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► **To cite this version:**

Laura Marang, Pascal E. Reiller, Monique Pepe, Marc F. Benedetti. Donnan membrane approach: From equilibrium to dynamic speciation. *Environmental Science and Technology*, 2006, 40 (17), pp.5496 -5501. <10.1021/es060608t>. <cea-00278074v2>

HAL Id: cea-00278074

<https://cea.hal.science/cea-00278074v2>

Submitted on 17 Dec 2020

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Experimental kinetic approach of the Donnan Membrane Technique

Laura Marang ^{a,b}, Monique Pepe ^b, Pascal Reiller ^a, Marc F. Benedetti ^{b}*

^aCEA Saclay, Nuclear Energy Division, DPC/SECR, Laboratoire de Spéciation des
Radionucléides et des Molécules, BP 11, 91191 Gif sur Yvette, France

^bLaboratoire de Géochimie des Eaux, Université Paris 7, UMR CNRS 71574 and IPGP, Case
Postale 7052, 75251 Paris Cedex 05, France

benedett@ipgp.jussieu.fr

ABSTRACT

The Donnan Membrane Technique has been recently developed to measure free divalent concentration by waiting the free metal equilibration between a donor and an acceptor solution. Addition of a ligand in the acceptor solution can lower the duration of the measurement as well as the detection limit. In this study, experimental calibrations of the system were performed in the case when the flux of ions is controlled either by diffusion in the membrane or in the solution. Depending on the degree of complexation in the sample, the appropriate calibration curve was used to determine the free metal concentration.

Experiments were performed with cobalt and magnesium in the presence of different ligands at various pH and for a wide range of metal concentrations. In the experiment with Mg and EDTA, the free magnesium concentration measured and the calculated one are in good agreement. For more complex systems including humic acid, this kinetic approach is an elegant way to obtain binding isotherms in a shorter time (30 min instead) and also to determine very low free ion concentration when the complexation degree is high in the system. The binding isotherms were used to calibrate the NICA-Donnan model for cobalt. The very low free Co concentrations (10^{-10} M) that were measured were in good agreement with the one modeled using the NICA-Donnan model.

KEYWORDS: Donnan Membrane Technique, humic Acid, cobalt, speciation, modeling

Introduction

In the environment, metal exists in various chemical forms namely “solids, particulate, colloidal and dissolved”. The latter includes free metal ions and complexes with natural organic ligands. Humic substances (HS) represent up to 70% of the natural organic matter (1). They play a key role in metal behavior in the environment because of their ability to complex metal ions and thus to partly control metal ion concentrations in soils and natural aquifers (2). Knowledge of complexation data with HS is required for the comprehension of pollutants behavior in the environment and, particularly in the case of radioactive waste disposal, for the comprehension of radionuclides transport from the source term to the biosphere. Despite of the large number of studies on the topic, only few data sets available for radionuclide binding to Humic and Fulvic acids (HA, FA) describes the complexation over a wide range of free metal concentration ($[M]_{free}$) and pH and which permits the comprehension of competition with major cations (3).

Free ion concentration is recognized as one of the key parameter for ion bioavailability. It is

therefore necessary to use a technique which allows the determination of the $[M]_{\text{free}}$ as well as the bound metal ion ($[M]_{\text{bound}}$) under different experimental conditions. These experimental data are also useful to calibrate models that describe metal HS complexation over a large range of pH and ionic strength and to evaluate the validity of their predictions for field systems (4,5).

Numerous methods are developed to measure the speciation of elements in presence of HS (1). Some of them involve a physical separation of the humic bound metal ion from the free metal ion like equilibrium dialysis (6,7), ultrafiltration (2), diffusive gradient in thin film method (8), and the Donnan Membrane Technique (DMT) (8). Once the separation is achieved, analytical determination of the total metal concentration ($[M]_{\text{total}}$) is required. The range of concentration that can be investigated depends upon the sensitivity of the chosen analytical method.

The DMT has been developed (9) and used for $[M]_{\text{free}}$ measurement of divalent cations such as Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} (10,11). Through the use of a cation exchange membrane the separation of the free metal from its complexed species is possible. The specificity of the DMT is that it uses a negatively charged membrane discriminating the free ions according to their charge. If donor and acceptor background electrolyte concentration are equal, then an equal $[M]_{\text{free}}$ on both side of the membrane is measured. The Donnan Membrane theory is described in detail elsewhere (9).

The main limitation of the technique are: i) a rather long equilibration time (2 days) and ii) the limit of detection depends upon the amount of free metal ion separated by the DMT. To overcome the latter limitation, Weng et al. (12) proposed a modification of the DMT by adding a strong ligand that increases the amount of free metal ion transported through the membrane. The conditions under which the diffusion in the solution film at the solution-membrane interface or in the membrane becomes the limiting step were discussed and

analytical solutions were presented (12). The $[M]_{\text{free}}$ that can be measured using the analytical solution are much lower than the one obtained in equilibrium mode. In this study, we will show that an experimental calibration of the metal ion transport in the DMT can be used to overcome the detection limitation. We also report a modification of the procedure that reduces the experimentation time.

