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Kinetics and equilibria of tea infusion, Part 15. Transport of caffeine across a teabag membrane in a modified rotating diffusion cell

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Abstract

The rates of transfer of aqueous caffeine through a membrane of teabag paper were measured by means of a modified rotating diffusion cell. The reciprocals of the transfer rates were found to be directly proportional to the inverse square root of the rotation speed. These results are consistent with the rate-controlling step being diffusion of caffeine through the Nernst diffusion layers on each side of the membrane. At both 25 and 80°C the resistance to transfer through the teabag membrane itself was negligible, showing that the material was well suited to the brewing of tea, coffee or other food materials. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In Britain alone, some 87% of the tea consumed is currently sold in the form of teabags. There has therefore been much interest in the structure of teabags and the traditional square shape has in recent years been supplemented by round and pyramidal designs. Although the quality of the resulting tea brew depends on the quality of the tea leaf and of the water used, the rate of infusion is affected by the teabag structure and the hydrodynamic conditions. But whatever the shape of the teabag, common to all of them is the interfacial system: tea leaf/internal tea solution/teabag membrane/external tea solution (the tea brew).

The kinetics of the tea leaf/tea solution system have been investigated previously (Spiro, 1997; Spiro & Jago, 1982) and we now report a study of the kinetics of transfer across the teabag membrane. To simplify the problem, we have chosen an aqueous solution of caffeine to model the internal tea solution with the expectation that similar considerations would apply to other soluble tea constituents.

In the cell used and described in detail below, a caffeine solution was put into an outer compartment O and the caffeine allowed to diffuse through a membrane of teabag paper (TBP) into an inner compartment I which was regularly sampled to determine the rate of caffeine transfer.

2. Theory

The model used is similar to that employed by Albery, Burke, Leffler and Hadgraft (1976) and is shown in Fig. 1. On each side of the central TBP membrane (thickness d_m) there is a thin Nernst diffusion layer, of thickness δ_0 in the outer compartment O and δ_i in the inner compartment I. The diffusion coefficients of caffeine in O, the membrane, and I are D_o, D_m, and D_i, respectively. The partition constant of caffeine between either of the dilute aqueous phases and the membrane phase is given by

$$K = c_{\text{membrane}}/c_{\text{soln}} = k_1/k_{-1} \quad (1)$$

where k_1 and k_{-1} are first order transfer rate constants as shown in Fig. 1.

If the geometrical cross-sectional area of the membrane is A and α is the area of the pores of the membrane per unit geometrical area, then

$$A_{\text{membrane}} = \alpha A \quad (2)$$

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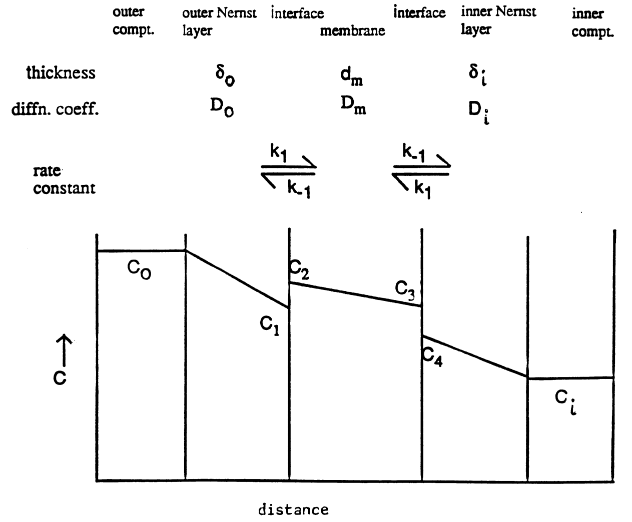

Fig. 1. Concentration profiles of the model used (schematic).

