Neutron imaging of liquid-liquid systems containing paramagnetic salt solutions

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The method of neutron imaging was adopted to map the concentration evolution of aqueous paramagnetic Gd(NO$_3$)$_3$ solutions. Magnetic manipulation of the paramagnetic liquid within a miscible nonmagnetic liquid is possible by countering density-difference driven convection. The formation of salt fingers caused by double-diffusive convection in a liquid-liquid system of Gd(NO$_3$)$_3$ and Y(NO$_3$)$_3$ solutions can be prevented by the magnetic field gradient force.

In this study, we use neutron imaging to track the concentration distribution of aqueous paramagnetic gadolinium(III) nitrate (Gd(NO$_3$)$_3$) solutions in a liquid-liquid system with a miscible nonmagnetic counterpart. This direct method consists of measuring the attenuation of a white neutron beam on passing through a sample and has potential for applications in a variety of fields$^{21-23}$. Neutrons interact with the nuclei of the sample, which makes the measurement element-specific, allowing the direct study of liquids that are both miscible and visually indistinguishable under normal conditions. Gd is the element with the highest neutron absorption cross section ($\sigma_a = 46 \, 700$ barn for thermal neutrons$^{21}$). In addition, Gd$^{3+}$ possesses a large magnetic moment of $7 \mu_B$ by virtue of unpaired 4f electrons. Consequently, solutions of Gd(NO$_3$)$_3$ are ideal candidates for neutron imaging of paramagnetic solutions, enabling the direct observation of their response to magnetic fields. Recent advances in detector systems have provided the means for neutron imaging with both high spatial and temporal resolutions$^{25-27}$. Here, we monitor the interplay of convection, magnetic field gradient force, and diffusion by variations in the neutron transmission profile.

Neutron imaging experiments were carried out at the IMAGINE station$^{28}$ located in the neutron guide hall of the Orphée reactor at the Laboratoire Léon Brillouin just before its final shutdown. The spectrum of the white neutron beam contained cold neutrons (λ = 2-20 Å), which emerged from a 10 mm pinhole and travelled 2.5 m to the detector where the neutron flux was $2 \times 10^7 \text{cm}^{-2} \text{s}^{-1}$. The detection system consisted of a 50 µm thick $^6$LiF/ZnS scintillator, with a resolution of 18 µm/pixel, coupled to an sCMOS camera. Recorded images of 2560×2160 pixels correspond to a field of view of 46×39 mm$^2$. All images shown here were obtained with an acquisition time of 60 s. The spatial resolution is on the order of 50 µm.

Quartz cuvettes with path lengths of 1 mm were filled with the liquid solutions and placed 5 mm in front of the detector (see sketch in Fig. 1(a)). The outside dimensions of the cuvettes were 40 mm × 23.6 mm × 3.5 mm (height × width × depth). Incoherent scattering by water molecules ($\sigma_{inc} = 160.5 \text{barn}$) was minimized by dissolving salts in D$_2$O ($\sigma_{inc} = 4.1 \text{barn}$). For max-
The intensity of the white beam from a neutron beam is a simplification. This approximation is not a consequence of a single value for a polychromatic neutron beam but rather considering the fact that the neutron wavelengths constituting the beam (2-20 Å) lie within one order of magnitude of each other. A calibration of the transmitted intensity to the Gd³⁺ concentration was performed by recording images of solutions in 1 mm path length cuvettes (see Fig. 2). The attenuation follows the Beer-Lambert law up to a concentration of about 0.4 M, when the beam is almost completely absorbed and the transmitted intensity originates predominately from incoherent scattering. An offset exponential fit with an extra variable (b = 0.07) captures the behavior, but quantitative statements cannot be readily made at concentrations higher than 0.5 M. The latest development of black body correction opens the possibility to quantify the contribution of background and sample scattering to the transmittance, but it would require a black body grid. The magnetic susceptibility of a 1 M Gd(NO₃)₃ heavy water solution (χ₁M = 322 x 10⁻⁶) is the sum of the diamagnetic D₂O contribution (χD₂O = −8 x 10⁻⁶) and the paramagnetic Curie-law contribution of the Gd³⁺ ions. This value and the magnetic field distribution of the Nd-Fe-B magnet allow the computation of the magnetic field gradient force in the vicinity of the magnet (see Fig. 3(b)). The magnetic field was calculated by approximating the magnet as two uniform sheets of magnetic charge. In the case of an inhomogeneous solution comprising a paramagnetic and nonmagnetic component, a magnetic field gradient orthogonal to the concentration gradient alters the equilibrium state. The Gd(NO₃)₃ solution climbs up the side of the cuvette until the balance between buoyancy (Fg = Δρg) and magnetic field gradient forces is re-established. This can be seen in Fig. 3. Here, 100 µL of 0.4 M Gd(NO₃)₃ solution (ρ = 1180 kg m⁻³) at the bottom of a 1 mm path length cuvette was covered with 400 µL D₂O (ρ = 1110 kg m⁻³). A magnet was placed at the side and the diffusion of the Gd(NO₃)₃ was monitored for 3 h. The magnetic field gradient draws the Gd(NO₃)₃ solution towards the magnet, although homogenization by diffusion continues in its presence. An estimate for the diffusion coefficient D of 0.4 M Gd(NO₃)₃ in D₂O can be obtained from the vertical concentration profile by a fit with the solution of the one-

