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Diffusion Coupling in Associating Non–ideal Multi-Electrolyte Solutions.

Tesis que presenta el
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*Dedicado a
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ABSTRACT

A theoretical formalism to describe the diffusion coupling process in multiply non–ideal associating aqueous electrolyte solutions is presented. Association considers complexes formation to arbitrary order. Non–ideality is taken into account with the use of the mean spherical approximation (MSA). The internal electrical field due to the major electrolyte, is calculated using the dynamical electroneutrality condition and the general equations are solved in two ways: (i) a classic finite differences method and (ii) a linearization procedure or normal mode (NM) analysis. This last approximation gives closed analytical relations showing explicitly the coupling between association and non–ideality phenomena. To illustrate both methodologies, new experimental results are presented for the diffusion of an electrolyte mixture of $ZnCl_2$ and $LiCl$ where Cl^- ions and tracer Zn^{2+} ions can associate to form complexes up to $ZnCl_4^{2-}$ (pentamers). The theoretical results are in good agreement with the experimental data.

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CHAPTER 1

INTRODUCTION

Aqueous electrolytes are ubiquitous on earth. They may be found, for instance, in natural waters like oceans and lakes and also in almost all living beings. They have a huge influence on the development and functioning of life on the planet. Moreover the motion of ionic species is an important process that governs the local amount of ions. In this respect, aqueous electrolytes have the particular property that the motions of different ions in a medium are strongly coupled through the effect of electrostatic interactions [1].

Diffusion coupling thus can be observed in many natural and industrial domains and systems, such as in geochemistry (when studying diagenetic fluxes in sediments [2, 3]), in biophysics (e.g. for a description of permeation through ionic channels of cells [4]), in engineering processes (e.g., when using membranes for industrial separations [5]), in materials science (e.g., for the assessment of chemical ageing of concrete and composite materials [6]).

Diffusion coupling in aqueous ionic solutions has been investigated at a fundamental level for a long time [1]. Theoretical descriptions have been developed that assume linear transport theory, in which fluxes are linear functions of forces [7]. Multicomponent diffusion has been examined in the framework of Onsager formalism of irreversible thermodynamics [8].

A phenomenon that has great influence on coupled diffusion in electrolytes is ionic association, consisting either of ion pairing or chemical reaction. In geochemistry, Lasaga first examined the influence of ion pair formation on diagenetic fluxes in marine sediments [3]. Ion pairing is important because it modifies the charge of the diffusing species and so changes their response to the electrostatic diffusion field that is created by the diffusing ions. A clear example is that of a monovalent tracer ion that associates with a monovalent anion, which forms a neutral species that is insensitive to the diffusion field.

Some time ago, were investigated the effect of ion pairing caused by magnesium(II) ion on the transient transport of sulfate ion by carrying out experiments in a special diffusion cell (closed capillary) [9]. Later, was also investigated the effect of a pH gradient on sulfate and phosphate ions [10]. In these works, the diffusion-reaction equations were solved by using two types of treatments: a 'normal–mode' (NM) analysis in which the equations are linearized and solved analytically [11]; and a classical numerical finite-difference method in which time and space are sliced and the equations are solved incrementally in the

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course of time. In these treatments, the equations were written in the ideal case in which activity coefficients are taken equal to unity. Besides, the associations involved only one type of complex, leading to an ion pair $MgSO_4^0$ in the case of Mg^{2+} and SO_4^{2-} [9], or to the hydrogen sulfate ion HSO_4^- in the case of sulfate in the pH gradient.

In environmental media, the ionic pollutants exist in various forms. For instance, toxic heavy metal ions of various valencies such as zinc, cadmium, lead, and mercury, may form a series of complexes with complexing ions like chloride, nitrate and hydroxide, among others. The speciation of these ions in the environment is an important issue because complexation modifies the electric charge borne by the ions. Consequently it modifies the transport of trace metal ions when they are submitted to diffusion electric fields caused by major ions in the environmental medium and the physical and chemical behavior of the ion interacting with the environment.

Various softwares exist commercially which permit estimations of the speciation for many metal ions in aqueous solutions. One may cite the following which have been developed in various countries: MINTEQ [12], MINEQL+ [13], JCHESS [14], PHREEQC [15] and CHEAQS [16]. The calculation of the speciation is based on a solution to the chemical association equilibria which involve the introduction of thermodynamic association constants (cumulative constants β_n for $n = 1, 2, 3, ...$) and the use of formulas for the computation of the activity coefficients of the species. The softwares rely on previous determinations of the association constants, which can be found in famous books (e.g., in the book by Sillen and Martell [17]) or in the NIST Database [18]. In general deviations from ideality were computed using equations of the Debye–Hückel type (like the Davies equation). Depending on the values taken for the β_n's and on the equation used, the softwares may give speciations that differ in magnitude. Because the speciation is generally very difficult to determine experimentally without ambiguity, there may be some uncertainty in the determination of speciation in electrolyte solutions.

We propose to study transient diffusion patterns produced by some metal cations giving rise to multiple association. The metal cation used in tracer amount is placed in the diffusion electric field originating from the diffusion of a major salt. Then, this type of experiment is an extension of the experiments we had carried out with magnesium(II) ion and sulfate ion [9,10] which gave one ion pair to the case of electrolytes leading to a series of stepwise associations. It is a way of probing the validity of traditional approaches to describe the motion of such complex associating salts in internal electric fields.

In this work, we carried out experiments with zinc(II) cation which can multiply associate with the chloride anion. In the configuration used zinc(II) ion can give 4 complexes: $ZnCl^+$, $ZnCl_2^0$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ [17]. These complexes should be of covalent nature, except for the monochloro-complex $ZnCl^+$ which may be essentially ionic [19]. The zinc ion was taken in radioactive form, $^{65}Zn^{2+}$. A special technique consisting of a silica capillary inserted in a cylinder of scintillating plastic was utilized to observe the transient concentration profiles of the radioactive tracer [20]. The major salt producing the internal electric field was LiCl. It was chosen because it produces a strong electric field, which is due to the greatly differing values of the diffusivities of the two ions Li^+ and Cl^-. The observed experimental transient profiles were modeled by using finite differences and normal–mode techniques. In contrast with previous work about coupling diffusion, the deviations from ideality were included in the algorithms and complexation was taken into account to arbitrary order. For this purpose the activity coefficients of

all species were calculated using the mean spherical approximation. The results obtained from these methods were compared with the experimental data.

CHAPTER 2

ELECTROLYTES AT EQUILIBRIUM

2.1   Physical System

A mixture of two aqueous electrolyte solutions is considered: an MA salt (or the major electrolyte) combined with an TA salt (where cation T is radiactive) with arbitrary ion's valences and both salts having the same anion. Moreover, in this work we are considering that we have a non-ideal solution where the only associating ions are the cation T and the anion A, such that each cation T can bind an arbitrary number of anions.
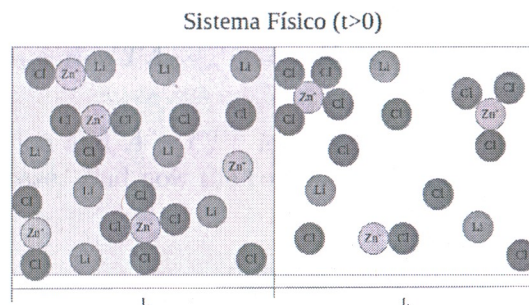
Figure 2.1: Physical system: A mixture of an MA salt (or the major electrolyte) combined with an TA salt with arbitrary ion's valences and both salts having the same anion where only the cation T associates with the anion A to make complexes. We show the case of LiCl with $ZnCl_2$ to illustrate our system.

We start our analysis describing the physical electrolyte model that we are considering on this work. The electrolyte in question considers complex formation, i.e. we have the formation of different "species" inside our solution, specifically the ones which includes the binding of zinc ion with one clhoride ion, the binding of zinc-chloride with one chloride anion, the binding of zinc-2chloride with one chloride ion and so on until complete four chloride binded ions to the zinc. The Figure 2.1 show us the two ion with its respective binding sites.
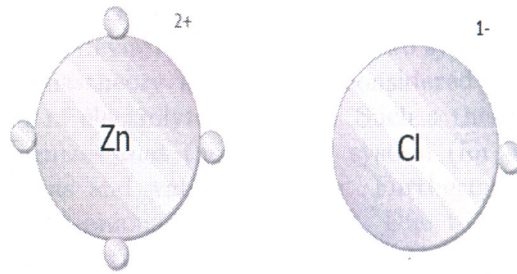
Figure 2.2: In this figure we show both ions with its respective binding sites. The different species were done with some particular combinations of these ions.

Now we write the reaction equations who describe our system where we include the activity coefficients. Those are given next:

$$T + A = TA \qquad K_1 = \frac{\gamma_D C_D}{\gamma_T C_T (\gamma_A C_S)}$$

$$TA + A = TA_2 \qquad K_2 = \frac{\gamma_{TR} C_{TR}}{\gamma_D C_D (\gamma_A C_S)}$$

$$TA_2 + A = TA_3 \qquad K_3 = \frac{\gamma_{TE} C_{TE}}{\gamma_{TR} C_{TR} (\gamma_A C_S)}$$

$$TA_3 + A = TA_4 \qquad K_4 = \frac{\gamma_{PE} C_{PE}}{\gamma_{TE} C_{TE} (\gamma_A C_S)} \qquad (2.1)$$
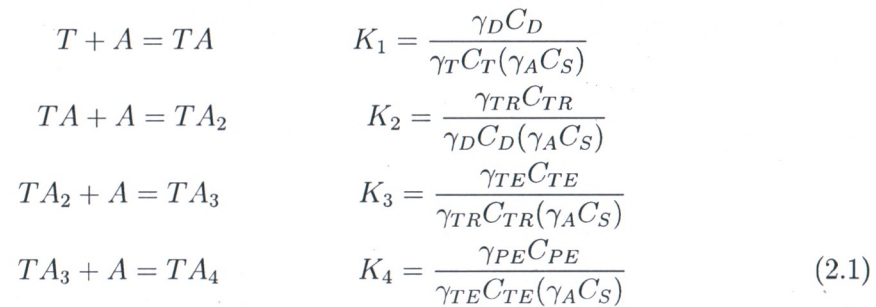
Where $T = Zn^{*2+}$ ion and $A = Cl^{1-}$ ion, i.e. the zinc ion is the tracer (radiactive ion) in this particular case. And now the complex concentrations takes the form

$$C_D = \frac{\beta_1 \gamma_T C_T (\gamma_S C_S)}{\gamma_D}$$

$$C_{TR} = \frac{\beta_2 \gamma_T C_T (\gamma_S C_S)^2}{\gamma_{TR}}$$

$$C_{TE} = \frac{\beta_3 \gamma_T C_T (\gamma_S C_S)^3}{\gamma_{TE}}$$

$$C_{PE} = \frac{\beta_4 \gamma_T C_T (\gamma_S C_S)^4}{\gamma_{PE}} \qquad (2.2)$$

Where we can see that all the concentrations depends on the salt concentration and the tracer concentration. Moreover the $\beta_i's$ variables are the so called cummulative equilibrium constants defined by:

$$\beta_i = K_1 \cdot K_2 \cdot K_3 \cdots K_{i-1} \cdot K_i, \qquad i = 1, \ldots, n \qquad (n = \text{positive integer}) \qquad (2.3)$$

2.2   The Debye–Hückel theory and primitive model

The Debye–Hückel (DH) theory is a theoretical explanation proposed by P. Debye and E. Hückel in 1923, to explain the deviation of ideality for two systems of interest: electrolyte solutions and plasmas. This theory nowadays is considered as the starting point for treatments of non–ideality of electrolyte solutions. Such a theory is based on the next considerations: 1) it recognizes that the physical system (for aqueous electrolytes) is conformed by cations, anions and water molecules. Furthermore, the water molecules can hydrate the cations and anions in some ways. Due to the fact that there is to difficult to consider water structure, Debye and Hückel decide to "remove" the water molecules, retaining only its dielectric effect via its electrical permitivity. This physical space is knowed as the "dielectric continuum". 2) On average, each ion is surrounded by counterions (ions of opposite charge) and they will aggregate to form clusters: choose an arbitrary ion with charge $z_c e$ at the center, then many counterions will surround the ion forming a "charge's cloud" neutralizing the ion's charge $z_c e$. Besides, that first "cloud" will result in the emergence of a new neighbour "cloud" that will surround the first and it will be of opposite sign. And so on. These "clouds" are called "cospheres" and the center ion has a group of cospheres surrounding it. Placing a test charge e at a distance $\mathbf{r}$ from the center ion will interact with the center ion and the cospheres ions via Coulomb's equation. The average electrostatic potential (AEP) $\Psi(\mathbf{r})$ (which is the sum of the Coulomb interaction with $z_c e$ and all the cosphere interactions that the test charge will experience coming from $r = \infty$ to r) that the unit charge will experience in the solution was described by Debye and Hückel with the use of Poisson's equation. 3) The ions in the cospheres follows a *Boltzmann distribution*. 4) It is possible to *linearize* the resulting Poisson-Boltzmann equation. 5) The cations and anions don't have volume which means that they're *point charges*. This kind of model is called the primitive model (PM). If we consider a neutral mixture of charged hard spheres (insted of point charges) of the same or different diameter σ_i and charge $z_i e$ we are talking about the restricted and unrestricted primitive model (RPM and UPM) [21].

2.3   The mean spherical approximation for the restricted primitive model

The principal problem with the DH theory is that it doesn't takes into account the interactions at short range level between the particles (ions, in the case of electrolytes) which is a very important fact when the solute concentration is increased. The mean spherical approximation (MSA) deals with this problems considering the sizes of the particles and the electrostatic long-range interactions. The MSA is an analytical theory that could be used for electrolyte solutions in the ionic approach. The name cames because this approximation is a generalization of the mean spherical model (MSM) of Ising spin systems was introduced. The spherically symmetric case (all the ions has the same diameter) has the next general form for the potential

$$v(\boldsymbol{r}) = \infty \qquad\qquad \boldsymbol{r} < \sigma$$
$$\qquad = v_1(\boldsymbol{r}) \qquad\qquad \boldsymbol{r} > \sigma \tag{2.4}$$

where σ is the hard-sphere diameter. Similarly, in terms of the pair distribution function and direct correlation function it states

$$g(\boldsymbol{r}) = 0 \qquad\qquad \boldsymbol{r} < \sigma$$
$$c(\boldsymbol{r}) = -\beta v_1(\boldsymbol{r}) \qquad\qquad \boldsymbol{r} > \sigma. \tag{2.5}$$

On the other hand, the Ornstein-Zernike (OZ) equation which is a definition of the direct correlation function $c(\mathbf{r})$ can be written down mathematically as

$$h(\mathbf{r}) - c(\mathbf{r}) = \sum_{\mathbf{k}} \int d\mathbf{r_1} h(\mathbf{r_1}) c(|\mathbf{r} - \mathbf{r_1}|) \tag{2.6}$$

Combining the expressions (2.4), (2.5) and (2.6) we obtain an integral equation for the pair distribution function $g(r)$. Furthermore, an attractive feature of the MSA is that the integral equation can be solved analytically for a various potential models of physical interest, per example, the hard core Yukawa fluid, simple models of electrolyte solutions and polar liquids [22].

Next, we proceed to give a description of the different contributions to the thermodynamics and the radial distribution functions of a primitive model, within the MSA description.

Thermodynamics

The density of free energy f (defined as $f = F/V$) is the charged hard-spheres mixture's density, and it's naturally separated in the next terms

$$\beta f = \beta f^{id} + \beta f^{hs} + \beta f^{el} \tag{2.7}$$

with f^{id} the ideal contribution, f^{hs} the hard-sphere (i.e., the excluded-volume) and f^{el} the electrostatic free energy contribution terms.

Ideal contribution

The ideal contribution is equal to the free energy of the same composition ideal-gas

$$\beta f^{id} = \sum_i \rho_i (\beta \mu_i^{id} - 1) \tag{2.8}$$

with the equallity $\beta \mu_i^{id} = \ln(\Lambda_i^3 \rho_i)$ (a term who depends on the species's density and mass) and Λ_i the knowed i-th thermal de Broglie's wavelength $\Lambda_i = (\frac{h}{2\pi m_i k_B T})^{\frac{1}{2}}$.

Hard-sphere contribution or Excluded Volume Contribution

The hard sphere contribution βf^{HS} is calculated from the Carnahan-Starling approximation [23, 24] to get

$$\frac{\pi}{6} \beta f^{HS} = \left(\frac{X_2^3}{X_3^2} - X_0 \right) \ln(\Delta) + \frac{3X_1 X_2}{\Delta} + \frac{X_2^3}{X_3 \Delta^2} \tag{2.9}$$

where

$$X_n = \frac{\pi}{6} \sum_k \rho_k \sigma_k^n$$

$$x = \Delta = 1 - X_3 \tag{2.10}$$

Electrostatic contribution

The electrostatic contribution obtained by the MSA solution has the form

$$\beta f^{el} = \beta \Delta E + \frac{\Gamma^3}{3\pi} \tag{2.11}$$

where the definition of the excess internal energy is

$$\beta \Delta E = -\frac{\beta e^2}{\epsilon} \left[\Gamma \left(\sum_i \frac{\rho_i z_i^2}{1 + \Gamma \sigma_i} \right) + \eta \sum_k \frac{\rho_k \sigma_k z_k}{1 + \Gamma \sigma_k} \right] \tag{2.12}$$

where Γ could be seened as the generalization of the inverse Debye's length (κ_D, definded below) and can be obtained from the next implicit equation

$$2\Gamma = \left[\frac{4\pi \beta e^2}{\epsilon} \sum_j \rho_j \left(\frac{z_i - \sigma_i^2 \eta}{1 + \Gamma \sigma_i} \right)^2 \right]^{\frac{1}{2}} \tag{2.13}$$

and

$$\eta = \frac{1}{\Omega} \frac{\pi}{2\Delta} \sum_j \frac{\rho_j \sigma_j z_j}{1 + \Gamma \sigma_j} \tag{2.14}$$

$$\tag{2.15}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k} \tag{2.16}$$

with Δ defined by (2.10)

Usually, (2.13) and (2.16) is easily solved by iteration starting with the initial value $2\Gamma_1 = \kappa_D$, where κ_D is the Debye screening parameter:

$$\kappa_D = \left(\frac{4\pi \beta e^2}{\epsilon} \sum_i \rho_i z_i^2 \right)^{1/2} \tag{2.17}$$

With the mean ionic parameter approximation $\sigma_i = \sigma$ (which mean that all the species have the same diameter) eq. (2.10) becomes

$$\Gamma = [(1 + 2\kappa_D \sigma_S)^{1/2} - 1]/(2\sigma_S)$$

$$\kappa_D = \left(4\pi\lambda \sum_i \rho_i z_i^2\right)^{\frac{1}{2}}$$

$$\kappa_D \cong (8\pi\lambda\rho_S)^{\frac{1}{2}} \tag{2.18}$$

with

$$\lambda = \frac{1}{kT} \frac{e^2}{4\pi\epsilon_0\epsilon_r} \cong 7.14\text{Å} \tag{2.19}$$

for $\epsilon_0 = 8.85 \times 10^{-12}$ the vacuum permittivity and $\epsilon_r = 78.38$ the dielectric constant of water at $T = 25\ ^\circ$C.

Activity Coefficients Using the MSA

The activity coefficients using the MSA (on the laboratory system of reference, i.e., the reference frame in which the experiment is done) are [25, 26]

$$\ln\gamma_i^{LR} = \ln\gamma_i^{MM} - C \cdot V_i\phi^{MM} \tag{2.20}$$

where C is the total concentration and is equal to $2C_S$ in our case.
While for a salt S in a mixture the activity coefficient is:

$$\ln\gamma_S^{LR} = \ln\gamma_S^{MM} - 2C_S V_S\phi^{MM}/\nu_S$$
$$\ln\gamma_S^{LR} = \ln\gamma_S^{MM} - C_S V_S\phi^{MM}/ \tag{2.21}$$

with $\nu_S = \nu_+ + \nu_- = 2$ and V_S the mean partial molar volume of salt S defined by

$$V_S = \frac{M_S - d'_S}{d - C_S d'_S} \tag{2.22}$$

where M_S is the molar mass of S, C_S its molar concentration and $d'_S = \partial d/\partial C_S$ and d is the density of the solution and is given as a polinomial function of the salt concentration as

$$d = d_w + d_1 C_S - d_2 C_S^{3/2} \tag{2.23}$$

d_w is the density of the pure solvent (water, in our particular case), d_1 and d_2 are constant coefficients whose value depends on the solvent in question.

