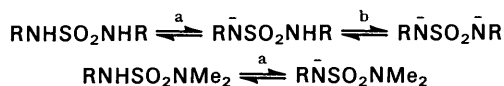# Basicity of Nitrogen–Sulphur(VI) Compounds. Part 4.[1] Ionization of Di- and Tri-substituted Sulphamides

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Potentiometric and u.v. methods have been used to study the ionization equilibria of di- and tri-substituted sulphamides:

$$RNHSO_2NHR \xrightarrow{a} R\bar{N}SO_2NHR \xrightarrow{b} R\bar{N}SO_2\bar{N}R$$

$$RNHSO_2NMe_2 \xrightarrow{a} R\bar{N}SO_2NMe_2$$

pK_a Values for equilibrium a have been determined for nine di- and five tri-substituted sulphamides, sulphamide, and phenylsulphamide in 60% v/v ethanol–water. Ionization data for equilibrium b have been measured for seven diarylsulphamides in aqueous potassium hydroxide. Since neither H_- nor H_{2-} acidity functions are suitable for describing the ionizations occurring a number of other methods, e.g. the modified Marziano–Cimino–Passerini method, have been used to obtain thermodynamic pK_a values. The agreement between the pK_a values obtained by the various methods is good. The effect of substituents on both equilibria (a and b) is similar.

In this series we have examined the protonation and ionization of various types of sulphamates ($>NSO_3^-$) using potentiometric, conductiometric, and u.v. and n.m.r. (^{13}C and ^1H) spectroscopic methods. While extensive studies have been made on the protonation [2] and ionization [3] of the medicinally important sulphonamides ($C-NHSO_2-C$), no work appears to have been carried out on the study of the acid–base equilibria of the related sulphamides ($>NSO_2N<$) despite the fact that (di-)anion(s) are clearly involved or implicated in many sulphamide reactions.[4] Further, the study of the acid dissociation of say, symmetrically disubstituted sulphamides, $RNHSO_2NHR$, would be of interest *per se* in that while the first proton would be removable in the pH region the second proton might require stronger base to effect its removal and thus a H_- or similar ' basicity function ' would be needed to describe adequately the ionizations occurring. In this paper we have examined the ionizations of such a series of disubstituted sulphamides, using both aryl, alkyl, and alicyclic compounds. Additionally, we have looked at a series of trisubstituted (one ionizable proton) sulphamides, N-phenylsulphamide, and the parent compound, sulphamide.

In general, the potentiometric method has been used to examine the first ionization and the u.v. method has been employed to study the second acid dissociation.

EXPERIMENTAL

Materials.—The disubstituted sulphamides (1)—(4), (6) and (7) (see Scheme 1) were reported previously by us.[5] Compounds (5), (8), and (9) were prepared by the method of Parnell,[6] involving reaction of their amines with sulphuryl chloride. The m.p.s of compounds (8) and (9) agreed with the values given in the literature.[7,8] Compound (5) melted at 192—194° (lit.,[6] 205°). The trisubstituted sulphamides (10)—(14) were prepared by the reaction of NN-dimethyl-sulphamyl chloride with the appropriate amines. After recrystallization the following m.p.s were obtained: (10) 53—55° (lit.,[8] 56°), (11) 89—91° (lit.,[9] 90—91°), (12) 85—87° (lit.,[9] 84—85°), (13) 86—88° (lit.,[8] 88.5°), and (14) 124—126° (lit.,[8] 127°). The i.r. spectra of the trisubstituted sulphamides displayed the following characteristic vibr-

ations [10] (in cm^{-1}): 3 225—3 280 (s, m) (v_{NH}), 1 320—1 340 (m) (v_{SO_2} asymm), 1 140—1 150 (s) (v_{SO_2} symm.), 1 030—1 080 (m, w) (v_{CN}), and 795—820 (m, w) (v_{SN}). Sulphamide (Fluka) was used as obtained and N-phenylsulphamide, m.p. 106—108° (lit.,[11] 105—107°), was synthesised by the method given by Kirsanov and Zolotov.[11] Potassium hydroxide (1.0M) was prepared from Volucon (May and Baker) standards. Solutions of lesser concentration were prepared by dilution. 2—10M-KOH solutions were prepared by dissolving potassium hydroxide pellets in distilled water. The concentrations of the resulting solutions were checked by titration with standard HCl. Buffered solutions for pH 4.0, 7.0, and 9.2 were prepared from buffer tablets (B.D.H.). A buffered solution of pH 12 was prepared by dilution of a Puffer-Titrisol (Merck). The observed pH values were reduced by 0.22 units to take into account the change from water to 60% v/v EtOH–H$_2$O.[12a]

