

DISSOCIATION CONSTANTS  
OF MONOSUBSTITUTED DIPHENYLAMINES  
AND AN OPTIMIZED CONSTRUCTION OF ACIDITY FUNCTION

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Eleven monosubstituted diphenylamines have been synthesized, and concentration ratio of the protonated and free bases has been measured in aqueous sulphuric acid in the concentration range  $1.0 \cdot 10^{-3}$  to  $9.0 \text{ mol l}^{-1}$ . An algorithm has been suggested and used for determination of optimized values of  $pK$  and  $H'$  acidity function within sulphuric acid concentration range  $0.05$  to  $9.0 \text{ mol l}^{-1}$ . The results have been compared with literature data and discussed in terms of theory of acidity functions and linear free energy relationships.

Dissociation constants of monosubstituted diphenylamines in water have only been published for 4-nitro derivative<sup>1,2</sup> and the parent compound<sup>2-4</sup> so far. The paper<sup>5</sup> gives dissociation constants of a greater series of derivatives in 20% ethanol and uses indicators for construction of  $H$  acidity function in sulphuric acid. Carpentier and Lemetais<sup>2</sup> dealt with the problem of incorporation of the acidity-function defined with diphenylamines, and earlier Carpentier and Fleury<sup>6</sup> suggested five basic types of acidity functions and their classification. Bunnett and Olsen<sup>7</sup> laid the foundations for a more general classification, and their ideas were developed by Marziano and co-workers<sup>8-12</sup> (the  $M_c$  function of activity coefficients) and Cox and Yates<sup>13</sup> ( $X$  function). These authors started from the definition of dissociation constant in general medium

$$K = a_B a_{H^+} / a_{BH^+} = (c_B / c_{BH^+}) c_{H^+} (f_B f_{H^+} / f_{BH^+}). \quad (1)$$

On introduction of the usual symbol for the ratio  $c_{BH^+} / c_B = I$  and transformation into logarithmic form Eq. (1) gives definition equation of the  $H$  acidity function in the form

$$pK - \log I = H = -\log c_{H^+} - \log (f_B f_{H^+} / f_{BH^+}). \quad (2)$$

The mentioned authors<sup>9,14</sup> proved that the last term of Eq. (2) for a general indicator is proportional to the same quantity defined for a standard (even though hypothetical<sup>13</sup>) indicator. So Eq. (2) can be modified by application of, e.g., the  $X$  function

by Cox and Yates<sup>13</sup> to give

$$pK - \log I = H = -\log c_{H^+} - m^*X, \quad (3)$$

where

$$X = \log (f_B \cdot f_{H^+} / f_{B \cdot H^+}), \quad (4)$$

and

$$m^* = \log (f_B f_{H^+} / f_{B \cdot H^+}) / X, \quad (5)$$

B and B\* pertaining to the general and the standard indicators, respectively. This approach makes it possible to determine pK from known log I and log c<sub>H<sup>+</sup></sub> only, construction of the proper acidity function being unnecessary.

Cox and Yates<sup>13</sup> also suggested a simple way of construction of acidity function applicable to computer treatment.

Our aim was to measure dissociation constants of monosubstituted diphenylamines in water, to construct the H<sup>n</sup> acidity function in aqueous sulphuric acid on the basis of these indicators and with the use of original algorithm, and to incorporate these results in theory of acidity functions and free energy relationships.

## EXPERIMENTAL

Synthesis of the monosubstituted diphenylamines. 0.1 mol substituted acetanilide, 25 g bromobenzene, 50 g nitrobenzene, 7 g potassium carbonate, and 1 g fresh cuprous iodide were mixed and boiled 15 h. The mixture was steam distilled to remove volatile components, and the residue was dissolved in 100 ml ethanol and boiled with 30 ml concentrated hydrochloric acid 3 h. Purification methods and physical constants are given in Table I.

