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Acid-Base Equilibria of Aniline Derivatives in *n*-Butanol[1]

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Acid-base equilibria of the aniline derivatives in *n*-BuOH were investigated. The over-all dissociation constant ($K_{BH}^{n\text{-BuOH}} = K_{HX}^{\circ}/K_B K_{BHX} = [H^+][B]f_H/[BH^+]f_{BH}$) and the dissociation constant of ion pair ($K_{BHX} = [BH^+][X^-]f_{BH}f_X/[BH^+X^-]$) were estimated. The ion pair (BH^+X^-) existed to a considerable extent. The values of $pK_{BH}^{n\text{-BuOH}}$ and pK_{BHX} were respectively: 3.47, 2.83 for 4-methyl-3-nitroaniline; 3.33, 2.66 for 4-carbethoxyaniline; 2.94, 2.42 for 2-methoxy-5-nitroaniline; 2.84, 2.74 for *m*-nitroaniline; 2.79, 2.84 for 2-methyl-5-nitroaniline. The basicity of the anilines in *n*-BuOH increased as compared with that in water ($\Delta pK = pK_{BH}^{n\text{-BuOH}} - pK_a = 0.4$—$0.8$).

Keywords——acid-base equilibria in *n*-BuOH; UV- and visible absorption spectrophotometry; nitroanilines; dissociation constant; ion pair dissociation constant; perchloric acid as a standard acid

In the previous paper,[3] the dissociation constants (pK_{BH}^{MeOH}) of the aniline derivatives were determined in MeOH. The pK_{BH}^{MeOH} values could be measured by the usual spectrophotometry as well as in aqueous solution. This method, however, could not be applied to acid-base equilibrium in alcoholic solvents with much lower dielectric constant (D) than that of MeOH. It has generally been known that, when the dielectric constant of the solvent is lowered, the ions become associated to form ion pairs.[4–7] Kolthoff and Bruckenstein[4,8] pointed out that, although it was virtually complete in MeOH(D=32.6) and EtOH(D=24.3), the dissociation of ion pair became incomplete in alcoholic solvents with lower dielectric constant such as iso-propyl alcohol(D=18.3). Marple and Fritz[9] elucidated the acid-base equilibrium of organic acids in *tert*-BuOH(D=11.2) by considering ion pair formation. In this paper, a method is developed to estimate the base strength of the aniline derivatives in *n*-BuOH(D=17.1).

Theoretical

The equilibria of the base, B, in the presence of an acid, HX, are written

$$B + HX \overset{K_B}{\rightleftharpoons} BH^+X^- \qquad \text{(I)}$$

$$BH^+X^- \overset{K_{BHX}}{\rightleftharpoons} BH^+ + X^- \qquad \text{(II)}$$

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[1] This work was presented at the 95th Annual Meeting of the Pharmaceutical Society of Japan, Nishinomiya, 1975.

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[3] T. Kitagawa and S. Mizukami, *Chem. Pharm. Bull.* (Tokyo), **26**, 53 (1978).

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[5] E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

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[7] R.G. Bates, "Determination of pH," 2nd ed., John Wiley and Sons, Inc., New York, 1973, pp. 170—210.

[8] I.M. Kolthoff, J.J. Lingane, and W.D. Larson, *J. Am. Chem. Soc.*, **60**, 2512 (1938); I.M. Kolthoff and L.S. Guss, *ibid.*, **60**, 2516 (1938); L.S. Guss and I.M. Kolthoff, *ibid.*, **62**, 249 (1940).

[9] L.W. Marple and J.S. Fritz, *Anal. Chem.*, **35**, 1223, 1431 (1963).

$$HX \overset{K^i_{HX}}{\rightleftarrows} H^+X^- \overset{K^d_{HX}}{\rightleftarrows} H^+ + X^- \tag{III}$$

The equilibrium constants, K_B, K_{BHX}, K^i_{HX} and K^d_{HX} are defined as follows:

$$K_B = \frac{[BH^+X^-]}{[B][HX]} \tag{1}$$

$$K_{BHX} = \frac{[BH^+][X^-]}{[BH^+X^-]}\,{}_{BH}f_X \tag{2}$$

$$K^i_{HX} = \frac{[H^+X^-]}{[HX]} \tag{3}$$

$$K^d_{HX} = \frac{[H^+][X^-]}{[H^+X^-]} f_H f_X \tag{4}$$

The over-all dissociation constant of the acid, K°_{HX}, is defined as eq(5).

