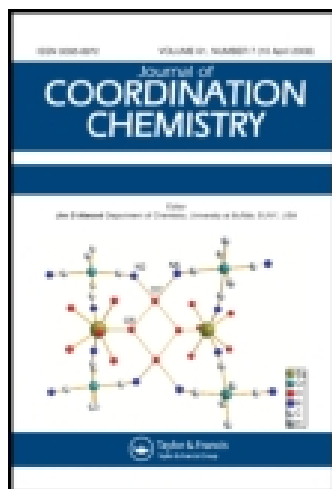


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Emf(H) data analysis of weak metallic complexes using reduced formation functions

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A general method for the study of weak metal complexes by emf(H) measurements has been developed using reduced formation functions instead of classical formation functions. This approach consists of subtracting the contribution of the products of the hydrolysis (protolysis) of the metallic cation (anion), as well as the possible protonated species of the ligand from the total number of associated H^+ , and from the total concentrations of metal or ligand, observing only the contribution of the reaction of interest. This was carried out using the FONDO version of the generalized least-squares computer program LETAGROP, written to analyze these reduced formation functions. The aim of this communication was to show in greater detail than in previous publications the data analysis of reactions in solution using these reduced formation functions. The method is illustrated using emf(H) data for the three-component systems H^+ –Be(II)–serine, H^+ –Mo(VI)–NTA and H^+ –V(IV)–V(V) investigated recently.

Keywords: Emf(H) data analysis; Weak metallic complexes; Reduced formation functions; Stability constants; FONDO version; LETAGROP program

1. Introduction

Experimental techniques as well as graphical methods and computer programs have been developed for the determination of equilibrium constants in solution [1–3]. Thus, in the early 1960s, with the arrival of digital computers, the first versions of the generalized least-squares program LETAGROP were developed to complement the graphical methods used up until then [4–9]. Later, different kinds of least-squares

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programs, such as MINQUAD, SUPERQUAD, HYPERQUAD [10], POLET [11] and LAKE [12], came into common use.

In dealing with solution equilibrium, the initial step is determination of the stoichiometry and the stability of the species formed, the law of mass action (activity factors held constant by ionic medium) being the basis of all such work [1,2].

The symbols used in the present paper are the same as those adopted in previous work; chemical symbols are in roman and concentrations in italic type [13–17]. In particular, we consider a system where three reagents (omitting charges), H^+ ($=H$), a metallic ion $B^{n\pm}$ ($=B$) and a ligand C^{m-} ($=C$), form one or several complexes $H_pB_qC_r$, (p, q, r) in brief, according to the general reaction (1), each with a formation constant β_{pqr} .



Then we have the law of mass action (2),

$$c_{pqr} = [H_pB_qC_r] = \beta_{pqr} h^p b^q c^r \quad (2)$$

where h, b, c and c_{pqr} are the equilibrium concentrations of reagents H, B, C and complex (p, q, r), respectively. The mass balance for the total (analytical) concentrations H, B and C , and the average number of H^+ bound per B, Z_B , or per C, Z_C , are given by the expressions (3)–(5), respectively, where K_w is the water dissociation constant.

$$H - h + K_w h^{-1} = BZ_B = CZ_C = \sum_p \sum_q \sum_r p \beta_{pqr} h^p b^q c^r \quad (3)$$

$$B = b + \sum_p \sum_q \sum_r q \beta_{pqr} h^p b^q c^r \quad (4)$$

$$C = c + \sum_p \sum_q \sum_r r \beta_{pqr} h^p b^q c^r \quad (5)$$

The electromotive force measurement, $\text{emf}(H)$, is a well-established method for studying equilibria in solution [13]. If we know H, B and C by analysis and we measure h with a reversible electrode to H^+ , the primary experimental data (emfs, analysis, volumes) can be given in terms of the formation functions (6) or (7),

$$Z_B = (H - h + K_w h^{-1}) / B = \sum_p \sum_q \sum_r p c_{pqr} / \left(b + \sum_p \sum_q \sum_r q c_{pqr} \right) \quad (6)$$

$$Z_C = (H - h + K_w h^{-1}) / C = \sum_p \sum_q \sum_r r c_{pqr} / \left(c + \sum_p \sum_q \sum_r r c_{pqr} \right) \quad (7)$$

as $Z_B(\log h, B, C)$ or $Z_C(\log h, B, C)$, most suited for mathematical treatment [6].

In these equations the products of hydrolysis or protolysis ($p, q, 0$) of the metallic ion according to reactions (8) or (9), respectively, as well as the possible acid species ($p, 0, 1$) of the ligand formed after reaction (10), are included.



