

ASSESSMENT OF GRAPHICAL METHODS FOR THE
STUDY OF THE INTERACTIONS OF METAL IONS WITH
SOIL AND WATER ORGANIC MATTER

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Abstract

Scatchard, Buffle and van den Berg/Ruzic graphical methods for the analysis of complexation reactions of metal ions by soil and water organic matter (SWOM) samples using a simple 1:1 model, were assessed. Simulated and experimental (SWOM sample: Laurentian fulvic acid, FA) data sets were analysed. Simulated data shows that the presence of ligand heterogeneity results in deviations from linearity of the Scatchard and Buffle plots, while van den Berg/Ruzic plots remains linear. Average conditional equilibrium constants (K) and ligand concentration (L_T) can be estimated from van den Berg/Ruzic plots. The graphical analysis of experimental data for the system FA plus Cu(II), obtained with a Cu(II) ion selective electrode, shows that the sample is characterised by ligand heterogeneity. The equilibrium parameters obtained from van den Berg/Ruzic plots are the following (standard deviation in parentheses): $\text{Log } K = 5.56(1)$; $L_T = 44(2) \mu\text{M}$ [$\{L\} = 1.76(8) \text{ mmol/g FA}$].

Keywords: Complexation reactions; soil and water; graphical methods; Scatchard method; Buffle method; van den Berg/Ruzic method; fulvic acids.

1. INTRODUCTION

Electrochemical techniques, particularly potentiometric and voltametric methods, are suitable to monitor the speciation of metal ions in the environment [1]. Indeed, potentiometric methods allow the rapid direct measurement of the concentration of the ionic species in the solution under analysis, showing detection limits in the micromolar range, while ion selective electrodes (ISE) are particularly suitable to detect the free metal ion without disturbing chemical equilibrium. Voltametric methods involve electrolytic detection steps, and usually show lower detection limits. However, this family of methods is subject to a great number of interferences, for example adsorption. Equilibrium constants calculated from voltametric data are usually higher than those calculated from potentiometric data [2].

Studies of metal ion speciation in environmental compartments have to include soil and water organic matter (**SWOM**) as important ligand species. Indeed, **SWOM** is ubiquitous in environment and has the capacity of strong metal ion complexation [1,3]. The major constituents of **SWOM** are the humic substances (**HS**). The fraction of **HS** called fulvic acids (**FA**) is particularly reactive in the association with metal ions because it is highly soluble in water and has a relatively high concentration of oxygen organic functionalities (carboxylic, hydroxylic and phenolic structures) that give origin to ligand structures with the capacity to form metal ion quelates [3].

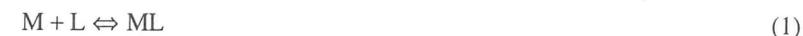
Data analysis approaches usually employed in the treatment of electrochemical experimental data involve graphic methods or computational fittings of non-linear models. The last procedure can only be successfully used if the chemical system under analysis is completely characterized (concentration and structure of the chemical species). This is not the case for **SWOM**, which can be classified as quite fuzzy substances. For this reason, the study of chemical equilibrium or speciation of metal ions in natural soil or water is usually done with the aid of graphical methods [1,3-15].

Although **SWOM** has a quite complex nature, as far as the complexation of metal ions is concerned, macroscopically only one main ligand structure is usually observed to play an important role in that phenomenon. As consequence, the analysis of experimental data is usually done using simple 1:1 (ligand: metal ion) complexation models [16-22]. Based on this model, three linear equations have been proposed and named after their authors: (i) Scatchard [1,3-9]; (ii) Buffle [10,11]; and, (iii) van den Berg/Ruzic [12-15].

The objectives of this paper is to assess the ability of the three graphical methods to generate information about the interaction of a **FA** sample with Cu(II). Before the analysis of potentiometric experimental data acquired with Cu(II) ion selective electrodes at pH 6 and at 25 mg/L **FA** concentration, a simulation study was performed to study the effect of ligand heterogeneity in the results obtained by graphical methods.

2. THEORY

The interaction of metal ions (M) with ligands (L) existing in **SWOM** is usually expressed by the simple complexation equilibrium equation (charges omitted for simplification),



and by the corresponding conditional equilibrium constant (K) expression,

$$K = \frac{[ML]}{[M][L]} \quad (2)$$

where [ML], [L] and [M] are the equilibrium molar concentration of the complex species (ML), free ligand (L) and free metal ion (M).