### Measurement of the Dissociation Constants and Construction of the H<sup>n</sup> Function

Absorbances of the indicators were measured in aqueous sulphuric acid solutions at (25.0 ± 0.1)°C using a VSU-2 spectrophotometer (Zeiss, Jena) at the wavelengths given in Table I and at the sulphuric acid concentrations whose number is given in Table II. The log I values were calculated from dependences of the absorbances on sulphuric acid concentrations, the indicators were ordered according to the expected basicity decrease, and the pK value was assessed for the most basic one. The pK difference between two adjacent indicators was calculated from the formula

$$\Delta pK^{i+1} = pK^i - pK^{i+1} = \left( \int_{c_1^{i+1}}^{c_2^{i+1}} \log I^i - \int_{c_1^{i+1}}^{c_2^{i+1}} \log I^{i+1} \right) / (c_2^{i+1} - c_1^{i+1}), \quad (6)$$

where  $c_1^{i+1}$ ,  $c_2^{i+1}$  are the acid concentrations limiting the concentration range used simultaneously for two indicators, and the integrals were obtained by numerical integration. Then Eq. (2) was used for calculation of the H function at all the acid concentrations, the function was smoothed, absorbances of the protonated ( $A_{B \cdot H^+}$ ) and non-protonated forms ( $A_B$ ) were optimized

so that scattering of the  $pK$  values calculated from Eq. (2) was minimum and  $H = pH$  at concentrations below  $5 \cdot 10^{-3} \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ , and, at last,  $pK$  of the first indicator was corrected. The whole procedure was repeated until the  $pK$  difference between two subsequent iterations was less than 0.001 (about 20 iterations). The experimental data were treated according to the algorithm described, with the use of our original program. All the calculations were carried with an EC 1033 computer.

## RESULTS AND DISCUSSION

Generally, the modification of Eq. (2) according to Marziano<sup>8-12</sup> or Cox and Yates<sup>13</sup> can be considered as incorporation of acidity functions into the concept of linear free energy relationships. If difference between  $\log c_{H^+}$  and  $\log I$  is expressed as concentration equilibrium constant ( $pK_c$ , see Eqs (1) and (2)), then it can be written

$$pK_c = pK - m^*X. \quad (7)$$

The relation thus expressed represents a three-parameter equation in which  $pK_c$  is an experimentally measurable quantity,  $X$  is a parameter describing the free enthalpy change  $\Delta \Delta G^*$  of standard due to a perturbation — change in composition of acid (base),  $m^*$  represents selectivity of a particular indicator as compared with the standard in the same process ( $\Delta \Delta G/\Delta \Delta G^*$ ), and  $pK$  means the  $pK_c$  values in the absence of the perturbation ( $\Delta \Delta G = 0$ ). The expression in terms of the Gibbs energies follows from thermodynamic definition of equilibrium constant.

In principle, validity of Eq. (7) can be extended also to the acidity functions constructed in mixtures water — organic solvent. This statement is supported, *e.g.*, by close correlation between  $H^+ + \log c_{H^+}$  (20% ethanol, sulphuric acid<sup>5</sup>) and the  $X$  scale ( $m^* = 1.41 \pm 0.01$ ,  $n = 41$ ,  $s = 0.079$ ,  $r = 0.9991$ ), there are, however, not enough data in literature for further comparisons. In the given case the  $m^*$  value is surprisingly high, the value expected in water being close to 1. Obviously, addition of organic solvent increases „sensitivity” of indicator to solvent composition change (a general trend in the Hammett correlations<sup>19</sup>). Grunwald and Berkowitz<sup>20</sup> tried to describe quantitatively the solvent effect in protonizing media and arrived at similar conclusions.

The treatment of experimental data with the aim of obtaining  $pK$  values was carried out in two ways — with application of the mentioned method by Cox and Yates<sup>13</sup> and by the procedure suggested by us. Although formulation of the generalized activity function  $X$  (or  $M_c$ ) represents a theoretical contribution, its practical application is limited to higher acid concentrations only, because, for  $c_{H^+}$  approaching to zero,  $X$  approaches zero, too, and  $pK_c$  approaches  $pK$ . Then the regression by Eq. (7) at low concentrations only correlates experimental error of  $pK_c$  or  $\log I$  measurement with  $X$ , and the whole procedure becomes meaningless. A certain improvement is achieved by incorporation of the term describing the dependence on the pro-

ton concentration (see Eq. (3)), which leads to double linear regression according to the equation

$$\log I = pK + n^* \log c_{H^+} + m^* X, \quad (8)$$

and by testing statistical significance of the individual parameters. Insignificant parameters are neglected, and a new simple linear regression is carried out. This procedure has a drawback in that often  $n^*$  in Eq. (8) is not statistically significantly