When the complexes (*p*, *q*, *r*) are too weak, it is necessary to use the appropriate ligand/metal ratio, *R*, such that these species can be formed in appreciable amounts. Undoubtedly, excess ligand could also mask the contribution of these complexes and it is sometimes difficult to detect them by analyzing the formation functions (6) and (7). In these circumstances, we have found that it is possible to achieve a more efficient approach to the problem, besides visualizing it graphically in the $Z(\log h, B, C)$ dimensions, using instead of the relationships (6) and (7), the reduced formation functions Z_{Bf} [equation (11)] and Z_{Cf} [equation (12)],

$$Z_{Bf} = \left(BZ_B - \sum_p \sum_q p c_{pq0} - \sum_p p c_{p01} \right) / \left(B - \sum_p \sum_q q c_{pq0} \right) \quad (11)$$

$$Z_{Cf} = \left(CZ_C - \sum_p \sum_q q c_{pq0} - \sum_p p c_{p01} \right) / \left(C - \sum_p p c_{p01} \right) \quad (12)$$

where c_{pq0} denotes the equilibrium concentration of the products of the hydrolysis or protolysis of the metallic ion, reactions (8) or (9), and c_{p01} the equilibrium concentration of the ligand acid species, reaction (10), the stability constants of which are known from previous experiments under identical conditions (temperature, ionic medium, total concentrations *H*, *B* and/or *C*, etc.).

The fundamental purpose of the present communication was to explain in greater detail than in previous publications [14–17] the analysis of data of reactions in solution using these reduced formation functions.

2. Experimental

In this section we provide only information on computational work. The data treatment consists of subtracting from the total number of associated H^+ , BZ_B , or $CZ_C = (H - h + K_w h^{-1})$, and from the total concentration *B* or *C*, respectively, the contribution of reactions (8) or (9) and (10), as well as, if this were the case, the contribution of some other particular species (*P*, *Q*, *R*) whose stability constant β_{PQR} was known. Then, we only observe the contribution of the species of the reaction (1) of interest.

This has been carried out by using the so-called FONDO† version of LETAGROP [18], written to analyze the functions (11) and (12)‡. However, this procedure can be

†FONDO is a Spanish word meaning the contribution of background species (*p*, *q*, 0) and (*p*, 0, 1), and also, if it were the case, any other complex with a well-known equilibrium constant.

‡In our case, its implementation consisted substantially of modifying the procedure APFEL of the block UBBE of LETAGROP. For instance, in the case of function (11), it would be as follows, coded in Turbo Pascal 7:

```
BZB := H - h + Kw*h-1; BEGIN yy[1]:=0; xx[1]:=0; For ix:=ag3 to ag4 DO Begin yy[ix]:=yy[ix-1]+p[ix]*c[ix]; [ix]:=xx[ix-1]+q[ix]*c[ix] End; ZBf := (BZB-yy[ag4])/(B-xx[ag4]); yyy[1]:=0; xxx[1]:=b; For ix:=ag5 to ag6 DO begin yyy[ix]:=yyy[ix-1]+p[ix]*c[ix]; xxx[ix]:=xxx[ix-1]+q[ix]*c[ix] end; ZBf := yyy[ag6]/xxx[ag6]; fel := (ZBf-ZBf*) END;
```

ag3 and *ag4* (*ag5* and *ag6*) being the lower and upper *nk* values of the FONDO species (remaining complexes) given in *Rurik*=6, respectively. Therefore, the equilibrium constants in *Rurik*=7 should be given in the following order: metal hydrolysis or protolysis constants, ligand acidity constants, and equilibrium constants of the remaining complexes.

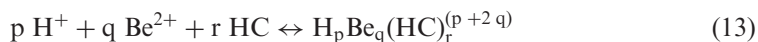
used in any computational program that deals with the formation functions (6) and (7) [11,12] or similar ones [19].

3. Results and discussion

The term FONDO was introduced in 1987 during the study of the systems H^+-Be^{2+} -IDA (IDA = iminodiacetic acid), H^+-Be^{2+} -MIDA (MIDA = *N*-methyliminodiacetic acid), H^+-Be^{2+} -EIDA (EIDA = *N*-ethyliminodiacetic acid) and H^+-Be^{2+} -PIDA (PIDA = *N*-propyliminodiacetic acid) by means of emf measurements in 0.5 M $NaClO_4$ ionic medium at 25° C [14]. Later, the FONDO treatment was used successfully in the study of the H^+-VO^{2+} -glutathione [15], H^+-VO^{2+} -carnosine [16] and $H^+-Cr(III)$ -glutathione [17] systems. Now, with the aim of explaining the better performance of the FONDO version than that shown in previous references [15–17], a summary is given below of the results obtained by its application to other recently investigated three-component systems.

