Monatshefte für Chemie 111, 235—248 (1980)

Monatshefte für Chemie

An Analytical Approach to the Study of Coupled Chemical Equilibria

Bohumila Schreiber, Helga Martinek,
Maria Hoffmann-Ostenhof, Peter Wolschann, and **Peter Schuster***

Institut für Theoretische Chemie und Strahlenchemie,
Universität Wien, A-1090 Wien, Austria

(Received 10 October 1979. Accepted 17 October 1979)

Two classes of coupled chemical equilibria

$$(1)\ \mathrm{A}+\mathrm{B}\overset{K_1}{\rightleftharpoons}\mathrm{C}\ \text{and}\ \mathrm{B}+\mathrm{D}\overset{K_2}{\rightleftharpoons}\mathrm{E},\quad\text{and}$$

$$(2)\ \mathrm{A}+\mathrm{B}\overset{K_1}{\rightleftharpoons}\mathrm{C}\ \text{and}\ \mathrm{B}+\mathrm{D}\overset{K_2}{\rightleftharpoons}\mathrm{E}+\mathrm{F}$$

have been studied by a combination of analytical and numerical mathematical techniques. Both equilibrium constants and/or one unknown initial concentration ($[D]_0 = d_0$) can be obtained simultaneously and with relatively high accuracy. In order to illustrate the usefulness of this procedure we determined some equilibrium constants for donor-acceptor complex formation and proton transfer reactions in non-aqueous solvents.

(Keywords: Chemical equilibria, coupled; Donor-acceptor complexes; Mathematical analysis of chemical equilibria; Proton-transfer equilibria)

Ein mathematisch-analytischer Ansatz zum Studium von gekoppelten chemischen Gleichgewichten

Es wurden zwei Typen von gekoppelten chemischen Gleichgewichten mit kombinierten analytischen und numerischen Methoden untersucht:

$$(1)\ \mathrm{A}+\mathrm{B}\overset{K_1}{\rightleftharpoons}\mathrm{C}\ \text{und}\ \mathrm{B}+\mathrm{D}\overset{K_2}{\rightleftharpoons}\mathrm{E}$$

$$(2)\ \mathrm{A}+\mathrm{B}\overset{K_1}{\rightleftharpoons}\mathrm{C}\ \text{und}\ \mathrm{B}+\mathrm{D}\overset{K_2}{\rightleftharpoons}\mathrm{E}+\mathrm{F}$$

Beide Gleichgewichtskonstanten und/oder eine unbekannte Anfangskonzentration ($[\mathrm{D}]_0 = d_0$) können gleichzeitig mit großer Genauigkeit erhalten werden.

0026-9247/80/0111/0235/$ 02.80

Um den Nutzen dieses Verfahrens zu demonstrieren, wurden einige Gleichgewichtskonstanten für Donor-Acceptor-Komplexe und Protonierungsreaktionen in nichtwäßrigen Lösungsmitteln bestimmt.

1. Introduction

The mathematical techniques most frequently applied to the determination of equilibrium constants fall mainly into two categories: either, one tries to linearize the experimentally determined function of concentration variables by a suitable transformation[1] or one applies direct numerical simulation and obtains the constants by a curve fitting procedure[2]. In the first example the mathematical method used is simply linear regression. Both techniques may suffer from certain shortcomings: linearization in general requires special conditions to be fulfilled and consequently the information contained in the experimental data which do not meet these conditions is lost. Moreover, it may be hard to sample enough data in the linear range because of various experimental difficulties and then the determination of the constants of interest inevitably becomes less accurate. Purely numerical methods, on the other hand, usually suffer from the lack of insight into the mathematical problem lying beyond parameter fitting. Very often these techniques work properly in close vicinity of the ultimate solutions only. Parameter fitting may lead to physically insignificant local minima in parameter space. Usually, the determination of a single equilibrium constant does not lead to serious problems, provided sufficiently accurate experimental data are accessible. Simultaneous determination of several equilibrium constants in coupled equilibria is not as simple[3]. We made an attempt to overcome these difficulties by performing a detailed analysis of the functional relations to be determined by measurements prior to numerical computation. In this paper we report a study on two classes of coupled association and exchange equilibria.

