A New Model for the Full Inclusion of Precipitation Reactions in the General Ionic Equilibrium Framework of Homogeneous Solutions Based on the Fraction of Species Concept in Heterogeneous Systems

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Abstract: This study aims at extending the general methodology for the study of predominance and reactivity of ionic homogeneous solutions to precipitation reactions. This extension was satisfactorily formulated by the definition of the fraction of species concept in heterogeneous systems for the first time. An easy form to fully integrate the ion product concept with other descriptions of homogeneous ionic reactions, to obtain predominance zone diagrams (PDZ), to enrich the use logarithmic relative diagrams, to generate continuous equations from titration curves, and to generalize side-reaction coefficients to heterogeneous systems using easy-to-compute algorithms of calculation is shown.

The new representation was applied in a study case exemplified by the hydrolysis of copper (II) in the absence and the presence of complexing ligands considering soluble and insoluble species of the metal ion. The results perfectly compare to those obtained by established numerical and graphical methods of analysis of solution equilibria showing the equivalence among the different descriptions.

Pre-nucleation clusters (PNCs) theory of precipitation reactions was used as a mean to interpret the theoretical implication that this view engendered.

Keywords: Distribution fraction diagram, predominance zone diagram, precipitation reactions, side-reaction coefficients, modeling precipitation reactions.

1. INTRODUCTION

The object of analytical chemistry is to obtain qualitative and quantitative information about the chemical composition and structure of materials. Analytical chemistry investigates the type of components present in materials, their amount, and their structural relationships [1]. From the analytical chemistry point of view, the structure of aqueous solutions of ions and neutral molecules is related to the inner relationships that the different species establish among them due to fundamental chemical principles, such as the conservation of matter and charge, and the thermodynamic equilibrium. Basic theory of solution chemistry is essential to the study the physicochemical phenomena that are applied in chemical analysis, allowing the understanding of sample pretreatment and preparation methods used in conjunction with modern instrumental techniques. The importance of accurate sample preparation techniques cannot be overstated, as even the best analytical techniques cannot rectify problems generated by sloppy sample pretreatment [2]. With the extended use of analytical methods among different chemical and non-chemical related disciplines, there is an increasing need to conceptualize the principles of solution chemistry in such a form that problem descriptions are simplified, common methodologies to plan and resolve complex problems of analytical and industrial chemistry can be employed, and non-expert users of analytical methods can have an easy comprehension of the rules lying behind the use of diverse chemical operations in aqueous solutions (pH buffering, use of masking and precipitating reagents, control of redox potential, etc.). On this subject, general approaches to include in a single scheme homogeneous ionic reaction, e.g., acid/base, complex, and redox systems, have been proposed as an appropriate conceptual framework from which the composition and reactivity of complex ionic media can systematically be analyze [3-6]. One of the great interests in the analytical chemistry practiced in aqueous solutions lies in the fact that it can be quasi-systematically described by mathematical equations, which can be grouped themselves in mathematical determined systems [7]. Consequently, the arithmetic structures of such systems and methods for the treatment of solution equilibria by different approaches have been reported over time [7-9]. With the availability of personal computers with spreadsheet and mathematical software, various computer methods and graphical approaches based on the concept of master variables can be now easily implemented [10-13]. Such approaches use the concepts of "particle exchange" and "distribution or fraction diagrams" as fundamental starting points from which predominance-zone diagrams (PZD) can be constructed and reactivity of a system deduced [3, 14-17]. However, as for precipitation reactions is concerned, they have generally been treated separately from this general framework. There are at least two probably reasons for this: the intrinsic heterogeneous character of the reaction that leads to a phase separation phenomenon, and the absence of a linking frame from which different approaches to study such reactions can be integrated. As for the second reason, it is reasonable to think that if, ultimately,

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precipitation reactions are complexation ones with the characteristic that the complex is in a sparingly soluble form, it should be possible to treat them as such with some particularity. In this regard, Fernández-Pereira *et al.* [18] based on the concept of acceptance potential has established a correlation of the precipitation-solubility equilibrium with other ionic equilibria; however, the theoretical implication of such inclusion and a complete view of the panorama of all the possibilities allowed by such incorporation have not been deeply examined up to now. In this work, it will be shown that the possibility to include precipitations reactions in the general ionic equilibrium framework of homogeneous reactions just requires an appropriate definition of the fraction of species concept in the heterogeneous system using a modified equilibrium constant value. It is the intention of the manuscript to shed light upon the advantages of such approach to simplify the description of precipitation reactions based on previous knowledge of homogeneous ionic reactions and to promote critical reflection about the implications of such view.

In a first instance, and for the sake of clarity in the presentation, preliminary concepts in solution chemistry exemplified with acid/base reactions will be reviewed; then, the generalization of the homogeneous framework to include precipitation reactions will be formally introduced. To show the feasibility and applicability of the approach, the results of the use of the proposed methodology to analyze the composition of a complex heterogeneous system will be compared to that obtained by established numerical methods. Furthermore, it will be shown how an established graphical method can take advantage of the new approach to enrich its range of application by obtaining easily PDZ diagrams in heterogeneous systems. Finally, titration curves for precipitation reactions will be computed using the framework commonly used for homogeneous reactions, and the generalization of side-reaction coefficients [19, 20] to heterogeneous systems will be performed in a straightforward form. Overall, the integration of precipitation reactions in the homogeneous equilibrium framework will then be demonstrated and its applications and implications in the chemical descriptions of solution chemistry problems properly analyzed.

2. THEORETICAL BASIS

Review of the general ionic equilibrium framework of homogeneous solutions as applied to acid/base reactions

HA/A^- system

As an illustrative example well found in the literature [4, 21, 22], considering the proton exchange between a donor (acid, HA) and an acceptor (base, A^-) species of this particle according to the reaction:

$$HA + H_2O \leftrightarrow A^- + H_3O^+ \tag{1}$$
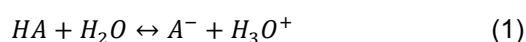
the mole fraction of both species in a system with total concentration C_{HA} may be computed from[1]:

$$x_{HA} = \frac{[HA]}{C_{HA}} \text{ and } x_{A^-} = \frac{[A^-]}{C_{HA}} \tag{2}$$

Where

$$C_{HA} = [HA] + [A^-] \tag{3}$$

Using the acid equilibrium constant, K_a, under ideal conditions, i.e., the activities of the species correspond to their concentrations, defined by:

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{4}$$

And the mass balance (Eq. (3)), x_{HA} and x_{A^-} are expressed as:

$$x_{A^-} = \frac{[A^-]}{[HA]+[A^-]} = \frac{K_a/_{[H^+]}}{1+K_a/_{[H^+]}} = \frac{K_a}{[H^+]+K_a} = \frac{10^{-pK_a}}{10^{-pH}+10^{-pK_a}} = 1 - x_{HA} \tag{5}$$

$$x_{HA} = \frac{[HA]}{[HA]+[A^-]} = \frac{1}{1+K_a/_{[H^+]}} = \frac{[H^+]}{[H^+]+K_a} = \frac{10^{-pH}}{10^{-pH}+10^{-pK_a}} = 1 - x_{A^-} \tag{6}$$

taking into account that $pH = -log[H^+]$ and $pK_a = -logK_a$.

From Figure **1a** it is clearly noted that when $[H^+] > K_a$ $(pH < pK_a)$, $x_{HA} > x_{A^-}$, and when $[H^+] < K_a$ $(pH > pK_a)$, $x_{HA} < x_{A^-}$; clearly at $[H^+] = K_a$ $(pH = pK_a)$, $x_{HA} = x_{A^-}$. From the same Figure, it is observed that in a rigorous sense both species, the acid and the base, are simultaneously present within all pH range; however, its relative abundance or predominance is determined by the conditions indicated before.

