Diffusion coupling in multiply associating electrolyte solutions

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ABSTRACT

Diffusion coupling in multiply associating aqueous electrolyte solution is studied. The process is illustrated in the case of zinc(II) ion which forms a set of complexes, $ZnCl_n^{2-n}$ (with $n = 1,...,4$), in the presence of chloride ions. The transport of zinc ion, taken in radioactive form $^{65}Zn^{2+}$, in the electric field created by a gradient of LiCl, is investigated experimentally by employing an adaptation of the closed capillary technique. The transient diffusion process is modeled by using two different treatments: finite difference (FD) simulation and normal-mode (NM) analytic solution. Deviations from ideality are taken into account with the use of the mean spherical approximation (MSA), and the internal electric field is calculated using the dynamical electroneutrality condition. The theoretical FD and NM results are compared with the experimental data about the diffusion of zinc.

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1. Introduction

Aqueous electrolytes are ubiquitous on earth. They may be found in natural waters (e.g., in oceans, lakes, sediments), in most living beings and in plants, trees,… They have a huge influence on the development and functioning of life on the planet. The motion of ionic species governs the local amount of ions. In this respect, aqueous electrolytes have the particular property that the movements of the ions in a medium are strongly coupled through the effect of electrostatic interactions [1,2].

Diffusion coupling thus can be observed in many natural and industrial domains and systems, such as in geochemistry (when studying diagenetic fluxes in sediments [3,4]), in biophysics (e.g. for a description of permeation through ionic channels of cells [5]), in engineering processes (e.g., when using membranes for industrial separations [6]), in materials science (e.g., in the study of diffusion of ions in concrete [7] or for the assessment of chemical aging of concrete and composite materials [8]).

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 [9]. Multicomponent diffusion has been examined in the framework of Onsager formalism of irreversible thermodynamics [10].

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

[4]. Ion pairing is important because it modifies the effective charge of the diffusing species and so changes their response to the internal electric field created by the diffusing ions. A clear example is that of a monovalent tracer ion that associates with a monovalent anion and forms a neutral species that is insensitive to the diffusion field [4].

Some time ago, we 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) [11]. Later we investigated the effect of a pH gradient on sulfate and phosphate ions [12]. In these works, the diffusion–reaction equations were solved by using two types of treatments: a 'normal-mode' analysis in which the equations are linearized and solved analytically [13]; and a classical numerical finite-difference method in which time and space are 'sliced' and the equations are solved incrementally in the 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 the ion pair $MgSO_4^0$ in the case of Mg^{2+} and SO_4^{2-} [11], or to the hydrogen sulfate ion HSO_4^- in the case of sulfate in the pH gradient.

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

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 [14], MINEQL+ [15], JCHESS [16], PHREEQC [17] and CHEAQS [18]. 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 $n = 1,2,3,\ldots$) 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 [19]) or in the NIST Database [20]. 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, softwares may give speciations that differ in magnitude. Because the speciation is generally very difficult to determine experimentally, there is uncertainty in the determination of speciation in electrolyte solutions.

In the present work, we propose to study transient diffusion patterns in the case of a metal cation giving rise to multiple association. The metal cation (in tracer amount) is placed in the electric field created by the diffusion of a major salt. This type of experiment is a variation on the theme of experiments we had carried out with magnesium(II) and sulfate ions [11,12]. The latter system gave one type of ion pair. In the present work we investigate the case of electrolytes leading to a set of complexes of increasing stoichiometries through a series of stepwise associations.

Moreover, in contrast with our earlier work about coupling diffusion, we now include the effect of deviations from ideality. Accounting for activity coefficients in the treatment has several consequences. It modifies the speciation of the metal cation under study, and therefore the diffusion rate of the various forms (free species and complexes). It also introduces a new driving force associated to the variation in space of the activity coefficients of the chemical species, and it modifies the magnitude of the internal diffusion electric field created by the major ions. The experimental observable is the result of these different effects.