2. Recording of Data, Initial Conditions and Mass Conservation

Throughout this paper we shall assume that the free concentration of one component is accessible to some direct or indirect physical measurement. In particular, this will be always the component denoted by A. For free concentrations, more precisely activities, we shall use small letters: $[A] = a$. In the concrete examples which will be presented in the experimental section the physical parameter to be determined is the optical density. Hence, we require a certain range in the electronic spectra of our systems within which the absorption is practically due to a single component only. All the results presented here can be generalized in a straight-forward way to systems in which more components absorb at the same wavelengths.

The titration curves to be analysed yield the free concentration of A as a function of the initial concentrations, $a = f(a_0, b_0, \ldots)$. In order to make this expression more handy we have to impose certain conditions on the initial concentrations in order to obtain a dependence on a single input parameter only, e.g. $a = f(a_0)$; $b_0 = \beta a_0, \ldots$ etc. This is not to be considered as a restriction since we can change the relations imposed on the total concentrations in a systematic way and thereby derive two and higher dimensional surfaces as families of curves with gradually changing parameters.

Mass conservation leads to some relations between variables in both systems to be studied here:

(1) $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}, \ \mathrm{B} + \mathrm{D} \rightleftharpoons \mathrm{E}$

$$a + c = a_0 + c_0 \tag{1a}$$
$$b + c + e = b_0 + c_0 + e_0 \tag{1b}$$
$$d + e = d_0 + e_0 \tag{1c}$$

and (2) $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}, \ \mathrm{B} + \mathrm{D} \rightleftharpoons \mathrm{E} + \mathrm{F}$

$$a + c = a_0 + c_0 \tag{2a}$$
$$b + c + e = b_0 + c_0 + e_0 \tag{2b}$$
$$d + f = d_0 + f_0 \tag{2c}$$
$$e - f = e_0 - f_0 \tag{2d}$$

In order to facilitate further treatment we may choose some initial concentrations equal to zero and find:

(1) $c_0 = e_0 = 0$:

$$a + c = a_0 \tag{1a'}$$
$$b + c + e = b_0 \tag{1b'}$$
$$d + e = d_0 \tag{1c'}$$

or (2) $c_0 = e_0 = f_0 = 0$:

$$a + c = a_0 \tag{2a'}$$
$$b + c + e = b_0 \tag{2b'}$$
$$d + f = d_0 \tag{2c'}$$
$$e = f \tag{2d'}$$

In the first example we do not lose any generality whereas in the latter case we exclude all initial conditions for which $e_0 \neq f_0$. In the kind of titration curve to be studied later we shall further assume that one initial concentration, in particular d_0, is constant for each individual curve:

$$a = f(a_0, b_0, d_0); \quad b_0 = \beta a_0, \ d_0 = \text{const.}$$

3. Mathematical Analysis

Appropriately we analyse the equations for the coupled equilibria (1) and (2) seperately and start with the more simple example.

A. The System $A + B \rightleftharpoons C$, $C + D \rightleftharpoons E$

From the relations determined by the two equilibrium constants

$$K_1 = \frac{[C]}{[A]\cdot[B]} = \frac{c}{a\cdot b} \tag{3}$$

and

$$K_2 = \frac{[E]}{[C]\cdot[D]} = \frac{e}{c\cdot d} \tag{4},$$

the mass conservation laws as well as the initial conditions ($a_0, b_0 = \beta a_0, c_0 = 0, d_0 = \text{const}$, $e_0 = 0$) discussed above we can easily derive an implicit equation for the equilibrium concentration a:

$$F(a, a_0) = a^3 + (m_4 + m_3 a_0) a^2 + (m_2 + m_1 a_0) a_0 a + m_0 a_0^2 = 0 \tag{5}$$