Osmotic coefficient

The osmotic coefficient at the MacMillan-Mayer level has the next form

$$\phi^{MM} = 1 + \phi^{MSA} + \phi^{HS} \tag{2.24}$$

where the mean spherical approximation or the electrical contribution is written as

$$\phi^{MSA} = -\frac{\Gamma^3}{3\pi\rho_t}, \tag{2.25}$$

$\rho_t \approx 2\rho_S$ = total density of the system, with ρ_S the salt density. The hard sphere (HS) contribution becomes

$$\phi^{HS} = \frac{X_3}{1 - X_3} + \frac{3X_1 X_2}{X_0(1 - X_3)^2} + \frac{X_2^3(3 - X_3)}{X_0(1 - X_3)^3} \qquad (2.26)$$

with the terms $X_i's$ defined by (2.10)

For now, we'll keep our attention just on MacMillan-Mayer's activity coefficients relation for the complex and the tracer. So we need both contributions: the one due to the electrostatic contribution and the other one due the hard sphere.

Hard Sphere contribution This contribution is given by the equation:

$$ln(\gamma_i)^{(HS)} = -\ln x + \sigma_i \cdot F_1 + \sigma_i^2 \cdot F_2 + \sigma_i^3 \cdot F3 \qquad (2.27)$$

and

$$F_1 = \frac{3X_2}{x}$$

$$F_2 = 3\frac{X_1}{x} + 3\frac{X_2^2}{X_3}\frac{1}{x^2} + 3\frac{X_2^2}{X_3^2}\ln x$$

$$F_3 = \left(X_0 - \frac{X_2^3}{X_3^2}\right)\frac{1}{x} + \frac{3X_1 X_2 - X_2^3/X_3^2}{x^2} + 2\frac{X_2^3}{X_3^3}\ln x \qquad (2.28)$$

where X_n and x are obtained from (2.10).

From 2.27 we can write the activity coefficient's HS contribution for every zinc's complexes and for the salt

$$\ln \gamma_T^{HS} = -\ln x + \sigma_T F_1 + \sigma_T^2 F_2 + \sigma_T^3 F_3$$

$$\ln \gamma_D^{HS} = -\ln x + \sigma_D F_1 + \sigma_D^2 F_2 + \sigma_D^3 F_3$$

$$\ln \gamma_{TR}^{HS} = -\ln x + \sigma_{TR} F_1 + \sigma_{TR}^2 F_2 + \sigma_{TR}^3 F_3$$

$$\ln \gamma_{TE}^{HS} = -\ln x + \sigma_{TE} F_1 + \sigma_{TE}^2 F_2 + \sigma_{TE}^3 F_3$$

$$\ln \gamma_{PE}^{HS} = -\ln x + \sigma_{PE} F_1 + \sigma_{PE}^2 F_2 + \sigma_{PE}^3 F_3$$

$$\ln \gamma_S^{HS} = -\ln x + \sigma_S F_1 + \sigma_S^2 F_2 + \sigma_S^3 F_3$$

$$(2.29)$$

2.4 Activity Coefficient Curves

We start writing the Zinc system's total concentration

$$C_{TOT} = C_T + C_D + C_{TR} + C_{TE} + C_{PE} \qquad (2.30)$$

where we are considering the zinc clhoride electrolyte's complex formations: Dimer $[ZnCl](z_2 = 1+)$ Trimer $[ZnCl_2](z_3 = 0)$, Tetramer $[ZnCl_3](z_4 = 1-)$ and Pentamer $[ZnCl_4](z_5 = 2-)$. Using the BiMSA paper notation [26] for the activity coefficients, the

concentration equations 2.2 becames

$$C_D = \frac{\beta_1 \cdot \gamma_T^{(LR)} \cdot C_T \cdot \gamma_S^{(LR)} \cdot C_S}{\gamma_D^{(LR)}}$$

$$C_{TR} = \frac{\beta_2 \cdot C_T \cdot \gamma_T^{(LR)}(\gamma_2^{(LR)} \cdot C_S)^2}{\gamma_{TR}^{(LR)}}$$

$$C_{TE} = \frac{\beta_3 \cdot C_T \cdot \gamma_T^{(LR)}(\gamma_S^{(LR)} \cdot C_S)^3}{\gamma_{TE}^{(LR)}}$$

$$C_{PE} = \frac{\beta_4 \cdot C_T \cdot \gamma_T^{(LR)}(\gamma_S^{(LR)} \cdot C_S)^4}{\gamma_{PE}^{(LR)}} \tag{2.31}$$

And then equation (2.30) becames

$$C_{TOT} = \frac{\beta_1 \cdot \gamma_T^{LR} \cdot C_T \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot C_T \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}}$$
$$+\frac{\beta_3 \cdot C_T \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot C_T \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}} \tag{2.32}$$

Now, if we define the concentration fractions (denoted by $X_i's$) as

$$X_T = \frac{C_T}{C_{TOT}}$$

$$X_D = \frac{C_D}{C_{TOT}}$$

$$X_{TR} = \frac{C_{TR}}{C_{TOT}}$$

$$X_{TE} = \frac{C_{TE}}{C_{TOT}}$$

$$X_{PE} = \frac{C_{PE}}{C_{TOT}} \tag{2.33}$$

Then, substituting eqs. (2.31) and (2.32) on (2.33) gets

$$X_T = \frac{1}{\frac{\beta_1 \cdot \gamma_T^{LR} \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}} + \frac{\beta_3 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}}} \tag{2.34}$$

$$X_D = \frac{\frac{\beta_1 \cdot \gamma_{TLR} \cdot \gamma_{2LR} \cdot C_S}{\gamma_{DLR}}}{\frac{\beta_1 \cdot \gamma_T^{LR} \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}} + \frac{\beta_3 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}}} \tag{2.35}$$

$$X_{TR} = \frac{\frac{\beta_2 \cdot \gamma_{TLR}(\gamma_{2LR} \cdot C_S)^2}{\gamma_{TRLR}}}{\frac{\beta_1 \cdot \gamma_T^{LR} \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}} + \frac{\beta_3 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot \gamma_T^{LR}(\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}}} \tag{2.36}$$

$$X_{TE} = \frac{\frac{\beta_3 \cdot \gamma_{TLR} (\gamma_{2LR} \cdot C_S)^3}{\gamma_{TELR}}}{\frac{\beta_1 \cdot \gamma_T^{LR} \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}} + \frac{\beta_3 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}}} \tag{2.37}$$

$$X_{PE} = \frac{\frac{\beta_4 \cdot \gamma_{TLR} (\gamma_{2LR} \cdot C_S)^4}{\gamma_{PELR}}}{\frac{\beta_1 \cdot \gamma_T^{LR} \cdot \gamma_S^{LR} \cdot C_S}{\gamma_D^{LR}} + \frac{\beta_2 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^2}{\gamma_{TR}^{LR}} + \frac{\beta_3 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^3}{\gamma_{TE}^{LR}} + \frac{\beta_4 \cdot \gamma_T^{LR} (\gamma_S^{LR} \cdot C_S)^4}{\gamma_{PE}^{LR}}} \tag{2.38}$$

Note that in equations (2.34)-(2.38) the dependence on C_T vanishes. The curves on 2.3 were obtained using Maple13 [27].
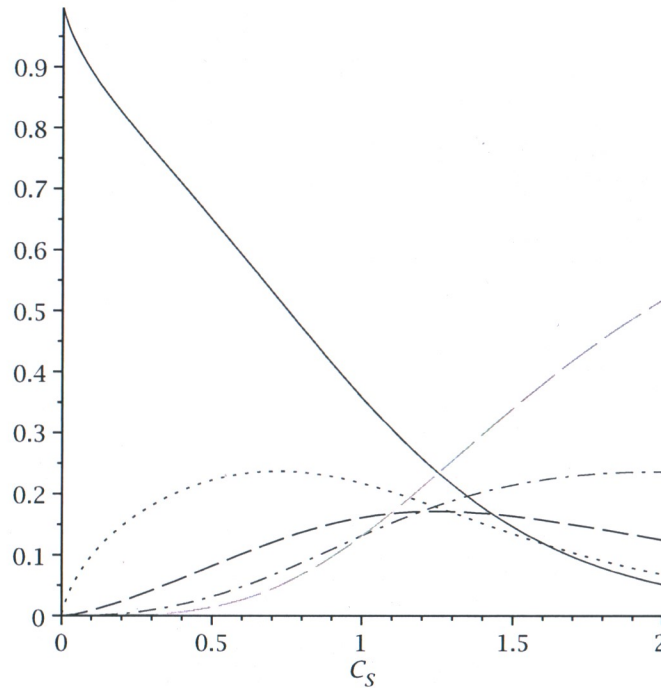
Figure 2.3: "Molar fractions" of the complexes on the system. Solid is for Tracer, dot for Dimer, dash for Trimer, dashdot for Tetramer and longdash for Pentamer

2.5 Multiply associating electrolytes in the binding mean spherical approximation (BiMSA)

The MSA has provided poor results for a highly-charged systems with low solvent dielectric constant that presents strong electrostatic attraction, where the association of free ions to create complexes is favoured. The development of a theory which permits bond's formation between ions via a sticky-point potential which is a generalization of the MSA,

is due to Blum and Bernard. From now on, we'll consider a binary ionic solution consti-
tuted from a salt (a cation and an anion) in a solvent (usually water). We assume that
one of the ions has multiple association sites and binds to its one-site counterion. This ion
will be called polyion, denoted by p and the counterion denoted by c. The two ions have
number densities ρ_i, charge ez_i and hard core diameter σ_i. The solvent is regarded as a
continuum of relative permittivity ϵ_r. The temperature of the system is T, Boltzmann's
constant is k_B and we set $\beta = 1/k_B T$ throughout. The sites on the ions are randomly
positioned on their surface. These binding sites will be denoted by S_k, with k an integer
running from 1 to N for the polyion. For this model, the free energy can now be written
as [28]

$$\beta \Delta A = \beta \Delta E^{el} + \frac{[\Gamma^B]^3}{3\pi} - \beta(\hat{\rho}_{pc} W_{pc}^{el} + \hat{\rho}_{cc} W_{cc}^{el}) + \beta \Delta A^{ass} \tag{2.39}$$

where

$$\left[\frac{\partial \Delta E^{el}}{\partial \hat{\rho}_p^{(a)}} \right]_{\Gamma^B} = \frac{e^2}{\epsilon} \frac{2\chi_p^0 \chi_c^0}{\sigma_p + \sigma_c} \equiv W_{pc}^{el}, \tag{2.40}$$

$$\left[\frac{\partial \Delta E^{el}}{\partial \hat{\rho}_p^{(ab)}} \right]_{\Gamma^B} = \frac{e^2}{\epsilon} \frac{2(\chi_c^0)^2}{(\sigma_p + 2\sigma_c)(1 + \Gamma^B \sigma_p)} \equiv W_{cc}^{el}. \tag{2.41}$$

Osmotic and mean activity coefficients

The osmotic coefficient can be separated in electrostatic and associative contribution
like

$$\Delta \phi = \Delta \phi^{el} + \phi^{as} \tag{2.42}$$

with

$$\Delta^{el} = -\frac{[\Gamma^B]^3}{3\pi\zeta_0} - \frac{e^2 \beta}{\epsilon\zeta_0} \frac{2}{\pi} [\eta^T]^2 \tag{2.43}$$

and

$$\Delta \phi^{as} = -\frac{1}{\zeta_0} \rho_c (1 - \alpha_c) \left[1 + \sum \rho_k \frac{\partial ln g_{pc}^{HS}(\sigma_{pc})}{\partial \rho_k} \right] \tag{2.44}$$

Meanwhile the mean activity coefficient can also be separated in two contributions

$$\Delta ln\gamma_{\pm} = \Delta ln\gamma_{\pm}^{el} + \Delta ln\gamma_{\pm}^{as} \tag{2.45}$$

with

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$$\Delta ln\gamma_{\pm}^{el} = \frac{e^2\beta}{\epsilon\zeta_0}\left[\sum_k \rho_k z_k M_k^0 - \eta^T \sum_k \rho_k \sigma_k \left(\chi_k^0 + \frac{\eta^T}{3}\sigma_k^2\right)\right] \tag{2.46}$$

and

$$\Delta ln\gamma_{\pm}^{as} = \frac{\rho_{pc}}{\zeta_0}ln\alpha_c + \frac{\rho_p}{\zeta_0}ln\alpha_p - \frac{1}{\zeta_0}\rho_c(1-\alpha_c)\sum_k \rho_k \frac{\partial ln g_{pc}^{HS}(\sigma_{pc})}{\partial \rho_k}. \tag{2.47}$$

We included section 2.5 to show that Equations (2.45) to (2.47) (for the activity coefficient's) considers the dependence on complex densities and can be used as an extension of that obtained via MSA. We assume that in our particular case, the use of the later extensions weren't necessary because we work at not so high concentrations for the present salts.

CHAPTER 3

NON–EQUILIBRIUM ELECTROLYTES

3.1 Flows and currents

A non–equilibrium thermodynamic system is submitted to various internal and external forces who are responsible of the irreversible processes and chemical reactions inside the system. Chemical reactions don't require inhomogeneities on the space such like the transport phenomena who really needs an intensive variable gradient to produce flows which are proportional to those gradients at low particle concentrations. Regularly, transport phenomena and chemical reactionss are coupled, and therefore they present a series of complexes physicochemical phenomena [29].

In a system where the particles are represented by $X_i (i = 1, 2, \ldots, k)$, with local concentrations $c_i(\vec{r}, t)$ and velocities $\vec{v}_i(\vec{r}, t)$ a particle's flow $\vec{J}_i$ has an origin taken in relation with a velocity of reference $\vec{v}_{ref}$.

$$\vec{J}_i = c_i(\vec{v}_i - \vec{v}_{ref}); \qquad \vec{v}_{ref} = \sum_i g_i \vec{v}_i; \qquad \sum_i g_i = 1 \qquad (3.1)$$

with g_i as a weight factor dependent on the choice of the reference system. The reference system can be Hittorf or Fick and the reference velocity in Hittorf and Fick systems are, respectively, the velocity of the solvents and the mean velocity of all particles. Moreover, the velocity of reference may be ignored which is our case. The flow of particles X_i passing across an arbitrary surface S inside our system yields a diffusion current ϕ_i

$$\phi_i = \iint \vec{J}_i d\vec{S}. \qquad (3.2)$$

The flow across a closed surface surrounding a volume V yields the integral form of continuity equation

$$\oint \vec{J}_i d\vec{S} = -\iiint_V \partial_t c_i dV, \qquad (3.3)$$

or using the normal vector $\hat{n}$ notation and the divergence theorem

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$$\oint \vec{J_i} \cdot d\vec{S} = \oint J_i \hat{n} \cdot d\vec{S} = \iiint_V \nabla \cdot \vec{J_i} dV$$

i.e.

$$\iiint_V (\nabla \cdot \vec{J_i} + \partial_t c_i) = 0$$
$$\implies \qquad \nabla \cdot \vec{J_i} = -\partial_t c_i \qquad (3.4)$$

The later equation is valid when there is no other process inside volumen V who can change the concentrations c_i, or, broadly speaking, if there are no negative or positive sources of particle X_i in V.

Particularlly, if there are some chemical reactions ocurring on our system changing the concentrations c_i at a rate χ_i, the continuity equation (3.4) shows the generalized form

$$\frac{\partial c_i(\vec{r}, t)}{\partial t} + \nabla \cdot \vec{J_i}(\vec{r}, t) = \chi_i(\vec{r}, t) \qquad i = 1, 2 \ldots, k \qquad (3.5)$$

One typical example is the creation of an ion-pair

$$X_1 + X_2 \underset{k}{\overset{k'}{\rightleftharpoons}} X_3; \qquad K_A = \frac{k}{k'} \qquad (3.6)$$
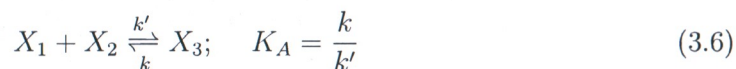
with X_1, X_2 and X_3 the cation, anion and ion pair, respectively; k, k' are the rate constants of formation and decomposition, and K_A the association constant.

The particle sources for this particular example yields

$$\chi_1 = k'c_3 - kc_1c_2$$
$$\chi_2 = k'c_3 - kc_1c_2$$
$$\chi_3 = kc_1c_2 - k'c_3$$

$$(3.7)$$

The above relations (3.5) are valid in the following cases:

- If do not exist chemical reactions inside the volume V ($\chi_i = 0$) which implies that (3.5) reduces to (3.4)

- They apply to any system having an equilibrium perturbation due to some internal sources.

- They apply to systems with spontaneous fluctuations, where the variables must satisfy the following relations:

$$c_i(\vec{r}, t) = <c_i> + \delta c_i$$
$$\vec{J_i}(\vec{r}, t) = <\vec{J_i}> + \delta \vec{J_i}$$
$$\chi_i(\vec{r}, t) = <\chi_i> + \delta \chi_i \qquad (3.8)$$

where $< c_i >$, $< \vec{J}_i >$, $< \chi_i >$ are the mean values, and δC_i, $\delta \vec{J}_i$ and $\delta \chi_i$ are its fluctuations, respectively. In equilibria $< \vec{J}_i >=< \chi_i >= 0$ and $\partial_t < c_i >= 0$, then the fluctuations should satisfy equation (3.5) in the following manner

$$\partial_t [\delta c_i] + \nabla \cdot [\delta \vec{J}_i] = [\delta \chi_i]; \quad i = 1, 2, \ldots, k \tag{3.9}$$

- They apply to non–equilibrium steady-states systems having time-constant concentrations but not space-constant concentrations. Here the quantities $< \vec{J}_i >$ and $< \chi_i >$ can have non-zero values without any dependence in time and space..

- The relation (3.9) has validity even when external perturbations lead to relaxations.

The equation's system (3.5) are far from being a closed system. To achieve this we add a "constitutive relations" or "closure equations" who relates flows J_i and concentrations c_i. Needless to say that the reference velocity vanishes, at this level of discussion and the resulting action-force particle's velocity $\vec{F}_i$ on particle X_i could be considered proportional to this force.

$$\vec{J}_i(\vec{r}, t) = c_i(\vec{r}, t)\vec{v}(\vec{r}, t)$$
$$\vec{v}_i(\vec{r}, t) = \omega_i \vec{F}_i(\vec{r}, t), \tag{3.10}$$

where ω_i and $\vec{F}_i$ are the generalized mobility of particle X_i and the force acting on particle X_i, respectively. This force can be seen as a gradient of the electrochemical potential per particle X_i

$$\tilde{\mu}_i(p, T) = \mu_i(p, T) + \mathcal{F} z_i \phi$$
$$\mathcal{F} = \text{Faraday number}$$
$$\phi = \text{Galvani potential of the liquid}$$
$$\mu_i = \text{Chemical potential}$$

$$\vec{F}_i = -\frac{1}{N_A}\mathbf{grad}\tilde{\mu}_i(p, T)$$
$$\vec{F}_i = -\frac{1}{N_A}\nabla\mu_i(p, T) - \frac{\mathcal{F} z_i}{N_A}\nabla\phi$$

where N_A is the Avogadro's number. If we use the definition of the chemical potential in terms of the concentration and Farday's constant definition ($\mathcal{F} = e N_A$ is the electric's charge magnitud per mole of electrons), we obtain the force is rewrited as

$$\vec{F}_i = -\frac{1}{N_A}\left[\nabla\mu_i^0(p, T) + RT\nabla ln(c_i\gamma_i)\right] - z_i e\nabla\phi$$

or

$$\vec{F}_i = -kT\nabla ln(c_i\gamma_i) - z_i e\nabla\phi \tag{3.11}$$

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with the universal gas constant $R = k_B N_A$.

Similarly, if we use kinetic theory Einstein's relation ($D_i = \omega_i kT$) and the usual expression between electric field and potential ϕ ($\vec{E} = -\nabla\phi$) on (3.10), we obtain for the expression for the flux

$$\vec{J}_i = c_i\omega_i\vec{F}_i = c_i\omega_i\left[-kT\nabla ln(c_i\gamma_i) + z_i e\vec{E}\right] = -D_i\nabla c_i - D_i c_i\nabla ln\gamma_i + z_i e\frac{D_i c_i}{kT}\vec{E} \quad (3.12)$$

and for an ideal system

$$\vec{J}_i = -D_i\nabla c_i + z_i e\frac{D_i c_i}{kT}\vec{E} \quad (3.13)$$

In the latest equations the first term(s) concerns to the chemical forces producing a Fick's law type flow. The second term results from the electrical forces which are caused by external and internal electric fields. Here the only electric parameters of interest are the internal fields as a result of local fluctuations of electroneutrality. The external fields and high frequency contributions as well as relaxations effecs (second order effects) hasn't been considered.

