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Determination of the diffusion coefficient of sucrose in water and its hydrodynamic radius

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ABSTRACT

In this work, the diffusion coefficient of sucrose was determined in four experiments by varying the initial concentrations at different time rates. The amount of sucrose that diffused into the solvent column was determined via a coulometric assay developed by Dubois et al. In 200secs and at initial concentration of 0.5gmL^{-1} , the rate of diffusion was 99.43% while at the initial concentration of 3.0gmL^{-1} and in 800 secs the rate of diffusion was 99.88%. From the concentrations obtained after diffusion was allowed at the different time ranges, the average diffusion coefficient of $4.64 \times 10^{-8}\text{cm}^2\text{s}^{-1}$ was obtained. This value is in agreement with that obtained from literature ($4.586 \times 10^{-8}\text{cm}^2\text{s}^{-1}$). The hydrodynamic radius of the sucrose was consequently evaluated to be 51.34pm.

Key words: Diffusion coefficient, solvent column, hydrodynamic radius.

INTRODUCTION

Studies of reaction kinetics and the bulk fluid properties of liquids often require fundamental knowledge of mass transport in the condensed phase. The movement of molecules (considered in this experiment as the solute in a dilute solution) arises from one of the most basic properties of fluids, namely, the constant random motion of the constituent molecules. Even when there is no directed driving force for mass transport, such as a concentration gradient or a gravitational field (i.e., an isotropic medium), molecules are observed to undergo constant random displacements. A well-known example of this phenomenon is Brownian motion in which a particle moves in continual zigzag patterns. Over a long time period there is no *net* displacement of the particle because in the absence of a concentration, chemical, or potential energy gradient the probability of motion in any one direction is equal to the probability of motion in exactly the opposite direction.[1]

In this experiment, the directed displacement of molecules in solution will be considered. The driving force for this motion is a *concentration gradient*; thus solute will spontaneously flow from a region of higher concentration to one of lower concentration in a one-phase system. This process results in an entropy increase corresponding to the increase in the volume available to the solute as it moves into a more dilute environment; in this sense, we are dealing with an “entropy of mixing” phenomenon.

In the most general case, the driving force causing the change in local concentration of a solute is expressed in terms of the anisotropy (spatial asymmetry) of the chemical potential, μ . If we consider one-dimensional motion (along the

x axis), the instantaneous velocity of a molecule, v_x , is proportional to the gradient of the chemical potential at that point, thus

$$v_x = -u \left(\frac{\partial \mu}{\partial x} \right)_x \quad (\text{cm s}^{-1}), \quad (1)$$

where the proportionality constant, u , is called the *mobility*. The negative sign indicates that the molecule moves in a direction from higher to lower chemical potential, i.e., opposite to the gradient. u can also be expressed in terms of another constant, D , called the *diffusion coefficient* as

$$u = \frac{D}{kT} \quad (\text{sg}^{-1}), \quad (2)$$

where k is the Boltzmann constant and T is the absolute temperature. Equation (2) is known as the *Nernst-Einstein relation*, from which it can be seen that D has dimensions of $\text{cm}^2 \text{s}^{-1}$ [2]

If the concentration of the solute, C , is the number of moles per dm^3 , the *flux*, J_x , is defined as the number of moles passing through a unit cross section, (cm^2) per second, hence $J_x = v_x C$, and equations (1) and (2) can be combined and written

$$J_x = v_x C = -\frac{D}{RT} C \left(\frac{\partial \mu}{\partial x} \right)_x \quad (\text{moles cm}^{-2} \text{s}^{-1}) \quad (3)$$