It is possible to demonstrate that the same information may be attained using logarithmic diagrams without the need of computing the fraction of species as described above, as this alternative representation just requires performing pertinent approximations to the equilibrium relationship (Eq. (4)) and the mass balance condition (Eq. (3)) to get lineal relationships that can be easily drawn [4, 22-25]. Accordingly, when $pH < pK_a$, $[HA] \gg [A^-]$ and $[HA] \approx C_{HA}$ and two lineal forms, one for each species can be deduced:

$$log[HA] = logC_{HA} \tag{7}$$

$$log[A^-] = -pK_a + logC_{HA} + pH \tag{8}$$

Similarly, when $pH > pK_a$, $[HA] \ll [A^-]$ and $[A^-] \approx C_{HA}$ and

$$log[A^-] = logC_{HA} \tag{9}$$

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[1]Mole fractions have been represented with different symbols in the literature, mainly α_i. In the following, it was decided to employ x_i to avoid a confusion with the α_i symbol employed for side-reactions coefficients and to be consistent with most physicochemical textbooks.

$$log[HA] = pK_a + logC_{HA} - pH \qquad (10)$$

To perform a comparison between both procedures Eqs. (2) are transformed to their logarithms forms to get:

$$log[HA] = logC_{HA} + \log x_{HA} \qquad (11)$$

$$log[A^-] = logC_{HA} + logx_{A^-} \qquad (12)$$

In Figure **1b**, created using Excel, it is seen that the horizontal line at $logC_{HA} = log[HA] \, or \, log[A^-]$ is a graphic representation of the mass balance condition (Eq. (3)), and the equilibrium condition (Eq. (4)) is represented by the two straight lines given by Eqs. (8) and (10).

In Figure **1b** both procedures are compared as well. As observed, the main difference arises from the nature of the approximation done when drawing the lineal equations, as strictly speaking, at the system point $pH = pK_a$ neither species can be neglected in the mass balance condition, where $[HA] = [A^-] = C_{HA}/2.$ So it is found that the true curves for HA and A^- in the lineal logarithmic equations must intersect at $pH = pK_a$ but 0.3 units (log 0.5) below the mass balance line, as obtained using Eqs. (11) and (12) which do not use any approximation.

The PZD (Figure **1c**) visually simplifies the $x_i = f(pH)$ diagram in a unidimensional representation such that the more abundant species in each pH region is easily identified considering that in the coexistence line pH = pK_a both species have the same relative abundance. From this scale, the reactivity of an acid/base system is easily deduced considering that acid/base species can coexist in pH regions that agree with their predominance zone, otherwise species should be transformed by particle exchange to meet this requirement [17].

Alternatively, Eqs. (5) and (6) may be expressed in terms of the global stability constant of the system defined by:

$$\beta_1 = \frac{[HA]}{[A^-][H^+]} \qquad (13)$$

as:

$$x_{A^-} = \frac{[A^-]}{C_{HA}} = \frac{[A^-]}{\beta_1[H^+][A^-]+[A^-]} = \frac{1}{1+\beta_1[H^+]} \qquad (14)$$

$$x_{HA} = \frac{[HA]}{C_{HA}} = \frac{\beta_1[H^+]}{1+\beta_1[H^+]} = 1 - x_{A^-} \qquad (15)$$

Although such constants are scarcely employed in the literature concerning acid/base reactions the advantage of its use will be shown subsequently.

H_nA/A^{n-} system

For a polyprotic system of the type

$$HA^{(n-1)-} \leftrightarrow A^{n-} + H^+ \qquad\qquad K_{a1} = \frac{[A^{n-}][H^+]}{[HA^{(n-1)-}]} \qquad (16)$$
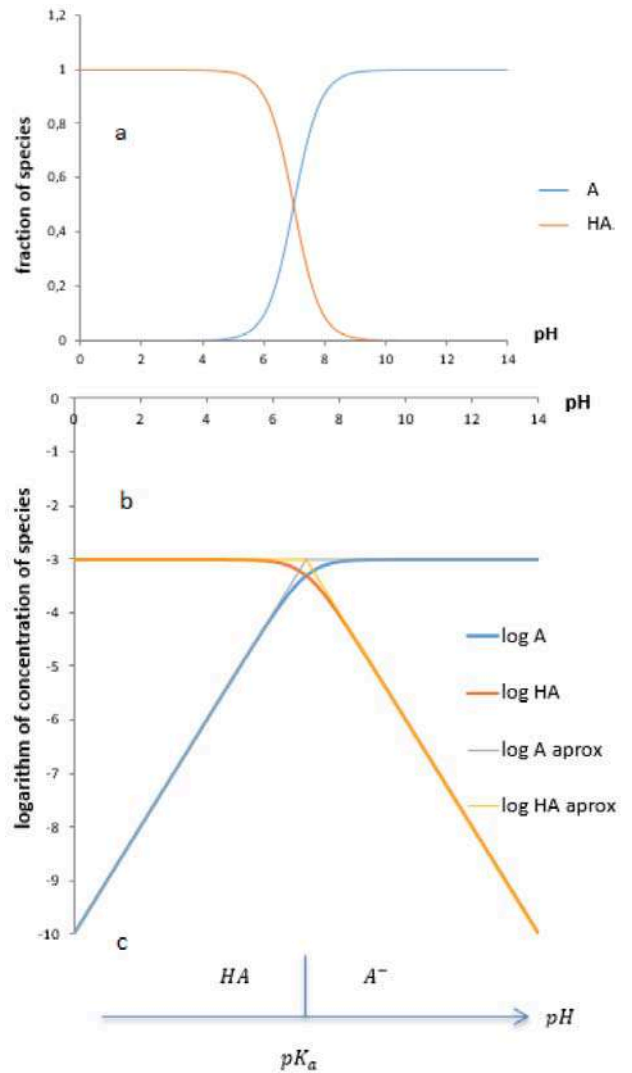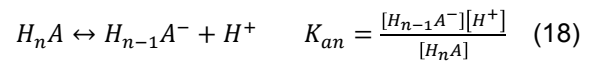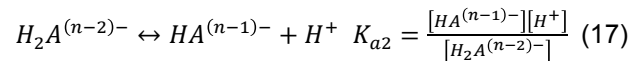

Figure 1: (a) Distribution or fraction diagram of an acid/base system with $pK_a = 7$ as a function of pH computed from Eqs. 5 and 6 using Excel. (b) Logarithmic diagram of the same system showing the concentration of the species as a function of pH. The diagram was constructed using Eqs. (7) to (10) and Eqs. (11) and (12) for comparative purposes. (c) PDZ diagram constructed from the above Figures showing the predominant species in each pH zone defined by the pK_a value.

$$H_2A^{(n-2)-} \leftrightarrow HA^{(n-1)-} + H^+ \quad K_{a2} = \frac{[HA^{(n-1)-}][H^+]}{[H_2A^{(n-2)-}]} \quad (17)$$

$$H_nA \leftrightarrow H_{n-1}A^- + H^+ \qquad K_{an} = \frac{[H_{n-1}A^-][H^+]}{[H_nA]} \quad (18)$$

The corresponding β_i expressions:

$$\beta_1 = \frac{1}{K_{a1}} = \frac{[HA^{(n-1)-}]}{[A^{n-}][H^+]} \qquad (19)$$

$$\beta_2 = \frac{1}{K_{a1}K_{a2}} = \frac{[H_2A^{(n-2)-}]}{[A^{n-}][H^+]^2} \qquad (20)$$

$$\beta_n = \frac{1}{K_{a1}K_{a2}...K_{an}} = \frac{[H_nA]}{[A^{n-}][H^+]^n} \qquad (21)$$

allow to easily formulate the fractions of species equations as:

$$x_{A^{n-}} = \frac{[A^{n-}]}{C_{HA}} = \frac{[A^{n-}]}{[A^{n-}] + [H_2A^{(n-2)-}] + \cdots + [H_nA]}$$
$$= \frac{1}{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \cdots + \beta_n[H^+]^n} \tag{22}$$

$$x_{HA^{(n-1)-}} = \frac{[HA^{(n-1)-}]}{C_{HA}} = \frac{[A^{n-}][HA^{(n-1)-}]}{C_{HA}[A^{n-}]} = x_{A^{n-}}\beta_1[H^+] \tag{23}$$

$$x_{H_2A^{(n-2)-}} = \frac{[H_2A^{(n-2)-}]}{C_{HA}} = \frac{[A^{n-}][H_2A^{(n-2)-}]}{C_{HA}[A^{n-}]} = x_{A^{n-}}\beta_2[H^+]^2 \tag{24}$$

$$x_{H_nA} = \frac{[H_nA]}{C_{HA}} = x_{A^{n-}}\beta_n[H^+]^n \tag{25}$$

Moreover, as these expressions have a general character, they can be applied for the exchange of other particles different from H^+. The utility of this formulation will be appreciated later when analyzing the simultaneous participation of OH^- particles in precipitation and complexation equilibria.