3.1. $H^+-Be(II)$ -*D,L*-serine system

The chemistry of Be(II) with different ligands has been an area of interest to us for many years [20]. In particular, the system H^+-Be^{2+} -*D,L*-serine (HC) was recently studied by emf(H) measurements in 3.0 M $NaClO_4$ ionic medium at 25° C, according to reaction (13), using the ratios $R=4, 8$ and 16 [21,22].



Figures 1 and 2 show our results in terms of $Z_B(\log h)$ and $Z_{Bf}(\log h)$, respectively, assuming that $FONDO = [Be_2(OH)]^{3+}$, $[Be_3(OH)_3]^{3+}$, $[Be_5(OH)_6]^{4+}$, $[Be(OH)_2]$, H_2C^+

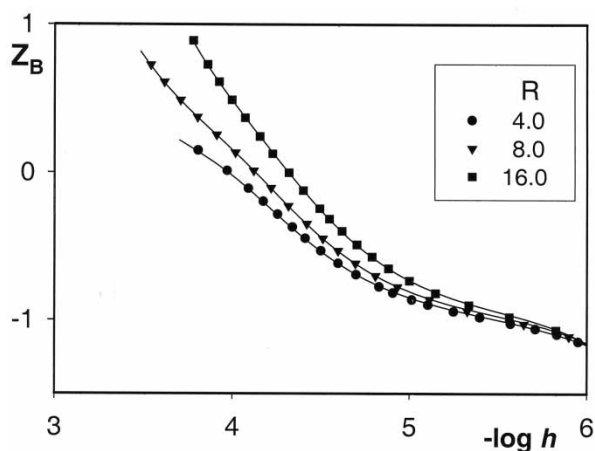


Figure 1. Z_B , average number of H^+ associated per mol of Be(II) vs $-\log h$ for the system H^+-Be^{2+} -serine (H_2C) in 3.0 M $NaClO_4$ ionic medium at 25° C, for $B=8.27$ mM and ratios $R=4.0$ (\square), 8.0 (Δ) and 16.0 (\bullet), according to reaction (13). The lines represent theoretical curves calculated with the equilibrium constants of table 1 (column 2).

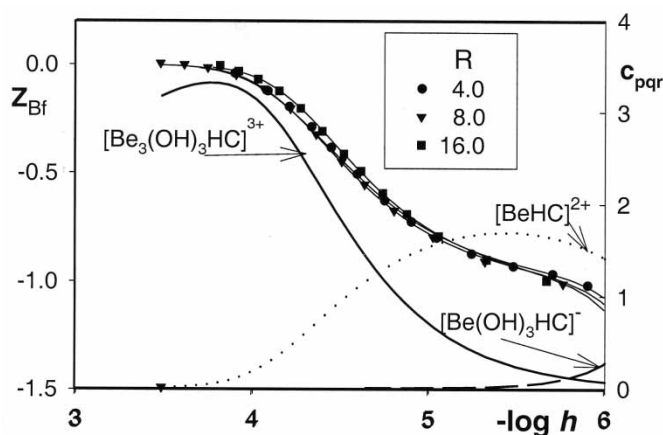


Figure 2. (a) Z_{Bf} vs $-\log h$ for the system $\text{H}^+ - \text{Be}^{2+} - \text{serine (HC)}$ in 3.0 M NaClO_4 ionic medium at 25° C, for $B = 8.27$ mM and ratios $R = 4.0$ (\square), 8.0 (Δ) and 16.0 ($+$), according to reaction (13) and assuming that $\text{FONDO} = [\text{Be}_2\text{OH}]^{3+}$, $[\text{Be}_3(\text{OH})_3]^{3+}$, $[\text{Be}_5(\text{OH})_6]^{4+}$, $[\text{Be}_6(\text{OH})_8]^{4+}$, $\text{Be}(\text{OH})_2$, H_2C^+ and C^- species. The lines represent theoretical curves calculated with the equilibrium constants of table 1 (column 3). (b) Species distribution diagram for $B = 10$ mM and ratio $R = 8$.

Table 1. Equilibrium constants for the system $\text{H}^+ - \text{Be}^{2+} - \text{serine (HC)}$ in 3.0 M NaClO_4 ionic medium at 25° C according to reaction (13).