Now if the chemical potential is expressed in terms of a concentration standard state, $C^\circ \equiv 1 \text{ mole dm}^{-3}$, $\mu = \mu^\circ + RT \ln C$, the concentration dependence of $d\mu$ becomes $d\mu = RT d(\ln C) = (RT/C)dC$, and if this relation is substituted into equation (3), we obtain

$$J_x = -D \left(\frac{\partial C}{\partial x} \right)_x \quad (4)$$

This is known as Fick's first law and is a more specific statement of mass transport than equation (3). Another fundamental law of mass transport, known as *Fick's second law*, is obtained from equation (4) through an application of the conservation of mass known as the *law of continuity*. The change in the flow rate (flux) after a system has moved from one volume element to another is equal to the concentration difference of the volume elements (per unit time). Mathematically, this is expressed as

$$\left(\frac{\partial J}{\partial x} \right)_t = - \left(\frac{\partial C}{\partial t} \right)_x \quad (5)$$

By differentiating equation (4) with respect to x and equating the result with that in equation (5), one obtains

$$\left(\frac{\partial J}{\partial x} \right)_t = \frac{d}{dx} \left[D \left(\frac{\partial C}{\partial x} \right)_t \right] \quad (6)$$

If we take D to be independent of the diffusion distance x , which is to say the solute concentration, Fick's second law then reads

$$\left(\frac{\partial C}{\partial t} \right)_x = D \left(\frac{\partial^2 C}{\partial x^2} \right)_t \quad (7)$$

The solution of equation (7) will describe the space and time dependence of the solute concentration as it undergoes diffusion. In order to solve this differential equation and apply the solution to the determination of the diffusion coefficient, it is important to consider the physical methodology of the experiment. A homogenous solution containing the solute at a concentration C is placed in a cylindrical vessel. This solution is suddenly but quiescently (i.e., without disturbance) placed in contact with pure solvent contained in a cylinder of the same diameter such that

the circular surfaces of the two liquids come into direct contact. The solution and solvent columns, which are quiescent i.e., no physical agitation), remain in contact for a measured period of time during which the solute spontaneously diffuses into the solvent. The two liquid columns are then separated at the same place as their original contact, and the amount of solute that has diffused into the solvent column is then determined. The procedure is shown schematically in Figure 1. The apparatus used in this experiment was devised by Polson [1,2] for use in determining the diffusion coefficient of a virus and is described in more detail below. The foregoing discussion of the experimental design allows us to establish the boundary conditions appropriate to the solution of equation (7)

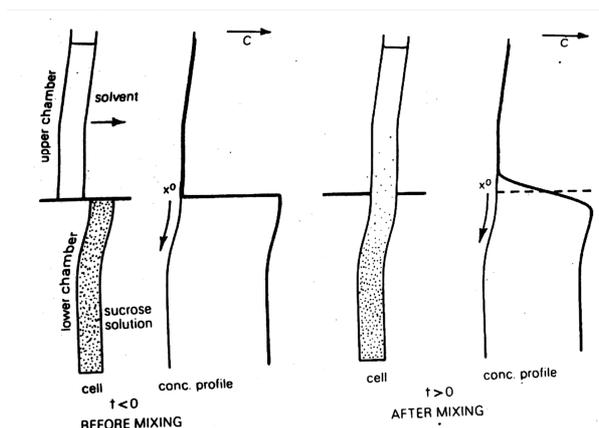


Fig. 1: Polson cell positions and concentration profiles before mixing (left) and after mixing (right)

$$\text{At } t \leq 0, C = C_0 \text{ for } x > 0 \quad \text{and} \quad C = 0 \text{ for } x < 0. \quad (8a)$$

$$\text{At } t > 0, C \rightarrow C_0 \text{ as } x \rightarrow +\infty \quad \text{and} \quad C \rightarrow 0 \text{ as } x \rightarrow -\infty, \quad (8b)$$

and

$$\text{As } t \rightarrow \infty, C \rightarrow \text{constant}.$$

As is indicated in equation (8b) the columns of liquid are presumed at this point to be infinitely long.