The above framework can be applied to redox (through the incorporation of the $p\varepsilon$ or $pE = -log[e^-]$ and pK_{red} or $pE^0 = -logK_{red}$ concepts) and complex equilibria as well, allowing a straightforward generalization of acid/base, complex, and redox ionic systems in a unique framework [3-5]. However, as previously discussed, when heterogeneous precipitation reactions are presented, i. e., the lack of expressions for the fractions of species related to this type of systems represents one big drawback to integrate precipitation reactions with other descriptions of homogeneous ionic reactions. Alternatively, the "ion product" concept plays a fundamental and useful role in the explanation of the precipitation concept, but in a first instance, it does not seem to be related in any form with the fraction of species concept or the PZD method outlined above. Although some attempts have been previously reported to include precipitation reactions in the PZD framework [6, 18] a full integration of the concept has not been realized nor the implication of such inclusion deeply discussed up to now. However, in the following sections it will be shown how precipitation reactions may be included in a simple form in the scheme of homogeneous ionic equilibria of the type acid/base, complex and redox systems through the deduction of the fraction of species concept in such heterogeneous systems.

The new extension of the general ionic equilibrium framework of homogeneous solutions to include precipitation reactions

$MX \downarrow$ system

The generalization of the homogeneous framework to include precipitation reactions may be satisfactorily accomplished in an experiment where X^- is added to a solution of M^+ at total C_M concentration (where $[X^-]$ can be measured and/or controlled) to form $MX \downarrow$, by defining a modified global formation constant (β_1^*) as demonstrated below.

The law of conservation of matter establishes that the total amount of mole, n_M, is maintained constant in

the whole system. Taking as reference the total or initial concentration of the metal ion in solution, it is possible to write:

$$\frac{n_M}{V} = C_M = \frac{n_{MX\downarrow}}{V} + \frac{n_{M^+}}{V} = \frac{n_{MX\downarrow}}{V} + [M^+] \tag{26}$$

Considering the definition of the mole fraction for the precipitate, $x_{MX\downarrow} = \frac{n_{MX\downarrow}}{n_M}$, in the above equation:

$$C_M = \frac{x_{MX\downarrow}n_M}{V} + [M^+] = C_M x_{MX\downarrow} + [M^+] \tag{27}$$

By defining:

$$\{MX\downarrow\} = C_M x_{MX\downarrow} = \frac{n_{MX\downarrow}}{V} \tag{28}$$

The mass balance equation (27) is expressed as:

$$C_M = \{MX\downarrow\} + [M^+] \tag{29}$$

in which as shown, the term $\{MX\downarrow\}$ represents the fraction of the total concentration that is in the precipitate form or, equivalently, the number of moles of precipitate in contact with the volume of the solution. Consequently, from the above equation:

$$[M^+] = C_M(1 - x_{MX\downarrow}) = C_M x_{M^+} \tag{30}$$

Then, the solubility, $[M^+]$, is the fraction of the total concentration that is in the soluble form, as expected.

As for the chemical equilibrium:

$$MX \downarrow \leftrightarrow M^+ + X^- \tag{31}$$

in which not ion pairing of the ions is presented due to a high polarity of the solvent, commonly water, with equilibrium constant defined by:

$$K_s = \frac{a_{M^+}a_{X^-}}{a_{MX\downarrow}} \tag{32}$$

and considering the relationship between activity and molality or mole fraction following the analogous of convention III [26] for activities and activity coefficients for condensed phases in a mixture with dissolved species, i.e., expressing the activity of the condensed phase on the mole fraction scale and those of the dissolved species on the molality scale (unsymmetrical activity coefficients convention), Eq. (32) can be written as:

$$K_s = \frac{\gamma_{M^+}m_{M^+}\gamma_{X^-}m_{X^-}}{\gamma_{MX\downarrow}x_{MX\downarrow}} \tag{33}$$

The application of this convention to the dissolution of salts has previously proved to be an efficient form to derive equations of states for model electrolyte solutions with multiple salts [27] and to predict the precipitation of salts from aqueous solutions using organic solvents [28]. This is possible as none of the scales in which the species concentration may be expressed is more fundamental than the others, and which scale is used is simply a matter of convenience.

Considering dilute solutions $m_i \to [i]$, then Eq. (33) is transformed to:

$$K_s = \frac{\gamma_{M^+}[M^+]\gamma_{X^-}[X^-]}{\gamma_{MX\downarrow}x_{MX\downarrow}} \tag{34}$$

Furthermore, as in such solutions $\gamma_{MX\downarrow} \to 1, \gamma_{M^+} \to 1$ and $\gamma_{X^-} \to 1$, Eq. (34) reduces to:

$$K_s = \frac{[M^+][X^-]}{x_{MX\downarrow}} \tag{35}$$

Substituting Eq. (28) in (35):

$$K_s = \frac{[M^+][X^-]C_M}{\{MX\downarrow\}} \tag{36}$$

which after rearrangement takes the form:

$$\beta_1^* = \frac{C_M}{K_s} = K_{f,precipitate} \, C_M = \frac{\{MX\downarrow\}}{[X^-][M^+]} \tag{37}$$

The modified global formation constant β_1^* is basically the product of the formation constant of the precipitate, $(K_{f,precipitate})$, times the total concentration of the metal in solution. In the following sections, the utility of Eq. (37) will be further demonstrated.

Ion Product

Once again considering the same system, the fractions of the different metallic species exchanging the X^- anion are defined according to the previously shown theory (see acid base concepts) and using Eq. (37) as:

$$x_{M^+} = \frac{[M^+]}{C_M} = \frac{[M^+]}{[M^+]+\{MX\downarrow\}} = \frac{1}{1+\beta_1^*[X^-]} = \frac{1}{1+C_M/K_s[X^-]} = \frac{K_s}{K_s+C_M[X^-]} \tag{38}$$

$$x_{MX\downarrow} = \frac{\{MX\downarrow\}}{C_M} = x_{M^+}\beta_1^*[X^-] = \frac{C_M[X^-]}{K_s+C_M[X^-]} = 1 - x_{M^+} \tag{39}$$

From these equations and using Excel Figure **2a** was created. It is clearly noted that when $K_s > C_M[X^-]$, $x_{M^+} > x_{MX\downarrow}$ and when $K_s < C_M[X^-]$, $x_{M^+} < x_{MX\downarrow}$; clearly at $K_s = C_M[X^-]$, $x_{M^+} = x_{MX\downarrow}$. Interestingly these observations based on the fraction of species concept just make it then equivalent the rules lying behind the comparison between the ion product concept and the K_s value as a mean to evaluate the degree of precipitation with those analyses done to evaluate the predominance of the different species in homogeneous ionic solutions, as this comparison determine the abundance of the soluble or insoluble metallic species, as shown below.

From Eq. (38) the generalization of the ion product concept to a continuous function which denotes the relationship between the fraction of soluble metal, x_{M^+}, in a solution at C_M total metal concentration at a determined value of $[X^-]$ is given by:

$$C_M[X^-] = \frac{K_s(1-x_{M^+})}{x_{M^+}} \tag{40}$$

From this it is possible to evaluate that if $x_{M^+} = 0.999$ (99.9% predominance of M^+):

$$C_M[X^-] = \frac{K_s(1-0.999)}{0.999} \approx 0.001K_s \tag{41}$$

so that the ion product equals one thousandth of the K_s value, i.e., $C_M[X^-] < K_s$ and the soluble species is more abundant than the precipitated one in agreement with the regular rules to evaluate precipitation reactions.

If $x_{M^+} = 0.001$ (0.1% predominance of M^+):

$$C_M[X^-] = \frac{K_s(1-0.001)}{0.001} \approx 1000K_s \tag{42}$$

so that the ion product equals thousand times the K_s value, i.e., $C_M[X^-] > K_s$ and the precipitated species is more abundant than the soluble one in agreement with the regular rules to evaluate precipitation reactions.

Clearly at $x_{M^+} = 0.5$ this equation simplifies to $C_M[X^-] = K_s$, the classical ion product, and both species have the same abundances in accordance with Figure **2b**.

