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Spectrophotometric Determination of Formation Constants and Estimation of Molar Absorption Spectra of Individual Components in Chemical Equilibria. Infrared Study of Intermolecular Hydrogen Bonding of 2-Aminopyridine

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A general method is developed for evaluating formation constants and molar absorption coefficients of constituent species from spectrophotometric data for a multicomponent equilibrium system. The method is applied to analyzing infrared spectra for the intermolecular hydrogen bond system of 2-aminopyridine in carbon tetrachloride solution. 2-Aminopyridine assumes a cyclic dimer structure by dint of an intermolecular hydrogen bonding and the formation constant for the dimerization is 1.4±0.1 mol^{-1} dm^3 at 30 °C.

Spectroscopic methods have widely been used for studying equilibria in solutions. In very complex systems in which numerous equilibria exist, absorption curves of constituent species will overlap each other to give rise to complex envelopes of bands. For such complex systems methods for evaluating equilibrium constants from spectrophotometric data with the nonlinear least-squares method have been discussed by many investigators.[1-5] In their treatments the solution of mass balance equations and Jacobian matrix in the least-squares method were evaluated by numerical computations without resorting to analytical equations.

In this paper a general method for least-squares determination of formation constants and molar absorption coefficients of constituent species from spectrophotometric data is worked out in terms of matrix formulation and programed for electronic computers; a general method for solving mass balance equations for a multicomponent equilibrium system is derived; derivatives of equilibrium concentrations of constituent species with respect to formation constant are given in an analytical form; and a method for recasting the problem of least-squares determination in a simplified form is treated by using methods[6,7] for eliminating linear parameters in nonlinear least-squares adjustment. The method derived is applied to analyzing the intermolecular hydrogen bond system of 2-aminopyridine in carbon tetrachloride solution. Infrared spectra of 2-aminopyridine have been measured by Ramiah and Puranik[8] and Spinner,[9] and a normal coordinate treatment has been carried out by Berezin and Elkin,[10] but no quantitative analyses on intermolecular hydrogen bonding have yet been worked out. Therefore, the present infrared study on the intermolecular hydrogen bond of 2-aminopyridine was undertaken to investigate the molecular structure and formation constant of the hydrogen bond.

Method

Chemical Equilibrium of Multicomponent System. Let us consider the chemical equilibrium of a multicomponent system which consist of reactants X_i $(i=1,\cdots,m)$ and products Y_p $(p=1,\cdots,f)$. Let reaction equation for the system be given by

$$\sum_{i=1}^{m} n_{pi}X_i \rightleftharpoons Y_p \quad (p=1,\cdots,f), \tag{1}$$

where n_{pi} is the stoichiometric coefficient. Denoting the equilibrium concentrations of reactants X_i and products Y_p as $\tilde{\boldsymbol{x}}=[x_1\cdots x_m]$ and $\tilde{\boldsymbol{y}}=[y_1\cdots y_f]$, respectively, the total concentration of reactant X_i as $\tilde{\boldsymbol{x}}^t=[x_1^t\cdots x_m^t]$, and the formation constant of products Y_p as $\tilde{\boldsymbol{K}}=[K_1\cdots K_f]$ where $\sim$ represents the transpose of matrix, we have following equations for ideal solutions:

$$y_p = K_p \prod_{i=1}^{m} x_i{}^{n_{pi}}, \tag{2a}$$

$$\ln \boldsymbol{y} = \ln \boldsymbol{K} + \boldsymbol{N} \ln \boldsymbol{x}, \tag{2b}$$

$$x_i^t = x_i + \sum_{p=1}^{f} n_{pi} y_p, \tag{3a}$$

$$\boldsymbol{x}_i^t = \boldsymbol{x} + \tilde{\boldsymbol{N}}\boldsymbol{Y}, \tag{3b}$$

where $\ln \boldsymbol{x}$ represents the vector given by

$$\ln \tilde{\boldsymbol{x}} = [\ln x_1 \cdots \ln x_m], \tag{4}$$

and $\boldsymbol{N}$ is the stoichiometric coefficient matrix whose elements are n_{pi}. For a given set of stoichiometry $\boldsymbol{N}$, we can derive the following relations among infinitesimal changes in variables x_i, y_p, K_p, and x_i^t by differentiation of Eqs. 2a—3b:

$$[\boldsymbol{Y}]^{-1}\Delta \boldsymbol{y} = [\boldsymbol{K}]^{-1}\Delta \boldsymbol{K} + \boldsymbol{N}[\boldsymbol{X}]^{-1}\Delta \boldsymbol{x}, \tag{5a}$$