Fick's second law, equation (7) subject to the above boundary conditions, has the following solution $C(x,t)$ [3]. It is important to realize that this solution is valid only for finite times, i.e., after diffusion has commenced ($t > 0$).

$$C(x, t) = \frac{C_0}{2} \left\{ 1 - \text{erf} \left[\frac{x}{2(Dt)^{1/2}} \right] \right\}, \quad (9)$$

where erf denotes the error function,

Values of erf (w) can be obtained from standard mathematical tables. It should be noted that in this one-dimensional solution of Fick's second law, the space and time variables, x and t , are linked in the form $(xt^{-1/2})$; see equation (9). In order to express the diffusion coefficient in terms of experimentally measurable quantities, equation (9) is first differentiated with respect to x :

$$\left(\frac{\partial C}{\partial x} \right)_t = \frac{-C_0}{2} \left[\frac{1}{(\pi Dt)^{1/2}} \right] \exp \left(\frac{-x^2}{4Dt} \right). \quad (11)$$

This is the concentration gradient expressed as a function of x and t . If we now evaluate this gradient at the original interface, $x = 0$ (see Figure 1), we have

$$\left(\frac{\partial C}{\partial x} \right)_{x=0} (t) = \frac{-C_0}{2(\pi Dt)^{1/2}} \quad (12)$$

The concentration gradient in equation (12) can now be substituted in Fick's first law, equation (4), and defining the flux as $J = (1/A)dn/dt$, we have

$$\frac{dn}{dt} = -AD \frac{-C_0}{2(\pi Dt)^{1/2}} = \frac{AD^{1/2}C_0}{2(\pi t)^{1/2}}, \quad (13)$$

where dn is the number of moles transported through the cross-sectional area, A , (across the original boundary at $x = 0$) in the time dt . Equation (13) may now be integrated to provide the total number of moles of solute that diffuses across the $x = 0$ boundary during a time t :

$$\int_0^n dn = \frac{AD^{1/2}C_0}{2\sqrt{\pi}} \int_0^t \frac{dt}{t^{1/2}} \quad (14)$$

or

$$n = A \left(\frac{D}{\pi}\right)^{1/2} C_0 t^{1/2} \quad (15)$$

The length of the “solvent” cylinder is, in fact, finite, i.e., h cm high. The *bulk* (mixed) concentration of solute that has diffused during the time interval t is then $C = n/Ah$. Substituting n into equation (15) and solving for D provides the final result for the measured diffusion coefficient [4]:

$$D = \frac{h^2(C/C_0)^2\pi}{t} \text{ (cm}^2\text{s}^{-1}\text{)} \quad (16)$$

Interestingly, the diffusion coefficient can be used to determine not only quantitative transport properties of a solute but also certain structural characteristics of the solute in a given solvent environment. The relationship between the diffusion coefficient and the “size” of the solute is contained in the *Stokes-Einstein equation*. It expresses D_0 , the diffusion coefficient at *infinite dilution*, in terms of the solvent viscosity, η , and the “effective” radius, R' , of the solute:

$$D_0 = \frac{kT}{6\pi\eta R'} \quad (17)$$

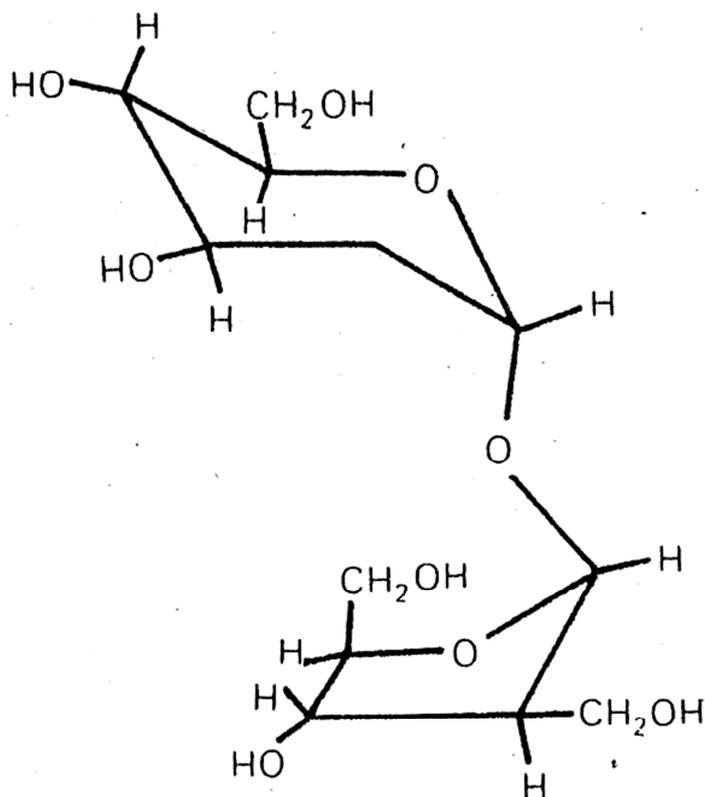
k is the Boltzmann constant and T is the absolute temperature. There are several important assumptions implicit in equation (17). Two of these are that the solute is spherical, and considerably larger than the solvent molecules. Deviations from spherical geometry (such as oblate or prolate ellipsoids) could cause equation (17) to be in error up to about 30 to 40 percent [3]. For solutes of similar size to that of the solvent, the 6 in the denominator of (17) is sometimes replaced by 4. Stoke’s law was actually developed to deal with macroscopic particles, and Einstein successfully applied it to the quantitative observation of the random displacements (Brownian motion) of colloidal particles. The falling-sphere method of measuring viscosities is an explicit application of Stoke’s law to a macroscopic body. Stoke’s law was also invoked in the treatment of falling oil drops in the famous experiment by Millikan *et al.* in 1909. [5]

It is remarkable that a fluid dynamic treatment of mass transport pertaining to 0.01 – to 1-cm objects (which underlies the development of the Stokes-Einstein equation) can be successfully extended to the level of molecular dimensions, i.e., $\sim 10\text{\AA}$. Einstein’s application of Stoke’s law to Brownian motion (1905) provided a theoretical basis that was used to support the then still unaccepted idea of atomicity – that molecules are specific, discrete entities.

The diffusion coefficient reflects the transport properties of the solute under *solvated* conditions and therefore the “effective radius,” R , represents the radius of the solute that may contain bound (e.g., hydrogen-bonded) solvent molecules that on a time-averaged basis are part of the solute structure. The effective radius, which includes the associated solvation shell, is referred to as the *hydrodynamic radius*.

Using the Stokes-Einstein equation (17) to estimate the hydrodynamic radius of a solute requires knowledge of D_0 . Some of the assumptions that underlies this equation would seem to make its application semiquantitative at best [after all, the measurement of *one number* (the diffusion coefficient) cannot provide much information about something as complex as molecular structure]. Nevertheless, some insight into the gross structure of solvated molecules (including biologically significant macromolecules) can be obtained. In this experiment, the diffusion

coefficient of sucrose in aqueous solution will be determined at different concentrations, and D_0 will be obtained by extrapolation. The concentration dependence of D is observed to be very slight, and a linear extrapolation to zero concentration can be empirically justified [6]. The hydrodynamic radius will be estimated from D_0 and the Stokes-Einstein equation. Sucrose is a disaccharide in which two cyclic forms of simple sugars, glucose and fructose, are linked together. The structure is shown below.



It is obvious that in aqueous solution there is appreciable hydrogen bonding between the solvent and the sucrose molecule.

MATERIALS AND METHODS

The Polson apparatus is shown in Figure 2.

It consists of two cylinders constructed from an inert material such as stainless steel, brass, or bronze. Six 1/4-in-diameter cylindrical holes, or columns, precisely spaced 60° apart, are drilled into the two cylinders. The six holes completely pass through the upper cylinder and terminate in a blind end in the lower one. The two cylinders are in close, fluid-tight contact, the upper one being designed to rotate smoothly with respect to the lower one.