$$K^\circ_{HX} = K^i_{HX}K^d_{HX} = \frac{[H^+][X^-]}{[HX]} f_H f_X \tag{5}$$

According to Kolthoff,[10] activity coefficient is written

$$f_H = f_{BH} = f_X = f \tag{6}$$

From the rule of the electroneutrality

$$[X^-] = [H^+] + [BH^+] \tag{7}$$

The total concentrations of the base and the acid, C_B and C_{HX}, are expressed by eq(8) and (9), respectively.

$$C_B = [B] + [BH^+] + [BH^+X^-] \tag{8}$$

$$C_{HX} = [HX] + [H^+X^-] + [X^-] + [BH^+X^-] \tag{9}$$

A molar ratio of the base to its protonated form is defined as P.

$$P = \frac{[B]}{[BH^+]+[BH^+X^-]} \tag{10}$$

Combining eq(1)—(6) with eq(10) yields

$$\frac{1}{P[H^+][X^-]f^2} = \frac{K_B K_{BHX}}{K^\circ_{HX}}\,\frac{1}{[X^-]f^2} + \frac{K_B}{K^\circ_{HX}} \tag{11}$$

The coefficient, $K_B K_{BHX}/K^\circ_{HX}$, in the right-hand side of eq(11) represents the reciprocal of the over-all dissociation constant of the base, $K^{n\text{-BuOH}}_{BH}$, in the solvent as follows:

$$K^{n\text{-BuOH}}_{BH} = \frac{[H^+][B]}{[BH^+]} = \frac{K^\circ_{HX}}{K_B K_{BHX}} \tag{12}$$

When P, $[H^+]$, $[X^-]$ and f are able to evaluate successfully, therefore, the $K^{n\text{-BuOH}}_{BH}$ value may be estimated by eq(11). The P value is measurable spectrophotometrically.

$$P = \frac{\varepsilon - \varepsilon_{BH}}{\varepsilon_B - \varepsilon} \tag{13}$$

where ε is the molar extinction coefficient at a given wavelength which is apparently observed for the test solution, and ε_B and ε_{BH} are the coefficients at the wavelength of the base and its protonated form, respectively.[11] If a very strong acid is used and the undissociated species is negligible in the solvent($[HX]=0$ and $[H^+X^-]=0$), $[H^+]$ can be calculated by eq(14) which is derived from eq(7), (8), (9) and (10).

$$[H^+] = C_{HX} - \frac{C_B}{1+P} \tag{14}$$

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[10] I.M. Kolthoff and M.K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965); I.M. Kolthoff and M.K. Chantooni, Jr., *J. Phys. Chem.*, 70, 856 (1966).

[11] On measurement of P, the wavelength in general was chosen in the region where the difference between the absorbances of the base and the protonated form was large.

When the concentration of the base is much smaller than that of the acid, *i.e.*, $[X^-] \gg [BH^+X^-]$, $[X^-]$ is approximately equal to C_{HX}. Thus, f may be calculated by Debye-Hückel equation[12] as shown

$$-\log f = 5.02\sqrt{\mu} \quad (\mu = [X^-]) \tag{15}$$

Results and Discussion

In this work, perchloric acid, $HClO_4$, was used as an acid. Potentiometry revealed that $HClO_4$ dissociated almost completely in *n*-BuOH in the concentration from 2×10^{-5} M to 2×10^{-2} M. The e.m.f. (electromotive force(mV)) of the acid solution was measured and the relationship between e.m.f. and the logarithmic value of hydrogen ion activity ($[H^+]f$) was examined. Fig. 1 shows the plot of e.m.f. against $-\log C_{HX}f$ in two ranges in the concentrations; 2×10^{-5}—5×10^{-4} M and 6×10^{-4}—2×10^{-2} M. The relation was shown as a straight line. The slopes of the straight lines were calculated to be about -60 mV according to the method of least-squares, which were illustrated in Table I. As explained by Nernst equation, this fact may indicate that $HClO_4$ dissociated almost completely in such concentrations in the solvent. Accordingly, $[H^+]$ can be determined from eq(14) using C_{HX}, C_B and P. The spectral change on addition of $HClO_4$ of 4-methyl-3-nitroaniline (**1**) and 4-carbethoxyaniline (**2**) were shown in Fig. 2 and 3, respectively. Since the concentration of the sample was kept constant independently of an increasing amount of the acid, the P values were calculated using the absorbances, A, A_B and A_{BH} in a series of spectra at a given wavelength. Plots of $1/P[H^+]C_{HX}f^2$ against $1/C_{HX}f^2$ for both anilines are shown in Fig. 4 and 5. The plot yielded a straight line (correlation coefficient, $r=0.9988$ for **1**; $r=0.9993$ for **2**). The slope of the straight line ($1/K_{BH}^{n\text{-BuOH}}$) was calculated by the method of least-squares.

