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Analyses of three-way data from equilibrium and kinetic investigations

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Abstract

In kinetic or equilibrium investigations it is common to measure two-way multiwavelength data, e.g. absorption spectra as a function of time or reagent addition. Often it is advantageous to acquire experimental data at various initial conditions or even on different instruments. A collection of these measurements can be arranged in three-dimensional arrays, which can be analysed as a whole under the assumption of a superimposed function, e.g. a kinetic model, and/or common properties of the subsets, such as molar absorptivity. As we show on selected formation equilibria (Zn^{2+}/phen) and kinetic studies (Cu^{2+}/cyclam) from our own research, an appropriate combination of multivariate data can lead to an improved analysis of the investigated systems.

Keywords: Metal complexation; Three-way data; Kinetics; Equilibria

1. Introduction

Increasing the dimensionality of measurements from one-way to two-way and three-way data has several obvious and also not so obvious advantages. There is, at least potentially, more information if additional data are available. It is less clear that radically different ways of analyses are applicable to the differently dimensioned data sets [1].

A typical example of a one-way data set is a monovariate chromatogram, e.g. conductivity or absorption at one wavelength versus retention time. Such data allow the identification of well-resolved peaks based on retention time and quantitative analysis after appropriate calibration. Such data are efficiently arranged as vectors, i.e. one-dimensional arrays. Two-way data can be arranged in matrices or two-dimensional arrays. Analysis methods for two-way data can be much more powerful than those for one-way data, e.g. in HPLC with diode array detection or GC–MS, even severely overlapped peaks of unknown components can be resolved automatically or model-free and identified via their response, i.e. MS or UV-Vis spectrum. Note that this is not generally possible for any two-way data set, bilinearity is the precondition for such analyses [2,3]. Bilinear data sets are fairly common while two-way data which are not bilinear are rather scarce (e.g. 2D NMR spectra). As a convenient definition, the matrices of bilinear data can be written as a product of two usually much smaller matrices, see Eq. (1).

Three-way data can be written as three-dimensional arrays. The equivalent to bilinearity is trilinearity. However, it is not as straightforward to define trilinearity. Instead, an example may illustrate the concept. Consider a set of samples which contains the same

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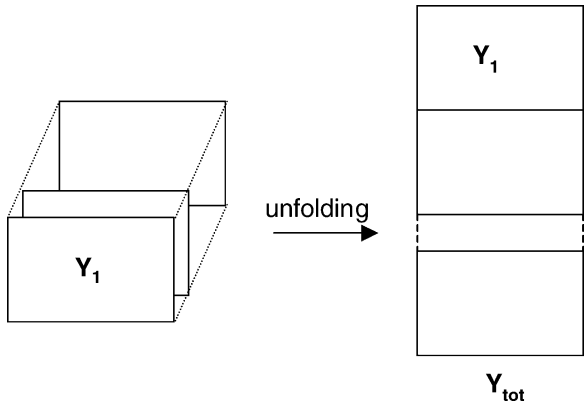
components in different concentrations. Imagine each sample is analysed chromatographically, say by HPLC, using an array detector. Each chromatogram represents a bilinear data set, under ideal conditions the collection of these bilinear data is trilinear. It can be decomposed into three smaller matrices that contain the molar absorptivity spectra and the chromatographic elution profiles for the pure components as well as a matrix with the concentrations of the components in each sample. If, however, chromatographic conditions, such as temperature or solvent, change trilinearity is lost as each chromatogram will have different elution profiles for its components.

Three-way data allow additional more powerful methods of resolution, particularly if they obey prerequisites such as trilinearity. However, such rather restrictive prerequisites rarely apply. Depending on the nature of the data several straightforward model-free data analysis tools are available which exploit the specific advantages of three-way data sets, they include Tucker [4–6], PARAFAC [7–10], GRAM [11] DTD [12] and ALS [13].

