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HYPERFILTRATION-INDUCED FRACTIONATION OF LITHIUM ISOTOPES IN GEOLOGIC SYSTEMS

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ABSTRACT

Effective modeling of hyperfiltration-induced fractionation of lithium isotopes is hindered by a lack of data concerning aqueous diffusion coefficients of ${}^6\text{Li}^+$ and ${}^7\text{Li}^+$. Several experiments were conducted this past year concerning fractionation of lithium isotopes. Reported here are results from the most successful of these which yielded a value for the ratio of diffusion coefficients between $D_{{}^6\text{Li}^+\text{Cl}^-}/D_{{}^7\text{Li}^+\text{Cl}^-}$.

A 0.9450 molal LiCl solution was placed within sealed dialysis tubing and osmoted against a kilogram of deionized water at 22° C. Osmotic equilibrium occurred at 143 minutes, and the ratio of $\omega_{{}^6\text{Li}^+\text{Cl}^-}/\omega_{{}^7\text{Li}^+\text{Cl}^-}$ was measured to be 1.011. Because this experimentally-determined value is very close to the square root of the mass ratio between ${}^7\text{LiCl}$ and ${}^6\text{LiCl}$ ($= 1.012$), then Graham's Law may be a convenient way to calculate such ratios in the absence of data for aqueous diffusion coefficients of individual isotopic components comprising the solute of interest.

In the evolution of this closed-system osmotic cell as a function of time, the Li isotopic ratios of the beaker and bag solutions exhibit a minimum and a maximum before the ${}^6\text{Li}/{}^7\text{Li}$ ratios of both solutions assume the inevitable asymptotic approach toward isotopic equilibrium. The maximum difference in the ${}^6\text{Li}/{}^7\text{Li}$ ratio between the beaker and bag solution was 0.00156 (± 0.00015).

ACTIVITIES SINCE START OF GRANT (APRIL 1, 1991)

Effective modeling of hyperfiltration-induced fractionation of solute isotopes is hindered by a lack of data for diffusion coefficients of isotopic components comprising those solutes. Lithium provides a case in point. Utilizing concatenation of key words ('lithium', 'isotope', 'diffusion coefficient') in computer-aided searches of ChemAbstracts, GeoRef, GeoBase, and GeoArchive data bases, this author found only a single study in which the $D^{6}\text{Li}^{+}\text{Cl}^{-}/D^{7}\text{Li}^{+}\text{Cl}^{-}$ was quoted. Barr and Elmessiery (1979) extrapolated Kunze and Fuoss' (1962) conductance data for $^{6}\text{LiCl}$ and $^{7}\text{LiCl}$ to infinite dilution, thereby computing a $D^{6}\text{Li}^{+}\text{Cl}^{-}/D^{7}\text{Li}^{+}\text{Cl}^{-}$ ratio of 1.0035 based on the ratio of their limiting conductances. Described herein is a simple experiment involving dialysis tubing in which the ratio of diffusion coefficients for ^{6}Li and ^{7}Li in a LiCl solution is measured directly. The results show that the measured ratio of $\omega_{6}\text{Li}^{+}\text{Cl}^{-}/\omega_{7}\text{Li}^{+}\text{Cl}^{-}$ (assumed to be equivalent to $D^{6}\text{Li}^{+}\text{Cl}^{-}/D^{7}\text{Li}^{+}\text{Cl}^{-}$) is within 0.001 of this ratio as calculated by Graham's Law.

METHODS

Concentrations of all lithium chloride solutions were analyzed by potentiometric titration for the chloride ion with AgNO_3 in the presence of a $\text{Ag}^{+}/\text{S}^{2-}$ specific-ion electrode. Solutions to be titrated were weighed on a top-loading balance having a readability of ± 0.01 grams. Normality of the AgNO_3 was 0.01958 (± 0.00007) N, and the titrant was delivered from a 10-ml automatic buret graduated in units of 0.05 ml. With repeated practice, the sharp potentiometric endpoints for these titrations were attained with a precision of 0.025 ml. To minimize the relative error of titration, most solutions were

weighed out in amounts that anticipated an endpoint volume close to the graduated 10-ml capacity of the buret. Since the titrated solutions were measured out gravimetrically, density corrections were made for titration results of concentrated solutions of LiCl. Densities for various dilutions of the LiCl stock solutions were performed by a pycnometer which was weighed on an analytical balance to the nearest 0.0001 gram. The following equation relates volume (V in liters) of LiCl solution at 22°C versus the moles of LiCl per kilogram of water (n):

$$V = 1.001 + 0.01389 \cdot n + 0.003145 \cdot n^2. \quad (1)$$

A 0.9088 Formal aqueous solution of lithium chloride was prepared from reagent-grade LiCl. This stock solution was funnelled into a 45-mm diameter dialysis tubing (pre-soaked in deionized water) and tied off at one end. After filling about half of the tubing with the stock solution, the other end was knotted. No air bubbles were entrapped. The filled bag was weighed to the nearest 0.01 gram and the net weight of solution (45.93 g) was obtained by subtracting the weight of the soaked bag prior to its receiving the solution. Thus the initial mass of the LiCl in the bag/beaker system was 41,740 μ moles (= 908.8 mF x 45.93g). The dialysis tubing (Spectra/Por) has a molecular-weight cutoff of 3500. Micrometer measurements of a single ply of the wetted sheet gave a thickness of 0.005 cm. A later hydraulic conductivity measurement of this sheeting gave a single-measured value of 1.86×10^{-11} cm $\cdot$ sec $^{-1}$. Surface area of the dialysis bag is estimated to be 75 cm 2 .