Potentiometric Measurements.—A Pye–Unicam model 290 MK 2 pH meter standardized with buffers of pH 4.0, 7.0, 9.2, and 12.0 was used. The following procedure represents the conditions of a typical measurement.[12b] Compound (3) (0.031 g) was dissolved in 60% v/v ethanol–water (37.5 ml) in a 100 ml titration flask which was placed in a water-bath maintained at 25 °C. A magnetic stirring bar and a glass electrode were placed in the flask. After reading the initial pH, 0.05M-KOH in 60% v/v ethanol–water (2.5 ml) was added in 0.2 ml portions. The solution was stirred during the addition of titrant and for *ca.* 20 s afterwards. The pH was then recorded. In the calculation of the pK values, allowance was made for the dilution caused by the addition of the titrant.

U.v. Measurements.—U.v. measurements were made at 25 °C using a Perkin-Elmer 124 spectrophotometer. The following procedures were typical.

Method A. A 5 × 10^{-4}M stock solution of compound (3) was prepared by dissolving (3) (0.0062 g) in 1.0M-KOH (50 ml). 0.5 ml of this solution was pipetted into 4.5 ml of base of known strength giving a 5 × 10^{-5}M solution. The solution was well shaken and the spectrum scanned in the region 320—220 nm. Figure 1 illustrates the spectral changes observed for compound (3) over this wavelength range for various strengths of base.

Method B. This was identical to method A except that the stock solution was made up in 0.1M-KOH.

Method C. This was identical to method A except that

the stock solution was made up in 0.001M-KOH. In the case of compound (7) the spectrum was scanned in the region 380—220 nm. In general the pK_a values in Table 1 and the ionisation data in Tables 2 and 4 were not determined in duplicate. When a second determination was made it was found to give value(s) identical to the original values.
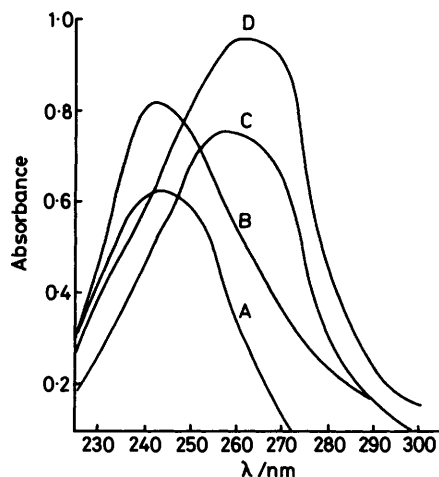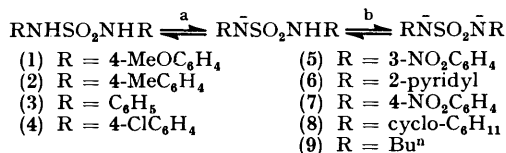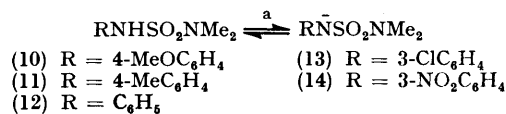

FIGURE 1 Absorption spectra of compound (3) in A, 0.25M-KOH, B, 2.0M-KOH, C, 4.0M-KOH, and D, 10.0M-KOH
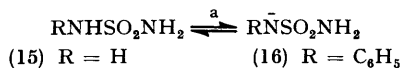
RESULTS AND DISCUSSION

Equilibrium a.—In Table 1 pK_a values are given for equilibrium a for the 16 sulphamides shown in Schemes 1—3. Ionization data were determined potentiometric-

$$RNHSO_2NHR \underset{}{\overset{a}{\rightleftharpoons}} R\bar{N}SO_2NHR \underset{}{\overset{b}{\rightleftharpoons}} R\bar{N}SO_2\bar{N}R$$

(1) R = 4-MeOC$_6$H$_4$	(5) R = 3-NO$_2$C$_6$H$_4$
(2) R = 4-MeC$_6$H$_4$	(6) R = 2-pyridyl
(3) R = C$_6$H$_5$	(7) R = 4-NO$_2$C$_6$H$_4$
(4) R = 4-ClC$_6$H$_4$	(8) R = cyclo-C$_6$H$_{11}$
	(9) R = Bu^n