If the equation (3.13) is used on (3.5) we obtain the non–ideal diffusion equation

$$\frac{\partial c_i(\vec{r}, t)}{\partial t} - D_i\nabla\cdot\left(\nabla c_i + c_i\nabla ln\gamma_i - \frac{z_i e c_i}{kT}\vec{E}\right) = \chi_i(\vec{r}, t) \qquad i = 1, 2\ldots, k \quad (3.14)$$

or

3.2 Principles of normal mode analysis

A general strategy to solve a differential equation's system (4.21) where flows and source terms have been related by some "adecuated" closure relations, is to transform that system into a set of algebraic equations using Fourier and Laplace transformations.

The main property of Fourier transformation is the effect on the derivatives of the space variable $\vec{r}$ of the form

$$\int \boldsymbol{grad} c_i(\boldsymbol{r}, t)\exp(\boldsymbol{iq}\cdot\boldsymbol{r})d\boldsymbol{r} = -\boldsymbol{iq}\int c_i(\boldsymbol{r}, t)\exp(\boldsymbol{iq}\cdot\boldsymbol{r}) = -\boldsymbol{iq}c_i(\boldsymbol{q}, t) \quad (3.15)$$

$$\int \mathrm{div}\boldsymbol{grad} c_i(\boldsymbol{r}, t)\exp(\boldsymbol{iq}\cdot\boldsymbol{r})d\boldsymbol{r} = -\boldsymbol{q}^2 c_i(\boldsymbol{q}, t) \quad (3.16)$$

For its part, a time derivative Laplace transformation of a variable $c_i(\boldsymbol{q}, t)$ gives

$$\int_0^\infty \frac{\partial c_i(\boldsymbol{q}, t)}{\partial t}\exp(-st)dt = sc_i(\boldsymbol{q}, s) - c_i(\boldsymbol{q}, t = 0) \quad (3.17)$$

where $c_i(\boldsymbol{q}, t = 0)$ is the state of the system at time's origin (t=0).

Once the algebraic equations have been established, their generalization in the $(\boldsymbol{q}, s)$ space is carried out simply by retaining only the first order terms of the perturbations. As a result, the linear system of algebraic equations of the type of

$$M(q, s)c(q, s) = c(q, t = 0) \tag{3.18}$$

in the Fourier-Laplace space is obtained. The matrix of $M(q, s)$ contains the relevant information from the input.

The boundary or initial conditions are stored in vector $c(q, t=0)$. The response of the system to a perturbation or fluctuation is reflected by the vector $c(q, s)$.

$$c(q, s) = M^{-1}(q, s)c(q, t = 0) \tag{3.19}$$

With a system of k starting equations of type (4.21), an algebraic system of k linear equations is obtained. The determinant $|M(q, s)|$ od this system yields a polynomial of degree k in the variables s with k roots, real or complex, $s_1 \ldots s_k$

$$|M(q, s)| = (s - s_1)(s - s_2) \cdots (s - s_k) \tag{3.20}$$

from which the reciprocal is obtained with the help of partial fraction expansion

$$\frac{1}{|M(q, s)|} = \frac{A_1}{(s - s_1)} + \frac{A_2}{(s - s_2)} + \cdots + \frac{A_k}{(s - s_k)} \tag{3.21}$$

The relevant property of retransformation is the exponential $exp[-s_i t]$ as the Laplace original of $(s - s_i)^{-1}$. For stable systems all roots of $|M(q, s)|$ have negative real parts, indicating that all fluctuations or heterogeneities decay in time

$$c(q, t) = \sum_{i=1}^{k} B_i(q)\exp(s_i t) \tag{3.22}$$

The roots of $|M(q, s)|$ are the normal modes of the system. With the exception of a few cases there is no need to evaluate the retransformation of $c(q, t)$ to the Fourier original $c(r, t)$ because all the relevant physics and chemistry can be understood in the Fourier space. Linearization is generally the strongest limitation of the method. No approximations are needed when the starting equations are themselves linear. For practical applications this hardly relevant case would occur for first order reactions of the kinetic sources. Linear approximation is, however, always possible but may meet difficulties for highly non-linear systems.

3.2.1 Normal modes

Let us now to exemplify the simple cases which gives single modes

The relaxation modes (produced by chemical reactions) could be obtained by the first order differential equation

$$\frac{dc}{dt} = -kc \tag{3.23}$$

They do not dependt on the Fourier-space variable q and that's why is not correlated with a space propagation but only to a time decay

$$c = c_0\exp[-kt] \tag{3.24}$$

The Migration modes are correlated to convective or migrational transport leaded by the equation

$$\frac{\partial c(\boldsymbol{r}, t)}{\partial t} + \omega \boldsymbol{F} \, \boldsymbol{grad} \, c(\boldsymbol{r}, t) = 0 \tag{3.25}$$

The evaluation of this pure mode involves migration in a uniform force-field $\boldsymbol{F}$, div $\boldsymbol{F} = 0$, (e.g., uniform external electric field). The Fourier and Laplace transformations, respectively are

$$\frac{\partial c(\boldsymbol{q}, t)}{\partial t} = i\boldsymbol{q}\omega \, F \, c(\boldsymbol{q}, t); \quad sc(\boldsymbol{q}, s) - c(\boldsymbol{q}, t = 0) = i\boldsymbol{q}\omega \, \boldsymbol{F} \, c(\boldsymbol{q}, s) \tag{3.26}$$

Solving for $c(\boldsymbol{q}, s)$ (Laplace transformation of $c(\boldsymbol{q}, t)$) and taking the inverse Laplace transform

$$c(\boldsymbol{q}, s) = \frac{c(\boldsymbol{q}, t = 0)}{s - i\boldsymbol{q} \, \boldsymbol{F}\omega t}; \quad c(\boldsymbol{q}, t) = c(\boldsymbol{q}, t = 0)\exp[i\boldsymbol{q} \, \boldsymbol{F}\omega t] \tag{3.27}$$

Is characteristic for a migration mode a root proportional to $i\boldsymbol{q}$. A traslational movement is defined for (3.27)

The diffusion modes are characterized by the equation

$$\frac{\partial c(\boldsymbol{r}, t)}{\partial t} - D \operatorname{div} \boldsymbol{grad} \, c(\boldsymbol{r}, t) = 0. \tag{3.28}$$

We ca obtain the Fourier-Laplace transform of $c(\boldsymbol{q}, s)$ and the inverse Laplace transform

$$c(\boldsymbol{q}, s) = \frac{c(\boldsymbol{q}, t = 0)}{s + q^2 D}; \quad c(\boldsymbol{q}, t) = c(\boldsymbol{q}, t = 0)\exp[-q^2 D t]. \tag{3.29}$$

A diffusion mode is characteristic for a root proportional to q^2.

3.3 Coupled diffusion of a multiply associating non–ideal Case

Generalities

The subtance's movement process (atom, molecule, etc.) from higher to lower concentration on a certain region is called diffusion. At first order this process is ruled by Fick's law $\mathbf{J}_i = -D_i \mathbf{grad} c_i$. the different types of diffusion are:

- Self-diffusion (or tracer diffusion). It is a special case carried out in pure substances or a same constitution solutions where the substance's particles display an spontaneous mixing under equilibrium without gradients of concentration or chemical potential. The participating species in this particular diffusion have different physical characteristics but same chemical properties like radiactive isotopes (isotope tracers) wich can be observed using various techniques. The closed capillary technique is a common one to measure self diffusion coefficients.

- Chemical diffusion. It is a non–equilibrium process that takes place with the existence of gradients of concentration or gradients of chemical potential in order to produce a net transport of mass.

- Coupled diffusion. It is achieved when we pass from self-diffusion to chemical diffusion. This process takes place when there are concentration gradients on a solution with some tracer inside.

Theory

A multicomponent non–ideal electrolyte solutions requires, for the representation of its coupled diffusion, a set of equations of the type of (3.9), $\chi_i \neq 0$, $i = +, -, 1, 2 \ldots, N$

$$\frac{\partial C_i}{\partial t} + \mathrm{div}\vec{J_i} = \chi_i \qquad (3.30)$$

where the following notation is used: for the mayor electrolyte, $+$ is for the cation, and - is for the anion. For the species: 1 is for tracer, 2 for dimer, 3 for trimer, ...,N for N-mer. The flux J_i of the ith species at position x and time t, can be derived according to the linear transport theory to obtain

$$\vec{J_i} = -C_i D_i \nabla ln\gamma_i - D_i \nabla C_i + \beta D_i z_i e C_i \vec{E}, \qquad (3.31)$$

where D_i are the diffusion coefficient, γ_i are the activity coefficients associated to each species and $z_i e$ and the charge of the i-th species respectively. $\vec{E}$ is the electrical field created by the diffusion of the ions originally forming the salt.

Explicitly fluxes associated with the major electrolyte are

$$\vec{J_+} = -C_+ D_+ \nabla ln\gamma_+ - D_+ \nabla C_+ + \beta D_+ z_+ e C_+ \vec{E},$$
$$\vec{J_-} = -C_- D_- \nabla ln\gamma_- - D_- \nabla C_- + \beta D_- z_- e C_- \vec{E}. \qquad (3.32)$$

The electrical field $\vec{E}$ is calculated demanding local dynamical electroneutrality

$$\nu_+ z_+ \vec{J_+} + \nu_- z_- \vec{J_-} = \vec{0}. \qquad (3.33)$$

This implies

$$z_- \nu_- (-C_- D_- \nabla ln\gamma_- - D_- \nabla C_- + \beta D_- z_- e C_- \vec{E})$$
$$= -z_+ \nu_+ (-C_+ D_+ \nabla ln\gamma_+ - D_+ \nabla C_+ + \beta D_+ z_+ e C_+ \vec{E})$$

which could be writed for $\vec{E}$

$$\vec{E} = \frac{1}{z_+^2 \nu_+ D_+ C_+ + z_-^2 \nu_- D_- C_-} \frac{kT}{e} \cdot$$
$$[z_+ \nu_+ C_+ D_+ \nabla ln\gamma_+ + z_- \nu_- C_- D_- \nabla ln\gamma_- + z_+ \nu_+ D_+ \nabla C_+ + z_- \nu_- D_- \nabla C_-]$$

or using the identity (with $\gamma_i = \gamma_i(C_s)$) $\nabla ln\gamma_i = \nabla C_+ \partial_{C_+} ln\gamma_i + \nabla C_- \partial_{C_-} ln\gamma_i$

$$\vec{E} = \frac{1}{z_+^2 \nu_+ D_+ C_+ + z_-^2 \nu_- D_- C_-} \frac{kT}{e} [z_+ \nu_+ C_+ D_+ (\nabla C_+ \partial_{C_+} ln\gamma_+ + \nabla C_- \partial_{C_-} ln\gamma_+)$$
$$+ z_- \nu_- C_- D_- (\nabla C_+ \partial_{C_+} ln\gamma_- + \nabla C_- \partial_{C_-} ln\gamma_-) + z_+ \nu_+ D_+ \nabla C_+ + z_- \nu_- D_- \nabla C_-]$$

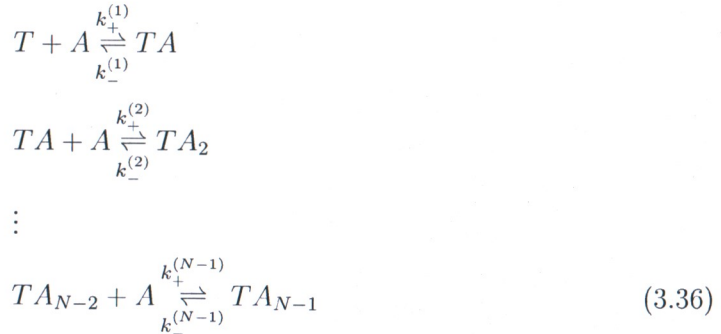Considering $\partial_{C_+} + \partial_{C_-} = \partial_{C_s}$ and $C_+ \approx C_- \approx C_s$

$$\vec{E} = \frac{kT}{(z_+^2 \nu_+ D_+ + z_-^2 \nu_- D_-)e} [z_+ \nu_+ D_+ \nabla C_s \partial_{C_s} ln\gamma_+$$
$$+ z_- \nu_- D_- \nabla C_s \partial_{C_s} ln\gamma_- + z_+ \nu_+ D_+ \frac{\nabla C_s}{C_s} + z_- \nu_- D_- \frac{\nabla C_s}{C_s}]$$

$$\vec{E} = \frac{kT}{e} \frac{z_+ \nu_+ D_+ + z_- \nu_- D_-}{z_+^2 \nu_+ D_+ + z_-^2 \nu_- D_-} \frac{\nabla C_s}{C_s} + \frac{kT}{e} \nabla C_s \frac{z_+ \nu_+ D_+ \partial_{C_s} ln\gamma_+ + z_- \nu_- D_- \partial_{C_s} ln\gamma_-}{z_+^2 \nu_+ D_+ + z_-^2 \nu_- D_-} \quad (3.34)$$

In our case we have a 1:1 electrolyte ($z_+ = -z_- = 1$ and $\nu_+ = \nu_- = 1$). The electrical field equation has the form

$$\vec{E} = \frac{kT}{e} \frac{D_+ - D_-}{D_+ + D_-} \frac{\vec{\nabla} C_s}{C_s} + \frac{kT/e}{D_+ + D_-} \vec{\nabla} C_s \left(D_+ \frac{\partial ln\gamma_+}{\partial C_s} - D_- \frac{\partial ln\gamma_-}{\partial C_s} \right) \quad (3.35)$$

On the other hand, to obtain the source terms and to consider association first of all it is necessary to know the equilibrium equations (that ones) who gives us the N-mers formation. Such a relations could be written as (where $T=$ Tracer and $A=$ Anion, $TA=$Dimer, $TA_2=$Trimer,$\cdots$,$TA_{N-1}=$N-mer)

$$T + A \underset{k_-^{(1)}}{\overset{k_+^{(1)}}{\rightleftharpoons}} TA$$

$$TA + A \underset{k_-^{(2)}}{\overset{k_+^{(2)}}{\rightleftharpoons}} TA_2$$

$$\vdots$$

$$TA_{N-2} + A \underset{k_-^{(N-1)}}{\overset{k_+^{(N-1)}}{\rightleftharpoons}} TA_{N-1} \quad (3.36)$$

where $K_1 = \frac{k_+^{(1)}}{k_-^{(1)}}$, $K_2 = \frac{k_+^{(2)}}{k_-^{(2)}} \ldots K_{N-1} = \frac{k_+^{(N-1)}}{k_-^{(N-1)}}$.

The source terms including the activity coefficients are given by

$$\chi_1 = k_-^{(1)} \gamma_2 [TA] - k_+^{(1)} \gamma_A \gamma_1 [T][A]$$
$$\chi_2 = k_+^{(1)} \gamma_1 \gamma_A [T][A] - k_-^{(1)} \gamma_2 [TA] + k_-^{(2)} \gamma_3 [TA_2]$$
$$- k_+^{(2)} \gamma_2 \gamma_A [TA][A]$$

$$\vdots$$

$$\chi_N = k_+^{(N-1)} \gamma_{N-1} \gamma_A [TA_{N-2}][A] - k_-^{(N-1)} \gamma_N [TA_{N-1}] \quad (3.37)$$

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Moreover, it is important to say that we are working with a 1-dimensional spatial system such that we are "following" the diffusion process in only one direction as time goes on. That's why we need to write expressions in terms of this restriction, like (3.15) or the eq. for the electrical field. Let's choose the spatial variable as x and let's start writing the equation (3.35) for the electrical field in terms of that variable and substituting in the expression (3.31) for the flux

$$E_x = \frac{kT}{e} \frac{D_+ - D_-}{D_+ + D_-} \frac{\partial_x C_s}{C_s} + \frac{kT/e}{D_+ + D_-} \partial_x C_s \left(D_+ \frac{\partial ln\gamma_+}{\partial C_s} - D_- \frac{\partial ln\gamma_-}{\partial C_s} \right)$$

and

$$J_{ix} = -C_i D_i \partial_x ln\gamma_i - D_i \partial_x C_i + \beta D_i z_i e C_i E_x \tag{3.38}$$

Then if we subtitute eq. (3.38) and (3.37) in (3.30) we have

$$\frac{\partial C_i}{\partial t} + \partial_x J_i x = \chi_i$$

$$\frac{\partial C_i}{\partial t} + \partial_x \{ -C_i D_i \partial_x ln\gamma_i - D_i \partial_x C_i + \beta D_i z_i e C_i E_x \} = \chi_i$$

(where as usual $(\nabla \cdot \vec{J_i})_x = \partial_x J_i x$)
or

$$\frac{\partial C_i}{\partial t} - D_i \partial_x C_i \partial_x ln\gamma_i - D_i C_i \partial_x^2 ln\gamma_i - D_i \partial_x^2 C_i + \beta D_i z_i e \partial_x C_i E_x + \beta D_i z_i e C_i \partial_x E_x \} = \chi_i.$$

$$\tag{3.39}$$

As can see, in the third-left term of the above equation there is a second derivative of $ln\gamma_i$ and in the fifth-left term will appear a similar expression. To obtain that cuadratic derivative terms, let us remind that we have the one dimensional equation $\partial_x ln\gamma_i = \partial_x C_s \partial_{C_s} ln\gamma_i$. So, then

$$\frac{\partial^2 ln\gamma_i}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial C_s}{\partial x} \frac{\partial ln\gamma_i}{\partial C_s} \right)$$

$$= \frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_i}{\partial C_s} + \frac{\partial C_s}{\partial x} \frac{\partial}{\partial x} \left(\frac{\partial ln\gamma_i}{\partial C_s} \right)$$

or

$$\frac{\partial^2 ln\gamma_i}{\partial x^2} = \frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x} \right)^2 \frac{\partial^2 ln\gamma_i}{\partial C_s^2}.$$

Now we can get the partial derivative of the electrical field $\partial_x E_x$

$$\frac{\partial E_x}{\partial x} = \frac{\partial}{\partial x}\left[\frac{kT}{e}\frac{D_+ - D_-}{D_+ + D_-}\frac{\partial_x C_s}{C_s} + \frac{kT/e}{D_+ + D_-}\partial_x C_s\left(D_+\frac{\partial ln\gamma_+}{\partial C_s} - D_-\frac{\partial ln\gamma_-}{\partial C_s}\right)\right]$$

$$= \frac{kT}{e}\frac{D_+ - D_-}{D_+ + D_-}\left[\frac{\partial_x^2 C_s}{C_s} - \frac{(\partial_x C_s)^2}{C_s^2}\right] + \frac{kT/e}{D_+ + D_-}\partial_x^2 C_s\left(D_+\frac{\partial ln\gamma_+}{\partial C_s} - D_-\frac{\partial ln\gamma_-}{\partial C_s}\right) \quad (3.40)$$

$$+ \frac{kT/e}{D_+ + D_-}(\partial_x C_s)^2\left(D_+\frac{\partial^2 ln\gamma_+}{\partial C_s^2} - D_-\frac{\partial^2 ln\gamma_-}{\partial C_s^2}\right) \quad (3.41)$$

From (3.37), (3.41) and (3.39) we have

$$\frac{\partial C_i}{\partial t} - D_i\partial_x C_i\partial_x ln\gamma_i - D_i C_i\partial_x^2 ln\gamma_i - D_i\partial_x^2 C_i$$

$$+\beta D_i z_i e\partial_x C_i\left[\frac{kT}{e}\frac{D_+ - D_-}{D_+ + D_-}\frac{\partial_x C_s}{C_s} + \frac{kT/e}{D_+ + D_-}\partial_x C_s\left(D_+\frac{\partial ln\gamma_+}{\partial C_s} - D_-\frac{\partial ln\gamma_-}{\partial C_s}\right)\right]$$

$$+\beta D_i z_i e C_i\{\frac{kT}{e}\frac{D_+ - D_-}{D_+ + D_-}\left[\frac{\partial_x^2 C_s}{C_s} - \frac{(\partial_x C_s)^2}{C_s^2}\right] + \frac{kT/e}{D_+ + D_-}\partial_x^2 C_s\left(D_+\frac{\partial ln\gamma_+}{\partial C_s} - D_-\frac{\partial ln\gamma_-}{\partial C_s}\right)$$

$$+\frac{kT/e}{D_+ + D_-}(\partial_x C_s)^2\left(D_+\frac{\partial^2 ln\gamma_+}{\partial C_s^2} - D_-\frac{\partial^2 ln\gamma_-}{\partial C_s^2}\right)\} = k_+^{(i-1)}\gamma_{i-1}\gamma_A[TA_{i-2}][A] - k_-^{(i-1)}\gamma_i[TA_{i-1}]$$

or doing some algebra

$$\frac{\partial C_i}{\partial t} = D_i\frac{\partial^2 C_i}{\partial x^2} + D_i C_i\left[\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x}\right)^2\frac{\partial^2 ln\gamma_i}{\partial C_s^2}\right] + D_i\frac{\partial C_i}{\partial x}\frac{\partial C_s}{\partial x}\frac{\partial ln\gamma_i}{\partial C_s}$$

$$- D_i z_i\frac{\partial C_i}{\partial x}\frac{D_+ - D_-}{D_+ + D_-}\frac{1}{C_s}\frac{\partial C_s}{\partial x} - D_i z_i\frac{\partial C_i}{\partial x}\frac{1}{D_+ + D_-}\frac{\partial C_s}{\partial x}\left(D_+\frac{\partial ln\gamma_+}{\partial C_s} - D_-\frac{\partial ln\gamma_-}{\partial C_s}\right)$$

$$- D_i C_i z_i\frac{D_+ - D_-}{D_+ + D_-}\left(\frac{1}{C_s}\frac{\partial^2 C_s}{\partial x^2} - \frac{1}{C_s^2}\left(\frac{\partial C_s}{\partial x}\right)^2\right) - D_i C_i z_i\frac{D_+}{D_+ + D_-}\left(\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_+}{\partial C_s} + \frac{\partial^2 ln\gamma_+}{\partial C_s^2}\left(\frac{\partial C_s}{\partial x}\right)^2\right)$$

$$+ D_i C_i z_i\frac{D_-}{D_+ + D_-}\left(\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_-}{\partial C_s} + \frac{\partial^2 ln\gamma_-}{\partial C_s^2}\left(\frac{\partial C_s}{\partial x}\right)^2\right) + k_+^{(i-1)}\gamma_{i-1}\gamma_A[TA_{i-2}][A] - k_-^{(i-1)}\gamma_i[TA_{i-1}]$$

$$(3.42)$$

For the major electrolyte (the salt), we can obtain the diffusion equation using the expression (3.39) for the flux with the electrical field equal zero (because the salt generates that field) and without sources to get

$$\frac{\partial C_s}{\partial t} - D_s\frac{\partial C_s}{\partial x}\left(\frac{\partial C_s}{\partial x}\frac{ln\gamma_s}{\partial C_s}\right) - D_s C_s\left(\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x}\right)^2\frac{\partial^2 ln\gamma_i}{\partial C_s^2}\right) - D_s\frac{\partial^2 C_s}{\partial x^2} = 0.$$

i.e.