\[ I = I₀ e^{−εcl}, \]  

with the molar neutron absorption coefficient ε, the Gd³⁺ concentration c and the sample thickness l. Strictly speaking, ε depends on the neutron energy and the assumption of a single value for a polychromatic neutron beam is a simplification. This approximation is not a concern, considering the fact that the neutron wavelengths constituting the beam (2-20 Å) lie within one order of magnitude of each other.
dimensional diffusion equation (see Fig. 3(c)):

\[ c(z, t) = \frac{c_0}{2} \text{erf} \left( \frac{z}{\sqrt{4Dt}} \right), \tag{4} \]

with Gd\(^{3+}\) starting concentration \(c_0\). The value of \(D = 1.2 \times 10^{-9} \text{m}^2\text{s}^{-1}\) obtained for the nonmagnetized region after 3 h is reasonable for rare-earth ions in water.\(^{33}\) However, this value should be treated with caution, as the initial interface was smeared by introducing the liquids into the cuvette before the onset of diffusion. The diffusion coefficient from the fit for the magnetized region is higher at \(D = 1.5 \times 10^{-9} \text{m}^2\text{s}^{-1}\), but the one-dimensional expression does not account for horizontal diffusion from the warped concentration profile.

The density difference between the Gd(NO\(_3\))\(_3\) solution and the nonmagnetic liquid can be adjusted by addition of Yttrium(III) nitrate (Y(NO\(_3\))\(_3\)), which is transparent to neutrons (\(\sigma_n = 7.0 \text{ barn}^{22}\)), to the D\(_2\)O. Decreasing the density difference leads to more vigorous magnetically induced migration and facilitates magnetic confinement. If the density of the Gd solution is higher than that of the Y solution, the removal of the magnet before homogenization has taken place prompts a

FIG. 3. Neutron image of a 1 mm path length quartz cuvette with 100 µL 0.4 M Gd(NO\(_3\))\(_3\) solution overlain with 400 µL of D\(_2\)O. A 20 mm magnet cube to the right skews the Gd\(^{3+}\) concentration profile. (a) After 3 min (b) after 3 h. (c) Fits of Eq. (4) to the vertical cross sections (broken lines in neutron images) of the concentration profiles 3 mm (\(\nabla B \neq 0\)) and 19 mm (\(\nabla B = 0\)) away from the magnet show good agreement and the diffusion coefficient \(D\) can be obtained.

FIG. 4. (a)-(f) Neutron images of 100 µL 0.4 M Gd(NO\(_3\))\(_3\) above 300 µL 1.3 M Y(NO\(_3\))\(_3\) solution (\(\Delta \rho = 140 \text{ kg m}^{-3}\)) in a 1 mm path length quartz cuvette. The view is restricted to the area below the surface in the vicinity of the liquid-liquid interface. (a) 2 min after the Gd(NO\(_3\))\(_3\) solution is suspended above the Y(NO\(_3\))\(_3\) surface. (b)-(c) Double-diffusion imposes Gd salt fingers which protrude into the Y(NO\(_3\))\(_3\) solution after 90 min and begin to sink due to the loss of buoyancy. The fingers have a width of 1.2 mm and persist for over 8 h (Multimedia view). (d) A cubic 20 mm magnet at the side of the cuvette halts the instability growth and destroys the stratification instantly (\(t_2\): time since magnetization; Multimedia view). (e)-(f) Once the magnet is removed, the control over the Gd(NO\(_3\))\(_3\) is relinquished and it fans out. The system snaps back into the stratified state in less than 10 min and the cascading salt fingers homogenize the mixture after 2 h (\(t_3\): time since removal of magnet; Multimedia view). (g) Horizontal cross sections (broken lines in the neutron images) of the salt fingers in (b), (c), and (e) show a periodic variation of the Gd\(^{3+}\) concentration by \(\approx 0.02 \text{ mol L}^{-1}\). The plotted data was smoothed with a Savitzky-Golay filter.
buoyancy-driven Rayleigh-Taylor instability and the Gd solution plunges to the bottom of the cuvette in a matter of seconds. A different situation arises when the density difference is inverted and the Gd solution floats above the Y solution. To investigate this, 100µL 0.4 M Gd(NO$_3$)$_3$ solution was injected on top of 300 µL 1.3 M Y(NO$_3$)$_3$ solution ($\rho = 1320$ kg m$^{-3}$) in a cuvette (see Fig. 4(a)). After 1 h the system was beset by a salt-finger instability due to double diffusive convection (see Fig. 4(b)-(c) and animations for greater visibility). This phenomenon is encountered at the interface of solutions that diffuse into each other at unequal rates. The diffusivity of Y$^{3+}$ in the 1.3 M solution exceeds that of the Gd in the 0.4 M solution. It follows that Y(NO$_3$)$_3$ will diffuse laterally into small portions of Gd(NO$_3$)$_3$ solution that cross the interface. The increase in density due to the gained Y(NO$_3$)$_3$ makes the Gd(NO$_3$)$_3$ solution plummet in form of 1.2 mm wide fingers (see cross sections in Fig. 4(g)), which continue to leech Y(NO$_3$)$_3$ from their surroundings during their descent. These transport the Gd(NO$_3$)$_3$ advectively, two orders of magnitude faster than regular diffusion and trigger a stratification with neighboring fingers that rise thanks to the buoyancy acquired by the loss of Y(NO$_3$)$_3$. Hence, the usually stabilizing factor of diffusion can destabilize a system in which the density decreases upwards. The stratification persists for over 8 h (see Fig. 4(c) and animations in supplementary material). Viscous friction between the liquid and the cuvette walls plays a role in the horizontal scale of the individual fingers, which is inversely proportional to the distance between the cell walls. Thus, a horizontal expansion of the fingers beyond the gap width is achievable in thin cuvettes. A magnet next to the cuvette erases the stratification and restabilizes the system by capturing the paramagnetic solution (see Fig. 4(d)). This does not reverse the mixing that has occurred and the Gd$^{3+}$ ions can be seen to continuously diffuse into the Y(NO$_3$)$_3$ solution. The magnetic field gradient merely prevents the collapse of the liquid-liquid interface. Nonetheless, the system undergoes an immediate change upon its withdrawal (see Fig. 4(e)). Bereft of the confining magnetic field gradient force, the boundary between the solutions is once again disrupted. The ensuing release of the paramagnetic liquid is accompanied by convective mixing of the solutions amidst which the salt fingering instability can be witnessed anew. After two hours the system equilibrates as homogenization sets in (see Fig. 4(f)).