In this contribution, we will discuss a particular family of three-way data sets that are formed by collections of bilinear two-way measurements taken at different experimental conditions. These three-way data sets generally are not trilinear and, therefore, the powerful algorithms for the decomposition of trilinear data cannot be applied. Typical examples of such collections are encountered in investigations of solution chemistry such as kinetics and equilibrium studies [14,15]. One two-way measurement consists of a series of spectra acquired as a function of time in the case of kinetics or of reagent addition in equilibrium studies. With reasonably complex systems it is often not possible to find one set of conditions which allows the complete and robust analysis of the whole system under investigation. As an example, consider the determination of the formation kinetics for an ML_2 complex (M is a metal ion, L any ligand interacting with M to form the complexes ML and ML_2). If M is mixed with 2 equivalents of L, the intermediate ML might not be formed to a significant extent and thus its properties are not well defined. Measurements with 1:1 initial concentrations will not reveal much about the formations of ML_2. In order to gain robust information about both steps it is imperative to perform the measurement under different initial conditions. It is advantageous to analyse the set of data globally, as one unit.



Scheme 1.

It is often possible to unfold three-way data into two-way arrays in such a way that traditional two-way analysis methods can be adapted and applied without major difficulties (see Scheme 1). This idea applies to hard-modelling [14,16] as well as soft-modelling [8,13,17] approaches. Such unfolding can be regarded as a matter of convenience or even cosmetics. The important aspect of both soft- and hard-modelling is the definition of the quality of fit as a function of the parameters (hard-modelling) or the decomposition matrices (soft-modelling). The way in which the software is written is not primarily relevant. For the matrix based program MATLAB it is, for example, most convenient to arrange the data in such a way that the matrix operations can be used efficiently.

There is a relatively rich literature on soft-modelling of three-way data. For example, see the review in [1] or the special issue on multiway analysis [18]. Much less is published on hard-modelling of such data sets [14–16,19,20]. For this reason, we will concentrate here on hard-modelling. Nonetheless, it is important to stress that the advantages of three-way data sets apply to both hard- and soft-modelling techniques.

2. Two-way analyses

The two-way analysis of bilinear data consists of the decomposition of the matrix $\boldsymbol{Y}$ of measured data into the product of two smaller matrices. In the case of

a series of absorption spectra, $\boldsymbol{Y}$ is decomposed into the product of $\boldsymbol{C}$, containing concentration profiles, and $\boldsymbol{A}$ of absorption spectra.

$$\boldsymbol{Y} = \boldsymbol{C} \times \boldsymbol{A} + \boldsymbol{R} \quad (1)$$

Due to experimental error the decomposition is never perfect and the difference between the matrix $\boldsymbol{Y}$ of data and its decomposition $\boldsymbol{C} \times \boldsymbol{A}$ is a matrix $\boldsymbol{R}$ of residuals.

Both hard- and soft-modelling methods aim at finding those matrices $\boldsymbol{C}$ and $\boldsymbol{A}$ for which the matrix $\boldsymbol{R}$ of residuals is minimal, or more precisely, for which the Euclidean norm, the sum over all the squares of the elements of $\boldsymbol{R}$, is minimal.

In hard-modelling, the sum of squares, ssq, is defined as a function of a chemical model and its parameters.

$$\text{ssq} = \sum \boldsymbol{R}_{i,j}^2 = f(\boldsymbol{Y}, \text{ model, parameters}) \quad (2)$$

In kinetics, the model is the reaction mechanism and the parameters are the rate constants, in equilibrium studies, the model is the collection of equilibria between the components and the parameters are the equilibrium constants. It has been shown that the molar absorptivities, the elements of the matrix $\boldsymbol{A}$, are linear parameters that can effectively be eliminated during the fitting of the non-linear parameters [21,22]. An important step is the calculation of the molar absorptivities $\boldsymbol{A}$ as a function of the non-linear parameters, which define the matrix $\boldsymbol{C}$ of concentrations. This is a linear and thus explicit calculation.

$$\boldsymbol{A} = \boldsymbol{C}^+ \times \boldsymbol{Y} \quad (3)$$

There are powerful algorithms available for this task and we refer to the literature for detailed descriptions [23]. This computation also forms the core of the ALS algorithm [13]. In the examples presented later, we used the common Newton–Gauss–Marquardt/Levenberg algorithm for the non-linear fitting [22]. In this context, the choice of the algorithm is not crucial, any iterative non-linear least-squares algorithm such as the simplex could be used. Apart from differences in the computation times the results will be identical.