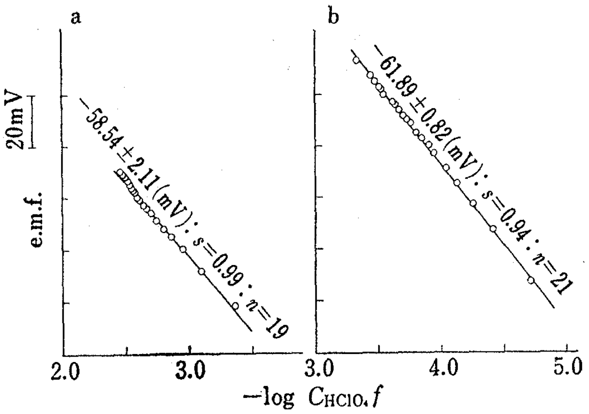

Fig. 1. Plot of e.m.f. (mV) against $-\log C_{HClO_4}f$ for Perchloric Acid Solution

a) C_{HClO_4}: 6.15×10^{-4}—1.79×10^{-2} M,
b) C_{HClO_4}: 2.00×10^{-5}—4.63×10^{-4} M.

TABLE I. Electromotive Force (mV) of Perchloric Acid in *n*-BuOH

Exp. No.	Slope (mV)	
	C_{HClO_4}: 2.00×10^{-5}—4.63×10^{-4} (M)	C_{HClO_4}: 6.15×10^{-4}—1.79×10^{-2} (M)
	(r: correlation coefficient)	
1	$-61.89\pm0.82(0.9991)$	$-58.54\pm2.11(0.9980)$
2	$-62.70\pm0.89(0.9991)$	$-59.52\pm2.28(0.9996)$

± values: 95% confidence interval.

On the other hand, another equilibrium constant, K_{BHX}, may be evaluated from $K_{BH}^{n\text{-BuOH}}$. The concentration, [B], is calculated from eq(8) and (10) according to the equation

$$[B] = \frac{PC_B}{1+P} \tag{16}$$

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[12] The constant term (5.02) in eq (15) was calculated using dielectric constant, $D=17.1$, absolute temperature, $T=298$ (°K).

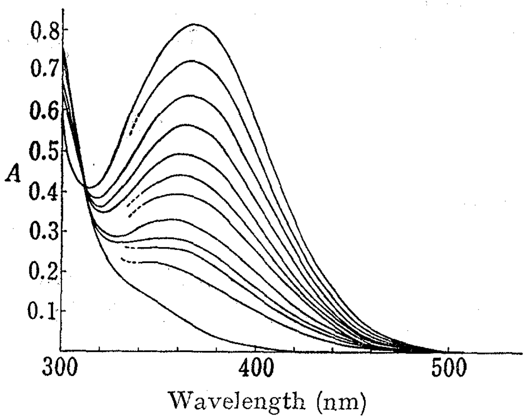


Fig. 2. Visible Absorption Spectra of 4-Methyl-3-nitroaniline in Perchloric Acid Solutions of Various Concentrations: (from the above) $C_{\mathrm{HClO_4}}$: 0 (*n*-BuOH), 1.075×, 2.150×, 3.225×, 4.300×, 5.375×, 6.450×, 8.600×, 10.750×, 12.901×, 16.126×10^{-4}M and 0.1M

