sensitivity of the indicator to the acidifying medium. The pK_a values obtained agree well with the literature data.

Key words: Acidity functions; 2,6-Disubstituted anilines; Chemometrics; Latent variables; Substituent effects.

Construction of acidity function is usually a means of determining the dissociation constants of weak bases or also acids with conformable type of structural, so-called indicators, in media of highly concentrated acids and bases. However, even the acidity function itself (in a certain medium and for a given indicator, and its changes with temperature, or the method of construction) can become a subject of study. More frequent are constructions of acidity functions in acid solutions than those in alkaline solutions. The most frequent indicators involve substituted anilines (*H*₀ function) but the palette of indicators is surprisingly varied. The choice of acidifying medium prefers aqueous solutions of sulfuric acid, but studies in perchloric acid are also common. Other acids such as hydrochloric, phosphoric, and methanesulfonic have been used less often. A detailed survey can be found

in literature¹⁻⁵. Several procedures have been suggested for construction of acidity function^{6,7}. The input data include the log I values usually obtained by measuring the absorbance changes in visible and UV spectral ranges, a method using NMR being described, too⁸. The large number of acidity functions initiated efforts to generalize them, the most significant approaches being those of Bunnett and Olsen⁹, Marziani *et al.*^{3-5,10-13}, and Cox *et al.*¹⁴⁻¹⁶. All the procedures mentioned start from the physico-chemical ideas of behaviour of the indicators in the medium given, the mathematical description consisting in linear regression with a universally explaining variable which is a function of the acid concentration. Similarity of acidity functions has not been studied by other means of chemometrics yet.

Perchloric acid has been a frequently used medium for construction of acidity function^{2,6,17,18}, and it is certainly a suitable medium for determination of dissociation constants of little basic indicators. We were interested in 2,6-disubstituted anilines, in the context of our studies of 2,6-disubstituted benzene derivatives with various reaction centres¹⁹. The aim of the present work is to construct an acidity function H_0 in perchloric acid with selected anilines as indicators and to compare the acidity functions thus obtained with the H functions in perchloric acid obtained by other authors and with different indicators.

EXPERIMENTAL

Chemicals

2-Methyl-6-nitroaniline was obtained²⁰ by nitration of 2-methylacetanilide and hydrolysis of the respective derivative isolated from its mixture with 4 isomer by the Vitt-Uterman separation method²¹. Similar procedure was also adopted for synthesis of 2-chloro-6-nitroaniline. 2,4-Dichloro-6-nitroaniline was synthesized²² by nitration of 2,4-dichloroacetanilide with fuming nitric acid in a mixture of acetic and sulfuric acids and subsequent hydrolysis. The synthesis of 2,6-dinitroaniline²³ was based on nitration of chlorobenzene and nucleophilic substitution of chlorine for amino group. The synthesized derivatives were identified by NMR. Their purity was determined by GC/MS. The other anilines were commercial samples (Fluka). Before the measurements, the anilines were purified by recrystallization from ethanol (2-NO₂, 2-CH₃-6-NO₂, 2,4-di-NO₂, 2,6-di-NO₂) or hexane (the other). Analytical grades of perchloric acid (Carlo Erba), sodium hydroxide (Lachema Neratovice), and methanol for UV (Lachema) were used without purification.

Measurement of Dissociation Constants

The measurements were carried out spectrophotometrically using an SP 8-100 (Pye Unicam) apparatus. The exact concentrations of perchloric acid were determined by alkalimetry. Stock solutions of individual anilines in methanol had the concentrations of 10⁻¹ to 10⁻² mol dm⁻³.

The solutions were pipetted (0.05 cm^3) into 25-ml calibrated flasks and the volumes were filled up to the mark with aqueous perchloric acid of appropriate concentrations. The absorbance changes and perchloric acid concentration changes were read at the wavelength of the longest-wave maximum. Some of the measurements were repeated several times. The acidity function was constructed from the dependence of $\log I$ vs $c(\text{HClO}_4)$ using known algorithm⁷, the $\text{p}K_a$ values of the indicators being obtained simultaneously. The acidity functions selected from literature and that obtained by us were treated by the Principal Components Analysis²⁴ (PCA).