$$\Delta \ln \boldsymbol{y} = \Delta \ln \boldsymbol{K} + \boldsymbol{N} \Delta \ln \boldsymbol{x}, \tag{5b}$$

$$\begin{aligned} \Delta \boldsymbol{x}^t &= \Delta \boldsymbol{x} + \tilde{\boldsymbol{N}}\Delta \boldsymbol{y} \\ &= \tilde{\boldsymbol{N}}[\boldsymbol{Y}][\boldsymbol{K}]^{-1}\Delta \boldsymbol{K} + \{[\boldsymbol{X}] + \tilde{\boldsymbol{N}}[\boldsymbol{Y}]\boldsymbol{N}\}[\boldsymbol{X}]^{-1}\Delta \boldsymbol{x} \\ &= \tilde{\boldsymbol{N}}[\boldsymbol{Y}][\boldsymbol{K}]^{-1}\Delta \boldsymbol{K} + \boldsymbol{H}[\boldsymbol{X}]^{-1}\Delta \boldsymbol{x} \qquad (6a) \\ &= \tilde{\boldsymbol{N}}[\boldsymbol{Y}]\Delta \ln \boldsymbol{K} + \boldsymbol{H}\Delta \ln \boldsymbol{x}, \qquad (6b) \end{aligned}$$

where

$$\boldsymbol{H} = [\boldsymbol{X}] + \tilde{\boldsymbol{N}}[\boldsymbol{Y}]\boldsymbol{N}, \tag{7}$$

and $[\boldsymbol{X}]$, $[\boldsymbol{Y}]$, and $[\boldsymbol{K}]$ are the diagonal matrices whose elements are x_i, y_p, and K_p, respectively, and $\Delta \ln \boldsymbol{x}$ represents the vector given by

$$\Delta \ln \boldsymbol{x} = \begin{bmatrix} \Delta \ln x_1 \\ \Delta \ln x_2 \\ \vdots \\ \Delta \ln x_m \end{bmatrix} = \begin{bmatrix} \Delta x_1/x_1 \\ \Delta x_2/x_2 \\ \vdots \\ \Delta x_m/x_m \end{bmatrix} = [\boldsymbol{X}]^{-1}\Delta \boldsymbol{x}. \tag{8}$$

For a given set of formation constants $(\boldsymbol{K})$ and experimental formal concentrations of reactants $(\boldsymbol{x}^t)$, equilibrium concentrations of reactants $(\boldsymbol{x})$ can be calculated according to the method of Newton-Raphson iteration by making use of the following partial derivatives of total concentration $\boldsymbol{x}^t$ with respect to equilibrium concentration $\boldsymbol{x}$ which can be derived from Eqs. 6a and 6b under the condition of $\Delta\boldsymbol{K}=0$:

$$(\partial\boldsymbol{x}^t/\partial\boldsymbol{x})_{\Delta\boldsymbol{K}=0} = \boldsymbol{H}[\boldsymbol{X}]^{-1}, \tag{9}$$

$$(\partial\boldsymbol{x}^t/\partial\ln\boldsymbol{x})_{\Delta\boldsymbol{K}=0} = \boldsymbol{H}, \tag{10}$$

where $(\partial\boldsymbol{x}^t/\partial\boldsymbol{x})$ represents the matrix whose i,j elements are $(\partial x_i^t/\partial x_j)$. Partial derivatives of equilibrium concentrations with respect to formation constant for a given set of experimental formal concentrations of the reactants are required for the least-squares determination of formation constants from spectrophotometric data. These derivatives can be derived from Eqs. 5a—6b under the condition of $\Delta\boldsymbol{x}^t=0$ as

$$(\partial\boldsymbol{x}/\partial\boldsymbol{K})_{\Delta\boldsymbol{x}^t=0} = -[\boldsymbol{X}]\boldsymbol{H}^{-1}\tilde{\boldsymbol{N}}[\boldsymbol{Y}][\boldsymbol{K}]^{-1}, \tag{11}$$

$$(\partial\ln\boldsymbol{x}/\partial\ln\boldsymbol{K})_{\Delta\boldsymbol{x}^t=0} = -\boldsymbol{H}^{-1}\tilde{\boldsymbol{N}}[\boldsymbol{Y}], \tag{12}$$

