



Application the computational method KINMODEL(AGDC) to the simultaneous determination of kinetic and analytical parameters



M.M. Canedo Alonso^{*}, J.L. González-Hernández, S. Encinar del Dedo

Department of Physical Chemistry, Faculty of Chemistry, University of Salamanca, Pza. de los Caídos s/n, E-37008 Salamanca, Spain

ARTICLE INFO

Keywords:

Unconstrained optimization
Computational program
Computational chemical kinetics
Kinetic modeling
Resolution of mixtures

ABSTRACT

In a preliminary work we developed a computational method of kinetic treatment (KINMODEL(AGDC)) and studied the possibilities of its application for the determination of kinetic and non-kinetic parameters. In this new work, we studied the kinetic and/or analytical applicability of the KINMODEL(AGDC) program in a broad series of reactions of different complexities: (a) Simple reactions (reversible and irreversible), (b) Consecutive (reversible and irreversible), (c) Concurrent, (d) Competitive, (e) Cyclic. KINMODEL(AGDC) is a computational method that uses the AGDC mathematical optimization algorithm to determine different types of parameters. It is valid for the treatment of any reaction mechanism and allows the determination of different parameters from absorbance data. In all the reactions system included in the a, b, c, d and e groups, the KINMODEL(AGDC) methodology was applied for the determination of the initial concentrations of the species involved in the reaction mechanism, individually or jointly, with the kinetic constants of the elementary reactions comprising the mechanism. We analyze the influence of an extensive series of factors affecting the optimization process: the nature and number of the parameters to be optimized, the initial estimations of the parameters, the reaction mechanism and the relative values of the different rate constants of the mechanism considered. Since parameters of different natures and orders of magnitude are determined, we analyze the possibility of the existence of ambiguity in the solutions since it is common to find several (two or more) groups of parameters that fit the experimental kinetic data.

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1. Introduction

In a preliminary work [1] we developed a computational method (KINMODEL(AGDC)) for the treatment of kinetic data, this program was used for the determination of kinetic and non-kinetic parameters, rate constants and molar absorption coefficients. In the present work we studied the kinetic and/or analytical applicability of the computational program and we determined different kinetic and analytical parameters by means of the treatment of kinetic absorbance data. The computational treatment of kinetic data in order to determine kinetic and/or analytical parameters and reaction mechanisms is of great importance in different fields of chemistry. The literature contains many references to works in which different computational treatments have been used to study reaction mechanisms, with both kinetic aims, for the determination of rate constants and the discrimination of reaction mechanisms, and for analytical purposes for the resolution of homogeneous

^{*} Corresponding author.

E-mail addresses: mcanedo@usal.es (M.M. Canedo Alonso), jlgh93@usal.es (J.L. González-Hernández), sonsoles_e@usal.es (S. Encinar del Dedo).
URL: <http://web.usal.es/jlgh93> (M.M. Canedo Alonso).

mixtures [2]. In all the various works, the authors use different mathematical algorithms and a broad set of software options has been developed for these algorithms to be implemented. Here we shall consider some of the most important ones and those most closely related to the present investigation.

Traditional methods of curve-fitting [3–10] allow the determination of kinetic, analytical and thermodynamic parameters through application of different mathematical algorithms implemented in computational programs by means of the treatment of spectrophotometric data. Other relevant methods of data treatment used for the determination of kinetic and/or analytical parameters, are the Classic Curve Resolution techniques and their modifications: Classical Curve Resolution-Hard modeling (CCR-HM) [11,12], Classical Curve Resolution-Soft modeling (CCR-SM) [13] or a combination of both, Classical Curve Resolution-Combining Hard-Soft modeling (CCR-CHSM) [14,15]. Other techniques used the so-called Kalman filter algorithm, in its extended version [16–18], which evaluates spectrophotometric data, allowing the prediction of concentrations and rate constants, and there are also methodologies based on Artificial Neural Networks (ANN) techniques [19–25]. In general, the methodologies for kinetic treatment can be found in different text books [26–28], which gather and describe both classic and current methods for data treatment and the determination of different parameters.