The theory derived from this model is based on the assumption that in the steady state the flux J (mol s^{-1}) of the solute caffeine is the same through all interfaces and all phases. Hence, using Fick's first law,

$$\begin{aligned} J &= -\mathrm{d}(c_\mathrm{o}V_\mathrm{o})/\mathrm{d}t = AD_\mathrm{o}(c_\mathrm{o}-c_1)/\delta_\mathrm{o} \\ &= \alpha A(k_1c_1 - k_{-1}c_2 = \alpha AD_\mathrm{m}(c_2-c_3)/d_\mathrm{m} \\ &= \alpha A(k_{-1}c_3 - k_1c_4) = AD_\mathrm{i}(c_4-c_\mathrm{i})/\delta_\mathrm{i} \\ &= \mathrm{d}(c_\mathrm{i}V_\mathrm{i})/\mathrm{d}t \end{aligned} \tag{3}$$

where V stands for the volume of the subscripted compartment. Concentrations c_1, c_2, c_3, c_4 can now be eliminated in reverse order to yield

$$c_\mathrm{o} = c_\mathrm{i} + J/Ak \tag{4}$$

where

$$\frac{1}{k} = \frac{2}{\alpha k_1} + \frac{\delta_\mathrm{i}}{D_\mathrm{i}} + \frac{d_\mathrm{m}}{\alpha KD_\mathrm{m}} + \frac{\delta_\mathrm{o}}{D_\mathrm{o}} \tag{5}$$

A second relation between c_o and c_i can be obtained from the mass conservation of caffeine within the system as a whole. With superscript $^\mathrm{o}$ indicating the initial conditions, it follows that

$$\begin{aligned} c_\mathrm{o}^\mathrm{o}(V_\mathrm{o}^\mathrm{o} + \delta_\mathrm{o}A) = c_\mathrm{o}V_\mathrm{o} + \delta_\mathrm{o}A(c_\mathrm{o}+c_1)/2 + d_\mathrm{m}\alpha A(c_2+c_3)/2 \\ + \delta_\mathrm{i}A(c_4+c_\mathrm{i})/2 + c_\mathrm{i}V_\mathrm{i} \end{aligned} \tag{6}$$

Eliminating c_1, c_2, c_3 and c_4 by means of Eq. (3), and ignoring the second order terms δ^2, δd_m and d_m^2, leads to

$$c_\mathrm{o} = c_\mathrm{o}^\mathrm{o} - c_\mathrm{i}(V_\mathrm{i}' + K\alpha Ad_\mathrm{m})/V_\mathrm{o}' - Jd_\mathrm{m}/k_{-1}V_\mathrm{o}' \tag{7}$$

where it has been assumed that the volumes remain constant throughout an experiment so that V_o equals V_o^o, and where V' represents the whole solution volume in either compartment, i.e.

$$V' = V + \delta A \tag{8}$$

Combination of Eqs. (4) and (7) allows us to eliminate c_o. Incorporation of $J = d(c_\mathrm{i}V_\mathrm{i})/\mathrm{d}t$ then gives the following linear differential equation in c_i:

$$\mathrm{d}c_\mathrm{i}/\mathrm{d}t + Pc_\mathrm{i} = Q \tag{9}$$

where

$$P = G/F \tag{10}$$

$$Q = c_\mathrm{o}^\mathrm{o}/F \tag{11}$$

$$F = \frac{V_\mathrm{i}}{A}\left(\frac{1}{k} + \frac{Ad_\mathrm{m}}{k_{-1}V_\mathrm{o}'}\right) \tag{12}$$

$$G = 1 + \frac{V_\mathrm{i}'}{V_\mathrm{o}'} + \frac{K\alpha Ad_\mathrm{m}}{V_\mathrm{o}'} \tag{13}$$

Using $\exp(Pt)$ as an integrating factor and the assumption that $c_\mathrm{i} = 0$ at $t = 0$ leads to

$$c_\mathrm{i} = Q(1 - \exp[-Pt]/P \tag{14}$$

An interesting corollary is that

$$\ln\{c_\mathrm{i}^\infty/(c_\mathrm{i}^\infty - c_\mathrm{i})\} = Pt \tag{15}$$

where the infinity superscript denotes the final equilibrium condition. This is a kinetic equation of the same form as that applicable to the infusion of caffeine and other solubles from loose tea leaves (Spiro, 1997; Spiro & Jago, 1982), ground coffee beans (Spiro, 1988; Spiro & Selwood, 1984), and other plant products (Spiro & Kandiah, 1989) where internal diffusion is the rate-determining step. However, in the present research only the early stages of the infusions were followed, for which the relevant equation is

$$c_\mathrm{i} = Qt \tag{16}$$

Thus plots of c_i versus t should be straight lines of slope Q.

