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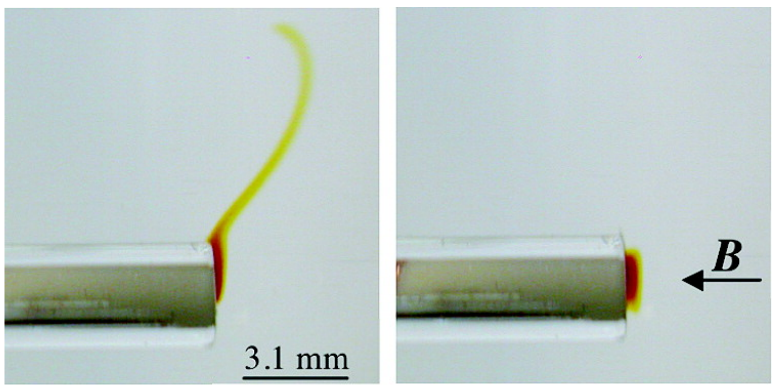

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Demonstration of the Elusive Concentration-Gradient Paramagnetic Force

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A unit volume element that contains magnetic dipoles, *j*, may experience two paramagnetic forces, the field-gradient force, $\mathbf{F}_{\nabla B}$, and the concentration-gradient force, $\mathbf{F}_{\nabla C}$.[1,2] $\mathbf{F}_{\nabla B}$ is proportional to the magnetic field gradient ($\mathbf{B}\cdot\nabla\mathbf{B}$; eq 1)[3] and is associated with

$$\mathbf{F}_{\nabla B} = 2N_A C_j[(g\mu_B)^2/4kT]\mathbf{B}\cdot\nabla\mathbf{B} \quad (1)$$

magnetic attraction,[4] certain types of magnetohydrodynamic (MHD) convection,[5,6] and levitation.[7] $\mathbf{F}_{\nabla C}$ is proportional to the concentration gradient of *j* (∇C_j; eq 2),[3] and it remains ambiguous despite a

$$\mathbf{F}_{\nabla C} = N_A[(g\mu_B)^2/4kT]\ |\mathbf{B}|^2\ \nabla C_j \quad (2)$$

known electrostatic analogue in media of inhomogeneous dielectric constant.[8,9] Thus, early attempts to involve $\mathbf{F}_{\nabla C}$ in enhanced magnetic diffusion through membranes,[10] or enhanced convection during electrolysis in solutions with paramagnetic ions,[11] have been questioned.[12] More recently, $\mathbf{F}_{\nabla C}$ was used to explain magnetic effects on the open circuit potential of ferromagnetic electrodes (Fe, Co, Ni) in corrosive paramagnetic solutions.[13] But, since magnetized ferromagnetic electrodes attract paramagnetic ions through field-gradient-type forces,[14] the $\mathbf{F}_{\nabla C}$ involvement has also been questioned.[15] In several other occasions, the presence of $\mathbf{F}_{\nabla C}$ has been denied based on magnitude comparisons with the driving force of diffusion.[16] But as shown here, being a body force $\mathbf{F}_{\nabla C}$ affects modes of mass transfer different from diffusion. Lately, $\mathbf{F}_{\nabla C}$ has been evoked in phenomena where, if of any consequence, it may be convoluted either with kinetics and MHD transport as in microelectrodes facing the magnetic field[17] or with natural convection both with[18] and without complications associated with $\mathbf{F}_{\nabla B}$.[19]

With this background, our strategy was to isolate $\mathbf{F}_{\nabla C}$ from other magnetic forces and demonstrate its properties by letting it compete and reverse the effects of another body force, gravity, the cause of density-gradient driven natural convection. This strategy was implemented with concentration gradients produced and probed electrochemically in homogeneous magnetic fields using bent nonferromagnetic Au and Pt disk millielectrodes (0.5−3 mm in diameter) facing the magnetic field. This experimental setup was first introduced by White in conjunction with microelectrodes,[20] which, owing to radial currents,[21] produce cyclonic MHD flows, while voltammograms are always sigmoidal. Millielectrodes, on the other hand, can generate linear diffusion resulting in a peak−current response,[21] which, if used in conjunction with quantitative criteria such as the linear relationship between the peak current and (potential sweep rate)$^{1/2}$, can confirm absence of convection. Finally, to ensure that our observations are due to $\mathbf{F}_{\nabla C}$, and not to $\mathbf{F}_{\nabla B}$-type forces, control experiments with magnetizable Fe electrodes were also run in parallel for comparison.