wherein

$$m_0 = \frac{K_2}{K_1(K_2 - K_1)} \tag{5a}$$

$$m_1 = \frac{K_2}{K_2 - K_1}(1 - \beta) \tag{5b}$$

$$m_2 = \frac{K_1 - 2K_2 + K_1 K_2 d_0}{K_1(K_2 - K_1)} \tag{5c}$$

$$m_3 = \beta - 1 - \frac{K_2}{K_1(K_2 - K_1)} \tag{5d}$$

and

$$m_4 = \frac{1}{K_1}\left(1 - \frac{K_1 K_2 d_0}{K_2 - K_1}\right) \tag{5e}$$

Although nobody has succeeded so far to obtain solution curves of equation (5) in algebraic form, we may find answers to certain problems as analytic expressions. An important example of this kind which will be discussed in some detail here, concerns the appearance of a maximum in the plot $a = f(a_0)$. The position of such a maximum which may be determined experimentically with rather high precision, can be derived from equation (5) by implicit differentiation:

$$\frac{\mathrm{d}\,a}{\mathrm{d}\,a_0} = -\frac{\left(\dfrac{\partial F}{\partial a_0}\right)}{\left(\dfrac{\partial F}{\partial a}\right)} =$$

$$= -\frac{m_3\,a^2 + (m_2 + 2\,m_1\,a_0)\,a + 2\,m_0\,a_0}{3\,a^2 + 2\,(m_4 + m_3\,a_0)\,a + (m_2 + m_1\,a_0)\,a_0} \tag{6}$$

At the maximum, $(\bar{a}_0, \bar{a})$, we find $\left(\dfrac{\mathrm{d}\,a}{\mathrm{d}\,a_0}\right)_{\bar{a}_0} = 0$ provided $\left(\dfrac{\partial F}{\partial a}\right)_{\bar{a}_0} \neq 0$ and consequently obtain further:

$$\bar{a}_0 = \frac{(m_3\,\bar{a} + m_2)\,\bar{a}}{2\,(m_1\,\bar{a} + m_0)} \tag{7}$$

Combining equations (5) and (7) we find an expression for $\bar{a}$ which ultimately may be simplified to a quadratic equation:

$$\bar{a}_{1,2} = \frac{1}{b_2}\,(b_1 \pm \sqrt{b_1{}^2 - b_0\,b_2}\,) \tag{8}$$

wherein

$$b_0 = m_2{}^2 - 4\,m_0\,m_4, \tag{8a}$$

$$b_1 = 2\,m_0 + 2\,m_1\,m_4 - m_2\,m_3 \tag{8b}$$

and

$$b_2 = m_3{}^2 - 4\,m_1 \tag{8c}$$

The further condition which determines the extremum to be a maximum simply follows from

$$\left.\frac{\mathrm{d}^2\,a}{\mathrm{d}\,a_0{}^2}\right|_{\bar{a}_0} = -\left.\frac{\left(\dfrac{\partial^2 F}{\partial\,a_0{}^2}\right)}{\left(\dfrac{\partial F}{\partial a}\right)}\right|_{\bar{a}_0} < 0 \tag{9}$$

and reads:

$$\frac{2\,(m_1\,\bar{a} + m_0)}{3\,\bar{a}^2 + 2\,(m_4 + m_3\,\bar{a}_0)\,\bar{a} + (m_2 + m_1\,\bar{a}_0)\,\bar{a}_0} > 0 \tag{9a}$$

The functional relations fulfilled by the maximum and the conditions of its appearance will be discussed later by means of concrete examples.

B. The System $A + B \rightleftharpoons C$, $B + D \rightleftharpoons E + F$

Again we start from the two equilibrium constants

$$K_1 = \frac{c}{a \cdot b}$$

and

$$K_2 = \frac{e \cdot f}{b \cdot c}$$

Now we introduce initial conditions ($b_0 = \beta a_0$, $c_0 = 0$, $d_0 = \text{const.}$, $e_0 = f_0 = 0$) and the mass conservation relations as in the previous example and find the following implicit equations for the equilibrium concentration a:

$$F(a, a_0) = a^4 + (m_6 + m_7 a_0) a^3 + (m_3 + m_4 a_0 + m_5 a_0^2) a^2 + (m_1 + m_2 a_0) a_0 a + m_0 a_0^2 = 0 \tag{10}$$