In our experiments the optical absorbances of small samples in compartment I were determined at various times t. It then follows from Eq. (16) and the

Beer–Lambert law that plots of absorbances against time should be linear, i.e.

$$\mathrm{Abs} = a + bt \tag{17}$$

It will be convenient to represent the results in terms of the rate R (mol s^{-1}) at which the caffeine appears in the inner compartment, so that

$$R = \mathrm{d}(c_{\mathrm{i}}V_{\mathrm{i}})/\mathrm{d}t = bV_{\mathrm{i}}/\varepsilon\ell \tag{18}$$

where ε is the extinction coefficient of caffeine and ℓ the length of the cuvette. It then follows from Eq. (16) that

$$\begin{aligned}\frac{1}{R} &= \frac{1}{QV_{\mathrm{i}}} = \frac{F}{c_{\mathrm{o}}^{\mathrm{o}}V_{\mathrm{i}}} \\ &= \frac{1}{c_{\mathrm{o}}^{\mathrm{o}}A}\left(\frac{2}{\alpha k_1} + \frac{\delta_{\mathrm{i}}}{D_{\mathrm{i}}} + \frac{d_{\mathrm{m}}}{\alpha K D_{\mathrm{m}}} + \frac{\delta_{\mathrm{o}}}{D_{\mathrm{o}}} + \frac{Ad_{\mathrm{m}}}{k_{-1}V'_{\mathrm{o}}}\right)\end{aligned} \tag{19}$$

For dilute solutions of caffeine at a given rotation speed of f (Hertz) it is reasonable to write

$$\delta_{\mathrm{i}} = \delta_{\mathrm{o}} = \delta \tag{20}$$

$$D_{\mathrm{i}} = D_{\mathrm{o}} = D \tag{21}$$

For the rotating diffusion cell used here, δ is given by the Levich equation (Opekar & Beran, 1976)

$$\delta = 0.643\nu^{1/6}D^{1/3}f^{-1/2} \tag{22}$$

where ν is the kinematic viscosity of the solution. Hence,

$$\begin{aligned}\frac{1}{R} &= \frac{1}{c_{\mathrm{o}}^{\mathrm{o}}A}\left(1.286\nu^{1/6}/D^{2/3}f^{1/2}\right) \\ &+ \frac{1}{c_{\mathrm{o}}^{\mathrm{o}}A}\left(\frac{2}{\alpha k_1} + \frac{d_{\mathrm{m}}}{\alpha K D_{\mathrm{m}}} + \frac{Ad_{\mathrm{m}}}{k_{-1}V'_{\mathrm{o}}}\right)\end{aligned} \tag{23}$$

The first term on the right-hand side is a mass transport term arising from diffusion of caffeine through the two Nernst layers while the second term expresses the resistance due to transfer through the membrane. The latter can thus be obtained from the intercept of a plot of $1/R$ versus $1/\sqrt{f}$.

3. Materials and methods

Since diffusion was bound to play a major part in the overall transfer process, the rate of flow towards and away from the membrane of teabag paper needed to be controlled. The most appropriate method was by rotating disk hydrodynamics (Opekar & Beran, 1976). We therefore employed a modified form of the cylindrical rotating diffusion cell devised by Albery et al.(1976) and Albery and Hadgraft (1979) for studying interfacial transfer between an aqueous and a non-aqueous medium. In our case the basic arrangement involved a TBP membrane separating an outer compartment (O) containing an aqueous solution of caffeine and an inner compartment (I) containing water and a stationary baffle. The rotation of the cylinder produced well-defined fluid motion both above and below the membrane. The rate of transfer of caffeine from O to I through the membrane was then measured by sampling the solution in I at various times and analysing it spectrophotometrically.

Several changes to the Albery cell and the experimental procedure were necessary for the present work. First, the cell design had to allow easy replacement of the membrane after runs. Second, the interfacial tension between an aqueous and a non-aqueous solution, which had facilitated the filling of the Albery cell and had stabilised the interface, was now absent. Furthermore, the TBP membrane proved to be much more porous than the filters previously employed. Great care had therefore to be taken to avoid extraneous flow and leakage due to thermal, gravitational and mechanical factors, and only low rotation speeds could be employed. These precautions were particularly important at higher temperatures and are described below. Several cell modifications and handling methods were tried before a suitable cell was constructed and satisfactory filling and running procedures were established.