Species	$\log \beta_{\text{pqr}} (3\sigma)$	
	LETAGROP [18]	FONDO
$[\text{Be}(\text{HC})]^{2+}$	1.244 (4)	1.045 (5)
$[\text{Be}_3(\text{OH})_3(\text{HC})]^{3+}$	7.045 (8)	7.042 (9)
$[\text{Be}(\text{OH})_3(\text{HC})]^-$	16.18 (2)	16.18 (2)
$\sigma(Z_{\text{B}})$	0.007	
$\sigma(Z_{\text{Bf}})$		0.010
Refs	[21, 22]	[21, this work]

and C^- species. Figure 2 also shows the species distribution diagram for $B = 10$ mM and $R = 8$.

The experimental data are in the range $-1 \leq Z_{\text{Bf}} \leq 0$, which led us to assume that two important reactions are probably taking place in the system, one that does not liberate or consume H^+ and another in which at least one mole of H^+ is liberated by the metal to form $[\text{Be}(\text{HC})]^{2+}$ ($Z_{\text{Bf}} \rightarrow 0$) and $[\text{Be}_3(\text{OH})_3(\text{HC})]^{3+}$ ($Z_{\text{Bf}} \rightarrow -1$) complexes, respectively. Nevertheless, at $-\log h > 5.8$ this model did not fit the data well, indicating an additional reaction that involves liberation of a larger amount of H^+ . However, because $\text{Be}(\text{OH})_2(\text{s})$ precipitates at $-\log h \approx 6$, only small amounts of this supposed species should theoretically prevail at basic $-\log h$. At first, the $[\text{BeC}]^+$ and $[\text{Be}_3(\text{OH})_3\text{C}]^{2+}$ complexes were considered, which did not improve the fit, but when $[\text{Be}(\text{OH})_3(\text{HC})]^-$ was included, excellent agreement was achieved. Table 1 contains the equilibrium constants as well as the standard deviations $\sigma(Z_{\text{B}})$ and $\sigma(Z_{\text{Bf}})$ determined with LETAGROP [18] and its FONDO version, the values obtained being the same order of magnitude, indicating the accuracy of the method.

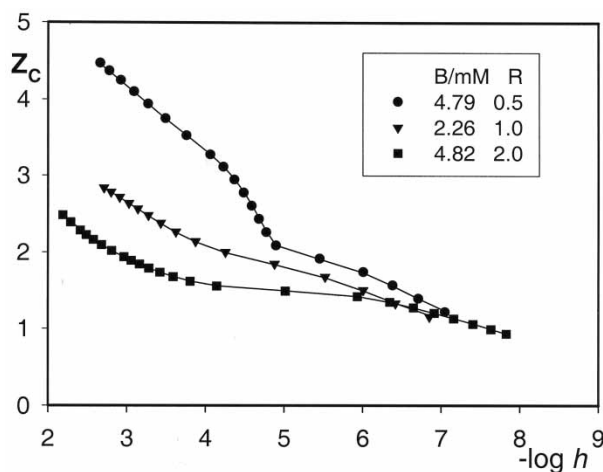
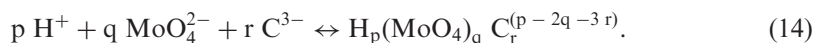


Figure 3. Z_C , average number of H^+ associated per mol of NTA as a function of $-\log h$ for the system $H^+-MoO_4^{2-}-NTA$ (H_3C) in 1.0 M NaCl ionic medium at 25°C, for $(B/mM, R) = 4.79, 0.5$ (\bullet), 2.26, 1.0 (\blacktriangle) and 4.82, 2.0 (\blacksquare), according to reaction (14). The lines represent theoretical curves calculated with the equilibrium constants of table 2 (column 2).

3.2. $H^+-Mo(VI)-NTA$ system

The system $H^+ - MoO_4^{2-} - NTA$ ($NTA = \text{nitrilotriacetic acid, } H_3C$) was studied by means of emf(H) measurements in 1.0 M NaCl at 25°C, according to reaction (14) and using the ratios $R = 0.5, 1$ and 2 [23].



This system was previously studied by Cruywagen *et al.* [19] in the same ionic medium and at the same temperature.

