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The magnetic concentration gradient force—Is it real?

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Abstract There are suggestions in the electrochemical literature that a body force $F_{\nabla c}$ acts when an electrolyte with a non-uniform concentration c of paramagnetic ions is subject to a uniform magnetic field. We demonstrate, experimentally and theoretically, that no such magnetic body force exists, to first order. A second-order correction associated with the demagnetizing field does lead to a very small concentration-dependent body force, which is not expected to produce any observable effect in electrochemistry.

Introduction

The energy of a permanent magnetic moment **m** subject to a constant magnetic field **H** is $U = -\mu_0 \mathbf{m} \cdot \boldsymbol{H}$, where μ_0 is the permeability of free space. When a solution of susceptibility χ is subject to the magnetic field, a magnetization $\boldsymbol{M} = \chi \boldsymbol{H}$ is induced. Magnetization is the magnetic moment per unit volume. Hence, the energy density E_{mag}, of an electrolyte in the presence of a magnetic field is often written as

$$E_{\mathrm{mag}} = -(1/2)\mu_0 MH, \tag{1}$$

where the factor 1/2 arises because the magnetization M is not permanent, but it is induced by the field H, and lies parallel to it. The expression can as well be written as $E_{\mathrm{mag}} = -(1/2)MB$, where B is the flux density. In free space, $\boldsymbol{B} = \mu_0 \boldsymbol{H}$ [1].

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Differentiating the energy density gives a force density $\boldsymbol{F}_{\mathrm{mag}} = -\nabla E_{\mathrm{mag}}$. Writing $\chi = \chi^{water} + \chi_{mol} c$, where χ_{mol} is the molar susceptibility of the dissolved ions, c is their ionic concentration in mole per m^3 and χ^{water} is the susceptibility of water, we obtain

$$\boldsymbol{F}_{mag} = \mu_0 \chi H \nabla H + (\mu_0/2)\chi_{mol} H^2 \nabla c \tag{2}$$

The first term,

$$\boldsymbol{F}_{\nabla H} = \mu_0 \chi H \nabla H, \tag{3}$$

is the well-known field gradient force. When the applied field is non-uniform, the paramagnetic ions are drawn towards regions of higher field, where they can lower their potential energy. Here $H = |\boldsymbol{H}|$. The second term,

$$\boldsymbol{F}_{\nabla c} = (\mu_0/2)\chi_{mol} H^2 \nabla c \tag{4}$$

is a force that is thought to arise when a uniform magnetic field acts on a non-uniform concentration of magnetic ions, such as exists near the electrode in the diffusion layer. If this were a body force, related to potential energy, it would tend to inhibit diffusion and confine the ions, as it acts in the direction of increasing c.

In addition, when an electric current density j flows, there is the Lorentz force per unit volume, $\boldsymbol{F}_{\mathrm{L}}$,

$$\boldsymbol{F}_{\mathrm{L}} = \boldsymbol{j} \times \boldsymbol{B} \tag{5}$$

There are some short reviews of the influence of magnetic fields in electrochemistry [2–4]. Numerous experimental reports show clearly the effects of the field gradient force [5–7] and the Lorentz force [8–11]. However, the concentration gradient force is controversial. It was introduced by Waskaas [12] to account for the influence of a magnetic field on diffusion through a membrane. Waskaas and Kharkats [13, 14] subsequently invoked the concentration gradient force to account for the

shift of the rest potential of ferromagnetic electrodes in a magnetic field.

It has been discussed in relation to convection in solutions containing paramagnetic ions by O'Brien and Santhanam [15] and Rabah et al. [16] and solutions with functionalized nanoparticles and paramagnetic ions by Chen, Yang et al. [17, 18]. Krause et al. [19] have attributed a decreased rate of electrodeposition of cobalt in a field applied perpendicular to the electrode to $F_{\nabla c}$. Bund and Kuehnlein associated the corrosion of recessed micro-electrodes partly with this force [20]. Most recently, Leventis and Dass [21] have claimed that the concentration gradient force can counteract gravity in the diffusion layer, showing that the weight of paramagnetic electrolyte supported magnetically scales as B^2.