SCHEME 1

$$RNHSO_2NMe_2 \overset{a}{\rightleftharpoons} R\bar{N}SO_2NMe_2$$

(10) R = 4-MeOC$_6$H$_4$	(13) R = 3-ClC$_6$H$_4$
(11) R = 4-MeC$_6$H$_4$	(14) R = 3-NO$_2$C$_6$H$_4$
(12) R = C$_6$H$_5$	

SCHEME 2

$$RNHSO_2NH_2 \overset{a}{\rightleftharpoons} R\bar{N}SO_2NH_2$$

(15) R = H	(16) R = C$_6$H$_5$

SCHEME 3

ally. Using equation (1) pK_a values were calculated at each pH at which measurements were made, in the range

$$pK_a = pH + \log[HA]/[A^-] \quad (1)$$

20—80% ionization. A Hammett ρ value of 2.78 can be obtained for the diaryl compounds if the pK_a values for compounds (1)—(7) in Table 1 are plotted against the appropriate σ values using a value of 0.75 for the 2-pyridyl compound [13] and the exalted value of 1.24 for the 4-nitro-compound. The correlation coefficient r for the plot is 0.992 and the percentage error is 5.4. If $\sigma_{p\text{-NO}_2} = 0.78$ is used for compound (7) then r falls to 0.944 and the percentage deviation for compound (7) is

12.5 compared with 1.36 when the exalted value is used. Strong resonance interaction between the 4-nitro-substituent and the ionization site is clearly indicated. In the case of the *meta*-placed nitro-group in compound (5) such interaction is not possible and the usual $\sigma_{m\text{-NO}_2}$

TABLE 1

pK_a Values at 25 °C for $RNHSO_2NHR$, $RNHSO_2NMe_2$, and $RNHSO_2NH_2$ in equilibrium a in 60% v/v $EtOH-H_2O$

Compound	pK_a	Spread ($\pm$) [a]	n
(1)	10.57	0.04	11
(2)	10.49	0.02	6
(3)	10.13	0.04	12
(4)	8.95	0102	5
(5)	8.13	0.03	5
(6)	8.00	0.07	6
(7)	6.39	0.08	10
(8)	12.30	0.10	7
(9)	12.29	0.05	8
(10)	10.64	0.06	7
(11)	10.73	0.09	8
(12)	10.26	0.04	7
(13)	9.74	0.12	7
(14)	8.32	0.04	7
(15)	10.42 [b]	0.09	8
(16)	11.10	0.02	6

[a] The spread or scatter was calculated as before. [b] This value refers to aqueous solution.

is appropriate to use. The above ρ value of 2.78 may be compared with the values obtained for sulphonamide acid dissociations.[3] Willi [3a] gives a value of 1.74 for the ionization $C_6H_5SO_2NHC_6H_4X \rightleftharpoons C_6H_5SO_2\bar{N}C_6H_4X$ in water (for nine *m*- and *p*-substituted sulphonanilides). The change from water to a medium of lower dielectric constant, *e.g.* 60% v/v ethanol (which was necessary in order to dissolve a sufficient quantity of the sulphamides) would be expected to increase the ρ value. A Russian group [3d] using an almost aqueous media report a ρ value of 1.8 for a similar sulphonamide ionization. Our value is however in close agreement with the ρ values obtained in 50% ethanol, *i.e.* ρ 2.6 [3b] and 2.5.[3e,f]

The pK_a values for the five trisubstituted sulphamides (10)—(14) (Scheme 2) gave a ρ value of 2.34 (r 0.965, percentage error 15.6).

Equilibrium b.—The 'second' acid dissociation of the eight diarylsulphamides (3)—(7) has been examined by u.v. at 25 °C (Table 2). For compounds (5)—(7) all or almost all of whose ionizations took place in the pH region the $(H_-)_{\frac{1}{2}}$ values were taken as being equivalent to the thermodynamic pK_a values. The ionization ratios for compounds (1)—(7) were calculated from equation (2)

$$I = \frac{\varepsilon_{HA^-} - \varepsilon}{\varepsilon - \varepsilon_{A^2-}} \quad (2)$$

where ε_{HA^-} and ε_{A^2-} are the absorbances at the chosen wavelengths (see Table 2) of the monoanion ($R\bar{N}SO_2$-NHR) and the dianion ($R\bar{N}SO_2\bar{N}R$), respectively. ε is the absorbance at the wavelength monitored for various intermediate base strengths. The base strengths at which the monoanion was generated could be estimated from the previously determined 'first' pK_a value. Equilibrium b was then examined by a progressive in-

