Evaluation of Novel Local Structural Parameters of Acids and Bases for 1:1 Hydrogen-Bond Complexation. II. *p*-Fluorophenol, 5-Fluoroindole and Various Bases in Carbon Tetrachloride

Shozi Mishima,* Tsuyoshi Nakajima, and Nobuaki Tanaka†

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University,
Wakasato 4-17-1, Nagano 380-8533

†Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University,
Wakasato 4-17-1, Nagano 380-8533

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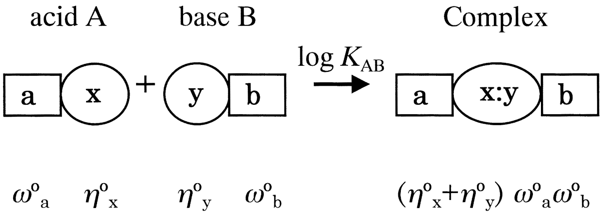
For 1:1 hydrogen-bond complexation in CCl_4, novel local structural parameters, η° and ω°, representing the nature of the functional group and the residual moiety (supporting group) of acids and bases have been evaluated for two acids and 26 bases. An evaluation of the η° and ω° was carried out by using convergent linear relationships observed among the log *K* values of the bases against each couple of reference acids. The values of log *K* experimentally obtained were reproduced from the η° and ω° values within ±0.21 in the log *K* unit, excluding three exceptions. Family-independent linear relationships were observed between ω_b° and the solute hydrogen bond basicity (β_2^H), and between ω_a° and the solute hydrogen bond acidity (α_2^H) of the bases and acids. Linear relationships could be applied to estimate the ω_a° and ω_b° values from α_2^H and β_2^H values existing in the literature.

The present authors[1–3] have shown for 1:1 hydrogen-bond complexation in CCl_4 that the strengths of the acids and bases closely correlate with the local structures of the molecules. Namely, an acid can be expressed as x–a, where x is the functional group and a is the residual moiety (called the supporting group, hereinafter); similarly, a base can be expressed as y–b, where y is the functional group and b is the supporting group. Thus, the 1:1 hydrogen-bond complexation of acid A and base B can be expressed as follows (Scheme 1):



Scheme 1.

As shown in a preceding paper,[3] the change of the enthalpy (ΔH_{AB}) and the formation constant (K_{AB}; $dm^3\ mol^{-1}$) of 1:1 hydrogen-bond complexation between acid A and base B can be expressed as follows:

$$\Delta H_{AB}^\circ = (\eta_x^\circ + \eta_y^\circ)\,\omega_a^\circ\,\omega_b^\circ, \tag{1}$$

$$\log K_{AB} = -\frac{(\eta_x^\circ+\eta_y^\circ)\omega_a^\circ\,\omega_b^\circ}{2.303RT} + \frac{\Delta S_f^\circ}{2.303R}, \tag{2}$$

where, as shown in Scheme 1, η_x° and η_y° represent the nature of the functional group of the acid and base, respectively; ω_a° and ω_b° represent the nature of the supporting group of the acid and the base, respectively. ΔS_f° is an entropy term, which can be regarded as being virtually constant ($-35.4\ J mol^{-1}\ K^{-1}$);[2] and *R* and *T* are the gas constant ($8.314\ J mol^{-1}\ K^{-1}$) and the temperature, respectively. As described in previous papers,[1,3] the parameter η° may be related to the size, or a size-related factor, of the functional group, and the parameter ω° may be related to the electronic factors (electron-donating or -withdrawing ability) of the supporting group. In the preceding paper,[3] the values of local structural parameters, η° and ω°, of OH-, NH-acids and phosphorus compounds were evaluated for the first time by introducing three numerical criteria: $\omega_a^\circ = 10.0$ and $\eta_x^\circ = 5.00$ for phenol and $\eta_y^\circ = 5.00$ for carbonyl bases.

In the present study, the η°-ω° methodology was applied to the reaction between various bases and three acids, to examine the generality of the methodology.