Combining the equilibrium constant expression with the material balances of the ligand and metal ions, the following three different model expressions are obtained [1,3-15]:

$$\frac{[M]_r - [M]}{\{L\}[M]} = \frac{K}{MM_L} - K \frac{[M]_r - [M]}{\{L\}} \quad (3)$$

$$\frac{\{L\}}{[ML]} = \frac{MM_L}{K} \frac{1}{[M]} + MM_L \quad (4)$$

$$\frac{[M]}{\{[M]_r + \Delta[M]\} - [M]} = \frac{1}{K[L]_r} + \frac{1}{[L]_r} [M] \quad (5)$$

where $[M]_T$ and $[L]_T$ are the total metal ion and ligand concentrations, respectively; $\{L\}$ is the total ligand concentration expressed as g/L; MM_L is the molar mass of the ligand species; and $\Delta[M]$ is the increment in the total metal ion concentration.

Equations 3 to 5 are known as Scatchard [1,3-9], Buffle [10,11] and van den Berg/Ruzic [12-15] equations, respectively. If the simple 1:1 complexation model is observed, the plot of these equations should give a linear representation, allowing the estimation of K and MM_L .

3. DATA SIMULATION

3.1 – Simulation equations

All simulations performed in this work were based on a one ligand to one metal ion complexation. Several simulations were done for different ligand type mixtures.

When only one ligand type is presented, the following relationship between K, $[M]$, $[M]_T$ and $[L]_T$ is observed,

$$K[M]^2 + [M](-K[M]_T + 1 + K[L]_T) - [M]_T = 0 \quad (6)$$

The free concentration of metal ion ($[M]$) can be calculated for any value of the other parameters after resolution of the second order equation.

A general equation that can be used for the simulation of complexation titrations for any mixture of different types of ligands (nL – number of ligand types) is the following,

$$[M] - [M]_T + \sum_{n=1}^{nL} \frac{K_n \times [L]_T}{\frac{1}{[M]} + K_n} = 0 \quad (7)$$

The free concentration of M corresponds to the root of this non-linear equation, which can be calculated, for example, using the Solver function of Microsoft Excel.

3.2 – Simulation models

Four simulation models were used in this work: Sim1 – one type of ligand ($K = 4.0 \times 10^5 \text{ M}^{-1}$); Sim2 – two different types of ligands (L1 and L2) having somewhat similar complexation constants ($K_{L1} = 4.0 \times 10^5 \text{ M}^{-1}$ and $K_{L2} = 4.0 \times 10^4 \text{ M}^{-1}$); Sim3 – two different types of ligands (L1 and L2) having somewhat different complexation constants ($K_{L1} = 4.0 \times 10^5 \text{ M}^{-1}$ and $K_{L2} = 4.0 \times 10^3 \text{ M}^{-1}$); and, Sim4 – ten different types of ligands whose stability constants ranges from 1.0×10^5 to $1.0 \times 10^3 \text{ M}^{-1}$. The total ligand concentration was $5.0 \times 10^{-5} \text{ M}$ for Sim1 ($MM_{L1} = 1000 \text{ g/mol}$), Sim2 ($MM_{L1} = MM_{L2} = 500 \text{ g/mol}$) and Sim3 ($MM_{L1} = MM_{L2} = 500 \text{ g/mol}$), and $1.0 \times 10^{-4} \text{ M}$ for Sim4 ($MM_{Li} = 100 \text{ g/mol}$, $i=1$ to 10). $[M]_T$ ranged from 1×10^{-7} to $1 \times 10^{-1} \text{ M}$.

4. EXPERIMENTAL SECTION

4.1 – Reagents and solutions

A sample of a Laurentian FA was purchased from Fredriks Research Products (The Netherlands). 25 mg/L FA solutions were prepared in 0.1 M potassium nitrate solution. For adjusting the FA solutions to pH 6, a decarbonated 0.05 M potassium hydroxide solution was used.

4.2 – Instruments

The experiments were made with a PC controlled system assembled with two Crison MicropH 2002 pH meters and a Crison MicroBu 2031 microburette, a Metler Toledo U262-S7/120 glass electrode, an Ingold 373-90-WTE-ISE-S7/105-120 (double junction) reference electrode, and a Cu(II) Orion ion selective electrode model 9429. The pH electrode was calibrated with two buffer solutions with ionic strength adjusted to 0.1 M. The experiments were conducted at 25 °C under nitrogen. After initial pH adjusting, the procedure sequence was the following: (i) addition of metal ion solution; (ii) pH verification and readjust if necessary with decarbonated potassium hydroxide solution; (iii) potential readings. ISE was calibrated at the end of the experiments, when the metal ion concentration was much higher than the ligand concentration.