crease in the strength of the base. When the absorbance showed very little change with increase in base strength, the dianion was considered to have been fully formed. Figure 2 shows a typical sigmoidal type curve obtained
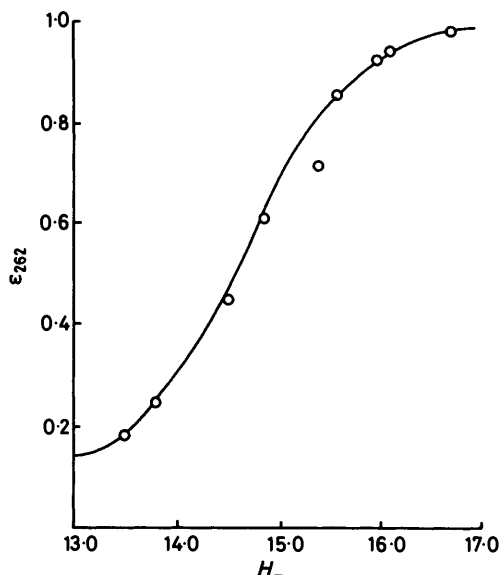

FIGURE 2   Plot of absorbance at 262 nm *versus* H_- for compound (3) in KOH at 25 °C

for one of the compounds studied. In the case of compound (7), $\varepsilon_{A^{2-}}$ was varied by small increments until the correlation coefficient of plots of $\log_{10} I$ *versus* H_- were maximised.

In examining the ionization behaviour of the sulphamides in equilibrium b it seemed appropriate to consider using both the H_- and H_{2-} acidity function for bases.[14-16] The H_{2-} function was developed to describe the ability of an aqueous basic solution to abstract a proton from a monoanion and has been set up for aqueous KOH using substituted indolecarboxylates as indicators. Irrespective of the base used H_{2-} increases more rapidly with increasing concentration of base than does the corresponding H_- scale. For the present work, H_{2-} values for aqueous KOH were calculated from the existing H_- values and the differences, $H_{2-} - H_-$, given by Yagil.[17]

Plots of $\log_{10} I$ *versus* H_{2-} [equation (3)] gave good straight lines but for a majority of the compounds the slopes(m) were not close to unity (see Table 2). (H_{2-})-

$$\log_{10} I = -m H_{2-} + pK_a \qquad (3)$$

Values have been calculated using equation (3) for the situation at half-ionization, *i.e.* when $[HA^-] = [A^{2-}]$; then $-m(H_{2-})_{\frac{1}{2}} = pK_a$. The $(H_{2-})_{\frac{1}{2}}$ values in Table 2 were obtained by dividing the intercepts of the plots by the m values. A plot of $(H_{2-})_{\frac{1}{2}}$ *versus* σ gave a good (r 0.995, error 4.2%) straight line with a slope (ρ) of 3.22. Again, use of the σ value of 1.24 for compound (7) gave a better fit.

The effect of varying the wavelength at which measurements were taken was checked in the case of compound (3) by plotting $\log_{10} I$ values determined at 270 nm against H_{2-}. These gave a $(H_{2-})_{\frac{1}{2}}$ value of 15.32 slope(m) = 0.88 ($r = 0.996$) compared with the values of $(H_{2-})_{\frac{1}{2}} = 15.20$ and 0.95(m) determined at 262 nm (Table 2).

Table 2 contains the results of plots of $\log_{10} I$ *versus* H_-. The slopes (m) obtained are closer to unity and it would thus seem that the H_- acidity function describes more accurately the ionization occurring in equilibrium b (Scheme 1). Perhaps the less satisfactory agreement with H_{2-} in the present instance may be due to the fact that for the sulphamides, two nitrogen anions are involved, whereas the indicators used for establishing H_{2-} have an oxygen and a nitrogen anion.

pK_a Values for some of the diarylsulphamides (1)—(4) have been calculated by several other methods. For compounds (5)—(7) the ionization represented in equilibrium b occurs in the pH region and the application of these methods would be inappropriate for these diarylsulphamides. Using the method of More O'Ferrall and Ridd [14,18] we estimated pK_a values for compounds (1)—(4) from equation (4) by plotting $\log_{10} I - \log_{10} [OH^-]$ *versus* $[OH^-]$ and extrapolating to zero concentration of base (where a_w and all solute activity coefficients are zero by definition).