The result of the fitting procedure is a set of non-linear parameters, which define the matrix $\boldsymbol{C}$, and additionally the matrix $\boldsymbol{A}$ of molar absorptivity spectra for all absorbing species. Often the most difficult aspect of the above procedure is to define the correct chemical model. The fitting of the parameters is usually comparatively fast and reliable. The process of determining the correct model, e.g. the correct mechanism, can be supported by prior model-free analyses of the data. The resulting matrix $\boldsymbol{C}$ can often be interpreted in terms of a chemical mechanism and the spectra in $\boldsymbol{A}$ indicate the structure of the species.

In soft-modelling, decomposition according to Eq. (1) is attempted without relying on a chemical model. Only straightforward physical restrictions such as non-negativity of concentrations $\boldsymbol{C}$ and molar absorptivities $\boldsymbol{A}$ are applied. Often the decomposition is not unique [24] and additional constraints such as unimodality, etc. can be applied in order to reduce the range of possible solutions [25]. There are several model-free analysis methods, most prominent are: ALS [13], EFA [26], RFA [27] amongst many others [28].

It is important to be aware of the limitations and potential difficulties of both hard- and soft-modelling approaches. Clear understanding only will allow the development of improved methods. The main difficulties encountered with both of the above analysis methods include: (a) linear dependence or near linear dependence of concentration profiles (columns of $\boldsymbol{C}$) [29]; this prohibits the calculation of the matrix $\boldsymbol{A}$ and thus $\boldsymbol{R}$, and the sum of squares (ssq). (b) Minor species, or species, which only reach relatively low concentrations during the complete reaction. Their contributions, spectra and corresponding constants are only poorly defined [15]. (c) There are special cases like a reaction scheme of two consecutive reactions $\text{X} \rightarrow \text{Y} \rightarrow \text{Z}$, where the sequence of the two first-order rate constants is not defined [30]. In soft-modelling analyses, we have to deal with the additional problem of rotational ambiguity [31] due to non-unique solutions.

Often it is possible to repeat the measurement under different experimental conditions in such a way that any of the above difficulties are avoided. Referring to the earlier example of the formation of ML and ML_2, the concentration [ML] might not reach substantial concentration under conditions of excess of L, while [ML_2] will not form substantially if a 1:1 mixture is analysed. Global analysis of both sets together will result in a robust result as all species are well defined in some part of the total measurement.

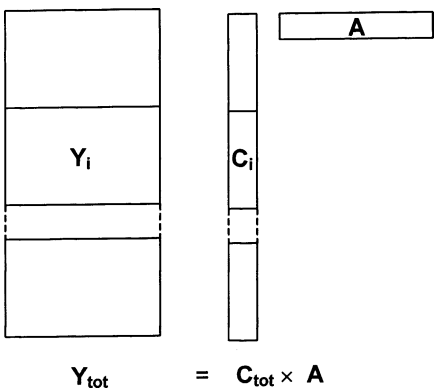
3. Two-way analyses of three-way data sets

In order to allow the application of two-way software, the three-way data sets have to be unfolded in any of the three dimensions. Unfolding means rearranging the data in such a way that the individual slices of two-way arrays are combined into a large two-way array [14,15]. For the analyses proposed here the individual matrices $\boldsymbol{Y}_i$ (see Scheme 1) are concatenated into a long matrix $\boldsymbol{Y}_{\text{tot}}$. Each submatrix $\boldsymbol{Y}_i$ is the product of its corresponding concentration matrix $\boldsymbol{C}_i$ and the matrix $\boldsymbol{A}$ of molar absorptivities, which usually is identical for all measurements; this is, however, not a critical prerequisite [14] as can also be seen in the kinetic example presented later.

The structure of the equation represented in Scheme 2 is essentially the same as in Eq. (1). The crucial difference between them is that it is possible to perform the individual experiments $\boldsymbol{Y}_i$ under conditions which ensure that $\boldsymbol{Y}_{\text{tot}}$ and $\boldsymbol{C}_{\text{tot}}$ have full rank. Thus, the calculation of the pseudo-inverse $\boldsymbol{C}_{\text{tot}}^{+}$ is not hampered by linear dependences between its columns, as it would be for only one bilinear subset $\boldsymbol{C}_i$ in Eq. (3). This alleviates most of the problems mentioned above. It often also narrows down the range of solutions in non-unique model-free analyses [31].