Data for Analysis

The values of log (K/$dm^3\ mol^{-1}$) subjected to the present analysis were obtained from the literature,[4–7] and are listed in Table 1. Phenol, *p*-fluorophenol and 5-fluoroindole and 26 bases are included as acids and bases. The bases can be classified into four families: =O (carbonyl and oxide bases), –O– (ethers), =N– (pyridines, guanidine and urea) and >N– (tertiary amines). It has been confirmed, as reported in a previous paper,[1] that family-independent or -dependent LFERs (linear free-energy relationships), both of which converge on the magic point (−1.1, −1.1) found by Abraham et al.,[8–13] were observed among the log *K* values of the bases against each couple

Table 1. Values of log (K/dm^3 mol^{-1}) for the 1 : 1 Hydrogen-Bond Complexation of Various Bases against *p*-Fluorophenol, 5-Fluoroindole and Phenol in CCl_4 at 298.15 K

Base	log K [a]		
	p-Fluorophenol[b]	5-Fluoroindole[c]	Phenol[d]
(=O Bases)			
Triphenylphosphine oxide	3.16(3.15)	2.05(2.12)	2.80(2.91)
Trimethyl phosphate	2.40(2.38)	1.49(1.51)	2.26[f](2.25) 2.19[i](2.18)
Hexamethylphosphoramide	3.56(3.54)	2.31(2.43)	3.27[f](3.37) 3.18[i](3.28)
Dimethyl sulfoxide	2.53(2.53)	1.49(1.62)	2.26(2.32)
N,*N*-Dimethylacetamide	2.38(2.36)	1.47(1.49)	2.13(2.16)
Tetramethylurea	2.30(2.29)	1.43(1.43)	— (2.09)
N,*N*-Dimethylformamide	2.06(2.05)	1.25(1.24)	1.81(1.86)
Diphenyl sulfoxide	2.03(2.01)	1.19(1.22)	1.85[f](1.89) 1.79[i](1.83)
N,*N*-Dimethylchloroacetamide	1.68(1.66)	1.06(0.94)	— (1.50)
Cyclohexanone	1.30(1.30)	0.75(0.65)	1.23[f](1.20) 1.18[i](1.15)
p-Methoxyacetophenone	1.33[e](1.31)	0.72(0.66)	— (1.16)
Benzaldehyde	0.83(0.82)	0.43(0.27)	0.68[f](0.73) 0.64[i](0.69)
(–O– Bases)			
Tetrahydrofuran	1.26(1.25)	0.34(0.36)	1.20(1.10)
Diethyl ether	0.98(0.97)	0.23(0.17)	0.78[h](0.80) 0.81[i](0.84)
(=N– Bases)			
sym-Tetramethylguanidine	3.14[e](3.13)	1.65(1.67)	— (2.89)
4-Dimethylaminopyridine	2.81(2.81)	1.41(1.45)	— (2.59)
Pyridine	1.88(1.87)	0.75(0.78)	1.70(1.69)
3-Bromopyridine	1.26(1.25)	0.42(0.35)	1.18[f](1.16) 1.13[i](1.11)
3,5-Dichloropyridine	0.75(0.74)	−0.01(−0.01)	— (0.62)
(>N– Bases)			
Quinuclidine	2.63[e](2.64)	0.79(1.07)	— (2.43)
N,*N*-Dimethylcyclohexylamine	2.07(2.08)	0.73(0.71)	1.96[g](1.87) 1.98[i](1.89)
1,4-Diazabicyclo[2.2.2]octane	2.20[e](2.22)	0.73(0.80)	2.48(2.02)
Triethylamine	1.91(1.93)	0.53(0.61)	1.84(1.75)
Tributylamine	1.57(1.58)	0.42(0.38)	1.46[f](1.47) 1.40[i](1.42)
N,*N*-Dimethylaniline	0.45[e](0.46)	0.17(−0.35)	— (0.35)
Triallylamine	1.23(1.25)	0.14(0.17)	1.29[g](1.08) 1.31[i](1.10)

a) Values in parenthesis are those calculated from η° and ω°. b) See Ref. 4. c) See Ref. 5. d) See Ref. 6. e) See Ref. 7. f) Values obtained at 293 K. g) Values obtained at 300 K. h) Values obtained at 302 K. i) Values at 298.15 K calculated by applying Eq. 3.

of reference acids. In the present study, the LFERs were reanalyzed in order to evaluate the local structural parameters, η° and ω°, of the acids and bases.