$$pK_w - pK_a = \log_{10} I - \log_{10} [OH^-] + \log_{10} \gamma_{A^-} \cdot a_w/\gamma_{HA} \cdot \gamma_{OH^-} \qquad (4)$$

The intercept gives a value for $pK_w - pK_a$ and hence for pK_a, *i.e.* $pK_{(4)}$ in Table 4. Where the extrapolation involved is not too long the method is considered reliable. In our case the points on the plots ranged from *ca.* 0.5—9M-base and the extrapolat ions involved were $\leqslant 1.0$M-base (gauged from the OH^- axis).

Stewart and his co-workers have modified and used the Bunnett and Olsen and the Marziano–Cimino–Passerini methods for the study of acid dissociations.[19-21] According to the modified Bunnett–Olsen treatment the pK_a

TABLE 2

Ionization data for diarylsulphamides in equilibrium b measured in KOH at 25 °C

Compound	λ	$\dfrac{d \log_{10} I}{d(H_{2-})}$ [a]	$(H_{2-})_{\frac{1}{2}}$ [b]	r [c]	$\dfrac{d \log_{10} I}{d(H_-)}$ [d]	$(H_-)_{\frac{1}{2}}$ [e]	r
(1)	270	0.70	16.28	0.987 (7)	0.87	15.59	0.987
(2)	260	0.55	15.80	0.991 (6)	0.83	15.47	0.988
(3)	262	0.95	15.20	0.999 (6)	1.27	14.70	0.999
(4)	270	0.84	14.22	0.993 (9)	0.99	13.91	0.992
(5)	270	0.52	12.44	0.969 (6)	0.96	12.83	0.972
(6)	260	0.77	13.00	0.994 (7)	0.83	12.90	0.994
(7)	350	1.06	11.36	0.992 (6)	1.06	11.36	0.992

[a] *I.e.* the slopes (m) of plots of $\log_{10} I$ *versus* H_{2-}. [b] Calculated from equation (3). [c] The figures in parentheses are the number of points taken. [d] *I.e.* the slopes (m) of plots of $\log_{10} I$ *versus* H_-. [e] Calculated from equation (3), when H_- is substituted for H_{2-}.

can be found from equation (5) by plotting $H_- - \log_{10}I$ versus $(H_- - pK_w - \log_{10}[OH^-] + \log_{10}a_w)$. In order

$$H_- - \log_{10}I = -\phi(H_- - pK_w - \log_{10}[OH^-] + \log_{10}a_w) + pK_a \quad (5)$$

to use this method (and also in order to use the modified Marziano–Cimino–Passerini treatment, see below) water activities in potassium hydroxide solutions are needed. They did not appear to be available in the literature so they were calculated [22] from the osmotic coefficients using equation (6) where ν (the number of ions produced)

$$\log_{10}a_w = -0.007\,824\,\nu m n \quad (6)$$

$= 2$ for potassium hydroxide, m is the molality, and n is the osmotic coefficient. Molalities and molarities were interconverted using densities of potassium hydroxide solutions.[23] The Marziano–Cimino–Passerini approach makes use of a single reference compound rather than an acidity function. We have employed the procedure used by Cox and Stewart [19] to calculate values of log $(f_{A_*^-}/f_{HA_*}f_{OH^-})$ for a reference indicator HA_* in potassium hydroxide solutions in the range 0.5—12.5M. Graphs were plotted according to equation (7) for two acids HA_0 (an anchor compound of known pK_a) and HA_1 with which it overlaps, using ionization data for successive

$$pK_w + \log_{10}[OH^-] - \log_{10}a_w - \log C_{A_1^-}/C_{HA_1}$$
$$= m(pK_w + \log_{10}[OH^-] - \log_{10}a_w - \log C_{A_*^-}/C_{HA_*} - pK_{HA_*}) + pK_{HA_1} \quad (7)$$

pairs of the indole derivatives originally employed by Yagil in setting up the H_- scale. Then values of log

according to equation (9) gave pK_a values for compounds (1)—(3). The Marziano plots show better linearity than the corresponding Bunnett–Olsen plots, which was also the case in the deprotonation of heterocyclic methiodide

TABLE 3

log $(f_{A_*^-}/f_{HA_*}f_{OH^-})$ as a function of potassium hydroxide concentration calculated by the method of Cox and Stewart [19]