An exploded view of the body of the final cell is shown in Fig. 2. It was made of Perspex to allow visual inspection of the internal flow when $KMnO_4$ was added as a test reagent, and had a height of 95 mm and an outer diameter of 89 mm. The cylindrical baffle, of height 82 mm and outer diameter 50 mm, was 4.5 mm thick and made of Teflon. It was fitted onto a central stainless steel inlet tube. The hole at the top of the baffle and in the inlet tube allowed air to escape during setting up and acted as a sampling path from the inner compartment. Movement of the baffle was prevented by a removable locking collar. The cell was rotated via a drive band with a velodyne motor connected to an Oxford Electrodes motor controller.

The circular hole in the bottom plates through which diffusion took place had a diameter of 19.8 mm. The layers of Parafilm “M” (American National Can) acted as essential seals between the TBP and the stainless steel plates. The latter were machined as shown, flat on the sides facing the membrane and with angles of 10° on the other sides to ensure a defined pattern of liquid flow. The bottom plate could be screwed onto the stainless steel ends of the cell walls as indicated.

The cell was placed in a double-walled thermostatted vessel made of glass which formed the outer compartment. Its temperature was controlled by connection to a

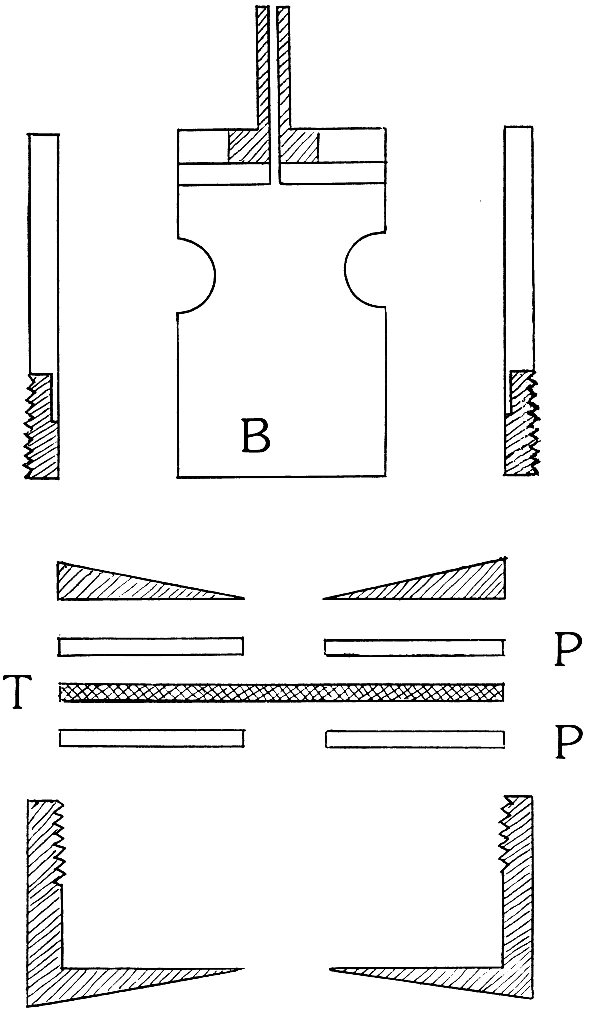

Fig. 2. Schematic exploded view of the inner compartment of the modified rotating diffusion cell. B, baffle; P, Parafilm; T, teabag paper. Hatched sections were made of stainless steel.

thermostatic circulator type LKB 2219 Multitemp II. At high temperature, evaporation from the surface was minimised by covering it completely with cling film apart from the central area around the rotating shaft. Another problem encountered at high temperature, softening of the Araldite glue used to join certain parts of the cell together, was solved by replacing it with a silicone rubber seal.

