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1 Study of salt free-diffusion by 1D transport numerical simulations and 2 shadowgraph experiments

3 C.O. Oko^a, A.T. Ndjaka^a, R. Minhas^a, A. Lassin^b, M. Azaroual^{b,c}, F.Croccolo^a, H. Bataller^{a*}

4 ^a Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, TotalEnergies, LFCR UMR5150,
5 Anglet, France

6 ^b BRGM, F-45060 Orléans, France

7 ^cISTO, UMR 7327, Univ. Orléans, CNRS, BRGM, OSUC, F-45071, Orléans, France

8 * Corresponding author: henri.bataller@univ-pau.fr

9 Abstract

10 Applying the Nernst-Planck formalism of 1D diffusive flux equations for ionic species of salts
11 dissolved in water, Pitzer formalism for activity coefficients and PHREEQC software for species
12 diffusion coefficients, with ionic strength-dependence coefficients optimized, we obtained
13 expressions for apparent diffusion coefficients of sodium chloride, calcium chloride, and sodium
14 sulphate, prevalent in deep aquifers. PHREEQC 1D transport simulations of free-diffusion
15 experiments yielded temporal evolution of the concentration and gradient verticals profiles. The
16 dynamics of concentrations non-equilibrium fluctuations during the free-diffusion experiments have
17 been recorded by shadowgraphy. Thanks to the calculated gradient profiles the thickness of the
18 sample has been integrated in the analysis equations of the structure functions. From the earliest
19 stages of the diffusion process we measured the diffusion coefficients for the three salts, in very
20 good agreement with reference measurements, validating the technique and method of analysis for
21 studying free-diffusion in reservoirs targeted for CO₂ and energy vectors storage.

22

23 Keywords

24 Salts, PHREEQC, concentration gradient profiles, shadowgraphy, free-diffusion, diffusion coefficients

25

26 1. Introduction

27 Mass diffusion is an important transport mechanism involved in various process, either natural or
28 industrial. In natural environments, the diffusion of contaminants to and from low-permeability
29 zones is a key issue for safety and remediation operations. In the case of underground nuclear waste
30 storage, diffusion is a key mechanism to help reducing the migration of radionuclides and toxic
31 chemicals around the geological repository (Delay et al., 2007). For CO₂ geological storage, diffusion
32 may play a significant role too: the injected CO₂ flows through the preferential flow-paths of high
33 hydraulic conductivity, in contact with the host rock matrix of lower permeability offering a large
34 volume for storing dissolved CO₂. Diffusion is then an important process in surrounding geological
35 levels especially in the low permeability parts as the non-conductive porosity and the cap rock. This
36 transport mechanism could be encountered in soils that are also characterized by variable chemical
37 and high concentration gradients and hydraulic heterogeneities due to the presence of roots,
38 microorganisms, interactions with the soil surface (Staunton, 2008). Industrial applications are also
39 concerned by diffusion processes for separation purposes like filtration, sieving, or selective
40 extraction operations.

41 In the particular case of CO₂ storage in deep saline aquifers, understanding Fickian mass diffusion of
42 electrolytic aqueous solutions requires a detailed description of the physicochemical and
43 electrochemical solute-solute and solute-water interactions with charged phase interfaces. The
44 concentration-driven mass transfer rate of salt mixtures is described by the specific diffusion
45 coefficients of the different species. Additionally, these coefficients depend on the thermodynamic
46 conditions (temperature, pressure, composition of the mixtures). Due to the conservation of the
47 neutrality of the electric charge, the species associate and the diffusive behavior resembles that of
48 molecules. As a result, the experimental measurements of the diffusion coefficients of salts provide
49 an effective or apparent value, equivalent to that of a neutral molecule. The link with the diffusion
50 coefficients of species, depending on thermodynamic conditions, is not trivial. This motivated us to
51 perform tentative original measurements of the diffusion coefficients of a limited number of salts in
52 order to get a better understanding of the link between apparent measurements and species
53 diffusion coefficients. The comparison between the two has been obtained by computing the species
54 diffusion coefficients by numerical simulations by means of the PHREEQ-C solver, on one side, and,
55 on the other side, by experimentally measuring the effective mass diffusion coefficients by means of
56 the optical technique of shadowgraphy.

57 PHREEQC is a geochemical software commonly used for speciation, batch-reaction, one-dimensional
58 transport, and inverse geochemical calculations (Appelo, 2017; Muniruzzaman and Rolle, 2019;
59 Parkhurst and Appelo, 2013). For the experiments we used dynamic shadowgraphy, a light scattering
60 technique in the near field which allows us to study the non-equilibrium density fluctuations during
61 free-diffusion experiments, thus measuring the mass diffusion coefficients of the salts, as done in a
62 number of previous studies (Bataller et al., 2016; Crococo et al., 2013, 2012; Giraudet et al., 2014;
63 Lizarraga et al., 2017, 2016; Ndjaka et al., 2022). In section 2, we provide the theoretical bases of the
64 diffusion of ionic species in a solution. We introduce PHREEQC and carry out free-diffusion
65 simulations of the main salts present in deep aquifers, sodium chloride *NaCl*, calcium chloride *CaCl₂*
66 and sodium sulfate *Na₂SO₄*. The values of the concentration profiles simulated before allow us to
67 develop an improved method for analyzing the shadowgraph data. In section 3 we describe the
68 experimental procedure. In section 4 we discuss the results. Finally, in section 5 we provide
69 concluding remarks and some perspectives.

70

71 2. Theoretical framework

72 2.1. Modelling of multicomponent ionic transport in water

73 In aqueous electrolyte systems, charge-induced ion-ion interactions lead to the electrostatic coupling
74 of ionic fluxes that results in a coordinated movement of charged species to maintain local charge
75 balance. The relevance of these Coulomb effects has been explored in details under diffusion-
76 dominated and macroscopic advection-dominated conservative and reactive transport conditions,
77 which led to the development of multicomponent diffusion theories and the concept of
78 multicomponent ionic dispersion (Appelo and Wersin, 2007; Muniruzzaman and Rolle, 2019).
79 Formulations of ionic diffusion are commonly based on the gradient of thermodynamic
80 electrochemical potential μ_i , rather than on the gradient of concentration (Appelo and Wersin,
81 2007):

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \phi \quad (1)$$

82 where μ_i^0 (*J/mol*) is the electrochemical potential at the standard state, R ($= 8.31446 \text{ J/mol/K}$) is
83 the ideal gas constant, T (*K*) is the absolute temperature, a_i (-) is the activity of specie i ($a_i =$
84 $\gamma_i c_i / c^0$ with γ_i (-), c_i (*mol/L*), and $c^0 = 1 \text{ mol/kg H}_2\text{O}$, being the activity coefficient,

85 concentration, and reference concentration, respectively), z_i (-) is the charge number, F (= 96485 C/mol) is Faraday's constant, and ϕ (V) is the electrical potential.

87 The diffusive flux (\vec{J}_i [mol/m²/s]) of a charged species i is derived from the electrochemical potential
88 spatial gradient (Muniruzzaman and Rolle, 2019):

$$\vec{J}_i = -\frac{u_i c_i}{|z_i|F} \vec{\nabla} \mu_i = -\frac{u_i RT}{|z_i|F} c_i \vec{\nabla} \ln a_i - \frac{u_i}{|z_i|} c_i z_i \vec{\nabla} \phi \quad (2)$$

89 where u_i (m²/s/V) is the mobility, which is related to the self-diffusion coefficient ($D_{aq,i}$ [m²/s]) of
90 species i by $D_{aq,i} = u_i RT / |z_i| F$. Eq. (2) represents the Nernst-Planck equation for the flux of a
91 charged species and can also be expressed as follows:

$$\vec{J}_i = -D_{aq,i} \left(\vec{\nabla} c_i + c_i \vec{\nabla} \ln \gamma_i + \frac{z_i F}{RT} c_i \vec{\nabla} \phi \right) \quad (3)$$

92 By considering the activity gradients as

$$c_i \vec{\nabla} \ln \gamma_i = c_i \frac{\partial \ln \gamma_i}{\partial c_i} \vec{\nabla} c_i = \frac{\partial \ln \gamma_i}{\partial \ln c_i} \vec{\nabla} c_i \quad (4)$$

93 The Nernst-Planck equation can be further rearranged to

$$\vec{J}_i = -D_{aq,i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \vec{\nabla} c_i - \frac{D_{aq,i} z_i F}{RT} c_i \vec{\nabla} \phi \quad (5)$$

94 The electrical potential gradient ($\vec{\nabla} \phi$) can be calculated using the Poisson equation. However, in the
95 absence of any external electric field, the null current condition ($\sum_{j=1}^N z_j \vec{J}_j = \vec{0}$) is valid and is
96 considered in continuum description of multicomponent ionic transport (Muniruzzaman and Rolle,
97 2019). Thus, $\vec{\nabla} \phi$ in Eq.(5) can be eliminated as an unknown by expressing this gradient term as
98 follows:

$$\vec{\nabla} \phi = -\frac{\sum_{j=1}^N \left[z_j D_{aq,j} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \vec{\nabla} c_j \right]}{\frac{F}{RT} \sum_{j=1}^N (z_j^2 D_{aq,j} c_j)} \quad (6)$$

99 Upon substituting Eq. (6), the flux equation can be recast in term of known parameters:

$$\vec{J}_i = -D_{aq,i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right) \vec{\nabla} c_i + \frac{D_{aq,i} z_i c_i}{\sum_{j=1}^N (z_j^2 D_{aq,j} c_j)} \sum_{j=1}^N \left[z_j D_{aq,j} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \vec{\nabla} c_j \right] \quad (7)$$

100 This equation can be rearranged in a more compact form:

$$\vec{J}_i = -\sum_{j=1}^N \left[D_{ij} \left(1 + \frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \vec{\nabla} c_j \right] \quad (8)$$

101 where D_{ij} are the interdiffusion species coefficients, which include both the pure diffusive and the
102 electromigration flux components (Eq. 3), defined as:

$$D_{ij} = \delta_{ij} D_{aq,i} - \frac{z_i z_j D_{aq,i} D_{aq,j} c_i}{\sum_{j=1}^N (z_j^2 D_{aq,j} c_j)} \quad (9)$$

103 with δ_{ij} the Kronecker delta function.