$$(\partial\boldsymbol{y}/\partial\boldsymbol{K})_{\Delta\boldsymbol{x}^t=0} = [\boldsymbol{Y}]\{\boldsymbol{E} - \boldsymbol{N}\boldsymbol{H}^{-1}\tilde{\boldsymbol{N}}[\boldsymbol{Y}]\}[\boldsymbol{K}]^{-1}, \tag{13}$$

$$(\partial\ln\boldsymbol{y}/\partial\ln\boldsymbol{K})_{\Delta\boldsymbol{x}^t=0} = \boldsymbol{E} - \boldsymbol{N}\boldsymbol{H}^{-1}\tilde{\boldsymbol{N}}[\boldsymbol{Y}], \tag{14}$$

where $\boldsymbol{E}$ represents unit matrix.

Least-squares Treatment of Spectrophotometric Data. Suppose a set of absorbance data at λ points in a given wavenumber region for s solutions of different concentrations containing n absorbing components in a chemical equilibrium system. The absorbance per unit path length, $D_{\nu r}$, at wavenumber ν in the rth solution, is expressed by the sum of absorptions of the n components in the system on the assumption of Beer's law:

$$D_{\nu r} = \sum_{i=1}^{n} A_{\nu i}C_{ir}(\boldsymbol{K}) \quad (\nu=1,\cdots,\lambda;\ r=1,\cdots,s), \tag{15}$$

where $A_{\nu i}$ is the molar absorption coefficient of the ith species at wavenumber ν, and C_{ir} is the concentration of the ith species in the rth solution which is a function of formation constants $\boldsymbol{K}$ and can be calculated by the method as described above. Equation 15 may be written in the matix notation as

$$\boldsymbol{D} = \boldsymbol{A}\boldsymbol{C}(\boldsymbol{K}), \tag{16}$$

where $\boldsymbol{D}$ is a $\lambda\times s$ absorbance matrix, $\boldsymbol{A}$ is a $\lambda\times n$ matrix of molar absorption coefficients, and $\boldsymbol{C}$ is an $n\times s$ concentration matrix. Introducing absorbance vector $\boldsymbol{d}$ and vector $\boldsymbol{a}$ of molar absorption coefficients as defined by

$$\tilde{\boldsymbol{d}} = [\tilde{\boldsymbol{D}}_1\tilde{\boldsymbol{D}}_2\cdots\tilde{\boldsymbol{D}}_\lambda], \tag{17}$$

$$\tilde{\boldsymbol{a}} = [\tilde{\boldsymbol{A}}_1\tilde{\boldsymbol{A}}_2\cdots\tilde{\boldsymbol{A}}_\lambda], \tag{18}$$

where $\tilde{\boldsymbol{D}}_\nu$ and $\tilde{\boldsymbol{A}}_\nu$ are row vectors of absorbance and molar absorption coefficients which are the νth rows of matrices $\boldsymbol{D}$ and $\boldsymbol{A}$, respectively,

$$\boldsymbol{D} = \begin{bmatrix} \tilde{\boldsymbol{D}}_1 \\ \vdots \\ \tilde{\boldsymbol{D}}_\lambda \end{bmatrix}, \tag{19}$$

$$\boldsymbol{A} = \begin{bmatrix} \tilde{\boldsymbol{A}}_1 \\ \vdots \\ \tilde{\boldsymbol{A}}_\lambda \end{bmatrix}, \tag{20}$$

Eq. 16 may be written as

$$\tilde{\boldsymbol{D}}_\nu = \tilde{\boldsymbol{A}}_\nu\boldsymbol{C}(\boldsymbol{K}) \quad (\nu = 1,\cdots,\lambda). \tag{21}$$

Now let us consider the problem of determining f formation constants $\boldsymbol{K}$ and $\lambda\times n$ molar absorption coefficients $\boldsymbol{A}$ from $\lambda\times s$ observed absorbances $\boldsymbol{D}^{\text{obsd}}$ by the least-squares method. In Eqs. 16 or 21 absorbances $D_{\nu r}$ are of linear function of molar absorption coefficients $A_{\nu i}$ but of nonlinear function of formation constants K_p. In such cases we can simplify the least-squares treatment into a reduced model by elimination of linear parameters as described in Appendix. For a given set of formation constants $\boldsymbol{K}$, the best least-squares estimate of molar absorption coefficients, $\boldsymbol{A}'(\boldsymbol{K})$, can be given in an explicit form as described in Appendix [Eq. A.6]:

$$\tilde{\boldsymbol{A}}'_\nu = \tilde{\boldsymbol{D}}_\nu^{\text{obsd}}\tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}, \tag{22}$$

$$\boldsymbol{A}' = \boldsymbol{D}^{\text{obsd}}\tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}. \tag{23}$$