It is the task of good experimental design to choose the conditions under which the individual measurements $\boldsymbol{Y}_i$ are acquired. In fact one could use the condition number of the matrix $\boldsymbol{C}_{\text{tot}}$ as a measure for the quality of the experimental design.

In the following, we will present two examples of investigations undertaken as part of our research on coordination compounds. They illustrate different aspects of difficulties encountered with traditional two-way data and how improved experimental design and appropriate analyses can improve the quality of the outcome. The first example is an equilibrium, the second a kinetic investigation.



Scheme 2.

3.1. Zn^{2+}/phenanthroline equilibrium investigation

The effects of combining measurements taken under different conditions are demonstrated by the example of an equilibrium study on the complexation of Zn^{2+} with 1,10-phenanthroline (phen) in aqueous solution.

Zn^{2+} compounds feature no d–d transitions and thus do usually not absorb in a useful range of the UV-Vis spectrum unless the ligand(s) themselves absorb in this range. This is the case with phenanthroline, which features a rich spectrum in the wavelength region from 270 to 340 nm. The absorption spectrum of phenanthroline is influenced by protonation of the nitrogen sites as well as by coordination with metal ions.

There are several protonation and complexation equilibria. They are fully described by Scheme 3. Note that there is no measurable metal hydrolysis occurring in the pH range of the measurements (pH < 6.5). This is the case for the free metal as well as the partially complexed metal for which the hydrolysis is weaker.

Phenanthroline and $Zn(NO_3)_2$ were from commercial sources. Titrations were performed directly in 1 cm absorption cells. A Hitachi 220A spectrophotometer, a Metrom 665 Dosimat and the pH electrode were under full computer control [32]. Different ratios of M:L (metal:ligand) were investigated. In all titrations, the initial concentration of phen was [phen] $= 3 \times 10^{-5}$ M, while the concentrations of Zn^{2+} were [Zn^{2+}]: 0 M in the 0:1 titration, 3×10^{-5} M in the 1:1 titration, 1.5×10^{-5} M in the 1:2 titration, 1×10^{-5} M in the 1:3 titration and 0.75×10^{-5} M in the 1:4 titration. Acidified (HCl) solutions were titrated with 0.1 M NaOH to cover a pH range of approximately 2–6.5. Spectra were measured between 272 and 340 nm at 4 nm intervals. The ionic strength was adjusted to 0.1 M with KCl, the temperature was maintained at 25 °C.

The most obvious experiment is the titration of 1:3 mixture of Zn^{2+} and phenanthroline, as under such conditions ML, ML_2, and ML_3 are expected to form. However, analysis of such a measurement fails

$$Zn^{2+} + phen \xrightleftharpoons{K_{110}} Zn(phen)^{2+}$$
$$Zn(phen)^{2+} + phen \xrightleftharpoons{K_{120}} Zn(phen)_2^{2+}$$
$$Zn(phen)_2^{2+} + phen \xrightleftharpoons{K_{130}} Zn(phen)_3^{2+}$$

$$phen + H^+ \xrightleftharpoons{K_{011}} phenH^+$$
$$(phenH^+ + H^+ \xrightleftharpoons{K_{012}} phenH_2^{2+})$$ only at very low pH, not encountered in our measurements

Scheme 3.

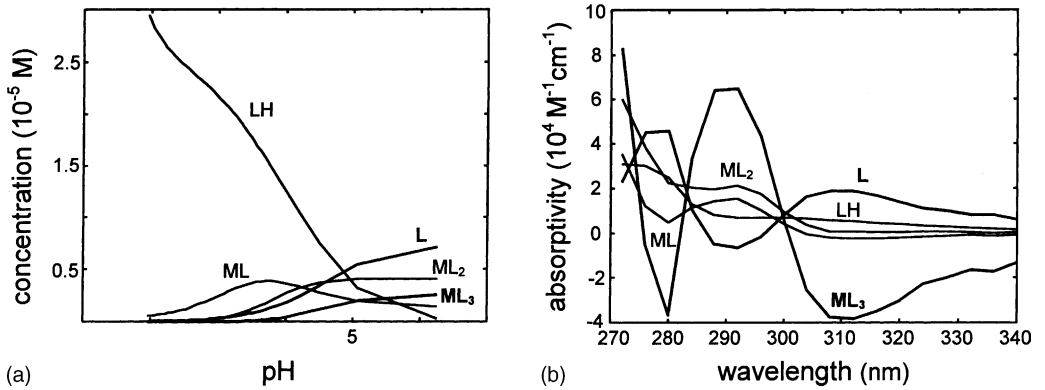
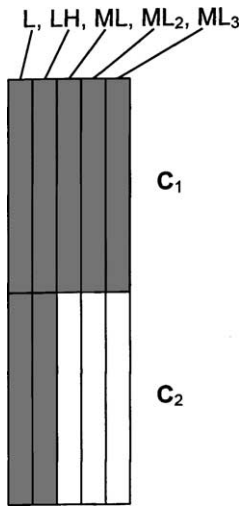