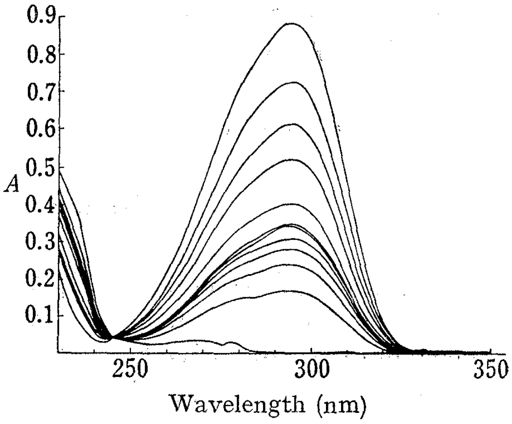


Fig. 3. UV-Spectra of 4-Carbethoxyaniline in Perchloric Acid Solutions of Various Concentrations: (from the above) $C_{\mathrm{HClO_4}}$: 0(*n*-BuOH), 1.073×, 2.146×, 3.219×, 5.366×, 6.439×, 6.439×, 7.512×, 8.585×, 10.732×, 16.097×, 6.439×10^{-4}M and 0.1M

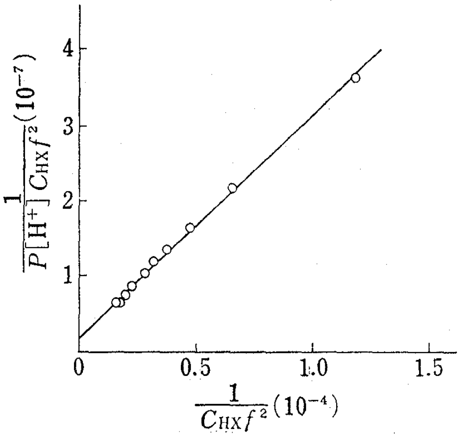


Fig. 4. Plot of $1/P[\mathrm{H}^+]C_{\mathrm{HX}}f^2$ (=Y) against $1/C_{\mathrm{HX}}f^2$ (=X) for 4-Methyl-3-nitroaniline

$Y=0.198\times10^7+2.960\times10^3\ X$; $s=0.048\times10^7$; $n=10$.

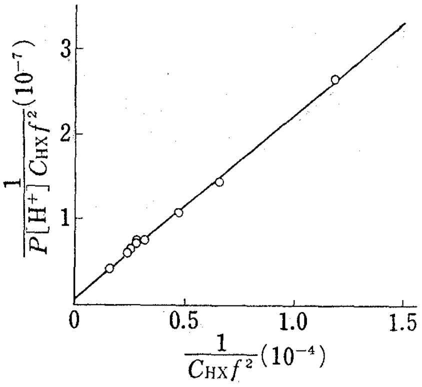


Fig. 5. Plot of $1/P[\mathrm{H}^+]C_{\mathrm{HX}}f^2$ (=Y) against $1/C_{\mathrm{HX}}f^2$ (=X) for 4-Carbethoxyaniline

$Y=0.101\times10^7+2.148\times10^3\ X$; $s=0.027\times10^7$; $n=10$.

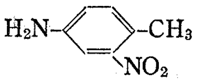
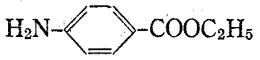
Therefore, $[\mathrm{BH}^+]$ and $[\mathrm{BH}^+\mathrm{X}^-]$ will be calculated from eq(8), (12), (14) and (16). Table II shows $[\mathrm{BH}^+]$ and $[\mathrm{BH}^+\mathrm{X}^-]$ calculated for **1** and **2**. This method was attempted for some other nitroanilines; 2-methoxy-5-nitroaniline(**3**), *m*-nitroaniline (**4**) and 2-methyl-5-nitroaniline (**5**). The plot according to eq(11) was successful for all the anilines. The values of $K_{\mathrm{BH}}^{n\text{-BuOH}}$ and K_{BHX} for these anilines were calculated.

In order to estimate the over-all dissociation constant of the base, $K_{\mathrm{BH}}^{n\text{-BuOH}}$, more accurately, a successive approximation procedure was developed.

(1) From the absorbance at a given concentration of the acid, an approximate value of $K_{\mathrm{BH}}^{n\text{-BuOH}}$ is calculated from eq(17), which is derived from eq(11), neglecting $[\mathrm{X}^-]$.

$$\frac{1}{P[\mathrm{H}^+]} = \frac{K_{\mathrm{B}}K_{\mathrm{BHX}}}{K_{\mathrm{HX}}^{\circ}} + \frac{K_{\mathrm{B}}}{K_{\mathrm{HX}}^{\circ}}[\mathrm{X}^-]f^2 \qquad (17)$$

Table II. Concentrations of BH^+, BH^+X^- and X^-, and the K_{BHX} Values of 4-Methyl-3-nitroaniline and 4-Carbethoxyaniline