Substitution of Eqs. 22 and 23 for Eqs. 21 and 16 gives the observation equations for the reduced model:

$$\tilde{\boldsymbol{D}}'_\nu = \tilde{\boldsymbol{A}}'_\nu\boldsymbol{C} = \tilde{\boldsymbol{D}}_\nu^{\text{obsd}}\tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C}, \tag{24}$$

$$\boldsymbol{D}' = \boldsymbol{A}'\boldsymbol{C} = \boldsymbol{D}^{\text{obsd}}\tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C}, \tag{25}$$

where the prime represents quantities for the reduced model which are functions of $\boldsymbol{K}$ only.

Small changes in absorbance, $\Delta\boldsymbol{D}$, caused by small increments in formation constants, $\Delta\boldsymbol{K}$, are expressed in terms of Jacobian matrix $\boldsymbol{J}'$ for reduced model:

$$\Delta\boldsymbol{D}'_\nu = \boldsymbol{J}'_\nu\Delta\boldsymbol{K}, \tag{26}$$

$$\Delta\boldsymbol{d}' = \boldsymbol{J}'\Delta\boldsymbol{K}, \tag{27}$$

$$\boldsymbol{J}' = \begin{bmatrix} \boldsymbol{J}'_1 \\ \vdots \\ \boldsymbol{J}'_\lambda \end{bmatrix}, \tag{28}$$

$$\boldsymbol{J}'_\nu = [(\partial\boldsymbol{D}'_\nu/\partial K_1)\cdots(\partial\boldsymbol{D}'_\nu/\partial K_f)]. \tag{29}$$

Elements $\partial D'_{\nu r}/\partial K_p$ of Jacobian matrix $\boldsymbol{J}'$ are given according to Eqs. A. 10—A. 12 derived in Appendix:

$$\begin{aligned}\partial\boldsymbol{D}'_\nu/\partial K_p &= (\partial\tilde{\boldsymbol{C}}/\partial K_p)\boldsymbol{A}'_\nu + \tilde{\boldsymbol{C}}(\partial\boldsymbol{A}'_\nu/\partial K_p) \\ &= [\boldsymbol{E} - \tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C}](\partial\tilde{\boldsymbol{C}}/K_p)\boldsymbol{A}'_\nu \\ &\quad + \tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}(\partial\boldsymbol{C}/\partial K_p)(\boldsymbol{D}_\nu^{\text{obsd}} - \boldsymbol{D}'_\nu),\end{aligned} \tag{30}$$

$$\begin{aligned}\partial\boldsymbol{A}'_\nu/\partial K_p &= -(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C}(\partial\tilde{\boldsymbol{C}}/\partial K_p)\boldsymbol{A}'_\nu \\ &\quad + (\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}(\partial\boldsymbol{C}/\partial K_p)(\boldsymbol{D}_\nu^{\text{obsd}} - \boldsymbol{D}'_\nu).\end{aligned} \tag{31}$$

Derivatives $(\partial C_{ir}/\partial K_p)$ can be calculated by the method established in the preceding section (Eqs. 11 and 13). Equations 30 and 31 may be written with reference to Eqs. 19 and 20 as follows:

$$\begin{aligned}\partial\boldsymbol{D}'/\partial K_p &= \boldsymbol{A}'(\partial\boldsymbol{C}/\partial K_p) + (\partial\boldsymbol{A}'/\partial K_p)\boldsymbol{C} \\ &= \boldsymbol{A}'(\partial\boldsymbol{C}/K_p)[\boldsymbol{E} - \tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C}] \\ &\quad + (\boldsymbol{D}^{\text{obsd}} - \boldsymbol{D}')(\partial\tilde{\boldsymbol{C}}/\partial K_p)(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}\boldsymbol{C},\end{aligned} \tag{32}$$

$$\begin{aligned}\partial\boldsymbol{A}'/\partial K_p &= -\boldsymbol{A}'(\partial\boldsymbol{C}/\partial K_p)\tilde{\boldsymbol{C}}(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1} \\ &\quad + (\boldsymbol{D}^{\text{obsd}} - \boldsymbol{D}')(\partial\tilde{\boldsymbol{C}}/\partial K_p)(\boldsymbol{C}\tilde{\boldsymbol{C}})^{-1}.\end{aligned} \tag{33}$$

