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DIFFUSION OF SODIUM ALGINATE IN AQUEOUS SOLUTIONS AT INFINITESIMAL CONCENTRATION AND AT PHYSIOLOGICAL TEMPERATURE

Keywords: Diffusion coefficient; Transport; Sodium alginate; Polyelectrolyte; Solutions.

Taylor dispersion technique has been used for measuring mutual diffusion coefficients of sodium alginate at infinitesimal concentration at 25 °C and 37 °C. From these experimental data, it was possible to estimate the limiting ionic conductivity, the tracer diffusion coefficient of the alginate anion, and the hydrodynamic radius of the unit of sodium alginate ($\text{NaC}_6\text{H}_7\text{O}_6$) at both temperatures, as well as, to discuss the influence of the temperature on the behavior diffusion of alginate in aqueous solutions at infinitesimal concentration, supplying the scientific and technological communities with data on these important parameters in solution transport processes.

Ключевые слова: коэффициент диффузии, транспорт, альгинат натрия, полиэлектrolит, растворы.

Резюме: Метод дисперсионного анализа Тейлора был использован для измерения коэффициентов взаимодиффузии альгината натрия в бесконечно малой концентрации при 25 °C и 37 °C. На основе этих экспериментальных данных, было возможно оценить предельную ионную проводимость, коэффициент диффузии меченого аниона альгината, и гидродинамический радиус фрагмента альгината натрия ($\text{NaC}_6\text{H}_7\text{O}_6$) при обеих температурах, а также обсудить влияние температуры на характер диффузии альгината в водных растворах при бесконечно малой концентрации, и ознакомить научно-техническое сообщество с данными о вкладе этих важных параметров в процессы переноса в растворе.

1. Introduction

Alginates are polysaccharides characterized by a wide variety of industrial applications including food, pharmaceuticals and biomedical [1-6]. For example, as biomaterials, these compounds can easily be formulated into a variety of soft, elastic gels, fibers and foams at physiological conditions ensuring the preservation of cell viability and function [1]. Among them, sodium alginate ($\text{NaC}_6\text{H}_7\text{O}_6$, Fig. 1) is water soluble taking a form of viscous hydrocolloid, dispersions or gels by cross linking [2] with the ability to hydrate in hot or cold water to form viscous solutions, dispersions or gels.

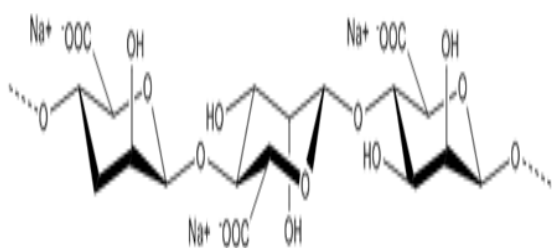


Fig. 1 - Sodium alginate general structure (Andersen et al., 2012) [1]

However, the properties and behavior of these chemical systems are poorly known, even though this is a prerequisite to obtain adequate understanding, e.g., some problems that appear in industrial applications and that involve mass transfer. In fact, as shown in the literature, there are a few studies on the transport of alginate in aqueous media (e.g., [2-6]). This has provided the impetus for the present study of the diffusion of the alginate in aqueous solutions [4].

In this work, we propose to extend our studies of diffusion using Taylor technique, already started with some concentrations of alginate, to infinitesimal concentrations [4] at 25 °C and 37 °C.

From these diffusion coefficients at infinitesimal concentration, the hydrodynamic radius and the limiting ionic conductivity of the unit of sodium alginate ($\text{NaC}_6\text{H}_7\text{O}_6$), as well as, the mutual and the tracer-diffusion coefficients, are computed and discussed. However, it is necessary to distinguish between two last parameters: tracer diffusion D^* (intradiffusion, single ion diffusion, ionic diffusion) and mutual diffusion D (interdiffusion, concentration diffusion, salt diffusion) [7-10]. Many techniques are used to study diffusion in aqueous solutions. Methods such as NMR, polarographic, and capillary-tube techniques with radioactive isotopes measure tracer-diffusion coefficients ("intradiffusion coefficients"). However, for bulk ion transport the appropriate parameter is the mutual diffusion coefficient, D . Relationships derived between intradiffusion and mutual diffusion coefficients, D^* and D , have had limited success and consequently mutual diffusion coefficients are much needed.