	 $(1/K_{BH}^{n\text{-BuOH}})_{obsd}=2.960\times10^3$				 $(1/K_{BH}^{n\text{-BuOH}})_{obsd}=2.148\times10^3$			
	$[BH^+]$ (10^4)	$[X^-]$ (10^4)	$[BH^+X^-]$ (10^4)	K_{BHX} (10^3)	$[BH^+]$ (10^4)	$[X^-]$ (10^4)	$[BH^+X^-]$ (10^4)	K_{BHX} (10^3)
1	0.607	1.051	0.024	2.14	0.0724	1.069	0.0037	1.65
2	1.093	2.012	0.138	1.22	0.1235	2.141	0.0054	3.49
3	1.499	2.955	0.271	1.18	0.1591	3.207	0.0123	2.74
4	1.832	3.890	0.411	1.19	0.2064	5.345	0.0209	3.09
5	2.123	4.864	0.512	1.30	0.2139	6.400	0.0391	1.95
6	2.360	5.846	0.604	1.40	0.2085	6.391	0.0483	1.53
7	2.717	7.853	0.747	1.59	0.2240	7.466	0.0463	1.78
8	2.995	9.950	0.801	1.88	0.2318	8.532	0.0528	1.90
9	3.195	12.060	0.839	2.14	0.2487	10.678	0.0544	2.29
10	3.118	14.890	1.237	1.16	0.2624	16.023	0.0743	2.24
Mean (σ)				1.52 ± 0.40				2.27 ± 0.65

(2) As a first approximation, $[BH^+]$ is calculated from eq(12) using the approximate value of $K_{BH}^{n\text{-BuOH}}(K_{HX}^{\circ}/K_BK_{BHX})$, $[H^+]$ and $[B]$. The concentrations, $[H^+]$ and $[B]$, are obtained independently of this approximation by eq(14) and (16), respectively.

(3) Knowing $[H^+]$ and an approximate $[BH^+]$, an approximate value of $[X^-]$ is calculated from eq(7).

(4) The activity coefficient, f, is calculated from eq(15) using the approximate value of $[X^-]$.

(5) A plot of $1/P[H^+][X^-]f^2$ against $1/[X^-]f^2$ is carried out (eq(11)) using the approximate value of $[X^-]$. From the slope of the linear plot, a better approximate value of $1/K_{BH}^{n\text{-BuOH}}$ is obtained. The entire cycle, (1)—(5), is iterated until constant values of $[X^-]$, $[BH^+]$, f and $K_{BH}^{n\text{-BuOH}}$ are obtained.

Calculations were made with the aid of computer. Sample calculations for **1** were started with an approximate value of $K_{BH}^{n\text{-BuOH}}$ calculated from the spectrum at $C_{HX}=1.613\times10^{-3}$.

Table III. Result of the Computation for the Data of 4-Methyl-3-nitroaniline $C_B=5.250\times10^{-4}$ (M), $C_{HX}=1.613\times10^{-3}$ (M)

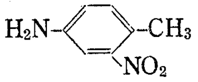
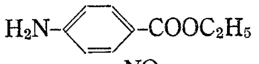
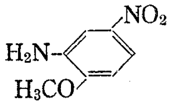
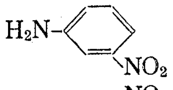
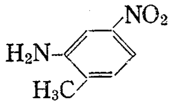
Iteration	I			II			III			
	$[X^-]$ (10^4)	$[BH^+]$ (10^4)	f	$[X^-]$ (10^4)	$[BH^+]$ (10^4)	f	$[X^-]$ (10^4)	$[BH^+]$ (10^4)	$[BH^+X^-]$[a] (10^4)	f
1	1.2899	0.84585	0.87697	1.0439	0.59986	0.88861	1.0489	0.60484	0.026092	0.88836
2	2.4422	1.5253	0.83473	1.9993	1.0802	0.84922	2.0082	1.0892	0.14176	0.84891
3	3.5428	2.0879	0.80447	2.9356	1.4807	0.82033	2.9479	1.4930	0.27707	0.81999
4	4.6088	2.5515	0.78024	3.8668	1.8095	0.79668	3.8818	1.8245	0.41815	0.79633
5	5.6972	2.9564	0.75889	4.8374	2.0967	0.77551	4.8548	2.1141	0.52017	0.77516
6	6.7708	3.2852	0.74024	5.8154	2.3298	0.75673	5.8347	2.3491	0.61528	0.75638
7	8.9223	3.7853	0.70803	7.8215	2.6845	0.72378	7.8437	2.7068	0.75627	0.72345
8	11.123	4.1692	0.68018	9.9107	2.9568	0.69497	9.9352	2.9813	0.81480	0.69465
9	13.321	4.4531	0.65581	12.026	3.1581	0.66975	12.052	3.1843	0.84800	0.66946
10	16.125	4.3532	0.62867	14.859	3.0873	0.64046	14.885	3.1129	1.2404	0.64021
$K_{BH}^{n\text{-BuOH}}$		3.4194×10^{-4}			3.3912×10^{-4}			3.3918×10^{-4}		
γ[b]		0.9986			0.9986			0.9986		