Figures 3 and 4 present our results in terms of $Z_C(\log h)$ and $Z_{Cr}(\log h)$, respectively, assuming that $FONDO = [Mo_7O_{24}]^{6-}, [HMo_7O_{24}]^{5-}, [H_2Mo_7O_{24}]^{4-}, [H_3Mo_7O_{24}]^{3-}, [HMoO_4]^{-}, H_2MoO_4, HC^{2-}, H_2C^{-}, H_3C$ and H_4C^+ species. The data are in the ranges $0.5 \leq Z_{Cr} \leq 3.5$ and $2 \leq -\log h \leq 8$, indicating the presence of the monomers $[HMoO_4C]^{4-}$ ($Z_{Cr} \rightarrow 1, pK_a = 9.5$), $[H_2MoO_4C]^{3-}$ ($Z_{Cr} \rightarrow 2, pK_a = 8.2$), $[H_3MoO_4C]^{2-}$ ($Z_{Cr} \rightarrow 3, pK_a = 3.3$) and $[H_4MoO_4C]^{-}$ ($Z_{Cr} \rightarrow 4, pK_a = 1.6$), as well as the dimers $[H_8(MoO_4)_2C_2]^{2-}, [H_5(MoO_4)_2C]^{2-}$ and $[H_6(MoO_4)_2C]^{2-}$ at $-\log h < 4$, which are less abundant than the monomer species at low B values.

Table 2 contains the equilibrium constants and also the standard deviations $\sigma(E)$, $\sigma(Z_C)$ and $\sigma(Z_{Cr})$ determined with SUPERQUAD [10b], HYPERQUAD [10d], LETAGROP [18] and its FONDO version, respectively. Both the equilibrium constants and the deviations $\sigma(Z_C)$ and $\sigma(Z_{Cr})$ are of the same order of magnitude, indicating the goodness of the fit.

Even though HYPERQUAD gives good results, it did not show any trace of $H(MoO_4)C^{4-}$, nor did LETAGROP, but when data were treated with its FONDO version, it was easily seen that this species exists at $-\log h > 6$. In fact, when the $[H(MoO_4)C]^{4-}$ complex was assumed with the HYPERQUAD and LETAGROP

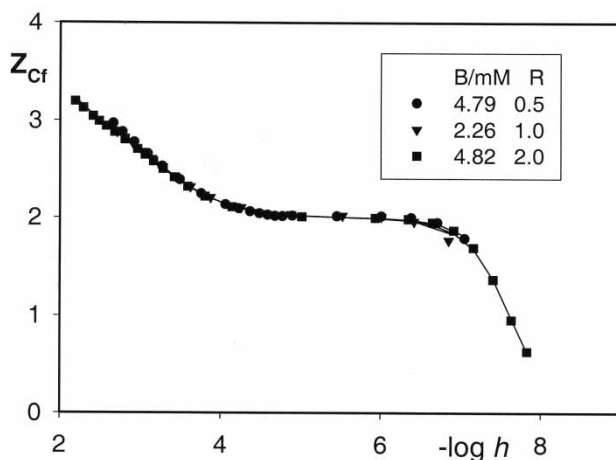


Figure 4. Z_{Cf} vs $-\log h$ for the system $H^+-MoO_4^{2-}-NTA$ (H_3C) in 1.0 M NaCl ionic medium at 25°C, for (B/mM , R) = 4.79, 0.5 (\square), 2.26, 1.0 (Δ) and 4.82, 2.0 ($+$), according to reaction (14) and assuming that $FONDO = [Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, $[H_3Mo_7O_{24}]^{3-}$, $[HMoO_4]^-$, H_2MoO_4 , HC^{2-} , H_2C^- , H_3C and H_4C^+ species. The lines represent theoretical curves using the equilibrium constants of table 2 (column 3).

Table 2. Equilibrium constants for the system $H^+-MoO_4^{2-}-NTA$ (H_3C) in 1.0 M NaCl ionic medium at 25°C, according to reaction (14).

Species	$-\log \beta_{pqr}(3\sigma)$			
	SUPERQUAD [10b]	HYPERQUAD [10d]	LETAGROP [18]	FONDO
$[HmoO_4C]^{4-}$	–	9.61 (7)	–	9.5 (1)
$[H_2MoO_4C]^{3-}$	17.78(2)	17.670(1)	17.674(4)	17.673(4)
$[H_3MoO_4C]^{2-}$	21.02(2)	20.910(2)	20.925(5)	20.923(6)
$[H_4MoO_4C]^-$	22.57(7)	22.51(2)	22.51(1)	22.51(2)
$[H_7(MoO_4)_2(C)_2]^{3-}$	45.16(5)	–	–	–
$[H_8(MoO_4)_2(C)_2]^{2-}$	47.95(2)	47.76(5)	47.79(2)	47.79(4)
$[H_5(MoO_4)_2(C)_2]^{2-}$	30.7(1)	30.3(1)	30.3(2)	30.2(2)
$[H_6(MoO_4)_2(C)]^-$	33.09(4)	32.6(1)	32.6(1)	32.6(1)
$\sigma(E)$		1.5 mV		
$\sigma(Z_C)$			0.008	
$\sigma(Z_{Cf})$				0.014
Refs	[19]	[23, this work]	[23, this work]	[23, this work]