To prevent bulk flow through the membrane caused by gravitational instability, the cell had been increased in size to hold a large volume of liquid and only very small samples were taken during a run. In addition, the heavier caffeine solution was placed in the outer compartment and distilled water in the inner. In more detail, for an experiment the cell with wetted TBP membrane was lowered into the outer compartment containing 930 ml preheated degassed distilled water. Any blocking air bubble below the membrane was sucked out with a syringe with a curved needle. The liquid then rushed into the inner compartment through the TBP until the levels of the two compartments were equal. The apparatus was left to attain thermal equilibrium at the chosen rotation speed for 10 min. The experiment was started by adding 20 ml of 0.1 mol dm^{-3} caffeine solution (0.2 mol dm^{-3} at higher temperature) to the top of the outer compartment; mixing within it was rapid. Then, at various times, volumes of 100 μl were sampled from the inner compartment (containing 250 ml) via the central stainless steel inlet. A microsyringe (type SGE) with a very long needle was used for this purpose. The samples were transferred into 5 ml volumetric flasks and diluted to the mark with distilled water. The absorbances were then measured at 273 nm in a Perkin–Elmer Lambda 2 computer-controlled spectrophotometer. Calibration plots with solutions of AnalaR caffeine (Merck BDH) gave an extinction coefficient of 9.88×10^3 dm^3 mol^{-1} cm^{-1}, close to other values in the literature (Cesaro, Russo & Crescenzi, 1976).

The membranes were made from a roll of teabag paper no. 17 supplied by Dexter Nonwovens. Three layers of TBP together were used to reduce problems of bulk flow and provided a more rigid membrane system.

4. Results and discussion

Typical plots of the optical absorbance readings against time are shown in Fig. 3 for both 25 and 80°C. The latter temperature is close to that obtained during tea brewing with teabags. The points in Fig. 3 are seen to fall on straight lines as expected from Eq. (17). The rates of transfer R calculated from the slopes of such lines at various rotation speeds are listed in Table 1.

The values of R from Table 1 have been plotted against $1/\sqrt{f}$ in Fig. 4. The intercepts, which represent the caffeine transfer rates at infinite rotation speed, were -0.55 ± 0.26 at 25°C and -0.17 ± 0.09 at 80°C on applying least squares fitting. Such negative intercepts are physically meaningless since caffeine cannot pass spontaneously through the membrane from the more dilute to the more concentrated side, and arise partly from the difficulty of making the measurements and partly from the long extrapolations involved because the system was not sufficiently stable at higher rotation speeds. However, the points at both temperatures do fit reasonably well on straight lines passing through the origin, which points to virtually zero transfer resistance within the TBP membrane.

The slopes of the lines in Fig. 4 can now be compared with the theoretical prediction in Eq. (23). Since the caffeine solutions are very dilute we can use the viscosity and density of water (Robinson & Stokes, 1959) to evaluate the kinematic viscosity ν, and take the limiting values of the diffusion coefficients of caffeine as reported by Price (1989) and Price, Trickett and Harris (1989).

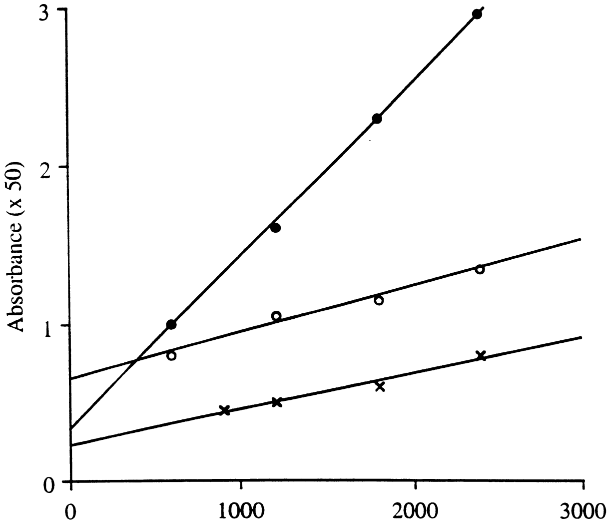

Fig. 3. Variation with time of the absorbances (×50) at 273 nm of diluted samples of caffeine solution, from rotation at 1.21 Hz of three TBP at 25°C (○) and at 80°C (●) and of an 8 µm pore Millipore filter (X) at 25°C.