Fig. 1. Result of the hard-modelling fit of a 1:3 mixture of Zn^{2+} and phenanthroline. (a) The concentration profiles for L and ML_3 are almost linearly dependent and, therefore, their spectra in (b) are not well defined.

because some of the concentration profiles of the absorbing species are almost linearly dependent.

Fig. 1 displays the result of the hard-modelling fit. Due to linear dependence, predominantly between the concentration profiles of L and ML_3, which are almost multiples of each other, the computation of $\boldsymbol{C}^+$ is ill-conditioned and this results in obviously wrong molar absorption spectra for those two species. We have chosen not to apply the non-negativity constraint to the calculated spectra $\boldsymbol{A}$ in Eq. (3). This leads to the obviously wrong result as shown in Fig. 1. Application of a non-negative least-squares algorithm to calculate $\boldsymbol{A}$ would result in physically possible spectra, but it does not avoid the problem of linear dependence in $\boldsymbol{C}$.

In line with the proposed globalisation of the analysis of a series of measurements, it is possible to analyse the combined matrices, e.g. those for the titrations of L only and the 1:3 mixture of M and L. The combined concentration matrix $\boldsymbol{C}_{tot}$ for this case can be represented by Scheme 4.



Scheme 4.

Table 1
Basicity and stability constants $\log K_{MLH}$ for phenanthroline and its complexation with zinc(II) at 25.0 (1) °C

	This work	[33]
$\log K_{011}$([HL]/[H] × [L])	4.84 (2)	4.93 (8)
$\log K_{110}$([ML]/[M] × [L]	6.58 (2)	6.4 (2)
$\log K_{120}$([ML_2]/[M] × $[L]^2$)	11.91 (12)	12.2 (4)
$\log K_{130}$([ML_3]/[M] × $[L]^3$)	17.12 (36)	17.1 (4)

The uncertainties are given in brackets and represent two standard deviations of the last significant digit(s).

The linear dependence between the columns of $\boldsymbol{C}_1$ are removed by the concatenation with matrix $\boldsymbol{C}_2$. Only the shaded parts of $\boldsymbol{C}_{tot}$ have positive entries, the white part only contains zeros. The complete matrix has full rank and the spectra of all absorbing species are well defined.

In order to improve the definition of all equilibrium constants and all spectra and thus the robustness of the analysis, we globally analysed a complete series of measurements of compositions 0:1 (L only), 1:1, 1:2, and 1:4. The results are compiled in Table 1.

Potentiometric titrations are the standard method for the quantitative determination of complexation equilibria. Spectrophotometric titrations deliver, in addition to the equilibrium constants, also absorption spectra of all species and this provides a certain level of structural information which is completely absent in potentiometric investigations. Fig. 2 displays the calculated absorption spectra.

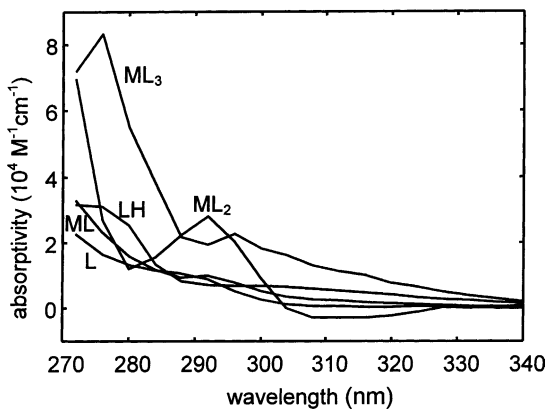


Fig. 2. Calculated molar absorption spectra resulting from the global analysis of the 0:1, 1:1,1:2 and 1:4 mixtures of Zn^{2+} and phenanthroline.