programs, both $\sigma(E)$ and $\sigma(Z_C)$ values improved. Finally, figure 5 shows the species distribution diagram for $B = 4.82$ mM and $R = 2.0$.

3.3. $H^+-V(V)-V(IV)$ system

It is well established that in acid medium the cations VO^{2+} and VO_2^+ hydrolyze, forming the $[VO(OH)]^+$, $[V_2O_2(OH)_2]^{2+}$ and $[VO(OH)_2]$ species [24], and the decavanadate series $[H_{3-n}V_{10}O_{28}]^{(n+3)-}$ ($n = 0-3$) [25], respectively. The formation of $[V_2O_3]^{3+}$ has been reported in very acidic solutions of V(V) and V(IV) [26].

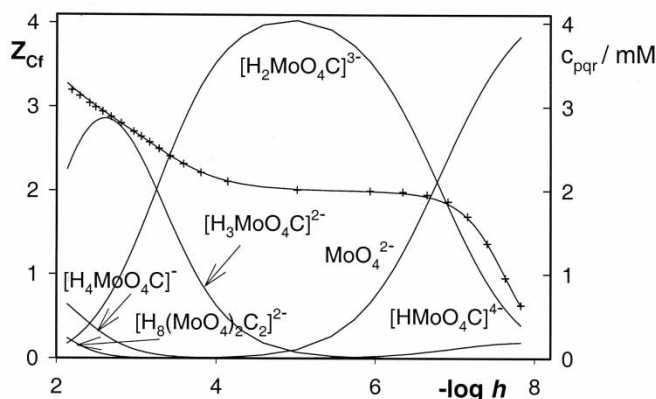


Figure 5. Z_{Cr} vs $-\log h$ and species distribution diagram for the system $H^+ - MoO_4^{2-} - NTA (H_3C)$ in 1.0 M NaCl ionic medium at 25°C and for $B = 4.82$ mM and $R = 2.0$.

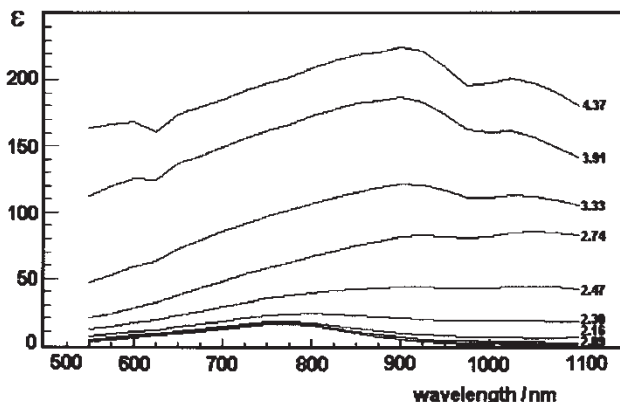


Figure 6. Electronic spectra $\varepsilon(\lambda)_{-\log h}$ of solutions containing equimolar mixtures of V(V) and V(IV) at a total concentration of 3.5 mM in 3.0 M KCl ionic medium at 25°C ($-\log h$ values are indicated in the figure).

We have studied the system $H^+ - VO_2^+ - VO^{2+}$ by emf(H) and spectrophotometric measurements in 3.0 M KCl ionic medium and an inert atmosphere of N_2 free of O_2 and CO_2 at 25°C, reaction (15),



at the following intervals of total V(V) concentrations, ratios V(IV)/V(V), $-\log h$ and wavelengths: $5.0 \leq B \leq 18.8$ mM, $R = 1.0, 1.4$ and 2.2 , $1 \leq -\log h \leq 4$ and $550 \leq \lambda \leq 1100$ nm. In this wavelength range, neither the cation VO_2^+ nor the decavanadate anions absorb, but the cation VO^{2+} has a characteristic spectrum with a maximum at 775 nm [$\varepsilon_{VO} = 7.6(2) \text{ cm}^{-1} \text{ M}^{-1}$]. When $-\log h > 2$, the solution color changes from the typical vanadyl(IV) blue to a more intense green color, increasing considerably the molar absorptivity $\varepsilon(\lambda)_{-\log h}$ of an electronic spectrum, which presents three maxima at 575, 900 and 1025 nm (figure 6).