On the other hand, Grant et al. explained the magnetic support of paramagnetic ions using only the Lorentz force and the field gradient force [22]. Hinds et al. [23] pointed out that the concentration gradient force (Eq. 4), like the entropic force driving diffusion $F_D=RT\nabla c$, is proportional to, and directed along ∇c. The ratio of the two terms, $\mu_0\chi_{mol}H^2/2RT$, is of order 10^{-4} to 10^{-5} in one-molar solutions, and so they argued that $F_{\nabla c}$ should have a negligible effect on diffusion or mass transport. Efficient convective mass transport results when Lorentz force or gravity act in a direction perpendicular to ∇c. Several authors [20, 21] however have signaled a difference between F_D and $F_{\nabla c}$ stating that the latter, unlike the former, is a body force, which can modify convection.

Here we demonstrate, experimentally and theoretically, that the quantity given by Eq. 4 is *not* a body force, and that it has no effect on paramagnetic or diamagnetic solutions. The term disappears when the correct expression is used for the free energy. There is a second-order concentration gradient force related to the demagnetizing field, but this is negligible in the paramagnetic or diamagnetic solutions used in electrochemistry, although it is significant in ferrofluids.

Susceptibility

It is useful to begin by considering the definitions and magnitudes of the magnetic susceptibility of solutions, as this can be a source of some confusion. For clarity, we use SI units, which permit the dimensions of any combination of quantities to be determined by inspection. Solutions are isotropic, so susceptibility is scalar.

The dimensionless susceptibility χ is the ratio of the magnetization of a sample to the field which induces it; $\chi=M/H$. Magnetic moment m has units Am^2, so M and H each have units Am^{-1}.

It is often convenient to consider unit mass of sample, or a mole of material, rather than unit volume. The susceptibility is then no longer dimensionless. The mass susceptibility χ_m is χ/ρ, where ρ is the density in kilogram per m^3. Unit of χ_m is therefore cubic meter per kilogram (m^3 kg^{-1}). Water is diamagnetic, with dimensionless susceptibility $\chi^{water}=-9.0$ 10^{-6}, a value which is practically independent of temperature. The mass susceptibility is $\chi_m^{water} = -9.0 \cdot 10^{-9} m^3 kg^{-1}$, as the density of water is 1,000 kg m^{-3}.

The susceptibility of isolated ions with unpaired electrons is paramagnetic, varying as inverse temperature according to the Curie law. For a mole of ions with noninteracting, spin-only moments, the molar susceptibility is $\chi_{mol}=C_{mol}/T$, where the Curie constant $C_{mol} = \mu_0 N_A g'^2 \mu_B^2 S(S+1)/3k_B$. Here N_A is Avogadro's number, μ_B is the Bohr magneton, k_B is Boltzmann's constant and $g'=2$ if the ion has a purely spin moment with 2S unpaired electrons. The Curie constant has dimensions of temperature, and it can be written as

$$C_{mol} = 1.571 \cdot 10^{-6} p_{eff}^2,$$

where the effective Bohr magneton number $p_{eff} = g'[S(S+1)]^{1/2}$. Hence, the susceptibility of a liter of solution of molarity c_{mol} is $-9 \cdot 10^{-9} + c_{mol}\chi_{mol}$. The dimensionless susceptibility of the solution is

$$\chi^{soln} = -9.0 \cdot 10^{-6} + cC_{mol}/T$$

where c is the concentration in mole per cubic meter (mol m^{-3}). For example, c for a one-molar solution is $\approx 1,000$.

Table 1 lists data for ions with different values of S, and it includes the susceptibility of a 1-molar solution at 295 K as an example. There is a concentration where the paramagnetic contribution of the ions just cancels the diamagnetic susceptibility of water, and the net susceptibility of the solution is zero. For ions such as Cu^{2+} with $S=1/2$, this crossover concentration is 0.57 M. From the table, it can be seen that the order of magnitude of χ^{soln} for one-molar solutions of 3d ions is 10^{-5} to 10^{-4}.