Because some of the log K values obtained from the literature were those evaluated at temperatures other than 298.15 K, they were converted to the value at 298.15 K by applying the following equation, introduced in the previous paper:[2]

$$\log K_{\mathrm{AB}}^{T_2} = \frac{T_1}{T_2}\log K_{\mathrm{AB}}^{T_1} + \left(1-\frac{T_1}{T_2}\right)\frac{\Delta S_{\mathrm{f}}^\circ}{2.303R}, \tag{3}$$

where T_1 and T_2 represent two different temperatures. The log K values at 298.15 K calculated by applying Eq. 3 are also listed in Table 1. As stated in a previous paper,[2] because the point (−1.85, −1.85) is more reasonable as the magic point than the point (−1.1, −1.1), the former point was adopted as the magic point in the present analysis. The slopes of the LFERs at 298.15 K, evaluated by applying the least-squares method, are listed in Table 2. In an estimation of the slopes, the log K values of quinuclidine and *N,N*-dimethylaniline against *p*-fluorophenol and 5-fluoroindole were neglected because these values deviate from the linear relationship observed for other >N– bases. Similarly, the log *K* values of 1,4-diazabicyclo[2.2.2]octane and triallylamine against phenol and 5-fluoroindole are also neglected in estimating the slope of the straight line.

Results and Discussion

Evaluation of η°_{y} of Bases. When Eq. 2 is applied to the reaction of a set of bases, B (y–b), with two reference acids, A_1 (a_1–x_1) and A_2 (a_2–x_2), the following equations are obtained:

$$\log K_{\mathrm{A_1B}} = -\frac{(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y}})\omega^\circ_{\mathrm{a_1}}\omega^\circ_{\mathrm{b}}}{2.303RT}+\frac{\Delta S^\circ_{\mathrm{f}}}{2.303R}, \tag{4}$$

$$\log K_{\mathrm{A_2B}} = -\frac{(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y}})\omega^\circ_{\mathrm{a_2}}\omega^\circ_{\mathrm{b}}}{2.303RT}+\frac{\Delta S^\circ_{\mathrm{f}}}{2.303R}. \tag{5}$$

From the above equations, the following equation can be derived:

$$\log K_{A_2B} = R_{\mathrm{y}}\log K_{A_1B} +(1-R_{\mathrm{y}})\frac{\Delta S^\circ_{\mathrm{f}}}{2.303R}, \tag{6}$$

where R_{y} is defined as

$$R_{\mathrm{y}} = \frac{(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y}})\omega^\circ_{\mathrm{a_2}}}{(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y}})\omega^\circ_{\mathrm{a_1}}}. \tag{7}$$

It is important that R_{y} in Eq. 6 and the slopes given in Table 2 have the same physical meaning, because both represent the slope of log $K_{\mathrm{A_2B}}$ vs. log $K_{\mathrm{A_1B}}$ plots.

When Eq. 7 is applied to the reaction of two families of bases with different functional groups, y_1 and y_2, against reference acids, A_1(x_1–a_1) and A_2(x_2–a_2), the following equations can be derived:

$$R_{\mathrm{y_1}} = \frac{(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y_1}})\omega^\circ_{\mathrm{a_2}}}{(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y_1}})\omega^\circ_{\mathrm{a_1}}}, \tag{8}$$

$$R_{\mathrm{y_2}} = \frac{(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y_2}})\omega^\circ_{\mathrm{a_2}}}{(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y_2}})\omega^\circ_{\mathrm{a_1}}}, \tag{9}$$

and then

$$\frac{R_{\mathrm{y_2}}}{R_{\mathrm{y_1}}} = \frac{(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y_2}})(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y_1}})}{(\eta^\circ_{\mathrm{x_1}}+\eta^\circ_{\mathrm{y_2}})(\eta^\circ_{\mathrm{x_2}}+\eta^\circ_{\mathrm{y_1}})}. \tag{10}$$