104 In the case of free diffusion of $NaCl$ in water, which is a symmetrical electrolyte, elementary
105 developments of Eq. (9) allow to find $D_{Na^+Na^+} = D_{Cl^-Na^+}$ and $D_{Na^+Cl^-} = D_{Cl^-Cl^-}$, which give
106 $\vec{J}_{Na^+} = \vec{J}_{Cl^-}$. Since the ionic species gradients are the same during $NaCl$ diffusion, both species
107 behave as a single molecule during the process.

108 Dissolution of the asymmetrical electrolyte Na_2SO_4 in water can be written $Na_2SO_4 \rightarrow 2Na^+ +$
109 SO_4^{2-} . So, Na^+ ion gradient is twice that of SO_4^{2-} . The application of Eq. (9) allows to find that
110 $D_{Na^+Na^+} = 2D_{SO_4^{2-}Na^+}$ and $D_{Na^+SO_4^{2-}} = 2D_{SO_4^{2-}SO_4^{2-}}$, which gives $\vec{J}_{Na^+} = 2\vec{J}_{SO_4^{2-}}$. Here again, during
111 the diffusion process in the simple binary system $Na_2SO_4 - H_2O$, the two ionic species will behave
112 as a single Na_2SO_4 molecule. Similar consideration would apply to the diffusion of $CaCl_2$.

113 2.2. PHREEQC software

114 PHREEQC is a geochemical software for speciation, batch-reaction, one-dimensional transport, and
115 inverse geochemical calculations (Appelo, 2017; Muniruzzaman and Rolle, 2019; Parkhurst and
116 Appelo, 2013). Based on the numerical resolution of the full Nernst-Planck equation, it allows to
117 include external electric fields effects, the medium porosity as well as temperature and
118 concentration dependencies on species diffusion coefficients. The latter are correction factors for
119 aqueous concentrations to account for the non-ideal behaviour of solutes in real solutions. PHREEQC
120 uses specific databases of thermodynamic and physicochemical properties of solutes, minerals and
121 gases. These databases include, in particular, information about the activity coefficient model used
122 consistently with the tabulated thermodynamic data of the chemical compounds. Thus, their domain
123 of validity is limited by that of the associated activity coefficient model. These databases were
124 established according to either ion-association equations (Davies, B-dot, Debye-Hückel (Debye and
125 Hückel, 1923), extended Debye-Hückel equations) or specific ion-interaction equations (Pitzer
126 equations (Pitzer, 2017)).

127 More specifically, the diffusion coefficient concentration-dependence is calculated with Kohlrausch's
128 law, according to the formulation proposed by Appelo (Appelo, 2017):

$$D_{aq,i} = D_{aq,T,i}^0 \exp\left(\frac{-a_{1i}A|z_i|\sqrt{I_s}}{1 + \kappa a}\right) \quad (10)$$

129 Where $D_{aq,T,i}^0$ is the diffusion coefficient at infinite dilution at temperature T , a_{1i} is a coefficient, A is
130 the Debye-Hückel parameter ($0.51 \text{ (mol/dm}^3\text{)}^{-0.5}$ at 25°C), I_s is the ionic strength and κa is

$$\kappa a = \kappa \sqrt{I_s} \frac{a_{2i}}{1 + I_s^{0.75}} \quad (11)$$

131 With a_{2i} a second coefficient and κ is the Debye length, defined by: $\kappa = \frac{1}{F} \sqrt{\frac{\epsilon_w RT}{2000 I_s}}$, where ϵ_w is the
132 dielectric permittivity of water ($6.94 \cdot 10^{10}$ F/m at 25°C). The diffusion coefficients are corrected for
133 temperature by a relation proposed by Smolyakov (Appelo, 2017):

$$D_{aq,T,i}^0 = D_{aq,298,i}^0 \frac{\eta_{298}^0 T}{\eta_T^0 298.15} \exp\left(\frac{d_i}{T} - \frac{d_i}{298.15}\right) \quad (12)$$

134 Where η_7^0 is viscosity of pure water (Pa.s) at temperature T and d_i is a coefficient. The exponential
 135 term dampens the temperature dependence of the diffusion coefficient, which is smaller than the
 136 variation of viscosity with temperature. Note that no physical meaning was given by the author to
 137 the $a_{1,i}$, $a_{2,i}$ and d_i coefficients.

138 The coefficients $a_{1,i}$, $a_{2,i}$ and d_i were optimized by Appelo to cover a wide range of applications
 139 (Appelo, 2017). The values for the species of interest in this work, with the $D_{aq,298,i}^0$, are given in the
 140 following table. They constitute the Appelo database of PHREEQC.

141 **Table 1: Appelo values (Appelo, 2017) for diffusion coefficients of selected species at 25°C and infinite**
 142 **dilution, as well as coefficients for calculating their temperature- and ionic strength-dependence. In**
 143 **parentheses, the values modified in the current work in order to best fit the experimental apparent diffusion**
 144 **coefficient literature data.**

Species	$D_{aq,298}^0$ ($10^{-9}m^2/s$)	d	a_1	a_2
Na^+	1.33	122	1.52 (0.09)	3.7 (1.55)
Ca^{2+}	0.793	97	3.4 (0.97)	24.6 (5.18)
Cl^-	2.03	194	1.6 (5.61)	6.9 (9.99)
SO_4^{2-}	1.07	34	2.08 (2.53)	13.4 (13.4)

145

146 2.3. Apparent diffusion coefficients

147 The diffusive behavior of salts in water, like the one of a molecule, allows us to derive the expression
 148 of an apparent diffusion coefficient. For $NaCl$, developments from Eq. (8) and (9) lead to:

$$D_a = \frac{D_{aq,Na^+}D_{aq,Cl^-}}{D_{aq,Na^+} + D_{aq,Cl^-}} \left(2 + \frac{\partial \ln \gamma_{Na^+}}{\partial \ln c_{Na^+}} + \frac{\partial \ln \gamma_{Cl^-}}{\partial \ln c_{Cl^-}} \right) \quad (13)$$

149 The mean activity coefficient of an electrolyte $C_{v^+}A_{v^-}$, where C is the cation, A is the anion and v^+
 150 and v^- are their respective stoichiometric coefficient, is defined by: $\gamma_{C_{v^+}A_{v^-}} = (\gamma_C^{v^+} \gamma_A^{v^-})^{1/(v^++v^-)}$.

151 In the case of $NaCl$, the mean activity coefficient is thus $2 \ln \gamma_{NaCl} = \ln \gamma_{Na^+} + \ln \gamma_{Cl^-}$, and we
 152 obtain:

$$D_a = \frac{2D_{aq,Na^+}D_{aq,Cl^-}}{D_{aq,Na^+} + D_{aq,Cl^-}} \left(1 + \frac{\partial \ln \gamma_{NaCl}}{\partial \ln c_{NaCl}} \right) \quad (14a)$$

153 In a similar way, the respective average diffusion coefficients for the asymmetric electrolytes Na_2SO_4
 154 and $CaCl_2$ are:

$$D_a = \frac{3D_{aq,Na^+}D_{aq,SO_4^{2-}}}{D_{aq,Na^+} + 2D_{aq,SO_4^{2-}}} \left(1 + \frac{\partial \ln \gamma_{Na_2SO_4}}{\partial \ln c_{Na_2SO_4}} \right) \quad (14b)$$

$$D_a = \frac{3D_{aq,Ca^{2+}}D_{aq,Cl^-}}{2D_{aq,Ca^{2+}} + D_{aq,Cl^-}} \left(1 + \frac{\partial \ln \gamma_{CaCl_2}}{\partial \ln c_{CaCl_2}} \right) \quad (14c)$$

155 With $3 \ln \gamma_{Na_2SO_4} = 2 \ln \gamma_{Na^+} + \ln \gamma_{SO_4^{2-}}$ and $3 \ln \gamma_{CaCl_2} = \ln \gamma_{Ca^{2+}} + 2 \ln \gamma_{Cl^-}$.

