$m^*|\mathbf{B}|/kT \ll 1$. Therefore, $\tanh(m^*|\mathbf{B}|/kT) \approx m^*|\mathbf{B}|/kT$, and eq 7 becomes

$$\langle \mathbf{m} \rangle_j = [(m^*)^2/kT]\mathbf{B} \tag{8}$$

The average magnetic energy per dipole, $\langle U_M \rangle_j$, in the distribution of dipoles is given by eq 9.[4d] Meanwhile, the unit volume

$$\langle U_M \rangle_j = -\langle \mathbf{m} \rangle_j \cdot \mathbf{B} \tag{9}$$

element of the electrolyte contains $C_j N_A$ dipoles of species j, where C_j is the concentration and N_A is Avogadro's number. So the total magnetic energy per unit volume containing j_{max} dipolar species (all with spin $^1/_2$) is given by

$$U_M|_{\text{per unit volume}} = -N_A \sum_{j=1}^{j_{max}} C_j \langle \mathbf{m} \rangle_j \cdot \mathbf{B} \tag{10}$$

Reasoning by analogy to the method of deriving $\mathbf{F}_B$ (eq 6) from the $\mathbf{F}_L$ forces acting on individual ions, the total force, $\mathbf{F}_\nabla$, on the unit volume element containing j_{max} kinds of paramagnetic species is described by the sum of all forces on individual dipoles and is given by eq 11.[4d]

$$\mathbf{F}_\nabla = -\nabla U_M|_{\text{per unit volume}} \tag{11}$$

Because of eqs 8 and 10, eq 11 gives eq 12.[14]

$$\mathbf{F}_\nabla = \mathbf{F}_{\nabla B} + \mathbf{F}_{\nabla C} = 2N_A \sum_{j=1}^{j_{max}} C_j[(m^*)^2/kT]\mathbf{B}\cdot\nabla\mathbf{B} +$$
$$N_A \sum_{j=1}^{j_{max}} [(m^*)^2/kT]|\mathbf{B}|^2\nabla C_j \tag{12}$$

Because of the first term of eq 12, $\mathbf{F}_{\nabla B}$, a volume element containing paramagnetic species is attracted toward areas of higher $\mathbf{B}$, and because of the second term, $\mathbf{F}_{\nabla C}$, is attracted toward areas of higher concentration.

Overall, the three possible types of magnetic forces acting upon a unit volume element are given by eqs 6 and 12. The first type of force, $\mathbf{F}_B$, is exerted when the unit volume element carries electric current ($\mathbf{i} \neq 0$), the second type of force, $\mathbf{F}_{\nabla B}$, is exerted when the volume element (a) contains radicals and (b) is located in a magnetic field gradient where $\mathbf{B}\cdot\nabla\mathbf{B} \neq 0$, and the third type of force, $\mathbf{F}_{\nabla C}$, is exerted when the concentration of radicals is nonuniform.[2d,16] Importantly, $\mathbf{F}_{\nabla C}$ is present in homogeneous fields as well, and in typical electrochemical systems, it acts upon the diffusion layer.

The motion of the unit volume element accelerated by the total force $\mathbf{F}_{mag} = \mathbf{F}_B + \mathbf{F}_{\nabla B} + \mathbf{F}_{\nabla C}$, is described by the Navier–Stokes

(14) Note that $\nabla(\langle \mathbf{m} \rangle_j \cdot \mathbf{B}) = (\langle \mathbf{m} \rangle_j \cdot \nabla)\mathbf{B} + (\mathbf{B}\cdot\nabla)\langle \mathbf{m} \rangle_j + \langle \mathbf{m} \rangle_j \times \nabla \times \mathbf{B} + \mathbf{B} \times \nabla \times \langle \mathbf{m} \rangle_j$.[15] But since $\nabla \times \mathbf{B}=0$ (i.e., $\mathbf{B}$ is not due to currents within our system), $\nabla(\langle \mathbf{m} \rangle_j \cdot \mathbf{B}) = (\langle \mathbf{m} \rangle_j \cdot \nabla)\mathbf{B} + (\mathbf{B}\cdot\nabla)\langle \mathbf{m} \rangle_j$. Because of eq 8, $\nabla(\langle \mathbf{m} \rangle_j \cdot \mathbf{B}) = 2[(m^*)^2/kT]\ \mathbf{B}\cdot\nabla\mathbf{B}$.
(15) Borisenko, A. I.; Tarapov, I. E. *Vector and Tensor Analysis with Applications*; Dover Publications: New York, 1979; p 180.
(16) Waskaas, M.; Kharkats, Y. I. *J. Phys. Chem. B* **1999**, *103*, 4873.