The KINMODEL(AGDC) computational method [1] allows the determination of different kinetic, non-kinetic and analytical parameters from kinetic absorbance data through application of the ADGC mathematical optimization algorithm [29–36]. This algorithm has been used in many computational methods for the treatment of different chemical systems and it turn has been used for the treatment of different types of kinetic data (potentiometric, spectrophotometric, ...) for kinetic, analytical and thermodynamic purposes. Taking into account the results obtained with these methodologies, we have adapted the AGDC algorithm, developing a new version that allows the treatment of kinetic data of absorbance at one or several different wavelengths. The AGDC algorithm can be adapted easily for the processing of kinetic experimental data acquired with other techniques, introducing in the expression that allows to obtain the value of the sum of quadratic deviations (SSQ) the corresponding relation between the monitored variable and the concentration. The new version of the algorithm was implemented in the generalized KINMODEL(AGDC) kinetic computational program [1]. The program was used for the treatment of different system of reaction, determining the rate constants of the elementary stages comprising the mechanism and the molar absorption coefficients of the species involved and it was also applied for discrimination among reaction mechanisms. Currently, there are two versions of the program: one version in FORTRAN 90 for use in a DOS environment and another in C++, using JAVA applications, which allows it to be used in a WINDOWS environment. Both versions are based on a generalized numerical method that allows the treatment of any reaction mechanism and the determination of different parameters with different orders of magnitude.

The KINMODEL(AGDC) model is a numerical method for kinetic treatment that allows the determination of a series of kinetic, non-kinetic and analytical parameters: (1) the kinetic constants (k_r) of the “r” elementary reactions comprising the reactions system, (2) the molar coefficients of the “j” species at different working wavelengths ($\epsilon_{j,\lambda}$), (3) the kinetic constants (k_r) and molar absorption coefficients ($\epsilon_{j,\lambda}$) simultaneously, (4) the initial concentrations of the “j” species $[B_j]_0$ involved, (5) the kinetic constants (k_r) and initial concentrations ($[B_j]_0$) jointly and simultaneously via a single optimization process. In that preliminary work [1], we discussed the application of the KINMODEL(AGDC) program for the determination of the parameters indicated in points 1, 2 and 3; i.e., kinetic constants and molar absorption coefficients. Here we analyze the possibility of using the methodology for the determination of the parameters reflected in points 4 and 5; i.e., the initial concentrations of the species involved (point 4) and the initial concentrations and kinetic constants simultaneously (point 5). For these optimization processes (points 4 and 5) we studied the effect of a series of factors that affect the optimization process, such as the nature and number of parameters to be optimized, the value of the initial estimates of the parameters, the reaction mechanism and the relative values of the various rate constants of the mechanism considered. In the optimization process mentioned in point 5, we performed a joint determination of parameters of different types (initial concentrations and rate constants), such that we analyzed the possibility of the existence of several groups of parameters that fit the kinetic experimental data.

2. Theoretical and computational aspects

2.1. Theoretical aspects

The computational methodology KINMODEL(AGDC) [1] carries out the determination of the parameters whose values one wishes to know by means of the AGDC mathematical optimization algorithm [29–36], it is a second-order gradient method that minimizes the numerical function (SSQ) given by:

$$SSQ = \sum_{i=1}^{N_d} \sum_{\lambda=1}^{N_w} ((A_{i,\lambda})_C - (A_{i,\lambda})_E)^2, \quad (1)$$

where: N_d = Number of experimental data pairs; N_w = Number of working wavelengths; N_c = Number of chemical species; $(A_{i,\lambda})_E$ = Total absorbance value obtained at a wavelength λ ; $\epsilon_{j,\lambda}$ = Molar absorption coefficient of the species j at a wavelength λ ; $[B_j]_i$ = Molar concentration of the species j at time i ; $(A_{i,\lambda})_C$ = Total absorbance value calculated.

According to the Beer–Lambert law the total absorbance, $A_{i,\lambda}$, of a mixture formed by N_c chemical species ($l = 1$ cm), will be:

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