156 Note that when the derivative term of the activity coefficients is negligible, equations (14) reduce to
157 the Nernst equation in the case of homogeneous diffusion. From Eqs. (10) to (12) it is possible to
158 calculate the species diffusion coefficients at any concentration and temperature. Given the high
159 concentrations of solutes, up to $6 \text{ mol}\cdot\text{kg}^{-1}$, the activity coefficients are calculated according to the
160 Pitzer equations (Pitzer, 2017) associated with reliable sets of specific interaction parameters,
161 namely (Lach et al., 2017) for NaCl , (Lach et al., 2016) for Na_2SO_4 , and (Lassin and André, 2023) for
162 CaCl_2 . In Fig. 1 we report the apparent diffusion coefficient calculations and the measured values
163 from the literature for the three salts as a function of the concentration at 25°C and atmospheric
164 pressure.

165

166 **Figure 1: Calculated and literature values of the mass diffusion coefficients as a function of the concentration**
167 **at $T = 25^\circ\text{C}$ and atmospheric pressure of a) NaCl b) CaCl_2 and c) Na_2SO_4 electrolytes in water.**

168

169 For NaCl (Fig. 1a), the measurements of Vitagliano and Lyons date from the 1950s and were carried
170 out by Gouy interferometry (Hall et al., 1953; Lyons and Riley, 1954). The measurements of Rard and
171 Miller were made in the late 1970s by Rayleigh interferometry (Rard and Miller, 1979a). The
172 measurement of Guo et al. has been performed in the late 1990s by phase shifting interferometer
173 (Guo et al., 1999). These three series of measurements are in very good agreement and show a non-
174 ideal behaviour of the diffusion coefficient of NaCl in water as a function of concentration. More
175 recently, Torres et al. (Torres et al., 2012) and Nimdeo et al. (Nimdeo et al., 2014) have made
176 measurements that confirm the non-ideal behaviour, but disagree with the initial measurements,
177 mainly at higher concentrations. The dashed black line in Fig. 1a represents the calculations of the
178 apparent diffusion coefficient obtained by PHREEQC with the Appelo values of the ionic strength-
179 dependence coefficients. The obtained values describe well the steep decrease of the diffusion
180 coefficient at very low concentrations less than $0.1 \text{ mol}\cdot\text{L}^{-1}$, but not at medium and high
181 concentrations. They also do not describe the second extremum, even qualitatively. To improve the
182 fit between experimental data and calculated values, the coefficients a_{1,Na^+} , a_{2,Na^+} , a_{1,Cl^-} and
183 a_{2,Cl^-} have been optimized by minimizing the cost function based on the deviations between the
184 experimental and the calculated diffusion coefficients at every concentration. However, it was found
185 that the $a_{1,i}$ and $a_{2,i}$ coefficients influence the diffusion coefficient computed from the combination
186 of Eqs (10), (11) and (14a) mostly at high concentrations (above c.a. $1 \text{ mol}\cdot\text{L}^{-1}$). Therefore, in the
187 optimization process, the weight set to diffusion coefficient data was greater at the highest
188 concentrations than at lower concentrations. As a result, a set of $a_{1,i}$ and $a_{2,i}$ coefficients was
189 obtained (Table 1) that significantly improves the calculated diffusion coefficients of NaCl over the
190 whole range of concentration, and more specifically above the concentration of $2 \text{ mol}\cdot\text{L}^{-1}$. These
191 calculations are represented by the solid red line in Fig. 1a

192 For CaCl_2 , optical measurements of the mass diffusion coefficient (Fig. 1b) were made first by Gouy
193 interferometry (Hall et al., 1953; Lyons and Riley, 1954). They were confirmed by Rayleigh
194 interferometry in the late 1970s by Rard and Miller (Rard and Miller, 1979b). Again, the dashed black
195 line in Fig. 1b represents the apparent diffusion of CaCl_2 calculated using the a_1 and a_2 coefficients
196 for Ca^{2+} and Cl^- proposed by (Appelo, 2017). Clearly, the calculations based on these values rapidly
197 deviate dramatically from the experimental data, above $0.5 \text{ mol}\cdot\text{kg}^{-1}$, which made it necessary
198 optimizing new $a_{1,\text{Ca}^{2+}}$ and $a_{2,\text{Ca}^{2+}}$ coefficients while keeping the a_{1,Cl^-} and a_{2,Cl^-} coefficient
199 previously optimized, for consistency. The same optimization procedure as described above was
200 applied. The results are represented by the red full line in Fig. 1b, illustrating the improvement

201 obtained. Note that experimental data above $4 \text{ mol}\cdot\text{kg}^{-1}$ of CaCl_2 where not considered because of
202 the appearance of the CaCl^+ aqueous species (Lassin and André, 2023), what makes Eq. (14c)
203 inapplicable above this concentration.

204 The Na_2SO_4 diffusion coefficient was measured by Rayleigh interferometry (Rard and Miller, 1979c)
205 in the entire concentration range (Fig. 1c). More recent measurements at high (Annunziata et al.,
206 2000; Fu et al., 2001) and low concentrations (Rard, 2021) have confirmed the first measurements.
207 The most recent measurements have benefited from computerized image acquisition and processing
208 means. As above, the dashed black line in Fig. 1c represents the apparent diffusion of
209 Na_2SO_4 calculated using the a_1 and a_2 coefficients for Na^+ and SO_4^{2-} proposed by (Appelo, 2017).
210 The decreasing trend of the apparent diffusion coefficient is correctly described, but the match with
211 experimental data could be improved by optimizing the a_1 and a_2 coefficients for SO_4^{2-} , while
212 keeping fixed the values of the a_1 and a_2 coefficients for Na^+ obtained for NaCl . The red full line in
213 Fig. 1c represents the results of this new optimization.

214 In summary, the theoretical framework developed by (Appelo, 2017) for considering
215 multicomponent diffusion in water, and that is implemented in the PHREEQC geochemical software,
216 can help describing aqueous electrolyte diffusion measurements in concentrated simple brines, up to
217 several $\text{mol}\cdot\text{kg}^{-1}$. However, Appelo (Appelo, 2017) optimized the initial values of the coefficients that
218 describe the ionic strength-dependence of the species self-diffusion coefficient on an aqueous
219 solutions specific conductance database. These values had to be corrected in the present work to
220 reproduce the apparent diffusion coefficients reference experimental data. They are given in Table 1.
221 In summary, the values were decreased for cations and increased for anions, compared to the values
222 proposed by Appelo. However, our optimized values do not degrade significantly the description of
223 the specific conductance, as shown in the appendix. Besides, when aqueous complexation reactions
224 occur, interpreting the diffusion processes based on a single apparent diffusion coefficient may not
225 be relevant anymore since it is necessary to integrate explicitly the additional charged species
226 (aqueous complex).

227

228 2.4. Numerical simulations

229 A typical free-diffusion experiment consists in the superposition of two horizontal layers of two
230 different and miscible mixtures stable in the gravity field (Fig. 2). Here, we focus on the free-diffusion
231 of two mixtures of the same salt solution, but at two different concentrations (Fig. 2). The two
232 superimposed layers are thus ideally separated by an initially sharp, horizontal interface. As soon as
233 the fluids are put in contact, a diffusive flow begins to transport mass across the interface so that the
234 concentration close to the boundary begins to change. As time goes by, the thickness of the
235 dissolving region grows diffusively. For experiments performed in the gravity field, the densest layer
236 is usually placed at the bottom of the diffusion cell in order to avoid any initial convective instability.
237 Mass flux can be considered unidirectional in the vertical direction (z).

238

239

Figure 2: Schematic diagram of a free-diffusion experiment

240

241 For binary mixtures (a solute or molecule in a solvent) the free-diffusion process is well understood,
242 nowadays (Vailati and Giglio, 1998). The concentration at the top ($z = h$) and the bottom ($z = 0$) of
243 the sample is assumed to remain constant for a long time (Dirichlet condition). This assumption is
244 true in the case of unbounded diffusion, where two infinitely thick layers of binary fluids are allowed

245 to diffuse into each other. In practice the assumption is valid only during a given time interval after
 246 the beginning of the diffusion process. This time is called characteristic diffusive time τ_d and depends
 247 on the vertical size of the vessel and on the value of the mixture mass diffusion coefficient. As soon
 248 as the concentration at the boundaries begins to change, the features of the macroscopic diffusion
 249 process cease to depend on the diffusion coefficient only, and are influenced by the height of the
 250 vessel, too.

251 To obtain quantitative information about the concentration profile $c(z, t)$ of the solute and the
 252 gradient $\partial c/\partial z(z, t)$ we need to formalise the problem using the one-dimensional continuity
 253 equation for concentration since, due to the symmetry of the problem, $\partial/\partial x = 0$ and $\partial/\partial y = 0$:

$$\frac{\partial c}{\partial t} = -\frac{\partial J_z}{\partial z} \quad (15)$$

254 In a 1D transport simulation with PHREEQC, the percolation column is discretized in a number of
 255 cells, which are considered at each time step as perfect homogeneous batch reactors. With such a
 256 principle, each cell is considered as a closed system, so that the mass is conserved, the aqueous
 257 solutions are electrically neutral and the chemical reactions and the solutions are systematically at
 258 thermodynamic equilibrium. These assumptions are considered for applying the mass action law and
 259 calculate the activity-concentration relationship over space and time for all chemical species involved
 260 in a specified cell (in PHREEQC the resolution is done by considering each independent species and
 261 their mutual influence). Then flow and transport of species are performed by transferring part of the
 262 aqueous solution of one cell to the next according to mixing factors that are defined by the flow
 263 and/or the diffusion rates of the system.