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$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \left(1 + C_s \frac{\partial ln\gamma_s}{\partial C_s}\right) + D_s \left(\frac{\partial C_s}{\partial x}\right)^2 \left[\frac{\partial ln\gamma_s}{\partial C_s} + C_s \frac{\partial^2 ln\gamma_s}{\partial C_s^2}\right] \tag{3.43}$$

with $D_s = \frac{2D_+D_-}{D_+ + D_-}$ and represents the *Nernst-Hartley diffusion coefficient of the salt.*

The system of equations that we need to solve are the sum over all species, i.e. the sum from $i = 1$ to N of the eqs. (3.42)

$$\sum_{i=1}^{N} \frac{\partial C_i}{\partial t} = \sum_{i=1}^{N} D_i \frac{\partial^2 C_i}{\partial x^2} + \sum_{i=1}^{N} D_i C_i \left[\frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x}\right)^2 \frac{\partial^2 ln\gamma_i}{\partial C_s^2}\right] + \sum_{i=1}^{N} D_i \frac{\partial C_i}{\partial x} \frac{\partial C_s}{\partial x} \frac{\partial ln\gamma_i}{\partial C_s}$$

$$- \sum_{i=1}^{N} D_i z_i \frac{\partial C_i}{\partial x} \frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s} \frac{\partial C_s}{\partial x} - \sum_{i=1}^{N} D_i z_i \frac{\partial C_i}{\partial x} \frac{1}{D_+ + D_-} \frac{\partial C_s}{\partial x} \left(D_+ \frac{\partial ln\gamma_+}{\partial C_s} - D_- \frac{\partial ln\gamma_-}{\partial C_s}\right)$$

$$- \sum_{i=1}^{N} D_i C_i z_i \frac{D_+ - D_-}{D_+ + D_-} \left(\frac{1}{C_s} \frac{\partial^2 C_s}{\partial x^2} - \frac{1}{C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right)$$

$$- \sum_{i=1}^{N} D_i C_i z_i \frac{D_+}{D_+ + D_-} \left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_+}{\partial C_s} + \frac{\partial^2 ln\gamma_+}{\partial C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right)$$

$$+ \sum_{i=1}^{N} D_i C_i z_i \frac{D_-}{D_+ + D_-} \left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_-}{\partial C_s} + \frac{\partial^2 ln\gamma_-}{\partial C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right) + \sum_{i=1}^{N} Q_i \tag{3.44}$$

From the last equation we can see that to guarantee mass conservation it is necessary to have $\sum_{i}^{N} Q_i = 0$. To obtian such a sums (from the above equation) we note that species concentrations can be writed in terms of the binding constants and in terms of the salt concentration according to the mass action law (MAL)

$$K_1 = \frac{\gamma_2 C_2}{\gamma_1 C_1 \gamma_A C_A}$$

$$K_2 = \frac{\gamma_3 C_3}{\gamma_2 C_2 \gamma_A C_A}$$

$$\vdots$$

$$K_i = \frac{\gamma_{i+1} C_{i+1}}{\gamma_i C_i \gamma_A C_A}$$

$$\vdots$$

$$K_{N-1} = \frac{\gamma_N C_N}{\gamma_{N-1} C_{N-1} \gamma_A C_A},$$

solving for the species's concentrations

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$$C_2 = \frac{K_1 \gamma_1 C_1 \gamma_A C_A}{\gamma_2}$$

$$C_3 = \frac{K_2 \gamma_2 C_2 \gamma_A C_A}{\gamma_3} = C_1 \frac{K_1 K_2 \gamma_1 \left(\gamma_A C_s\right)^2}{\gamma_3}$$

$$\vdots$$

$$C_i = \frac{K_i \gamma_i C_i \gamma_A C_A}{\gamma_{i+1}} = C_1 \frac{K_1 K_2 \cdots K_{i-1} \gamma_1 \left(\gamma_A C_s\right)^{i-1}}{\gamma_i}$$

$$\vdots$$

$$C_N = \frac{K_{N-1} \gamma_{N-1} C_{N-1} \gamma_A C_A}{\gamma_N} = C_1 \frac{K_1 K_2 \cdots K_{N-1} \gamma_1 \left(\gamma_A C_s\right)^{N-1}}{\gamma_N},$$

i.e.

$$C_2 = C_1 \beta_1' C_s$$

$$C_3 = C_1 \beta_2' C_s^2$$

$$\vdots$$

$$C_i = C_1 \beta_{i-1}' C_s^{i-1}$$

$$\vdots$$

$$C_N = C_1 \beta_{N-1}' C_s^{N-1} \tag{3.45}$$

where by convention $\beta_i' = \beta_i \frac{\gamma_1 \gamma_A^i}{\gamma_{i+1}}$ and β_i are the cummulative equilibrium constants defined by $\beta_i = \prod_{i=1}^{N} K_i = K_1 \cdot K_2 \cdots K_{i-i} \cdot K_i$.

The next step is to analize term by term the sums of eq. (3.44). Note that this term could be rewrited as

$$\sum_{i=1}^{N} \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial t} \sum_{i=1}^{N} C_i = \frac{\partial}{\partial t} C_{Tot} \tag{3.46}$$

where C_{Tot} is the total tracer concentration. The first sum is given in terms of the partial derivative with respect to time of the total tracer concentration as we want. The total tracer concentration by convention is

$$C_{Tot} = C_1 \sum_{i=0}^{N} \beta_{i-1}' C_s^{i-1} = C_1 \sum_{i=0}^{N-1} \beta_i' C_s^i = C_1 \Delta_1 \tag{3.47}$$

where we define $\Delta_1 = \sum_{i=0}^{N-1} \beta_i' C_s^i$. The above relations implies that

$$\frac{\partial}{\partial t} C_{Tot} = \frac{\partial}{\partial t} (C_1 \Delta_1) = \Delta_1 \frac{\partial}{\partial t} C_1 + C_1 \frac{\partial}{\partial t} \Delta_1 = \Delta_1 \frac{\partial}{\partial t} C_1 + C_1 \frac{\partial \Delta_1}{\partial C_s} \frac{\partial C_s}{\partial t}$$

$$= \Delta_1 \frac{\partial C_1}{\partial t} + C_1 \Delta_2 \frac{\partial C_s}{\partial t}$$

with the next definition $\Delta_2 = \frac{\partial \Delta_1}{\partial C_s}$. Doing some algebra this quantity becomes

$$\Delta_2 = \frac{\partial \Delta_1}{\partial C_s} = \frac{\partial \Delta_1}{\partial C_s} = \frac{\partial \sum_{i=0}^{N-1} \beta_i' C_s^i}{\partial C_s} = \sum_{i=0}^{N-1} \left[C_s^i \frac{\partial \beta_i'}{\partial C_s} + \beta_i' \frac{\partial C_s^i}{\partial C_s} \right] \tag{3.48}$$

Analizing the derivative terms one by one we can see that the second derivative term is obtained easily $\frac{\partial C_s^i}{\partial C_s} = iC_s^{i-1}$, meanwhile the first term requires some little algebra

$$\frac{\partial \beta_i'}{\partial C_s} = \beta_i \frac{\partial}{\partial C_s} \left(\frac{\gamma_1 \gamma_A^i}{\gamma_{i+1}} \right) = \beta_i \left[\frac{1}{\gamma_{i+1}^2} \left(\left(\gamma_A^i \partial_{C_s} \gamma_1 + \gamma_1 i \gamma_A^{i-1} \partial_{C_s} \gamma_A \right) \gamma_{i+1} - \gamma_1 \gamma_A^i \partial_{C_s} \gamma_{i+1} \right) \right]$$

$$= \frac{\beta_i \gamma_1 \gamma_A^i}{\gamma_{i+1}} \left[\frac{\partial_{C_s} \gamma_1}{\gamma_1} + i \frac{\partial_{C_s} \gamma_A}{\gamma_A} - \frac{\partial_{C_s} \gamma_{i+1}}{\gamma_{i+1}} \right] = \beta_i' \left(\Gamma_1 + i\Gamma_A - \Gamma_{i+1} \right)$$

where we define $\Gamma_i = \left(\frac{\partial \gamma_i}{\partial C_s} \right) / \gamma_i$. On this way Δ_2 is

$$\Delta_2 = \sum_{i=1}^{N-1} C_s^i \beta_i' \left(\Gamma_1 + i\Gamma_A - \Gamma_{i+1} \right) + \beta_i' i C_s^{i-1}$$

$$\Delta_2 = \sum_{i=1}^{N-1} C_s^{i-1} \beta_i' \left[\left(\Gamma_1 + i\Gamma_A - \Gamma_{i+1} \right) C_s + i \right]$$

rewriting

$$\Delta_2 = \sum_{i=0}^{N-2} C_s^i \beta_{i+1}' \left[\left(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+2} \right) C_s + (i+1) \right] \tag{3.49}$$

The next term to analize is the first-right term of eq. (3.44)

$$\sum_{i=1}^{N} D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial^2}{\partial x^2} \sum_{i=1}^{N} D_i C_i = \frac{\partial^2}{\partial x^2} \sum_{i=1}^{N} D_i C_1 \beta_{i-1}' C_s^{i-1}$$

$$= \frac{\partial^2 C_1}{\partial x^2} \sum_{i=1}^{N} D_{i+1} \beta_i' C_s^i + C_1 \sum_{i=1}^{N} D_i \left(\frac{\partial^2 \beta_{i-1}'}{\partial x^2} C_s^{i-1} + \frac{\partial^2 C_s^{i-1}}{\partial x^2} \beta_{i-1}' \right) \tag{3.50}$$

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$$\sum_{i=1}^{N} D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial^2 C_1}{\partial x^2} \sum_{i=0}^{N-1} D_{i+1} \beta_i' C_s^i$$

$$+C_1 \sum_{i=1}^{N} D_i \left[\left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial \beta_{i-1}'}{\partial C_s} + \left(\frac{\partial C_s}{\partial x} \right)^2 \frac{\partial^2 \beta_{i-1}'}{\partial C_s^2} \right) C_s^{i-1} + \left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial C_s^{i-1}}{\partial C_s} + \left(\frac{\partial C_s}{\partial x} \right)^2 \frac{\partial^2 C_s^{i-1}}{\partial C_s^2} \right) \beta_{i-1}' \right]$$

$$= \frac{\partial^2 C_1}{\partial x^2} \sum_{i=0}^{N-1} D_{i+1} \beta_i' C_s^i$$

$$+C_1 \frac{\partial^2 C_s}{\partial x^2} \sum_{i=1}^{N} D_i C_s^{i-1} \frac{\partial \beta_{i-1}'}{\partial C_s} + C_1 \left(\frac{\partial C_s}{\partial x} \right)^2 \sum_{i=1}^{N} D_i C_s^{i-1} \frac{\partial^2 \beta_{i-1}'}{\partial C_s^2}$$

$$+C_1 \frac{\partial^2 C_s}{\partial x^2} \sum_{i=1}^{N} D_i \beta_{i-1}' \frac{\partial C_s^{i-1}}{\partial C_s} + C_1 \left(\frac{\partial C_s}{\partial x} \right)^2 \sum_{i=1}^{N} D_i \beta_{i-1}' \frac{\partial^2 C_s^{i-1}}{\partial C_s^2}$$

where by convention we have

$$\sum_{i=1}^{N} D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial^2 C_1}{\partial x^2} \sum_{i=0}^{N-1} D_{i+1} \beta_i' C_s^i$$

$$+C_1 \frac{\partial^2 C_s}{\partial x^2} \sum_{i=0}^{N-1} D_{i+1} C_s^i \frac{\partial \beta_i'}{\partial C_s} + C_1 \left(\frac{\partial C_s}{\partial x} \right)^2 \sum_{i=0}^{N-1} D_{i+1} C_s^i \frac{\partial^2 \beta_i'}{\partial C_s^2}$$

$$+C_1 \frac{\partial^2 C_s}{\partial x^2} \sum_{i=0}^{N-1} D_{i+1} \beta_i' \frac{\partial C_s^i}{\partial C_s} + C_1 \left(\frac{\partial C_s}{\partial x} \right)^2 \sum_{i=0}^{N-1} D_{i+1} \beta_i' \frac{\partial^2 C_s^i}{\partial C_s^2} \tag{3.51}$$

with $\frac{\partial^2}{\partial x^2} = \frac{\partial^2 C_s}{\partial x^2} \frac{\partial}{\partial C_s} + \left(\frac{\partial C_s}{\partial x} \right)^2 \frac{\partial^2}{\partial C_s^2}$. Moreover, let's define the next delta terms

$$\Delta_3 = \sum_{i=1}^{N} D_i \beta_{i-1}' C_s^{i-1}$$

$$\Delta_3 = \sum_{i=0}^{N-1} D_{i+1} \beta_i' C_s^i \tag{3.52}$$

$$\Delta_4 = \frac{\partial \Delta_3}{\partial C_s} = \frac{\partial}{\partial C_s} \sum_{i=0}^{N-1} D_{i+1} \beta_i' C_s^i = \sum_{i=0}^{N-1} D_{i+1} \frac{\partial(\beta_i' C_s^i)}{\partial C_s}$$

$$= \sum_{i=1}^{N-1} D_{i+1} \left[\beta_i' (\Gamma_1 + i\Gamma_A - \Gamma_{i+1}) C_s^{i-1} + \beta_i' i C_s^{i-1} \right]$$

similarly, making the index runs from zero by convention, like the other delta terms

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$$\Delta_4 = \sum_{i=0}^{N-2} D_{i+2} \beta'_{i+1} C_s^i \left[(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+2}) C_s + i + 1 \right] \tag{3.53}$$

where the second derivative element is

$$\frac{\partial^2 \beta'_i}{\partial C_s^2} = \frac{\partial[\beta'_i(\Gamma_1 + i\Gamma_A - \Gamma_{i+1})]}{\partial C_s} = \frac{\partial \beta'_i}{\partial C_s}(\Gamma_1 + i\Gamma_A - \Gamma_{i+1}) + \frac{\partial(\Gamma_1 + i\Gamma_A - \Gamma_{i+1})}{\partial C_s}\beta'_i$$

$$= (\beta'_i(\Gamma_1 + i\Gamma_A - \Gamma_{i+1}))(\Gamma_1 + i\Gamma_A - \Gamma_{i+1}) + (\Gamma_{1,2} + i\Gamma_{A,2} - \Gamma_{i+1,2})\beta'_i$$

$$= \beta'_i[(\Gamma_1 + i\Gamma_A - \Gamma_{i+1})^2 + (\Gamma_{1,2} + i\Gamma_{A,2} - \Gamma_{i+1,2})] \tag{3.54}$$

and the term

$$\frac{\partial^2 C_s^i}{\partial C_s^2} = \frac{\partial(iC_s^{i-1})}{\partial C_s} = i(i-1)C_s^{i-2}$$

Now we can define the delta parameter

$$\Delta_7 = \frac{\partial \Delta_4}{\partial C_s} = \frac{\partial^2 \Delta_3}{\partial C_s^2} = \sum_{i=0}^{N-1} D_{i+1} \frac{\partial^2(\beta'_i C_s^i)}{\partial C_s} = \frac{\partial}{\partial C_s}\left(C_s^i \frac{\partial \beta'_i}{\partial C_s} + \beta'_i \frac{\partial C_s^i}{\partial C_s}\right)$$

$$= \sum_{i=0}^{N-1} D_{i+1}\left[C_s^i \frac{\partial^2 \beta'_i}{\partial C_s^2} + 2\frac{\partial C_s^i}{\partial C_s}\frac{\partial \beta'_i}{\partial C_s} + \beta'_i \frac{\partial^2 C_s^i}{\partial C_s^2}\right]$$

$$= \sum_{i=0}^{N-1} D_{i+1}\left\{C_s^i \beta'_i[(\Gamma_1 + i\Gamma_A - \Gamma_{i+1})^2 + (\Gamma_{1,2} + i\Gamma_{A,2} - \Gamma_{i+1,2})]\right.$$

$$\left. + 2iC_s^{i-1}\beta_i(\Gamma_1 + i\Gamma_A - \Gamma_{i+1}) + \beta'_i i(i-1)C_s^{i-2}\right\}$$

$$= \sum_{i=0}^{N-1} D_{i+1} \beta'_i C_s^{i-2}\left\{C_s^2[(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+1})^2 + (\Gamma_{1,2} + (i+1)\Gamma_{A,2} - \Gamma_{i+1,2})]\right.$$

$$\left. + 2(i)(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+1})C_s + (i-1)i\right\}. \tag{3.55}$$

Then

$$\sum_{i=1}^{N} D_i \frac{\partial^2 C_i}{\partial x^2} = \Delta_3 \frac{\partial^2 C_1}{\partial x^2} + C_1 \Delta_4 \frac{\partial^2 C_s}{\partial x^2} + C_1 \Delta_7 \left(\frac{\partial C_s}{\partial x}\right)^2 \tag{3.56}$$

Next element of (3.44) to develop is

$$\sum_{i=1}^{N} D_i C_i \left[\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x}\right)^2 \frac{\partial^2 ln\gamma_i}{\partial C_s^2}\right] \tag{3.57}$$