When the solution is not dilute, there are dipolar and exchange interactions between the ions, which modify the susceptibility. These interactions can be represented by

Table 1 Susceptibility of ions and ionic solutions at 295 K

Ion	Configuration	S	p_{eff}^2*	χ_{mol} (m^3 mol^{-1})	χ^{soln} (1 mol)
Ti^{3+} V^{2+} Cu^{2+}	3d^1, 3d^9	1/2	3	15.7×10^{-9}	6.7×10^{-6}
V^{3+}, Ni^{2+}	3d^2, 3d^8	1	8	41.9	32.9
Cr^{3+}, Co^{2+}	3d^3, 3d^7	3/2	15	78.6	69.6
Mn^{3+}, Fe^{2+}	3d^4, 3d^8	2	24	125.7	116.7
Mn^{2+}, Fe^{3+}	3d^5	5/2	35	183.3	174.3

* assuming g'=2

internal magnetic fields. Exchange is represented by a "molecular field." Dipolar interactions are represented by a demagnetizing field $H_d = -NM$, where the demagnetizing factor N is a number between 0 and 1, which depends on the shape of the magnetized region. For the solutions used in electrochemistry, the demagnetizing field $H_d = N\chi^{so\,ln}H$ is no more than 10^{-5} to 10^{-4} times the applied field H, and it can generally be neglected. For magnetic liquids such as ferrofluids whose susceptibility is much higher, 10^{-1} or more, this is no longer the case.

The flux density B, measured in tesla (T), is related to the magnetization and magnetic field at a point by $B = \mu_0(H + M)$; μ_0 is $4\pi\,10^{-7}\,TmA^{-1}$. In free space, $M = 0$ and $B = \mu_0 H$.

Experiments

Solutions were prepared from 99% pure $CoCl_2$ and deionized water. The natural pH of the paramagnetic solution resulting from the mixture of 1.5 M $CoCl_2$ and water is about 7. The susceptibility of the solution (χ^{soln}) is 109×10^{-6}, and its density is 1,160 kg m^{-3}. A large electromagnet was used (pole face diameter 200 mm, airgap 50 mm), which produces a horizontal field $\mu_0 H$ of up to 1.5 T that is homogeneous to better than one part in 10^3 over a volume of 30 cm^3 at the center ($\mu_0 \nabla H < 0.05$ T m^{-1}). All experiments were conducted in passive conditions, with no corrosion or electrodeposition, hence, no Lorentz force.

1) First, consider a simple experiment (Fig. 1a). A long tube with open ends is half-filled with carbon tetrachloride and topped up with the $CoCl_2$ solution. The long tube is then placed horizontally, with the interface between the liquids at the center of the airgap of an electromagnet. On switching on the field, in either direction, the interface is drawn along the tube until $CoCl_2$ fills the segment of the tube in the airgap.

The field gradient force acts on the $CoCl_2$ which is subject to the fringing field of the electromagnet. Integrating Eq. 3 along x over a cylindrical volume extending from a point a, where the field H is near-zero to a point b in the airgap, where H is constant, we find the force $f_{\nabla H} = (\mu_0/2)A\chi H_b^2$, where A is the cross-sectional area of the tube. Integrating Eq. 4 from a point d, where the concentration is c, to a point e, where it is zero, and multiplying by the cross-sectional area, A, yields the force, $f_{\nabla c} = -(\mu_0/2)A\chi_{mol}H^2 c = -(\mu_0/2)A\chi H_b^2 = f_{\nabla H}$. The forces given by Eqs. 3 and 4 are equal and opposite. If both existed, the liquid would not move when the field was switched on. The argument is independent of whether the interface is abrupt or diffuse, if the Co^{2+} ions diffuse some distance into the carbon tetrachloride.
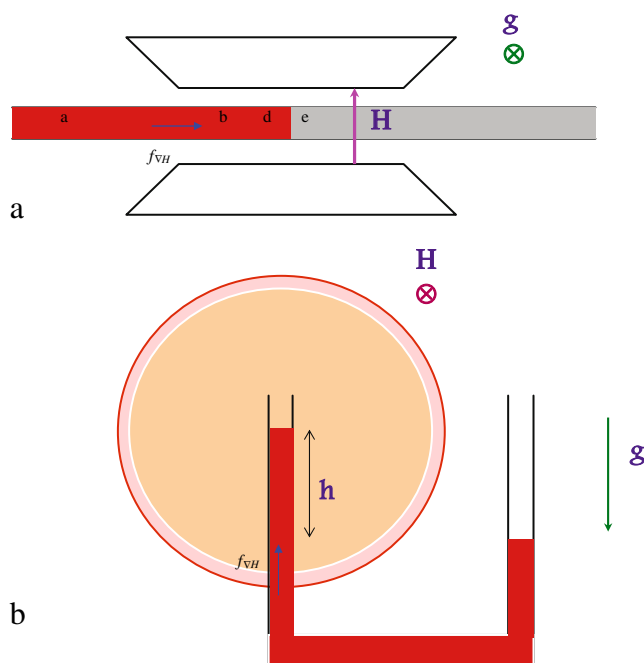
Fig. 1 Experimental configurations for observing the magnetic force on paramagnetic liquids. **a** Horizontal tube with an interface between paramagnetic and nonmagnetic liquids placed in the airgap of an electromagnet; **b** Quincke's method of measuring magnetic susceptibility using a vertical U tube with one arm placed in the airgap of the magnet