When Eq. 10 is applied to the family-dependent LFERs observed among log *K* of =O bases and –O–, =N– or >N– bases against 5-fluoroindole and *p*-fluorophenol (or phenol), the following substitution is possible: x_1 = OH, x_2 = NH, y_1 = =O and y_2 = –O–, =N–, or >N–. Thus, $\eta^\circ_{\mathrm{y_2}}$ of the bases can be expressed as

$$\eta^\circ_{\mathrm{y_2}} = -\frac{R_{\mathrm{=O}}\,\eta^\circ_{\mathrm{NH}}(\eta^\circ_{\mathrm{=O}}+\eta^\circ_{\mathrm{OH}})-R_{\mathrm{y_2}}\,\eta^\circ_{\mathrm{OH}}(\eta^\circ_{\mathrm{=O}}+\eta^\circ_{\mathrm{NH}})}{R_{\mathrm{y_2}}(\eta^\circ_{\mathrm{=O}}+\eta^\circ_{\mathrm{NH}})-R_{\mathrm{=O}}(\eta^\circ_{\mathrm{=O}}+\eta^\circ_{\mathrm{OH}})}, \tag{11}$$

where the subscripts stand for the functional group. As reported in the preceding paper,[3] because the values of η°_{OH} (= 5.00), η°_{NH} (= 7.57) and $\eta^\circ_{\mathrm{=O}}$ (= 5.00) are already known, $\eta^\circ_{\mathrm{y_2}}$ may be calculated by substituting the values of slope R_{y} given in Table 2 to Eq. 11. For example, for the reaction of the ethers against *p*-fluorophenol and 5-fluoroindole, the value of $\eta^\circ_{\mathrm{-O-}}$ may be calculated by substituting the values of $R_{\mathrm{=O}}$ (= 0.789) and $R_{\mathrm{y_2}}$ (= 0.718). The results are given in Table 3. It is known that the value of η°_{y} of various bases can be evaluated from the slope of the family-dependent LFERs among the log *K* values of the bases. In the table, the values of η°_{y} of the –O– and =N– bases are the mean of two values obtained for the two sets of reference acids. The η°_{y} value of the >N– bases was evaluated from the slope of the bases against *p*-fluorophenol and 5-fluoroindole.

Table 2. The Slope of Famiy-Dependent LFERs Conversing on the Magic Point (−1.85, −1.85) Observed between log (K/dm^{3}mol^{-1}) Values of Various Bases against *p*-Fluorophenol (PFP), 5-Fluoroindole (5FI) and Phenol (Ph) in CCl_4 at 298.15 K

Reference acid				Standard
Acid 1	Acid 2	Base Family	Slope R_{y}	Deviation[a)]
PFP	5FI	=O	0.789	0.0861(12)
		–O–	0.718	— (2)
		=N–	0.704	0.0362(5)
		>N–	0.647[b)]	0.0438(5)
Ph	5FI	=O	0.837	0.0805(9)
		–O–	0.746	— (2)
		=N–	0.745	— (2)
		>N–	0.662[c)]	0.0871(4)
PFP	Ph	all	0.950	0.0822(19)

a) In parenthesis are number of data points. b) Estimated by excluding the data of *N*,*N*-dimethylaniline and quinuclidine. c) Estimated by excluding the data of 1,4-diazabicyclo[2.2.2]octane and triallylamine.

From the η°_{y} values obtained here and those obtained in a preceding paper,[3] the strength of the basic functional groups on the η°_{y} scale increases in the following order: =Se (η°_{y} = 0.55) < =S (0.67) < =O (5.00) < –O– (14.6) < =N– (16.3) < >N– (77). This order suggests that the basic functional groups with a π-electron and with a larger atomic number are generally weak in strength. It is interesting that the order is qualitatively in accord with the hardness–softness factor proposed by Pearson.[14–16] Such a comparison is difficult when the four parameter equations proposed by Drago et al. (*E*–*C* equation),[17–19] Maria et al.[20] and Abraham et al.[21] (*S*–*F* equation) are applied, because, in their methodologies, little attention was paid to the structure–strength relationship observed for the interaction between acids and bases. Thus, the η°_{y} scale is of importance as a new quantitative scale which represents the nature of the functional group of bases.

It has been demonstrated, as described above, that the η°_{y} of various bases can be evaluated and that it is important as a new quantitative scale for the hydrogen-bond basicity.