Figure 1 shows cyclic voltammograms (CVs) obtained with Pt and Fe disk millielectodes in a CH_3CN solution of nitrobenzene (NB) in the presence and absence of a homogeneous magnetic field at two orientations: $\theta = 90°$, $\theta = 0°$ (Figure 1-inset).[20] NB is reduced by the electrode into paramagnetic $NB^{\bullet-}$, whose concentration in the forward voltage sweep is the highest at the solution/electrode interface, fading away in the bulk (Appendix II).

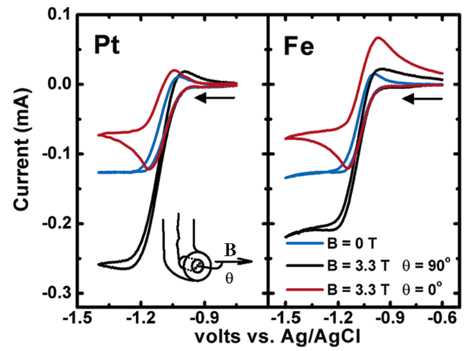

Figure 1. Voltammetry at 10 mV s^{-1} of NB (0.1 M) in CH_3CN/0.5 M tetrabutylammonium perchlorate (TBAP) with inlaid Pt and Fe disk millielectrodes (1.00 mm diameter) at two orientations, θ, relative to **B**.

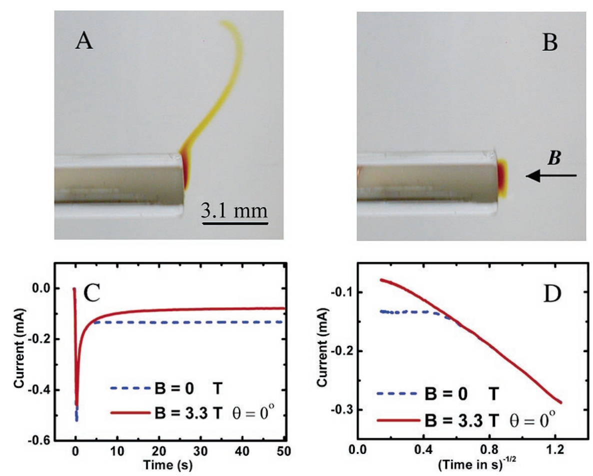

Figure 2. Potential step (PS) experiments with a Au electrode (1 mm diameter) in an NB solution as in Figure 1 (see also Movie S4). (A, B) 40 s after the PS, with $|\mathbf{B}| = 0$ (A) or $|\mathbf{B}| = 3.3$ T, $\theta = 0°$ (B). (C) Current/time curves in the two situations. (D) Corresponding Cottrell plots.

For $|\mathbf{B}| = 0$ T (blue lines) both electrodes show identical quasi-steady-state CVs indicative of natural convection. For $|\mathbf{B}| = 3.3$ T at $\theta = 90°$ (black lines) both electrodes show enhanced steady-state currents due to MHD stirring.[22] But, for $|\mathbf{B}| = 3.3$ T at $\theta = 0°$ (red lines), i.e., for electrodes facing the field, both electrodes show characteristic peak-current response suggesting absence of natural convection and, therefore, retention of the paramagnetic layer close to the electrode. Although this realization might be counterintuitive for nonmagnetic electrodes in homogeneous fields, nevertheless it is confirmed easily by visual examination. Figure 2A shows that at $|\mathbf{B}| = 0$ T the layer containing the red $NB^{\bullet-}$ rises.[20] In contrast, Figure 2B shows that in a 3.3 T field normal to a diamagnetic Au electrode the red layer is held close to the electrode

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(see also Movies S1−S3). Similar results have been obtained with other redox couples as well (Appendix III and Movies S5, S6).

Forces holding the paramagnetic layer must oppose gravity; hence they are body forces. With ferromagnetic electrodes, those forces should include both $\mathbf{F}_{\nabla B}$ and $\mathbf{F}_{\nabla C}$.[6] With Au and Pt electrodes, however, there is no field gradient and the only force left to oppose gravity is $\mathbf{F}_{\nabla C}$. Further insight for the role of $\mathbf{F}_{\nabla C}$ comes from the conspicuous absence of a strong return wave with the Pt electrode at $\theta = 0°$ (compare the red lines in Figure 1) implying an efficient mechanism, other than natural convection, for removal of $NB^{\bullet-}$ from the vicinity of the electrode. In general, along the return wave the $NB^{\bullet-}$ concentration is maximal *near* the electrode, decaying sharply toward the electrode and more smoothly toward the bulk (Appendix II). That profile generates two $\mathbf{F}_{\nabla C}$ forces upon the paramagnetic layer: a weaker one toward the electrode and a stronger one toward the bulk; the net result is detachment of the $NB^{\bullet-}$ layer and loss of the return wave. (The different behavior of the Fe electrode is attributed to the $\mathbf{F}_{\nabla B}$ force, which is always retentive.)