Cobalt is an essential element to human life as it is involved in B12 vitamin. Its main problem in the nuclear field comes from the stellite alloy particles activated within the reactor core. These particles can also be dissolved during reprocessing leading to a ^{60}Co release in the environment. Among the studies on HS complexation of cobalt, only two data sets cover a sufficiently large range of $[M]_{\text{total}}$ and pH (6,13), but these data sets have poor statistics (3). Hence, new experimental data are needed.

In order to fix the potential of the membrane, a divalent cation has to be used as background electrolyte. Magnesium is chosen to avoid interferences during Co detections by ICP-MS and because Mg is a major cation in the environment. Knowledge of Mg and Co competition in natural system will be gained from this choice.

The approach was first validated by comparing $[\text{Mg}]_{\text{free}}$ measured with $[\text{Mg}]_{\text{free}}$ calculated when EDTA was added to the system. Metal speciation were estimated using ECOSAT (14). Cobalt adsorption isotherms on HA from Gorleben aquifer were acquired for a wide range of concentration and pH. The NICA-Donnan model (5) was then used to describe the data and a comparison between experimental and modeled speciation for different conditions are done.

Theoretical Basis

Process controlling the metal ion transport in the DMT

The DMT system can be represented by 5 zones: bulk solution in the donor side, diffusion layer at the donor-membrane interface, the cation exchange membrane, diffusion layer at the membrane –acceptor interface and the bulk solution in the acceptor. There is no gradient

concentration in the acceptor and donor bulk solutions, because the circulation of each solution is assured with a peristaltic pump. When there is no ligand in the acceptor side and the salt level is not very high, the concentration gradient in the membrane (donnan phase) for cation is much larger than the concentration gradient in the diffusion layer (12,15). Therefore, for cations, the diffusion in the solution diffusion layer is usually the rate limiting step under these conditions. When a ligand is add in the acceptor side, cation transport in the system can be limited either by diffusion in the solution or by diffusion in the membrane depending on the complexation factor P_i (Ratio of total to free concentration of ion i) and on the ionic strength (12).

We assumed that diffusion coefficients of all ionic species are the same as the diffusion coefficient of the free ion (D_i).

The ion diffusion flux in the solution diffusion layer is:

$$J_{i,sol} = -D_i \frac{\Delta C_{i,tot}}{\Delta \delta} = -D_i \cdot P_i \frac{\Delta C_i}{\Delta \delta} \quad (1),$$

and the ion diffusion flux in the membrane is:

$$J_{i,m} = -D_{i,m} \cdot B^{z_i} \frac{\Delta C_i}{\Delta \delta_m} \quad \text{with} \quad D_{i,m} = \frac{D_i}{\lambda_i} \quad (2),$$

with B the Boltzmann factor related to the ionic strength (9), C_i the free concentration of ion i in solution (mol.L^{-1}), $C_{i,tot}$ the total concentration of ion i in solution (mol.L^{-1}), D_i the diffusion coefficient of ion i in water ($\text{m}^2\cdot\text{s}^{-1}$), $D_{i,m}$ the apparent diffusion coefficient on ion i in the membrane ($\text{m}^2\cdot\text{s}^{-1}$), λ_i tortuosity factor for ion i in the membrane, $J_{i,sol}$ the flux of ion i in solution ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), $J_{i,m}$ the flux of ion i in the membrane ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), z_i the charge of ion i , δ the thickness of diffusion layer in solution (m) and δ_m the thickness of the membrane (m).

The ion transport in the DMT can be approximated using the classical linear driving force approximation from equations (1) and (2) as described in detail elsewhere (12).

Under these conditions, the $[M]_{\text{free}}$ in the acceptor is much smaller than the $[M]_{\text{free}}$ in the donor. Ratios of concentration in both cases are linearly related with time. The ratio of total metal ion concentration in the acceptor vs. total concentration in the donor can be calculated when the transport is controlled by diffusion in the solution by:

$$\frac{C_{i,\text{tot,acc}}}{C_{i,\text{tot,donor}}} = A_1 \cdot t \text{ with } A_1 = \frac{A_e \cdot D_i}{V_{\text{acc}} \cdot \delta} \quad (3),$$

with A_e the effective surface area of a membrane (m^2) and V_{acc} the volume of the acceptor solution (m^3).

The ratio of total concentration in the acceptor vs. the free concentration in the donor can be calculated when the transport is controlled by diffusion in the membrane by:

$$\frac{C_{i,\text{tot,acc}}}{C_{i,\text{donor}}} = A_2 \cdot t \text{ with } A_2 = \frac{A_e \cdot D_i \cdot B^{z_i}}{V_{\text{acc}} \cdot \delta_m \cdot \lambda} \quad (4)$$

The comparison of equations (1) and (2) suggests that in some cases either the diffusion in solution or in the membrane is the rate-limiting step. Increasing P_i and the background electrolyte concentration values, as well as decreasing z_i will result in a transition from a solution controlled transport towards a membrane controlled transport mechanism.