Evaluation of $\omega^\circ_{\mathrm{a}}$ of Acids. When Eq. 8 is applied to the LFER of the bases against phenol and *p*-fluorophenol, the following equation can be derived, because these acids have the same functional group, OH ($\eta^\circ_{\mathrm{x_1}}$ = $\eta^\circ_{\mathrm{x_2}}$ = 5.00):

$$\omega^\circ_{\mathrm{PFP}} = \frac{\omega^\circ_{\mathrm{Ph}}}{R_{\mathrm{y}}}. \tag{12}$$

Since the value of $\omega^\circ_{\mathrm{Ph}}$ (= 10.0) is already known, $\omega^\circ_{\mathrm{PFP}}$ can be

Table 3. Values of Local Structural Parameters, η°_y and ω°_b, and Solute Hydrogen Bond Basicity Scale β^H_2 of Various Bases

Base	Functional Group	η°_y	ω°_b	$\beta^{H\ a)}_2$
Triphenylphosphine oxide	=O	5.00	−266	0.919
Trimethyl phosphate	=O	5.00	−231	0.762
Hexamethylphosphoramide	=O	5.00	−293	1.000
Dimethyl sulfoxide	=O	5.00	−238	0.775
N,*N*-Dimethylacetamide	=O	5.00	−229	$0.730^{b)}$
Tetramethylurea	=O	5.00	−225	$0.743^{b)}$
N,*N*-Dimethylformamide	=O	5.00	−212	$0.663^{b)}$
Diphenyl sulfoxide	=O	5.00	−210	$0.667^{b)}$
N,*N*-Dimethylchloroacetamide	=O	5.00	−191	—
Cyclohexanone	=O	5.00	−171	$0.523^{b)}$
p-Methoxyacetophenone	=O	5.00	−172	$0.526^{b)}$
Benzaldehyde	=O	5.00	−145	$0.415^{b)}$
Triphenyl phosphate	=O	5.00	$-198^{c)}$	0.624
Tetrahydrofuran	–O–	14.6 (±1.8)	−86.0	$0.510^{b)}$
Diethyl ether	–O–	14.6	−78.3	0.450
sym-Tetramethylguanidine	=N–	16.3 (±0.3)	−127	$0.915^{b)}$
4-Dimethylaminopyridine	=N–	16.3	−119	$0.859^{b)}$
Pyridine	=N–	16.3	−95.0	0.625
3-Bromopyridine	=N–	16.3	−79.2	$0.508^{b)}$
3,5-Dichloropyridine	=N–	16.3	−66.2	—
Quinuclidine	>N–	77	−29.6	$0.805^{b)}$
N,*N*-Dimethylcyclohexylamine	>N–	77	−25.9	$0.700^{b)}$
1,4-Diaza-bicyclo[2.2.2]octane	>N–	77	−26.8	$0.805^{b)}$
Triethylamine	>N–	77	−24.9	0.699
Tributylamine	>N–	77	−22.6	$0.597^{b)}$
N,*N*-Dimethylaniline	>N–	77	−15.2	$0.351^{b)}$
Triallylamine	>N–	77	−20.4	$0.537^{b)}$

a) See Ref. 2. b) Caculated from log K^H_B values using the equation $\beta^H_2 = (\log K^H_B + 1.1)/4.636$ obtained from Ref. 11.
c) See Ref. 3.

calculated by substituting the slope R_y (= 0.950) of the bases against phenol and *p*-fluorophenol, given in Table 2 to Eq. 12.

When Eq. 8 is applied to the LFER observed for =O bases against *p*-fluorophenol and 5-fluoroindole, the following equation can be derived:

$$\omega^\circ_{5FI} = R_y\,\omega^\circ_{PFP}\,\frac{\eta^\circ_{PFP}+\eta^\circ_{=O}}{\eta^\circ_{5FI}+\eta^\circ_{=O}}. \qquad (13)$$

Since the values of η° and ω° in the right-hand terms of the above equation have already been known, the value of ω°_{5FI} can be calculated by substituting the slope R_y (= 0.789) of the bases against *p*-fluorophenol and 5-fluoroindole given in Table 2.