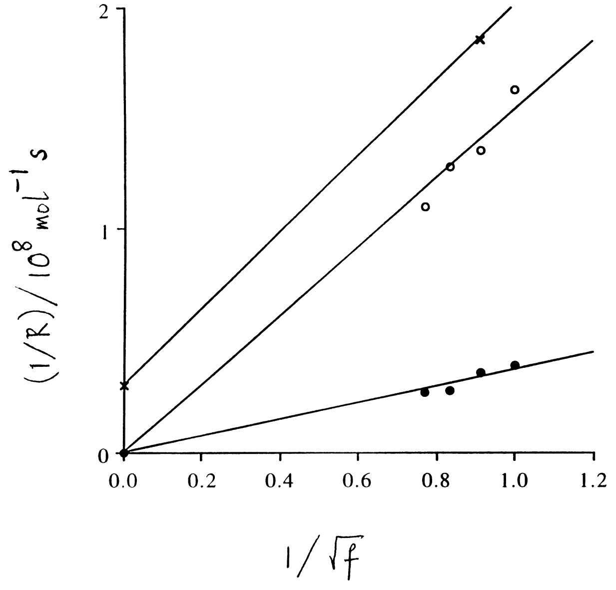

Fig. 4. Variation of the inverse caffeine transfer rates $(1/R)/10^8$ mol^{-1} s with the inverse square root of the rotation speed f, using membranes of three TBP at 25°C (○) and at 80°C (●) and of an 8 µm pore Millipore filter (X) at 25°C.

Also listed in Table 2 are the initial concentrations of caffeine in the 700 ml of solution in the outer compartment after the 20 ml of 0.1 (or 0.2) mol dm^{-3} caffeine had been added. The resulting theoretical slope is seen to be 10% higher than the experimental one at 25°C and 5% lower at 80°C. Bearing the uncertainties in mind there is satisfactory agreement between the theoretical and experimental slopes, which supports the line fitting adopted in Fig. 4.

A few additional experiments were also carried out with MF-Millipore Membrane Filters. These filters are hydrophilic with a thickness of 250 µm, similar to the thickness of three teabag papers. The pore size chosen was 8 µm, the largest available. Since even these filters were not sufficiently porous to permit bulk water from the outer compartment to flow easily through the membrane into I, the filling procedure of the cell had to be modified. The inner compartment was therefore filled directly with 250 ml distilled water through the sampling outlet by means of a large syringe with a long needle attached.

The slope of the absorbance-time plot obtained with the Millipore membrane rotating at 1.21 Hz was found to be 27% smaller than the slope for the TBP membrane at the same temperature (Fig. 3). The Millipore filter's rate of transfer was correspondingly lower and its $1/R$ was 37% greater than that of the TBP membrane (Fig. 4). As shown in this diagram, a line drawn with the theoretical slope through the Millipore membrane point leads to a positive intercept of 0.31×10^8 mol^{-1} s. This represents significant resistance to caffeine transfer through the Millipore membrane itself, in contrast to the absence of such resistance within the TBP membrane. This comparison illustrates the high porosity of teabag paper and its suitability for tea brewing.

These experiments, together with those carried out previously (Spiro, 1997; Spiro & Jago, 1982), show that the rate of tea brewing in teabags is determined by diffusion within the tea leaves plus the hydrodynamic flow inside and outside the teabag. Similar conclusions have recently been reached by Dr. A.J. Marquis (private

Table 1
Rates of transfer (R) of caffeine into the inner compartment I at various rotation speeds (f) and temperatures

f (s^{-1})	R (25°C) (10^{-8} mol s^{-1})	R (80°C) (10^{-8} mol s^{-1})
1.00	0.61_3	2.53
1.21	0.73_9	2.76
1.44	0.78_0	3.48
1.69	0.90_6	3.65

Table 2
Comparison of experimental and theoretical slopes of plots of $1/R$ versus $1/\sqrt{f}$ at 25 and 80°C

Parameter	Value at 25°C	Value at 80°C
$D/10^{-9}$ m^2 s^{-1}	0.773 (Price, 1989)	2.250 (Price et al., 1989)
$\nu/10^{-6}$ m^2 s^{-1}	0.8929	0.3657
c_0^0/mol m^{-3}	2.857	5.714
Theoretical slope/10^8 s$^{1/2}$ mol^{-1}	1.70	0.360
Experimental slope/10^8 s$^{1/2}$ mol^{-1}	1.54 ± 0.04	0.377 ± 0.013

communication) by computer simulation and flow visualisation. It follows that any motion which decreases the thickness of the inner and outer Nernst layers adjacent to the TBP membrane will increase the rate of tea brewing. This readily explains the empirical findings of tea drinkers that stirring the brew around a teabag, moving the teabag up and down, and jiggling the teabag all speed up the brewing of tea. Similar comments can obviously be made about the rates of infusion of herb teas (tisanes) and ground coffee sold in "teabag" type containers.

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