A standard task for students is to measure the susceptibility of a paramagnetic liquid by Quincke's method (http://www.shef.ac.uk/physics/teaching/second/labscripts/G4.pdf), whereby a U tube is placed with one arm between the poles of the electromagnet, and the other arm is outside it (Fig. 1b). The force due to the fringing field draws the liquid up on the magnet side, and a column of liquid of height h is supported, which exerts a pressure equal to $f_{\nabla H}/A$. Hence, the susceptibility is deduced as $h\rho g/\mu_0 H^2$. For our example of 1.5 M $CoCl_2$ in 1.5 T, $h = 10$ mm. If there was a concentration gradient force ($f_{\nabla c} = -f_{\nabla H}$), it would act at the interface in the field to exactly balance $f_{\nabla H}$, and no student would ever have managed to measure susceptibility in this way.[1] Quincke's method would not work if there were a concentration gradient force!

2) A second, even simpler experiment is to observe a large drop of paramagnetic liquid placed on a teflon-coated horizontal surface at the center of the airgap. On turning on the field, no change of shape of the drop can be observed. The magnetic pressure related to Eq. 4 is $(\mu_0/2)\chi H^2$, or 98 N m^{-2} for the 1.5 M $CoCl_2$ in 1.5 T. This is comparable to the hydrostatic pressure in the drop. There is no evidence for the "magnetic pressure"

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[1] Again the interfaces can be sharp or diffuse; diffuse interfaces are achieved by adding identical drops of water, or some other solvent, above each free interface.

that would be expected if the concentration gradient force acted on the interface between the $CoCl_2$ droplet and air because there is no discernable influence of the field on the shape of the droplet.

3) A drop of the paramagnetic solution was introduced into a beaker of water at the center of the electromagnet, in the presence or absence of the 1.5 T field. The droplet disperses regardless of the presence of the field. No effect of the concentration gradient force (Eq. 4) or magnetic pressure on convection was observed. If the concentration gradient force was present, the droplet might be expected to hold its shape in the presence of a uniform magnetic field. No difference in the dispersion was observed when the field was switched on or off.

4) A final experiment demonstrates the confining effect of the field gradient force (Eq. 3), and its ability to inhibit convection. Two 1-mm-diameter iron wires and a 1-mm copper spacer were set into a disc of perspex, which was placed in a bath of water in the airgap of the magnet, as shown in Fig. 2. The $CoCl_2$ solution was then injected into the water with a syringe, and the solution is trapped in three positions by the field gradient produced by the iron wires embedded in the plastic disc: between the wires, and to the left or to the right of them. The field gradient forces $F_{\nabla H}$ acting in this configuration are greater than 10^4 N m^{-3}, which is quite sufficient to inhibit