The values of ω°_{PFP} and ω°_{5FI}, estimated by applying Eqs. 12 and 13, are listed in Table 4, together with the η°_x values of the acids. The values of η°_x and ω°_a of various acids reported in the preceding paper[3] are also listed in the table. The electronic nature of the supporting groups can be compared quantitatively by applying the ω°_a scale; namely, a supporting group with a larger ω°_a value is stronger in the electron-withdrawing ability. It is interesting that the strength of the supporting group of phenol and indole increases by ca. 0.5 in the ω°_a unit by substituting a hydrogen atom with a fluorine atom.

As described above, the ω°_a value of *p*-fluorophenol and 5-fluoroindole has been successfully determined.

Evaluation of ω°_b of Bases. When Eq. 2 is applied to the log *K* values of the bases against *p*-fluorophenol, given in Table 1, the following equation can be derived:

$$\omega^\circ_b = -\frac{T(2.303R\log K-\Delta S_f)}{(\eta^\circ_{OH}+\eta^\circ_y)\,\omega^\circ_{PFP}}. \qquad (14)$$

Since the numerical values of the right-hand terms of the above equation are already known, the ω°_b value of the bases may be evaluated. The results of the calculations are listed in Table 3. In this table, the values of ω°_b and η°_y of triphenyl phosphate reported in a preceding paper[3] are also listed. The electronic nature of the supporting groups of the bases may be compared quantitatively by applying the ω°_b scale; namely, a supporting group with a smaller ω°_b value is stronger in the electron-donating ability.

As described above, it has been demonstrated that the ω°_b value of the 26 bases can also be determined reasonably.

Calculation of log *K* from η° and ω°. When the values of η° and ω° given in Tables 3 and 4 are applied to Eq. 2, the values of log *K* listed in Table 1 should be reproduced. In Table 1, the values in parenthesis are those calculated from the η° and ω° values. The plots in Fig. 1 show the relation between the log *K* values calculated and those experimentally obtained. It is

Table 4. Values of Local Structural Parameters, η°_x and ω°_a, and Solute Hydrogen Bond Acidity Scale α_2^H of Various Acids

Acid	Functional group	η°_x	ω°_a	α_2^{H} [a)]
Phenol	OH	5.00	10.0	0.596
p-Fluorophenol	OH	5.00	10.5	0.629[b)]
2-Naphthol	OH	5.00	10.5	0.612
1-Naphthol	OH	5.00	10.3	0.608
CF_3CH_2OH	OH	5.00	9.92	0.567
CCl_3CH_2OH	OH	5.00	8.91	0.500
CBr_3CH_2OH	OH	5.00	8.61	0.478
5-Fluoroindole	NH	7.57	6.63	0.468[b)]
Carbazole	NH	7.57	6.47	0.469
Indole	NH	7.57	6.15	0.436
Pyrrole	NH	7.57	5.69	0.408

a) See Ref. 9. b) See Ref. 10.

known that a good straight line with unit slope is obtained (data points = 80, standard deviation = 0.104). In this figure, only three points corresponding to the adducts (phenol: 1,4-diazabicyclo[2.2.2]octane, 5-fluoroindole: quinuclidine, and 5-fluoroindole: *N,N*-dimethylaniline) deviate from the regression line. Since the log *K* values of these adducts deviate from the corresponding LFERs among the log *K* values, the deviation from the regression line of the three points may be ascribed to some additional factors, such as the steric requirements, as stated by Mitsky et al.[5] As shown in Fig. 1, the remaining 77 log *K* values predicted from the η° and ω° values are in accord with those determined experimentally within ±0.21 in the log *K* unit. It is thus concluded that the η° and ω° values determined here can be applied quantitatively to predict the corresponding log *K* values.