Thus, formation constants $\boldsymbol{K}$ can be determined according to the usual procedure based on nonlinear least-squares with reference to observed data $\boldsymbol{D}^{\text{obsd}}$. The normal equations for the reduced model which give correction $\Delta\boldsymbol{K}$ in iteration cycles are given by

$$(\tilde{\boldsymbol{J}}'\boldsymbol{J}')\Delta\boldsymbol{K} = \tilde{\boldsymbol{J}}'(\boldsymbol{d}^{\text{obsd}} - \boldsymbol{d}') \tag{34}$$

$$\tilde{\boldsymbol{J}}'\boldsymbol{J}' = \sum_{\nu=1}^{\lambda}\tilde{\boldsymbol{J}}'_\nu\boldsymbol{J}'_\nu \tag{35}$$

$$\tilde{\boldsymbol{J}}'(\boldsymbol{d}^{\text{obsd}} - \boldsymbol{d}') = \sum_{\nu=1}^{\lambda}\tilde{\boldsymbol{J}}'_\nu(\boldsymbol{D}_\nu^{\text{obsd}} - \boldsymbol{D}'_\nu). \tag{36}$$

Experimental

2-Aminopyridine was recrystallized from carbon tetrachloride and dried. Spectroscopic grade carbon tetrachloride dried over molecular sieves 3A was used as the solvent. Solutions were prepared in the concentration range of 0.5—0.005 M (1 M = 1 mol dm^{-3}). Infrared spectra were measured with a JASCO A-3 infrared spectrophotometer at 30°C. Absorbances were digitized with an AD converter over the range from 3600 to 3000 cm^{-1}. Absorbance data at 10 cm^{-1} intervals from 3550 to 3360 cm^{-1} and at 20 cm^{-1} intervals from 3360 to 3120 cm^{-1} were used for data analysis.

Results and Discussion

The observed spectra in the NH_2 stretching region of three solutions of 2-aminopyridine in CCl_4 are shown in Fig. 1. In the dilute solution the symmetric (ν_sNH_2) and antisymmetric (ν_aNH_2) stretching vibrations of NH_2 group in free species are observed at 3415 and 3520 cm^{-1}, respectively. As the concentration increases both the peaks at 3520 and 3415 cm^{-1} decrease while the broad bands at 3315 and 3170 cm^{-1} grow up and the absorbances at about 3500 and 3390 cm^{-1} increase. These observations suggest that bands due to intermolecular association exist at those wavenumbers.

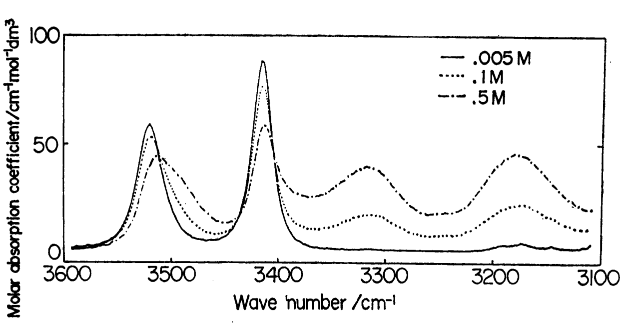

Fig. 1. Infrared spectra of 2-aminopyridine in CCl_4 solution.

The concentration dependence of the observed absorbances was analyzed on the basis of the monomer-dimer equilibrium model by the least-squares method as described above. The formation constant for dimerization (K=[dimer]/[monomer]^2) was calculated to be 1.4±0.1 M^{-1} at 30 °C. The calculated molar absorption coefficients for monomer and dimer species are shown in Fig. 2, in which those for dimer species are given in values per monomer unit. The observed spectra could be reproduced with a root-mean-squares deviation of 0.57 (in the unit of molar absorption). An example of comparison between observed and calculated spectra is shown in Fig. 3, together with contribution from monomer and dimer species for the 0.5 M solution. The concentration dependence of the degree of dimer formation is shown in Fig. 4. It turns out that the fraction of dimer changes from 1.4% at the lowest concentration of 0.005 M to 44% at the highest concentration of 0.5 M. The monomer-trimer model also was applied but the agreement between observed and calculated spectra was poor as compared with the monomer-dimer model. The least-squares treatment on the monomer-dimer-trimer model could give no convergence. Therefore, it can be concluded that dimerization is the predominant association in the concentration range employed.