TABLE I

Purification methods, physical properties, and the analytical wavelengths used in  $pK$  measurements of monosubstituted diphenylamines  $X-C_6H_4-NH-C_6H_5$

X	Purification method	M.p. (b.p., pressure), °C		Formula (mol.mass)	Calculated/ Found, % N	$\lambda$ nm
		M.p. (b.p., pressure), °C, ref.	°C			
4-CH <sub>3</sub> O	crystallization, hexane	103–104		C <sub>13</sub> H <sub>13</sub> NO (199·2)	7·03	275
		104·5–105, lit. <sup>5</sup>			7·17	
4-C <sub>2</sub> H <sub>5</sub> O	crystallization, hexane	68–71		C <sub>14</sub> H <sub>15</sub> NO (213·3)	6·57	275
		69–71, lit. <sup>15</sup>			6·47	
4-CH <sub>3</sub>	crystallization, hexane	87·5–88		C <sub>13</sub> H <sub>13</sub> N (183·2)	7·64	280
		87·5–88, lit. <sup>5</sup>			7·48	
3-CH <sub>3</sub>	vacuum distillation	(314, 99·2 kPa)		C <sub>13</sub> H <sub>13</sub> N (183·2)	7·64	280
		(315, 96·5 kPa), lit. <sup>16</sup>			7·70	
H	crystallization, hexane	52–53		C <sub>12</sub> H <sub>11</sub> N (169·2)	8·28	278
		53, lit. <sup>17</sup>			8·31	
3-CH <sub>3</sub> O	crystallization, heptane	69·5–70·0		C <sub>13</sub> H <sub>13</sub> NO (199·2)	7·03	278
		68·5–59, lit. <sup>5</sup>			6·97	
4-Cl	crystallization, heptane	67·5–68		C <sub>12</sub> H <sub>10</sub> ClN (203·67)	6·88	285
		68·5–69, lit. <sup>5</sup>			6·78	
3-Br	vacuum distillation	(318, 99·2 kPa)		C <sub>12</sub> H <sub>10</sub> BrN (248·1)	5·64	280
		—			5·68	
3-Cl	vacuum distillation	(330, 99·2 kPa)		C <sub>12</sub> H <sub>10</sub> ClN (203·7)	6·88	280
		(335, 98·52 kPa), lit. <sup>5</sup>			6·76	
3-NO <sub>2</sub>	crystallization, heptane–toluene 3 : 1	111–112		C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> (214·2)	13·08	270
		110–111, lit. <sup>5</sup>			13·26	
4-NO <sub>2</sub>	crystallization heptane–toluene 1 : 2	133–135		C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> (214·2)	13·08	400
		130–131, lit. <sup>18</sup>			13·30	

equal to one even in very close correlations). It is, of course, difficult to judge to what extent this result is due to correctness of the used  $c_{H^+}$  scale (with incompletely dissociated acids<sup>13</sup>).

Our method is based on the known idea following, *e.g.*, from Eq. (2) that the  $\log I$  difference between two indicators fulfilling the Hammett condition of proportionality of activity coefficients is equal to difference between the respective  $pK$  values at the same acid concentration. For a larger number of experimental points this difference can be easily obtained by numerical integration of the curve  $\log I$  vs  $c$  concentration within the acid concentration range common to the both indicators (from  $c_1$  to  $c_2$ ) and by calculation of the difference according to Eq. (6). In contrast to other methods, this procedure does not much depend on number and values of the acid concentrations used in the common range of acid concentrations. The subsequent construction of the acidity  $H$  function, its smoothing, optimization of absorbance of the limit forms, and repeated calculation of  $\Delta pK$  in several iterations improve the link between the individual indicators and, hence, the calculated  $pK$  and acidity function.

