Determination of the number of complex in equilibrium mixture

Zuzana FERENČÍKOVÁ, Milan MELOUN

University of Pardubice, Department of Analytical Chemisty, Studentská 673, Pardubice, 53210, Czech Republic; zuzka.ferencikova@seznam.cz

Potentiometry and spectrophotometry are often used to study solution equilibria. In the study of solution equilibria, it is not only necessary to determine the stability (protonation or dissociation) constant of each species, but also to find out how many such species are present. The expression "chemical model" means the number of species in mixture, their stoichiometry, values of protonation constants and values of other physical constants (e.g. molar absorption coefficient).

(a) In spectrophotometry we can determine the number of light-absorbing species using a factor analysis of absorbance-response surface. Algorithm INDICES [1] in program S-PLUS contains 12 methods of factor analysis. Precise methods are based on knowledge of the instrumental error of the absorbance data $s_{inst}(A)$, on the other hand if we don´t know $s_{inst}(A)$ we use approximate methods.

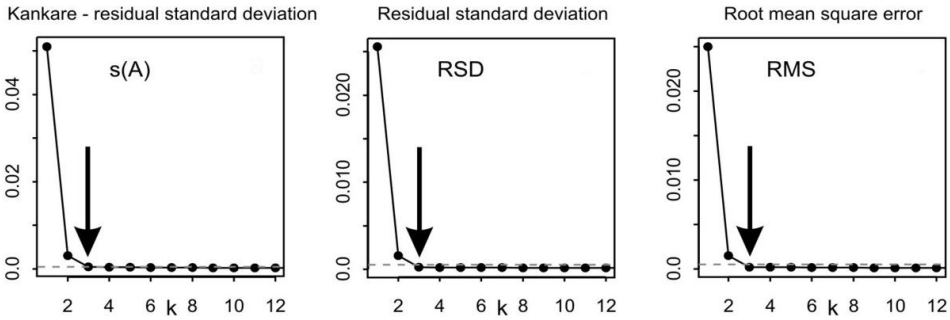

Figure 1: Precise methods of FA to determination of light-absorbing species. (S-PLUS)

(b) In potentiometry we can determine the number of complex species also with the method of factor analysis. The first step in to transform the titration curve into the form of normalizes variables $Z = f$ (pA), where the free equilibrium concentration of component A is usually measured potentiometrically as pA = -log [A] and Z represents the average number of one component (A) bound per another component (B): $Z = (c_A\text{-}[A])/c_B$. Each curve Z can be measured for different total concentration of component B to give finally the matrix **Z**. The rank of **Z** gives directly the number of complex species in solution [2].

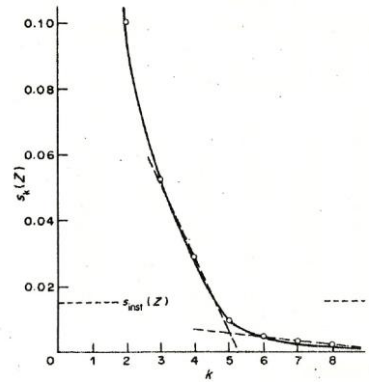

Figure 2: Graphical determination of the number of complex.

The last method for determination the number of species useable for both spectrophotometric and potentiometric data is searching of chemical model using the minimization process. When the minimization process of a regression analysis terminates in the minimum of the residual square sum function *U*, some diagnostic criteria are examined to determine whether the results should be accepted or rejected: the physical meaning of estimated parameters, physical meaning of the species concentrations, parametric correlation coefficient, goodness-of-fit test (standard deviation of absorbance, Hamilton *R*-factor). The minimization process is repeated for various hypothesis of chemical model and the lowest *U* value obtained indicates the most probable model (Table 1) [3, 4].

Table 1: The search for a protonation model of methotrexate with the SQUAD(84) analysis of A-pH spectra at 25ºC and an ionic strength I = 0.0012. The standard deviations in the last valid digits are in brackets.

Model hypothesis	L, LH	L, HL, H_2L	L, HL, H_2L, H_3L
k, $s_k(A)$ [mAU]	2, 4.00	3, 0.52	4, 0.46
pK_{a1}	5.532(7)	3.813(18)	3.086(167)
pK_{a2}	---	5.639(2)	4.403(63)
pK_{a3}	---	---	5.675(6)
$s(A)$ [mAU]	4.68	0.87	0.65
$s(e)$ [mAU]	4.68	0.87	0.65
$\lvert\bar{e}\rvert$ [mAU]	3.24	0.58	0.42
g_1	-0.53	-0.07	-0.28
g_2	4.29	3.21	3.32
R [%]	0.97	0.18	0.13
Model is	rejected	rejected	accepted

References:

[1] Meloun, M.; Syrový, T.; Vrána, A., Determination of number of light-absorbing species in protonation equilibria of selected drugs. *Anal. Chim. Acta* **2003**, 489, 137-151

[2] Havel, J.; Meloun, M., Multiparametric curve fitting VII: Determination of the number of complex species by factor analysis of potentiometric data. *Talanta* **1985**, 32(3), 171-175

[3] Meloun, M.; Havel, J.; Högfeldt, E., *Computation of solution equilibria: A guide to methods in potentiometry, extraction, and spectrophotometry,* Ellis Horwood: Chichster (England), **1988**, *pp.* 297

[4] Meloun, M.; Havel, J., *Computation of solution equilibria II. Potentiometry,* Folia Fac. Sci. Nat. Univ. Purkyn. Brunensis (Chemia)B: Brno, **1985,** *pp*. 144

[Topic: Computational modelling]