RESULTS AND DISCUSSION

Acidity Functions

The dependences of $\log I$ on the concentration of protonating acid are presented in Table I for all the indicators used. Their treatment⁷ gave the values of acidity function in dependence on molar concentration of perchloric acid in water, which are given in Table II. The residual deviation $s = 0.0363$ is very small in comparison with calculation on other data⁷, being comparable, for instance, with the same value calculated from literature quality data²⁵. The course of the dependences has a standard character.

In order to be able to carry out comparisons with other acidity functions in perchloric acid, we took suitable acidity functions (constructed for perchloric acid with various types of indicators or, as the case may be, in mixed solvents) from literature^{8,17,26-30}. For this purpose, the H_0 values from Table II and the literature values were interpolated into a scale of 23 concentrations in the interval from 0.1 to 10.0 mol dm^{-3} (see ref.¹⁷). The matrix thus created was treated by the PCA method. The first latent variable explained on incredible amount of 99.78% variability, which indicates high extent of similarity of the acidity functions. The rest of variability can be considered to be due to the experimental error, whose value is very low. The first principal component carries information about the course of the acidity function depending on concentration of perchloric acid, which is to a maximum extent common for all the acidity functions taken into the calculation. The statistical characteristics of regressions of these acidity function values upon this quantity are summarized in Table III. A number of interesting conclusions follow from the data of this table. First of all, the results for the acidity function constructed by us are virtually identical with those taken from literature for the same type of indicators and the same conditions. Also noteworthy is the very close correlation of the dependence mentioned regardless of the indicator type and composition of medium. The results given confirm unambiguously that the properties of perchloric

TABLE I
log *I* values for aniline derivatives depending on perchloric acid concentration in water

$c(\text{HClO}_4)$ mol dm ⁻³	Aniline derivatives		
	2,6-di-Cl	2-NO ₂	2-CH ₃ -6-NO ₂
0.0242	1.082, 1.180		
0.0483	0.958, 0.973		
0.0748	0.800, 0.976		
0.0992	0.628, 0.685		
0.1200	0.535, 0.535		1.616
0.132	0.500, 0.462		
0.148	0.490, 0.474		
0.164	0.378, 0.371		
0.181	0.369, 0.394		
0.214	0.252, 0.201	0.925	
0.250	0.176, 0.180		
0.264	0.124, 0.121		
0.280	0.111, 0.083		
0.303	0.049		
0.328	0.028		
0.345	0.030, -0.001		
0.369	-0.031	0.672, 0.627, 0.651	
0.412	-0.079, -0.098		
0.566	-0.279, -0.279	0.400, 0.392, 0.377	0.712, 0.744
0.723	-0.410, -0.369	0.279, 0.232, 0.242	0.543
0.803		0.145, 0.172, 0.178	
0.886	-0.510, -0.546		0.403, 0.482
0.910		0.071, 0.091	
0.981		0.083	
1.06	-0.604, -0.653	0.023	0.349, 0.386
1.20		-0.073, -0.095, -0.107	0.267, 0.280
1.39		-0.211, -0.227, -0.205	0.128, 0.165
1.50		-0.259	
1.55		-0.303, -0.265, -0.266	0.070, 0.107
1.65		-0.369, -0.353, -0.362	-0.007, 0.036
1.76			-0.051, -0.019
1.88		-0.468, -0.441, -0.453	-0.143, -0.085
2.04		-0.489	-0.225, -0.229
2.08		-0.558	
2.15		-0.599, -0.576, -0.607	
2.29		-0.701, -0.630, -0.656	-0.333, -0.282
2.59		-0.794, -0.807, -0.794	-0.508, -0.465
2.69			-0.537, -0.502
2.89		-0.931, -0.915	-0.619, -0.599
3.12			-0.743, -0.725
3.19		-1.084, -1.085	
3.41			-0.914, -0.902

TABLE I
(Continued)