Kinetic approach of the DMT

The addition of a ligand in the acceptor side influences the transport. The time of equilibration is directly related to P_i value: the higher the P_i value, the longer the equilibration time between the two compartments (12). In the following, a strong ligand (ethylene diamine tetracetic acid, EDTA) is always added in the acceptor solution. Then the ion transport is always controlled by membrane diffusion in the acceptor side.

In the donor side, the comparison of the flux of a divalent cation os obtained from equations (1) and (2):

$$\frac{D_i \cdot P_i}{\delta} \cdot \frac{\delta_m}{D_{i,m} \cdot B^{z_i}} = \frac{P_i}{X} \text{ with } X = \frac{D_{i,m} \cdot B^{z_i} \cdot \delta}{D_i \cdot \delta_m} \quad (5)$$

If we postulate that one flux has to be at least 5 times smaller than the other to be the rate limiting flux, then the flux is controlled by diffusion in solution when $P_i < X/5$, both by membrane and solution diffusion when $X/5 \leq P_i \leq 5X$, and finally by diffusion in the membrane when $P_i > 5X$. The transport is dominated by one type of flux only in the two extreme cases.

In order to be able to calculate $[M]_{\text{free}}$ in the donor side with $[M]_{\text{total}}$ measured on the acceptor side, calibration curves relating the two concentrations as a function of time for the two limiting cases are needed. The first calibration, corresponding to the transport controlled by the diffusion in solution on the donor side ($P_i < X/5$), is done without ligand on the donor side. The second calibration corresponding to the transport limited by diffusion in the membrane ($P_i > 5X$) is done with a high concentration of EDTA in the donor side. The limiting P_i values can be calculated for different ionic strengths (Table 1). A tortuosity factor value of 20 is used for the calculation as it was proposed by Weng et al. (12). The thickness of the solution diffusion layers on both side of the membrane is 0.1 mm and the thickness of the membrane is 0.16 mm.

For a given background electrolyte concentration, decreasing the ionic strength results in a transition from membrane towards solution diffusion control. Indeed, B increases when the ionic strength decreases (9). The ionic strength has to be much higher when using a monovalent electrolyte in order to have a system which is not exclusively controlled by diffusion in the solution. Knowing $[M]_{\text{total}}$ and the total ligand concentration in a given system, a preliminary calculation of the speciation can be done. Depending on the ionic strength and the estimated $[M]_{\text{free}}$ in the sample, the appropriate calibration will be used to determine $[M]_{\text{free}}$ on the donor side. When a weak ligand is present the first calibration is used (transport controlled by the diffusion in solution on the donor side, $P_i < X/5$), whereas when a strong

ligand is present the second calibration is used (transport limited by diffusion in the membrane, $P_i > 5X$) (Table 1).

Experimental Section

Donnan Membrane Technique (DMT)

The design of the cation exchange cell was described by Temminghoff et al. (9). In the cell, a cation exchange membrane is used to separate the substrate solution (donor) and a salt solution (acceptor). This cation exchange membrane (BDH, Laboratory Supplies) is a matrix of polystyrene and divinylbenzene with sulfonic acid groups, which are fully deprotonated at pH > 2 . Its ion exchange capacity and thickness are defined by the supplier as 0.8 meq.g^{-1} and $0.16 \pm 0.1 \text{ mm}$ respectively. The area of the membrane used in the DMT device is 7 cm^2 .

The reagents used are $\text{Co}(\text{NO}_3)_2$ (Normapur, Prolabo), $\text{Mg}(\text{NO}_3)_2$ (Normapur, Prolabo), KNO_3 (Panreac) and EDTA (Aldrich) and water (Milli Q, Millipore).

The membranes were preconditioned in three steps. The membrane is first soaked in 0.1 M HNO_3 to remove trace metal impurities. Secondly, the membrane is saturated with a solution of either $1 \text{ M Mg}(\text{NO}_3)_2$ or 1 M KNO_3 depending of the background electrolyte used in the experiment. In the last step the potential of the membrane is fixed by soaking in $2 \text{ mM Mg}(\text{NO}_3)_2$ or 0.1 M KNO_3 . All cells, bottles and tubes were washed with 0.1 M HNO_3 and rinsed with water (Milli Q). The background electrolyte is 0.1 M KNO_3 or $2 \text{ mM Mg}(\text{NO}_3)_2$ for magnesium and cobalt studies respectively.

Both donor and acceptor solutions were circulated at a constant rate of 2.5 mL.min^{-1} . The acceptor and donor volumes are equal to 25 mL and 200 mL , respectively. A large donor volume is used in order to ensure that the metal ion accumulation in the membrane is always negligible compared to the stock of metal ion in the donor solution. The pH was measured using a pH HANNA electrode. It was calibrated with N.I.S.T standards buffers pH (4.008, 6.986,

and 9.933). The pH of the solutions was adjusted with HNO₃ and freshly prepared KOH with a precision of 0.05. Solutions were buffered at pH 6 using 5.10⁻³ M MES (2-[N-Morpholino] ethanesulfonic acid, Sigma) and at pH 8 using 5.10⁻³ M HEPES (N-piperazine-N'-[2-ethane sulfonic acid], Sigma).