Certainly, it should possible to deduce approximate equations for the concentrations of species in logarithmic form without the need of computing the fraction of species in a similar form to that exemplified in acid/base reactions. Therefore, for the sake of symmetry in the representation, by defining:

$$K_{d,1}^* = \frac{[X^-][M^+]}{\{MX\downarrow\}} \tag{43}$$

and using the mass balance Eq. (29) when $pX < pK_{d,1}^*$, $\{MX\downarrow\} \gg [M^+]$ and $\{MX\downarrow\} \approx C_M$; thus, two lineal forms, one for each species can certainly be deduced:

$$log\{MX\downarrow\} = logC_M \tag{44}$$

$$log[M^+] = -pK_{d,1}^* + logC_M + pX \tag{45}$$

Similarly, when $pX > pK_{d,1}^*$, $\{MX\downarrow\} \ll [M^+]$ and $[M^+] \approx C_M$ and

$$log[M^+] = logC_M \tag{46}$$

$$log\{MX\downarrow\} = pK_{d,1}^* + logC_M - pX \tag{47}$$

To perform a comparison between both procedures Eqs. (38) and (39) are transformed to their logarithms forms to get:

$$log[M^+] = logC_M + logx_{M^+} \tag{48}$$

$$log\{MX\downarrow\} = logC_M + log\,x_{MX\downarrow} \tag{49}$$

In Figure **2b** it is seen that the horizontal line at $logC_M = log\{MX\downarrow\}$ or $log[M^+]$ is a graphic representation of the mass balance condition (Eq. (29)), and the equilibrium condition (Eq. (37)) is represented by the two straight lines given by Eqs. (47) and (49). In Figure **2b** both procedures are compared as well. It is also worth to observe that strictly speaking the concept that precipitation "starts" when $K_s = C_M[X^-]$ in this conceptualization is just a limiting condition generated

by the lineal approximation of the fraction diagram by the lineal logarithmic equations, in the same way as discussed in the acid/base case pointed out before, as the condition at which the ion product equals the solubility product constant determines in fact 50% of precipitation (0.3 units below the mass balance condition in a logarithmic representation). This result will be further confirmed by numerical methods in its corresponding section. The implications of such statement will be analyzed further below as well.

It is also straightforward to write down a PZD from Figure **2b** considering that the system's point, $pX_{50\% \, abundance}$, distinguishing the predominance zone of the different species (analogous to the pK_a value in acid/base systems) is given by:

$$pX_{50\% \, abundance} = log\beta_1^* = pK_s + logC_M = pK_{d,1}^* \quad (50)$$

This means that the pK_s parameter must be modified by a term accounting for the total concentration of the analyte ($logC_M$) to be useful as coexistence line value is this type of heterogeneous systems, as it has been experimentally observed. The combination of both terms defines a modified system point ($pK_{d,1}^*$) from which the PZD can be draw as shown in Figure **2c**.

The behavior predicted by the model line corresponding to the fraction of species of the precipitate shown in Figure **2** can be explained considering that in solutions of very low concentrations of precipitating reagent ($pX > pK_{d,1}^*$) the number of growth units per unit volume of solution is small and the growth units are relatively distant from one another. With the increase in concentration the unsaturated solution gradually reaches supersaturation ($pX < pK_{d,1}^*$) and spontaneous nucleation will happen when the supersaturation reaches a certain value ($pX = pK_{d,1}^*$). Between the unsaturated area and spontaneous nucleation area a metastable zone exists, in which spontaneous nucleation cannot happen without seed crystals, unless concentration reaches the nucleation zone. Then these nuclei can grow into crystals of visible sizes in the supersaturated system, giving rise to phase separation, and quantitative precipitation initiates. The most interesting point of the fraction of species treatment is the prediction of the presence of precipitation units before phase separation, i.e., before visual confirmation of precipitation (continuous curve in the unsaturated region). The understanding of the molecular mechanisms underlying phase separation and the formation of the first solid particles in aqueous solution during crystallization is rather limited. However, stable solute species, often called pre-nucleation clusters (PNCs), can exist in under-and supersaturated solutions, and participate in the process of phase separation. The role that PNCs have as solute precursors in the emergence of a new phase has recently been summarized, and the link between the chemical speciation of homogeneous solutions and the process of phase separation via pre-nucleation clusters highlighted as well [29]. The stoichiometry of

constituents in the PNCs may resemble that of the bulk phase with the addition of hydration water, as well as hydroxide or hydronium ions. Recent experimental and computational results suggest that Ca^{2+} and CO_3^{2-} ions can associate into stable complexes prior to the onset of liquid or solid $CaCO_3$ formation [30, 31]. Titration experiments coupled to characterization techniques have proved to be a form to study ion pairing and clustering phenomena in the pre-nucleation regime [32]. So that, the presence of latent particles of precipitate in the region in which $pX > pK_{d,1}^*$ assumed by the heterogeneous speciation fraction is then compatible with the presence of PNCs. However, further research in this topic is needed before drawing additional conclusions.
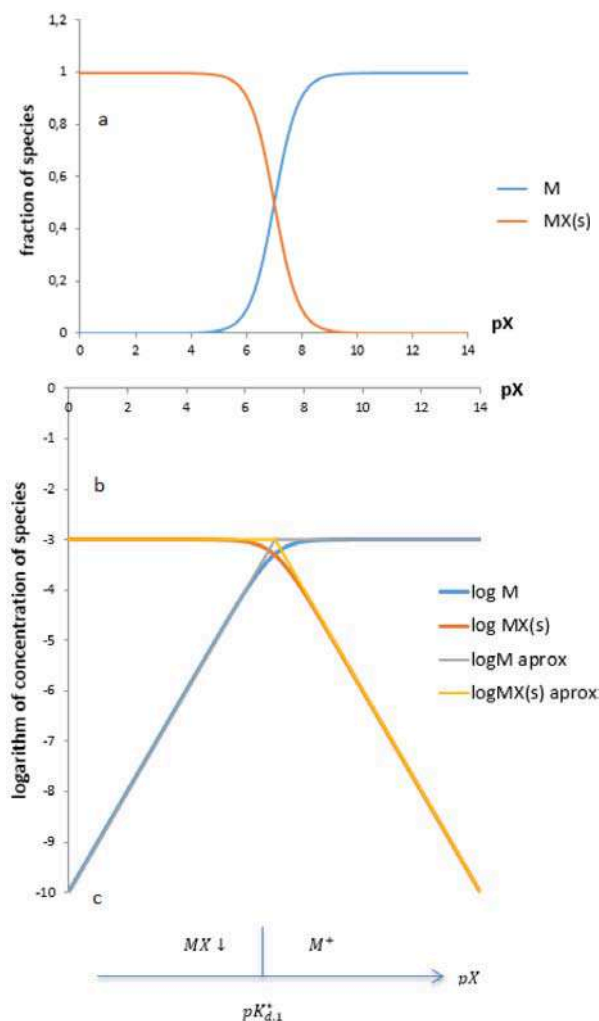

Figure 2: (a) Distribution diagram of a metal ion/precipitate system with $pK_s = 10$ as a function of pX at $C_M = 1mM$ computed from Eqs. (38) and (39) using Excel. (b) Logarithmic diagram of the same system showing the concentration of the species as a function of pX. The diagram was constructed using Eqs. (44) to (47) and Eqs. (48) and (49) for comparative purposes. (c) PDZ diagram constructed from the above Figures showing the predominant species in each pX zone defined by the $pK_{d,1}^*$ value.

$M_nX_m \downarrow$ system

The generalization of the above equations to a precipitate with a stoichiometry ratio different to one leads to:

Precipitation Equilibrium

$$M_n X_m \downarrow \leftrightarrow n M^{m+} + m X^{n-} \qquad (51)$$
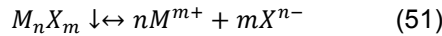
Fraction of soluble metal

$$x_{M^+} = \frac{K_s}{K_s + C_M^n [X^-]^m} \qquad (52)$$

Ion Product

$$C_M^n [X^-]^m = \frac{K_s(1 - x_{M^+})}{x_{M^+}} \qquad (53)$$

System Point

$$pX_{50\% \ abundance} = \frac{pK_{d,n,m}^*}{m} = \frac{1}{m} pK_s + \frac{n}{m} \log C_M \quad (54)$$

Modified Stability Constant

$$\beta_{n,m}^* = \frac{1}{K_{d,n,m}^*} = \frac{C_M}{K_s} = \frac{\{M_n X_m \downarrow\}}{[X^{n-}]^m [M^{m+}]^n} \qquad (55)$$

In this form, the $pK_{d,n,m}^* / m$ parameter plays the same role in precipitation reactions than that play by $pK_{d,n,m} / m$ in generalizing complexation reactions in homogeneous systems [3, 5, 6, 16].