$c(\text{HClO}_4)$ mol dm^{-3}	Aniline derivative		
	4-Cl-2-NO ₂	4-Cl-6-NO ₂	2,4-di-Cl-6-NO ₂
0.606	1.016		
1.06	0.803, 0.708		
1.15	0.672, 0.674		
1.20	0.600		
1.39	0.499, 0.603		
1.55	0.424, 0.498		
1.65	0.303, 0.374		
1.88	0.225, 0.268		
2.04	0.213, 0.194		
2.15	0.110, 0.122		
2.42	-0.043, 0.008		
2.59	-0.152, -0.155		
2.69	-0.209, -0.201		
2.89	-0.339, -0.299		
3.12	-0.371, -0.363		
3.19		1.030, 1.005	
3.41	-0.483, -0.464	0.967, 0.907	
3.55	-0.543, -0.592	0.900, 0.846	
3.71		0.718	
3.81	-0.717, -0.721	0.773, 0.688	
4.03		0.636, 0.625	
4.19	-0.976, -0.918	0.640, 0.542	1.128
4.35		0.488, 0.383	1.097, 1.163
4.46	-1.077, -1.102	0.315, 0.334	
4.64		0.225, 0.210	0.927, 0.978
4.85		0.164, 0.151	
5.00		0.128, 0.092	0.819, 0.845
5.15		0.028, 0.054	
5.35		-0.121, -0.137	0.659, 0.645
5.64		-0.162, -0.204	
5.76		-0.320, -0.327	0.439, 0.450
5.94		-0.402, -0.417	0.376, 0.390
6.09		-0.511, -0.515	0.291, 0.313
6.23			0.190, 0.220
6.36		-0.690, -0.692	
6.43			0.064, 0.081
6.62			-0.044, -0.008
6.91			-0.185, -0.170
7.02			-0.333, -0.317
7.43			-0.590, -0.586
7.92			-0.896, -0.990
8.33			-1.208
8.60			-1.422

TABLE I
(Continued)

$c(\text{HClO}_4)$ mol dm^{-3}	Aniline derivative	
	4-Cl-2-NO ₂	2,4-di-Cl-6-NO ₂
6.36	1.289	
6.62	1.073	
6.91	0.990, 1.051	
7.02	0.824, 0.858, 0.886	
7.28	0.688, 0.716, 0.689	
7.43	0.639, 0.606	
7.50	0.529, 0.471, 0.505	
7.61	0.260	
7.84	0.222	1.260, 1.251
7.92	0.162, 0.162, 0.170, 0.225	1.190, 1.181
8.13	0.067, 0.071	0.988, 0.988
8.33	0.009, -0.030, 0.000, -0.024	0.920, 0.929
8.47	-0.139, -0.125	0.874, 0.859
8.60	-0.197, -0.153, -0.189, -0.225	0.828, 0.833
8.72	-0.340, -0.301	0.682, 0.678
8.82	-0.500, -0.424, -0.412, -0.414	0.538, 0.536
8.99	-0.728, -0.728, -0.636, -0.649	0.410, 0.420
9.30	-802	0.230, 0.231
9.47		0.100, 0.079
9.56		0.049, -0.040
9.65	-1.095, -1.094	-0.152, -0.135
9.74		-0.334, -0.317
9.95		-0.593, -0.544
10.25		-0.718, -0.744
10.55		-1.024, -1.022

acid solutions only depend on its concentration, being independent of the indicator and probably the medium as well. Hence a given acid is associated with a single acidity function which can describe the acid-base properties in dependence on the concentration. This is in accordance with the efforts to create a general acidity function^{3-5,9-16}.

The type of indicator or medium is reflected by different regression coefficients a_1 . For instance, it is known that the acidity functions constructed with amides are less steep. Actually, the regression coefficient given in Table III for amides reaches two-thirds of the same quantity for anilines. On the other hand, the sensitivity of indoles and tertiary amines to protonating media is higher than that of standard anilines.