Aliquots of donor and acceptor solutions were sampled, acidified with HNO₃ (Suprapur, Prolabo) and analysed either with inductively coupled mass spectrometer (Plasmaquad PQ2+ (VG instrument), with a detection limit of 5.10⁻⁹ M, or with ELC (Extended Lifetime Cuvette) graphite furnace atomic absorption spectroscopy at 240.7 nm with a detection limit of 1.10⁻⁸ M for cobalt and with flame at 285.2 nm for magnesium with a detection limit of 1.10⁻⁶ M (Unicam Solaar M6).

Calibration of the system for magnesium and cobalt

The DMT was calibrated when transport in the donor side is controlled by diffusion in solution (case 1) and in the membrane (case 2) (Table 2a). In case 1, the calibration is performed with high concentration of EDTA ([EDTA]) in the acceptor side. In case 2, the calibration is performed with high [EDTA] on both sides of the membrane. The [EDTA] controls the metal speciation on both sides. The concentrations were chosen to obtain the desired free ion concentration on both sides and were calculated for each limiting case as given in Table 1. The influence of pH and [Co] in the donor side on the calibration curves were checked.

For case 1, the acceptor and donor solutions were sampled every 10, 20, 30, 40, 60, 80 min for both ions. For case 2, they were sampled every 10, 20, 30, 40 min, 1, 2, 3, 4 hours and every 16, 20, 30, 40, 60, 80 hours for magnesium and cobalt, respectively.

Validation the procedure

To test the validity of the approach, Mg complexation isotherm with EDTA is obtained at pH 6 with the $[Mg]_{free}$ varying from 10^{-7} to 10^{-2} M in the donor side. The $[Mg]_{free}$ measured with the appropriate calibration is then compared with the $[Mg]_{free}$ calculated with ECOSAT.

Two experiments were made to plot the complexation isotherm of Mg with EDTA (Table 2b). Experiments 1 correspond to high $[Mg]_{free}$ in solution and experiments 2 to low $[Mg]_{free}$ in solution. For all experiments the pH was adjusted to 6.00 ± 0.05 . The acceptor solution composition was 50 mM EDTA. Donor and acceptor sides were sampled every 30 min (calibration 1) for experiments 1, and every hour or every three hours (calibration 2) for experiments 2.

Cobalt complexation by HS

The humic acid used in this experiment was extracted from one of the deep groundwaters in the Gorleben area (Gohy-573, Germany). Its isolation, purification, and characterization are described in detail elsewhere (16). A stock solution of 1 g/L is prepared and stored for 12 hours at pH 10.

Firstly, the binding isotherms were acquired, and secondly, the ability of this technique to measure low $[M]_{free}$ was checked. The measured $[Co]_{free}$ was compared with $[Co]_{free}$ calculated using parameters derived from analysis of the binding isotherms.

In the first experiment, the donor side composition consisted of 50 mg/L of HA with a $[Co]_{total}$ varying from $8 \cdot 10^{-7}$ M to $4 \cdot 10^{-4}$ M. The acceptor side consisted of 5 μ M EDTA. The donor and acceptor sides were sampled after 30 min. The adsorption isotherms were acquired at pH 4, 6 and 8. Cobalt was always added to the HA containing solution, thus we considered that no precipitation of $Co(OH)_2(s)$ (17) during the experiments made at pH = 8.

In the second experiment, the composition of the donor solution consisted of 650 mg/L of HA with a $[Co]_{total}$ varying from $1 \cdot 10^{-8}$ M to $5.5 \cdot 10^{-8}$ M. The acceptor side consisted of 5 μ M

EDTA. The donor and acceptor sides were sampled after 48 hours. The pH was fixed at 6.00 ± 0.05 .

Results and discussion

Calibration of the system for magnesium and cobalt

The ratios of the $[M]_{\text{total}}$ in the acceptor side vs. the $[M]_{\text{free}}$ in the donor side are shown in Figure 1a,b and Figure 2a,b for case 1 and 2, respectively. The $[M]_{\text{free}}$ on the donor side is directly obtained from the measured $[M]_{\text{total}}$ in the acceptor solution for case 1 (Equation 3). After the calculation of cobalt and magnesium speciation on the donor side using the Mg and Co binding and acidity constants for EDTA (18,19), the $[M]_{\text{free}}$ on the donor can be related to the measured $[M]_{\text{total}}$ in the acceptor solution for case 2 (Equation 6).

As expected theoretically, the experimental ratio is a linear function of time. There is no evidence of a pH buffer influence on the flux through the membrane (Figure 1a). The metal ion complexation by pH buffer is thus negligible. The flux is independent of the initial total concentration of the metal in the donor (Figure 1 a). The y intercept is not zero for short measuring time (Figure 1) whereas it is zero for longer ones (Figure 2). This effect can be related to the initial accumulation time of the metal in the membrane that can be evidenced at short time but not apparent a longer time as it can be seen for Mg calibration 2 (Figure 2 b). Hence, the regression for calibration 2 was forced at y intercepts = 0.

The theoretical values of slopes A_1 and A_2 corresponding to the two limiting cases are first calculated with an effective surface value A_e of 20% of the initial value (7 cm^2) (12) (Table 3). The diffusion coefficient in water for cobalt and magnesium is $0.732 \cdot 10^{-5}$ and $0.706 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ respectively (20).