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If we analize that expression by parts

$$\sum_{i=1}^{N} D_i C_i \frac{\partial ln\gamma_i}{\partial C_s} = \sum_{i=1}^{N} D_i(C_1\beta'_{i-1}C_s^{i-1})\frac{\partial ln\gamma_i}{\partial C_s} = C_1 \sum_{i=1}^{N} D_i\beta'_{i-1}C_s^{i-1}\frac{\partial ln\gamma_i}{\partial C_s} = C_1\Delta_6 \quad (3.58)$$

defining

$$\Delta_6 = \sum_{i=1}^{N} D_i\beta'_{i-1}C_s^{i-1}\frac{\partial ln\gamma_i}{\partial C_s} = \sum_{i=0}^{N-1} D_{i+1}\beta'_i C_s^i \frac{\partial ln\gamma_{i+1}}{\partial C_s} = \sum_{i=0}^{N-1} D_{i+1}\beta'_i C_s^i \Gamma_{i+1} \quad (3.59)$$

and

$$\sum_{i=1}^{N} D_i C_i \left(\frac{\partial C_s}{\partial x}\right)^2 \frac{\partial^2 ln\gamma_i}{\partial C_s^2} = \left(\frac{\partial C_s}{\partial x}\right)^2 \sum_{i=1}^{N} D_i(C_1\beta'_{i-1}C_s^{i-1})\frac{\partial^2 ln\gamma_i}{\partial C_s^2}$$
$$= C_1 \left(\frac{\partial C_s}{\partial x}\right)^2 \sum_{i=1}^{N} D_i\beta'_{i-1}C_s^{i-1}\frac{\partial^2 ln\gamma_i}{\partial C_s^2} = C_1\Delta_8 \left(\frac{\partial C_s}{\partial x}\right)^2 \quad (3.60)$$

using the definition

$$\Delta_8 = \sum_{i=1}^{N} D_i\beta'_{i-1}C_s^{i-1}\frac{\partial^2 ln\gamma_i}{\partial C_s^2} = \sum_{i=0}^{N-1} D_{i+1}\beta'_i C_s^i \frac{\partial^2 ln\gamma_{i+1}}{\partial C_s^2} = \sum_{i=0}^{N-1} D_{i+1}\beta'_i C_s^i \Gamma_{i+1,2} \quad (3.61)$$

Substituting (3.60) and (3.58) on (3.57)

$$\sum_{i=1}^{N} D_i C_i \left[\frac{\partial^2 C_s}{\partial x^2}\frac{\partial ln\gamma_i}{\partial C_s} + \left(\frac{\partial C_s}{\partial x}\right)^2 \frac{\partial^2 ln\gamma_i}{\partial C_s^2}\right] = C_1\Delta_6 \frac{\partial^2 C_s}{\partial x^2} + C_1\Delta_8 \left(\frac{\partial C_s}{\partial x}\right)^2 \quad (3.62)$$

Examining the following term from equation (3.44): $\sum_{i=1}^{N} D_i \frac{\partial C_i}{\partial x}\frac{\partial C_s}{\partial x}\frac{\partial ln\gamma_i}{\partial C_s}$

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$$\sum_{i=1}^{N} D_i \frac{\partial C_i}{\partial x} \frac{\partial C_s}{\partial x} \frac{\partial ln\gamma_i}{\partial C_s} = \frac{\partial C_s}{\partial x} \sum_{i=1}^{N} D_i \frac{\partial(C_1 \beta'_{i-1} C_s^{i-1})}{\partial x} \frac{\partial ln\gamma_i}{\partial C_s}$$

$$= \left(\frac{\partial C_s}{\partial x}\right)^2 \sum_{i=1}^{N} D_i \frac{\partial(C_1 \beta'_{i-1} C_s^{i-1})}{\partial C_s} \frac{\partial ln\gamma_i}{\partial C_s}$$

$$= \left(\frac{\partial C_s}{\partial x}\right)^2 \sum_{i=1}^{N} D_i \frac{\partial ln\gamma_i}{\partial C_s} (\beta'_{i-1} C_s^{i-1} \frac{\partial C_1}{\partial C_s} + C_1 \frac{\partial(\beta'_{i-1} C_s^{i-1})}{\partial C_s})$$

$$= \left(\frac{\partial C_s}{\partial x}\right)^2 \left\{ \frac{\partial C_1}{\partial C_s} \sum_{i=1}^{N} D_i \beta'_{i-1} C_s^{i-1} \Gamma_i \right. \tag{3.63}$$

$$\left. +C_1 \sum_{i=2}^{N} D_i \Gamma_i C_s^{i-2} \beta'_{i-1} [(\Gamma_1 + (i-1)\Gamma_A - \Gamma_i)C_s + (i-1)] \right\}$$

$$= \left(\frac{\partial C_s}{\partial x}\right)^2 \left\{ \frac{\partial C_1}{\partial C_s} \Delta_6 + C_1 \Delta_9 \right\}$$

$$= \frac{\partial C_1}{\partial x} \frac{\partial C_s}{\partial x} \Delta_6 + C_1 \left(\frac{\partial C_s}{\partial x}\right)^2 \Delta_9$$

where we use the definition

$$\Delta_9 = \sum_{i=2}^{N} D_i \Gamma_i C_s^{i-2} \beta'_{i-1} [(\Gamma_1 + (i-1)\Gamma_A - \Gamma_i)C_s + (i-1)]$$

$$\Delta_9 = \sum_{i=0}^{N-2} D_{i+2} C_s^i \beta'_{i+1} \Gamma_{i+2} [(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+2})C_s + (i+1)] \tag{3.64}$$

Continuing the analysis of the equation's terms of (3.44)

$$\sum_{i=1}^{N} D_i z_i \frac{\partial C_i}{\partial x}$$

$$= \frac{\partial C_1}{\partial x} \sum_{i=1}^{N} D_i z_i \beta'_{i-1} C_s^{i-1} + C_1 \left(\frac{\partial C_s}{\partial x}\right) \sum_{i=2}^{N} D_i z_i C_s^{i-2} \beta'_{i-1} [(\Gamma_1 + (i-1)\Gamma_A - \Gamma_i)C_s + (i-1)]$$

$$= \frac{\partial C_1}{\partial x} \Delta_5 + C_1 \frac{\partial C_s}{\partial x} \Delta_{10} \tag{3.65}$$

with the delta's defined as

$$\Delta_5 = \sum_{i=1}^{N} D_i z_i \beta'_{i-1} C_s^{i-1} = \sum_{i=0}^{N-1} D_{i+1} z_{i+1} \beta'_i C_s^i \tag{3.66}$$

and

$$\Delta_{10} = \sum_{i=2}^{N} D_i z_i \beta'_{i+1} C_s^{i-2} [(\Gamma_1 + (i-1)\Gamma_A - \Gamma_i)C_s + (i-1)]$$

$$= \sum_{i=0}^{N-2} D_{i+2} z_{i+2} \beta'_{i+1} C_s^{i} [(\Gamma_1 + (i+1)\Gamma_A - \Gamma_{i+2})C_s + (i+1)] \tag{3.67}$$

The last term to examine is

$$\sum_{i=1}^{N} D_i C_i z_i = \sum_{i=1}^{N} D_i z_i (C_1 \beta'_{i-1} C_s^{i-1}) = C_1 \sum_{i=1}^{N} D_i z_i (\beta'_{i-1} C_s^{i-1}) = C_1 \Delta_5 \tag{3.68}$$

Substituting the equations (3.46),(3.56),(3.58),(3.62),(3.63),(3.65),(3.68) on (3.44) we obtain

$$\frac{\partial C_{Tot}}{\partial t} = \Delta_3 \frac{\partial^2 C_1}{\partial x^2} + C_1 \Delta_4 \frac{\partial^2 C_s}{\partial x^2} + C_1 \Delta_7 \left(\frac{\partial C_s}{\partial x}\right)^2$$

$$+ C_1 \Delta_6 \frac{\partial^2 C_s}{\partial x^2} + C_1 \Delta_8 \left(\frac{\partial C_s}{\partial x}\right)^2 + \frac{\partial C_1}{\partial x} \frac{\partial C_s}{\partial x} \Delta_6 + C_1 \left(\frac{\partial C_s}{\partial x}\right)^2 \Delta_9$$

$$- (\frac{\partial C_1}{\partial x} \Delta_5 + C_1 \frac{\partial C_s}{\partial x} \Delta_{10}) \frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s} \frac{\partial C_s}{\partial x}$$

$$- (\frac{\partial C_1}{\partial x} \Delta_5 + C_1 \frac{\partial C_s}{\partial x} \Delta_{10}) \frac{1}{D_+ + D_-} \frac{\partial C_s}{\partial x} \left(D_+ \frac{\partial ln(\gamma_+)}{\partial C_s} - D_- \frac{\partial ln(\gamma_-)}{\partial C_s}\right)$$

$$- C_1 \Delta_5 \frac{D_+ - D_-}{D_+ + D_-} \left(\frac{1}{C_s} \frac{\partial^2 C_s}{\partial x^2} - \frac{1}{C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right)$$

$$- C_1 \Delta_5 \frac{D_+}{D_+ + D_-} \left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln(\gamma_+)}{\partial C_s} + \frac{\partial^2 ln(\gamma_+)}{\partial C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right)$$

$$+ C_1 \Delta_5 \frac{D_-}{D_+ + D_-} \left(\frac{\partial^2 C_s}{\partial x^2} \frac{\partial ln\gamma_-}{\partial C_s} + \frac{\partial^2 ln(\gamma_-)}{\partial C_s^2} \left(\frac{\partial C_s}{\partial x}\right)^2\right) \tag{3.69}$$

which, after grouping like terms

$$\frac{\partial C_{Tot}}{\partial t} = \Delta_3 \frac{\partial^2 C_1}{\partial x^2} + C_1 \Delta_4 \frac{\partial^2 C_s}{\partial x^2} + C_1 \Delta_7 \left(\frac{\partial C_s}{\partial x}\right)^2$$

$$+ C_1 \Delta_6 \frac{\partial^2 C_s}{\partial x^2} + C_1 \Delta_8 \left(\frac{\partial C_s}{\partial x}\right)^2 + \frac{\partial C_1}{\partial x} \frac{\partial C_s}{\partial x} \Delta_6 + C_1 \left(\frac{\partial C_s}{\partial x}\right)^2 \Delta_9$$

$$- (\frac{\partial C_1}{\partial x} \Delta_5 + C_1 \frac{\partial C_s}{\partial x} \Delta_{10})(\frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s} \frac{\partial C_s}{\partial x} + \frac{D_+ \Gamma_+ - D_- \Gamma_-}{D_+ + D_-} \frac{\partial C_s}{\partial x})$$

$$+ C_1 \Delta_5 \frac{\partial^2 C_s}{\partial x^2}(-\frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s} - \frac{D_+ \Gamma_+ - D_- \Gamma_-}{D_+ + D_-})$$

$$+ C_1 \Delta_5 \left(\frac{\partial C_s}{\partial x}\right)^2 \left[\frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s^2} - \frac{D_+ \Gamma_{2,+} - D_- \Gamma_{2,-}}{D_+ + D_-}\right] \tag{3.70}$$

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And finally, using eq. (3.47) we obtain the total tracer diffusion equation written as

$$
\frac{\partial C_{Tot}}{\partial t} = \frac{\partial^2 C_{Tot}}{\partial x^2}\frac{\Delta_3}{\Delta_1} + \frac{\partial^2 C_s}{\partial x^2}\frac{C_{Tot}}{\Delta_1}\left(\Delta_4 + \Delta_6 - \Delta_5 A - \frac{\Delta_2\Delta_3}{\Delta_1}\right)
$$

$$
\left(\frac{\partial C_s}{\partial x}\right)^2\frac{C_{Tot}}{\Delta_1}\left[\Delta_7 + \Delta_8 + \Delta_9 - \Delta_{10}A + \Delta_5 B + 2\left(\frac{\Delta_2}{\Delta_1}\right)^2\Delta_3 - \frac{\Delta_2\Delta_6}{\Delta_1} + \frac{\Delta_5\Delta_2}{\Delta_1}A - \frac{\Delta_3}{\Delta_1}\frac{\partial\Delta_2}{\partial C_s}\right]
$$

$$
+\frac{\partial C_s}{\partial x}\frac{\partial C_{Tot}}{\partial x}\frac{1}{\Delta_1}\left(-2\frac{\Delta_2\Delta_3}{\Delta_1} + \Delta_6 - \Delta_5 A\right) \tag{3.71}
$$

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where

$$\Delta_1 = \sum_{l=0}^{N-1} \beta_l' (C_s)^l$$

$$\Delta_2 = \sum_{l=0}^{N-2} \beta_{l+1}' C_s^l \left[(l+1) + C_s \frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1} \gamma_1}{\gamma_{l+2}} \right]$$

$$\Delta_3 = \sum_{l=0}^{N-1} D_{l+1} \beta_l' C_s^l$$

$$\Delta_4 = \sum_{l=0}^{N-2} D_{l+2} \beta_{l+1}' C_s^l \left[(l+1) + C_s \frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1} \gamma_1}{\gamma_{l+2}} \right]$$

$$\Delta_5 = \sum_{l=0}^{N-1} D_{l+1} z_{l+1} \beta_l' C_s^l$$

$$\Delta_6 = \sum_{l=0}^{N-1} D_{l+1} \beta_l' C_s^l \frac{\partial}{\partial C_s} ln\gamma_{l+1}$$

$$\Delta_7 = \sum_{l=0}^{N-1} D_{l+1} \beta_l' C_s^{l-2} \left[\left(\frac{\partial^2 ln\gamma_1}{\partial C_s^2} + (l+1) \frac{\partial^2 ln\gamma_A}{\partial C_s^2} - \frac{\partial^2 ln\gamma_{l+1}}{\partial C_s^2} \right) C_s^2 \right.$$

$$+ \left(\frac{\partial ln\gamma_1}{\partial C_s} + (l+1) \frac{\partial ln\gamma_A}{\partial C_s} - \frac{\partial ln\gamma_{l+1}}{\partial C_s} \right)^2 C_s^2$$

$$\left. +2i \left(\frac{\partial ln\gamma_1}{\partial C_s} + (l+1) \frac{\partial ln\gamma_A}{\partial C_s} - \frac{\partial ln\gamma_{l+1}}{\partial C_s} \right) C_s + i(i-1) \right]$$

$$\Delta_8 = \sum_{l=0}^{N-1} D_{l+1} \beta_l C_s^l \frac{\partial^2 ln\gamma_{l+1}}{\partial C_s^2}$$

$$\Delta_9 = \sum_{l=0}^{N-2} D_{l+2} \beta_{l+1}' C_s^l \frac{\partial ln\gamma_{l+2}}{\partial C_s} \left[C_s \left(\frac{\partial ln\gamma_1}{\partial C_s} + (l+1) \frac{\partial ln\gamma_A}{\partial C_s} - \frac{\partial ln\gamma_{l+2}}{\partial C_s} \right) + (l+1) \right]$$

$$\Delta_{10} = \sum_{l=0}^{N-2} D_{l+2} z_{l+2} \beta_{l+1}' C_s^l \left[C_s \left(\frac{\partial ln\gamma_1}{\partial C_s} + (l+1) \frac{\partial ln\gamma_A}{\partial C_s} - \frac{\partial ln\gamma_{l+2}}{\partial C_s} \right) + (l+1) \right]$$

$$A = \frac{1}{D_+ + D_-} \left[(D_+ - D_-) \frac{1}{C_s} + D_+ \frac{\partial ln\gamma_+}{\partial C_s} - D_- \frac{\partial ln\gamma_+}{\partial C_s} \right]$$

$$B = \frac{1}{D_+ + D_-} \left[(D_+ - D_-) \frac{1}{C_s^2} - D_+ \frac{\partial^2 ln\gamma_+}{\partial C_s^2} + D_- \frac{\partial^2 ln\gamma_+}{\partial C_s^2} \right]$$

$$\beta_l' = \beta_l \frac{\gamma_1 \gamma_A^l}{\gamma_{l+1}}$$

$$(3.72)$$

Similarly, the diffusion equation for the salt has the form

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \left(1 + C_s \frac{\partial ln\gamma_s}{\partial C_s} \right) + D_s \left(\frac{\partial C_s}{\partial x} \right)^2 \left(\frac{\partial ln\gamma_s}{\partial C_s} + C_s \frac{\partial^2 ln\gamma_s}{\partial C_s^2} \right) \qquad (3.73)$$

As a particular case, for an ideal solution we have

$$\vec{J_i} = -D_i \nabla C_i + \beta D_i z_i e C_i \vec{E}, \qquad (3.74)$$

with the electrical field taking the following simplified form

$$\vec{E} = \frac{kT}{e} \frac{D_1 - D_2}{D_1 + D_2} \frac{\vec{\nabla} C_s}{C_s} \qquad (3.75)$$

and the diffusion equation for the ideal case that considers formation of complexes to arbitrary order is

$$\frac{\partial C_{Tot}}{\partial t} = \frac{\partial^2 C_{Tot}}{\partial x^2} \frac{\Delta_3}{\Delta_1} + \frac{\partial^2 C_s}{\partial x^2} \frac{C_{Tot}}{\Delta_1} \left(\Delta_4 - \Delta_5 A - \frac{\Delta_2 \Delta_3}{\Delta_1} \right)$$

$$\left(\frac{\partial C_s}{\partial x} \right)^2 \frac{C_{Tot}}{\Delta_1} \left[-\Delta_{10} A + \Delta_5 B + 2 \left(\frac{\Delta_2}{\Delta_1} \right)^2 \Delta_3 + \frac{\Delta_5 \Delta_2}{\Delta_1} A - \frac{\Delta_3}{\Delta_1} \frac{\partial \Delta_2}{\partial C_s} \right]$$

$$- \frac{\partial C_s}{\partial x} \frac{\partial C_{Tot}}{\partial x} \frac{1}{\Delta_1} \left(2 \frac{\Delta_2 \Delta_3}{\Delta_1} + \Delta_5 A \right) \qquad (3.76)$$

where the expressions for Δ_i and coefficients A, B are obtained from (3.72) considering $\gamma_i = 1$. In the same way the diffusion equation for the salt takes the form

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \qquad (3.77)$$

A difference of the tracer concentration, for the salt, ideality implies linearity.

3.4   Diffusion coupling and the ideal case

The complete diffusion equation, for the ideal case of the i-th ion obtained from the continuity equation considering that all the activity coefficients γ_i are equal zero is given by the following expression

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - D_i z_i \frac{\partial C_i}{\partial x} \frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s} \frac{\partial C_s}{\partial x} + D_i C_i z_i \frac{D_+ - D_-}{D_+ + D_-} \left(\frac{1}{C_s} \frac{\partial^2 C_s}{\partial x^2} - \frac{1}{C_s^2} \left(\frac{\partial C_s}{\partial x} \right)^2 \right)$$

$$+ k_+^{(i)} [TA_{i-1}][A] - k_-^{(i)} [TA_i] + k_-^{(i+1)} [TA_{i+1}] - k_+^{(i+1)} [TA_i][A] \qquad (3.78)$$

where the source terms for i=1 and i=n, respectively, are

$$Q_1 = k_-^{(1)}[TA] - k_+^{(1)}[T][A]$$

$$Q_N = k_+^{(N-1)}[TA_{N-2}][A] - k_-^{(N-1)}[TA_{N-1}] \tag{3.79}$$

On the other hand, the diffusion equation for the salt has the form

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \tag{3.80}$$

CHAPTER 4

NORMAL MODE ANALYSIS FOR COUPLED DIFFUSION

4.1 Normal–mode analysis for coupled diffusion of a multiply associating non- ideal system

Since the first appearance on Schurr's work, the normal mode approximation technique has become a tool of choice for the study of transport process, specifically to study the diffusive processes on such a systems who are in stationary states subjected to small perturbations. NM treatment linearize the transport equations considering an arbitrary physical property, $A(\vec{r}, t)$, composed of two terms: an *equilibrium* term A^{∞} (t→ ∞) and a *non–equilibrium* or perturbation term $\delta A(\vec{r}, t)$. Linearization is implemented keeping only the first-order perturbation terms in the equations.