TABLE II
Acidity function (H_0) values depending on concentration (c , mol dm⁻³) of perchloric acid in water

c	H_0	c	H_0	c	H_0	c	H_0
0.04	1.398	1.0	-0.249	4.2	-1.932	7.4	-3.692
0.06	1.287	1.2	-0.393	4.4	-2.048	7.6	-3.893
0.08	1.166	1.4	-0.478	4.6	-2.161	7.8	-4.055
0.10	1.024	1.6	-0.608	4.8	-2.244	8.0	-4.160
0.15	0.809	1.8	-0.712	5.0	-2.321	8.2	-4.268
0.20	0.626	2.0	-0.796	5.2	-2.429	8.4	-4.375
0.25	0.530	2.2	-0.922	5.4	-2.536	8.6	-4.501
0.30	0.430	2.4	-1.020	5.6	-2.626	8.8	-4.724
0.35	0.357	2.6	-1.134	5.8	-2.752	9.0	-4.892
0.40	0.285	2.8	-1.210	6.0	-2.839	9.2	-4.984
0.45	0.207	3.0	-1.304	6.2	-2.944	9.4	-5.109
0.50	0.150	3.2	-1.412	6.4	-3.081	9.6	-5.365
0.60	0.056	3.4	-1.497	6.6	-3.187	9.8	-5.616
0.70	-0.004	3.6	-1.576	6.8	-3.297	10.0	-5.836
0.80	-0.118	3.8	-1.705	7.0	-3.427	10.2	-5.994
0.90	-0.195	4.0	-1.810	7.2	-3.548	10.4	-6.168

TABLE III
Selected acidity functions and their dependence on the first principal component t_1 (n is number of points in the regression (max. 23), a_0 and a_1 are regression coefficients, s residual standard deviation, and r correlation coefficient)

Acidity function	n	a_0	a_1	s	r
H_0 , anilines, water ^a	23	-5.746	6.574	$6.701 \cdot 10^{-2}$	0.9994
H_0 , anilines, water ¹⁷	20	-5.884	6.780	$5.801 \cdot 10^{-2}$	0.9995
H_0 , anilines, water ²⁸	20	-5.889	6.715	$7.873 \cdot 10^{-2}$	0.9991
H_0 , anilines, 60% 4-methylpent-3-en-2-one ²⁶	10	-8.398	10.880	$3.605 \cdot 10^{-2}$	0.9996
H''' , tertiary amines, water ³⁰	23	-8.262	9.247	$6.397 \cdot 10^{-2}$	0.9997
H_A , amides, water ³⁰	20	-4.072	4.229	$1.393 \cdot 10^{-1}$	0.9928
H_I , indoles, water ²⁷	15	-8.836	9.765	$4.572 \cdot 10^{-2}$	0.9997
H , hydroxy- and alkoxybenzenes, water ²⁹	11	-5.566	6.438	$1.562 \cdot 10^{-2}$	0.9916
H , 4-methylpent-3-en-2-one, ¹³ C NMR, water ⁸	7	-6.252	7.280	$1.031 \cdot 10^{-1}$	0.9946

^a This paper.

TABLE IV
Comparison of pK_a values obtained from the data of Table I with literature data (n number of experimental points in the series)

Indicator	n	pK_a (calc.)	\overline{pK}_a	pK_a (lit.)
2,6-Dichloraniline	20, 20	0.361, 0.355	0.358	
2-Nitroaniline	16, 16, 16	-0.296, -0.302, -0.302	-0.300	-0.31 ^a , -0.29 ^b , -0.282 ^c
2-Methyl-6-nitroaniline	17, 17	-0.619, -0.657	-0.638	
4-Chloro-2-nitroaniline	19, 21	-0.993, -1.006	-1.000	-1.03 ^a , -1.07 ^b , -1.030 ^c
2-Chloro-6-nitroaniline	18, 19	-2.440, -2.408	-2.424	-2.41 ^b
2,4-Dichloro-6-nitroaniline	16, 15	-3.143, -3.167	-3.155	-3.30 ^a
2,4-Dinitroaniline	12, 12, 11, 11	-4.283, -4.290, -4.298, -4.316	-4.297	-4.55 ^a , -4.26 ^b
2,6-Dinitroaniline	17,17	-5.283, -5.279	-5.281	-5.25 ^b

^a Ref.³¹, ^b Ref.²², ^c Ref.⁶.

pK_a Values of Indicators

Table IV presents the pK_a values of indicators obtained in the process of construction of the acidity function. From the data, it is obvious that the calculated pK_a values agree well with the literature data obtained with aqueous perchloric acid.

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