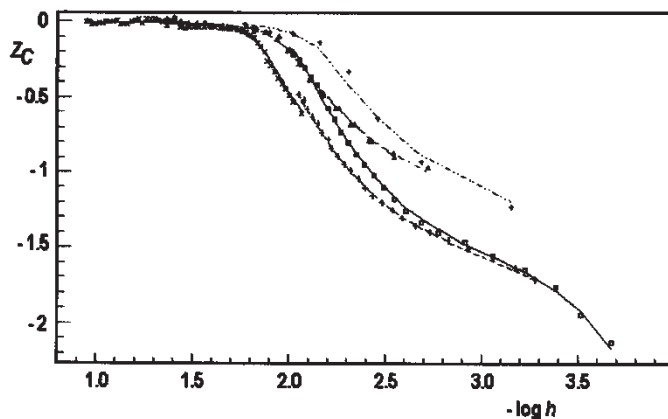


Figure 7. Z_C , average number of H^+ associated per mol of V(IV) as a function of $-\log h$ for the system $H^+ - VO_2^+ - VO^{2+}$ in 3.0 M KCl ionic medium at 25°C, for $(B/mM, R) = 18.8, 0.973$ (\times); 7.8, 0.961 ($+$); 5.0, 0.960 (\square), 8.8, 1.352 (Δ) and 9.8, 2.163 (\blacklozenge), according to reaction (15). The lines represent theoretical formation curves calculated with the equilibrium constants of table 3 (column 4).

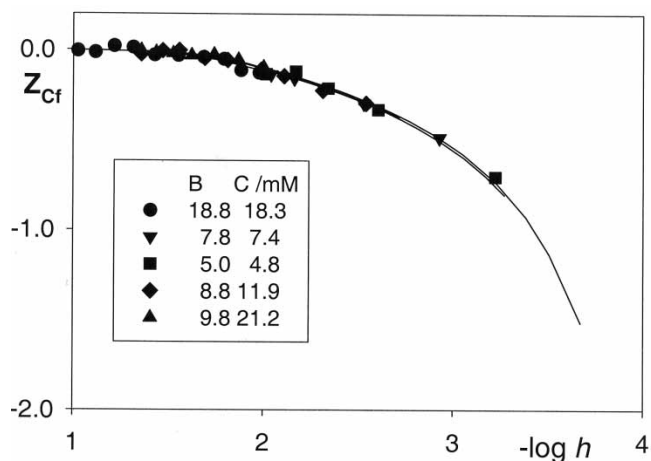


Figure 8. Z_{Cf} vs $-\log h$ for the system $H^+ - VO_2^+ - VO^{2+}$, in 3.0 M KCl ionic medium at 25°C, $(B/mM, R) = 18.8, 0.973$ (\times); 7.7, 0.961 ($+$); 5.0, 0.960 (\square); 8.8, 1.352 (Δ) and 9.8, 2.163 (\blacklozenge), according to reaction (15) and assuming that $FONDO = [H_3V_{10}O_{28}]^{3-}$, $[H_2V_{10}O_{28}]^{4-}$, $[HV_{10}O_{28}]^{5-}$, $[VO(OH)]^+$, $[V_2O_2(OH)_2]^{2+}$ and $VO(OH)_2$ species. The line represents theoretical curve calculated with the equilibrium constants of table 3 (column 5).

Figure 7 shows the results of the emf measurements as $Z_C(\log h)$ and figure 8 the application of the current *fondo* concepts assuming that $FONDO = [H_3V_{10}O_{28}]^{3-}$, $[H_2V_{10}O_{28}]^{4-}$, $[HV_{10}O_{28}]^{5-}$, $[VO(OH)]^+$, $[V_2O_2(OH)_2]^{2+}$ and $VO(OH)_2$. Figure 7 reveals little about the system composition, but figure 8 shows that all $Z_{Cf}(\log h)$ data are almost situated on the same theoretical curve corresponding to the so-called mononuclear wall [13,28], where at $-\log h < 2$ the ions VO_2^+ and VO^{2+} interact to form the dimeric $[V_2O_3]^{3+}$, which successively hydrolyzes to form the homonuclear V(V)–V(IV) mixed species $[V_2O_3(OH)]^{2+}$, $[V_2O_3(OH)_2]^+$, $[V_2O_3(OH)_3]$ and $[V_2O_3(OH)_4]^-$.