Thus, our main goal is to reach a better understanding of the structure of these polyelectrolytes in aqueous solutions that will give us a useful tool for the structural interpretation of these systems.

2. Experimental

2.1 Materials

Sodium alginate was supplied from Sigma-Aldrich Sigma (*pro analysis* > 99 %). Milli-Q® water (from A10 Millipore®) was used as solvent.

The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using Millipore-Q water. The solutions were freshly prepared

before each set of runs. The uncertainty concerning their compositions was usually within $\pm 0.1\%$.

2.2 Diffusion measurements

The Taylor dispersion method for measuring diffusion coefficients is based on the dispersion of a very small amount of solution injected into a laminar carrier stream of solvent or solution of different composition flowing through a long capillary tube (e.g., [11-16]). (Fig. 2).

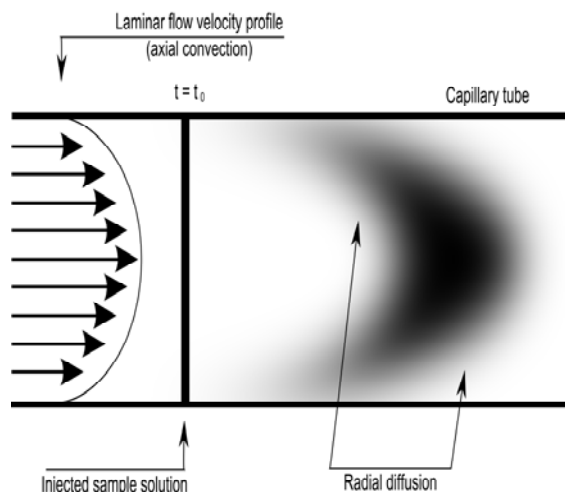


Fig. 2 - Schematic representation of the Taylor dispersion technique [11]

The length of the tube was determined by direct measurement by stretching it in a large hall and using two high quality theodolites and appropriate mirrors capable of focusing the capillary tube ends very accurately. This technique gave a tube length of $3.2799 (\pm 0.0001) \times 10^3$ cm, in agreement with less-precise check measurements using a good quality measuring tape. The radius of the tube was obtained by accurately weighing (resolution 0.1 mg) the tube when empty and when filled

with distilled water of known density. This procedure gave a tube radius of $0.05570 (\pm 0.00003)$ cm.

At the start of each run, a 6-port Teflon injection valve (Rheodyne, model 5020) was used to introduce 0.063 cm^3 of solution into the laminar carrier stream of slightly different composition. A flow rate of $0.23 \text{ cm}^3 \text{ min}^{-1}$ (corresponding to 3.5 rotations per minute of the peristaltic pump head) has been used, and was controlled by a metering pump (Gilson model Miniplus 3) to give retention times of about 8×10^3 s. The dispersion tube and the injection valve were kept at 298.15 K and 303.15 K (± 0.01 K) in an air thermostat.

Dispersion of the injected samples was monitored using a differential refractometer (Waters model 2410) at the outlet of the dispersion tube. Detector voltages, $V(t)$, were measured at accurately timed 5 s intervals with a digital voltmeter (Agilent 34401 A) with an IEEE interface. Binary diffusion coefficients were evaluated by fitting the dispersion equation

$$V(t) = V_0 + V_1 t + V_{\max} (t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2] \quad (1)$$

to the detector voltages. The additional fitting parameters were the mean sample retention time t_R , peak height V_{\max} , baseline voltage V_0 , and baseline slope V_1 .

In these experiments, small volumes, ΔV of the solution of different composition, c , were injected into water to measure the diffusion coefficients, D , at infinitesimal concentration.

3. Results and discussion

3.1 Mutual and tracer diffusion coefficient at infinitesimal concentration from Nernst-Hartley equation

The limiting mutual diffusion coefficient at infinitesimal concentration D^0 values for different molecular weights, were estimated by extrapolating experimental data to $c \rightarrow 0$ (Table 1), provided that the carrier stream is pure solvent.