wherein

$$m_0 = K(K - \varkappa) \tag{10a}$$

$$m_1 = (1 - \beta)(2K - \varkappa) \tag{10b}$$

$$m_2 = -[2K^2 + (d_0 - 2K)\varkappa] \tag{10c}$$

$$m_3 = (1 - \beta)^2 \tag{10d}$$

$$m_4 = (\beta - 2)(2K - \varkappa) \tag{10e}$$

$$m_5 = K^2 + (d_0 - K)\varkappa \tag{10f}$$

$$m_6 = 2(\beta - 1) \tag{10g}$$

$$m_7 = 2K - \varkappa \tag{10h}$$

For convenience we use $K = K_1^{-1}$ and $\varkappa = K_2/K_1$. Apparently equation (10) is somewhat more complicated than the implicit equation of the former system (9), since the degree of the polynomial in a is higher and eight coefficients instead of five are required.

The appearance of a maximum in the plot $a = f(a_0)$ can be analysed by means of implicit differentiation as before.

$$\frac{da}{da_0} = -\frac{m_7 a^3 + (m_4 + 2m_5 a_0)a^2 + (m_1 + 2m_2 a_0)a + 2m_0 a_0}{4a^3 + 3(m_6 + m_7 a_0)a^2 + 2(m_3 + m_4 a_0 + m_5 a_0^2)a + m_1 a_0 + m_2 a_0^2} \tag{11}$$

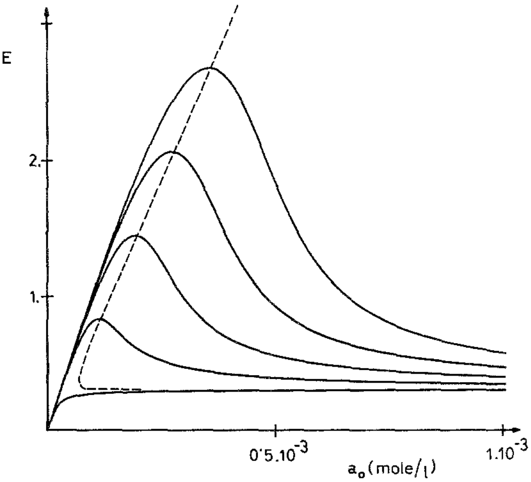

Fig. 1. Typical graphs of the function $F(\bar{a}, a_0)$ according to equation (7) and (8) at various concentrations d_0. The broken line shows the graph of the maxima of $F(a, a_0; d_0)$. Following parameters have been used: $K_1 = 8.55 \cdot 10^3$ l/mol, $K_2 = 8.40 \cdot 10^4$ l/mol, $\beta = 5.07$, $d_0 = 1 \cdot 10^{-4}$, $6 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$, $1.6 \cdot 10^{-3}$, $2.1 \cdot 10^{-3}$ mol/l

At the extremum $(\bar{a}_0, \bar{a})$ of the function $a = f(a_0)$ we find:

$$\bar{a}_0 = -\frac{(m_7 \bar{a}^2 + m_4 \bar{a} + m_1)\bar{a}}{2(m_5 \bar{a}^2 + m_2 \bar{a} + m_0)} \tag{12}$$

Now we insert eq. (12) into eq. (10). Due to cancellation of terms the coefficients of $\bar{a}^4$ and $\bar{a}^3$ vanish and the final result is obtained as a root of a quadratic equation:

$$\bar{a}_{1,2} = \frac{1}{b_2}(b_1 \pm \sqrt{b_1^2 - b_0 b_2}) \tag{13}$$

wherein

$$b_0 = 4m_0 m_3 - m_1^2 \tag{13a}$$

$$b_1 = m_1 m_4 - 2m_0 m_6 - 2m_2 m_3 \tag{13b}$$

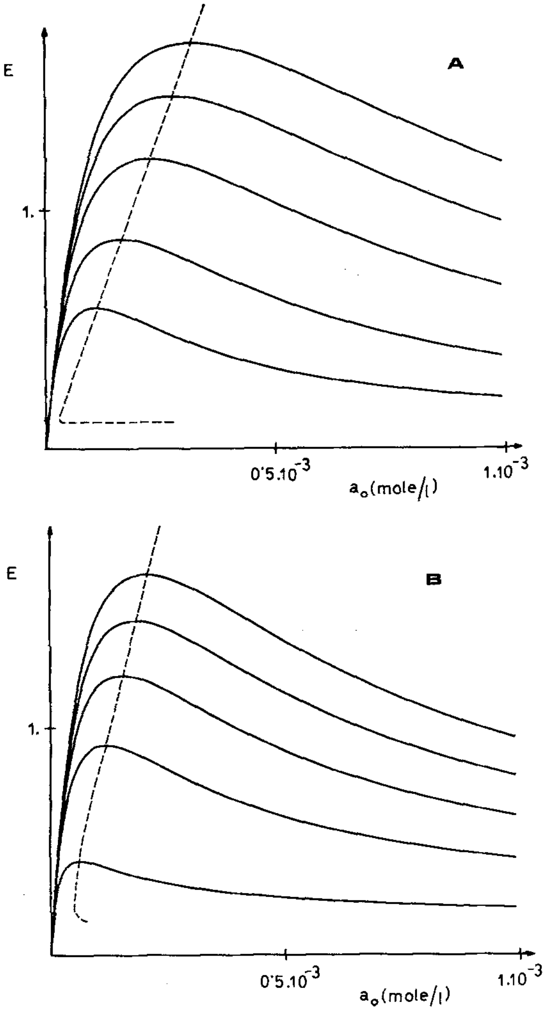

Fig. 2. Typical graphs of the function $F(\bar{a}, a_0)$ according to equation (12) and (13) at various concentrations d_0. The broken lines show the graphs of the maxima of $F(a, a_0; d_0)$. Following parameters have beeen used: *A* $K_1 = 2.60 \cdot 10^5$ l/mol, $K_2 = 0.413$, $\beta = 1.67$, $d_0 = 5 \cdot 10^{-4}$, $1.1 \cdot 10^{-3}$, $2.1 \cdot 10^{-3}$, $3.1 \cdot 10^{-3}$, $4.1 \cdot 10^{-3}$ mol/l; *B* $K_1 = 2.60 \cdot 10^5$ l/mol, $K_2 = 4.20$, $\beta = 1.80$, $d_0 = 1 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, $1.1 \cdot 10^{-3}$, $1.6 \cdot 10^{-3}$, $2.1 \cdot 10^{-3}$ mol/l

and
$$b_2 = 4\,m_0 + 4\,m_2\,m_6 + 4\,m_3\,m_5 - m_4^2 - 2\,m_1\,m_7 \qquad (13\text{c})$$

Again we may use eq. (9) to decide whether the extremum is a maximum or not.

C. Evaluation of Equilibrium Constants

Equations (7) and (8) or (12) and (13) respectively may be used to determine the equilibrium constants K_1 and K_2. The position of the maximum of $F(a, a_0) = 0$ depends characteristicly on the initial concentration d_0. Typical examples of curves $\{\tilde{a}(d_0), \tilde{a}_0(d_0)\}$ are shown in Figs. 1 and 2. These curves as well as the entire system of graphs $F(a, a_0; d_0) = 0$ may be used to fit values of both constants simultaneously. The accuracy obtained thereby is very satisfactory as we shall see in the next section.

Alternatively, one may also keep d_0 constant and vary the coefficient β; this procedure again results in a characteristic curve $\{\tilde{a}(\beta), \tilde{a}_0(\beta)\}$.

Finally, the graphs shown in Figs. 1 or 2 may be used also to determine d_0 and K_2 simultaneously provided the equilibrium constant K_1 is known from an independent measurement. This procedure turned out to be useful for the determination of impurities (see section 4B).

4. Experimental Examples

In order to test the usefulness of the relations derived in the preceding section we studied two types of coupled equilibria by recording curves as shown in Figs. 1 and 2, and determined the equilibrium constants from them.