The filled and sealed dialysis bag was placed into a 2-liter polyethylene beaker containing a large magnetic stirring bar and 1000.1 grams of deionized water whose initial conductivity was 1.143 μ mhos/cm. A combination conductivity/temperature probe (YSI Model 32) was placed into the beaker

solution to monitor these parameters during the run. The temperature of the beaker solution during the 10-hour run averaged $22.2 \pm 0.4^\circ\text{C}$. Measuring the conductivity of the beaker solution during the experiment provided an independent means to obtain this solution's LiCl concentration. Particularly valuable is the fact that conductivity can be read to 4 significant figures. The conductivity/concentration relationship was verified to be linear between 0.0001 and 0.1000 Formal LiCl. Calibration was performed at 22°C with gravimetric dilutions of the stock solution, and the following empirical equation relates LiCl formality (F_{LiCl}) to conductivity expressed in $\mu\text{mhos/cm}$:

$$F_{\text{LiCl}} = 10.09 \cdot (100.9962 \log[\text{cond}]) \quad (2)$$

The scheme to measure the ratio of diffusion coefficients for the two isotopes of lithium hinges on measuring the solute flux out of the bag when the net solution flux is zero. This dictates that the mass of solution in the dialysis bag be measured during the run. Accordingly, the bag was periodically withdrawn, daubed dry, weighed, then returned to the beaker. The timer clock was stopped whenever the bag was out of the beaker, and it resumed after the bag was put back into the beaker. During this interval two small aliquots were withdrawn--one for titration, the other for later analysis of the solution's $^6\text{Li}/^7\text{Li}$ ratio. A meticulous bookkeeping accounted for all but 1 gram of the 45 grams of mass lost from the beaker due to withdrawal of aliquots, evaporation, and daubing the dialysis bag prior to weighing it.

Isotopic analyses were performed at the Analytical Chemistry Division of Argonne National Laboratory on a VG-Isomass 54R thermal ionization mass spectrometer. Forty nanograms of lithium are loaded onto the filament, and the reported $^6\text{Li}/^7\text{Li}$ ratio is an average of 50 readings within the 90 minute sample run. Their reported precision of ± 0.00015 is based upon repeated

analyses of a Li_2CO_3 standard obtained from NBS. Flesch *et al* (1973) reported a ratio of 0.0832 ± 0.0002 for this material. Just prior to analyzing the LiCl precipitates from this experiment, the ACD performed 5 analyses of this standard and recorded an average $^6\text{Li}/^7\text{Li}$ ratio of 0.081149 ± 0.000059 . This compares favorably with the precision reported for the same standard (0.08281 ± 0.00007) by Chan and Edmond (1988).

RESULTS

Table 1 lists data from the run. Numbers in the table printed in bold type denote measured values; all other numbers were calculated from measured data. 'Stock' refers to the stock solution which is the concentration of LiCl in the dialysis bag at time equal to zero minutes. The last row entry, denoted as 'bag', refers to the solution in the dialysis bag at the termination of the experiment. Immediately after the last aliquot was withdrawn at 579 minutes, the dialysis bag was removed from the beaker and the contents sampled for LiCl content and analysis of the $^6\text{Li}/^7\text{Li}$ ratio. Within the limits of analytical uncertainty, chemical equilibrium was attained between the solution in the dialysis bag and the solution in the beaker at the 579-minute withdrawal (Table 1).

The $^6\text{Li}/^7\text{Li}$ ratio of the stock solution was 0.08059. Thus, of the 41,740 μmoles of LiCl in the bag at time equals zero minutes, $41,740/(1+0.08059)$ represents the micromoles of $^7\text{Li}^+$, and the remaining 3,113 micromoles are $^6\text{Li}^+$ (Table 2). One minute later the dialysis bag is removed, the beaker solution weighed, and then the two aliquots taken. The aliquot withdrawn for titration had a concentration of 1.17 mF, which (when multiplied by the beaker solution's pre-withdrawal net weight of 999.9 grams) translates to 1,170 micromoles of LiCl (Table 1). The accompanying aliquot was later measured to

have a ${}^6\text{Li}/{}^7\text{Li}$ ratio of 0.08159. This corresponds to 1,082 micromoles of ${}^7\text{Li}^+$ and 88 micromoles of ${}^6\text{Li}^+$. Thus, within the first minute, the dialysis bag has lost ${}^7\text{Li}^+$ and ${}^6\text{Li}^+$ equivalent to the amount gained by the beaker solution. Since the masses of both the beaker and bag solutions are known, then the concentrations of ${}^7\text{Li}^+$ and ${}^6\text{Li}^+$ can be computed on a mass basis, either as molality or formality, or in molarity via a density calculation.

With subsequent withdrawals, the mass lost from the beaker solution is recorded along with LiCl concentrations of those aliquots. This permits a continuous ledger-like accounting for mass of both water and solute. At any stage during the run, the micromolar sum of LiCl in the bag, the beaker, and the aliquots always added to within 10 micromoles of LiCl in the dialysis bag at the beginning of the experiment.

Figures 1a and 1b show that the diffusion of both isotopes out of the dialysis bag follows a first-order rate law, where n is the moles at any time (t in minutes), and n_0 and n_e are moles at t_0 and t_e (equilibrium), respectively.

$$n_{\text{Bag}} = (n_0 - n_e) \cdot \exp[-a \cdot t] + n_e. \quad (3)$$

For example 6n_0 is 0.003113 moles, corresponding to the starting mass for ${}^6\text{Li}^+$ in the bag, and 6n_e is the computed mass of this isotope in the bag at 579 minutes. Gain of solute mass in the beaker solution with time also conforms to a first-order rate law:

$$n_{\text{Bkr}} = n_e \cdot (1 - \exp[-b \cdot t]). \quad (4)$$

The errors associated with constructing these empirical equations are almost entirely based on the uncertainties of two measurements: the ${}^6\text{Li}/{}^7\text{Li}$ ratio and the LiCl concentration of the accompanying aliquot. Each isotopic ratio has a reported analytical uncertainty of ± 0.00015 . Although this

uncertainty is not insignificant, the level of this error in mass-balance calculations is overshadowed by the error in computing the moles of LiCl in the dialysis bag as the experiment progresses. This is especially true if the mass of solute in the bag is calculated from titration data. The first 3 withdrawals have large uncertainties for LiCl concentration because the potentiometric endpoint for the titration of these aliquots took less than 1 ml of the silver nitrate titrant. However, the large relative errors (between 4 and 17%) of the beaker solution's LiCl concentration translate to relative small errors in calculating the micromoles of LiCl in the bag at these early withdrawals due to the fact that the solute ratio between the bag and beaker solutions is greater than 10 during the first few effluents. The relative error of the beaker's LiCl reported concentration decreases in later effluents because the LiCl concentration of the beaker solution goes up, translating to higher volumes of the titrant necessary to achieve the potentiometric endpoint.