Table II gives the  $pK$  values of the indicators studied by us and determined by Eq. (8). Dependence of these  $pK$  values on the substituent  $\sigma$  constants<sup>21</sup> gives a fairly good correlation

$$pK = (0.700 \pm 0.053) - (2.543 \pm 0.110) \sigma \quad (9)$$

$$n = 11, \quad s = 0.160, \quad r = 0.9920.$$

TABLE II

Dissociation constants of monosubstituted diphenylamines in water at 25°C

X	$\sigma$	$pK^a$	$pK^b$	$s_{pK}^b$	$n^c$
4-CH <sub>3</sub> O	-0.28	1.413	1.355	0.079	24
4-C <sub>2</sub> H <sub>5</sub> O	-0.28 <sup>d</sup>	1.478	1.350	0.075	21
4-CH <sub>3</sub>	-0.14	1.208	1.123	0.041	24
3-CH <sub>3</sub>	-0.06	0.976	0.872	0.041	24
H	0.00	0.769	0.643	0.055	24
3-CH <sub>3</sub> O	0.10	0.318	0.429	0.080	24
4-Cl	0.22	-0.070	0.090	0.024	24
3-Br	0.37	-0.238	-0.242	0.020	24
3-Cl	0.37	-0.412	-0.332	0.067	22
3-NO <sub>2</sub>	0.71	-1.276	-1.270	0.046	15
4-NO <sub>2</sub>	1.25 <sup>e</sup>	-2.237	-2.634	0.093	16

<sup>a</sup> From Eq. (8); <sup>b</sup> according to the algorithm suggested (see Experimental); <sup>c</sup> number of the measurements at various acid concentrations; <sup>d</sup> the constant used is  $\sigma(4\text{-CH}_3\text{O})$ ; <sup>e</sup> the  $\sigma^-$  constant.

A substantially better correlation with  $\sigma$  is exhibited by the pK values obtained from the proper  $H''$  function calculated by the described algorithm

$$pK = (0.673 \pm 0.017) - (2.652 \pm 0.035) \sigma \quad (10)$$

$$n = 11, \quad s = 0.051, \quad r = 0.9992.$$

The Eqs (9) and (10) show no statistically significant differences both in absolute term ( $F(1.18) = 0.24$ ,  $F_{0.05}(1.18) = 4.41$ ) and in the value  $\rho$  ( $F(1.18) = 0.89$ ), hence the both calculation methods give the same results, application of the proper  $H''$  function being more accurate. A statistically significant difference is between pK of the parent compound in ref.<sup>2</sup> (0.775) and that obtained from the proper  $H''$  function (0.643) (Table II,  $t(23) = 2.40$ ,  $t_{0.05}(23) = 2.07$ ) in contrast to the value found from Eq. (7) (Table II,  $t(23) = 0.22$ ) presuming the published value to be correct. The reaction constant in Eq. (10) is significantly smaller than the same quantity for pK of substituted anilines<sup>19</sup> ( $F(1.31) = 11.85$ ,  $F_{0.05}(1.31) = 4.15$ ), which proves a compensation electronic effect due to addition of another benzene ring. Transition from water to 20% ethanol<sup>5</sup> causes a significant increase of  $\rho$  value ( $F(1.18) = 177$ ,  $F_{0.05}(1.18) = 4.41$ ) due to lowered stabilization by solvation<sup>19</sup>.

TABLE III

The  $H''$  acidity function constructed on the basis of monosubstituted diphenylamines in aqueous sulphuric acid at 25°C;  $c$  in  $\text{mol l}^{-1}$

$c$	$H''$	$c$	$H''$	$c$	$H''$	$c$	$H''$	$c$	$H''$
0.05	1.15	0.80	-0.16	1.55	-0.65	2.30	-1.06	3.40	-1.58
0.10	0.88	0.85	-0.20	1.60	-0.68	2.35	-1.08	3.80	-1.77
0.15	0.70	0.90	-0.23	1.65	-0.71	2.40	-1.11	4.20	-1.95
0.20	0.56	0.95	-0.27	1.70	-0.74	2.45	-1.13	4.60	-2.13
0.25	0.45	1.00	-0.30	1.75	-0.77	2.50	-1.16	5.00	-2.31
0.30	0.36	1.05	-0.34	1.80	-0.79	2.55	-1.18	5.40	-2.50
0.35	0.29	1.10	-0.37	1.85	-0.82	2.60	-1.21	5.80	-2.69
0.40	0.22	1.15	-0.40	1.90	-0.85	2.65	-1.23	6.20	-2.88
0.45	0.16	1.20	-0.44	1.95	-0.88	2.70	-1.26	6.60	-3.08
0.50	0.11	1.25	-0.47	2.00	-0.90	2.75	-1.28	7.00	-3.28
0.55	0.06	1.30	-0.50	2.05	-0.93	2.80	-1.30	7.40	-3.49
0.60	0.01	1.35	-0.53	2.10	-0.96	2.85	-1.33	7.80	-3.71
0.65	-0.03	1.40	-0.56	2.15	-0.98	2.90	-1.35	8.20	-3.93
0.70	-0.08	1.45	-0.59	2.20	-1.01	2.95	-1.38	8.60	-4.16
0.75	-0.12	1.50	-0.62	2.25	-1.03	3.00	-1.40	9.00	-4.39