The comparison between theoretical and experimental A_1 values shows a good agreement for Co but not for Mg (Table 3) when the effective surface is 20 % of the initial value. The use

of KNO_3 as background electrolyte may affect the effective surface area. Indeed, divalent ions can be more accumulated in the membrane than monovalent ones (9). A good agreement between experimental and theoretical values can be obtained if the effective surface A_e corresponds to 40% of the initial value. This latter effective surface value is therefore used to calculate the Mg theoretical slope for the conditions corresponding to case 2. The tortuosity factor is a variable parameter in the theoretical calculation of A_2 and so the calculations have been done with different values (20, 60). Using a tortuosity factor value of 60, experimental and theoretical values are in good agreement (Table 3). This value is reasonable compared to those found by Weng et al. (12) (values between 10-60). The good agreement between theoretical and experimental slopes confirms that the transport is controlled by diffusion in solution and by diffusion in the membrane in case 1 and 2, respectively.

Calibrations are used to adapt the time at which the samples will be collected: it can either be reduced (after 30 min, 5% of free cobalt is on the acceptor side in case 1) or one can let the free metal accumulate in the acceptor. The detection limit is then much lower when the $[\text{M}]_{\text{free}}$ accumulates during a longer time: after 48 hours, the $[\text{Co}]_{\text{free}}$ is increased by a factor of 52 on the acceptor side.

Validation of the procedure

In order to validate the proposed approach, the $[\text{Mg}]_{\text{free}}$ calculated with ECOSAT were compared to the measurements (Figure 3). For the experiments corresponding to high $[\text{Mg}]_{\text{free}}$ (experiment 1) the calibration curve given in Figure 2b was used. For the experiments corresponding to low $[\text{Mg}]_{\text{free}}$ (experiment 2), the calibration corresponding to case 2 was used. Experimental results are in good agreement with the calculated concentrations in both cases. The $[\text{Mg}]_{\text{free}}$ is between 80 % and 97 % of the $[\text{Mg}]_{\text{total}}$ in experiment 1 and between 0.16 % and 10% of the $[\text{Mg}]_{\text{total}}$ in experiment 2.

The limitations of this procedure can be discussed. Firstly, it is difficult to know exactly which diffusion mechanism actually controls the whole process and thus the validity of each calibration (Table 1). Secondly, the calibration validity strongly depends both upon the acidity constants values of the ligand and the metal-ligand complexation constants. Nevertheless, this new approach of the DMT reduces the experimental time (30 min instead of 2 days), but also allows much lower detection limits for the $[M]_{\text{free}}$ by accumulating the metal on the acceptor side for much longer time as it will be shown in the following.

Adsorption Isotherm for cobalt with Gorleben HA

Figure 4 shows the log-log plot of the $[Co]_{\text{bound}}$ vs. $[Co]_{\text{free}}$, for pH values of 4, 6 and 8. Modeling of Co binding to Gorleben HA was made using the NICA-Donnan model (5) which has been used previously to describe extensive data sets available for proton and metal binding to HS (3,21). Site density (Q_{max}) and protons parameters (non ideality parameter n_{H} and median affinity constant (\tilde{K}_{H}) were obtained for carboxylic-type and phenolic-type groups by the proton titration of the Gorleben HA (Figure S1, Supporting Information). A summary of the parameters used for modeling is given in Table 4. The description of the data was done by adjusting the Co parameters to the experimental data (Table 4) and using the Mg generic parameters proposed by Milne et al. (3). The description by the NICA-Donnan model of the Co^{2+} binding data is good over a wide range of $[M]_{\text{free}}$ and 4 pH units.

Like for other divalent cations, the Co^{2+} binding is pH dependant, with more Co bound at higher pH (5). The pH effect seems however smaller compared to other divalent ions. For instance a ΔpH of 1 corresponds, at a given $[M]_{\text{free}}$, to a $\Delta\log[M]_{\text{bound}}$ of 0.25 for Co whereas it corresponds to a $\Delta\log[M]_{\text{bound}}$ of 1 and 1.5 for Cd and Cu, respectively (5). This effect was also noticed by other authors (6,13). The ratio of metal exchanged per type of groups $n_{\text{M}}/n_{\text{H}}$ is close to unity (1.13, 1.33) (Table 4), indicating that the cobalt seems to be bound in a monodentate

way to both type of groups (5). The NICA-Donnan model was used to simulate the percentage of metal bound to the carboxylic-type and phenolic-type groups under our experimental conditions for cobalt and magnesium. Complexation of with carboxylic-type groups is dominant for low to neutral pH, but phenolic-type groups becomes as important for higher pH. Complexation by carboxylic-type groups is dominant for magnesium whatever the pH. The competition between magnesium and cobalt seems to be important because they are both bound to the same type of groups in a wide range of pH.