Fig. 2 Trapping of 1.5 M $CoCl_2$ solution injected into water in a nonhomogenous field produced by two Fe wires 1 mm in diameter. The *dashed line* in the *inset* corresponds to the interface between transoptic plastic and water. A spacer with 1 mm diameter spacer is placed between the Fe wires. Gravity is acting downward
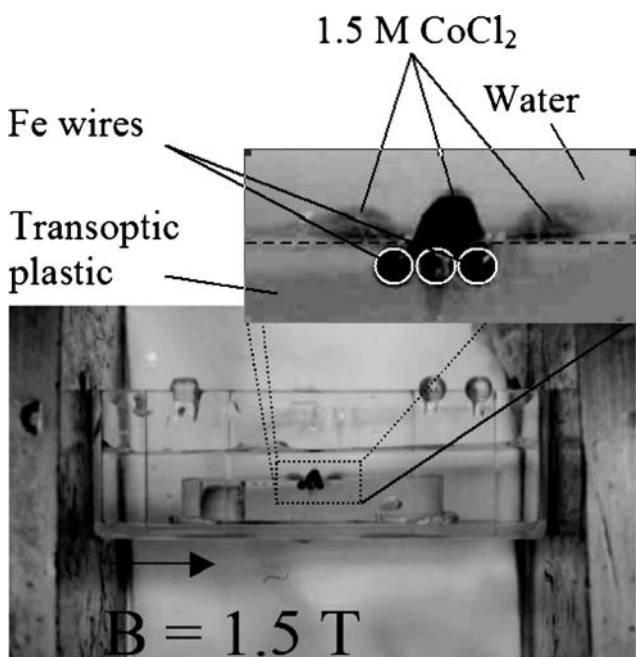
convection [24]. Forces of this magnitude are unable to impede diffusion, however, and we observed that as time passes the trapped paramagnetic solution eventually diffuses away. Further experiments indicate that the field gradient force is able to deform and hold paramagnetic droplets of $CoCl_2$, is water, but the concentration gradient force is not.

Discussion

The experiments provide no evidence for a concentration gradient force, so there must be something wrong with the derivation of Eq. 4. In fact, the magnetic energy density expression (Eq. 1) is not the correct one to calculate body forces. Two expressions are commonly used for magnetic work per unit volume [25]. One is $-\mu_0 H_0 \delta M$, where H_0 is the externally applied field, and M is the sample magnetization. This relates to a change of magnetic Gibbs free energy $G=U-TS-\mu_0 H_0 M$; $dG=-\mu_0 M dH_0 - S\, dT$ in which H_0 and T are the independent variables. The other expression, which should be integrated over all space, is $H\delta B$, where H and B are the fields inside the sample, and throughout the surrounding space.
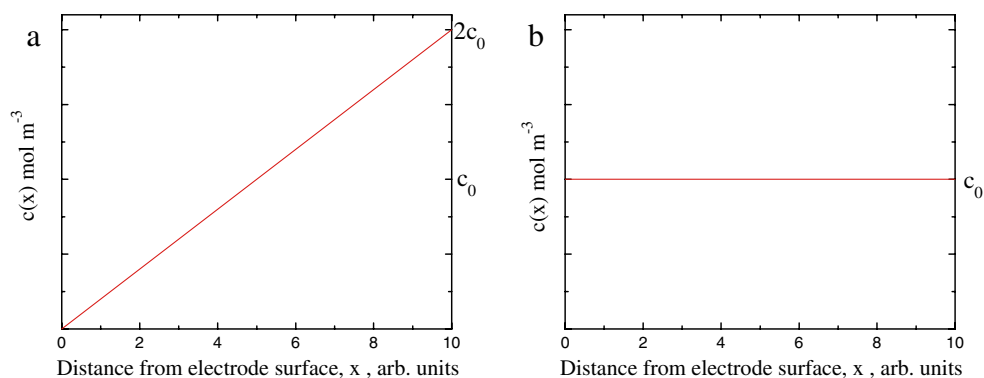
Considering further the first expression, which is more convenient because only the sample volume, where $M\neq 0$, has to be considered, a change in applied field leads to a change in free energy, and hence a body force. The magnetic energy density for a paramagnet is $E_{mag}=-(1/2)\mu_0 M H_0$. However, the magnetization of the sample depends on the internal field $H_{int}=H_0+H_d$, where $H_d=-NM$ is the demagnetizing field. The induced magnetization is χH_{int}, not χH_0. The internal susceptibility M/H_{int} is an intrinsic magnetic property of the material, given by the constitutive relation $M=M(H_{int})$, which is independent of such extraneous factors as sample shape. The divergent Curie law susceptibility at low temperature, for example, refers to the susceptibility in the internal field; the external susceptibility M/H_0 cannot exceed $1/N$.