In terms of error, the important figures are not the percent relative errors, but rather the absolute magnitude of the spread of values about the reported median. Table 2 shows the range of data for $^6\text{Li}^+$ and $^7\text{Li}^+$ in both the beaker and bag solutions at each aliquot. These ranges take into account the $\pm$ uncertainties of the $^6\text{Li}/^7\text{Li}$ ratio, the titration volume, and the net weights of the beaker and bag solutions. The median value was used to compute the coefficients for equations 3 and 4, and these coefficients are listed in Figure 1 as well as in Table 2. Linearizing these 4 equations to conform to a line plotted on semi-log graph paper result in linear correlation coefficients for all four equations greater than 0.9998 (Table 2).

If the concentrations of LiCl are derived from the conductivity data, then Table 2 shows that the spread for the uncertainties are much less than

that for the titration data. This is due to the fact that the conductivity measurements had a constant uncertainty of $\pm 5 \mu\text{mho/cm}$. However reduced the uncertainty for the values used to compute the coefficients of equations 3 and 4 for both isotopes of lithium, the conductivity-calculated concentrations for LiCl result in lower correlation coefficients for these 4 equations (Table 2).

Figure 2 depicts the variation of lithium's isotopic composition as a function of time. It appears that isotopic equilibrium has been achieved at 579 minutes as the difference between the measured $^6\text{Li}/^7\text{Li}$ ratios for the beaker and bag solutions (0.00017) is within the mutual overlap of the ± 0.00015 uncertainty reported for each measured ratio (Table 1). Equally encouraging is the close agreement between the measured $^6\text{Li}/^7\text{Li}$ ratio of the bag solution at equilibrium (0.08084) and the ratio for the bag solution at 579 minutes (0.08086) calculated with titration data and the reported $^6\text{Li}/^7\text{Li}$ ratios of the beaker solutions.

The lower mass lithium-6 cation should have a higher diffusion coefficient than lithium-7. As such, $^6\text{Li}^+$ would diffuse out of the bag faster than $^7\text{Li}^+$. And Figure 2 does indeed show this to be true as the very first effluent (1 minute) has the highest $^6\text{Li}/^7\text{Li}$ ratio of any of the 9 aliquots sampled from the beaker. The isotopic composition of the bag solution in the first few effluents is scantily different from the $^6\text{Li}/^7\text{Li}$ of the stock solution because only a tiny fraction of the bag's solute has diffused out of the bag.

Because $^6\text{Li}^+$ should diffuse out of the bag faster than $^7\text{Li}^+$, and also because the equilibrium $^6\text{Li}/^7\text{Li}$ ratio of the beaker solution must match that of the bag's starting solution in a closed system, then one would expect that the bag solution exhibit a 'bottoming out' of its $^6\text{Li}/^7\text{Li}$ ratio sometime during the system's evolution to equilibrium (Fig. 2). Unexpected though was the reversal of the $^6\text{Li}/^7\text{Li}$ ratio for the beaker solution which is manifested by an increase

of the $^6\text{Li}/^7\text{Li}$ ratio between the 7-minute and the 63-minute withdrawals. This phenomenon is explained by the lowering of the $^6\text{Li}^+/^7\text{Li}^+$ concentration gradient in the early stages of the experiment. This causes a momentary drop in the ratio of the accelerations between $^6\text{Li}^+$ and $^7\text{Li}^+$ through the membrane out into the beaker solution.

If time-vs-mass relationships of $^6\text{Li}^+$ and $^7\text{Li}^+$ in the bag and beaker solutions are correctly portrayed by equations 3 and 4, then the $^6\text{Li}/^7\text{Li}$ ratios of the beaker solution should never be below the bag solution's initial $^6\text{Li}/^7\text{Li}$ ratio of 0.08059. And they aren't (Table 1, Figure 2). Correspondingly, the $^6\text{Li}/^7\text{Li}$ ratio of the bag solution should never be above 0.08059. The *calculated* $^6\text{Li}/^7\text{Li}$ ratio of the bag solution lies above this figure for the last two withdrawals due, most probably, to levels of uncertainty which increase with ensuing withdrawals. Yet the actual $^6\text{Li}/^7\text{Li}$ measurement for the bag solution exceeds that of the last measured effluent (Table 1).

DISCUSSION

The physico-chemical evolution of an osmotic cell is described in length by Fritz (1986). A brief synopsis is given here to explain the meaning of 'osmotic equilibrium'--the key event in the life of an osmotic cell. Analogous to the short period of a total eclipse affording a fleeting opportunity to observe the sun's corona, the brief interval of osmotic equilibrium permits measuring the solute flux out of the membrane when there is no net solution flux across the boundary.

Phenomenological Coefficients

The birth, longevity, and ultimate demise of an osmotic cell are manifested by fluxes of solute and solvent through the membrane. And these fluxes are generated by hydraulic and chemical-potential gradients. The

interplays between the forces and fluxes in a membrane system are mediated by 3 phenomenological coefficients: L_p , σ , and ω . Taken together, the following two equations succinctly describe the evolution of an osmotic cell in an isothermal system having no imposed electrical gradients.