264 To solve the transport process through mesh cells, the initial and boundary conditions must be
 265 defined. In our case studies sketched in Fig. 2, initial concentrations are defined by a vertical step
 266 function:

$$c(z, t_0) = \begin{cases} c_{bottom} & z \in (0, a) \\ c_{top} & z \in (a, h) \end{cases} \quad (16)$$

267 where $t_0 = 0$ is the initial time, a is the vertical position of the initial boundary between the two
 268 layers and h is the total thickness of the two superimposed layers (Fig. 2). To match our experimental
 269 setup (see section 3) we took $a = h/2$ and $h = 10 \text{ mm}$. The liquid column, composed of the two
 270 layers, was divided into 100 cells, the thickness of each being therefore $\Delta z = 0.1 \text{ mm}$. The time step
 271 between two elementary calculation loops has been fixed to $\delta t = \Delta z^2/3D_a$ with D_a calculated at
 272 infinite dilution. To complete the equation setting, the boundary conditions must be specified. In our
 273 experimental setup, the walls of the vessel are impermeable to mass, which results in the condition:

$$\frac{\partial c}{\partial z} = 0 \Big|_{z=0, z=h} \quad (17)$$

274

275 The characteristic diffusive times were estimated with the formula $\tau_d = a^2/D_a$, which gives an
 276 estimation of the time to diffuse through half of the column taking D_a equal to the literature value at
 277 the mean concentration of the experiment. The maximum time for a simulation has been fixed to
 278 $\tau_{max} = 4\tau_d$, which gives an estimation of the time to diffuse through the entire column. The number
 279 of calculated time steps is thus set to $N = \tau_{max}/\delta t$. In Table 2 we report the configurations that we

280 have studied in this work, both experimentally and numerically. c is the mean of the molar
 281 concentration of the salt of the two layers, which corresponds to the equilibrium concentration at
 282 the end of the diffusion process. Δc is the difference of the molar concentration of the two initial
 283 layers. The temperature of the isothermal column was set at $T = 25^\circ\text{C}$. Experiments (see section 3)
 284 and simulations were performed at atmospheric pressure.

285

286 **Table 2: Average molar concentration c and molar concentration difference Δc between the two layers for**
 287 **the free-diffusion experiments and simulations reported in this work. τ_d is the characteristic diffusive time**
 288 **over the cell height and N is the number of PHREEQC simulation time steps.**

Experiment/simulation	Salt	c (mol/L)	Δc (mol/L)	τ_d (mn)	N
1	<i>NaCl</i>	2.700	2.000	269	31197
2	<i>CaCl₂</i>	0.460	0.800	364	35023
3	<i>Na₂SO₄</i>	0.500	0.700	523	46392
4		1.000	0.700	645	57119
5		1.484	0.700	727	64458

289

290 In Fig. 3 we show the time evolution of the simulated concentration profiles plotted as a function of
 291 the vertical position in the cell for the experiment #1. For experiments #2 and 4 the results obtained
 292 are given in Fig. B of the appendix.

293

294 **Figure 3: Simulations of the concentration profiles as a function of the vertical position and for different**
 295 **times for experiment #1 (NaCl, $c = 2.7$ mol/L, $\Delta c = 2.0$ mol/L). The concentration of the anions (cations)**
 296 **calculated by PHREEQC is represented with symbols (triangles: anions, circles: cations). Selected times**
 297 **correspond to fractions of the characteristic diffusive time τ_d as indicated in the legends.**

298

299 For the three salts, we can see in Figs. 3, Ba and Bb that the anions (triangles) evolve as fast as the
 300 cations (circles). This result had already been anticipated at the end of paragraph 2.1. and we
 301 retrieve the fact that the diffusive behavior of salts is equivalent to that of a neutral molecular
 302 species with an apparent diffusion coefficient given by Eq. (14). Knowing the vertical concentration
 303 profile as a function of time allows us to calculate the value of the concentration gradient at any
 304 point along the fluid column at any time. As we will see later, the value of the concentration gradient
 305 represents a fundamental quantity for the analysis of experimental data.

306 2.5. Concentration non-equilibrium fluctuations

307 In a binary mixture at equilibrium, there are spontaneous local temperature fluctuations δT and
 308 concentration fluctuations δc that represent small perturbations of the macroscopic spatial
 309 distribution of the temperature and concentration macroscopic fields. If the equilibrium state is
 310 perturbed by applying e.g. a concentration gradient, the fluctuations intensity will be modified
 311 significantly. These non-equilibrium fluctuations (NEFs) are orders of magnitude more intense than
 312 those occurring at equilibrium and they have been described theoretically and observed
 313 experimentally (Brogioli and Vailati, 2000; Croccolo et al., 2016; Vailati and Giglio, 1998). Such
 314 concentration NEFs (c-NEFs) originate from stochastic fluctuations in the velocity field that delocalise
 315 fluid volumes into layers of different concentration. The intensity enhancement is then induced by
 316 the coupling between the velocity fluctuations and the existing concentration gradient. The c-NEFs
 317 can provide an interpretation of the mass flow associated with the mass diffusion process (Brogioli
 318 and Vailati, 2017). It has been observed experimentally and predicted theoretically that gravity

319 strongly influences NEFs, damping them beyond a certain characteristic scale (Croccolo et al., 2006a;
 320 Vailati and Giglio, 1997). For even larger spatial scales other phenomena can be observed by the
 321 analysis of NEFS, like confinement effects and coupling between different modes (Croccolo et al.,
 322 2019b; García-Fernández et al., 2019; Ortiz de Zárate et al., 2020) generating propagating oscillations
 323 in the system at the Brunt–Väisälä frequency (Carpineti et al., 2021).

324 c-NEFs during the free-diffusion process have been extensively studied in the literature (Castellini et
 325 al., 2023; Croccolo et al., 2019a, 2007, 2006a, 2006b; Ndjaka et al., 2022), where it is common to use
 326 the dynamic structure factor $\tilde{S}(\vec{q}, t, \Delta t)$ to obtain valuable information about the statistical
 327 properties of δc :
 328

$$\tilde{S}(\vec{q}, t, \Delta t) = \langle \delta c(\vec{q}, t) \cdot \delta c(\vec{q}, t + \Delta t)^* \rangle \quad (18)$$

329 where \vec{q} is the 2D-spatial wave vector. We identify two different times scales Δt and t , the first is the
 330 fast one in which the c-NEFs take place, while the second is the slow one in which the evolution of
 331 the macroscopic state takes place, i.e. the time scale of the free-diffusion process. The brackets
 332 indicate the correlation operation.

333 Following first an original work (Vailati and Giglio, 1998), we assume having an infinitesimal layer of a
 334 solute in a solvent characterised by a concentration c which defines a diffusion coefficient $D(c)$ and
 335 a kinematic viscosity $\nu(c)$. In the approximations of small stabilizing concentration gradient $\vec{\nabla}c$ and
 336 $D(c)/\nu(c) \ll 1$, fluctuating hydrodynamics approach allows to find the following expression for the
 337 static structure factor (Croccolo et al., 2016; Ortiz de Zárate and Sengers, 2006; Vailati and Giglio,
 338 1998):

$$\tilde{S}(q, t) = S_{eq} \left[1 + \left(\frac{\vec{\nabla}c}{\vec{\nabla}c_{grav}} - 1 \right) \frac{1}{1 + \left(\frac{q}{q_{ro}} \right)^4} \right] \quad (19a)$$

339 where q is the radial component of the wave vector, q_{ro} is the characteristic spatial scale above
 340 which the effect of gravity on fluctuations becomes significant and is defined as:

$$q_{ro} = \left(\frac{\beta \vec{g} \cdot \vec{\nabla}c}{\nu(c)D(c)} \right)^{1/4} \quad (20)$$

341 $\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial c}$ is the expansion coefficient due to solute (ρ is the density, kg/m³), \vec{g} is the gravitational
 342 acceleration (9.81 m/s²). In Eq. (19), $\vec{\nabla}c_{grav} = \beta \vec{g} \left(\frac{\partial c}{\partial \mu} \right)_{p,T}$ is the equilibrium concentration gradient
 343 induced by barodiffusion, with $\left(\frac{\partial \mu}{\partial c} \right)_{p,T}$ the osmotic compressibility. $S_{eq} = \frac{k_b T}{16\pi^4 \rho} \left(\frac{\partial c}{\partial \mu} \right)_{p,T}$ is the static
 344 structure factor of the equilibrium fluctuations, in which T is the sample temperature and k_b the
 345 Boltzmann constant.