We have argued that no force is associated with a concentration gradient in the presence of a uniform magnetic field. This is strictly true when the demagnetizing field can be ignored, as is the case in electrolytes. The demagnetizing field takes account of the dipole–dipole interactions among the ions in solution. The energy of an ion subject to a uniform external magnetic field H_0 is no longer independent of position. It interacts with the dipolar field H_d created by the ions in the surrounding medium, and so its energy depends on the local ionic concentration c. The effect is very small in paramagnetic solutions, because $H_d/H_0\approx H_d/H_{int}=Nc\chi_{mol}$ is of order 10^{-4} (Table 1), but it is

Fig. 3 Two concentration profiles: a uniform concentration gradient (**a**) and a uniform concentration (**b**)

important in ferromagnetic solids and ferrofluids. The energy of an ion depends on the internal field to which it is subjected, and this field $H_{int}=H_0+H_d$ depends on position if there is a concentration gradient, even when H_0 is uniform. We have

$$H_{int} = H_0 - Nc\chi_{mol}H_{int} \approx (1 - Nc\chi_{mol})H_0 \qquad (7)$$

Consider a region of space, such as the diffusion layer, of cross-sectional area A, where there is a concentration gradient $c(x)$, as shown in Fig. 3. The energy density at position x is

$$E(x) = -(\mu_0/2)c\chi_{mol}(1 - Nc\chi_{mol})H_0^2$$

Comparing (a) a linear concentration profile $c(x)=2c_0x/x_0$ with (b) a uniform concentration profile $c(x)=c_0$ containing the same number of ions, we calculate the magnetic energy of the diffusion layer in the two cases:

$$\int E^a d^3r = -(\mu_0 c_0/x_0)A\chi_{mol}H_0^2 \int_0^{x0} (x - 2N\chi_{mol}c_0x^2/x_0)dx$$
$$= -(1/2)\mu_0 n\chi_{mol}H_0^2(1 - (4/3)Nc_0\chi_{mol})$$
$$\int E^b d^3r = -(1/2)\mu_0 n\chi_{mol}H_0^2(1 - Nc_0\chi_{mol})$$

Here $n=c_0Ax_0$ is the number of moles of ions in the diffusion layer. Note that the first term in the energy is the *same* in each case. There is no influence of a uniform applied field on the concentration profile to first order. It is only when $N\neq0$ that a difference in energy appears, which is due to the demagnetizing field. Furthermore, the uniform concentration profile is lower in energy. An effect of the demagnetizing field is to modify the concentration profile. The peaked structure adopted by the surface of a ferrofluid in a perpendicular applied field is a dramatic example of this effect [26].

The effect of the gradient of demagnetizing field can be represented by a body force by putting $\nabla H_d=-N\chi H\nabla c$ in Eq. 3:

$$F_{\nabla Hd} = \mu_0 c^2\chi_{mol}^2 H_0^2 N(\nabla c/c) \qquad (8)$$

In Quincke's experiment (Fig. 1b), there is a force acting at interface in the horizontal field, $f_{\nabla Hd} = -\mu_0 c^2\chi_{mol}^2 H_0^2 NA$, where $N=1/2$ for a tube with circular cross-section. Its effect is to decrease the height of the 10-mm supported column of $CoCl_2$ by just 1 μm.

If the diffusion layer has thickness 0.1 mm, $(1/c)\nabla c=10^4$, and if $c\chi_{mol}=10^{-4}$ and $\mu_0H_0=1.5$ T, the magnitude of this force is only 10^{-4} N m^{-3} when H_0 is perpendicular to the electrode surface layer ($N=1$), and zero when the field is parallel to the electrode surface ($N=0$). In regions where there are very large concentration gradients, in the double layer for instance, we can expect much greater force *densities*, but the *total* force acting on the layer is similar regardless of its thickness. It is $\approx10^{-8}$ N m^{-2}.