equation (eq 13) expressing Newton's second law of motion (mass

$$\rho(\partial\mathbf{v}/\partial t + \mathbf{v}\cdot\nabla\mathbf{v}) = -\nabla P + \eta\nabla^2\mathbf{v} + \mathbf{i} \times \mathbf{B} + \mathbf{F}_{\nabla B} + \mathbf{F}_{\nabla C} \tag{13}$$

$\times$ acceleration = sum of all forces) in an incompressible fluid ($\nabla\cdot\mathbf{v} = 0$) of constant density, ρ, and viscosity, η.[17] The velocity of the unit volume element is denoted as $\mathbf{v}$, and ∇P is the gradient of the dynamic pressure (the thermodynamic pressure gradient plus gravity). At steady state, $\partial\mathbf{v}/\partial t = 0$, and the $\mathbf{v}\cdot\nabla\mathbf{v}$ term describes the centripetal acceleration that maintains the vortices in the solution. The $\eta\nabla^2\mathbf{v}$ term assumes that the electrolyte is a Newtonian fluid and expresses the frictional forces between the unit volume element and the surrounding liquid.

It is noted now that the bulk migration current density, $\mathbf{i}$ (eq 6), is ultimately due to a faradaic process. Assuming for simplicity that the electrolytic solution contains a single diamagnetic redox-active species, O, that undergoes a one-electron reduction to yield paramagnetic R (eq 14), $\mathbf{i}$ is given in terms of the flux of species O at the electrode,

$$\text{O} + \text{e} \rightleftarrows \text{R} \tag{14}$$

$\mathbf{J}_O|_{\text{at the electrode}}$, via eq 15.

$$\mathbf{i} = -F\mathbf{J}_O|_{\text{at the electrode}} \tag{15}$$

In general, the flux of diamagnetic O is given by the Nernst–Plank equation (eq 16),[18a] where all previously defined symbols

$$\mathbf{J}_O = -D_O\nabla C_O(r,\phi,z,t) - [z_O C_O(r,\phi,z,t)D_O F/N_A kT]\nabla\phi + C_O(r,\phi,z,t)\mathbf{v} \tag{16}$$

have their usual meaning, while $C_O(r,\phi,z,t)$, D_O, and z_O are the concentration profile, the diffusion coefficient, and the ionic charge of O, respectively, and $\nabla\phi$ is the gradient of the electric potential.

With conventional disk millielectrodes, only the flux component normal to the electrode (in the z direction, Chart 1) contributes to the current density. One of the boundary conditions for the velocity profile $\mathbf{v}$ of eq 13 dictates that, at $z = 0$, $v_z = 0|_{z=0}$ (no slip condition). Furthermore, in the presence of a large excess of supporting electrolyte, there are no potential gradients in the electrolytic solution beyond the diffuse layer, i.e., $\Delta\phi \approx 0$. Therefore, eq 15 is simplified to eq 17.

$$\mathbf{i} = |i_z|\hat{\mathbf{z}} = FD_O\ \partial C_O(r,\phi,z,t)/\partial\mathbf{z}|_{z=0} \tag{17}$$

The concentration profile of species O cannot be calculated independently of the profile of species R, because the two profiles are coupled to one another via their boundary conditions at the electrode, which are as follows: (1) the flux balance of O and R ($\mathbf{J}_O|_{z=0} + \mathbf{J}_R|_{z=0} = 0$) and (2) the Nernst equation, if the O/R couple

(17) Newman, J. S. *Electrochemical Systems*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1991; Chapter 15.
(18) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications* 2nd ed.; John Wiley and Sons: New York, 2000. (a) p 29. (b) 138.