$$J_v = L_p \cdot \Delta P - \sigma \cdot L_p \cdot \Delta \Pi, \text{ and} \quad (5)$$

$$J_s = C_s \cdot (1 - \sigma) \cdot J_v - \omega \cdot \Delta \Pi. \quad (6)$$

Here, C_s (in $\text{mole} \cdot \text{cm}^{-3}$) is the average solute concentration on opposing sides of the membrane, equivalent to $(C_{\text{Bag}} + C_{\text{Beaker}})/2$. J_v is the solution flux in $\text{cm} \cdot \text{sec}^{-1}$, and ΔP (in $\text{dyne} \cdot \text{cm}^{-2}$) is the hydraulic pressure difference between the bag and beaker solutions. The filtration coefficient, L_p , is related to the hydraulic conductivity coefficient of Darcy's Law, K , by dividing K by the gravitational constant, g , the density of the permeating solution, ρ , and the thickness of the membrane, Δx . The single measurement for K of $1.86 \times 10^{-11} \text{ cm} \cdot \text{sec}^{-1}$ thus translates to a value for L_p of $3.80 \times 10^{-12} \text{ cm}^3 \cdot \text{dyne}^{-1} \cdot \text{sec}^{-1}$ for the 0.005-cm thick tubing. The osmotic pressure, $\Delta \Pi$, is calculated as:

$$\Delta \Pi = vRT \cdot \Delta C, \quad (7)$$

where R is the gas constant ($8.314 \times 10^7 \text{ dyne} \cdot \text{cm} \cdot \text{mole}^{-1} \cdot ^\circ\text{K}^{-1}$), T is temperature in $^\circ\text{K}$, ΔC is the concentration difference across the membrane in $\text{mole} \cdot \text{cm}^{-3}$, and v is the number of component ions of the dissolved solute. For 1:1 salts like LiCl, v equals 2.

The 3 phenomenological coefficients (σ , L_p , and ω) in equations 5 and 6 control the kinetic responses of the membrane in different ways. Of these 3, the reflection coefficient (σ) is the most important because its value translates directly to the all-important consideration of ideality. Should σ be zero, then consideration of the other 2 phenomenological coefficients is moot because

the porous medium is not acting like a membrane. If σ equals 1, then ω equals zero such that the membrane is ideal. In this case, solute can neither advect nor diffuse through the membrane (eqn. 6).

L_p dictates the sluggishness of response to fluid flowing through the membrane pores. Generally, low values of L_p translate to high values of σ because a membrane's ideality almost always increases with decreased porosity. Thus an extremely permeable barrier would have a sufficiently high porosity that the solute would not be retained relative to the passage of water. In other words, the σ for that material would be negligibly different from zero.

Osmotic systems are driven by the chemical potential gradient of solutes and solvent across the structure. Simply put: no concentration gradient, no osmosis, and no pressure buildup within the cell. Because all membranes are non-ideal, osmotic systems ultimately run down, and ω is instrumental in dictating the rate at which the membrane cell dies. That is, ω controls the rate at which solute diffuses out of the membrane to the point where the osmotic pressure becomes ineffectual as a hydraulic driving force.

Measurement of ω

A sign convention is adopted so that fluxes of both solution (J_v) and solute (J_s) are positive for transport into the bag and negative out of the bag into the beaker solution. This sign convention becomes geometrically apparent in examining Figure 3. The salt flux is equal to $(dn_s/dt)/\text{Area}$, or upon differentiating eqn. 3,

$$J_s = [-a \cdot (n_o - n_e) \cdot \exp[-a \cdot t]] / [\text{Bag Surface Area}]. \quad (8)$$

Thus J_s is always negative because the slope of any line tangential to the n_s -vs-time curve in Figure 3a is always negative.

Figure 3b depicts the net solution volume in the dialysis bag as a function of time. Volumes were computed from equation 1 using concentration and mass data. The volume/time data were fit to an equation having the following form:

$$V = [(V_e - V_o) + a \cdot \exp[-b \cdot t]] \cdot [1 - \exp[-c \cdot t]] + V_o, \quad (9)$$

where V_o is the initial volume of the bag solution (44.91 cm³), V_e is the bag volume at the termination of the run (48.67 cm³), and a , b , and c are empirical constants. Slopes of lines drawn tangential to the volume-vs-time curve in Fig. 3b are positive in the early stages of the experiment when the bag experiences a net gain of solution. Lines drawn tangential to this curve have negative slopes when the cell loses mass. In actuality, lines drawn tangential to the curve of Fig. 3b represent the solution flux multiplied by the area of the dialysis bag because $J_v = [(dV/dt)/\text{Area}]$.

Because $0 < \sigma < 1$, the dialysis bag functions as a membrane, thereby presenting an opportunity to measure the solute permeability coefficient (ω) of equation 6. The tangential line drawn parallel to the time axis of Figure 3b represents a unique event in the evolution of an osmotic system. This event, called 'osmotic equilibrium', is actually a transient-state phenomenon that represents, from a thermodynamic perspective, the point in time where the chemical potential of the solvent (water) is equal on opposing sides of the membrane. Unrequited is the balance of the solute's chemical potential; thus this imbalance drives the system to true equilibrium where the chemical potentials of all components in every part of the system are equal.

From an experimental point of view, osmotic equilibrium represents the point in time where there is no net solution flux across the membrane--that is, $J_v = 0$. This does not mean that there are no fluxes of solution components

across the membrane. Since J_v is the sum of the fluxes of the solution's components multiplied by their respective partial molar volumes, then at osmotic equilibrium, $J_w \cdot V_w = -J_s \cdot V_s$. Thus, at this juncture, the advective contribution to the solute flux in equation 6 (equivalent to the $C_s \cdot (1-\sigma) \cdot J_v$ term) can be ignored such that $J_s = -\omega \cdot \Delta\Pi$.

Osmotic equilibrium occurs at 143 (± 2) minutes (Fig. 3b). A value of J_s equal to $-1.92 \times 10^{-8} \text{ mole} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ results by differentiating the equation describing the solute flux out of the membrane depicted in Fig. 3a, and dividing the resultant $(dn_s/dt)_{t=143}$ by the membrane area of 75 cm^2 . Utilizing equations 3 and 4 to compute the concentration difference of Li^+Cl^- between the bag and beaker solutions at this event yields a value for $\Delta\Pi$ of $5.82 \times 10^6 \text{ dyne} \cdot \text{cm}^{-2}$, or 5.82 bars. Thus ω equals $3.30 \times 10^{-15} \text{ mole} \cdot \text{dyne}^{-1} \cdot \text{sec}^{-1}$. If J_s is calculated from the median of the ranges of data obtained from conductivity readings of the beaker solution, the value obtained for ω is $2.32 \times 10^{-15} \text{ mole} \cdot \text{dyne}^{-1} \cdot \text{sec}^{-1}$.