For comparison, typical field gradient forces $F_{\nabla H} = \mu_0\chi H_{int}\nabla H_{int}$ in the fringing field of an electromagnet where $\mu_0\nabla H_0 \approx100$ T m^{-1} and $\mu_0H_0\approx1.5$ T, are of order 10^4 N m^{-3} for $\chi\approx10^{-4}$. In supposedly uniform magnetic fields created by electromagnets, there may be gradients of approximately 0.1 T m^{-1} over the electrochemical cell, producing body forces of order 10 N m^{-3}, which scale as B^2. These are quite sufficient to influence convection, which if driven by density differences of 1% involves forces of order 100 N m^{-3}. It seems likely that some of the effects that have been attributed to a "concentration gradient force" actually have their origin in non-uniformity of the magnetic fields produced by electromagnets. Other effects, such as the magnetic rest potential shift, are due to the Lorentz force, acting on small-scale current flows in the vicinity of the electrode [11]. The Lorentz forces on current densities of 10^3 A m^{-2} in 1 T are 1,000 N m^{-3}.

The correct expression for the force on a paramagnetic or diamagnetic liquid in a magnetic field is not Eq. 2; at constant temperature, uniform pressure and in the absence of conduction currents it is given by the expression [27]:

$$\boldsymbol{F}_{\text{mag}} = (\mu_0/2)\boldsymbol{\nabla}\left[H^2\rho(\partial\chi/\partial\rho)\right] - (\mu_0/2)H^2\boldsymbol{\nabla}\chi. \qquad (9)$$

When the susceptibility is isotropic and depends linearly on density, $\chi=\alpha\rho$, this reduces to the Kelvin force [28],[2]

$$\boldsymbol{F}_{\text{mag}} = \mu_0 M\boldsymbol{\nabla}H_{int}, \qquad (10)$$

where H_{int} is the magnitude of the internal field. This, and not Eq. 2, is the correct expression for the force on the electrolyte. The force on a paramagnet is in the direction of the gradient of the magnitude of the field. Equation 10 is identical to the field gradient force Eq. 3, as $M=\chi H_{\text{int}}$. Equation 8 is also consistent with this expression.

There has been some controversy recently [29] arising from a suggestion, based on measurements on ferrofluids, that Eq. 10 should be replaced by $\boldsymbol{F}_{\text{mag}}=M\nabla B$. For our purposes, the expressions are indistinguishable, as if they differ at all [30], it is by no more than one part in χ^{-1}. Hence, there is no force in a uniform magnetic field, and no force depending on concentration gradient, other than that related to the demagnetizing field, discussed above.

A very simple demonstration that no magnetic concentration gradient force exists uses the pole representation of magnetized material. An arbitrary distribution of magnetization can be represented mathematically by a certain distribution of magnetic "poles" (the North and South poles of elementary school texts). The force on a magnetic pole q_{m} is $\mu_0 q_{\text{m}}\boldsymbol{H}$. Poles arise whenever the magnetization density is non-uniform, and the pole density ρ_{m} is $-\boldsymbol{\nabla}\cdot\boldsymbol{M}$, where $\boldsymbol{M}$ is the magnetization. In particular, they appear at surfaces where $M_\perp$ is discontinuous. The force density acting on a region of non-uniform magnetization is, therefore,

$$\boldsymbol{F}_{\text{mag}} = -\mu_0(\boldsymbol{\nabla}\cdot\mathbf{M})\mathbf{H} \qquad (11)$$

Now the flux density $\boldsymbol{B}$ is related to $\boldsymbol{M}$ and $\boldsymbol{H}$ by $\boldsymbol{B}=\mu_0(\boldsymbol{H}+\boldsymbol{M})$, and $\boldsymbol{B}$ is divergenceless, according to

Maxwell's equation $\boldsymbol{\nabla}\cdot\boldsymbol{B}=0$. Hence $\boldsymbol{F}_{\text{mag}}=\mu_0(\boldsymbol{\nabla}\cdot\boldsymbol{H})\boldsymbol{H}$, which is zero whenever $\boldsymbol{H}$ is uniform.

Finally, we mention the possibility of formally expressing the magnetic force $\boldsymbol{F}_{\text{mag}}$ in terms of the concentration gradient.