The ability of the DMT kinetic approach to detect very low $[\text{Co}]_{\text{free}}$ that could not be measured in the equilibrium mode was controlled for the following $[\text{Co}]_{\text{total}}$: $1.0 \cdot 10^{-8}$, $3.7 \cdot 10^{-8}$, $5.2 \cdot 10^{-8}$ M. The calibration curve in Figure 2a was used to determine the $[\text{Co}]_{\text{free}}$ on the donor side. The experimentally determined $\log [\text{Co}]_{\text{free}}$ (-9.76, -9.91, -9.62), and the one calculated using parameters given in Table 4 (-10.08, -9.44, -9.27), are in fair agreement. This agreement validates the DMT new approach and the NICA-Donnan parameters acquisition for cobalt. The detection limit of the DMT (10^{-9} M in equilibrium mode) is reduced but can be more reduced by accumulating the metal ion in the acceptor side during a longer time.

Acknowledgment. This work was financed through “FUNMIG project” (EC: FUNMIG-NUWASTE-2004-3.2.1.1-1), and the MRTRA project of the Risk Control Domain of CEA (CEA/DEN/DDIN). We thank Mr. Dominique Lavergne for technical support.

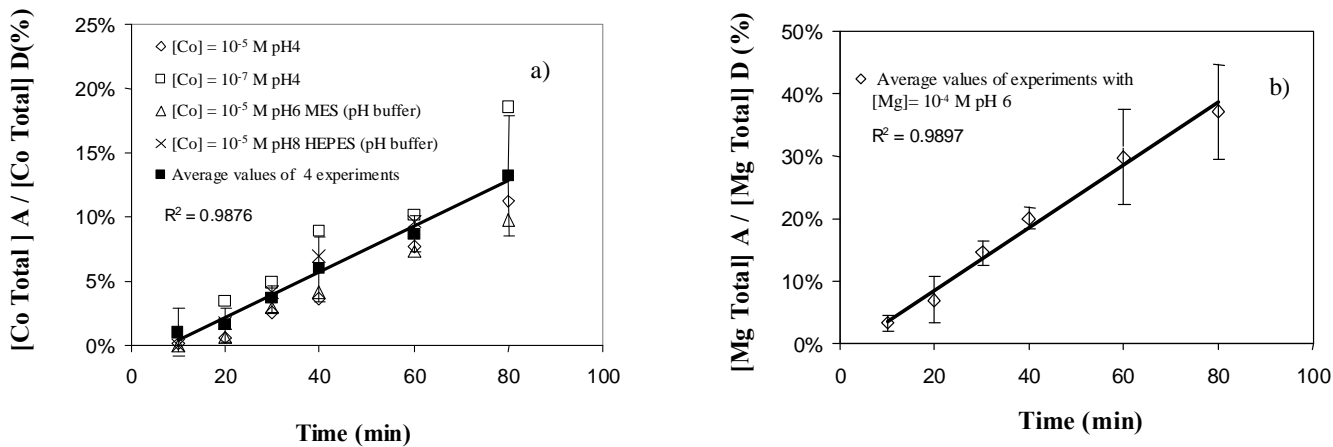


Figure 1. Case 1: Experimental calibration curves a) for cobalt b) for magnesium show the variation of ratio (total concentration of studied metal in the acceptor (A) / total concentration in the donor (D)) in function of time. The background electrolyte is 0.1 M KNO_3 or 2 mM $\text{Mg}(\text{NO}_3)_2$ for magnesium and cobalt, respectively. Each experiment has been replicated two times.

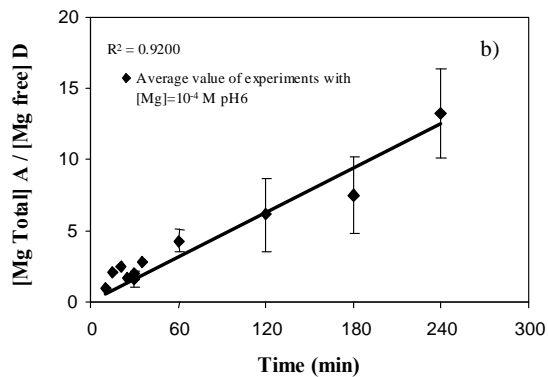
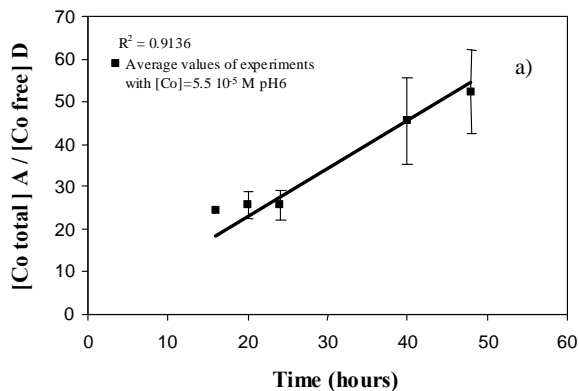


Figure 2. Case 2: Experimental calibration curves a) for cobalt and b) for magnesium show the variation of ratio (total concentration of studied metal in the acceptor side(A) / free concentration in the donor side (D)) in function of time. The background electrolyte is 0.1 M KNO_3 or 2 mM $\text{Mg}(\text{NO}_3)_2$ for magnesium and cobalt, respectively. Each experiment has been replicated twice.