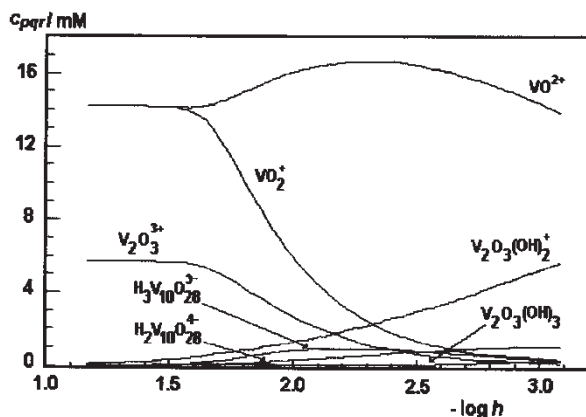


Figure 9. Species distribution diagram for the system $\text{H}^+ - \text{VO}_2^+ - \text{VO}^{2+}$ in 3.0 M KCl ionic medium at 25°C for $B = 20$ mM and $R = 1$.

Table 3. Equilibrium constants for the system $\text{H}^+ - \text{VO}_2^+ - \text{VO}^{2+}$ in 3.0 M KCl ionic medium at 25°C, according to reaction (15).

Species	$-\log \beta_{\text{pqr}} (3\sigma)$				
	VO^{2+} hydrolysis, LETAGROP	VO_2^+ hydrolysis, LETAGROP	$\text{V}_2\text{O}_3^{3+}$ hydrolysis, LETAGROP	$\text{V}_2\text{O}_3^{3+}$ hydrolysis, LETAGROP	$\text{V}_2\text{O}_3^{3+}$ hydrolysis, FONDO
$[\text{VO}(\text{OH})]^+$	6.4 (> 5.6)				
$[\text{V}_2\text{O}_2(\text{OH})_2]^{2+}$	7.45(4)				
$[\text{VO}(\text{OH})_2]$	10.0 (> 9.7)				
$[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$		6.83(4)			
$[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$		9.36(5)			
$[\text{HV}_{10}\text{O}_{28}]^{5-}$		14.23(8)			
$[\text{V}_{10}\text{O}_{28}]^{6-}$		20.5 (< 20.2)			
$[\text{V}_2\text{O}_3]^{3+}$			-1.46(4)	-1.48(3)	-1.48(3)
$[\text{V}_2\text{O}_3(\text{OH})]^{2+}$			1.9 (> 1.4)	1.6	1.6
$[\text{V}_2\text{O}_3(\text{OH})_2]^+$			2.82(2)	2.86(3)	2.87(3)
$[\text{V}_2\text{O}_3(\text{OH})_3]$			7.20(7)	7.1(2)	7.1(2)
$[\text{V}_2\text{O}_3(\text{OH})_4]^-$			10.54(3)	10.6(1)	10.5(1)
$\sigma(Z_B)$	0.002	0.010		0.028	
$\sigma(Z_{\text{Bf}})$					0.028
$\sigma(E)/\text{mV}$			0.5		
Refs	[24]	[27, this work]	[27, this work]	[27, this work]	[27, this work]

Table 3 gives the equilibrium constants as well as the standard deviations $\sigma(Z_B)$, $\sigma(Z_{\text{Bf}})$ and $\sigma(E)$ for the two- and three-component systems determined using LETAGROP [18] and its FONDO version. The equilibrium constants and the standard deviations $\sigma(Z_B)$ and $\sigma(Z_{\text{Bf}})$ for the $\text{H}^+ - \text{V}(\text{V}) - \text{V}(\text{IV})$ system are of the same order of magnitude, indicating the accuracy of the method. Figure 9 shows the species distribution diagram for $B = 10.0$ mM and $R = 1.0$.

In conclusion, we consider that when standard least-squares programs, which minimize the sum of the squared residuals of magnitudes such as potentials and total

concentrations, are used to analyze systems of more than two components, initially very little information can be gleaned about their composition. Instead, with this treatment we see the global behavior of the system graphically, starting from which we can attempt to achieve more acceptable models. This type of data analysis, especially in cases where weak complexes are formed, may contribute to the use of graphical methods to develop a more rational approach to solving problems of solution equilibria. This data treatment may prove useful for the study of systems with three or more components. At the very least, we believe it will be useful to determine behavior patterns for different complex systems, in order to design methods for equilibrium analysis by means of parallel and graphic-digital computation, using, for instance, expert systems and artificial neural networks [29].

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