Evidently, in a case of a homogeneous system with concentration C_X where $MX \downarrow$ is continuously formed due to progressive additions of the precipitating reagent M^+, and $[M^+]$ can be measured and/or controlled, the fraction of the different anion species exchanging the M^+ anion is defined in a similar way:

Fraction of soluble anion

$$x_{X^-} = \frac{[X^-]}{C_X} = \frac{K_s}{K_s + C_X^m [M^+]^n} \qquad (56)$$

Ion Product

$$C_X^m [M^+]^n = \frac{K_s(1 - x_{X^-})}{x_{X^-}} \qquad (57)$$

System Point

$$pM_{50\% \ abundance} = \frac{pK_{d,n,m}^*}{n} = \frac{1}{n} pK_s + \frac{m}{n} \log C_X \quad (58)$$

In this form Eqs. (54) and (58) perfectly agree with previous efforts to correlate precipitations reactions with other ionic equilibria through establishment of PZD diagrams [18].

3. APPLICABILITY OF THE NEW DESCRIPTION AND COMPATIBILITY WITH OTHER APPROACHES THROUGH THE ANALYSIS OF COPPER (II) HYDROLYSIS

The reliability and utility of the heterogeneous fraction of species concept in the description of precipitation reactions were established by comparing its results with two different established numerical and graphical approaches using the hydrolysis of copper (II) at three different total concentrations (1μM, 10 μM,

and 1mM) as illustrative example of application, as described below.

Equilibrium Computation Using Numerical Methods

First, the MEDUSA (Make equilibrium diagrams using sophisticated algorithms) software [33] was used to draw fraction diagrams for the system (Figures **3a-c**). The program is based on the SOLGASWATER [34], and HALTAFALL [35] algorithms which allow the computation of the chemical equilibrium composition of a system by two procedures: i) minimization of the free energy of the system, and ii) solving non-linear equations associated with the law of mass action using the master variable approach, respectively. As observed each of the soluble Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, and the $Cu(OH)_2 \downarrow$ solid species has characteristic predominance pH regions determined by the equilibrium constants of the copper (II)-hydroxide complexes (β_i), the solubility product constant value (K_s) and the total concentration of the metal ion (C_{Cu}). Clearly $Cu(OH)^+$ and $Cu(OH)_3^-$ are species with low predominance, i.e., low $x_{Cu(OH)_i^{2-i}}$ values, in the concentration range studied, reason why the Cu^{2+}, $Cu(OH)_2$, and $Cu(OH)_4^{2-}$ species completely determines each PZD that can be drawn for Figures **3a-c**. As expected, the pH value at which the solid species starts to predominate is a function of C_{Cu}. The logarithm diagram of all the species was additionally numerically computed and drawn at $C_{Cu} = 1 \mu M$ with the same software. From Figure **3d**, it is clear that the polynuclear $Cu_2(OH)_2^{2+}$ species plays a minor role in the equilibrium composition of the system at this copper concentration.

In the absence of the polynuclear complex, the fractions of species for all participating species are expressed as previously discussed (see acid base section) as:

$$x_{Cu^{2+}} = \frac{[Cu^{2+}]}{C_{Cu}} = \frac{[Cu^{2+}]}{[Cu^{2+}] + \sum_{i=1}^4 [Cu(OH)_i^{2-i}] + \{Cu(OH)_2\downarrow\}} =$$
$$\frac{1}{1 + \sum_{i=1}^4 \beta_i [OH^-]^i + \beta_2^* [OH^-]^2} \qquad (59)$$

$$x_{Cu(OH)_i^{2-i}} = \frac{[Cu(OH)_i^{2-i}]}{C_{Cu}} = x_{Cu^{2+}} \beta_i [OH^-]^i \quad (60)$$

$$x_{Cu(OH)_2\downarrow} = \frac{\{Cu(OH)_2\downarrow\}}{C_{Cu}} = x_{Cu^{2+}} \beta_2^* [OH^-]^2 \quad (61)$$

with

$$\beta_2^* = \frac{C_{Cu}}{K_s} = \frac{\{Cu(OH)_2\downarrow\}}{[OH^-]^2 [Cu^{2+}]} \qquad (62)$$

As Eqs. (59) to (61) depend only on pH they are easily draw with Excel considering the same equilibrium constants values used in MEDUSA evaluations (Figures **4a-c**, Cu^{2+}/OH^-: $\log\beta_1 = 6.04$, $\log\beta_2 = 11.76$, $\log\beta_3 = 15.3$, $\log\beta_4 = 16.4$, $pK_s = 19.84$). The comparison of these diagrams with those obtained with the numerical software reveals the
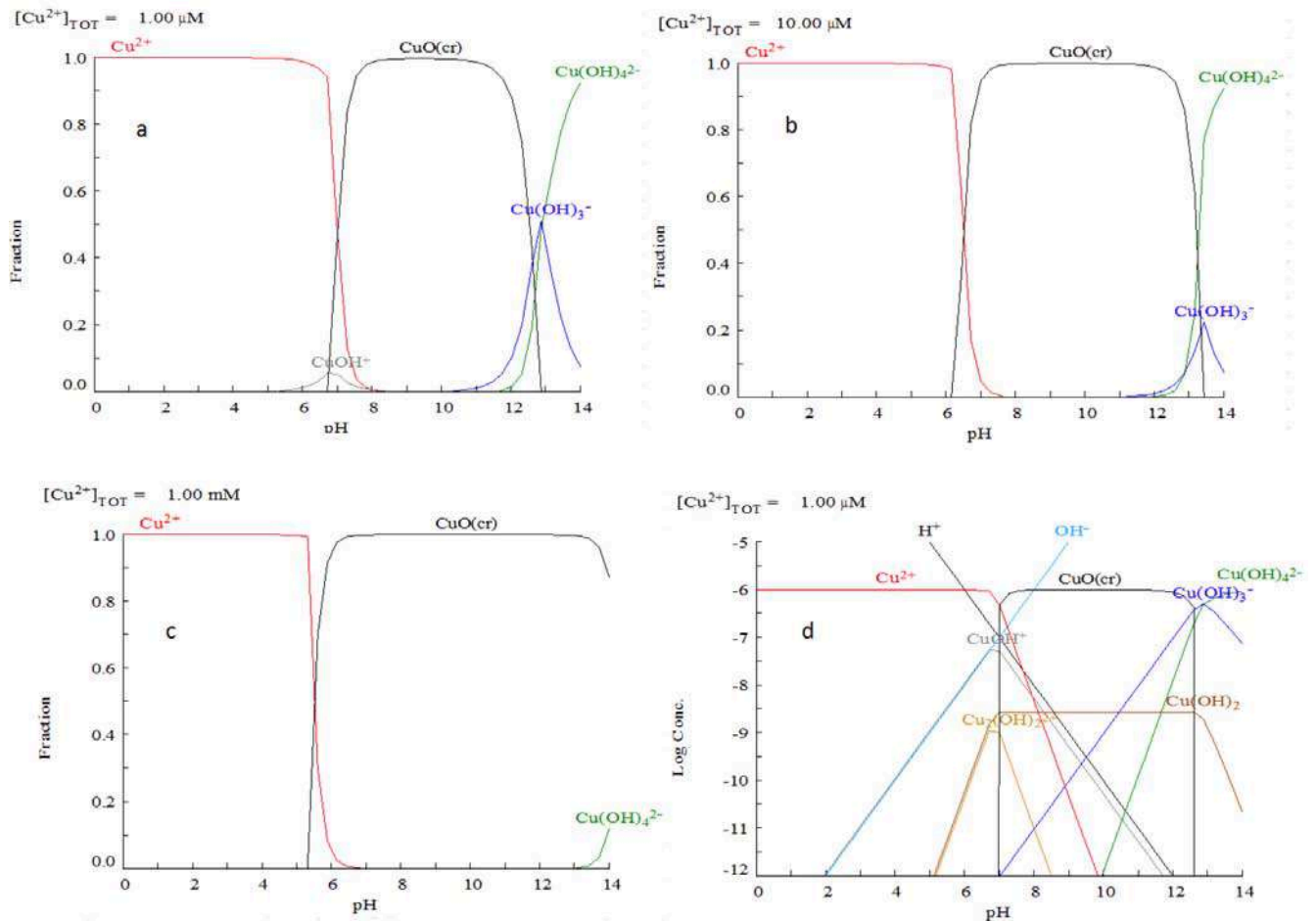
Figure 3: Fraction diagrams for copper (II) hydrolysis evaluated with the MEDUSA software at $C_M = 1\mu M\ (a), 10\mu M\ (b), 1mM\ (c)$. Logarithmic diagram of the same system at $C_M = 1\mu M\ (d)$.