The physical property to analyze is the concentration of the i-th species $C_i(\vec{r}, t)$, which we'll express as $C_i(\vec{r}, t) = C_i^{\infty} + \delta C_i(\vec{r}, t)$. We implement NM approximation given the spatial-temporal evolution of the concentrations. The technique, as we mention above, includes to retain only the linear terms on $\delta C_i(\vec{r}, t)$. Using this approximation on (3.71), a (linearized) diffusion tracer equation is obtained

$$\frac{\partial \delta C_{Tot}}{\partial t} - D^*_{Tot}\frac{\partial^2 \delta C_{Tot}}{\partial x^2} + a^*_{Tot}\frac{\partial^2 \delta C_s}{\partial x^2} = 0 \tag{4.1}$$

The involved parameters are defined as

$$D^*_{Tot} = \frac{\Delta_3^{\infty}}{\Delta_1^{\infty}}$$

$$a^*_{Tot} = -C_{Tot}^{\infty}\left(\frac{\Delta_6^{\infty}}{\Delta_1^{\infty}} - \frac{\Delta_5^{\infty}}{\Delta_1^{\infty}}A + \frac{\partial}{\partial C_s^{\infty}}\frac{\Delta_3^{\infty}}{\Delta_1^{\infty}}\right) \tag{4.2}$$

where we have used eq. (3.72) introducing the notation $\Delta_i^{\infty} \equiv \Delta_i(C_s = C_s^{\infty})$, i.e.

$$\Delta_1 = \sum_{l=0}^{n-1} \beta_l'^\infty (C_s^\infty)^l$$

$$\Delta_2 = \sum_{l=0}^{n-2} \beta_{l+1}'^\infty (C_s^\infty)^l \left[(l+1) + C_s^\infty \left(\frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1} \gamma_1}{\gamma_{l+2}} \right) \Bigg|_{C_s = C_s^o} \right]$$

$$\Delta_3 = \sum_{l=0}^{n-1} D_{l+1} \beta_l'^\infty (C_s^\infty)^l$$

$$\Delta_4 = \sum_{l=0}^{n-2} D_{l+2} \beta_{l+1}'^\infty (C_s^\infty)^l \left[(l+1) + C_s^\infty \left(\frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1} \gamma_1}{\gamma_{l+2}} \right) \Bigg|_{C_s = C_s^o} \right]$$

$$\Delta_6 = \sum_{l=0}^{n-1} D_{l+1} \beta_l'^\infty (C_s^\infty)^l \left(\frac{\partial ln \gamma_{l+1}}{\partial C_s} \right) \Bigg|_{C_s = C_s^\infty}$$

$$A = \frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s^\infty} + \frac{1}{D_+ + D_-} \left[D_- \left(\frac{\partial ln \gamma_-}{\partial C_s} \right) \Bigg|_{C_s = C_s^\infty} - D_+ \left(\frac{\partial ln \gamma_+}{\partial C_s} \right) \Bigg|_{C_s = C_s^\infty} \right] \quad (4.3)$$

The equation (4.1) is solved by using both Fourier transform on space (denoted by an asterisk) and Laplace transform on time (denoted by a tilde) with the help of equation (3.16) and (3.17). We obtain

$$\delta \tilde{C}_{Tot}^*(q, s) = \frac{\delta C_{Tot}^*(q, t = 0)}{(s + q^2 D_{Tot}^*)} + \frac{a^* q^2 \tilde{C}_s^*(q, s)}{(s + q^2 D_{Tot}^*)} \quad (4.4)$$

Similarly, the major electrolyte has a diffusion motion independent from the tracer, expressed by the next diffusion equation

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} \left[1 + C_s^\infty \left(\frac{\partial ln \gamma_s}{\partial C_s} \right) \Bigg|_{C_s = C_s^\infty} \right] = D_s^* \frac{\partial^2 C_s}{\partial x^2} \quad (4.5)$$

defining $D_s^* = D_s \left[1 + C_s^\infty \left(\frac{\partial ln \gamma_s}{\partial C_s} \right) \Big|_{C_s = C_s^\infty} \right]$.

The solution of eq. (4.5) in the Fourier-Laplace space using the equations (3.16) and (3.17) is

$$\tilde{C}_s^* = C_s^*(q, t = 0) / (s + q^2 D_s^*) \quad (4.6)$$

Substituing eq. (4.6) on (4.4) give us

$$\delta \tilde{C}_{Tot}^*(q, s) = \frac{\delta C_{Tot}^*(q, t = 0)}{(s + q^2 D_{Tot}^*)} + \frac{a^* q^2 \tilde{C}_s^*(q, s)}{(s + q^2 D_{Tot}^*)} = \delta C_{Tot}^{*(s)} + \delta C_{Tot}^{*(m)} \quad (4.7)$$

with $\delta C_{Tot}^{*(s)}$ as the self–diffusion propagator of the tracer, while $\delta C_{Tot}^{*(m)}$ describes the migration of the tracer in the diffusion field of the salt.

Let us note that we are concerning with the tracer migration part, because it takes into account the tracer diffusion from capillary part B to part A.

Using a Fourier series expansion for δC_{Tot}, we get

$$\delta C_{Tot}(x,t) = -\frac{4}{\pi}\frac{a^*_{Tot}C^0_s}{D^*_s - D^*_{Tot}}\sum_{l=0}^{\infty}\frac{\sin(q_l x)}{2l+1}\left[e^{-q^2_{2l+1}D^*_{Tot}t} - e^{-q^2_{2l+1}D^*_s t}\right] \qquad (4.8)$$

Substituting (5.2) in the the activity expression [30] considering a proper origin of a coordinate system, we get

$$\rho(t) = \frac{1}{I}\frac{4}{\pi}\frac{A^*_s C^0_s}{D^*_s - D^*_{Tot}}\sum_{l=0}^{\infty}\frac{e^{-D^*_{Tot}q^2_l t} - e^{-D^*_s q^2_l t}}{2l+1}\cdot$$

$$\int_0^1 (f_-(z) - f_+(z))\sin[(2l+1)\frac{\pi}{2}z]dz \qquad (4.9)$$

with $I = \int_0^1 (f_-(z) + f_+(z))dz$, $\phi(x)$ a geometry dependent function and C^0_{Tot} the initial tracer concentration.

The particular case which considers an ideal solution could be written as

$$\frac{\partial \delta C_{Tot}}{\partial t} - D^*_{Tot}\frac{\partial^2 \delta C_{Tot}}{\partial x^2} + A^*_s C^0_{Tot}\frac{\partial^2 C_s}{\partial x^2} = 0 \qquad (4.10)$$

The terms A^*_s and D^*_{Tot} are gived by (4.20) where $\Delta_i = \Delta^\infty_i$ and γ_i are equal to the identity.

The linearized-ideal diffusion equation for the salt has the form

$$\frac{\partial C_s}{\partial t} = D_s\frac{\partial^2 C_s}{\partial x^2} \qquad (4.11)$$

The coupled equations (4.10) and (4.11) are solved in the same way as above, obtaining similar solutions for the tracer concentration and activity expressions (5.2) and (4.24), respectively and writing D_s in the place of D^*_s (apart from the later considerations on the γ_i's and Δ_i's).

4.2   Normal modes and the ideal case

Now we made use of the normal mode approximation for the specie's concentrations $C_i = C^0_i + \delta C_i$, with C^0_i = concentration at infinite dilution and δC_i = non–equilibrium perturbation. Doing so, the next general diffusion tracer equation is obtained

$$\frac{\partial \delta C_{Tot}}{\partial t} - D^*_{Tot}\frac{\partial^2 \delta C_{Tot}}{\partial x^2} + A^*_s C^0_{Tot}\frac{\partial^2 C_s}{\partial x^2} = 0 \qquad (4.12)$$

$$D^*_{Tot} = \frac{\Delta_3}{\Delta_1}$$

$$A^*_s = -\left\{ \frac{\Delta_6}{\Delta_1} - \frac{\Delta_5}{\Delta_1}A + \left(\frac{\partial}{\partial C_s}\frac{\Delta_3}{\Delta_1}\right)\Big|_{C_s=C_s^0} \right\} \tag{4.13}$$

with

$$\Delta_1 = \sum_{l=0}^{n-1} \beta_l^0 (C_s^0)^l$$

$$\Delta_2 = \sum_{l=0}^{n-2} \beta_{l+1}^0 (C_s^0)^l (l+1)$$

$$\Delta_3 = \sum_{l=0}^{n-1} D_{l+1}\beta_l^0 (C_s^0)^l$$

$$\Delta_4 = \sum_{l=0}^{n-2} D_{l+2}\beta_{l+1}^0 (C_s^0)^l (l+1)$$

$$\Delta_6 = \sum_{l=0}^{n-1} D_{l+1}\beta_l^0 (C_s^0)^l$$

$$A = \frac{D_+ - D_-}{D_+ + D_-}\frac{1}{C_s^0} \tag{4.14}$$

The equation (4.19) is solved in the Fourier-Laplace space giving

$$\tilde{\delta}C^*_{Tot}(q,s) =$$
$$\frac{\delta C^*_{Tot}(q,t=0)}{[s+q^2 D^*_{Tot}]} + \frac{A^*_s C^0_{Tot} q^2 C^*_s(q,t=0)}{(s+q^2 D^*_{Tot})(s+q^2 D^*_{Tot})}$$
$$= \delta C^{*(s)}_{Tot} + \delta C^{*(m)}_{Tot} \tag{4.15}$$

where $\delta C^{*(s)}_{Tot}$ = autodiffusion term and $\delta C^{*(m)}_{Tot} = \delta C_{Tot}$ Total migration tracer term, $C_{Tot} = C_1 + C_2 + \cdots + C_N$ = Total tracer concentration and, by convention, we use the notation 1= Tracer, 2= Dimer, ..., N=n-mer.

At this point, we are concerning with the tracer migration part, because it takes into account the tracer diffusion from capillary part B to part A. Using a Fourier series expansion for $\delta C^{*(m)}_{Tot}$, we get ($q_l = \pi l/2L$)

$$\frac{\delta C_{Tot}(x,t)}{C^0_{Tot}} = -\frac{4}{\pi}\frac{A^*_s C^0_s}{D^*_s - D^*_{Tot}}\sum_{l=0}^{\infty}\frac{\sin(q_l x)}{2l+1}\left[e^{-q^2_{2l+1}D^*_{Tot}t} - e^{-q^2_{2l+1}D^*_s t}\right] \tag{4.16}$$

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Finally we obtain the activity expression in terms of the concentration [20]

$$\rho(t) = \frac{1}{I}\frac{4}{\pi}\frac{A_s^* C_s^0}{D_s^* - D_{Tot}^*} \sum_{l=0}^{\infty} \frac{e^{-D_{Tot}^* q_l^2 t} - e^{-D_s^* q_l^2 t}}{2l+1} \cdot$$

$$\int_0^1 (f_-(z) - f_+(z)) \sin[(2l+1)\frac{\pi}{2}z]dz \tag{4.17}$$

with

$$I = \int_0^1 (f_-(z) + f_+(z))dz$$

$$\tag{4.18}$$

where $f_\pm(z) =$ capillary geometry dependent function.

4.3 Normal modes and the non–ideal case

Now we made use of the normal mode approximation for the specie's concentrations $C_i = C_i^\infty + \delta C_i$, with $C_i^\infty =$ concentration at infinite dilution and $\delta C_i =$ non equilibrium perturbation. Doing so, the next general diffusion tracer equation is obtained

$$\frac{\partial \delta C_{Tot}}{\partial t} - D_{Tot}^* \frac{\partial^2 \delta C_{Tot}}{\partial x^2} + a_{Tot}^* \frac{\partial^2 C_s}{\partial x^2} = 0 \tag{4.19}$$

where $C_{Tot} = C_1 + C_2 + \cdots + C_N =$ Total tracer concentration and, by convention, we use the notation 1= Tracer, 2= Dimer, ..., N=n-mer.

$$D_{Tot}^* = \frac{\Delta_{III}}{\Delta_I}$$

$$a_{Tot}^* = -C_{Tot}^0 \left\{ \frac{\Delta_{VI}}{\Delta_I} - \frac{\Delta_V}{\Delta_I}A + \left(\frac{\partial}{\partial C_s}\frac{\Delta_{III}}{\Delta_I}\right)\bigg|_{C_s=C_s^0} \right\} \tag{4.20}$$

with

$$\Delta_I = \sum_{l=0}^{n-1} \beta_l^0 (C_s^0)^l$$

$$\Delta_{II} = \sum_{l=0}^{n-2} \beta_{l+1}^0 (C_s^0)^l.$$

$$\left[(l+1) + C_s^0 \left(\frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1}\gamma_1}{\gamma_{l+2}} \right) \Big|_{C_s=C_s^o} \right]$$

$$\Delta_{III} = \sum_{l=0}^{n-1} D_{l+1}\beta_l^0 (C_s^0)^l$$

$$\Delta_{IV} = \sum_{l=0}^{n-2} D_{l+2}\beta_{l+1}^0 (C_s^0)^l.$$

$$\left[(l+1) + C_s^0 \left(\frac{\partial}{\partial C_s} ln \frac{\gamma_A^{l+1}\gamma_1}{\gamma_{l+2}} \right) \Big|_{C_s=C_s^o} \right]$$

$$\Delta_{VI} = \sum_{l=0}^{n-1} D_{l+1}\beta_l^0 (C_s^0)^l \frac{\partial}{\partial C_s} ln\gamma_{l+1} \Big|_{C_s=C_s^0}$$

$$A = \frac{D_+ - D_-}{D_+ + D_-} \frac{1}{C_s^0} + \frac{1}{D_+ + D_-} \left[D_- \left(\frac{\partial}{\partial C_s} ln\gamma_- \right) \Big|_{C_s=C_s^0} \right.$$

$$\left. -D_+ \left(\frac{\partial}{\partial C_s} ln\gamma_+ \right) \Big|_{C_s=C_s^0} \right] \tag{4.21}$$

The equation (4.19) is solved in the Fourier-Laplace space giving

$$\tilde{\delta} C_{Tot}^*(q,s) =$$
$$\frac{\delta C_{Tot}^*(q,t=0)}{[s+q^2 D_{Tot}^*]} + \frac{a^* q^2 C_s^*(q,t=0)}{(s+q^2 D_{Tot}^*)(s+q^2 D_{Tot}^*)}$$
$$= \delta C_{Tot}^{*(s)} + \delta C_{Tot}^{*(m)} \tag{4.22}$$

where $\delta C_{Tot}^{*(s)}$ = autodiffusion term and $\delta C_{Tot}^{*(m)} = \delta C_{Tot}$ Total migration tracer term.

Here, we only need to consider the tracer migration's part, i.e., the part who takes into account the translation of the tracer from capillary part B to A. Using a Fourier series expansion for δC_{Tot}, we get

$$\delta C_{Tot}(x,t) = -\frac{4}{\pi} \frac{a_{Tot}^* C_s^0}{D_s^* - D_{Tot}^*} \sum_{l=0}^{\infty} \frac{\sin(q_l x)}{2l+1} \left[e^{-q_{2l+1}^2 D_{Tot}^* t} - e^{-q_{2l+1}^2 D_s^* t} \right] \tag{4.23}$$

Obtaining the activity expression in terms of the concentration [20]

$$\rho(t) = \int_{-L}^{L} \delta C_{Tot}(x,t)\phi(x)dx / \int_{-L}^{L} C_{Tot}^0 \phi(x) \tag{4.24}$$

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where $\phi(x)$ = geometry dependent function and C^0_{Tot} = initial tracer concentration.

CHAPTER 5

RESULTS

5.1 Experimental

It is worthwile to conduct diffusion experiments on an ion which is a pure β emitter in a cell made of scintillating plastic [9,10]. On the other hand if the tracer is both a β and a γ emitter then it is necessary to stop the β's so that only the γ emission can be analyzed. This was the case in the present work in which the diffusion of zinc(II) was investigated. The commercially available radioactive form of this ion, $^{65}Zn^{2+}$, is a β and γ emitter.

Thus the experimental technique utilized in this work was an adaptation of the closed capillary method [20]. The cell consists of a silica capillary (sealed at its bottom end) of 3 cm length and ca. 0.8 mm inner diameter which is introduced into a bore drilled through the center of a cylinder made of scintillating plastic (see Figure 5.1). The capillary (whose wall is ca. 1 mm thick) has the property of stopping the β^+ particles of low energy (0.33 MeV) emitted by $^{65}Zn^{2+}$. In order to avoid capillarity problems, the silica capillary was filled on a distance of 2.8 cm (i.e. 2 mm below the top of the capillary). Indeed, filling the capillary with liquid up to its mouth was observed to result in a significant loss of liquid in the course of the experiment. The top of the capillary was sealed with a piece of plastic paraffin film (Parafilm) to prevent evaporation. The silica capillary was adjusted within the plastic one so that the mid-point of the liquid phase coincided with the top of the scintillating plastic cylinder.

The diffusion experiments were conducted as follows. The bottom part of the capillary was filled with a solution containing 1 M LiCl, 10^{-3} M $ZnCl_2$ and radioactive zinc(II) in tracer amounts (of the order of 10^{-8} M). Then, the top part of the capillary was filled very carefully with a solution composed of 10^{-3} M $ZnCl_2$ and the same concentration of radioactive zinc(II). The solutions were introduced in the capillary by using a small plastic Pasteur pipette bearing a thin flexible Teflon tube at its end. This device allowed us to accurately handle very small volumes of liquid, of the order of 8 μL each time (half of the capillary). Next, the cell was introduced in a β radioactivity counter which counts the photons emitted in the scintillating plastic under the effect of the γ rays. The experiments were conducted with continuous monitoring of radioactivity, at a temperature of 25 $\pm$ 1 °C.
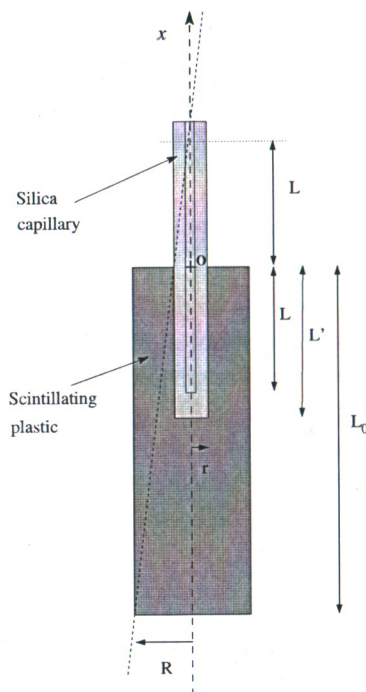
Figure 5.1: Sketch of the diffusion cell

Because it is expected that the γ rays can have only one efficient conversion in the plastic, it was shown [20] that the probability of conversion of a γ ray is proportional to the length of plastic it crosses. This property allows an explicit calculation of the counting intensity as a function of the tracer concentration profile in the capillary. Then one can measure self-diffusion coefficients of γ-emitters with this technique (as was done before in the case of a radiolabelled biological molecule [20]), and study diffusion processes like diffusion coupling.

The relative variation of the radioactivity intensity measured by the counter may be written as,

$$\rho(t) \equiv \frac{I(t)}{I(t=0)} - 1 \tag{5.1}$$

with $I(t)$ the measured intensity at time t, so that $\rho(t=0) = 0$.

With the notations of Ref. [20] we can write straightforwardly,

$$\rho(t) = \frac{\int_0^1 [\theta_-(z,t) f_-(z) + \theta_+(z,t) f_+(z)] dz}{\int_0^1 [f_-(z) + f_+(z)] dz} \tag{5.2}$$

in which $z \equiv x/L$, f_- and f_+ are functions proportional to the 'efficacy' of a γ-ray emitted at position x (f_- for $x < 0$ in the bottom part of the capillary and f_+ for $x > 0$ in the upper part), and $\theta_-(z,t)$ and $\theta_+(z,t)$ are the relative excesses of tracer concentration in bottom and upper parts of the capillary, respectively, that is

$$\theta_\pm(z,t) \equiv \frac{\delta C_T^{(\pm)}(z,t)}{C_T^{(0)}} \tag{5.3}$$

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where $\delta C_T^{(\pm)} \equiv C_T^{(\pm)} - C_T^{(0)}$, $C_T^{(-)}$ and $C_T^{(+)}$ are the tracer concentrations for $x < 0$ and $x > 0$, respectively, and $C_T^{(0)}$ is the initial uniform tracer concentration in the capillary. Expressions for the functions f_- and f_+ were given in ref. [20]. The concentration of the tracer is calculated below by using NM and FD techniques.

5.2 Application

As a case of study, we consider an electrolyte aqueous solution of $ZnCl_2$ at 0.02 M on LiCl at 1 M, where Zn^* is the tracer (* is for radiactive). We consider that the Zn^{*2+} ions can bind up to four Cl^-, i.e., considering complexes formation up to pentamers.