346 In most cases, $\nabla c_{grav} \ll \nabla c$ allowing to obtain a simplified expression for the static structure factor:

$$\tilde{S}(q, t) \approx S_{eq} \frac{\nabla c}{\nabla c_{grav}} \cdot \frac{1}{1 + \left(\frac{q}{q_{ro}} \right)^4} \quad (19b)$$

347 Dynamic and static structure factors are related by (Vailati and Giglio, 1998):

$$\tilde{S}(q, t, \Delta t) = \tilde{S}(q, t) \cdot \tilde{g}(q, t, \Delta t) \quad (21)$$

348 where $\tilde{g}(q, t, \Delta t)$ is the normalized correlation function describing the time evolution of the
 349 fluctuations. If we assume a diffusive behaviour for the fluctuations, in the case of a thin layer with a
 350 small stabilizing concentration gradient, the normalized correlation function can be written as a
 351 single exponential decay (Crocco et al., 2016; Segrè et al., 1993):

$$\tilde{g}(q, t, \Delta t) = e^{-\xi(q, t)\Delta t} \quad (22)$$

352 where $\xi(q, t) = \frac{1}{\tau(q, t)}$ is the reciprocal of the decay time of the c-NEFs. In the absence of propagating
 353 modes, the decay time of NEFs varies as a function of q according to a well-known scaling law
 354 (Crocco et al., 2007; Segrè et al., 1993; Segrè and Sengers, 1993) in which both the influence of
 355 mass diffusion (dominant at high q) and gravity (dominant at low q) appear, due to their impact on
 356 the fluctuations:

$$\xi(q, t) = D_a(c)q^2 \left[1 + \left(\frac{q_{ro}}{q} \right)^4 \right] \quad (23)$$

357 2.6. Dynamic Shadowgraphy

358 Light scattering methods allow to measure transport coefficients in fluid mixtures, thanks to their
 359 ability to analyse density fluctuations when a sample is irradiated (Berne and Pecora, 1976). The
 360 optical technique used in this work is Dynamic Shadowgraphy (Ndjaka et al., 2022), based on the
 361 analysis of differences between successive shadowgraph images to probe the system dynamics. The
 362 obtained result (more details will be given later) is the images structure function (SF) given by:

$$SF(q, t, \Delta t) = 2\{\tilde{T}(q)\tilde{S}(q, t)[1 - \tilde{g}(q, t, \Delta t)] + B(q, t, \Delta t)\} \quad (24)$$

363 where $B(q, \Delta t)$ is the image background, $\tilde{S}(q, t)$ is the static structure factor and $\tilde{g}(q, \Delta t)$ is the
 364 normalized correlation function, all having already been discussed in the previous section. The term
 365 $\tilde{T}(q)$ is the optical transfer function of the shadowgraph. We assume that $\tilde{T}(q)$ and $\tilde{S}(q, t)$ can be
 366 considered simultaneously as a single property, $A(q, t) = \tilde{T}(q)\tilde{S}(q, t)$, called the amplitude term.
 367 Thus, the expression for the structure function becomes:

$$SF(q, t, \Delta t) = 2\{A(q, t)[1 - \tilde{g}(q, t, \Delta t)] + B(q, t, \Delta t)\} \quad (25a)$$

368 Background term includes different contributions like electronic noise due to the camera and all the
 369 acquisition chain. For transient processes, it is customary to introduce a quadratic dependence as a
 370 function of the correlation time. This term is actually related to the imperfect planarity of the
 371 experimental cell, as recently reported (Castellini et al., 2024). Even if our cell is checked for planarity
 372 before each experiment, small misalignments can produce this drift effect.

373 The corresponding classical structure function for a simple exponential decay is then:

$$SF(q, t, \Delta t) \approx 2\{A(q, t)[1 - e^{-\xi(q, t)\Delta t}] + C(q, t) + E(q, t) \cdot \Delta t^2\} \quad (25b)$$

374 2.7. Thickness effect

375 During a Shadowgraph measurement, the signal is actually the superposition of signals coming from
 376 all the layers crossed by the detecting light beam through the fluid sample. The sample thickness can
 377 be in some cases not negligible, like it is the case in this work ($h = 10mm$). Following recent
 378 developments (Castellini et al., 2023; Zapf et al., 2022), the structure factor is therefore the integral
 379 of the structure factor of the infinitesimal layers (Eq. 21) over the entire thickness of the sample:

$$S(q, t, \Delta t) = \frac{1}{h} \int_0^h \tilde{S}(q, t) \cdot \tilde{g}(q, t, \Delta t) \cdot dz \quad (26)$$

380 Then, we introduce the distribution of reciprocal decay times $G(\xi, q, t)$, so that one can write:

$$g(q, t, \Delta t) = \int_{\xi_m}^{\xi_M} G(\xi, q, t) \cdot e^{-\xi(q,t)\Delta t} \cdot d\xi \quad (27)$$

381 where ξ_m et ξ_M correspond to the minimum and maximum values of the inverse decay times,
 382 respectively. Therefore, the structure function can be written as:

$$S(q, t, \Delta t) = S(q, t) \cdot g(q, t, \Delta t) \quad (28)$$

383 The problem is then shifted to the description of the distribution function $G(\xi, t, q)$. Different
 384 approaches have been proposed in the literature (Castellini et al., 2023). Here we propose a different
 385 strategy considering the following points:

- 386 1- With the concentration profile $c(t, z)$ obtained by the PHREEQC simulations described in the
 387 previous section, one can compute the concentration gradient profile within the sample
 388 $\vec{\nabla}c(t, z)$.
- 389 2- By means of Eq. 20, one can compute the roll-off wave number $q_{ro}(t, z)$, therefore also the
 390 inverse decay time $\xi(q, t, z)$ through Eq. 23.
- 391 3- By means of Eq. 19b, one can then compute the static structure factor $\tilde{S}(q, t, z)$ in any layer
 392 of the sample cell.
- 393 4- With the precedent results, one can then obtain the average static structure factor of the
 394 sample:

$$S(q, t) = \frac{1}{h} \int_0^h \tilde{S}(q, t) \cdot dz \quad (29)$$

- 395 5- By means of Eq. 22, one can compute the correlation function $\tilde{g}(q, t, \Delta t, z)$ at any layer of
 396 the sample cell.
- 397 6- By means of Eq. 26, one can compute the overall dynamic structure factor $S(q, t, \Delta t)$.
- 398 7- By means of Eq. 28, one can compute the overall correlation function $g(q, t, \Delta t)$.
- 399 8- After Eq. 27, the distribution of reciprocal decay times can be calculated by inverse Laplacian
 400 transform (ILT) of the overall correlation function $g(q, t, \Delta t)$. This can be achieved, for
 401 example, by means of CONTIN analysis (Liénard et al., 2022; Scotti et al., 2015).

402 In Fig. 4 we report the results for $g(q, t, \Delta t)$ in log-lin scale and the corresponding $G(\xi, q, t)$ in lin-log
 403 scale for the experiment #1.

a) b)
c) d)

404 **Figure 4: a) and c) Correlation functions of the c-NEFs $g(q, t, \Delta t)$ as a function of the correlation time Δt at**
 405 **different times t during the free-diffusion process for experiment #1 (NaCl, $c = 2.7 \text{ mol/L}$, $\Delta c =$**
 406 **2.0 mol/L): a) $q = 100 \text{ cm}^{-1}$ and c) $q = 400 \text{ cm}^{-1}$. b) and d) Corresponding distributions of the reciprocal**
 407 **decay times $G(\xi, q, t)$ as a function of the inverse relaxation time ξ . The solid red curves correspond to a**
 408 **Gaussian adjustment to the distributions.**

409

410 In Fig. 4a we report the correlation functions $g(q, t, \Delta t)$ as a function of the correlation time Δt at
 411 different times t during the free-diffusion process for wave vector $q = 100 \text{ cm}^{-1}$ and in in Fig. 4c for
 412 $q = 400 \text{ cm}^{-1}$. In Fig. 4b and 4d we report the corresponding distributions of the inverse decay
 413 times $G(\xi, q, t)$ after performing a CONTIN decomposition of the correlation functions.

414 In order to characterize the width of the distributions we performed Gaussian fits, as indicated by
 415 solid red lines in Fig. 4b and 4d, corresponding to the classical equation:

$$G(\xi) = ae^{-\frac{(\xi - \bar{\xi})^2}{2\sigma^2}} \quad (30)$$

416 with $\bar{\xi}$ the mean value of the distribution and σ its standard deviation. We introduce here a
 417 polydispersity index defined as $p = \sigma/\bar{\xi} \times 100\%$. In Fig. 5 we report the obtained values as a
 418 function of the reduced time t/τ_d for different wave numbers.