equivalence between both methods. To consider the minor contribution of the polynuclear $Cu_2(OH)_2^{2+}$ species, Eq. (59) was previously modified as:

$$x_{Cu^{2+}} = \frac{[Cu^{2+}]}{C_{Cu}} =$$

$$\frac{[Cu^{2+}]}{[Cu^{2+}] + \sum_{i=1}^{4}[Cu(OH)_i^{2-i}] + \{Cu(OH)_2 \downarrow\} + 2[Cu_2(OH)_2^{2+}]} = \frac{1}{1 + \sum_{i=1}^{4}\beta_i[OH^-]^i + \beta_2^*[OH^-]^2 + 2[Cu^{2+}]\beta_{2,2}[OH^-]^2} \quad (63)$$

where

$$\beta_{2,2} = \frac{[Cu_2(OH)_2^{2+}]}{[Cu^{2+}]^2[OH^-]^2} \quad (64)$$

Furthermore, the fraction of the polynuclear species is computed from:

$$x_{Cu_2(OH)_2^{2-}} = 2\frac{[Cu_2(OH)_2^{2+}]}{C_{Cu}} = 2x_{Cu^{2+}}[Cu^{2+}]\beta_{2,2}[OH^-]^2 \quad (65)$$

To plot Eqs. (60), (61), (63) and (65) in Excel, the term $[Cu^{2+}]$ first was determined at $C_{Cu} = 1\mu M$ solving at a constant pH value the mass balance condition:

$$2\beta_{2,2}[OH^-]^2[Cu^{2+}]^2 + (1 + \sum_{i=1}^{4}\beta_i[OH^-]^i + \beta_2^*[OH^-]^2)[Cu^{2+}] - C_{Cu} = 0 \quad (66)$$

Figure **4d** shows the comparison of the result obtained with this treatment with that obtained using MEDUSA ($log\beta_{2,2} = 17.65$). As observed comparable results are obtained from the fraction of species concept and the solution of the concentrations of the system by numerical methods.

Equilibrium Calculations Using Graphical Methods

Another way to get an idea of the distribution of the different species in a complex system is to use logarithmic relative diagrams. In this representation one species is selected as reference and the logarithmic ratios of the concentration between a specific species and the reference one is obtained using the equilibrium constants of the system. The relative diagram is easy to construct even in cases of several overlapping equilibria and has also found use in presenting redox equilibria [4, 36]. In Figure **5a** and using Excel such diagram is plotted for copper (II) hydrolysis at $C_{Cu} = 0.1mM$ taking as reference $[Cu^{2+}]$. The equations for the relative concentrations considering the same equilibrium constants used with MEDUSA evaluations are:

$$log\frac{[Cu^{2+}]}{[Cu^{2+}]} = 0 \quad (67)$$

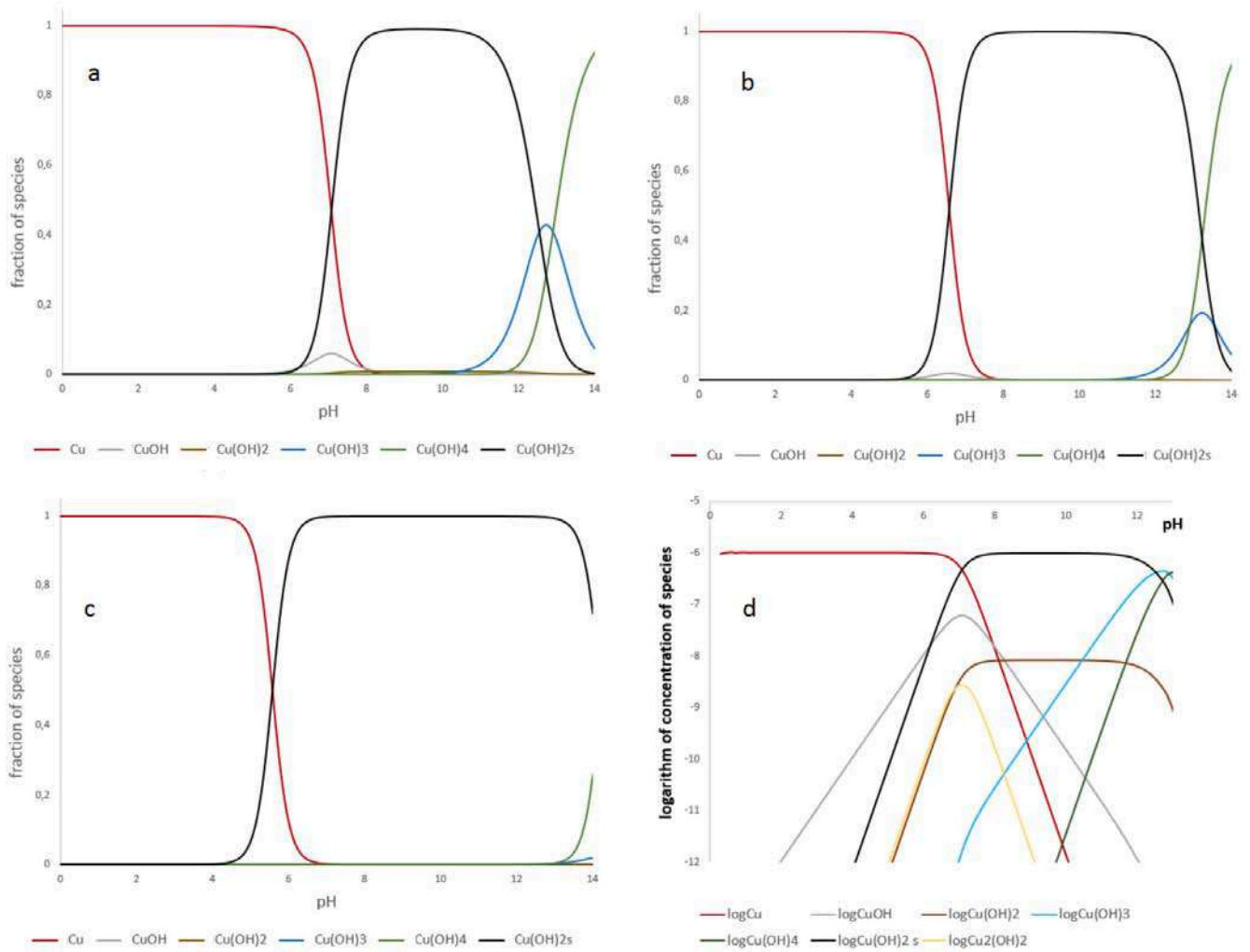$$log\frac{[Cu(OH)^+]}{[Cu^{2+}]} = log\beta_1 + logK_w + pH = -7.96 + pH \quad (68)$$

Figure 4: Fraction diagrams for copper (II) hydrolysis evaluated with Excel using the equilibrium constant values contained within the Hydra database of the MEDUSA software at $C_M = 1\mu M\ (a), 10\mu M\ (b), 1mM\ (c)$. Logarithmic diagram of the same system at $C_M = 1\mu M\ (d)$. For computing all species Eqs. (61), (60), (63) and (65) were used.

$$log \frac{[Cu(OH)_2^-]}{[Cu^{2+}]} = log\beta_2 + 2logK_w + 2pH = -16.24 + 2pH \quad (69)$$

$$log \frac{[Cu(OH)_3^-]}{[Cu^{2+}]} = log\beta_3 + 3logK_w + 3pH = -26.7 + 3pH \quad (70)$$

$$log \frac{[Cu(OH)_4^{2-}]}{[Cu^{2+}]} = log\beta_4 + 4logK_w + 4pH = -39.6 + 4pH \quad (71)$$

$$log \frac{\{Cu(OH)_2\downarrow\}}{[Cu^{2+}]} = -logK_s + 2logK_w + 2pH = -8.16 + 2pH \quad (72)$$

where it was assumed that $K_w = 10^{-14}$. As observed, the different predominance zones previously observed in Figure **3a** are clearly distinguished. However, this time the predominance of a species is determined by the uppermost straight line in each region. It is important to mention that Eq. (72) has a different meaning than the previous ones (67-71) as it serves as an auxiliary line from which precipitation can be analyzed. For the studied system, the precipitation condition in this type of representation is given by the following condition [36]:

$$log \frac{\{Cu(OH)_2\downarrow\}}{[Cu^{2+}]} - log \frac{[Cu^{2+}]}{[Cu^{2+}]} = -logC_{Cu} = 6 \quad (73)$$

which according to the diagram is accomplished at pH = 7.1, in agreement with the previous numerical results

(Figure **3a**) and in agreement with the evaluation using Eq. (54).