[KOH]/ mol dm^{-3}	$-\log (f_{A_*^-}/f_{HA_*}f_{OH^-})$	[KOH]/ mol dm^{-3}	$-\log (f_{A_*^-}/f_{HA_*}f_{OH^-})$
0.50	0.040	5.00	0.609
0.75	0.070	5.50	0.685
1.00	0.095	6.00	0.772
1.25	0.110	6.50	0.843
1.50	0.135	7.00	0.927
1.75	0.157	7.50	1.052
2.00	0.176	8.00	1.127
2.25	0.203	8.50	1.180
2.50	0.235	9.00	1.260
2.75	0.275	9.50	1.333
3.00	0.330	10.00	1.437
3.25	0.356	10.50	1.505
3.50	0.385	11.00	1.543
3.75	0.420	11.50	1.597
4.00	0.456	12.00	1.635
4.50	0.525	12.50	1.700

salts studied by Cox et al.[20] They have attributed this to the unsuitability of H_- for use with charged acids. The slops of the Bunnett–Olsen plots vary over a range of one unit. Variations of a similar magnitude were observed previously.[20]

The agreement between the pK_a values determined by the four different methods is quite good (Table 4). From

TABLE 4

pK_a Values for diarylsulphamides in equilibrium b by four methods

Compd.	$(H_-)_i$ [a]	$pK_{(4)}$ [b]	r	$pK_{(5)}$ [c]	r	ϕ	$pK_{(9)}$ [d]	r	m^*
(1)	15.59	15.55	0.921	15.34	0.950	-0.28	15.64	0.952	0.91
(2)	15.47	15.40	0.970	15.27	0.897	-0.35	15.51	0.981	0.92
(3)	14.70	15.06	0.999	14.93	0.980	0.66	14.94	0.996	1.78
(4)	13.91	14.05	0.870	13.92	e	0.09	f		

[a] Taken from Table 2. [b] Determined from equation (4). [c] Determined from equation (5), i.e. the Bunnett and Olsen approach. [d] Determined from equation (9), i.e. the Marziano–Cimino–Passerini method. [e] Correlation coefficient not given as it has no meaning when the slope is very close to zero. (J. F. Bunnett, R. L. McDonald, and F. P. Olsen, J. Am. Chem. Soc., 1974, 96, 2855). [f] This pK_a was not determined from equation (9) due to uncertainties in log $(f_{A_*^-}/f_{HA_*}f_{OH^-})$ below 0.5M-KOH.

$(f_{A_*^-}/f_{HA_*}f_{OH^-})$ for a reference indicator benzimidazole $(pK_a\ 12.86)$ were calculated using equation (8). The

$$\log(f_{A_*^-}/f_{HA_*}f_{OH^-}) = \frac{1}{m}\log(f_{A_1^-}/f_{HA_*}f_{OH^-})$$
$$= \frac{1}{mm^1}\log(f_{A_1^-}/f_{HA_*}f_{OH^-})$$
$$= \frac{1}{\pi m}\log(f_{A_n^-}/f_{HA_n}f_{OH^-}) \quad (8)$$

values of log $(f_{A_*^-}/f_{HA_*}f_{OH^-})$ when plotted against $[OH^-]$ are almost linear over the whole range (0.5—12.5M). Large scale plots of this type were used to determine values of log $(f_{A_*^-}/f_{HA_*}f_{OH^-})$ for use in equation (9). Values are given in Table 3. The intercepts of plots

$$pK_w + \log_{10}[OH^-] - \log_{10}a_w - \log_{10}I$$
$$= m^*[\log (f_{A_*^-}/f_{HA_*}f_{OH^-})] + pK_{HA} \quad (9)$$

the data in Table 4 the following average pK_a values, with standard deviations, can be calculated: 15.53 ± 0.11 [compound (1)], 15.41 ± 0.09 [compound (2)], 14.91 ± 0.13 [compound (3)], and 13.96 ± 0.06 [compound (4)].

A plot of $(H_-)_i$ values (from Table 2) versus σ gave a good straight line ($r\ 0.996$, error 4.3%) with $\rho\ 2.77$. A plot using the four Bunnett and Olsen $pK_{(5)}$ values from Table 4 for compounds (1)—(4) and the $(H_-)_i$ values from Table 2 for compounds (5)—(7) also gave a good straight line ($r\ 0.996$, error 4.1%) with a closely agreeing ρ value of 2.68.

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