4.3 – Calculations

All data analysis was done using standard functions and “Solver” from a spreadsheet (Microsoft Excel).

5. RESULTS AND DISCUSSION

5.1 Simulated data

Figs. 1 and 2 present the plots of the three graphical methods for the four simulated data sets.

Scatchard plots.

The Scatchard plots (Figs. 1.a, d, g and j) are curvilinear for all data sets but for Sim1. Indeed, a linear representation is only observed for the model that exactly fits the expected 1:1 complexation (Fig. 1.a, Sim1). The other three plots show an upward curvature resulting from the existence of more than one ligand type. These results show that Scatchard plots are highly sensitive to ligand heterogeneity and, consequently, can be used as a pre-processing diagnostic analysis of unknown composition ligands. As shown in Table 1, as expected, the calculated K and $[L_n]$ for Sim1 are exactly those used in the simulation.

There are studies that suggests that when a mixture of two different ligands are present in a mixture, Scatchard plots can be used for the estimation of the equilibrium information of the two ligands by adjusting to a straight line the two extremes of the curve [1,3,5-9]. This procedure was tried for the two simulated data sets that correspond to a mixture of two different ligands, Sim2 and Sim3 (as shown in Figs. 1.d and g) with the results presented in Table 1. Although there are some problems in the selection of the correct number of points to be included in the linear fitting (this selection is always somewhat arbitrary), the estimate of the logarithm of the equilibrium constants is good for $\text{Log } K_1$ and reasonable for $\text{Log } K_2$ (relative error about 6 and 10% for Sim2 and Sim3, respectively). However, as shown in Table 1, the estimates of $[L_n]$ are not always satisfactory, particularly those corresponding to the second and weaker ligand. In these two cases the quantitative analysis was not completely successful because of two main factors: (i) the number of points to be selected is somewhat arbitrary due to the overlap