Although the diagram shown in Figure **5a** is very useful, it is not very easy from it to determine the predominance zone of $Cu(OH)_2\downarrow$. The logarithmic relative diagram representation can be further improved including Eq. (62) in the graphical treatment in the same form as done with the soluble species to obtain a new relationship that replaces Eq. (72):

$$log \frac{\{Cu(OH)_2\downarrow\}}{[Cu^{2+}]} = log\beta_2^* + 2logK_w + 2pH = -14.2 + 2pH$$
$$(74)$$

This equation represents a true relative abundance line of the precipitate, as Eqs. (67) to (71) do. In Figure **5b**, the modified logarithmic relative diagram including Eqs. (67) to (71) and (74) is presented. As shown, this diagram allows a straightforward visualization of the predominance zone of the precipitate making easier to draw the PZD shown below (Figure **5c**). This PDZ is in perfect agreement with results shown in Figures **3a** and **3d**.
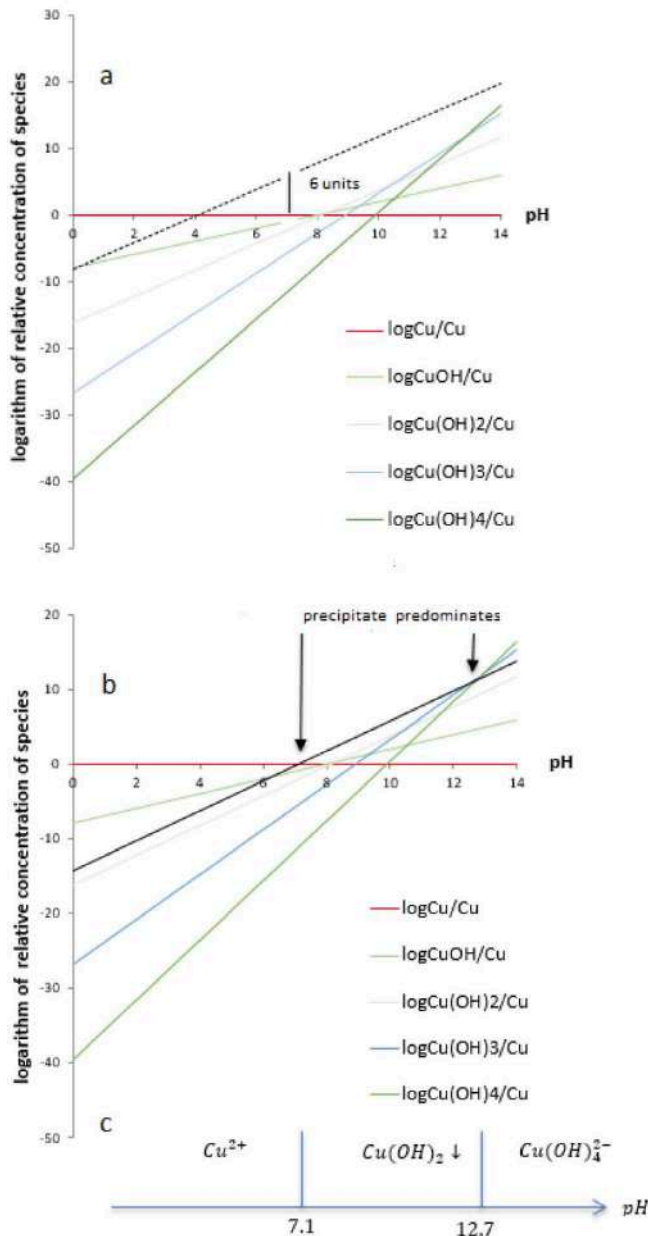
Figure 5: (a) Logarithm relative diagram for copper (II) hydrolysis evaluated with Excel using the equilibrium constant values contained within the Hydra database of the MEDUSA software and Eqs. (67) to (72). The black dotted line stands as an auxiliary relationship from which the starts of precipitation at $C_M = 1 mM$ is computed. (b) Modified logarithm relative diagram for the same system evaluated from Eqs. (67) to (71) and (74). (c) PDZ diagram computed from Fig. (b) showing the predominant species in each pH zone.

4. INCORPORATION OF THE HETEROGENEOUS FRACTION OF SPECIES CONCEPT IN TITRATION CURVES AND SIDE-REACTION (SPECIATION) COEFFICIENTS

Generalized Titration Curves

Following the procedure reported by de Levie [37] to compute acid/base, complexometric, and redox titration curves using explicit equations in terms of concentration, it is possible to generate that representation corresponding to the precipitation

titration of Cu^{2+} (dissolved initially as an strong electrolyte with initial volume V_0 at C_{Cu} concentration), considering the presence of its soluble complexes $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$ besides the $Cu(OH)_2 \downarrow$ solid species, through additions of the reagent OH^- (added as the strong electrolyte with v_{ad} volume at C_{OH^-} concentration) as further described.

Taking into account Cu^{2+} and H_2O as references, the proton condition of the system [4] is expressed by:

$$[H^+] - [OH^-] - \sum_{i=1}^{4} i\left[Cu(OH)_i^{2-i}\right] - 2\{Cu(OH)_2 \downarrow\} = -\frac{C_{OH^-} v_{ad}}{C_{Cu}V_0} \tag{75}$$

which can be expressed in terms of β_i as:

$$[H^+] - [OH^-] - [Cu^{2+}](\sum_{i=1}^{4} i\beta_i[OH^-]^i + 2\beta_2^*[OH^-]^2) = -\frac{C_{OH^-} v_{ad}}{C_{Cu}V_0} \tag{76}$$

Incorporating the heterogeneous fraction of species concept, Eq. (63), the above equation transforms to:

$$[H^+] - [OH^-] - \left(\frac{C_{Cu}V_0}{V_0+v_{ad}}\right)Z = -\frac{C_{OH^-} v_{ad}}{C_{Cu}V_0} \tag{77}$$

previous identification of the Z function [4], the average number of protons bound per Cu^{2+} species:

$$Z = ix_{Cu(OH)_i^{2-i}} + 2x_{Cu(OH)_2\downarrow} = x_{Cu^{2+}}(\sum_{i=1}^{4} i\beta_i[OH^-]^i + 2\beta_2^*[OH^-]^2) \tag{78}$$

Defining the fraction of titration, F, as:

$$F = \frac{C_{OH^-} v_{ad}}{C_{Cu}V_0} \tag{79}$$

once the autoprotolysis of water was included Eq. (77) is finally expressed as:

$$F = \frac{Z - \frac{[H^+] - K_W/[H^+]}{C_{Cu}}}{1 + \frac{[H^+] - K_W/[H^+]}{C_{OH^-}}} \tag{80}$$

This equation is important as it points out the degree of titration as a function of the evolution of the heterogeneous fraction of species of Cu^{2+}, as expected, in symmetry with the homogeneous fractions of species in acid/base, complexometric, and redox titrations [10]. As Eq. (80) express $F = f([H^+])$, it is possible to evaluate F for given values of pH using a spreadsheet[2]. In Figure **6** the titrations of several initial concentrations of $Cu(NO_3)_2$ with 0.01 mM $NaOH$ are shown. Clearly, Eq. 80 perfectly describes the expected behavior.