All spectra are well defined. The most interesting one is the spectrum of ML_2 with a characteristic maximum around 290 nm. This unique feature is a strong indication for a different structure of this complex, it could be either a square planar or a tetrahedral arrangement of the two phenanthroline ligands. The square planar geometry allows a strong-interaction between the two ligands via the central Zn^{2+}-ion, the tetrahedral geometry is very different from the octahedral arrangement of the ligands in the other complexes.

3.2. Cu^{2+}/cyclam formation kinetics

Our second example involves a kinetic investigation. We have applied the idea to the determination of the kinetics of the interaction between cyclam (1,4,8,11-tetraazacyclotetradecane) and Cu^{2+} in aqueous solution. The rate of this reaction is very strongly pH dependent as the relative concentrations of the differently protonated forms of the ligand, LH_x^{x+}, vary dramatically with pH. The rate constants k_{LH_x} cover several orders of magnitude with ligand protonation equilibria coupled to the kinetics, see Scheme 5 and Table 2.

In this example, it is impossible to cover the complete range of measurement times on one instrument. At relatively high pH, measurements are required on a time scale of seconds, whereas at low pH reaction times are up to 8 h. Therefore, in order to investigate the complete range of measurements we had to use stopped-flow instrumentation at high pH and conventional spectrophotometers at low pH (stopped-flow instruments do not have a long-term stability comparable to a double-beam spectrophotometer).

$$Cu^{2+} + LH_x^{x+} \xrightarrow{k_{LH_x}} CuL^{2+} + xH^+$$

$$L + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} LH^+$$

$$LH^+ + H^+ \overset{K_2}{\rightleftharpoons} LH_2^{2+}$$

$$LH_2^{2+} + H^+ \overset{K_3}{\rightleftharpoons} LH_3^{3+}$$

$$LH_3^{3+} + H^+ \overset{K_3}{\rightleftharpoons} LH_4^{4+}$$

Scheme 5.

Table 2
Basicity constants for cyclam and rate constants for its complexation with copper(II) at 25.0 (1) °C

	This work[a]	Other work
$\log K_3$	1.56 (1)	1.61 (2)[b]
$\log K_4$	2.34 (1)	2.42 (2)[b]
k_{LH} [10^6 (s M)$^{-1}$]	1.05 (5)	1.8 (4)[c], 8.0 (10)[d]
k_{LH_2} [(s M)$^{-1}$]	0.135 (5)	0.39 (6)[c], 0.076 (10)[d]

The uncertainties are given in brackets and represent two standard deviations of the last significant digit(s).

[a] $\log K_1$ and $\log K_2$ could not be determined at the investigated pH < 7 and have been fixed for the analysis to 11.59 and 10.62 according to [35,36]. The rate constants k_{LH_x} with x=0 and $x > 2$ cannot be observed.

[b] [35,36].

[c] [37].

[d] [38], $I = 0.2(NaClO_4)$.

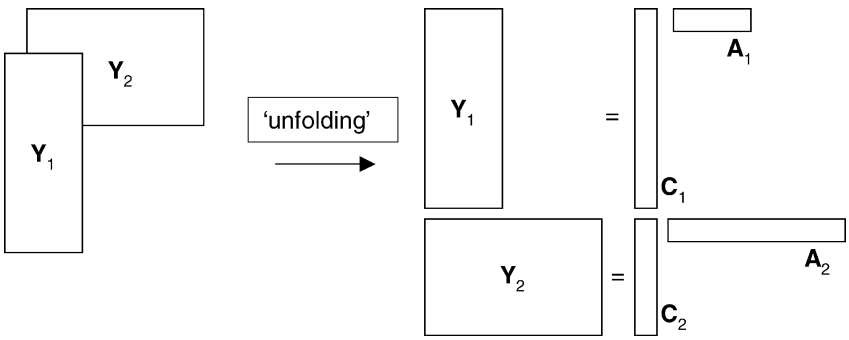
Copper(II) perchlorate hexahydrate and 1,4,8,11-tetraazacyclotetradecane (cyclam) were from commercial sources. The copper salt was dried in a desiccator under vacuum and solutions were standardised prior to use. The ionic strength of all solutions was adjusted to 0.5 M with $NaClO_4$. All reactions were thermostatted at 25 °C.