Abraham et al.[9,10,13] constructed the solute hydrogen bond acidity scale (α_2^H) and the basicity scale (β_2^H) for 1:1 hydrogen-bond complexation in CCl_4, where the strength scales can be correlated with log *K* by

$$\log K = m\alpha_2^H\beta_2^H + c, \tag{15}$$

where m (= 7.354) and c (= −1.1) are constant terms. The values of α_2^H and β_2^H of the acids and the bases noted here are also listed in Tables 3 and 4. Fig. 2 gives the relation between the values of log *K* obtained experimentally and those calculated from the α_2^H and β_2^H values by applying Eq. 15. A straight line with unit slope can be obtained. However, the plots of log *K* of the bases against 5-fluoroindole appreciably deviate from the regression line. As stated by Abraham et al.,[9,10] themselves, 5-fluoroindole is one of the exceptional acids to which Eq. 15 can not be applied. By comparing the results shown in Figs. 1 and 2, it is known that the two-parameter formalism proposed by Abraham et al.[9,10,13] is insufficient to predict the precise log *K* values of various acid-base adducts. It can be pointed out that the η°–ω° equation given by Eq. 2 should be applied, instead of Eq. 15, to the 1:1 hydrogen-bond complexation.

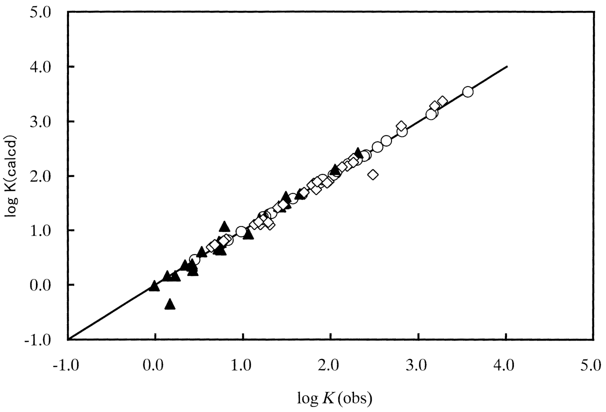


Fig. 1. Relation between the log (K/dm^3 mol^{-1}) values observed experimentally (log *K*(obs)) and those calculated from the η° and ω° values (log *K*(calcd)) for the various bases against three reference acids. Reference acids are ○: *p*-Fluorophenol, ▲: 5-Fluoroindole, ◇: Phenol.

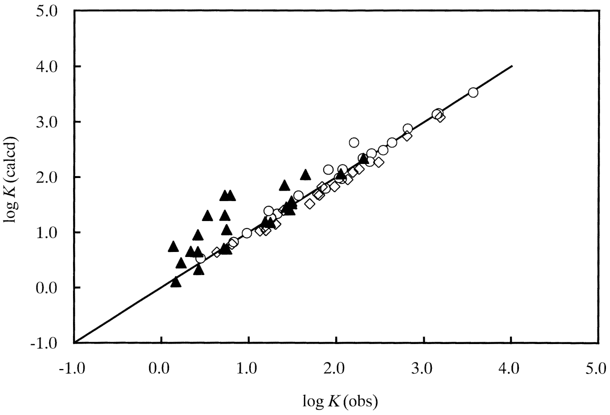


Fig. 2. Relation between the log (K/dm^3 mol^{-1}) values observed experimentally (log *K*(obs)) and those calculated from α_2^H and β_2^H values (log *K*(calcd)) for the various bases against three reference acids. Reference acids are ○: *p*-Fluorophenol, ▲: 5-Fluoroindole, ◇: Phenol.

Comparison of ω° with α_2^H and β_2^H. The relation between ω°_b and β_2^H obtained from the data given in Table 3 is shown in Fig. 3. A set of family-dependent straight lines converging on a point (0, −0.16) is obtained. From the results, the relation between β_2^H and ω°_b can be expressed as follows:

$$=\text{O bases: } \beta_2^H = -0.00396\omega^\circ_b - 0.160, \tag{16}$$

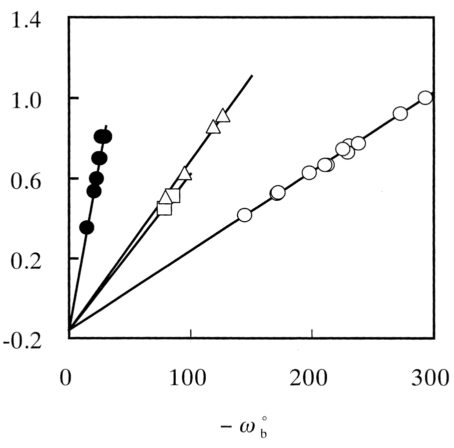


Fig. 3. Family-dependent linear relationships between β_2^H and ω_b° of various bases. ○: =O bases, □: –O– bases, △: =N– bases, ●: >N– bases. The convergence point of the straight lines is at (0, −0.16).