419

420 **Figure 5: Polydispersity index of the c-NEFs inverse decay times distributions as a function of the reduced**
 421 **time t for experiment #1 (NaCl, $c = 2.7 \text{ mol/L}$, $\Delta c = 2.0 \text{ mol/L}$) for wave numbers indicated in the**
 422 **legend.**

423

424 As can be seen from Fig. 4, the distribution of the inverse decay times has a Gaussian shape, i.e. it is
 425 spread around an average value $\bar{\xi}$ with a certain variance σ . For large wave numbers $q > 200 \text{ cm}^{-1}$,
 426 the average value does not change with the macroscopic evolution of the free-diffusion process, as
 427 the decay times in the diffusive regime are always determined by the $1/(D_a q^2)$ dependence and the
 428 mass diffusion coefficient does not vary along the process. The dispersion due to the concentration
 429 profile is a simple Gaussian with a constant dispersion of about 15% for sample #1. For smaller wave
 430 numbers $q < 200 \text{ cm}^{-1}$, the average value $\bar{\xi}$ changes along with the evolution of the free-diffusion
 431 process. In fact, the effect of gravity on fluctuations depends on the intensity of the concentration
 432 gradient that slowly decreases with time. The variation of the fluid properties is more important at
 433 small times and it affects more the smaller wave numbers because they correspond to larger spatial
 434 scales that are, consequently, more influenced by macroscopic variations within the sample. As
 435 visible in Fig. 4a, the departure from exponential behaviour is visible only for small times and for
 436 small wave number, similar to what previously reported in (Croccolo et al., 2007) where a more
 437 important density gradient was present in the fluid under investigation. This is visible also in Fig. 5,
 438 where the dispersion at larger wave number decreases significantly with time, while it is almost
 439 constant at small wave number.

440 When the polydispersity index of the distribution of the reciprocal decay times is small ($p < 20\%$),
 441 the cumulant method allows to develop the expression of the correlation function around the
 442 average value (Friskén, 2001; Liénard et al., 2022):

$$443 \quad g(q, t, \Delta t) \approx e^{-\bar{\xi}(q)\Delta t} \left[1 + \frac{\sigma^2}{2} \Delta t^2 \right]$$

444 A simple replacement in Eq. 25a or 25b yields the following SF expression, assumed to be valid for a
 445 free-diffusion process in thick samples with limited polydispersity:

$$SF(q, t, \Delta t) \approx 2 \left\{ A(q, t) \left[1 - e^{-\bar{\xi}(q,t)\Delta t} \left[1 + \frac{\sigma^2}{2} \Delta t^2 \right] \right] + C(q, t) + E(q, t) \cdot \Delta t^2 \right\} \quad (31)$$

446 For small wave numbers this approximation is not valid (Fig. 5). For intermediate wave numbers is
 447 only valid for times larger than 50% of the characteristic diffusive time τ_d . For large wave numbers it
 448 can be assumed valid at any time.

449

450 3. Experimental procedure

451 3.1. Materials and solution preparation

452 NaCl (Sigma-Aldrich, 746398-500G, anhydrous, ACS reagent, purity 99%), CaCl₂ (Labkem, Cach-AOP-
 453 1k0, anhydrous, purity $\geq 94\%$) and Na₂SO₄ (Sigma-Aldrich, 239313-500G, anhydrous, ACS reagent,
 454 purity 99%) were used without further purification. De-ionized water (with resistivity of about
 455 18.5 $M\Omega\text{ cm}$) retrieved from a Millipore Milli-Q filtration station, was degassed and used to prepare
 456 a volume of 100 mL for every saline solution to the required concentration in $\text{mol}\cdot\text{L}^{-1}$. The salt
 457 masses required to prepare the solutions were weighted using an analytical balance (Sartorius
 458 TE313S, with resolution of $10^{-2} \text{ g}/200 \text{ g}$).

459 3.2. Set-up

460 To determine the diffusion coefficient of a binary mixture, two layers of the same mixture but at
 461 different concentrations must be superimposed in a cell, with the denser one at the cell bottom. In
 462 this work we used a cell developed for the study of free-diffusion of a molecular binary mixture
 463 (Ndjaka et al., 2022). The experimental details and the procedure for analysing the c-NEFs to obtain
 464 the mass diffusion coefficient are similar to those used in our previous study. For a brief reminder of
 465 the filling procedure of the cell and of the experimental procedure, the diffusion cell is first filled with
 466 the less dense solution and subsequently, the denser solution is introduced from the bottom of the
 467 cell and, at the same time, the less dense solution is introduced from the top until both of them fill
 468 half of the cell. At this time, the valves are closed and the free-diffusion process starts. The difference
 469 of concentration Δc between the bottom and the top layers is an important parameter of the
 470 experiments. The experimental shadowgraph setup used in the present work operates on exactly the
 471 same principle as described in (Ndjaka et al., 2022). The only difference is in the camera sensor used,
 472 a CCD Allied Vision Technologies camera (PIKE-F421B), whose detection plane is positioned at a
 473 distance of $z = (10.0 \pm 0.5) \text{ cm}$ from the sample central plane. The camera attributes were adjusted
 474 with National Instruments Measurement & Automation Explorer acquisition software NI-MAX. This
 475 camera allows acquiring a series of raw images at a constant framerate by means of a custom
 476 'LabView' software. The camera is capable of acquiring images at a maximum frame rate of 15 Hz at
 477 full frame resolution of 2048×2048 square pixels with a pixel side of $l_{pix} = 7.32 \mu\text{m}$. Like in our
 478 precedent study, series of $N = 2500$ images of $1024 \times 1024 \text{ pix}^2$ have been recorded at frequency

479 $f = 7.8 \text{ Hz}$, every 5 minutes (after closing the valves) over the first 20 minutes of each experiment,
480 and then every 10 minutes until the equilibrium state.

481 3.3. Image processing

482 The images acquired in the near field consist of an intensity map $I(\vec{x}, t)$, generated by the
483 interference on the camera plane between the portion of the incident beam that has passed
484 undisturbed through the sample and the beams scattered by the refractive index fluctuations
485 occurring within the sample. Here, \vec{x} and t stand for the position in the image plane and the time
486 lapsed during the acquisition, respectively. Thanks to the interference of different beams, the
487 fluctuations in the fluid density, that are proportional to the fluctuations of the fluid refractive index,
488 are transformed into fluctuations of the light intensity at the detector plane. Therefore, in order to
489 study the dynamics of the density fluctuations in our samples, we calculate the SF of the light
490 intensity, i.e. of the acquired images, by means of an already proven Differential Dynamic Algorithm
491 (DDA) (Cerchiarì et al., 2012; Norouziadeh et al., 2021). The DDA algorithm consists of the following
492 main steps: first, each recorded image $I(\vec{x}, t)$ is Fourier transformed in the 2D spatial space of the
493 detector plane to obtain $I(\vec{q}, t) = \mathcal{F}(I(\vec{x}, t))$, then the Fourier transform (FT) is normalized by
494 dividing it by the zero spatial frequency $i(\vec{q}, t) = I(\vec{q}, t)/I(\vec{0}, t)$ in order to remove the source
495 intensity fluctuations. Then, the differences between normalized FTs at a given time difference Δt
496 (the correlation time) $\Delta i(\vec{q}, t, \Delta t) = i(\vec{q}, t) - i(\vec{q}, t + \Delta t)$ are calculated. These Δt 's are, of course,
497 multiples of the time delay dt_{min} of the recording process, and cannot be larger than the acquisition
498 duration. Finally, the 2D correlation functions are calculated by determining the square moduli
499 $|\Delta i(\vec{q}, t, \Delta t)|^2$ of the FT differences, and the individual spatial Fourier transforms of the image
500 differences are averaged, first over all times t and second over the modulus of the wave vector \vec{q} .
501 The result $\langle |\Delta i(q, \Delta t)|^2 \rangle_{q,t}$ is the SF of the recorded intensity fluctuations. In order to reduce the
502 computational time to calculate the structure function out of the image series, we make use of a
503 graphic card taking advantage of the massive parallelization on the Graphic Processing Unit (GPU)
504 and in-house developed software (Cerchiarì et al., 2012; Norouziadeh et al., 2021).

505 Examples of SF obtained 30 minutes after closing the valves in experiment #1 are shown in Fig. 6a, as
506 a function of q for different Δt , and in Fig. 6b as a function of Δt for different q .

507

508 Figure 6: Structure function a) as a function of the wave number q for different correlation times Δt and b) as a
509 function of the correlation time for different wave numbers for experiment #1 (NaCl, $c = 2.7 \text{ mol/L}$, $\Delta c =$
510 2.0 mol/L) 30 minutes after closing the valves.

511

512 The oscillatory behaviour shown in Fig. 6a is due to the optical transfer function (Eq. 24, 25, and 31)
513 of the shadowgraph. For wave numbers $q > 300 \text{ cm}^{-1}$ the signal intensity becomes comparable to
514 the background noise. According to the number of images and acquisition rate, the maximum
515 correlation time is 320 s in this study. However, in order to minimize the impact of the transient
516 effect and not consider noisy experimental points (related to a weak statistic at long correlation
517 times) the fitting of the SF with Eq. 31 is performed up to $\Delta t = 32 \text{ s}$ for all the measurements. We
518 found that the latter was enough to capture the “plateau” of the investigated wave numbers (see Fig.
519 6b as example).

520 $A(q, t)$, $\bar{\xi}(q, t)$, $\sigma(q, t)$, $C(q, t)$ and $E(q, t)$ are the fitting parameters at each wave number. The
521 fitting is performed through MatLab and an implemented Levenberg-Marquand non-linear least-

522 square fitting routine. At the end of the fitting, we proceed to the analysis of the dynamics of the
523 fluctuations through the reciprocal decay times $\bar{\xi}(q, t)$.