The complex formation kinetics of copper(II) (7.87×10^{-3} M) with cyclam were followed under second-order conditions (10% excess of ligand). Four measurements were performed under different total proton concentrations $[H^+]_{tot} = 1.73 \times 10^{-3}$ M (measurements 1 and 2); $[H^+]_{tot} = 1.92 \times 10^{-2}$ M (measurement 3); $[H^+]_{tot} = 1.31 \times 10^{-1}$ M (measurement 4) on an Applied Photophysics stopped-flow spectrophotometer DX-17 MV (measurements 1 and 3) and with a Hitachi 220-A UV-Vis spectrophotometer after manual mixing (measurements 2 and 4). Stopped-flow measurements were done using the "point by point" method, where kinetic traces were acquired individually at the wavelengths 470 ≤ λ ≤ 605 nm (15 nm intervals) for 1000 s at 1000 logarithmically spaced times. The manual measurements were followed over the wavelength range of 400 ≤ λ ≤ 800 nm (10 nm intervals) for 8 h at up to 100 evenly spaced times. The stopped-flow measurements cover the initial period of the overall reaction; the manual measurements cover the much slower parts of the reaction.

It has proven advantageous to globally analyse measurements acquired on both instruments [34]. The individual matrices of measurements have different dimensions as they cover different time and wavelength ranges. Thus, we need to generalise the concept of three-way data sets in order to encompass such collections. This is represented in Scheme 6 for a collection of two measurements with different numbers of rows (times) and columns (wavelengths).

Here, the chemical model combines two measurements; in our example we combined four of them. Fig. 3 displays the calculated concentration profiles, $\boldsymbol{C}_1$ and $\boldsymbol{C}_2$, of the absorbing species for the stopped-flow and the manually mixed measurement at $[H^+]_{tot} = 1.73 \times 10^{-3}$ M. In Fig. 3(a), the pH drops from approximately 6 to 3.5 and, in Fig. 3(b), from 3.5 to 2.

In this instance, due to the different spectral ranges measured, there are two matrices $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ of molar absorptivity spectra. Fig. 4 shows that they are virtually identical in the range covered by both measurements. Here, the problem solved by global analysis is not linear dependence as the only absorbing species



Scheme 6.