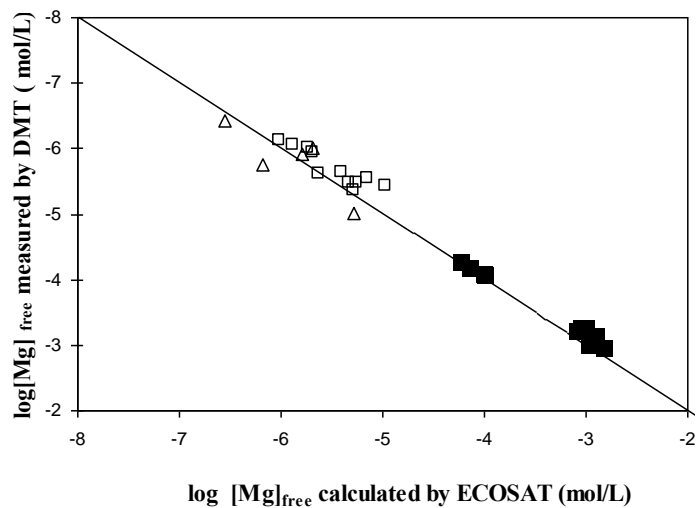


Figure 3. Plot of concentration calculated vs. concentration measured by DMT kinetic approach: calibration 1 (■); calibration 2: sampling after one hour (□), sampling after three hours (△) are used to determine the free magnesium concentration in the donor side.

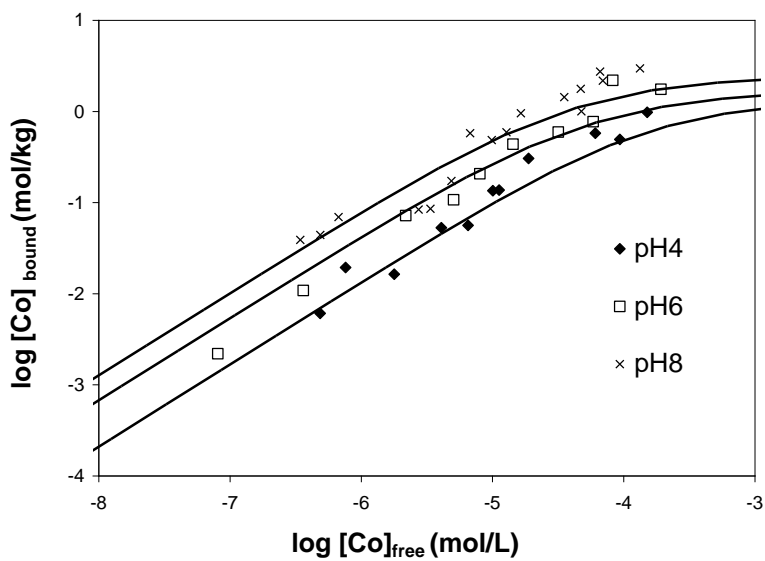


Figure 4. Adsorption isotherms ($\log [Co]_{\text{free}}$ vs. $\log [Co]_{\text{bound}}$) with Gorleben HA (50mg/L) at pH 4, 6 and 8. The points are the experimental data and the straight lines are the NICA-Donnan modelling.

Table 1. Limiting P_i (Ratio of total to free concentration of ion i) values and limiting % of free ion values as function of ionic strength characterizing transition between membrane or solution diffusion controlled.

Ionic strength	Transport controlled by diffusion in solution:		Transport controlled by diffusion in the membrane:	
	$P_{i<}$	% of free ion >	$P_{i>}$	% of free ion <
2 mM $Mg(NO_3)_2$	5.4	18	54	0.18
0.2 mM $Mg(NO_3)_2$	54	0.18	540	0.018
0.1 M KNO_3	7.6	13	76	0.13

Table 2. Experimental conditions of the DMT kinetic approach: a) for the cobalt and magnesium calibrations: transport controlled by diffusion in solution (case 1) or in the membrane (case 2) in the donor side. b) for the validation of the procedure: experiments 1 correspond to high free magnesium concentration and experiments 2 correspond to low free magnesium concentration in solution.

a)

	Mg: Case 1	Mg: Case 2	Co: Case 1	Co: Case 2
[EDTA] in Donor	0	5 mM	0	50 μ M
[EDTA] in Acceptor	5mM	50 mM	5 μ M	5 μ M
Background	0.1 M KNO ₃	0.1 M KNO ₃	2mM Mg(NO ₃) ₂	2mMMg(NO ₃) ₂
[Mg _{Total}] in donor	10 ⁻⁴ M	10 ⁻⁴ M	10 ⁻⁵ , 10 ⁻⁷ M	5.10 ⁻⁵ M
pH	6	6	4, 6, 8	6

b)

Experiments	[EDTA] in the donor side	[Mg total] in the donor side
1	50 μ M	10-100 μ M
	500 μ M	1-10 mM
2	1 mM	10-100 μ M
	50 mM	100 μ M-2 mM

Table 3. Comparison between experimental and theoretical slopes (A_1 and A_2) for both calibrations curves. Theoretical calculations are done with different parameters: ES = effective surface, i.v. = initial value, λ = tortuosity factor.