The solute permeability coefficient is not equivalent to the Fickian diffusion coefficient (D) in free solution because the ω term incorporates the physical and electrical impedance of the membrane to the diffusive path of the co-ion through this structure. The *maximum* value of ω is, however, related to the Fickian diffusion coefficient of the solute and the thickness of the membrane, Δx (Fritz, 1986).

$$\omega_{\max} = D/(R \cdot T \cdot \Delta x). \quad (10)$$

The diffusion coefficient for LiCl in a 0.01 M solution at 298°K is $1.312 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ (Robinson and Stokes, 1955). Since the dialysis tubing used in the experiment has a thickness of 0.005 cm , then the maximum value of

ω to be expected for diffusion of this solute through the tubing at 22° C is 1.07×10^{-13} mole·dyne⁻¹·sec⁻¹--a value 32 times greater than that measured.

Calculating the ratio of $\omega_{6\text{Li}+\text{Cl}^-}/\omega_{7\text{Li}+\text{Cl}^-}$

The Fickian coefficient (D) can be related to ω only through measurements of frictional coefficients between: 1) the solute and the water; 2) the solute and the membrane; and 3) the water and the membrane (Katchalsky and Curran, 1965). This would be a daunting task if one were concerned with measuring the absolute value of D. However, membrane systems can certainly be used to calculate ratios of ω values for individual isotopic components of a solute. Assumed here is that ratios of these ω values for individual isotopic species are equal to the ratios of their Fickian diffusion coefficients. In other words, the ratio of $\omega_{6\text{Li}+\text{Cl}^-}/\omega_{7\text{Li}+\text{Cl}^-}$ equals the ratio of $D_{6\text{Li}+\text{Cl}^-}/D_{7\text{Li}+\text{Cl}^-}$. This assumption would be erroneous if a membrane discriminates against the passage of, say 7Li^+ , relative to 6Li^+ solely on the basis of some property of these isotopes that can't ultimately be ascribed to their ionic mobility. An example would be if the membrane pores were larger than the hydrated radius of one species but smaller than the hydrated radius of the other isotopic species. Rather, differences of diffusive fluxes of 6Li^+ and 7Li^+ out of the membrane occur because of differences in their ionic mobilities.

Using $t=143$ minutes for attainment of osmotic equilibrium and a surface area of 75 cm², the solution fluxes for $6\text{Li}^+\text{Cl}^-$ and $7\text{Li}^+\text{Cl}^-$ are, respectively, -1.221×10^{-9} and -1.520×10^{-8} mole·cm⁻²·sec⁻¹. These same equations in Table 2 for the titration data are used to compute the moles of $6\text{Li}^+\text{Cl}^-$ and $7\text{Li}^+\text{Cl}^-$ in both the beaker and the bag at 143 minutes. The volume of the bag at that juncture is taken from the empirical equation in Fig. 3b to be $50.65 \pm .1$ cm³,

and the volume of the beaker (966.1 cm³) is calculated from the density-corrected mass of solution in the beaker after the last withdrawal at 127 minutes. Thus the molarity of ${}^6\text{Li}^+\text{Cl}^-_{\text{Bag}}$, ${}^7\text{Li}^+\text{Cl}^-_{\text{Bag}}$, ${}^6\text{Li}^+\text{Cl}^-_{\text{Bkr}}$, and ${}^7\text{Li}^+\text{Cl}^-_{\text{Bkr}}$ are, respectively, 1.133×10^{-5} , 1.420×10^{-4} , 2.654×10^{-6} , and 3.286×10^{-5} mole·cm⁻³. Expressed as concentration differences between the bag and beaker solutions, $\Delta C^6_{\text{Li}^+\text{Cl}^-} = 8.676 \times 10^{-6}$ mole·cm⁻³, and $\Delta C^7_{\text{Li}^+\text{Cl}^-} = 1.091 \times 10^{-4}$ mole·cm⁻³. The osmotic pressure as calculated by equation 7 gives 4.256×10^5 dyne·cm⁻² for the ${}^6\text{Li}^+\text{Cl}^-$ component and 5.354×10^6 dyne·cm⁻² contributed by ${}^7\text{Li}^+\text{Cl}^-$.

The ratio of the solute permeability for ${}^6\text{Li}^+\text{Cl}^-$ and ${}^7\text{Li}^+\text{Cl}^-$ is now obtained as:

$$\frac{\omega^6_{\text{Li}^+\text{Cl}^-}}{\omega^7_{\text{Li}^+\text{Cl}^-}} = \frac{[J_s^6_{\text{Li}^+\text{Cl}^-}/\Delta\Pi^6_{\text{Li}^+\text{Cl}^-}]}{[J_s^7_{\text{Li}^+\text{Cl}^-}/\Delta\Pi^7_{\text{Li}^+\text{Cl}^-}]} = 1.011. \quad (11)$$

Choosing different values for the time at which osmotic equilibrium is achieved will affect individual values for ω . However, the choice of the time is not really significant in computing ratios of ω values for ${}^6\text{Li}^+\text{Cl}^-$ and ${}^7\text{Li}^+\text{Cl}^-$. Assigning $t=133$ (rather than 143 minutes) gives a ratio calculated by the above equation equal to 1.010. A ratio of 1.012 is obtained if osmotic equilibrium is judged to occur at 153 minutes.

To reiterate, the $\omega^6_{\text{Li}^+\text{Cl}^-}/\omega^7_{\text{Li}^+\text{Cl}^-}$ ratio of 1.011 was computed from the median of the ranges of values for the titration-calculated data listed in Table 2. If this same ratio is calculated from the conductivity data in Table 2, the result is 1.008.

