Determination of the diffusion coefficient.

When the concertation of dissolved substance in various points of the solution is different, we observe the migration of the substance from the regions of higher concertation to those of lower concentrations. This migration is called the diffusion. In one dimensional diffusion, the rate of the diffusion , dn/dt of dn moles of dissolved substance that passes through the area A in the time dt is proportional to the concentration gradient, dc/dx:

$$\frac{dn}{dt} = -AD\left(\frac{\partial c}{\partial x}\right) \qquad [1]$$

The constant D is called the **diffusion coefficient**. The SI unit of D are meter squared per second (m^2/s).

A major problem in diffusion coefficient measurement is to make sure that the solute movement is solely a result of the diffusion, *i.e*, random molecular motion, and not by bulk liquid movement, *e.g,* convection. Bulk movement is prevented if the liquid is held in a gel. A gel is a comparatively rigid structure composed of a three-dimensional open network of polymer chains, the voids filled with liquids. Small molecules of solvent or solute can move about in a gel as freely as in ordinary liquid. This can easily be shown by measuring of conductivity of an ionic solute in a cooling solution of agar in water. The conductivity falls as the temperature falls, but there is no discontinuity as the mobile liquids turns into a firm gel.

A convenient experimental set for the diffusion coefficient measurement consist a concentrated solution of the solute under study. The glass cylinder (reservoir) is held vertical with the lower open end immersed in a baker with a large volume of stirred solvent. At the moment of immersion the solvent contains no solute, and the solute concentration from then on increase with time. Diffusion through the gel is in one dimension only, down the vertical axis. A mathematical analysis of this system, given by Hadgraft[i], shows that if less than 5% or so of the total amount of the solute in the gel has diffused out, then the number of the solute moles n_t diffused out at time t is

$$n_t = 2c_0 A\sqrt{\frac{Dt}{\pi}} \qquad [2]$$

where c_0 is the initial concentration in the gel, *D* denotes the diffusion coefficient of the solution and *A* – cross-section of the cylinder. By monitoring the solute concentration in the baker it is possible to determine the diffusion coefficient. Note, that the solute concentration c_t in the baker after time *t* is small but finite, and it can be calculated from [3]

$$c_t = \frac{n_t}{V_r} \qquad [3]$$

where Vr is the volume of the solvent in the reservoir. Combining [2] and [3] we obtain

$$\frac{c_t}{c_0} = \frac{2A}{V_r}\sqrt{\frac{Dt}{\pi}} \qquad [4]$$

Experimental

The goal of the experiment is to determine the diffusion coefficient of potassium chloride (KCl). Changes in KCl concentrations can be monitored conductometrically.

1. Dissolve about 0.4g KCl in 50cm^3 of water in a baker. Dilute with distilled water 5cm^3 (V_1) of prepared solution (of concentration c_0) to 250 cm^3 (V_2) volumetric flask.
2. Measure the conductance G_0 of the dilute solution, whose concentration is further denotes as c_0
3. Boil the remaining 45 cm3 of the initial solution and add 1g of agar crystals dissolve them on stirring.
4. Measure precisely the inner diameter, *d*, of the glass cylinder, pour the hot solution into this cylinder and leave it to cool.
5. When the room temperature gel is reached, which takes about 45 minutes, clamp the cylinder vertically at such a height that the lower end will be approximately 2 cm above the bottom of the 250 cm^3 baker containing 150 cm^3 (V_r) of water with a dipping conductivity cell immersed beforehand.
6. Note down the conductance of water G_{H2O} . The water should be vigorously stirred by magnetic stirrer.

7. At the moment of the immersion of the cylinder filled with gel into the reservoir start a stopwatch. In suitable time intervals (1, 2, 5, 10, 20, 30, 40, 55, 70 and 90 min) measure the conductance Gt of the solution in the baker.
8. At low electrolyte concentrations there is no significant error in assuming that conductance is linearly proportional to concentration. Thus, we can assume that Gt is proportional to ct, and G0 is proportional to c0. Taking into account that $c_0 = c_0 \frac{V_1}{V_2}$ and $A = \pi \left(\frac{d}{2}\right)^2$, where d is the cylinder diameter eq [4] can be transformed into:

$$\frac{G_t}{G_0} = \frac{d^2 V_2}{2 V_1 V_r} \sqrt{\pi D t} \qquad [5]$$

9. Using eq [5] calculate the values of *D* for different *t*. Calculate the diffusion coefficient of KCl as the arithmetic mean of the obtained D values.
10. Plot G_t vs. $\sqrt{t}$. Collect all data in table 1.

Table 1.

t	$\sqrt{t}$	G_t	D

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[i] Hagraft, J. *Init. J. Pharmaceut*. 1979, 2, 177-194