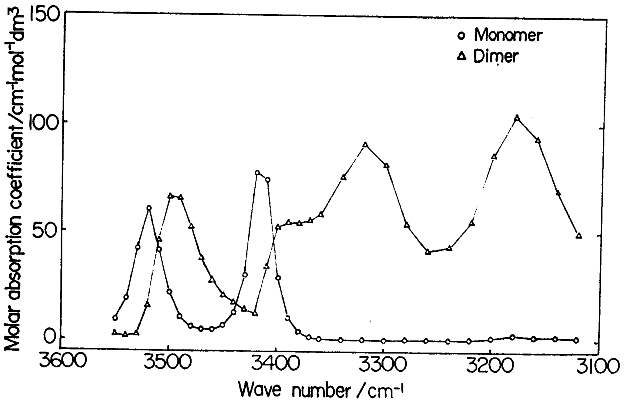

Fig. 2. Molar absorption coefficients for monomer and dimer of 2-aminopyridine.

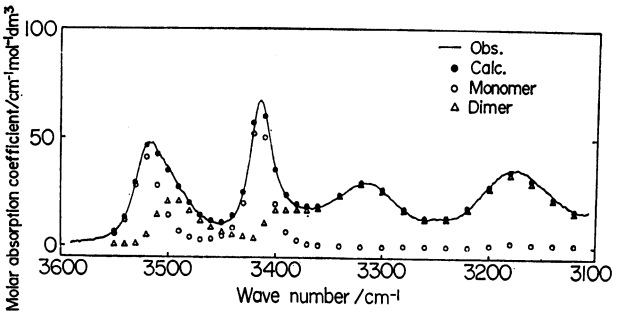

Fig. 3. Observed and calculated spectra for 0.25 M solution.

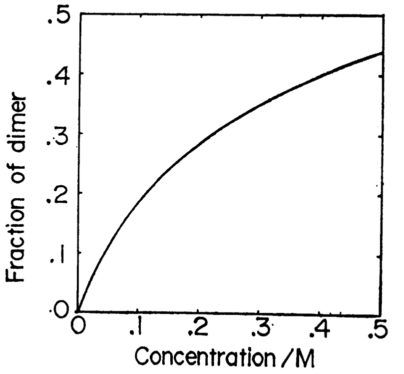

Fig. 4. Concentration dependence of the degree of dimer formation.

The calculated molar absorption coefficients in Fig. 2 show that the monomer species has bands at 3520 and 3415 cm^{-1} which are assigned to vibrations ν_aNH_2 and ν_sNH_2, respectively, in the non-hydrogen-bonded species. The calculated dimer spectrum has peaks at 3495, 3320, and 3180 cm^{-1} and a shoulder at about 3390 cm^{-1}. The band at 3495 cm^{-1} can be assigned to the free N-H stretching vibration in the $\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}\mathrm{-H\cdots N}$ hydrogen bond system. The two broad bands at 3320 and 3180 cm^{-1} can be assigned to the Fermi doublet caused by the resonance between the hydrogen-bonded N-H stretching vibration and the overtone of the NH_2

bending vibration at 1630 cm^{-1} in the $\overset{\text{H}}{\overset{|}{\text{N}}}\text{–H}\cdots\text{N}$ hydrogen bond system, similar resonance beeing observed in the hydrogen bond system of aniline by Wolf and Mathias.[11] The unperturbed hydrogen-bonded N–H stretching fundamental of dimer is estimated to be about 3240 cm^{-1}. The shoulder at 3390 cm^{-1} may be ascribed to the band caused by a Fermi resonance between the hydrogen-bonded N–H stretching fundamental and the overtone of the pyridine ring vibration at 1610 cm^{-1} or the combination tone of the NH_2 bending and ring vibrations.

From the fact that the calculated dimer spectrum has only one non-hydrogen-bonded N–H stretching band it turns out that one proton of NH_2 group is involved in the hydrogen bond while the other proton is free of the hydrogen bonding. It is consequently concluded that 2-aminopyridine in CCl_4 assumes a cyclic dimer structure by dint of an intermolecular hydrogen bond as shown in Fig. 5; it has been observed that 2-aminopyridine assumes the same cyclic dimer structure in the crystalline state.[12]

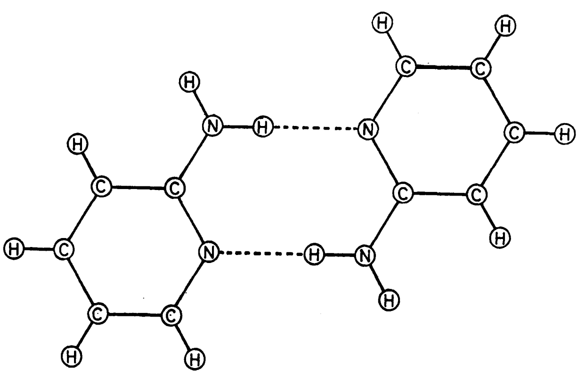

Fig. 5. Intermolecular hydrogen bonding of 2-aminopyridine.