Because the $\omega^6_{\text{Li}^+\text{Cl}^-}/\omega^7_{\text{Li}^+\text{Cl}^-}$ ratio can be measured only at a single moment during the evolution of the osmotic cell, it's difficult to place an uncertainty on this number. Nevertheless, the ranges of values in Table 2

provide some basis for stating an uncertainty. A computer program was written to assign values for each of the 4 species listed on that table by a random-number generator so as to compute coefficients for the 4 equations depicting the masses of ${}^6\text{Li}^+\text{Cl}^-$ and ${}^7\text{Li}^+\text{Cl}^-$ within the beaker and bag solutions at various times. Using the titration data in Table 2 as an example, the program would, for the first withdrawal, randomly assign a value between 73 and 104 μmoles for ${}^6n_{\text{Bkr}}$, a value between 910 and 1,273 μmoles for ${}^7n_{\text{Bkr}}$, a value between 3,009 and 3,040 μmoles for ${}^6n_{\text{Bag}}$, and a value between 37,360 and 37,730 μmoles for ${}^7n_{\text{Bag}}$. This process continues through all 9 effluents, ending up with a single calculation of ω values for ${}^6\text{Li}^+\text{Cl}^-$ and ${}^7\text{Li}^+\text{Cl}^-$. One hundred such iterations were computed, coming up with an average $\omega^{{}^6\text{Li}^+\text{Cl}^-}/\omega^{{}^7\text{Li}^+\text{Cl}^-}$ ratio of 1.023 (± 0.0201). The range of conductivity data at the bottom of Table 2 was input into the same program. The result for 100 iterations was a ratio averaging 1.010. Because the degree of uncertainty was less when the conductivity data was used to compute LiCl concentrations in the dialysis bag, the standard deviation was only 0.0030.

Comparison with Calculations using Graham's Law

Both lithium and chlorine have 2 stable isotopes. Lithium-6 comprises 7.5% of stable Li and ${}^7\text{Li}$ the remaining 92.5% (Walker *et al.*, 1977). Stable chlorine is composed of 75.77% ${}^{35}\text{Cl}$ and 24.23% ${}^{37}\text{Cl}$ (Walker *et al.*, 1977). These mole percents, multiplied by their respective formula weights, yield the formula weight for LiCl (42.41 $\text{grams}\cdot\text{mole}^{-1}$) upon which the value of diffusion coefficients for the 4 isotopic end-members can be computed by application of Graham's Law which states that the relative rates of diffusion for gases is inversely proportional to square roots of their densities. While not appropriate to calculating ratios of diffusion coefficients of isotopes in electrolyte solutions, nevertheless the mathematical form of Graham's Law is,

at the very least, a convenient yardstick to gauge the diffusion-coefficient ratio for $^6\text{Li}^+\text{Cl}$ and $^7\text{Li}^+\text{Cl}$.

There are 4 distinct isotopic species in LiCl: $^6\text{Li}^{35}\text{Cl}$, $^7\text{Li}^{35}\text{Cl}$, $^6\text{Li}^{37}\text{Cl}$, and $^7\text{Li}^{37}\text{Cl}$. In a stock solution of LiCl, the concentration of the 4 species are proportional to their isotopic abundance in the dissolved salt. For example, if 10.00 millimoles of LiCl are dissolved with deionized water to yield a liter of solution, then the concentration of individual ions are:

$$^6\text{Li}^+ = 0.7500 \text{ mM}; \quad ^7\text{Li}^+ = 9.250 \text{ mM}; \quad ^{35}\text{Cl}^- = 7.577 \text{ mM}; \quad ^{37}\text{Cl}^- = 2.423 \text{ mM}.$$

Cations and anions move together during advection and diffusion. It's assumed that there is no preferred association of, say $^6\text{Li}^+$, with $^{37}\text{Cl}^-$. Since $^6\text{Li}^+$ moves with an anion partner, it is likely that the association of $^6\text{Li}^+$ with a chloride anion will be proportional to the amount of that anionic isotope species present. In other words, 75.77% of $^6\text{Li}^+$ will be associated with $^{35}\text{Cl}^-$, and 24.23% will be associated with $^{37}\text{Cl}^-$. Using this reasoning, then the 4 isotopic end-members will have the following concentrations in a 10.00 mM LiCl stock solution:

$$^6\text{Li}^{35}\text{Cl} = 0.5683 \text{ mM}; \quad ^7\text{Li}^{35}\text{Cl} = 7.009 \text{ mM};$$

$$^6\text{Li}^{37}\text{Cl} = 0.1817 \text{ mM}; \quad ^7\text{Li}^{37}\text{Cl} = 2.241 \text{ mM}.$$

Diffusion coefficient values for these 4 components are calculated using the composite diffusion coefficient for LiCl at 25°C and a concentration of 0.01 M. Thus $D_{\text{LiCl}} = 1.312 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$ (Robinson and Stokes, 1955).

$$D_{^6\text{Li}^{35}\text{Cl}} = D_{\text{LiCl}} \cdot [(42.41/41)^{1/n}], \quad (12)$$

$$D_{^7\text{Li}^{35}\text{Cl}} = D_{\text{LiCl}} \cdot [(42.41/42)^{1/n}], \quad (13)$$

$$D_{^6\text{Li}^{37}\text{Cl}} = D_{\text{LiCl}} \cdot [(42.41/43)^{1/n}], \text{ and} \quad (14)$$

$$D_{^7\text{Li}^{37}\text{Cl}} = D_{\text{LiCl}} \cdot [(42.41/44)^{1/n}]. \quad (15)$$

If the assumption is made that an individual component's diffusion coefficient is proportional to the square root of the ratio of the solute's mass relative to the mass of one of the components in the composite salt, then $n=2$. Using this value for n , then $D^{6}\text{Li}^{35}\text{Cl}$ is 101.33% of D_{LiCl} , $D^{7}\text{Li}^{35}\text{Cl}$ is 100.12% of D_{LiCl} , $D^{6}\text{Li}^{37}\text{Cl}$ is 98.948% of D_{LiCl} , and $D^{7}\text{Li}^{37}\text{Cl}$ is 97.817% of D_{LiCl} .