Solution of the coupled diffusion eqs. (5.5) using (5.6) was obtained using a finite difference algorithm, with a number of cells, N=200, and a time step shorter than the mean diffusion time between contiguous cells for the faster ion, in such a way that if Δx and Δt are the space and time steps, is satisfied

$$\Delta t = \frac{1}{M} \frac{\Delta x^2}{max(D_l)}. \tag{5.4}$$

We choose M= 5, 10 or 20, for the diffusion of single species. M =2 is the lower limit for the convergence of the algorithm. Furthermore, close attention must be paid to the conservation of the total amount of matter in the course of time. The conservation of matter can be fulfilled by applying the following: i) The system is symmetrized at both ends. ii) One introduces two imaginary cells 0 and N + 1 in which the concentrations of the various species are equal to those of, respectively, cells 1 and N, the differential operators (first and second derivatives with respect to x) are written accordingly at both ends. iii) The reduced electrical field E is set equal zero in the latter two cells at each time incrementation. iv) To consider the association between ions, we assume a local chemical equilibrium and therefore we equilibrate the concentrations at each time step, after having let the particles diffuse individually according to eq. (5.6). This procedure may be used because we assume that the ion reactions are fast compared to the diffusion of matter at a macroscopic scale [9].

The diffusion equations that we are solving are obtained from the following one dimensional expressions

$$\frac{\partial C_i}{\partial_t} = D_i \left(\frac{\partial J_i}{\partial x} + \frac{\partial^2 C_i}{\partial x^2} \right), \tag{5.5}$$

$$J_i = C_i \left(\frac{\partial ln\gamma_i}{\partial x} - z_i \bar{E} \right), \tag{5.6}$$

where E is the one-dimensional magnitude of the electrical field due to equation (3.13) and the notation $\bar{E} = (e/kT)E$ has been used.

The parameters used to analyze the Zinc chloride on Lithium chloride are summarized in Table 5.1 [31–33]. The diffusion coefficients given on table 5.1 for every zinc

complex were obtained using the Stokes-Einstein equation, i.e., we assume an inversely proportional relation between the diffusion coefficients and the diameter's species.

The cummulative association constants were obtained from a previous work [34] and using a calculating computer software: CHemical Equilibria in AQuatic Systems (CHEAQS 4.1), see table 5.1.

Species	Parameters		
-	$\sigma(\text{Å})$	$D(10^{-6}cm^2/s)$	$\beta(\text{adim.})$
Li^+	4.3	10.29	-
Cl^-	3.6	20.32	-
Tracer	7.0	7.01	-
Dimer	6.8	7.22	0.49
Trimer	6.8	7.22	0.62
Tetramer	7.0	7.01	0.51
Pentamer	7.0	7.01	0.20

Table 5.1: Specie's parameters for $ZnCl_2$ on $LiCl$. Where σ's are the diameters, D's the Diffusion Coefficients and β's the cummulative association constants.

The experimental results were obtained specifically for this work using the closed capillary technique [35]. A bore of 1-mm diameter was drilled through the center of the cylinder. The bottom section, of length L = 1.29 cm, is made from scintillating plastic (Altustipe), whereas the top section is made of ordinary plastic of the same length L. The total length of the capillary is then 2L = 2.58 cm, corresponding to characteristic diffusion times in the system of about 2 or 3 days. The aqueous solutions are spiked with tracer amounts of [65](Zn)Cl radioactive aqueous solutions from the Radiochemical Centre, Amersham (U.K.).
The NM analysis for the particular case of pentamer formation is obtained from eqs. (4.19) and (4.24) only by taking the value N=5 on the delta parameters given by (4.20).

As expected, the finite difference non–ideal associated (NI-A) curve is the better approximation to the experimental results according to Figure 5.2, i.e., the complete diffusion equation who takes into account non–ideality and association phenomena. On the other hand, the ideal non-associated (I-NA) finite differences curve is clearly the approach more remote, so far, of the experimental results (see Figure 5.2), which means that both effects, non–ideality and association are importants. Moreover, according to Figure 5.3, the normal mode curves, we can see that the NI-A case is again a better approximation to experimental results. This shows that the NM approximation captures reasonably well the non–ideality and association phenomena. Nevertheless, compared with the full theory it seems that non-linear terms are necessary to have a better approximation. However the more remote approach to the experimental results is the non–ideal non-associated (NI-NA) case and the posible reason will be discussed below. Comparing the figures 5.2 and 5.3, we can see that the curves for the NI-NA and the I-NA cases are exchanged because in normal modes curves the minimum for the NI-NA case is greater than the

I-NA case, meanwhile in the full theory curves, the I-NA case is greater than the NI-NA case. This could happen due to the coupling between association and ideality in the normal modes expressions, i.e., if we turn off the association, taking all the cummulative association constants equal to zero, this implies necessarily to turn off non–ideality parameters (see eqs. (3.72)). On the contrary, in the case of the non-linear theory, the non–ideality and the association are not inextricably coupled, so that when we turn off the association, not necessarily it turns off non ideality, as we can see in eqs. (3.72) for the $\Delta'_i s$ parameter where association terms are coupled with non–ideality terms. Furthermore, the ideal associated (I-A) curves for finite differences and NM approximations have similar behaviours and are located above the experimental result curves in both cases. This could be telling that if we turn off non–ideality it doesn't necessarily means to turn off association, but we need to note that in the NM curve such a behaviour is decreased because it is farther from the experimental results. This is an expected result because of the linearization of the NM approximation.

We can see that the association phenomena is relevant for the description of our tracer diffusion process: the more we have specie's formation, the more we improve our diffusion results, i.e., to consider association formation until pentamers give us a more closer relation between the theory and experimental results.

The relevance of considering the specie's formation in our theory is very important because the fewer species consider, the further away the theoretical from the experimental results. Which meant that zinc complexe's formation proposed here is in agreement with that encountered in literature.

There is sensitivity to the size of the complexes, fundamentally in the γ_i's calculus, i.e., theres is sensitivity to the non–ideality description. In counterpart to vary the diffusion coefficients we have no a considerable activity variation, neither when we vary the association constants β_i's. The minima position is almost insensible to the order of the complex, however, curves gradually closer to the experimental results as the order of the complexes increases.

The theoretical development seems to inherit the sensitive diameter's dependence from the MSA theory via the activity coefficients. In counterpart the theoretical theory does not shows a perceptive sensitivity with respect to the discusion coefficients and neither if we vary the association constants β_i's. However, the species order complex shows that the curves gradually approach to the experimental results as the order of the complexes increases.
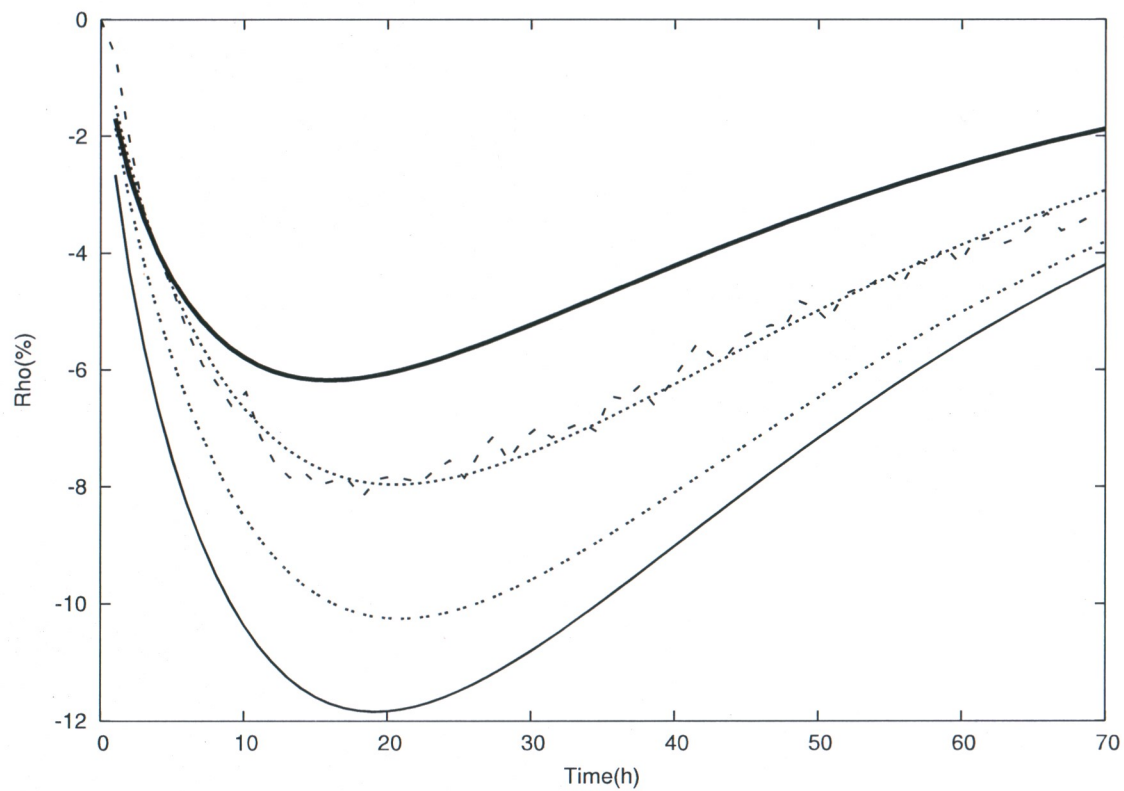
Figure 5.2: Finite Differences Curves. From top to bottom: curve including associanting effects but not an ideal solution, curve including non-associating effects and not an ideal solution, curve including non-associating effects but not an ideal solution, curve including non-associating effects and an ideal solution. The broken line is for the experimental results.

Figure 5.3: Normal Mode Curves. From top to bottom: curve including associanting effects but not an ideal solution, curve including non-associating effects and not an ideal solution, curve including non-associating effects but not an ideal solution, curve including non-associating effects and an ideal solution. The broken line is for the experimental results.
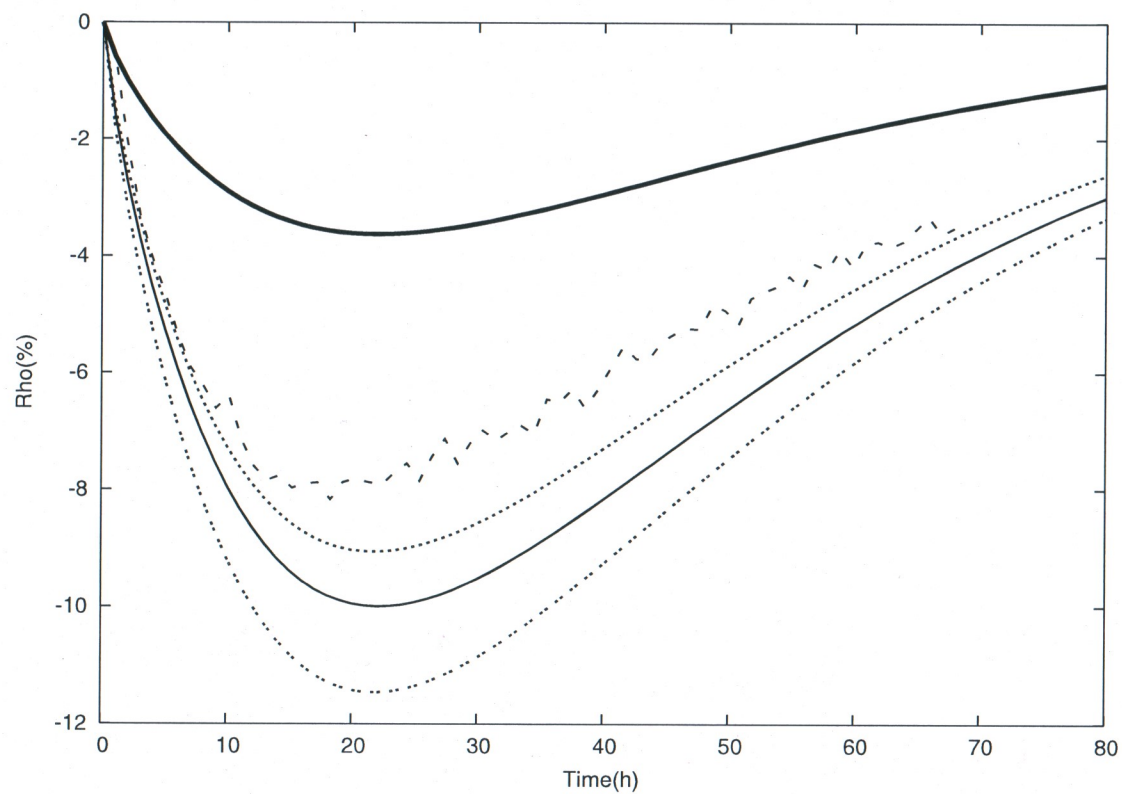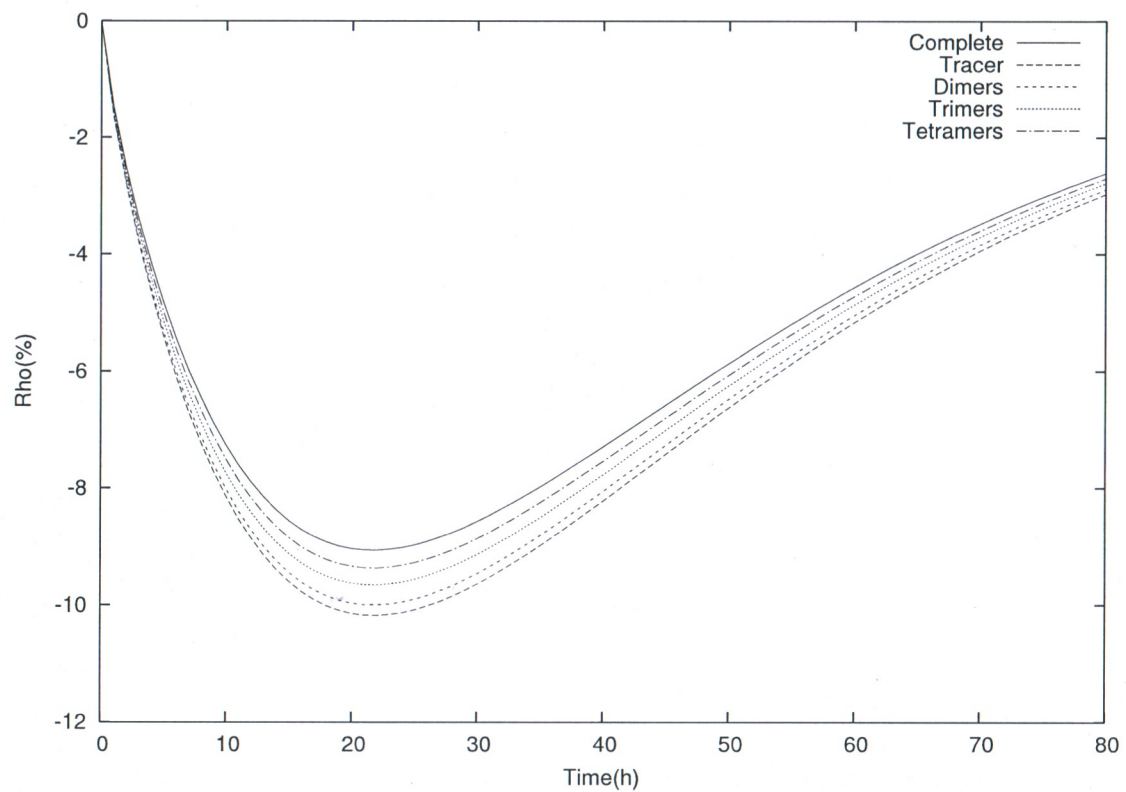
Figure 5.4: Here is shown the association relevance. Notice that the more we consider association closer we get to the complete NM theory.
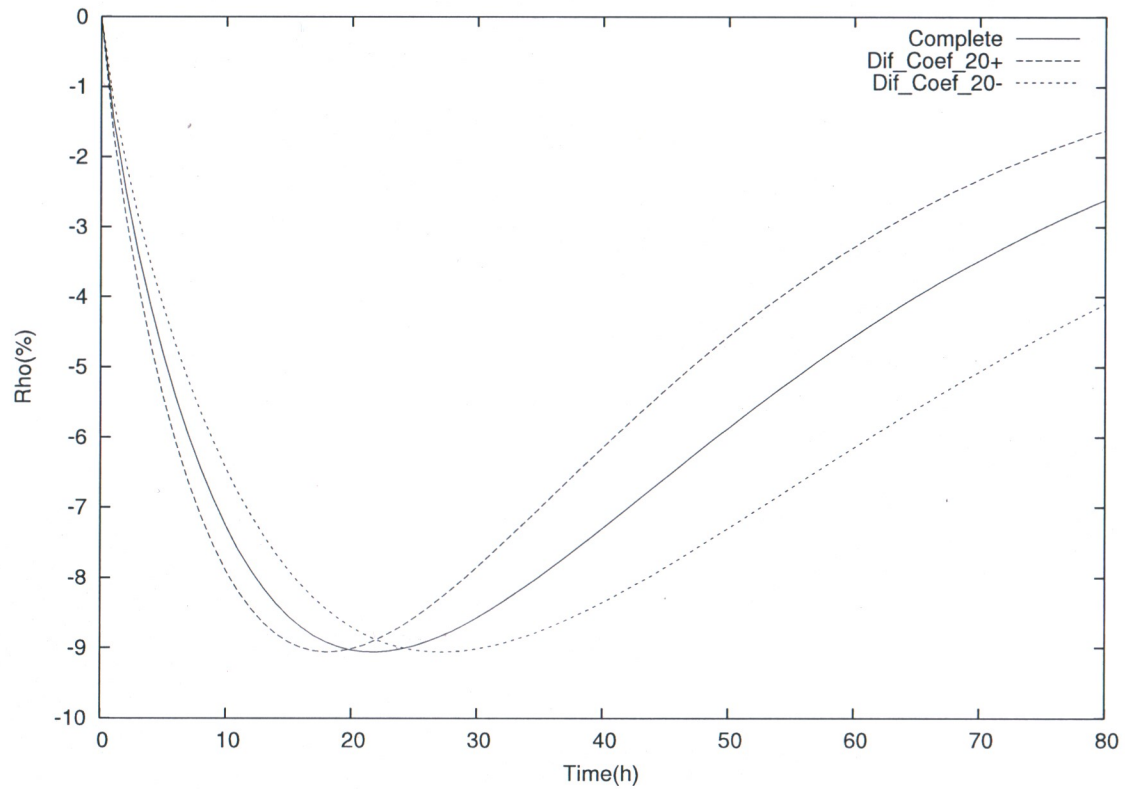
Figure 5.5: Modification NM curves considering an increase and a decrement of the diffsuion coefficient specie's values and its comparison with the complete NM approximation are shown. In those curves all specie's values at the same time and in the same proportion were modified. As expected, it can be seen that the smaller the diffusion coefficients the slower the tracer's diffusion process.