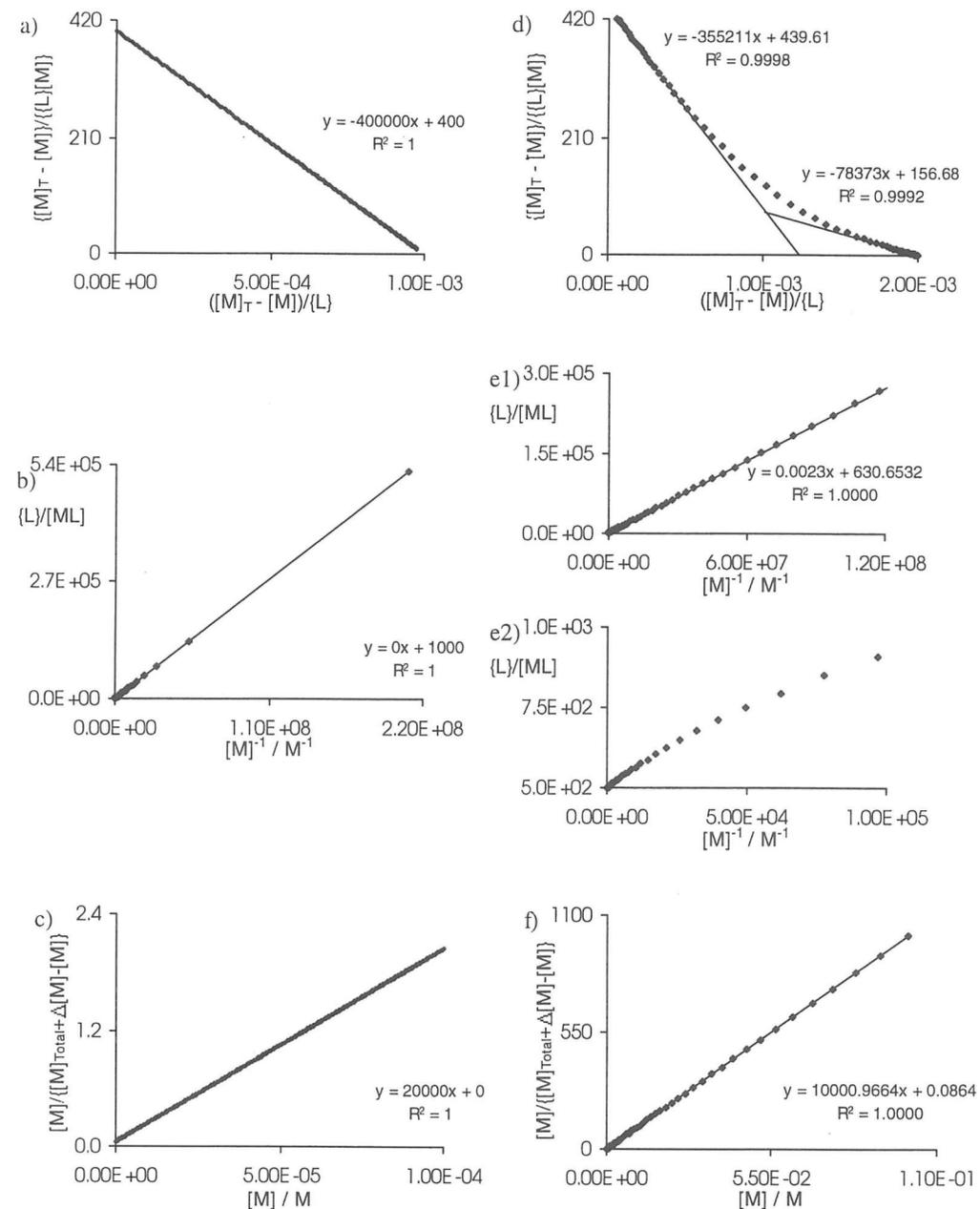


Fig. 1 – Plots of Sim1 [(a) – (c)] and Sim2 [(d) – (f)] simulated data. Scatchard, [(a), (d), (g) and (j)]; Buffle, [(b), (e), (h1), (h2), (k1) and (k2)]; and van den Berg / Ruzic [(c), (f), (i) and (l)] plots.