In actuality, the diffusion coefficient for ^6Li in a $\text{LiCl-H}_2\text{O}$ system is related to both $^6\text{Li}+^{35}\text{Cl}^-$ and $^6\text{Li}+^{37}\text{Cl}^-$. Put another way, the diffusion coefficient for the light isotope of lithium in a LiCl solution is computed on the basis of $^6\text{Li}+^{35.485}\text{Cl}^-$, where the subscripted fraction is the atomic weight of chlorine. This gives rise to a re-statement of the above 4 equations:

$$D^{6}\text{Li}^{35.485}\text{Cl} = D \cdot [(42.41/41.485)^{1/2}] , \text{ and} \quad (16)$$

$$D^{7}\text{Li}^{35.485}\text{Cl} = D \cdot [(42.41/42.485)^{1/2}] . \quad (17)$$

Dividing equation 16 by equation 17 results in the ratio of the two diffusion coefficients:

$$\frac{D^{6}\text{Li}^{35.485}\text{Cl}}{D^{7}\text{Li}^{35.485}\text{Cl}} = \frac{(1/41.485)^{1/2}}{(1/42.485)^{1/2}} = 1.0119. \quad (18)$$

This 1.0119 value compares very favorably with the $\omega^{6}\text{Li}^+\text{Cl}^-/\omega^{7}\text{Li}^+\text{Cl}^-$ ratio obtained from $^6\text{Li}/^7\text{Li}$ analyses in conjunction mass-balance calculations made with titration data (1.011) and mass balances computed with conductivity data (1.008). Based upon 100 computer iterations using concentrations of $^6n_{\text{Bkr}}$, $^7n_{\text{Bkr}}$, $^6n_{\text{Bag}}$, and $^7n_{\text{Bag}}$ that were randomly assigned to each of the 9 withdrawals based upon maximum measurement errors about their reported mean values, the calculated $\omega^{6}\text{Li}^+\text{Cl}^-/\omega^{7}\text{Li}^+\text{Cl}^-$ ratio for the titration data is 1.023 (± 0.0201). The same iterative technique using concentrations calculated with conductivity data gave a ratio of 1.010 (± 0.0030).

SUMMARY

Osmotic experiments can be used to measure the ratio of solute permeability coefficients (ω) of isotopes comprising a solute. The assumption employed here is that the ratio of such phenomenological coefficients is equal to the ratio of the Fickian diffusion coefficients. The close correspondence between the ratio of $D^6\text{Li}^{35.458}\text{Cl}/D^7\text{Li}^{35.458}\text{Cl}$ ($=1.0119$) as calculated by the mathematical form of Graham's Law and $\omega^6\text{Li}^+\text{Cl}^-/\omega^7\text{Li}^+\text{Cl}^-$ as measured with either the titration data (1.011) or the conductivity data (1.008) indicates this assumption may be reasonable. However, more precise works needs to be conducted if this osmotic technique is adopted to measure such ratios. Three recommendations for future designs of this type of experiment are: 1) the solute concentration of the outside (beaker) solution be monitored by conductivity; 2) the entire cell be placed within a water bath to minimize variation of conductivity readings due to temperature fluctuations; and 3) a micro pressure-transducer be installed inside the osmotic cell so that continuous pressure readings can be recorded. This last suggestion would obviate the need to remove the dialysis bag for weighing since the mass of solution in the cell can be computed from isothermal compressibility data of the solute. Continuous monitoring of the pressure inside the cell would also give a more precise time at which osmotic equilibrium occurs.

Should future experimental work on other solutes in aqueous systems (such as $^{23}\text{Na}+^{35}\text{Cl}^-$ and $^{23}\text{Na}+^{37}\text{Cl}^-$) show the continued close correspondence between measured ω ratios of isotopic components comprising that solute and the ratio as calculated by the square root of the mass ratio of the heavy-to-light isotopic component in that salt, then Graham's Law might be used to conveniently assess diffusion coefficients for isotopic components in a single-solute aqueous solution. Emphasized here is that this would be a purely

empirical observation--but nevertheless one that would have practical import, especially in research concerning membrane-induced fractionation of solute isotopes.

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TABLE 1

Sample	Withdrawal Time in Minutes	Cond. of Bkr. Sol'n $\mu\text{mhos/cm}$	Net Wt. Bag Sol'n	Net Wt. Bkr. Sol'n	--Micromoles of LiCl-- Σ_{out} in Bkr. in Bag			mF LiCl in Beaker	mF LiCl in Bag	$^6\text{Li}/^7\text{Li}$ in Beaker	$^6\text{Li}/^7\text{Li}$ in Bag
Stock	0	1.14	45.93	1000.0	0	0	41,740	0	908.8		0.08059
#1	1	55.50	46.07	999.9	0	1,170	40,570	1.17	880.6	0.08159	0.08056
#2	3	155.0	46.24	995.7	3	2,081	39,660	2.09	857.6	0.08108	0.08057
#3	7	377.0	46.58	988.7	15	3,895	37,830	3.94	812.1	0.08096	0.08054
#4	15	702.0	47.15	982.7	33	7,154	34,550	7.28	732.8	0.08098	0.08049
#5	31	1,327.	48.25	977.4	61	13,230	28,450	13.54	589.6	0.08117	0.08024
#6	63	2,250.	49.67	971.5	120	22,420	19,200	23.08	386.5	0.08127	0.07971
#7	127	3,230	50.67	966.3	206	32,540	9,000	33.67	177.6	0.08061	0.08038
#8	279	3,620	49.99	961.0	337	38,450	2,954	40.01	59.09	0.08070	0.08090
#9	579	3,890	48.67	955.2	509	39,210	2,020	41.05	41.52	0.08067	0.08086
Bag									41.50		0.08084

Numbers in bold type denote actual measurements. All other numbers on the table were calculated from these data. The column of numbers under Σ_{out} represent the running total of micromoles of LiCl withdrawn by successive aliquots. Thus, 3 μmoles were withdrawn in effluent #1, 12 μmoles withdrawn in effluent #2, 18 μmoles withdrawn in effluent #3, etc. Note the closeness of the mass balance agreement between the calculated LiCl concentration of the bag after sampling the last effluent and the actual concentration of the bag solution sampled immediately after the withdrawal of effluent #9. The very small concentration difference between the beaker and bag solutions show that equilibrium has been nearly achieved at 579 minutes into the run. The reported $^6\text{Li}/^7\text{Li}$ ratios have an uncertainty of ± 0.00015 .