A. Competitive Nucleophilic Addition

Kinetic and equilibrium studies on the nucleophilic addition of amines to electrophilic carbon-carbon double bonds were reported previously[4]. We may use systems of this type as a proper test case for coupled equilibria of our class (1): $A + B \rightleftharpoons C$, $B + D \rightleftharpoons E$; A and D are two acceptor molecules which compete for a base B. C and E are the corresponding addition-complexes. In Fig. 3 we summarize the structures of all four compounds used in our study. Acetonitrile was applied as solvent.

The curve-fit of the experimental points is shown in Fig. 4 and the numerical values are presented in Table 1. These simultaneously determined values compare favourably with those measured independently for the (uncoupled) single step equilibria $A + B \rightleftharpoons C$ and $B + D \rightleftharpoons E$ respectively.

B. Proton Transfer Equilibria

Coupled equilibria of class (2), $A + B \rightleftharpoons C$, $B + D \rightleftharpoons E + F$ were studied by means of the concrete system summarized in Fig. 5. B and F

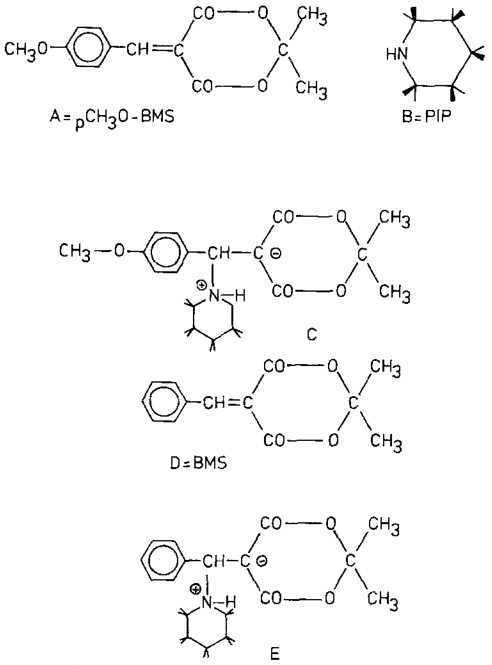

Fig. 3. Compounds used in testing equations (7) and (8) of the system $A + B \rightleftharpoons C$, $B + D \rightleftharpoons E$

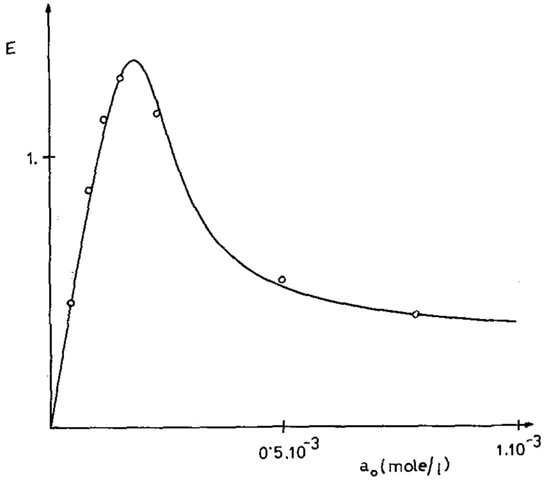

Fig. 4. Experimental points determined for the system shown in Fig. 3 with the curve-fit. The parameters used are the same as in Fig. 1. $d_0 = 1.03 \cdot 10^{-3}$ mol/l

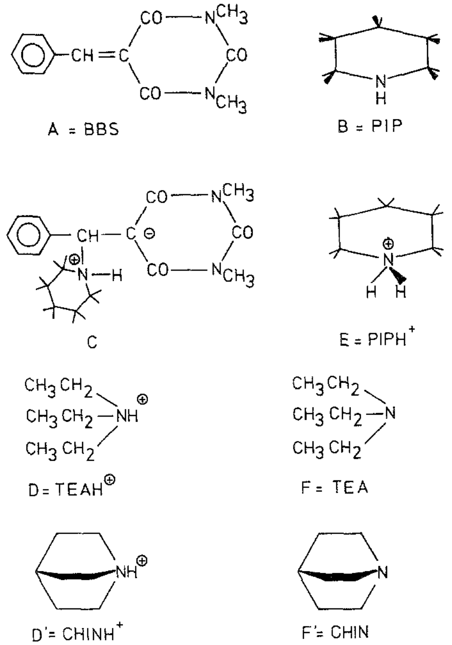

Fig. 5. Compounds used in testing equation (12) and (13) of the system $A + B \rightleftharpoons C$, $B + D \rightleftharpoons E + F$