In conclusion, neutron imaging is a viable method for capturing quasi two-dimensional convective and diffusive processes in solutions containing Gd$^{3+}$ ions. A pre-existing concentration of paramagnetic fluid in some region can be redistributed within a miscible liquid by the magnetic field gradient force, which counteracts density-difference driven convection. Furthermore, double-diffusive convection in the system of magnetic Gd(NO$_3$)$_3$ and nonmagnetic Y(NO$_3$)$_3$ salt solutions is suppressed. This manifests itself in the stratification by salt fingers when the magnet is absent. The implication of this is of great importance for the development of the magnetic separation of rare-earth ions, as even minor differences in diffusivity can precipitate salt fingering instabilities. If left unchecked, these will mix the separated solutions. A prerequisite for the generation of the liquid-liquid interface is a driving force that creates and preserves the concentration gradient of the paramagnetic ions. The magnetic field gradient is then able to bestow stability upon the system. Driving forces can range from the weak factor of evaporation to the more substantial injection of electrochemical energy, which can drive convection. In view of improvements in both imaging instrumentation and available neutron flux, higher resolution and frame rates are expected to improve the neutron imaging of hydrodynamic processes in the future. This may prove valuable for the analysis of ions in solutions.

See supplementary material for time sequenced images of liquid-liquid systems containing Gd(NO$_3$)$_3$ and Y(NO$_3$)$_3$ solutions: undisturbed double-diffusive convection and magnetic confinement of a Gd(NO$_3$)$_3$ drop.

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Supplementary Material:

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ADDITIONAL TIME SEQUENCED NEUTRON IMAGES

S1. Unhindered mixing by salt fingering

FIG. S1. Two 1 mm path length quartz cuvettes with 75 µL 0.4 M Gd(NO$_3$)$_3$ (left) and 100 µL 0.5 M Gd(NO$_3$)$_3$ (right) above 300 µL of 1.3 M Y(NO$_3$)$_3$. Gd(NO$_3$)$_3$ solutions were injected above the Y(NO$_3$)$_3$ solution surface in the left cuvette and below it in the right cuvette. Salt fingers form in both systems and mix the solutions within 7 h. Left cuvette: The surface profile is caused by capillary forces. The salt fingers begin to form at the side of the cuvette and propagate inwards. (Multimedia view)

S2. Magnetic confinement of a drop of Gd(NO$_3$)$_3$ solution

FIG. S2. 50 µL 0.5 M Gd(NO$_3$)$_3$ solution ($\rho = 1200$ kg m$^{-3}$) above 800 µL 1.3 M Y(NO$_3$)$_3$ solution ($\rho = 1320$ kg m$^{-3}$) in a 2 mm path length quartz cuvette. The acquisition time was 80 s for this measurement. The calibration from Fig 2 is not valid for path lengths above 1 mm. Therefore, the negative of the logarithm of the transmittance is shown. (a) The Gd(NO$_3$)$_3$ drop migrates to the cubic 20 mm magnet at the side of the cuvette within 2 min. (b) The trapped drop in the magnetic field gradient (see Fig. 1(b)) gradually diffuses into the Y(NO$_3$)$_3$ solution over the course of 4.5 h. (c) Salt fingers appear immediately after removal of the magnet at $\Delta t = 4$ h 30 min. (d) At $\Delta t = 6$ h 10 min, the stratification disappears after placing the magnet next to the cuvette again. (Multimedia view)