Homogeneous Side-Reaction Coefficients

Introduced by Gerold Schwarzenbach [19] and Anders Ringbom [20], side-reaction or speciation coefficients allow a simple form to account for the effect

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[2]Certainly, the deduction of continuous equations to represent titration curves for precipitation reactions is not new [13, 38], but previous approaches have not expressed the fraction of titration considering the presence of concomitant soluble species with a common ion, as done in the present methodology.

of simultaneous collateral reactions in a specific ionic equilibrium that is under study (the main reaction).
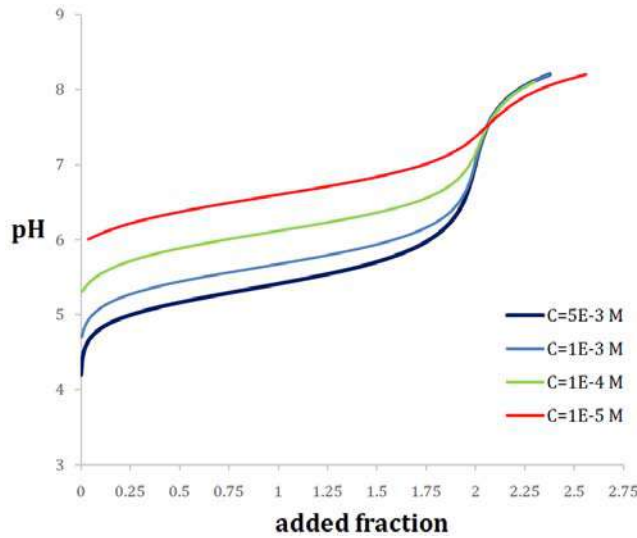

Figure 6: Titration curves of $Cu(NO_3)_2$ with 0.01 mM $NaOH$ at different initial copper (II) concentrations. The presence of the soluble complexes ($Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$) as well as the $Cu(OH)_2\downarrow$ solid species were considered in the simulation.

As an example of application, it is known that pectin (L^{z-}, where z = effective charge of the polyelectrolyte) is a polysaccharide that is largely present in the cell wall of plants, and in the flesh and peels of many fruits. It is used as gelling agents for food and as stabilizers for pulp drinks, in the production of biodegradable films for foods and in the pharmaceutical industry, as a carrier for drugs. Due to the presence of multiple carboxylate-binding sites in its structure, pectin can act as a sequestering agent for metal ions. For such reason, its use in different technical applications such as water and wastewater treatment, heavy metal removal in contaminated sites, metal recovery, etc. has been studied. At 0.1 M of ionic strength the following equilibrium constants are reported [39]:

Table 1: Reported Copper (II) / H^+/ Pectin (L^{z-}) Global Equilibrium Constants at 0.1 M of Ionic Strength

Equilibrium	$log\beta$
$L^{z-} + H^+ \Leftrightarrow HL^{1-z}$	3.77
$HL^{1-z} + H^+ \Leftrightarrow H_2L^{2-z}$	6.94
$Cu^{2+} + L^{z-} \Leftrightarrow CuL^{2-z}$	5.31
$Cu^{2+} + L^{z-} + H^+ \Leftrightarrow CuLH^{3-z}$	8.66

The effect of competing side reactions on Cu^{2+} complexation by L^{z-} can exert considerable influence on the main reaction such that the stability constant, β, is drastically altered. The alteration produces a conditional stability constant (β'), which is a realistic quantification of the stability of the complex under a set of conditions [20, 40]:

$$Cu^{2+}{}' + L^{z-}{}' \Leftrightarrow CuL^{2-z}{}' \qquad (81)$$
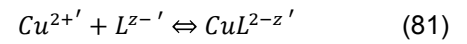
$$\beta' = \frac{[CuL^{2-z}{}']}{[Cu^{2+}{}'][L^{z-}{}']} \qquad (82)$$

where $Cu^{2+}{}'$ stands for the metal in all dissolved forms except CuL^{2-z}, $L^{z-}{}'$ for the ligand in all dissolved forms except CuL^{2-z}, and $CuL^{2-z}{}'$ for all forms of the reaction product.

According to the previous sections and using the data in Table **1** at $C_{Cu^{2+}} = 0.1\ mM$, conditional mass balance equations for all participating species in the main reaction are expressed as:

$$[Cu^{2+}{}'] = [Cu^{2+}] + \sum_{i=1}^{4}[Cu(OH)_i^{2-i}] = [Cu^{2+}](1 + \sum_{i=1}^{4}\beta_i[OH^-]^i) \qquad (83)$$

$$[L^{z-}{}'] = [L^{z-}] + \sum_{j=1}^{2}[H_jL^{j-z}] = [L^{z-}](1 + \sum_{j=1}^{2}\beta_j[H^+]^j) \qquad (84)$$

$$[CuL^{2-z}{}'] = [CuL^{2-z}] + [CuLH^{3-z}] = [CuL^{2-z}](1 + \beta_{CuL^{2-z}}^{H^+}[H^+]) \qquad (85)$$

where the side reaction coefficients, α_i, accounting for quantitative representations of all the competing side-reactions which tend to change the extent to which the main coordination reaction proceeds, are defined as:

$$\alpha_{Cu^{2+}(OH^-)} = \frac{[Cu^{2+}{}']}{[Cu^{2+}]} = 1 + \sum_{i=1}^{4}\beta_i[OH^-]^i \quad (86)$$

$$\alpha_{L^{z-}(H^+)} = \frac{[L^{z-}{}']}{[L^{z-}]} = 1 + \sum_{j=1}^{2}\beta_j[H^+]^j \quad (87)$$

$$\alpha_{CuL^{2-z}(H^+)} = \frac{[CuL^{2-z}{}']}{[CuL^{2-z}]} = 1 + \beta_{CuL^{2-z}}^{H^+}[H^+] \quad (88)$$

The relationship between both constants is then given by:

$$\beta' = \beta\frac{\alpha_{CuL^{2-z}(H^+)}}{\alpha_{Cu^{2+}(OH^-)}\alpha_{L^{z-}(H^+)}} \qquad (89)$$

From this equation, it is clear that β' has different values according to the pH of the solution, i.e., at pH = 7.0 $\beta' = 10^{5.26}$, where the predominant species of copper (II) in the homogeneous system is Cu^{2+}, while at pH= 9.5 the predominance of the $Cu(OH)_2$ soluble species reduces β' to $10^{2.48}$. However, these usual determinations of the α_i coefficients have been independent on considering precipitation reactions, in spike that insoluble hydroxide complexes may be formed depending on copper concentration (Figures **3**). If precipitation does occur, the solubility product constant fixes the dissolved free metal ion concentration, and the concentrations of all other dissolved species; consequently, the side-reactions coefficients should be affected in a form that cannot be easily accounted from the above equations.

Heterogeneous Side-Reaction Coefficients

Up to now, no information concerning the inclusion of precipitation reactions in side-reactions coefficients can be found in the literature in spite that commonly different insoluble species may be present in the system, e.g., hydroxide precipitates. This is a consequence of the extend use of the ion product or the use of logarithm diagrams to explain precipitation reactions, as these representations do not allow a simple incorporation of precipitation in the α_i mathematical structure. However, the inclusion of the fraction of species framework allows a straightforward generalization of side-reaction coefficients to heterogeneous systems due to the compatibility in structure that the heterogeneous fraction has with the homogeneous ones (Figures **1** and **2**). In such form, Eq. (83) is easily transformed to:

$$\left[Cu^{2+\prime}\right] = [Cu^{2+}] + \sum_{i=1}^{4}\left[Cu(OH)_i^{2-i}\right] + \{Cu(OH)_2 \downarrow\} = [Cu^{2+}](1 + \sum_{i=1}^{4}\beta_i[OH^-]^i + \beta_2^*[OH^-]^2) \quad (90)$$

with

$$\alpha_{Cu^{2+}(OH^-)} = \frac{\left[Cu^{2+\prime}\right]}{[Cu^{2+}]} = 1 + \sum_{i=1}^{4}\beta_i[OH^-]^i + \beta_{1,2}^*[OH^-]^2 \quad (91)$$

The last term in Eq. (91) has its usual meaning, i.e., relative abundance of the $Cu(OH)_2 \downarrow$ species, which depends on $C_{Cu^{2+}}$ by $\beta_{1,2}^*$, as expected.

5. CONCLUSIONS

The generalization of the fraction of species concept to precipitation reactions allows an easy form to fully integrate the ion product concept in a general ionic framework of homogeneous solutions, to obtain PDZ diagrams for soluble and insoluble species, to enrich the use logarithmic relative diagrams, to generate titration curves, and to generalize side-reaction coefficients to heterogeneous systems. The inclusion of precipitation reactions in the general ionic equilibrium framework of homogeneous solutions (acid/base, redox, and complex systems) is performed in a straightforward form using a modified equilibrium constant value, which is the constant corrected by the total concentration of the analyte, with the advantage that the structure of the fundamental equations and representations of the homogeneous solution framework is positively conserved. It was demonstrated that this modified and thermodynamically supported constant together with the implications of the approach are compatible with pre-nucleation clusters (PNCs) theory and well-established numerical and graphical methods of evaluation of solution equilibria. The new representation was successfully applied in the study of the hydrolysis of copper (II) in the absence and the presence of complexing ligands considering the precipitation of its hydroxide species using easy-to-compute algorithms of calculation.

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