TABLE 2

Mass-vs-Time Curves Calculated From Titration Data

Effluent	micromoles $^6\text{Li}^+$ in Beaker		micromoles $^7\text{Li}^+$ in Beaker		micromoles $^6\text{Li}^+$ in Dialysis Bag		micromoles $^7\text{Li}^+$ in Dialysis Bag	
	min.	max.	min.	max.	min.	max.	min.	max.
Stock						3,113		38,630
#1	73	104	910	1,273	3,009	3,040	37,360	37,730
#2	146	166	1,809	2,043	2,947	2,966	36,580	36,820
#3	279	302	3,455	3,729	2,810	2,833	34,890	35,160
#4	520	549	6,430	6,775	2,562	2,592	31,840	32,180
#5	976	1,907	12,050	12,380	2,104	2,134	26,220	26,550
#6	1,660	1,703	20,460	20,920	1,406	1,449	17,660	18,120
#7	2,397	2,445	29,780	30,280	662	710	8,271	8,771
#8	2,837	2,887	35,210	35,720	216	266	2,788	3,297
#9	2,889	2,939	35,870	36,380	161	211	2,094	2,602
moles $^6\text{n}_{\text{Bag}} = (0.007945) \cdot \exp[-0.01419 \cdot t] + 0.000186$ [r = 0.9993] moles $^7\text{n}_{\text{Bag}} = (0.03651) \cdot \exp[-0.01413 \cdot t] + 0.002348$ [r = 0.9998] moles $^6\text{n}_{\text{Bkr}} = (0.002942) \cdot (1 - \exp[-0.01436 \cdot t])$ [r = 0.9998] moles $^7\text{n}_{\text{Bkr}} = (0.03647) \cdot (1 - \exp[-0.01431 \cdot t])$ [r = 0.9998]								

Mass-vs-Times Curves Calculated From Conductivity Data

Effluent	micromoles $^6\text{Li}^+$ in Beaker		micromoles $^7\text{Li}^+$ in Beaker		micromoles $^6\text{Li}^+$ in Dialysis Bag		micromoles $^7\text{Li}^+$ in Dialysis Bag	
	min.	max.	min.	max.	min.	max.	min.	max.
Stock						3,113		38,630
#1	40	48	489	586	3,065	3,073	38,040	38,140
#2	117	125	1,447	1,544	2,987	2,996	37,080	37,180
#3	289	298	3,578	3,674	2,814	2,823	34,940	35,040
#4	541	550	6,687	6,785	2,561	2,571	31,830	31,920
#5	1,025	1,036	12,650	12,750	2,074	2,086	25,850	25,950
#6	1,740	1,753	21,440	21,540	1,355	1,369	17,030	17,140
#7	2,477	2,493	30,770	30,880	614	630	7,672	7,775
#8	2,779	2,795	34,480	34,580	308	325	3,925	4,029
#9	2,983	3,001	37,040	37,150	99	117	1,321	1,427
moles $^6\text{n}_{\text{Bag}} = (0.002723) \cdot \exp[-0.01157 \cdot t] + 0.000186$ [r = 0.9894] moles $^7\text{n}_{\text{Bag}} = (0.03378) \cdot \exp[-0.01154 \cdot t] + 0.002348$ [r = 0.9893] moles $^6\text{n}_{\text{Bkr}} = (0.002712) \cdot (1 - \exp[-0.01164 \cdot t])$ [r = 0.9895] moles $^7\text{n}_{\text{Bkr}} = (0.03364) \cdot (1 - \exp[-0.01161 \cdot t])$ [r = 0.9893]								

Masses of $^6\text{Li}^+$ and $^7\text{Li}^+$ in the dialysis bag can be calculated from either titration or conductivity data of the beaker solution. Displayed here are the minimum and maximum values based upon applying the uncertainties of measurements for $^7\text{Li}/^6\text{Li}$ ratio, titration-endpoint volumes, aliquot weights, weights of the bag/beaker solutions, and conductivity. Values of the coefficients given for the 4 sets of equations associated with each method were calculated from the median value between the reported minimum and maximum value. Although the degree of uncertainty is less for the conductivity data, the empirical equations calculated from conductivity data have lower correlation coefficients than r's calculated from titration data having a higher degree of uncertainty.

FIGURE 1

Figure 1. A time plot of μmoles of ${}^6\text{Li}$ and ${}^7\text{Li}$ in the dialysis bag and the beaker solutions. Each point plotted for the beaker solution was obtained directly from two measurements: the ${}^6\text{Li}/{}^7\text{Li}$ ratio, and the titration-determined concentration of LiCl . Masses of the two isotopes in the bag solution were calculated from these two measurements. Correlation coefficients for all 4 empirical equations listed on this figure exceed 0.9998.

FIGURE 2

Figure 2. Time versus $^6\text{Li}/^7\text{Li}$ ratios of the beaker and bag solutions. Except for the initial and final $^6\text{Li}/^7\text{Li}$ ratio of the bag solution, all other ratios for the bag solution were calculated by mass balance.

FIGURE 3

Figure 3. The top figure depicts the diffusion of the LiCl solute out of the dialysis bag. This decrease was fit to a first-order rate equation whose correlation coefficient was 0.9999. The bottom graph shows the temporal change of the bag volume. The data points were fit to the listed empirical equation. The solution flux, J_v , is equal to the $(dV/dt)/\text{Area}$. $J_v = 0$ at 143 minutes. If the slope of the line drawn tangential to the moles-vs-time curve at $t = 143$ minutes is divided by the surface area of the membrane, the result is the solute flux, J_s .

PROJECTED ACTIVITIES FOR THE UPCOMING YEAR

The final year of this 3-year grant will be devoted solely to hyperfiltration experiments in which different concentrations of LiCl solutions are hydraulically forced across thin clay and artificial membranes at various fluxes. These experiments will have a qualitative and a quantitative aim. Qualitatively speaking, will hyperfiltration generate fractionation of lithium isotopes to the degree seen here for simple osmotic measurements? On the quantitative side, I will focus the experimental goals toward the variation of fractionation engendered by solution flux across membranes.

Having successfully determined that the ratio of the diffusion coefficient of Lithium-6 to Lithium-7 can be calculated by Graham's Law, I will proceed to construct a mathematical model of hyperfiltration-induced fractionation of the stable isotopes of both lithium and chlorine in a LiCl system.

The research output of this grant has generated a manuscript sent to *Geochimica et Cosmochimica Acta* concerning the work detailed in this year's progress report. The hyperfiltration data and the mathematical model coming out of the upcoming year will generate additional manuscripts for submission to publish in internationally known geochemical journals.

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