But, what is the mode of mass transfer within the volume that is retained by $\mathbf{F}_{\nabla C}$? At $|\mathbf{B}| = 0$ T the current−time curve of the potential step experiment converges quickly to a convective steady-state behavior, but at $|\mathbf{B}| = 3.3$ T the current continues to decay even after 50 s (Figure 2C) showing "Cottrell" characteristics (Figure 2D), indicative of linear diffusion. Similarly, by voltammetry, Figure 3A shows that while at $|\mathbf{B}| = 0$ T onset of natural convection causes deviations at around 14 mV s^{-1} from the linear (Randles−Sevcik) relationship between peak current and (sweep rate)$^{1/2}$, at $|\mathbf{B}| = 3.3$ T that linear relationship is extended all the way down to ~2 mV s^{-1}. Hence, $\boldsymbol{F}_{\nabla C}$ simply holds the paramagnetic layer and does not interfere with diffusion processes within.

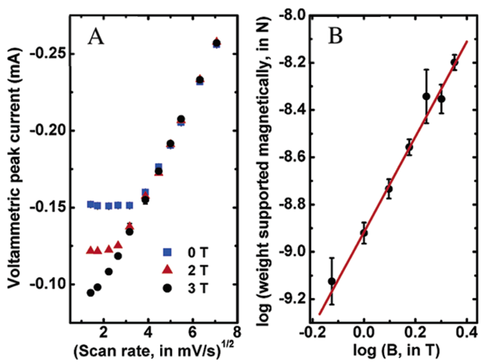

Figure 3. (A) Randles−Sevcik plots from waves similar to those shown in Figure 1 at $\theta = 0°$ (error bars: 1 SD). (B) log(weight supported magnetically) vs log $|\mathbf{B}|$ (average of 4 runs; slope = 2.01 ± 0.13; intercept = −8.91 ± 0.03; $R^2 = 0.997$; error bars: 1 SD).

Quantitative evidence for the identity of the magnetic force holding the diffusion layer is obtained by showing that the supported weight varies with $|\mathbf{B}|^2$ (eq 2). Thus, we note that the breakpoints in the linear parts of Figure 3A depend on $|\mathbf{B}|$. This is because the charge, Q, passing during voltammetry, i.e., the amount of NB electrolyzed and consequently the weight loss by the diffusion layer, all depends on the sweep rate (Appendix III); so, before each breakpoint $\mathbf{F}_{\nabla C}$ is stronger than the gravitational force; after each breakpoint gravity dominates. At the breakpoints, the magnetic force compensates gravity exactly. The excess weight balanced by the magnetic force at each breakpoint, W, is calculated via Newton's second law[6] and is equal to $\langle|\mathbf{F}_{\nabla C}|\rangle V \cos\phi$ (eq 3), where V is the

$$W = [(Q_B - Q_{|B|=0})/nF]\,[FW_+t_+ - FW_-t_-]\,|\boldsymbol{g}| = \langle|\mathbf{F}_{\nabla C}|\rangle V \cos\phi \quad (3)$$

volume and $\langle|\mathbf{F}_{\nabla C}|\rangle$ is the average magnetic force per unit volume of the diffusion layer, while ϕ is the angle of $\langle\nabla C_{NB^{\bullet-}}\rangle$ with the direction of gravity.[23] (For derivation of eq 3 and analysis of forces, see Appendix III.) A plot of log(W) vs log $|\mathbf{B}|$ is linear (Figure 3B) with slope = 2.01 ± 0.13, confirming that $\mathbf{F}_{\nabla C}$ is proportional to $|\mathbf{B}|^2$. In agreement with White's observations on cyclonic flows around 25 μm diameter electrodes,[20a] eq 3 is predicated on the fact that the diffusion layer is "skewed" upward by gravity. Quantitatively, at for example $|\mathbf{B}| = 2$ T, $W = 10^{-8.4}$ N (Figure 3B), while $\langle|\mathbf{F}_{\nabla C}|\rangle V = 3.95 \times 10^{-6}$ N (for the calculation see Appendix III). Hence, $\phi = 89.9°$; i.e., skewing is only very slight, explaining how a vertical force (gravity) is counteracted by a magnetic force that appears "horizontal."

Electrochemistry generates only transient concentration gradients. Permanent susceptibility gradients have been created by entrapping Fe particles in aerogels.[24] In homogeneous fields, such objects are accelerated toward the side of increasing C_j, and it is speculated that apart from the obvious relevance to magnetic confinement and levitation, $\mathbf{F}_{\nabla C}$ may also find application in propulsion.

Supporting Information Available: Appendices I−III; Experimental Section; concentration profiles of $NB^{\bullet-}$; derivation of eq 3, data analysis, other systems. Movies S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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