Table 1. *Typical results of the fitting procedure of equation (7) and (8) to experimental values.* p-CH_3O-*BMS*/*BMS*/*PIP*, solvent: acetonitrile

K_1 (l/mol)	K_2 (l/mol)	d_0 (mol/l)	β
$8.55 \cdot 10^3$	$8.40 \cdot 10^4$	$1.03 \cdot 10^{-3}$	5.08
$8.90 \cdot 10^3$	$7.93 \cdot 10^4$	$1.03 \cdot 10^{-3}$	4.06
$8.46 \cdot 10^3$	$7.45 \cdot 10^4$	$1.03 \cdot 10^{-3}$	5.08
$8.4 \cdot 10^3$*	$7.4 \cdot 10^4$*		

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* Independently determined[4].

represent two amines which compete for the protons in solution. The procedure may be applied quite generally to determine relative proton affinities of amines with only one restriction: F must not react with A ($A + F \rightleftharpoons G$) to an appreciable extent. This condition is fulfilled by tertiary amines in acetonitrile. The equilibrium constants for complex formation of *BBS* with tertiary amines are about four orders of

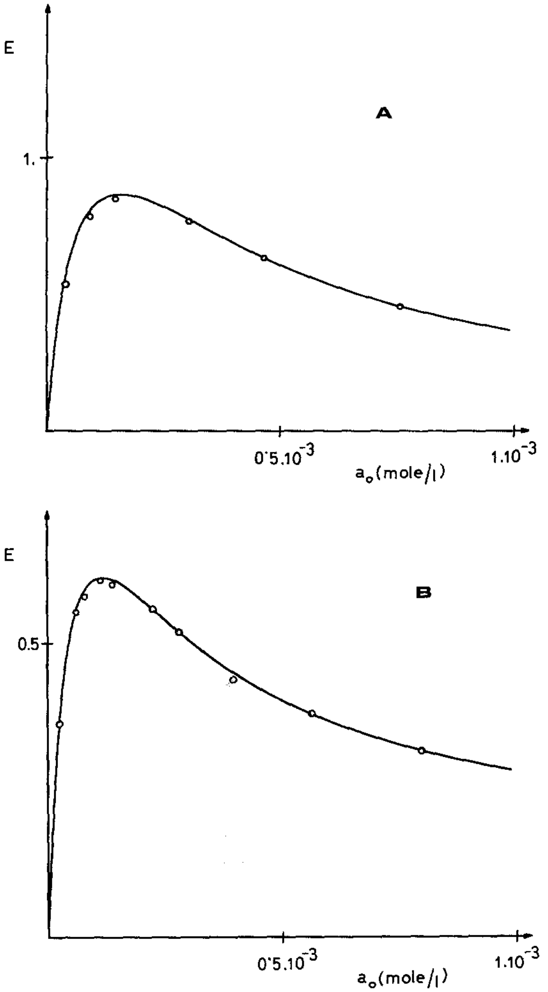

Fig. 6. Experimental points determined for the systems shown in Fig. 5 with the curve-fits. The parameters used are the same as in Fig. 2. A $d_0 = 1 \cdot 10^{-3}$; B $d_0 = 6 \cdot 10^{-3}$ mol/l

magnitude smaller than with piperidine (*PIP*) applied as amine B. The coupled reaction scheme at equilibrium

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}, \quad \mathrm{B} + \mathrm{D} \rightleftharpoons \mathrm{E} + \mathrm{F} \quad \text{and} \quad \mathrm{A} + \mathrm{F} \rightleftharpoons \mathrm{G},$$

wherein G is the addition complex of the tertiary amine and *BBS*, is approximated very well by the first two reaction steps except in the

Table 2. *Typical results of the fitting procedure of equation (12) and (13) to experimental values, solvent: acetonitrile*