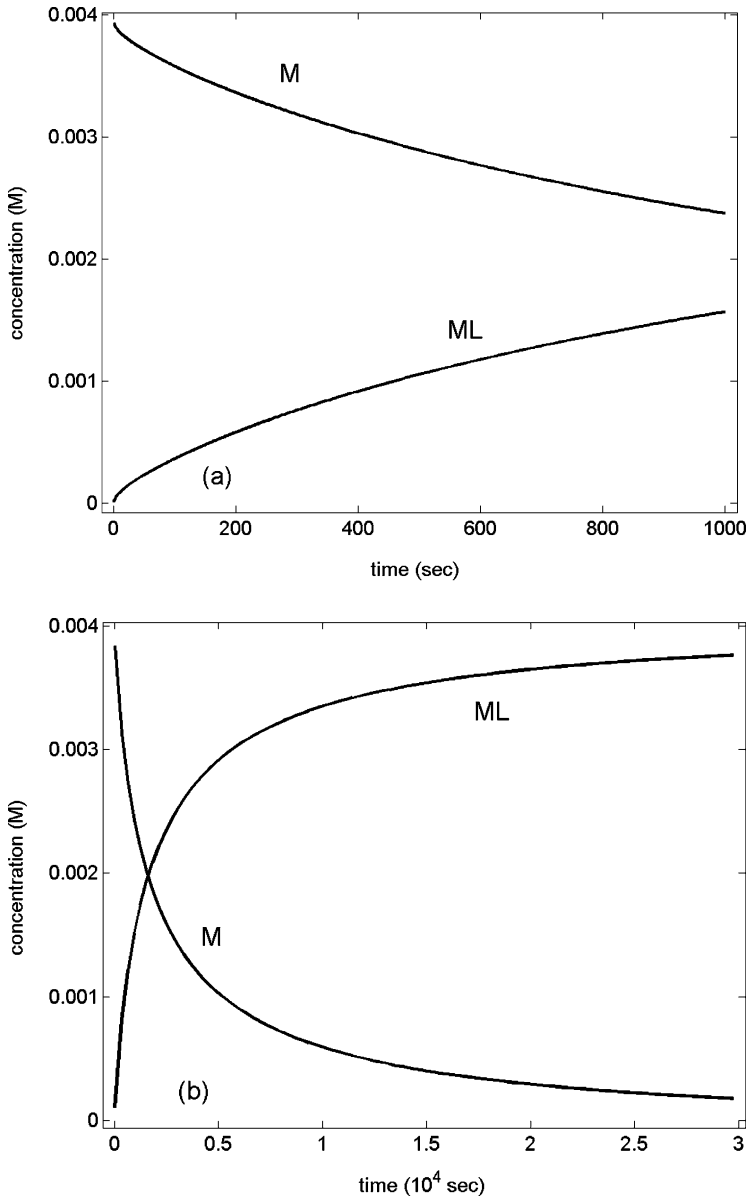


Fig. 3. Concentration profiles for Cu^{2+} (M) and $Cu(cyclam)^{2+}$ (ML) for: (a) the fast stopped-flow and (b) the slow manually mixed kinetic measurement at $[H^+]_{tot} = 1.73 \times 10^{-3}$ M, covering different pH ranges.

are Cu^{2+} and $Cu(cyclam)^{2+}$. The difficulty lies in the very wide range of reaction rates which prevents the acquisition of one particular measurement that covers the whole reaction.

Note that the pH is changing during the reaction as protons are released upon coordination of partially protonated ligand. Thus, the reaction is self-decelerating and this is the reason for the very wide range of rates, which in turn requires measurements at different instruments. The required software as well as details for the analysis of such data have been described elsewhere [34].

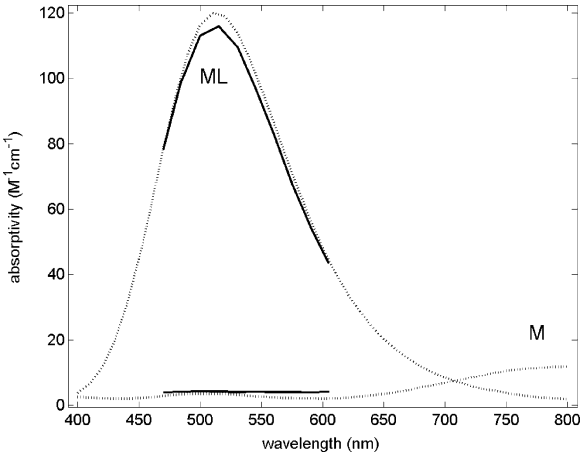


Fig. 4. Molar absorptivity spectra for Cu^{2+} (M) and $Cu(cyclam)^{2+}$ (ML) for: (—) the fast stopped-flow and (- -) the slow manually mixed kinetic measurement at $[H^+]_{tot} = 1.73 \times 10^{-3}$ M.

4. Conclusion

In the context presented here we define collections of two-way data sets, acquired under different conditions, such as initial concentrations, as three-way data sets. We have generalised the definition of three-way data to accommodate collections of two-way sets of different dimension.

We have demonstrated that the global, model based fitting of a complete three-way data set can result in an improvement of the analysis and the quality of the fitted parameters. This is because no individual two-way measurement defines all the required parameters of the model sufficiently. In the titration example, linear dependences of the concentration profiles were successfully eliminated; in the kinetic example, the analysis was only made possible by combining several two-way measurements. The measurements at low pH do not contain information about species that exist at high pH. It is often impossible to completely separate the different processes, i.e. there are minor effects which only disturb the data without being visible enough for proper definition. Global analysis combines all information gathered in the individual measurements; each parameter is defined in at least one of them.

It is convenient to unfold the three-way data sets into arrays of two-way data sets. This allows the relatively straightforward adaptation of existing fitting software.

The advantages of the globalisation are well documented for self-modelling analyses with ALS. Analysis of data sets with structures similar to the one represented in Schemes 2 and 6 clearly show that globalised soft-modelling analyses are more robust and results in narrower ranges of possible solutions [13,39,40].

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