In this work, we carried out experiments with the zinc(II) cation. This species has an important role in biological, geochemical and environmental media [22,23]. It is well known for giving rise to multiple association with various anions [19]. Here, we used zinc chloride, which can give 4 complexes: $ZnCl^+$, $ZnCl_2^0$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ [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 [24]. 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 difference (FD) and normal-mode (NM) methods. Deviations from ideality were included in the calculations by using the mean spherical approximation.

The main purpose of this paper is to investigate the validity of the modeling approach for the description of transient diffusion profiles for a multiply associating electrolyte. The theoretical descriptions include diffusion, ionic association and activity coefficients for all species. The maximum concentration of the major salt (LiCl) is sufficiently high to allow an appreciable influence of activity coefficients. However it is limited to 2 M in order to minimize the effect of hydrodynamic interactions and other subtle effects such as reference frame or ionic relaxation [25].

The remainder of this paper is organized as follows. The next section presents the experimental technique employed to probe the diffusion of the tracer in the cell, and the experimental conditions of this study. Then, a theoretical section exposes the basic equations governing the process and the methods used to calculate the observed effect. Next, the experimental data are compared with the results obtained from

the model in the Results and Discussion section. Finally a conclusion summarizes the main results of this work and presents some prospects.

2. Experimental

Diffusion experiments on an ion which is a pure β emitter can be conducted adequately by using a cell made of perspex and scintillating plastic [11,12]. On the other hand if the tracer is both a β and γ emitter then it is necessary to stop the β's so that only the γ emission can be analyzed (otherwise it would be impossible to distinguish the respective effects of the β and γ radiations in the scintillating plastic). In the present work, the commercially available radioactive isotope of the ion studied here, $^{65}Zn^{2+}$, is precisely a β and γ emitter.

In order to solve this difficulty, experiments were carried out by using an adaptation of the closed capillary technique [24]. It is depicted in Fig. 1. 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. The plastic cell was designed in such a way that the points A, B and C are on the same straight line [24]. The silica capillary (whose wall is ca. 1 mm thick) has the property of stopping the β^+ particles of 0.33 MeV energy emitted by $^{65}Zn^{2+}$. In this way, scintillation in the scintillating plastic is produced only by the γ radiation. In order to avoid capillarity problems at the mouth of the capillary, the latter 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 bore 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 (up to point O, see Fig. 1), of length L, was filled with a solution containing 1 M or 2 M LiCl + 10^{-2} M $ZnCl_2$ + radioactive zinc(II) in tracer amounts (of the order of 10^{-8} M). Then, the top part of the capillary, of the same length L, was filled very carefully
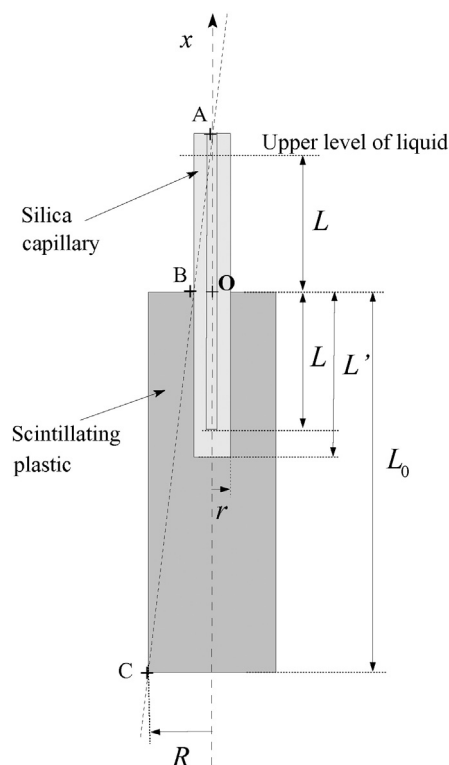

Fig. 1. Sketch of the diffusion cell. The points A, B and C are aligned.