The net force on a volume of liquid given by Eq. 10 is

$$\mathbf{f}_{mag} = \int_v \boldsymbol{F}_{\text{mag}} d^3r = (\mu_0/2)\int_v \chi\boldsymbol{\nabla}H^2 d^3r$$

If the susceptibility is uniform, using Gauss' theorem, this can be transformed into an integral over the boundary surface, with the susceptibility remaining outside the integral.

$$\mathbf{f}_{mag} = (\mu_0/2)\chi\int_s H^2\mathbf{e}_n d^2r$$

where $\mathbf{e}_{\text{n}}$ is the outward normal. In the case of the U tube in Fig. 1b, for example, the only surface on which there is a net force is the upper cross-section in the field. Therefore, the total force upward is $(\mu_0/2)\chi H^2 A$. This might be regarded as a concentration-gradient force $-(\mu_0/2)\chi_{\text{mol}}H^2 cA$ on the surface, which is exposed to a uniform horizontal field. This is an alternative way of regarding the body force of Eq. 3. It is not an additional term.

Conclusions

To first order in the susceptibility, *there is no concentration gradient force on a diamagnetic or paramagnetic solution subject to a uniform magnetic field*. There is, however, a second-order term in χ^2 related to the nonuniformity of the demagnetizing field, which does produce a very small concentration gradient force, directed perpendicular to the electrode surface. The effect of the demagnetizing force on diffusion is negligible—the diffusion constant is modified by one part in 10^8 for a 1 M solution in a field of 1 T. The effect on convection is likewise negligible, because the force is tiny, and it has no component parallel to the electrode surface.

There must be some other explanations for the effects that have been attributed in the literature to the 'concentration gradient force' of Eq. 4. Possibilities are forces due to small magnetic field gradients over the electrolytic cells, or secondary effects of the Lorentz force.

The energy of concentrated solutions are modified to some extent by exchange interactions, as shown by a concentration dependence of χ_{mol}. At the average distance between ions in a 1-molar solution, 1.2 nm, exchange interactions are supposedly negligible, but the random formation of ion pairs and clusters might have some

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[2] This can be written as $\boldsymbol{F}=\mu_0 M_{\text{j}}\boldsymbol{\nabla}H_{\text{j}}$, or in component form, $F_{\text{i}}=\mu_0 M_{\text{j}}\partial H_{\text{j}}/\partial x_{\text{i}}$, with a sum over repeated indices. It is only correct to write the Kelvin force as $\boldsymbol{F}=\mu_0(\boldsymbol{M}\cdot\boldsymbol{\nabla})\boldsymbol{H}$ when $\boldsymbol{H}$ and $\boldsymbol{\nabla}H$ are parallel. This is not usually the case; in Fig 1b, for example, $\boldsymbol{H}$ is horizontal, but $\boldsymbol{\nabla}H$ is vertical.

measurable consequences. This possibility merits further investigation.

List of quantities and symbols

A	Area	m^2
B	Magnetic flux density	T
c	Electrolyte concentration	$mol\ m^{-3}$
C	Curie constant	K
E	Energy density	$J\ m^{-3}$
f	Force	N
F	Force density	$N\ m^{-3}$
g	Acceleration due to gravity	$9.8\ m\ s^{-2}$
g′	g-factor	–
H	Magnetic field	$A\ m^{-1}$
j	Electric current density	$A\ m^{-2}$
k_B	Boltzmann's constant	$1.38 \cdot 10^{-23}\ J\ k^{-1}$
m	Magnetic moment	$A\ m^2$
M	Magnetization	$A\ m^{-1}$
N	Demagnetizing factor	$0 \leq N \leq 1$
p_{eff}	Effective Bohr magneton number	
q_m	Magnetic pole strength	$N\ T^{-1}$
S	Ion spin number	n/2; n integral
T	Temperature	K
U	Energy	J
χ	Dimensionless susceptibility	–
χ_m	Mass susceptibility	$m^3\ kg^{-1}$
μ_B	Bohr magneton	$9.27 \times 10^{-24}\ A\ m^2$
μ_0	Magnetic constant	$4\pi\ 10^{-7}\ T\ m\ A^{-1}$
ρ	Density	$kg\ m^{-3}$
ρ_m	Magnetic pole density	$N\ T^{-1}\ m^{-3}$

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