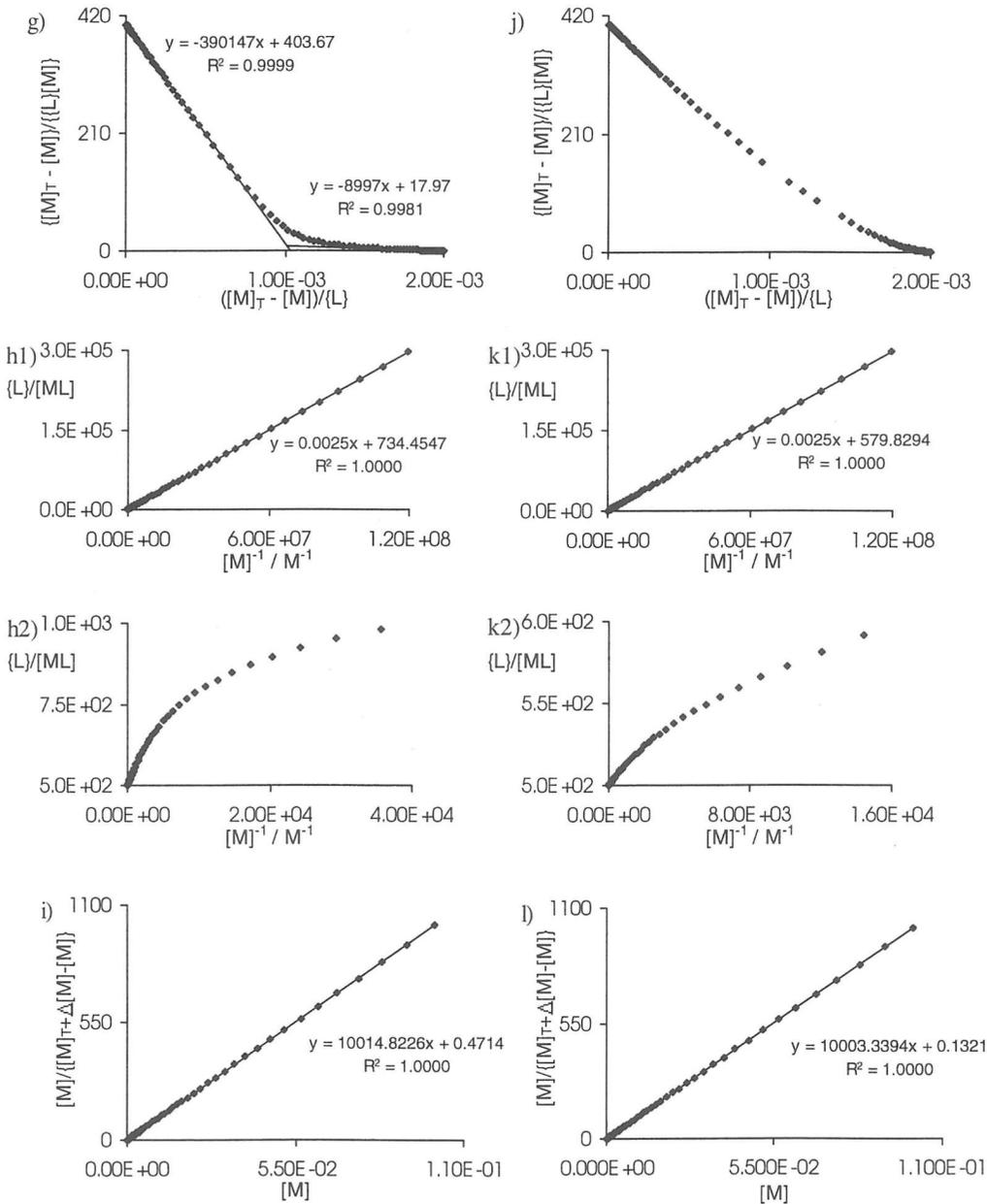


Fig. 1 (Continuation) – Plots of Sim3 [(g) – (i)] and Sim4 [(j) – (l)] simulated data. Scatchard, [(g) and (j)]; Buffle, [h1), h2), k1) and k2)]; and van den Berg / Ruzic [i) and l)] plots.

Table 1 – Results of simulated and experimental sets.

Method	Log K		$[L_n] / M^c$	
	Calculated value	error % ^a	Calculated value	error % ^b
Sim1				
Scatchard	5.60	0	5.00×10^{-5}	0
Buffle	5.60	0	5.00×10^{-5}	0
van den Berg / Ruzic	5.60	0	5.00×10^{-5}	0
Sim2				
Scatchard	Log $K_1 = 5.55$	0.93	$[L_1] = 6.19 \times 10^{-5}$	23.80
	Log $K_2 = 4.89$	6.26	$[L_2] = 1.00 \times 10^{-4}$	100.0
Buffle	5.41	6.04	7.93×10^{-5}	20.7
van den Berg / Ruzic	5.06	0.82	1.00×10^{-4}	0.0
Sim3				
Scatchard	Log $K_1 = 5.59$	0.22	$[L_1] = 1.24 \times 10^{-4}$	148.0
	Log $K_2 = 3.95$	9.66	$[L_2] = 2.78 \times 10^{-3}$	5460
Buffle	5.47	18.86	6.81×10^{-5}	31.9
van den Berg / Ruzic	4.33	5.91	9.99×10^{-5}	0.1
Sim4				
Buffle	5.37	5.17	8.62×10^{-5}	13.8
van den Berg / Ruzic	4.88	4.43	1.00×10^{-4}	0.0
AFLau				
van den Berg / Ruzic	5.56(1)	--	$4.4(2) \times 10^{-5}$	--

a – In Buffle and van den Berg / Ruzic methods, this value was calculated in relation to the mean of Log K_n values used in the simulations;

b – In Buffle and van den Berg / Ruzic methods, this value was calculated in relation to the sum of $[L_n]$ values used in the simulations.

c – In Buffle and Scatchard methods, $[L]_T$ was determined knowing that $[L]_T = \{L\} / MM_1$.

of the two ligands complexation equilibria; and, (ii) because the second ligand has relatively weak complexation properties, the ligand is not completely associated with the metal ion and, consequently, the observed Scatchard plot corresponds only to the beginning of the complexation.

The Scatchard plot of Sim4 data set cannot easily be adjusted to two or more straight lines and, in this case, there is no possible quantitative solution.

Buffle plots.

When all the available data is included in the Buffle plots (Figs. 1.b, e, h and k) they are apparently linear (Figs. 1.b, e1, h1 and k1). However, when only the data points that correspond to higher total metal ion concentrations (left side of the abscissas axis) are used in the analysis, the plots that correspond to mixtures of ligands show a downward curvature. This result shows that Buffle method is less sensible to ligand heterogeneity than the Scatchard method.

The analysis of Table 1 show that the equilibrium parameters estimated from the linear fit of the plots when all simulated data is used in calculations roughly corresponds to the average equilibrium constant and to the sum of the total ligand concentration.