Appendix: Elimination of Linear Parameters in Nonlinear Least-squares Treatment

Consider the problem of a least-squares estimation of the $m+n$ parameters of m nonlinear parameters $\tilde{\boldsymbol{\alpha}}=[\alpha_1\cdots\alpha_m]$ and n linear parameters $\tilde{\boldsymbol{\beta}}=[\beta_1\cdots\beta_n]$ with reference to the t observed values $\tilde{\boldsymbol{Z}}^{\text{obsd}}$ associated with the observation equations $\tilde{\boldsymbol{Z}}(\boldsymbol{\alpha},\boldsymbol{\beta})=[Z_1\cdots Z_t]$. Functions Z_q linear in β_k but nonlinear in α_i are generally written as

$$Z_q(\boldsymbol{\alpha},\boldsymbol{\beta}) = \sum_{k=1}^{n} F_{qk}(\boldsymbol{\alpha})\beta_k \ \ (q = 1, \cdots, t), \tag{A. 1}$$

where F_{qk} is the nonlinear function of α_i. Eq. A.1 may be written in the matrix notation as

$$\boldsymbol{Z}(\boldsymbol{\alpha},\boldsymbol{\beta}) = \boldsymbol{F}(\boldsymbol{\alpha})\boldsymbol{\beta}. \tag{A. 2}$$

Residual vector $\boldsymbol{\varepsilon}$ and the sum of squared residuals S are given by

$$\boldsymbol{\varepsilon} = \boldsymbol{Z}^{\text{obsd}} - \boldsymbol{Z} = \boldsymbol{Z}^{\text{obsd}} - \boldsymbol{F}\boldsymbol{\beta}, \tag{A. 3}$$

$$S = \tilde{\boldsymbol{\varepsilon}}\boldsymbol{\varepsilon} = \tilde{\boldsymbol{\beta}}\tilde{\boldsymbol{F}}\boldsymbol{F}\boldsymbol{\beta} - 2\tilde{\boldsymbol{\beta}}\tilde{\boldsymbol{F}}\boldsymbol{Z}^{\text{obsd}} + \tilde{\boldsymbol{Z}}^{\text{obsd}}\boldsymbol{Z}^{\text{cbsd}}, \tag{A. 4}$$

where ~ represents the transpose of matrix.

Lawton and Sylvester[6] have pointed out that the $m+n$ dimensional problem with m nonlinear and n linear parameters in a least-squares adjustment could be reduced to an m dimensional problem by elimination of linear parameters. Golub and Pereyra[7] have treated the mathematics and algorism associated with that problem in detail but their derivation requires a familiarity with a somewhat advanced mathematics and is not familiar to chemists. Thus, a rather simple derivation using the elementary algebra will be given in a form appropriate to the present study.

The best least-squares estimate $\boldsymbol{\beta}'(\boldsymbol{\alpha})$ of linear parameters $\boldsymbol{\beta}$ associated with a given set of nonlinear parameters $\boldsymbol{\alpha}$ can be derived from the minimum condition for the sum of squared residuals S:

$$\begin{aligned}(1/2)\partial S/\partial\boldsymbol{\beta} &= (1/2)\partial(\tilde{\boldsymbol{\varepsilon}}\boldsymbol{\varepsilon})\partial/\boldsymbol{\beta} = -\tilde{\boldsymbol{F}}\boldsymbol{\varepsilon}\\ &= \tilde{\boldsymbol{F}}\boldsymbol{F}\boldsymbol{\beta} - \tilde{\boldsymbol{F}}\boldsymbol{Z}^{\text{obsd}} = 0,\end{aligned} \tag{A. 5}$$

$$\boldsymbol{\beta} = \boldsymbol{\beta}'(\boldsymbol{\alpha}) = (\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}\tilde{\boldsymbol{F}}\boldsymbol{Z}^{\text{obsd}}. \tag{A. 6}$$