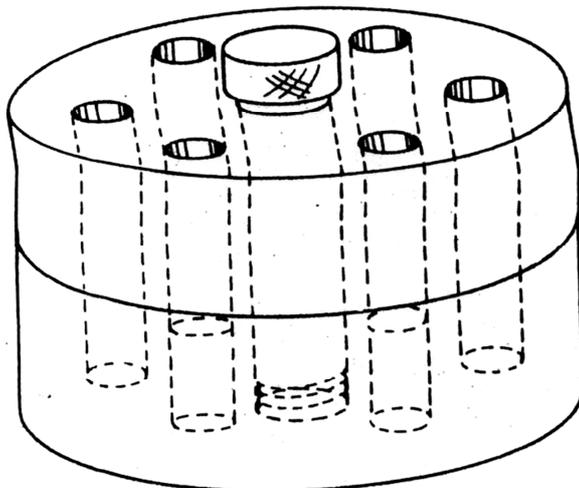


Figure 2: Diagram of the Polson cell

The upper cylinder is first rotated to a position in which the two columns are in precise alignment. The solution (concentration C_0) is then added to three *alternate* chambers so that the liquid levels are slightly *above* the boundary plane between the two cylinders. The upper cylinder is next rotated by about 1/12 revolution so that the three empty chambers are situated above the boundary surface of the lower cylinder. These chambers are then filled with solvent, and the upper cylinder is *slowly* and steadily rotated *ahead* (i.e., clockwise, viewed from above) so that the solvent-filled chambers are precisely (and quiescently) placed above the solution-filled chambers. The upper cylinder contains notches allowing the user to determine when the upper and lower cylinder holes are in alignment.

At this point, a discontinuous concentration gradient is created between the upper and lower chambers (the concentration profile now represents a step function). A timer is then started. After an appropriate time (t) has elapsed, the upper cylinder is *slowly* rotated *back* by 1/12 revolution to separate the upper and lower chambers, and the contents of the three isolated upper chambers are combined and mixed. The solute concentration (C) of the sampled liquid is then determined, and the diffusion coefficient is calculated through equation (16). This procedure can be repeated using different diffusing time and/or initial solute concentrations.

RESULTS AND DISCUSSION

Table 1 below gives results of diffusion measurements obtained.

Table 1: Diffusion Measurements

Expt	Upper Chamber height = 3cm		Temperature = 28°C (301K)	
	Initial conc. gmL ⁻¹	Contact time (secs)	Resulting conc. 10 ⁻⁴ gmL ⁻¹	D 10 ⁻⁸ cm ² S ⁻¹
1	0.5	200	2.85	4.584
2	1.0	400	8.05	4.581
3	2.5	600	24.67	4.590
4	3.0	800	35.02	4.820
				$\bar{D} = 4.64$

The diffusion of solute into solvent is, in fact, a bilateral process consisting of : (1) the solute molecules moving up into solvent; and (2) the solvent molecules moving down into solution. This intermingling of solute and solvent molecules goes on, so that ultimately a solution of uniform concentration results. It is this tendency to equalize concentration in all parts of the solution which is responsible for the diffusion of the solute. Thus diffusion of solute will also take place when two solutions of unequal concentration are in contact. This diffusion process is time and concentration dependent as depicted in equation (17). The measurements carried showed that diffusion rate increases with increase in both time and concentration. The average value of $4.64 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ obtained for sucrose did not deviate much from the value of $4.586 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ from literature.

Now, taking the value of D in Expt 4 as the diffusion coefficient at infinite dilution ($D_0 = 4.820 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$) and using the Stokes-Einstein equation the effective radius, R of the sucrose is estimated at 51.34pm. Again, this empirical value is reasonably rational.

Because the drift speed governs the rate at which charge is transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size. Experiments confirm these predictions for bulky ions (such as R_4N^+ and RCO_2^- but not for small ions. For example, the molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ even though the ionic radii increase. The paradox is resolved when we realize that the radius R in the formula is the *hydrodynamic radius* of the ion ie its effective radius in the solution taking into account all the H_2O molecules it carries in its hydrogen sphere. The very low value of the sucrose hydrodynamic radius goes to explain its high solubility in water.

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