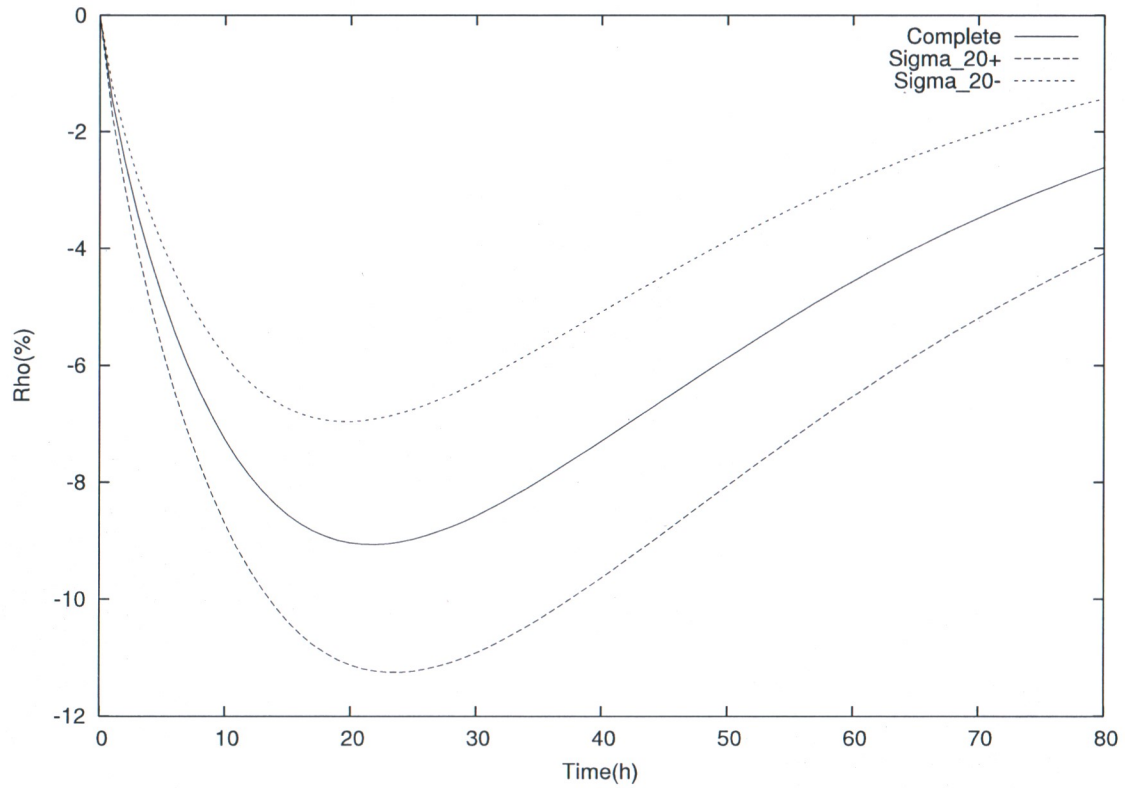Figure 5.6: NM curves obtained by modifying the specie's size and its comparison with the complete NM theory are shown. We can see that there is a considerable sensitivity of the NM theory with respect to the size of the species.
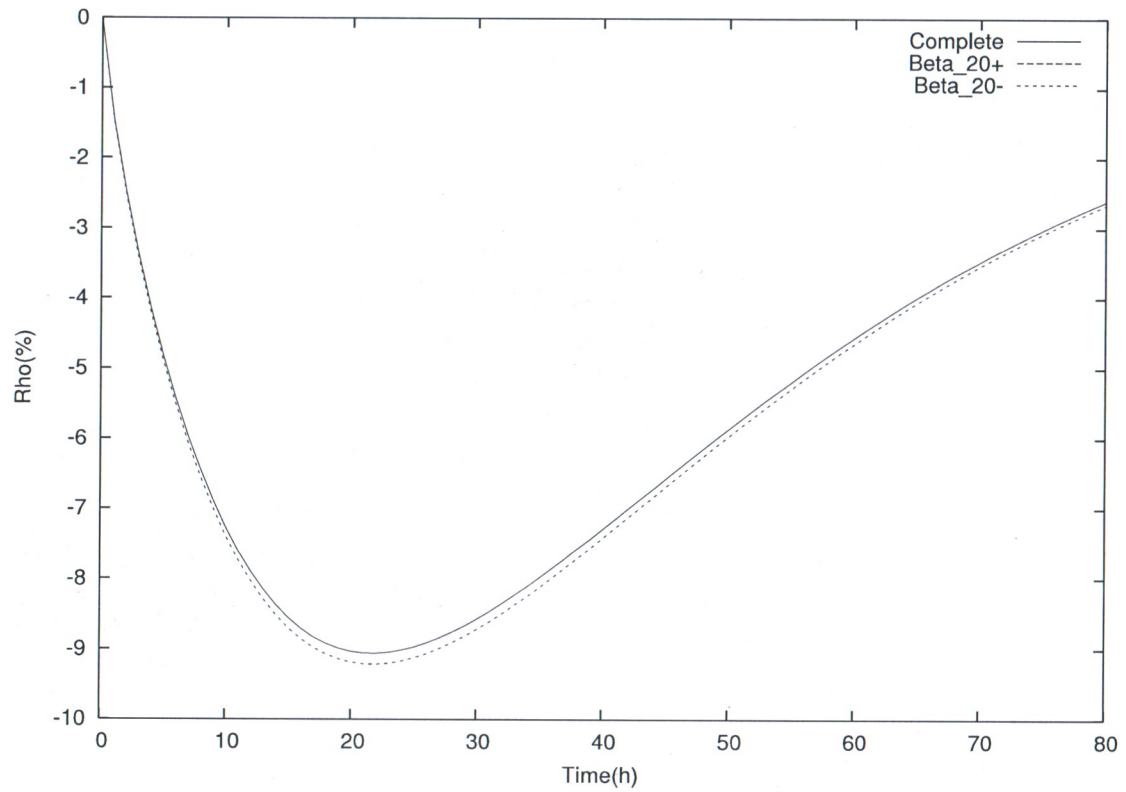
Figure 5.7: NM curves obtained by modifying the association constant values and its comparison with the NM complete theory are shown. It seems that there isn't significant difference between the curves.

CHAPTER 6

CONCLUSIONS AND PERSPECTIVES

A difusion coupling theory for non–ideal aqueous electrolytes that considers association to arbitrary order with a two electrolyte mixture sharing the same anion with arbitrary valences was developed. The theoretical formalism was obtained considering that the salt MA is in much larger amount (major electrolyte) than XA in order to have an internal electrical field "completely" due to the salt acting over all species. As a case of study we consider an electrolyte aqueous solution made of $ZnCl_2$ at 0.02 M diluted on LiCl at 1 M (major electrolyte) where we are considering up to pentamers complexes, i.e., Zn^{*2+} ions can bind up to four Cl^- ions.

Experimental results are in good agreement with our theoretical treatment. The presence of association and non–ideality in our system plays a crucial role in the description of the electrolyte solution's diffusion. The more accurate curves to the experimental results on both figures are those including association and non–ideality effects.

Moreover, even when we can use the activity coefficient analitycal expressions considering association up to pentamers given by the BiMSA [28] theory, that does not seem to be necessary because the expressions used are in good agreement with the reproduction of the non–ideality behavior until the concentrations used. Further work is needed in this direction.

The total tracer diffusion equation obtained using IT-NM approximation combination is a first order theory from those obtained with the IT itself. This could be relevant because in principle, we can develope a non-trivial second order approximation equation in order to have an improvement on the tracer's diffusion process description. In that sense we should have a more accurate NM curves to experimental results.

According to the theoretical development we see that there is a close relationship or coupling between association and non–ideality phenomena. This could be seen on the Δ's parameters where the association constants and the activity coefficients appears naturally related, such that if we turn off the association (when the constants $\beta's$ are zero) the non–ideal parameters are gone and at the contrary, if we turn off the non–idealization we don't necessarily lost the association phenomenom, because some association constant survives.

The theoretical development seems to inherit the sensitive diameter's dependence from the MSA theory via the activity coefficients. In counterpart the theoretical theory does

not shows a perceptive sensitivity with respect to the diffusion coefficients and neither if we vary the association constants β_i's. However, the species order complex shows that the curves gradually approach to the experimental results as the order of the complexes increases.

Similarly, we can use as a closure relation the poisson equation to calculate the electrical field instead of the dynamical electrolneutrality condition, having a stronger theoretical analysis in order to obtain a better approximation of the diffusion process.

As we mention above, we can use the activity coefficient analitycal expressions considering association up to pentamers given by the BiMSA [28] theory, where the activity coefficients depends explicitly, via the BiMSA coefficients, on the density of the complexes to give us a more accuracy on the non-ideal parameters. In addition to this we could consider different concentration regimes of our case of study ($ZnCl_2$ on $LiCl$), e.g., higher solute concentrations.

We could obtain a generalization of our case of study considering a three dimensional cylindrical system, generalizing the expressions for the activity, the normal modes and the finite differences; in order to obtain a three dimensional diffusion process to simulate a more realistic system.

APPENDIX A

FINITE DIFFERENCES APPROXIMATION

A.0.1   Von Neumann Stability analysis

The preceding stability analysis uses the eigenvalues of the matrix obtained from a semi-discretization of the partial differential equation at hand. Different spatial differencing schemes lead to different stability criteria for a given time advancement scheme. We shall refer to this type of analysis as the *matrix stability analysis*. Since boundary conditions are implemented in the semi-discretization, their effects are accounted for in the matriz stability analysis. The price paid for this generality is the need to know the eigenvalues of the matrix that arises from the spatial discretization. Unfotunately, analytacal expressions for the eigenvalues are ony available for very simple matrices, and therefore, the matrix stability analysis is not widely used. Experience has shown that in ost cases, numerical stability problems arise solely from the (full) discretization of the partial differential equation inside the domain and not from the boundary conditions. von Neumann's stability analysis is a widely used (back of an envelope) analytical procedure for determining the stability properties of a numerical method applied to a PDE that does not account for the effects of boundary conditions. In fact, it is assumed that the boundary conditions are periodic; that is, the solution and its derivatives are the same at the two ends of the domain. The technique works for linear, constant coefficient differential equations that are discretized on uniformly spaced apatial grids. Let's demonstrate von Neumann's technique by applying it to the discrete equation

$$u_j^{(n+1)} = u_j^{(n)} + \frac{\alpha \Delta t}{\Delta x^2} \left(u_{j+1}^{(n)} - 2u_j^{(n)} + u_{j-1}^{(n)} \right). \tag{A.1}$$

Equation (A.1) results from approximating the spatial derivative in (5.5) with the second-order central difference and using the explicit Euler for time advancement. The key part of von Neumann's analysis to assume a solution of the form

$$u_j^{(n)} = \sigma^n e^{ikx_j} \tag{A.2}$$

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for the discrete equation (A.1). Note that the assumption of spatial periodicity is already worked into the form of the solution in (A.2); the period is $2\pi/k$. To check whether this solution works, we substitute (A.2) into (A.1) and obtain

$$\sigma^{n+1}e^{ikx_j} = \sigma^n e^{ikx_j} + \frac{\alpha\Delta t}{\Delta x^2}\sigma^n(e^{ikx_{j+1}} - 2e^{ikx_j} + e^{ikx_{j-1}})$$

Noting that

$$x_{j+1} = x_j + \Delta x \qquad \text{and} \qquad x_{j-1} = x_j - \Delta x \tag{A.3}$$

and dividing both sides by $\sigma^n e^{ikx_j}$ leads to

$$\sigma = 1 + \frac{\alpha\Delta t}{\Delta x^2}(e^{ik\Delta x} - 2 + e^{-ik\Delta x})$$

and using the complex trigonometric identity $\sin^2(z) = -\frac{1}{4}[e^{2iz} + e^{-2iz} - 2]$ σ becomes

$$\sigma = 1 - \frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right)$$

Now, defining the amplification factor

$$G \equiv \frac{u_j^{n+1}}{u_j^n}$$

The necessary and sufficient condition for the error to remain bounded is that $|G| \leq 1$. However

$$G = \frac{\sigma^{n+1}e^{ikx_j}}{\sigma^n e^{ikx_j}} = \sigma$$

then we have $|\sigma| \leq 1$ (otherwise, σ^n in (A.2) would grow unbounded):

$$|1 - \frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right)| \leq 1 \tag{A.4}$$

In other words, we must have

$$-1 \leq 1 - \frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right) \leq 1 \tag{A.5}$$

The right hand inequality is always satisfied since $[\frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right)$ is always positive. The left-hand inequality can be recast as

$$-\frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right) \geq -2$$

or

$$\frac{4\alpha\Delta t}{\Delta x^2}\sin^2\left(\frac{k\Delta x}{2}\right) \leq 2 \tag{A.6}$$

For the above condition to hold at all $\sin^2(k\Delta x/2)$, we have

$$\Delta t \leq \frac{\Delta x^2}{2\alpha} \qquad (A.7)$$

In summary, the von Neumann analysis is an analytical technique that is applied to the full (space-time) discretization of a partial differential equation. The technique works whenever the space-dependent terms are eliminated after substituting the periodic form of the solution given in (A.2). For example, if in (5.5), α were a known function of x, then the von Neumann analyisis would not, in general, work. In this case σ would have to be a function of x and the simple solution given in (A.2) would no longer valid. The same problem would arise if a non-uniformly spaced spatial grid were used. Of course, in these cases the matrix stability analysis would still work, but (for variable α or on -uniform meshes) the eigenvalues would not be available via an analytical formula, moreover, one would have to restort to well-known numerical techniques to estimate the eigenvalue with the highest magnitude for a given N. However, in case such an estimate is not available, experience has shown us that using the maximum value of $\alpha(x)$ and/or the smallest Δx in (5.13) gives an adequate estimate for Δt_{max}.

The diffusion equations that we are solving are obtained from the next one dimensional expressions

$$\partial_t C_i = D_i \left(\frac{\partial J_i}{\partial x} + \frac{\partial^2 C_i}{\partial x^2} \right) \tag{A.8}$$

$$J_i = C_i \left(\frac{\partial ln\gamma_i}{\partial x} - z_i \bar{E} \right) \tag{A.9}$$

where $\bar{E} = (e/kT)E$, with k is the boltzmann constant, T is the temperature and E is the electric field.

and could be written as

$$C_{i,j}^{n+1} = C_{i,j}^n + \frac{\Delta t D_i}{(\Delta x)^2} \left(C_{i,j+1}^n - 2C_{i,j}^n + C_{i,j-1}^n \right) + \frac{D_i \Delta t}{\Delta x} \left(J_{i,j+1}^n - J_{i,j-1}^n \right) \tag{A.10}$$

Note that if we apply the Von Neumann stability analysis to this relation, the necessary and sufficient condition to the stability requirement for this *Forward-Time Central-Space* (FTCS) scheme is

$$\Delta t \leq \frac{(\Delta x)^2}{2D_i} \tag{A.11}$$

APPENDIX B

ALGORITHMS USED

There were various algorithms used on this work. The representative ones can be obtained from the next website:

https://dl.dropboxusercontent.com/u/49520808/DF_Zn_no_Ideal_asociativo.f
and
https://dl.dropboxusercontent.com/u/49520808/MN_Zn_noideal_asoc_1e-2.f

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León, Gto., 16 de Mayo, 2016

DR. LUIS ARTURO UREÑA LÓPEZ
COORDINADOR DE POSGRADO
DIVISIÓN DE CIENCIAS E INGENIERÍAS

Estimado Dr. Ureña López:

Por medio de la presente hago constar que he revisado la tesis titulada: "**Diffusion Coupling in Associating Non–ideal Multi-Electrolyte Solutions**" que para obtener el grado de Doctor en Física presenta el **M.F. José Miguel Ramos Moreno.**

En dicho trabajo se presenta un estudio teórico para describir el proceso de acoplamiento de difusión en soluciones electrolíticas acuosas. El trabajo constituye una aportación original en su campo debido a los formalismos teóricos que se discuten en el mismo para describir este tipo de sistemas.

Al mismo tiempo le comunico que he discutido cuidadosamente dicha tesis con el sustentante, al cual le he hecho llegar mis comentarios y correcciones. Le expreso además que en lo general me parece un buen trabajo por lo que avalo su presentación.

Atentamente

DR. MODESTO ANTONIO SOSA AQUINO

PROFESORA TITULAR "C"
Sinodal

DIVISION DE CIENCIAS E INGENIERÍAS, CAMPUS LEÓN
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<< 2016. Año deñ nuevo sistema de justicia penal>>

León, Gto., 16 de mayo de 2016

Dr. Luis Arturo Ureña López

Coordinador de Posgrado en Física

División de Ciencias e Ingenierías

Campus León

Estimado Dr. Ureña:

Por medio de la presente le informo que he revisado el trabajo de tesis *"Diffusion Coupling in Associating Non-ideal Multi-Electrolyte Solutions"* del Maestro en Física **José Miguel Ramos Moreno.** Considero que el trabajo es relevante y se puede proceder a la defensa de tesis. Reciba un cordial saludo.

A T E N T A M E N T E

"LA VERDAD OS HARÁ LIBRES"

DR. FRANCISCO SASTRE CARMONA

Director del Depto. de Ingeniería Física

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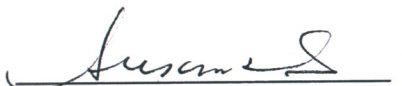
León, Gto., 25 de abril de 2016

Dr. Guillermo Mendoza Díaz
Director de la División de Ciencias e Ingenierías
Universidad de Guanajuato, Campus León
P R E S E N T E

Estimado Dr. Mendoza,

Por este conducto me permito comunicarle que, en relación a la tesis: **"Diffusion coupling in associating non-ideal multi-electrolyte solutions"**, que presenta el M. F. José Miguel Ramos Moreno para obtener el grado de Doctor en Física, he leído detenidamente el documento, retroalimentándolo con sugerencias, correcciones, y discutido su contenido con el estudiante.

Después de lo anterior expreso mi conformidad con su contenido considerando el documento del nivel requerido para un trabajo de doctorado, no teniendo inconveniente en que el mencionado trabajo sea defendido por el interesado cuando a él convenga.

Sin otro particular, aprovecho la presente para enviarle cordiales saludos.

Susana Figueroa Gerstenmaier
Profesora Titular

Universidad
de Guanajuato

León, Gto., Mayo 16, 2016

**DR. LUIS ARTURO UREÑA LÓPEZ
COORDINADOR DE POSGRADO
DIVISIÓN DE CIENCIAS E INGENIERÍAS**

Estimado Dr. Ureña:

Con la presente me permito hacer de su conocimiento que he revisado el trabajo titulado **"Diffusion Coupling in Associating Non-ideal Multi-Electrolyte Solutions"** que para obtener el Título de **Doctor en Física** pone a consideración el **M.F. José Miguel Ramos Moreno.**

Le comunico que en mi opinión el trabajo reúne las características de nivel y calidad necesarias para una tesis de doctorado. Asimismo he discutido con el Maestro Ramos algunos aspectos respecto a su trabajo y correcciones que he considerado pertinentes, las cuales se han incluido en la versión final del trabajo, no teniendo objeciones para la presentación del mismo de acuerdo a la reglamentación respectiva.

Sin otro en particular me despido

**ATENTAMENTE
"LA VERDAD OS HARÁ LIBRES"**

**Dr. Francisco Miguel Vargas Luna
Profesor Titular B**

C.c.p. Miguel Ramos
C.c.p. Archivo FMVL

Casa abierta al tiempo

UNIVERSIDAD AUTÓNOMA METROPOLITANA

Dr. Enrique Díaz Herrera

DIVISIÓN DE CIENCIAS BÁSICAS E INGENIERÍA
DEPARTAMENTO DE FÍSICA
AREA DE FÍSICA DE LÍQUIDOS

México, DF. 16 de mayo del 2016

Coordinación de Posgrado
División de Ciencias e Ingeniería, Campus León
Universidad de Guanajuato

Por medio de la presente, le informo que acepto el trabajo de tesis del estudiante José Miguel Ramos Moreno, con titulo Diffusion Coupling in Associating Non–ideal Multi-Electrolyte Solutions, para ser defendida.

Atentamente
Dr. Jesús Enrique Díaz Herrera

UNIDAD IZTAPALAPA
Av. San Rafael Atlixco No. 186, Col. Vicentina, Delegación Iztapalapa, C. P. 09340 México, D.F.
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León, Guanajuato, a 27 de abril de 2016

Dr. Guillermo Mendoza Díaz
Director
División de Ciencias e Ingenierías
PRESENTE

Estimado Dr. Mendoza Díaz:

Por medio de la presente le informo que he leído y revisado detalladamente el contenido de la tesis titulada *"Acoplamiento difusivo en soluciones electrolíticas no ideales"* desarrollada por el **M. en F. José Miguel Ramos Moreno** y dirigida por el Dr. José Torres Arenas y co-dirigida por el Dr. Jean Pierre Simonin.

La tesis está bien escrita y es auto-contenida. Esto favorece su fácil lectura y la comprensión de la misma. El principal resultado de la tesis doctoral del M. en F. Ramos es el desarrollo de un formalismo teórico que permite obtener la evolución temporal de la concentración de electrolitos. Este resultado, sin lugar a dudas, original es de suma importancia para entender, desde primeros principios, los procesos de transporte en soluciones electrolíticas.

Por dicho en el párrafo anterior, considero que la tesis reúne, y por mucho, los requisitos de calidad para ser defendida por el M. en F. Ramos, por lo que doy mi anuencia para formar parte del jurado de esta tesis, la cual puede defenderse en la fecha que sea más conveniente.

Atentamente,
"La Verdad Os Hará Libres"

Dr. Ramón Castañeda Priego
Profesor Titular C
Departamento de Ingeniería Física

DIVISIÓN DE CIENCIAS E INGENIERÍAS, CAMPUS LEÓN

León, Gto., a 16 de Mayo 2016

Dr. Susana Figueroa Gerstenmaier
Directora de la División de Ciencias e Ingenierías,
Campus León, Universidad de Guanajuato
PRESENTE

Por este medio, Comunico que he leído y revisado la tesis titulada **"Diffusion Coupling in**

Associating non-ideal Multi-Electrolyte Solutions" que presenta el M.F. José Miguel Ramos

Moreno, en esta División, para obtener el grado de Doctor en ciencias (Física). Considero que

el trabajo cumple con todos los requisitos de calidad que se exige para obtener el grado

mencionado. Por lo anterior, acepto en contenido, forma, y profundidad la mencionada tesis.

Atentamente,

Dr. David Delepine
Profesor Titular B
Departamento de Física, Campus León
Universidad de Guanajuato