A: *BBS/TEAH⁺/PIP*

K_1 (l/mol)	K_2	d_0 (mol/l)	β
$2.6 \cdot 10^5$	0.50	$3 \cdot 10^{-3}$	2.33
$2.6 \cdot 10^5$	0.41	$1 \cdot 10^{-3}$	1.67
$2.6 \cdot 10^5$	0.51	$1 \cdot 10^{-3}$	2.33

B: *BBS/CHINH⁺/PIP*

K_1 (l/mol)	K_2	d_0 (mol/l)	β
$2.6 \cdot 10^5$	5.3	$5 \cdot 10^{-3}$	2.16
$2.6 \cdot 10^5$	4.4	$3 \cdot 10^{-3}$	1.80
$2.6 \cdot 10^5$	4.4	$6 \cdot 10^{-3}$	1.80

range of vanishing concentration of the secondary amine $B = PIP$ (lim $b_0 \to 0$ what means lim $a_0 \to 0$ according to the experimental conditions chosen).

The experimental points were fitted numerically to the corresponding functions $F(a, a_0) = 0$ (Fig. 6). The results obtained are shown in Table 2. The technique reported allows direct measurements of relative acidities of amines in aprotic solvents. In acetonitrile we find the following decrease in basicity: $TEA > PIP > CHIN$.

Competitive equilibria of this kind came to our attention first as a disturbance by impurities during our studies on nucleophilic addition to carbon-carbon double bonds in acetonitrile[4]. The impurity actually resulted from *Hoffmann* type elimination taking place in small but not negligible amount on recrystallisation of quaternary, namely tetraethyl- and tetra-*n*-butyl-, ammonium salts from ethanol. This impurity then led to unexpected effects when the ammonium salts were added to solutions of *BMS* or *BBS* and piperidine in acetonitrile in order to obtain a current conducting medium.

5. Conclusion

Two handy equations were derived from competitive equilibria which facilitate the analysis of non-linear plots of experimental data. The non-linearity of the curves to be discussed offers the advantage that more information is contained in them than would be in straight lines. Therefore, the equilibrium constants can be determined simultaneously and, as the experimental data show, with appreciable accuracy.

The analysis of coupled equilibria in solution seems to provoke renewed interest at present. The refinement of experimental techniques allows to study multiple step reactions by flow and relaxation methods[5, 6], and for these studies a detailed knowledge of the underlying coupled equilibria is indispensable. We hope that the kind of analysis we propose here may serve properly for this purpose.

6. Materials and Recording of Experimental Data

Benzylidene-*Meldrum*'s acid (*BMS*, Fig. 3), *p*-methoxy-benzylidene-*Meldrum*'s acid (*p*-CH_3O-*BMS*) and benzylidene-*N*,*N*'-dimethyl barbituric acid (*BBS*, Fig. 5) were prepared and purified according to procedures described in the literature[7, 8].

Piperidine and triethylamine were freshly distilled from CaH_2 under nitrogen atmosphere. The tertiary ammonium salt was prepared by protonation of the correponding amine with gaseous hydrochloric acid in methanol. Quinuclidinehydrochloride was a commercial product. Both salts were recrystallized from ethanol.

Acetonitrile was a high-purity commercial product (Merck, Uvasol). We used it without further purification.

Solutions of *p*-CH_3O-*BMS*, *BBS* and piperidine as well as *BBS*, piperidine and triethylammonium or quinuclidinium chloride in acetonitrile were prepared and their extinctions at 390 nm and 320 nm respectively were recorded on a Zeiss PMQ II spectrophotometer. The temperature (25 °C) was controlled directly in the sample cell.

The processing of data was performed on the CDC-Cyber 73 computer of the *Interuniversitäres Rechenzentrum*, University of Vienna, using standard curve fitting programs (MINUIT).

Acknowledgements

Financial support by the Austrian *Fonds zur Förderung der wissenschaftlichen Forschung* (project no. 2015 and 2621) and generous supply with computertime by the *Interuniversitäres Rechenzentrum* is gratefully acknowledged.

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