Substitution of Eq. A.6 for Eq. A.2 gives reduced observation equations for the reduced model as

$$\boldsymbol{Z}'(\boldsymbol{\alpha}) = \boldsymbol{F}\boldsymbol{\beta}'(\boldsymbol{\alpha}) = \boldsymbol{F}(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}\,\tilde{\boldsymbol{F}}\boldsymbol{Z}^{\text{obsd}}, \tag{A. 7}$$

where $\boldsymbol{Z}'$ is a function of only nonlinear parameters $\boldsymbol{\alpha}$ and the prime is used for representing quantities for the reduced model. Jacobian matrix $\boldsymbol{J}'$ for the reduced model is defined as

$$J'_{qi} = \partial Z'_q/\partial\alpha_i = \sum_{k=1}^{n}[(\partial F_{qk}/\partial\alpha_i)\beta'_k + F_{qk}(\partial\beta'_k/\partial\alpha_i)], \tag{A. 8}$$

$$\boldsymbol{J}' = \partial\boldsymbol{Z}'/\partial\boldsymbol{\alpha} = [\partial\boldsymbol{Z}'/\partial\alpha_1 \cdots \partial\boldsymbol{Z}'/\partial\alpha_m], \tag{A. 9}$$

$$\partial\boldsymbol{Z}'/\partial\alpha_i = (\partial\boldsymbol{F}/\partial\alpha_i)\boldsymbol{\beta}' + \boldsymbol{F}(\partial\boldsymbol{\beta}'/\partial\alpha_i), \tag{A. 10}$$

where $\partial\boldsymbol{\beta}'/\partial\boldsymbol{\alpha}$ can be derived through differentiation of Eq. A.6:

$$\begin{aligned}\partial\boldsymbol{\beta}'/\partial\alpha_i = &-(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}[(\partial\tilde{\boldsymbol{F}}/\partial\alpha_i)\boldsymbol{F}\\ &+\tilde{\boldsymbol{F}}(\partial\boldsymbol{F}/\partial\alpha_i)](\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}\tilde{\boldsymbol{F}}\boldsymbol{Z}^{\text{obsd}}\\ &+(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}(\partial\tilde{\boldsymbol{F}}/\partial\alpha_i)\boldsymbol{Z}^{\text{obsd}}\\ = &-(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}\tilde{\boldsymbol{F}}(\partial\boldsymbol{F}/\partial\alpha_i)\boldsymbol{\beta}'\\ &+(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}(\partial\tilde{\boldsymbol{F}}/\partial\alpha_i)\boldsymbol{\varepsilon}.\end{aligned} \tag{A. 11}$$

Substitution of Eq. A.11 for Eq. A. 10 gives

$$\begin{aligned}\partial\boldsymbol{Z}'/\partial\alpha_i = &[\boldsymbol{E} - \boldsymbol{F}(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}\tilde{\boldsymbol{F}}](\partial\boldsymbol{F}/\partial\alpha_i)\boldsymbol{\beta}'\\ &+\boldsymbol{F}(\tilde{\boldsymbol{F}}\boldsymbol{F})^{-1}(\partial\tilde{\boldsymbol{F}}/\partial\alpha_i)\boldsymbol{\varepsilon}.\end{aligned} \tag{A. 12}$$

In terms of Jacobian matrix $\boldsymbol{J}'$ given by Eqs. A.9 and A.12 the normal equations for the reduced model are given by

$$(\tilde{\boldsymbol{J}}'\boldsymbol{J}')\Delta\boldsymbol{\alpha} = \tilde{\boldsymbol{J}}'\boldsymbol{\varepsilon}, \tag{A. 13}$$

and

$$\Delta\boldsymbol{\alpha} = (\tilde{\boldsymbol{J}}'\boldsymbol{J}')^{-1}\tilde{\boldsymbol{J}}'\boldsymbol{\varepsilon}. \tag{A. 14}$$

The improved nonlinear parameters $\boldsymbol{\alpha}+\Delta\boldsymbol{\alpha}$ for the next iteration are calculated from Eq. A.14 and the best companion linear parameters $\boldsymbol{\beta}$ are given by Eq. A.6. The method of least-squares with the reudced observation equations given by Eq. A.7 is evidently superior to the one with the original model given by Eq. A.2: The dimension of problem could be reduced to as low as m in the reduced model from $m+n$ in the original model by the elimination of n linear parameters. This reduced dimension could result in a faster convergence, a stabilization of convergence, and a reduction of memories. The initial guess requires only m nonlinear parameters rather than $m+n$ parameters in the original model.

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