524 4. Results and Discussion

525 In Table 2 we provided the experimental configurations studied in this work. In Fig. 7 we report the
526 obtained SFs as a function of the correlation time Δt for different wave numbers q (left panel) for
527 images acquired 30 minutes after closing the valves in experiment #1 together with the fitting
528 obtained through Eq. 25b and 31 and (right panel) the corresponding relative error.

529

530 Figure 7: a) Structure function of the concentration non-equilibrium fluctuations during the free-diffusion
531 experiment carried out at mean temperature of $T = 25^\circ C$ and 30 minutes after closing the valves, as a function of
532 the correlation time Δt for different wave numbers for experiment #1 (NaCl, $c = 2.7 \text{ mol/L}$, $\Delta c = 2.0 \text{ mol/L}$).
533 The dashed red curves correspond to the results of the fit with Eq. 25b, while the dotted black curves correspond
534 to the fit with Eq. 31. In b) we report the corresponding relative errors between the fitting and the experimental
535 points, in dashed curves with Eq. 25b and in circles with Eq. 31.

536

537 In Fig. 7b we report the corresponding relative errors between the fitting and the experimental
538 points, in dashed curves with Eq. 25b and in circles with Eq. 31. Colors correspond to the wave
539 number colors of Fig. 7a. For the three wave numbers, the relative error is slightly smaller with Eq.
540 31. At large wave numbers the residuals remain well below 1% and randomly distributed around zero
541 over the entire range of correlation times analysed. However, at small wave vectors the residuals are
542 more important, but do not exceed 2% with Eq. 31. This can be explained because, as already
543 anticipated at the end of paragraph 2.7, Eq. 25b does not consider coupling effects particularly
544 affecting the signal at small wave vectors, and moreover Eq. 31 is not valid for too high polydispersity
545 of reciprocal decay times.

546 The quantity $A(q, t)/C(q, t)$ provides a useful indication of the signal-to-noise ratio of the
547 measurements. In Fig. 8a, the signal-to-noise ratio is shown for experiment #1 at different times after
548 closing the valves. In Fig. 8b signal-to-noise ratio is shown for experiments #1, #2 and #3, at 11
549 minutes after closing the valves. In Fig 8c, a comparison of the signal-to-noise ratio at 11 minutes
550 after closing the valves is shown for the three concentrations (average and difference) of Na_2SO_4 . All
551 those reported results have been obtained with Eq. 31 for the analysis of the SFs .

552

553 Figure 8: Ratio between the static structure factor and the signal background as a function of the wave number a)
554 for experiment #1 at different times after closing the valves (NaCl, $c = 2.7 \text{ mol/L}$, $\Delta c = 2.0 \text{ mol/L}$); b) a
555 comparison between experiments #1, experiment #2 (CaCl₂, $c = 0.46 \text{ mol/L}$, $\Delta c = 0.8 \text{ mol/L}$) and
556 experiment #3 (Na₂SO₄, $c = 0.5 \text{ mol/L}$, $\Delta c = 0.7 \text{ mol/L}$) at 11 minutes after closing the valves. c) For the
557 three experiments performed with Na₂SO₄ at 11 minutes after closing the valves.

558

559 One can note that the positions of the maxima and minima in Fig. 8a, 8b and 8c remains the same,
560 being related to the optical transfer function of the shadowgraph setup that is the same for all the
561 experiments. From Fig. 8a one can appreciate that the signal-to-noise ratio decreases with time as
562 the experiment runs, witnessing the decrease of the overall concentration gradient within the
563 system.

564 From Fig. 8b one can detect that the overall signal-to-noise ratio is comparable for all the salt
565 mixtures presented, even though the q_{ro} are different from one experiment to another. For
566 example, for Na_2SO_4 , the second peak is remarkably more intense, showing that the q_{ro} should be
567 larger. On the contrary, the first peak is more intense for NaCl , showing that the intensity limit at
568 small q should be larger for this mixture couple.

569 From Fig. 8c, one can note that the intensity of NEFs is much larger for the molar concentration of
570 0.5 mol/L than in the other two cases.

571 From the fitting of the SFs , we obtained also the reciprocal decay times $\xi(q, t) = \frac{1}{\tau_c(q, t)}$ as a function
572 of q for different times after closing the valves. In Fig. 9 we report the decay times as a function of q
573 and for different times after closing the valves for the experiment #1. Only points for which the
574 $SN(q) > 1$ and $0.128s < \tau_c(q) < 3s$ are reported.

575

576 Figure 9: Decay times of the c-NEFs as a function of the wave number for different times after closing the valves
577 for experiment #1 (NaCl , $c = 2.7 \text{ mol/L}$, $\Delta c = 2.0 \text{ mol/L}$) with a fitting of the SFs with a) Eq. 25b and b) Eq. 31.
578 The continuous black lines correspond to the curves obtained fitting Eq. (23) to data points.

579

580 As can be seen in Fig. 9, the log-log plot of $\tau_c(q)$ vs. q shows the classical bell-shape curve at each
581 time. The time decays are slightly different depending on the used SF model adjustment. By
582 considering the data points of Fig. 9, the fitting of the c-NEFs decay times as a function of q was
583 performed with Eq. (23). The fit to the data turns out to be better with Eq. 31, particularly visible in
584 Fig. 9b at the smallest wave vectors. This fitting provides the values of the mass diffusion coefficient
585 D_a as well as the cut-off wave number q_{ro} , which corresponds to the q value of the maximum of the
586 bell-shape curve. As already reported in a number of publications (Crocco et al., 2012, 2006a), for
587 wave numbers larger than q_{ro} the system exhibits a diffusive behaviour for c-NEFs so that the mass
588 diffusion coefficient D_a is obtained from the fitting of the experimental data points through Eq. (23)
589 in this wave vector range. In Fig. 9, one can note that all the curves collapse onto a single one for
590 large wave numbers, meaning that the mean mass diffusion coefficient remains constant during the
591 free-diffusion process. This is consistent with the fact that the peak of the distribution of inverse time
592 decays shown in Fig. 4d does not move in time, as already mentioned above. Additionally, as time
593 goes by, the cut-off wave number decreases with time, therefore, the decay time curves move
594 towards larger decay times. This reflects the decrease of the concentration gradient with time due to
595 the diffusion process.

596

597 Figure 10: Distribution of reciprocal decay times standard deviation (only with Eq. 31) for different times after
598 closing the valves as a function of the wave number for experiment #1 (NaCl , $c = 2.7 \text{ mol/L}$, $\Delta c = 2.0 \text{ mol/L}$).
599 The dashed line corresponds to the standard deviations calculated from the simulated concentration profile 30
600 min after the start of the free diffusion experiment.

601

602 The standard deviation of the distribution of reciprocal decay times shown in Fig. 10 shows an
603 opposite behaviour with respect to the decay time. For small wave vectors, the standard deviation is
604 proportional to q^{-2} , while for large wave vectors it is proportional to q^2 . Like the decay time, the
605 standard deviation collapses in the diffusive regime. As the diffusive process evolves, standard
606 deviation for small wave numbers decreases, which is, again, a mark of the smoothing of the

607 concentration gradient, i.e. of the decreasing stratification of the layers in terms of fluid properties.
608 The dashed line corresponds to the standard deviations calculated from the simulated concentration
609 profile 30 min after the start of the free diffusion experiment. The calculations confirm the parabolic
610 trend. The adjustment with the data coming from the fit is remarkably good at medium and large
611 wave vectors.

612 In Fig. 11, we plot the mass diffusion coefficient D_a as a function of the normalised time (i.e. t/τ_d) for
613 the three binary mixtures obtained from analysis of the decay times after fitting the *SFs* with Eq. 31.

614

615 Figure 11: Mass diffusion coefficients D_a as a function of the normalized time for the free-diffusion experiments
616 carried out at $T = 25\text{ }^\circ\text{C}$, circles are for the experiment #1 (NaCl , $c = 2.7\text{ mol/L}$, $\Delta c = 2.0\text{ mol/L}$), squares for
617 the experiment #2 (CaCl_2 , $c = 0.46\text{ mol/L}$, $\Delta c = 0.8\text{ mol/L}$) and triangles for the experiment #3 (Na_2SO_4 , $c =$
618 0.5 mol/L , $\Delta c = 0.7\text{ mol/L}$) obtained from analysis of the decay times after fitting the *SFs* with Eq. 31.

619

620 The circles are for the experiment #1, squares for #2 and triangles for #3. Historical literature values
621 (Rard and Miller, 1979b, 1979c) are represented by the horizontal dashed lines for each binary
622 mixture of interest. The modeling of *SFs* with Eq. 31 gives constant values over time and in good
623 agreement with these literature values. According to the experimental procedure, the recording of
624 images started 5 minutes after introducing the fluids into the cell and closing the valves. We can see
625 in Fig. 11 that from the beginning of the experiment we obtain the correct estimation of the value of
626 the diffusion coefficient. We do not have to wait for the end of the diffusion process in order to
627 evaluate the diffusion coefficient, which is a major advantage compared to techniques which exploit
628 the kinetic evolutions of concentration profiles. Slightly different results are obtained after fitting the
629 *SFs* with Eq. 25b. The values are also constant over time, but they are systematically underestimated
630 respect to the reference values. In Fig. 1 we reported with red points the average apparent diffusion
631 coefficient values and associated uncertainties on the point series obtained from the modelling of
632 *SFs* with Eq. 31. Those mean values are given in the table A of the appendix.