a) The values of $[BH^+X^-]$ at Iteration No. I and II were not shown.
b) Correlation coefficient.

TABLE IV. Estimation of $K_{BH}^{n\text{-BuOH}}$ Values of Anilines by Computation

Compound	Initial value of $1/K_{BH}^{n\text{-BuOH}}$	Iteration	Regression line (slope$=1/K_{BH}^{n\text{-BuOH}}$)	Correlation coefficient	$(1/K_{BH}^{n\text{-BuOH}})_{obsd}$
1	3.0760×10^3	I	$Y=2.9456\times10^3X+2.1408\times10^6$	0.9986	2.960×10^3
	($C_{HX}=1.075\times10^{-4}$)	II	$Y=2.9483\times10^3X+2.1590\times10^6$	0.9986	
		III	$Y=2.9483\times10^3X+2.1586\times10^6$	0.9986	
	4.1237×10^3	I	$Y=2.9245\times10^3X+2.0150\times10^6$	0.9986	
	($C_{HX}=1.613\times10^{-3}$)	II	$Y=2.9488\times10^3X+2.1620\times10^6$	0.9986	
		III	$Y=2.9483\times10^3X+2.1585\times10^6$	0.9986	
2	2.6386×10^3	I	$Y=2.1544\times10^3X+9.7275\times10^5$	0.9993	2.148×10^3
	($C_{HX}=6.439\times10^{-4}$)	II	$Y=2.1555\times10^3X+9.7401\times10^5$	0.9993	
	2.7586×10^3	I	$Y=2.1541\times10^3X+9.7244\times10^5$	0.9993	
	($C_{HX}=1.610\times10^{-3}$)	II	$Y=2.1556\times10^3X+9.7401\times10^5$	0.9993	
3	1.0138×10^3	I	$Y=8.6623\times10^2X+3.3664\times10^5$	0.9979	8.689×10^2
	($C_{HX}=1.069\times10^{-3}$)	II	$Y=8.6658\times10^2X+3.3653\times10^5$	0.9980	
	1.1354×10^3	I	$Y=8.6594\times10^2X+3.3673\times10^5$	0.9979	
	($C_{HX}=4.277\times10^{-3}$)	II	$Y=8.6658\times10^2X+3.3653\times10^5$	0.9980	
4	8.4535×10^2	I	$Y=6.8912\times10^2X+2.9936\times10^5$	0.9846	6.840×10^2
	($C_{HX}=1.619\times10^{-3}$)	II	$Y=6.9136\times10^2X+3.0181\times10^5$	0.9850	
		III	$Y=6.9133\times10^2X+3.0177\times10^5$	0.9850	
	9.7196×10^2	I	$Y=6.8728\times10^2X+2.9767\times10^5$	0.9843	
	($C_{HX}=5.395\times10^{-3}$)	II	$Y=6.9139\times10^2X+3.0184\times10^5$	0.9850	
		III	$Y=6.9133\times10^2X+3.0177\times10^5$	0.9850	
5	7.4323×10^2	I	$Y=6.2619\times10^2X+4.0916\times10^5$	0.9990	6.193×10^2
	($C_{HX}=5.980\times10^{-4}$)	II	$Y=6.2865\times10^2X+4.0904\times10^5$	0.9991	
		III	$Y=6.2860\times10^2X+4.0904\times10^5$	0.9991	
	1.0245×10^3	I	$Y=6.2029\times10^2X+4.0972\times10^5$	0.9989	
	($C_{HX}=5.980\times10^{-3}$)	II	$Y=6.2877\times10^2X+4.0904\times10^5$	0.9991	
		III	$Y=6.2859\times10^2X+4.0904\times10^5$	0.9991	