		Case 1: A_1 value (s^{-1})		Case 2: A_2 value (s^{-1})	
		Experimental	Theoretical	Experimenta l	Theoretical
Cobalt	$3.0 \pm 0.5 \cdot 10^{-5}$		$4.1 \cdot 10^{-5}$	$3.1 \pm 0.2 \cdot 10^{-4}$	$1.12 \cdot 10^{-3}$ ($\lambda = 20$)
					$3.74 \cdot 10^{-4}$ ($\lambda = 60$)
Magnesium	$8.3 \pm 1.2 \cdot 10^{-5}$		$3.95 \cdot 10^{-5}$ (ES= 20% of i.v.)	$8.7 \pm 1.1 \cdot 10^{-4}$	$3.03 \cdot 10^{-3}$ ($\lambda = 20$)
			$7.91 \cdot 10^{-5}$ (ES= 40% of i.v.)		$1.01 \cdot 10^{-3}$ ($\lambda = 60$)

Incertainties 95%

Table 4. Nica-Donnan model parameters used in the description of cobalt and magnesium binding to HA.

	Q_{Max}	$\log K_H$	n_H	p	$\log K_{Mg}^a$	n_{Mg}^a	$\log K_{Co}$	n_{Co}
Carboxylic-type group	2.63	2.60	0.8	1	-0.6	0.77	2.5	0.9
Phenolic-type groups	3.08	3.50	0.65	0.41	0.6	0.59	3.5	0.9

^a parameters proposed by Milne et al. (3)

REFERENCES

- (1) Tipping, E. *Cation binding by humic substances*; Cambridge Environmental Chemistry Cambridge University Press, 2002.
- (2) Buffle, J. *Complexation Reactions in Aquatic Systems*; Ellis Horwood Series in Analytical Chemistry, 1988.
- (3) Milne, C. J.; Kinniburgh, G. G.; Van Riemsdijk, W. H.; Tipping, E. *Environ.Sci.Technol.* **2003**.
- (4) Tipping, E. *Aq. Geochem* **1998**, 4, 3 - 48.
- (5) Kinniburgh, D. G.; van Riemsdijk, W. H.; Koopal, L. K.; Borkovec, M.; Benedetti, M. F.; Avena, M. J. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1999**, 151, 166.
- (6) Glaus, M. A.; Hummel, W.; Van Loon, L. C., Experimental Determination and Modelling of Trace Metal-Humate Interactions: A pragmatic Approach for Applications in Groudwater.
- (7) Truitt, R. E.; Weber, J. H. *Anal.Chem* **1981**, 53, 337-342.
- (8) Zang, H.; Davison, W. *Anal. Chim. Acta* **1999**, 398, 329-340.
- (9) Temminghoff, E. J. M.; Plette, A. C. C.; Van Eck, R.; Van Riemsdijk, W. H. *Anal. Chim. Acta* **2000**, 417, 149-157.
- (10) Weng, L. P.; Temminghoff, E. J. M.; van Riemsdijk, W. H. *Environ. Sci. Tecnol.* **2001**, 35, 4436-4443.
- (11) Cances, B.; Ponthieu, M.; Castrec-Rouelle, M.; Aubry, E.; Benedetti, M. F. *Geoderma* **2003**, 113, 341-355.
- (12) Weng, L. P.; Van Riemsdijk, W. H.; Temminghoff, E. J. M. *Anal. Chem.* **2005**, 77, 2852-2861.
- (13) Westall, M. L.; Jones, J. D.; Turner, G. D.; Zachara, J. M. *Environ.Sci.Technol.* **1995**, 29, 951-959.
- (14) Keizer, M. G.; Van Riemsdijk, W. H. *A computer program for the Calculation of Chemical Speciation and Transport in Soil-Water Systems (ECOSAT 4.7)*. Agricultural University of Wageningen: Wageningen, 1994.
- (15) Yezek, L. P.; van Leeuwen, H. P. *Langmuir* **2005**, 21, 10342-10347.
- (16) Wolf, M.; Buckau, G.; Geyer, S. Isolation and characterization of new batches of Gohy-573 humic and fulvic acids. In *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field. Second Technical Progress Report* <<http://bibliothek.fzk.de/zb/berichte/FZKA6969.pdf>>; Buckau, G., Ed.: Karlsruhe, 2004; pp 111-124.
- (17) Wollery, T. J. W., T. J. EQ3/6, A computer program for geochemical aqueous speciation-solubility calculations. In *LLNL, Report UCRL-MA-110662*: Livermore, 1992.
- (18) Lindsay, W. L. *Chemica Equilibria in Soils*, 1979.
- (19) Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*; Environmental Science and Technology, A Wiley-Interscience Publication, 1996.
- (20) R.Lide, D. *Handbook of Chemistry and Physics 85 th Edition*; CRC Press, 2004-2005.
- (21) Milne, C. J.; Kinniburgh, G. G.; Tipping, E. *Environ.Sci.Technol.* **2001**, 35, 2049-2059.