It should be noted that when experimental points are available, the section of the plot that shows a linear behaviour (lower metal ion concentrations) is not available, or the corresponding data points are affected by a relatively greater error. Indeed, because this section corresponds to the lower concentration range the free metal ion measurements, is usually quite imprecise.

van den Berg/Ruzic plots.

The van den Berg/Ruzic plots (Figs. 1.c, f, i and l) are linear in all the range of data points. This result shows that this type of plot is insensitive to the heterogeneous properties of the ligand.

The analysis of Table 1 show that the equilibrium parameters estimated from the linear fit of the plots corresponds to the average equilibrium constants and to the sum of the total ligand concentrations – all the estimates have small relative errors.

5.2 Experimental data

Fig. 2 shows the representation of the three graphical methods that correspond to the experimental data of the system FA+Cu(II). The analysis of this figure shows that

the Scatchard and Buffle plots (Figs. 2.a and b) deviate markedly from linearity, as observed for the heterogeneous simulated models (Sim2, Sim3 and Sim4). This result shows that the main ligand of FA should be understood as fuzzy or heterogeneous structures.

The van den Berg/Ruzic representation shows a linear shape (Fig. 2.c). From the least squares fitting of eq. 5 (theory section) to the experimental data, the conditional equilibrium constant and total ligand concentration can be estimated (Table 1). The logarithm of K [5.56(1)] should be considered as an average value, and is in the range usually found for the FA complexation of Cu(II) at pH 6 [16,17,20,21]. The total quantity of ligand structures detected by this procedure is 1.76(8) mmol/g FA [under the experimental conditions used in this work this quantity corresponds to 44(2) mM].

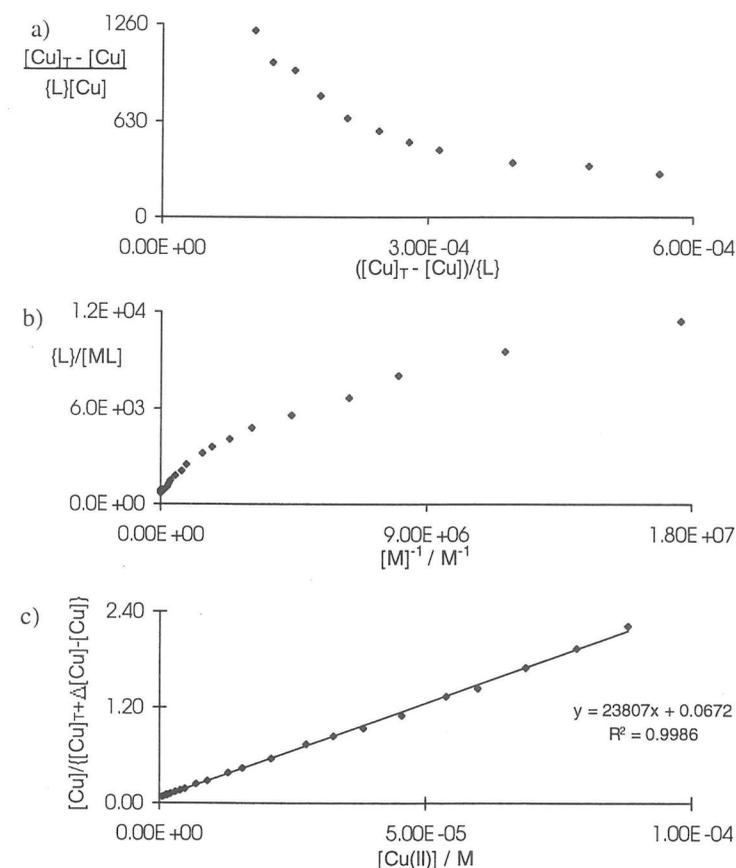


Fig. 2 – FA+Cu(II) experimental data plots: (a) Scatchard's plot; (b) Buffle's plot; and, (c) van den Berg / Ruzic plot.

6. CONCLUSIONS

The work reported in this paper shows that graphical methodologies of metal ion complexation analysis are a valuable approach for the study of **SWOM** complexation properties, either from a qualitative or from a quantitative perspective.

To obtain qualitative information about the ligand structure, Scatchard and Buffle plots give some insight on its heterogeneity characteristics. Furthermore, quantitative information can be obtained from van den Berg/ Ruzic plots, namely the conditional equilibrium constants (average values in the case of a mixture of heterogeneous ligands) and total ligand concentration.

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