The  $H^*$  acidity function constructed with eleven monosubstituted diphenylamines in aqueous sulphuric acid (total 242 measurements) using the method described in Experimental is given in Table III; Table IV gives coefficients of the polynomial expansion. Application of factor analysis to the  $H_0$  functions in aqueous sulphuric acid published in refs.<sup>4,22-24</sup> and to the  $H^*$  function constructed by us incorporates unambiguously the  $H^*$  function among other acidity  $H_0$  functions (common localiza-

TABLE IV

Coefficients of polynomial expansion of dependence of the  $H^*$  function on the acid concentration in  $\text{mol l}^{-1}$  and in % w/w (in the form  $H^* = a_0 + a_1z + a_2z^2 + \dots$ ,  $z = \ln c$ )

Coefficient	$a_0$	$a_1$	$a_2$
$c, \text{mol l}^{-1}$	-0.30354549	-0.69531452	-0.19670660
$c, \% \text{ w/w}$	0.86046779	-0.45675910 $\cdot 10^1$	0.16048056 $\cdot 10^2$
Coefficient	$a_3$	$a_4$	$a_5$
$c, \text{mol l}^{-1}$	-0.68318722 $\cdot 10^{-1}$	0.40445513 $\cdot 10^{-2}$	0.15370582 $\cdot 10^{-2}$
$c, \% \text{ w/w}$	-0.24525789 $\cdot 10^2$	0.19286865 $\cdot 10^2$	-0.95369542 $\cdot 10^1$
Coefficient	$a_6$	$a_7$	$a_8$
$c, \text{mol l}^{-1}$	-0.46262870 $\cdot 10^{-2}$	-0.17826194 $\cdot 10^{-2}$	-0.18025155 $\cdot 10^{-3}$
$c, \% \text{ w/w}$	0.21444936 $\cdot 10^1$	-0.285006790	0.15526616 $\cdot 10^{-1}$

TABLE V

Comparison of  $H^*$  (Table IV) with published  $H_0$  functions in aqueous sulphuric acid at 25°C according to the equation  $H^* = a + b H_0$

Ref.	$a$	$s_a$	$t(a=0)$	$b$	$s_b$	$t(b=1)$	$t_{0.05}$	$r$
4	-0.06	0.01	5.03	0.98	0.01	3.89	2.23	0.9999
22	-0.01	0.01	0.74	0.98	0.01	2.57	2.03	0.9998
23	0.09	0.02	5.28	1.01	0.01	1.30	2.06	0.9993
24	-0.04	0.02	1.82	1.02	0.01	1.99	2.16	0.9994

tion in the factor space). A close correlation is also found between the  $H''$  function constructed by us (as  $H'' + \log c_{H^+}$ ) and the X quantity by Cox and Yates<sup>13</sup>

$$H'' + \log c_{H^+} = -(0.007 \pm 0.010) + (1.037 \pm 0.006) X \quad (11)$$

$$n = 60, \quad s = 0.048, \quad r = 0.9989.$$

The  $H''$  function shows no statistically significant shift as compared with the X scale (the absolute term is equal to zero,  $t(58) = 0.64$ ,  $t_{0.05}(58) = 2.00$ ), the slope  $m^*$  in Eq. (11) corresponds to the same quantity of primary amines (1.02, ref.<sup>13</sup>). Comparison with several  $H_0$  functions for aqueous sulphuric acid<sup>4,22-24</sup> is given in Table V. The  $H''$  function shows a statistically significant shift when compared with the  $H_0$  by Paul and Long<sup>4</sup> (downwards) and with that by Rjabova and coworkers<sup>23</sup> (upwards), the steepness is significantly smaller when compared with that of  $H_0$  by Paul and Long<sup>4</sup> and by Bascomb and Bell<sup>22</sup>. The correlations are very close in all the cases.

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