

# Supporting Information

## Chemometric analysis of voltammetric data on metal ion binding by selenocystine

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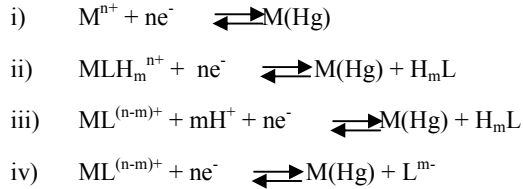
S1. Theory

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S3. Data Treatment

## S1. Theory

Consider a metal ion  $M^{n+}$  that is reversibly reduced at a mercury electrode to the amalgam  $M(Hg)$  and also reacts with a ligand  $H_mL$  to form the electrochemically inert and electroactive complex  $ML^{(n-m)+}$  in solution. Electrochemically inert means that the association-dissociation kinetics of the complex is so slow that it practically does not dissociate during the time scale of the electrochemical measurement. If the protonation equilibria of the ligand are involved in the electrochemical reaction, the reduction of  $M^{n+}$ -ions takes place according to different simultaneous processes:



Usually, reaction i) takes place at potentials quite less negative than those of processes ii)-iv), thus producing a separate signal for the reduction of the free metal ion, which, for the totally inert case, remains at constant potential. In contrast, processes ii) - iv) are simultaneous and compete with each other to produce a signal which moves along the potential axis, depending on the predominance of one or the other. It must be noted that reaction ii) will only occur when the complex is protonated without dissociation (*e.g.* if some electron pairs of the ligand remain available for coordination after metal ion binding). A very simple but still useful approach consists of writing the Nernst expression of half-reaction iii):

$$E = E^{0'} + \frac{0.058}{n} \log \frac{[H_mL]}{[ML^{(n-m)+}][H^+]^m} \quad (1)$$

where  $E^{0'}$  is the formal potential and 0.058 is given at 20°C. If we rearrange this equation, we find:

$$E = E^{0'} - 0.058 \frac{m}{n} \text{pH} + \frac{0.058}{n} \log \frac{[H_mL]}{[ML^{(n-m)+}]} \quad (2)$$

which suggests that the evolution of the peak potential of the signal ( $E_p$ ) as a function of pH should follow a linear relationship of the type:

$$E_p = k - 0.058 \frac{m}{n} \text{pH} \quad (3)$$

with  $k$  being a constant related to  $E^{0'}$ . This means that the slope of an  $E_p$  vs. pH linear plot leads to the obtaining of the ratio between the protons and electrons exchanged in the electrochemical reduction of the complex, which is useful in the formulation of complexation models.

Unfortunately, experimental systems do not behave in such a simple way. Firstly, Equations (1)-(3) depict a situation of electrochemical equilibrium, i.e. a reversible system, and the reduction of inert complexes is typically non-reversible.

Indeed, Koryta proposed for NTA a kinetic model with a pH-dependent dissociation constant of the complex ( $k_d$ ) according to the expression:

$$k_d = k^0 + k^1 [H^+] \quad (4)$$

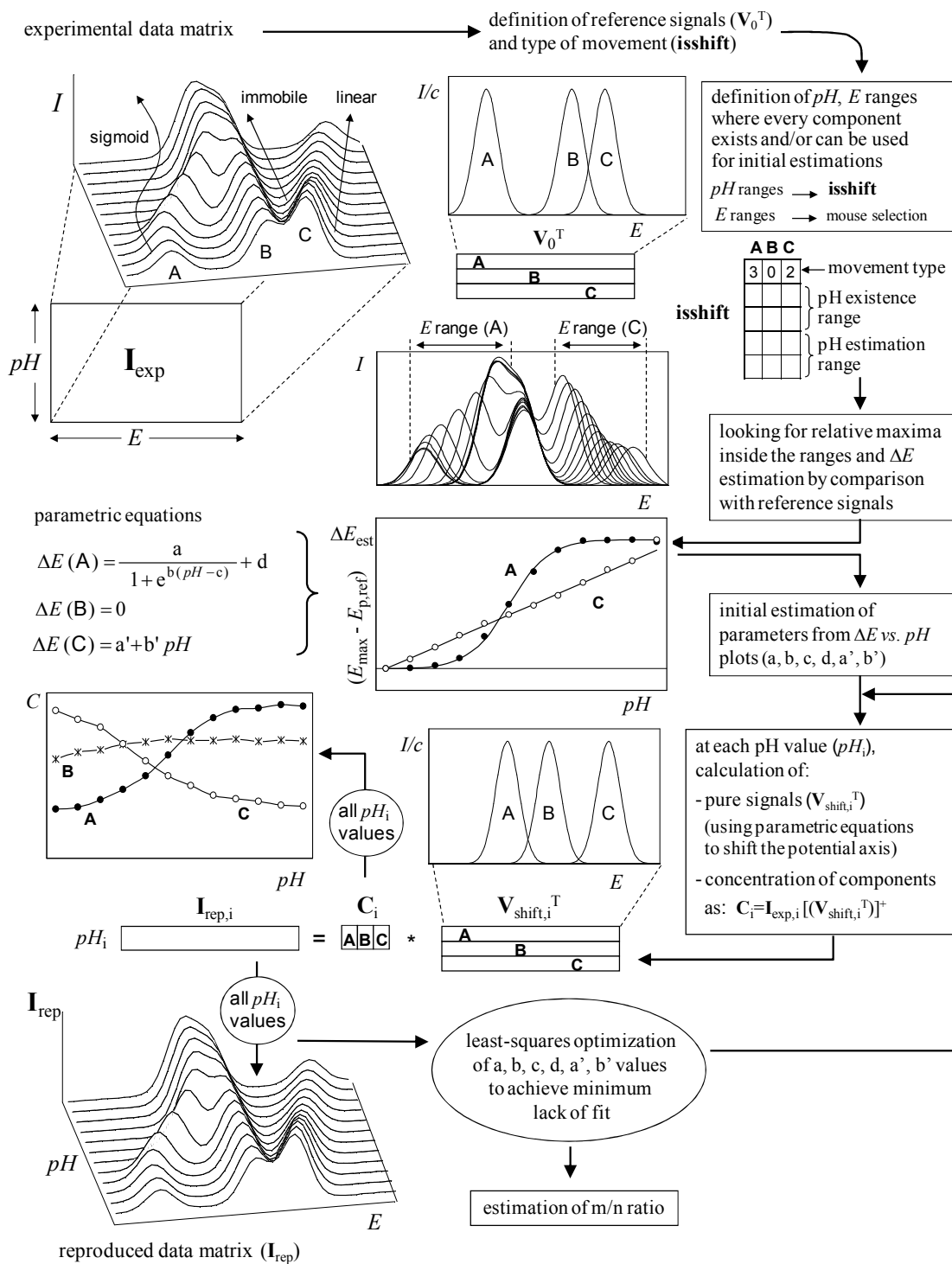
where  $k^0$  and  $k^1$  are rate constants. Secondly, the situation seems quite dependent on the distribution of the differently protonated species of the free ligand. For instance, process iii) becomes negligible at too high pH values (the concentration of  $H^+$  is too small to protonate either the ligand or the complex) or too acidic pH values (the ligand is already protonated in the complexed form or complexation is negligible), whereas processes ii) or iv) are unaffected by pH variation, provided that complexation still takes place and the free metal is not hydrolyzed. These considerations are confirmed by the sigmoid evolution of many experimental  $\Delta E$  vs. pH plots. To model this behavior, we chose a parametric sigmoid equation in the form:

$$\Delta E = \frac{a}{1 + e^{b(pH - c)}} + d \quad (5)$$

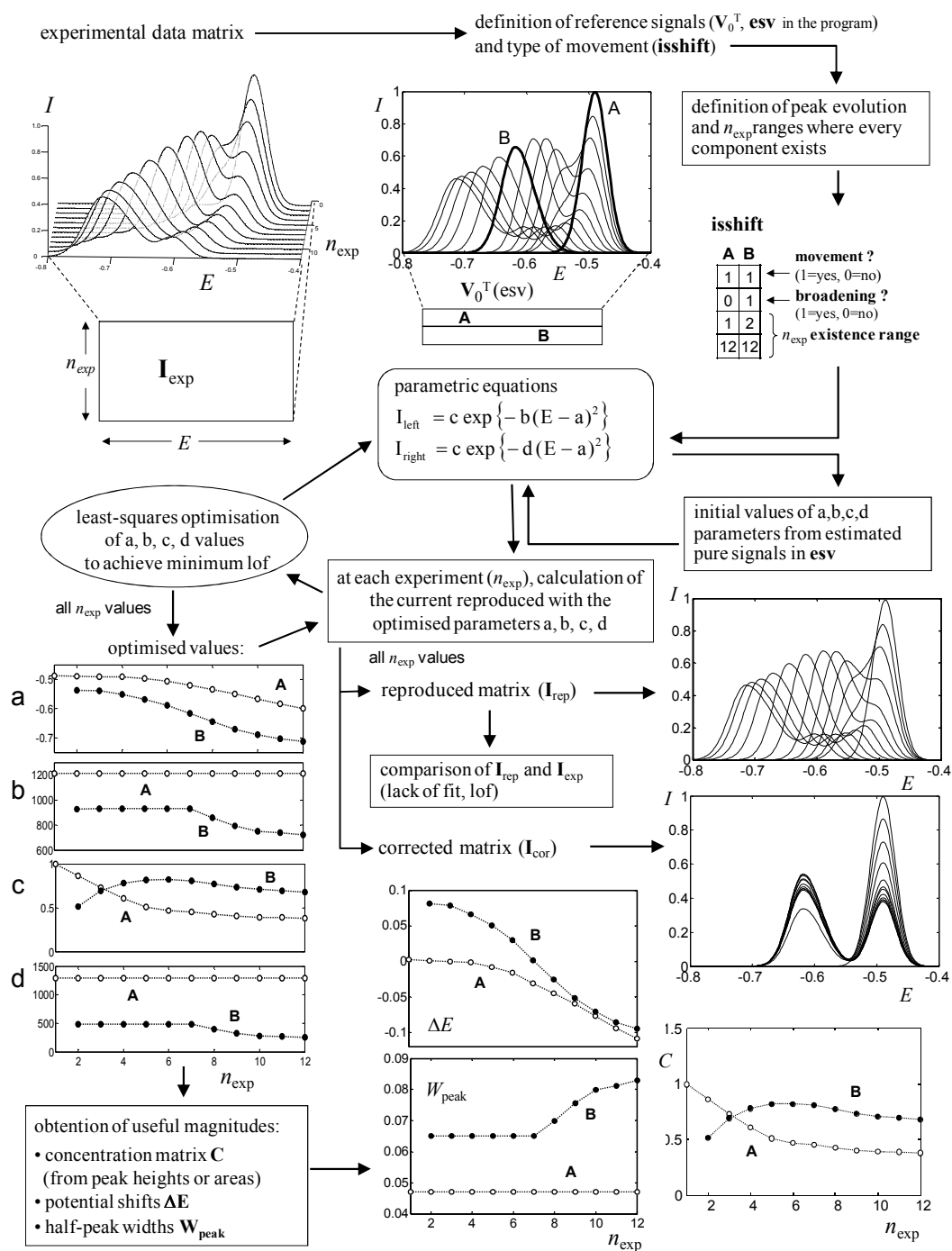
with a, b, c, d being adjustable parameters: a is the height of the function, *i.e.* the difference between the lower and upper limits of  $\Delta E$ , and can be positive or negative depending on the 'up-down orientation' of the function; b is related to the slope in the region close to the inflexion point and can also be positive or negative depending on the 'left-right orientation' of the function; c is the pH of the inflexion point; and d is the vertical displacement (positive or negative) of the sigmoid from the zero baseline ( $d \neq 0$  means a sigmoid with both a positive and a negative section).

Further reading on theoretical aspects of the data treatment can be found in Ref. 19 and 20.