633

634 5. Conclusions

635 Following the Nernst-Planck formalism we have developed the equations of the diffusive fluxes of
636 the ionic species of salts dissolved in water at high concentrations. As expected, due to the
637 conservation of the neutrality of the electric charge (electro-neutrality principle), the species
638 associate and the diffusive behavior resembles that of molecules. We obtained expressions for the
639 apparent diffusion coefficients of NaCl , CaCl_2 and Na_2SO_4 , depending on the diffusion coefficients
640 of corresponding species and the activity coefficients of the dissolved salts. Using the PHREEQC
641 geochemical software we calculated the species diffusion coefficients and the activity coefficients
642 thanks to the Pitzer formalism. A comparison with experimental literature reference measurements
643 shows that the calculations of apparent diffusion coefficient, carried out with default species ionic
644 strength-dependence coefficients, well describe the steep decrease of the diffusion coefficient at
645 very low concentrations but not at medium and high concentrations. By modifying the values of the
646 ionic strength-dependence coefficients it is possible to find the values of the apparent diffusion
647 coefficients at small and high concentrations, these values were optimized for the four ionic species
648 involved in the three salts studied in this work. The theoretical framework for considering
649 multicomponent diffusion in water implemented in the PHREEQC can help describing aqueous
650 electrolyte diffusion measurements in concentrated simple brines, up to several $\text{mol}\cdot\text{kgw}^{-1}$. When

651 aqueous complexation reactions occur, interpreting the diffusion processes based on a single
652 apparent diffusion coefficient may not be relevant anymore, as we saw with $CaCl_2$.

653 Then we simulated with PHREEQC free-diffusion experiments with the three salts, at different
654 average concentrations and for different concentration differences between the two layers of
655 superimposed saline solutions. Knowing the vertical concentration profile as a function of time
656 allows us to calculate the value of the concentration gradient at any point along the fluid column and
657 at any time. The value of the concentration gradient proved to be a fundamental quantity for the
658 analysis of experimental data.

659 We carried out experimentally the free-diffusion experiments simulated. Unlike classical optical
660 techniques, which measure horizontally the vertical concentration profile, we have studied by
661 shadowgraphy in the vertical direction the dynamics of c-NEFs in the horizontal plane during the
662 diffusion process.

663 Given the thickness of the system, the profile of the concentration gradients leads to a polydispersity
664 of the c-NEFs decay times. Since the shadowgraph measured signal is an integration of all the signals
665 coming from all the layers crossed by the detecting light beam through the fluid sample, we have
666 integrated the decay times polydispersity into the autocorrelation function of the c-NEFs, as reported
667 in recent literature. Starting from the concentration gradient profiles we found that the distribution
668 of the reciprocal decay times can be assumed to be Gaussian. When the polydispersity index is low
669 (valid all the time at large wave numbers and for times greater than 50% of the characteristic
670 diffusive time at intermediate wave numbers), the cumulants method allows to develop the
671 autocorrelation function around the mean value of the distribution and to introduce the standard
672 deviation of the distribution. We have therefore proposed an equation for fitting the image SFs and
673 integrating the thickness of the sample.

674 Based on an adapted measurement protocol, the analysis of the SFs allowed us to measure and from
675 the earliest stages of the diffusion process the diffusion coefficients for the three salts studied. They
676 are in very good agreement with literature reference measurements. This therefore validates the
677 technique and method of analysis of c-NEFs during the free-diffusion of salts with high initial
678 concentration gradient at 25°C and atmospheric pressure. The diffusion cell used in this work is
679 designed to operate at pressure up to 500 bars and, with the help of the Peltier elements which
680 finely regulate the temperature of the cell, it is possible to heat up to 70°C. Moreover, the diffusion
681 cell can be used with other aqueous electrolyte combinations. This allows for studies of salt diffusion
682 in more realistic reservoir conditions.

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688 [Author contributions](#)

689 H.B., M.A., A.L. and F.C. formulated the research questions, A.T.N, R.M. and C.O.O performed the
690 experiments, A.T.N, C.O.O. and A.L performed the simulations and A.T.N, H.B., M.A., A.L. and F.C.
691 wrote the manuscript. All authors analyzed the results and reviewed the manuscript.

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860

861

862 [Appendix:](#)

863 [Specific conductance calculations](#)

864 According to Appelo (Appelo, 2017), the specific conductance, SC , of a solution can be calculated
 865 after the individual contributions of electrically charged dissolved species:

866
$$SC = \sum \Lambda_{m,i} c_i$$

867 Where $\Lambda_{m,i}$ is the molar conductivity of ion i ($S \cdot m^{-1} \cdot (mol \cdot dm^{-3})^{-1}$), and c_i is the concentration ($mol \cdot dm^{-3}$).
 868

869 $\Lambda_{m,i}$ is related to the diffusion coefficient in the solution, $D_{aq,i}$ given in eq. (10), by:

870
$$\Lambda_{m,i} = \frac{z_i^2 F^2}{RT} D_{aq,i}$$

871 R ($= 8.31446 J/mol/K$) is the ideal gas constant, T (K) is the absolute temperature, z_i ($-$) is the
 872 charge number and F ($= 96485 C/mol$) is Faraday's constant.

873 These relationships are implemented in PhreeQC software so that the specific conductance of any
 874 aqueous solution can be calculated easily as soon as the parameters summarized in Table 1 are
 875 entered in the associated database.

876 We therefore calculated the specific conductivity of NaCl solutions as a function of NaCl
 877 concentration using either Appelo's (Appelo, 2017) a_1 and a_2 coefficients for Na^+ and Cl^- , or those
 878 revised in this work. Results are plotted in Figure A below.

879 In this figure, symbols are experimental data from (Chambers et al., 1956), the green dashed line
 880 represents specific conductivity calculated with Appelo's a_1 and a_2 and the green solid line with the
 881 revised coefficients. The match with experimental data is slightly degraded, mostly for NaCl
 882 concentration above $4 mol \cdot L^{-1}$.

883 In summary, and in comparison with Appelo (Appelo, 2017), the set of a_1 and a_2 coefficients
 884 proposed in the present work strongly improves the description of the diffusion coefficient of the
 885 NaCl aqueous electrolyte (Figure 1.a) without degrading significantly the calculation of the specific
 886 conductivity of the NaCl solution. Using this revised set of coefficients for Na^+ and Cl^- ions lead to
 887 propose new values for SO_4^{2-} and Ca^{2+} ions for consistency purpose and improve, in the same time,
 888 the calculation of diffusion coefficients for Na_2SO_4 and $CaCl_2$ electrolyte solution, as shown in Figure
 889 1, b and c, respectively.

890

891 **Figure A: Specific conductance of a NaCl aqueous solution as a function of NaCl concentration, modified after**
892 **Appelo (Appelo, 2017). Orange dots: experimental data from Chambers et al. (Chambers et al., 1956); in**
893 **green: results from this work. Green dashed line: specific conductance calculated with Appelo's α_1 and α_2**
894 **coefficients for Na^+ and Cl^- ; green solid line: specific conductance calculated with revised α_1 and α_2**
895 **coefficients.**

896 Simulated concentration profiles

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898

899 **Figure B: Simulations of the concentration profiles as a function of the vertical position and for different**
900 **times for a) experiment #2 (CaCl_2 , $c = 0.46 \text{ mol/L}$, $\Delta c = 0.80 \text{ mol/L}$) and b) experiment #4 (Na_2SO_4 , $c =$
901 **1.0 mol/L , $\Delta c = 0.7 \text{ mol/L}$). The concentration of the anions (cations) calculated by PHREEQC is**
902 **represented with symbols (triangles: anions, circles: cations). For a better visualization of the results, in Fig.**
903 **Ba the anion concentration was divided by 2, while in Fig. Bb the cation concentration was divided by 2.**
904 **Selected times correspond to fractions of the characteristic diffusive time τ_d as indicated in the legends.****

905

906 Apparent diffusion coefficients measured by shadowgraphy

907 **Table A: Values of the apparent diffusion coefficient of the salts D_a measured by shadowgraphy as a**
908 **function of the average molar concentration c and molar concentration difference Δc between the two**
909 **layers for the free-diffusion experiments performed in this work. The uncertainties correspond to the**
910 **standard deviation of the distribution of diffusion coefficients values obtained by experiment.**

Experiment	Salt	c (mol/L)	Δc (mol/L)	D_a ($10^{-5} \text{ cm}^2/\text{s}$)
1	<i>NaCl</i>	2.700	2.000	1.55 ± 0.03
2	<i>CaCl}_2</i>	0.460	0.800	1.14 ± 0.01
3	<i>Na}_2\text{SO}_4</i>	0.500	0.700	0.80 ± 0.02
4		1.000	0.700	0.670 ± 0.007
5		1.484	0.700	0.582 ± 0.015

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