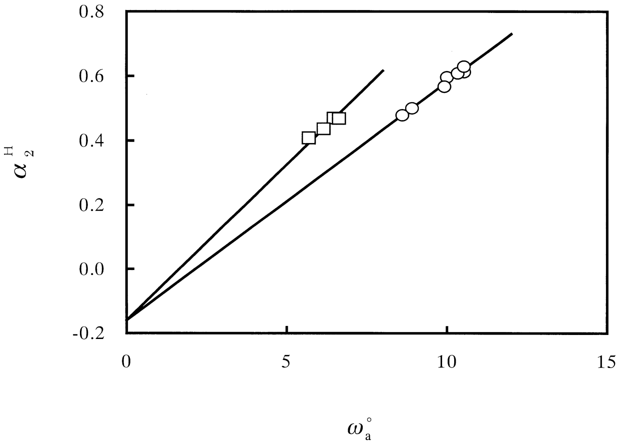


Fig. 4. Family-dependent linear relationships between α_2^H and ω_a° of various acids. ○: OH acids, ◇: NH acids. The convergence point of the two lines is at (0, −0.16).

$$\text{–O– bases: } \beta_2^H = -0.00779\omega_b^\circ - 0.160, \tag{17}$$

$$\text{=N– bases: } \beta_2^H = -0.00845\omega_b^\circ - 0.160, \tag{18}$$

$$\text{>N– bases: } \beta_2^H = -0.0339\omega_b^\circ - 0.160. \tag{19}$$

The relation between α_2^H and ω_a°, obtained by using the data given in Table 4, is shown in Fig. 4. Two family-dependent straight lines conversing on a point (0, −0.16) are obtained, so that the relation between α_2^H and ω_a° can be expressed as follows:

$$\text{OH acids: } \alpha_2^H = 0.0742\omega_a^\circ - 0.160, \tag{20}$$

$$\text{NH acids: } \alpha_2^H = 0.0970\omega_a^\circ - 0.160. \tag{21}$$

The linear-relationships expressed by Eqs. 16–21 suggest that the parameters α_2^H and β_2^H are similar to ω_a° and ω_b°, respectively, in a family of acids or bases. Thus, it may be pointed out that α_2^H and β_2^H as well as ω° are related to the electron-donating or -withdrawing ability. It is important that Eqs. 16–21 can be applied to evaluate the values of ω_a° and ω_b° from the α_2^H and β_2^H values, respectively. Since Abraham et al.[9,10] have been reported 150 α_2^H and 500 β_2^H values for various families of acids and bases, it is expected that numerous numbers of ω_a° and ω_b° for various acids and bases can be determined quantitatively from the α_2^H and β_2^H values. It is thus concluded that the log *K* values of 75,000 adducts can be predicted by using ω° values calculated from α_2^H and β_2^H values.

Conclusion

As described above, it has been demonstrated that novel local structural parameters, η° and ω°, can be evaluated for various bases and two new acids, and that the values of η° and ω° can be applied to a quantitative prediction of the log *K* values. It may be concluded from the results that the η°–ω° equation given by Eq. 2 can be applied as a general equation for a quantitative comparison and prediction of the log *K* values of the 1 : 1 hydrogen-bond complexation in CCl_4.

Since, at the present stage, the values of η° and ω° of eleven acids and 29 bases have already been known, 319 log *K* values at various temperatures can be predicted directly. Furthermore, as described above, because the value of ω° of numerous numbers of acids and bases can be determined from the α_2^H and β_2^H values reported by Abraham et al.,[9,10] parameters η° and ω° may be applied as new practical scales to interprete the 1 : 1 hydrogen-bond complexation. In addition, the η°–ω° function, as described in the preceding paper,[3] can be applied reasonably to predict a reversal in the order of the log *K* values.

From the results described above, it is concluded that the η°–ω° methodology can be applied widely as a new approach to interpret the fundamental factors governing acid-base interactions for the 1 : 1 hydrogen-bond complexation in CCl_4, and give a new view of acid-base chemistry.

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