TABLE V. $pK_{BH}^{n\text{-BuOH}}$ and pK_{BHX} Values of Anilines in *n*-BuOH

Compound		$pK_{BH}^{n\text{-BuOH}}$	pK_{BHX}	pK_a	$\Delta pK^{a)}$
1		3.47	2.83	3.02	0.45
2		3.33	2.66	2.51 (2.50)$^{b)}$	0.82
3		2.94	2.42	2.52	0.42
4		2.84	2.74	2.41 (2.41)$^{c)}$	0.43
5		2.79	2.84	2.32$^{d)}$	0.47

a) $\Delta pK=pK_{BH}^{n\text{-BuOH}}-pK_a$.
b) R.A. Robinson and A.I. Biggs, *Australian J. Chem.*, **10**, 128 (1957).
c) E. Högfeldt and J. Bigeleisen, *J. Am. Chem. Soc.*, **82**, 15(1960).
d) Determined in 5%(v/v) methanolic solution.

After three times iterations, $[X^-]$, $[BH^+]$, f and $K_{BH}^{n\text{-BuOH}}$ reached the constant value as shown in Table III. Such calculations were made at the other points of C_{HX}. The values, $[X^-]$, $[BH^+]$, f and $K_{BH}^{n\text{-BuOH}}$ estimated at all the points agreed with one another. The $K_{BH}^{n\text{-BuOH}}$ values for the other anilines obtainable at the two different points of C_{HX} are summarized in Table IV.

Such calculations indicated that $[X^-]$ was much larger than $[BH^+X^-]$ for all the anilines. The result shows that the former manual method is applicable to the estimation of the overall dissociation constant, $K_{BH}^{n\text{-BuOH}}$. The $K_{BH}^{n\text{-BuOH}}$ value by the method actually agreed with the computed value. The manual method is more rapid and simple than the computer method.

The difference of both dissociation constants between water (pK_a) and *n*-BuOH($pK_{BH}^{n\text{-BuOH}}$) is shown in Table V. It was found that the basicity increased in *n*-BuOH as compared with that in water. The degree of the increase is about 0.4—0.8 p*K* unit.

Experimental

Materials——Commercial *n*-BuOH (analytical grade) was purified by distillation. The distillate was collected at bp 117—118° after refluxing the solvent on the molecular sieves (Type 4A-1/16, Nakarai Chemical Co., Ltd.) for 16 hr. The apparatus was set up for the condensed solvent to pass through the column containing the molecular sieves. Water content of the distillate was within the range of 0.005 to 0.010% (w/v).

A solution of $HClO_4$ was prepared from the reaction of $AgClO_4$ with HCl. Commercial $AgClO_4$ (Merck, reagent grade) was dried over P_2O_5 for 3 days. To a solution of $AgClO_4$ in *n*-BuOH was added an equivalent amount of a solution of HCl, which was prepared by the introduction of HCl gas into *n*-BuOH. The mixture was allowed to stand for a day. The precipitates were filtered in a stream of nitrogen. The water content of the solution was within the range of 0.04 to 0.07% (w/v). The acid was standardized in MeOH using diphenylguanidine as standard material and methyl yellow as an indicator.

Substituted aniline derivatives were of reagent grade and were purified by recrystallization.

Measurement of e.m.f. of $HClO_4$-Solution——The electromotive force (e.m.f. (mV)) of $HClO_4$-solution was measured using Metrohm potentiometer (Type E 436). Glass and calomel electrodes, type EA 109UX and type EA 404 were respectively used. The glass electrode was dipped in the cell containing $HClO_4$-solution. The calomel electrode was in a separate compartment connected to the cell with a salt bridge. The bridge contained *n*-BuOH-solution saturated with LiCl.

Measurement of UV Spectra——The UV-spectra of the anilines were measured using a Hitachi EPS-2U spectrophotometer. The measurements were carried out at C_B: $0.4\times10^{-4}-7\times10^{-4}$ M. About 10 spectra were recorded for the various amount of the acid solutions (C_{HX}: $1\times10^{-4}-5\times10^{-3}$ M). The spectra of the protonated anilines were measured in 0.1—0.5 N $HClO_4$.

Measurement of p*K*a——The pK_a values of the anilines were determined by the usual spectrophotometric method.[13] The value for **5** was determined in 5% (v/v) methanolic solution because of its poor solubility.

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[13] A. Albert and E.P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, 1962, pp. 69—92.