## S2. Data Treatment

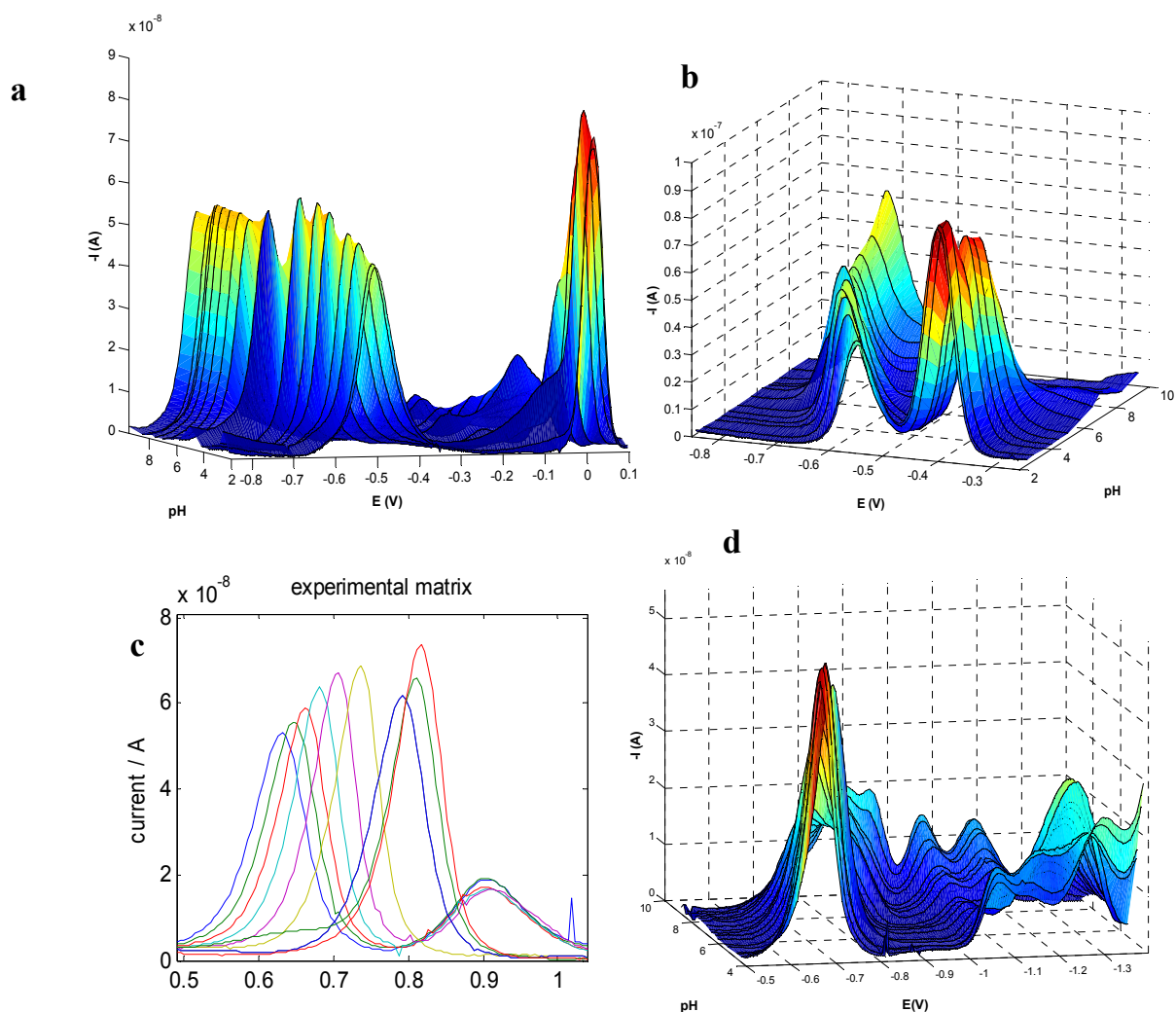


**Flowchart 1** - Method for non-linear multivariate curve resolution analysis of voltammetric pH titration datasets by means of pHfit program, as seen in reference 19. The proposed example includes three kinds of signals depending on their evolution with pH: sigmoid (A), immobile (B) and linear (C).



**Flowchart 2** - Methodology for non-linear multivariate curve resolution analysis of a voltammetric titration dataset by means of GPA programs, as seen in Reference 20.

### S3. Voltammetric pH titration



**Figure S1** – Voltammetric data matrix (current vs. potential vs. pH) obtained in the DPP pH titration of 3:2 SeCyst :  $M^{3+}$  (a –  $Bi^{3+}$ ; b –  $Cr^{3+}$ ) and equimolar SeCyst :  $M^{2+}$  (c –  $Pb^{2+}$ ; d –  $Co^{3+}$ ) systems, in 50 mmol  $L^{-1}$   $KNO_3$ . The unitary concentration is indicated with respect to SeCyst ( $10 \mu mol L^{-1}$ ). Axes are differently disposed for a better perspective of signals evolution.