Table 1 - Mutual diffusion coefficients, D , of sodium alginate in aqueous solutions at different injection concentrations using pure water as carrier stream, obtained from the Taylor technique, at $T = 25^\circ\text{C}$ and $T = 37^\circ\text{C}$

$c / (\text{g dm}^{-3})$	$D \pm S_D^a / (10^{-9} \text{ m}^2 \text{ s}^{-1})$	$D \pm S_D^a / (10^{-9} \text{ m}^2 \text{ s}^{-1})$
0.0010	0.599 ± 0.021	0.835 ± 0.020
0.0030	0.580 ± 0.018	0.820 ± 0.018
0.0050	0.566 ± 0.012	0.811 ± 0.012
0.0075	0.543 ± 0.002	0.796 ± 0.002
0.0100	0.521 ± 0.010	0.781 ± 0.010
	$D^0 = 0.607 \times 10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ b}}$	$D = 0.840 \times 10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ b}}$

^a D is the mean diffusion coefficient value from 4-6 experiments and S_D is the standard deviation of that mean. ^bExtrapolated values obtained from the D least-squares for total number of injections.

The limiting tracer diffusion coefficients at 25°C and 37°C , D_T^0 , can be estimated through the Nernst equation (equation 2) [7-9]

$$\lambda_{\text{alginate}}^0 = \frac{D_T^0 Z_a F^2}{RT} \quad (2)$$

where $\lambda_{\text{alginate}}^0$ represent the equivalent conductance at infinitesimal concentration of the alginate at temperature T , whose value is estimated by using the Nernst-Hartley equation (3) [7-9],

$$D^0 = \frac{RT}{F^2} \left(\frac{|Z_c| + |Z_a|}{|Z_c Z_a|} \right) \frac{\lambda_c^0 \lambda_a^0}{\lambda_c^0 + \lambda_a^0} \quad (3)$$

in which we are assuming that the experimental values of mutual D^0 (Table 1) are equal to the values obtained by this equation (3) and Z_c and Z_a , and λ_c^0 and λ_a^0 represent the algebraic valences and the equivalent

conductance at infinitesimal concentration of Na^+ and alginate ions respectively. By taking the limiting ionic conductivity of sodium ion as equal to $50.51 \times 10^{-4} \text{ m}^2 \text{ mol}^{-1}$ for 25°C and $63.94 \times 10^{-4} \text{ m}^2 \text{ mol}^{-1}$ for 37°C [8], we obtained $\lambda_{\text{alginate}}^0$ equal to $14.72 \times 10^{-4} \text{ S.m}^2 \text{ mol}^{-1}$ and $39.10 \times 10^{-4} \text{ S.m}^2 \text{ mol}^{-1}$, respectively. From these values, the corresponding limiting tracer diffusion coefficients, D_T^0 , were estimated and shown in Table 2.

Table 2 - Hydrodynamic radius, R_h , of sodium alginate, limiting ionic conductivity, $\lambda_{\text{alginate}}^0$, tracer diffusion coefficients, D_T^0 , and limiting mutual diffusion coefficients, D^0 , at $T = 25^\circ\text{C}$ and $T = 37^\circ\text{C}$

$T/^\circ\text{C}$	$\lambda_{\text{alginate}}^0 / (10^{-4} \text{ m}^2 \text{ mol}^{-1} \text{ S})$	$R_h / (\text{nm})$	$D^0 / (10^{-9} \text{ m}^2 \text{ s}^{-1})$	$D_T^0 / (10^{-9} \text{ m}^2 \text{ s}^{-1})$
25	14.72	0.628	0.607	0.391
37	39.10	0.303	0.840	1.083

From the analysis of Table 2, we can see that the mutual diffusion coefficients values of this system at infinitesimal concentration are significantly larger (1.5 times and 1.3 times for 25°C and 37°C , respectively) than those of the corresponding tracer diffusion coefficients. This increase characterises the electrostatic dragging effect of the sodium ions on the alginate ions.

3.2 Hydrodynamic radius of the sodium alginate

As it is well-known, the Stokes–Einstein equation for spherical particles (equation 4) [8,9] can be used to estimate the size of solute molecules treated as Brownian particles immersed in a continuum fluid, provided that the solute particle is at infinitesimal concentration and it is large compared to the solvent molecules. Equation (4) (where η^0 is the macroscopic viscosity value of the solvent [10], T the absolute temperature and k_B the Boltzmann constant) establishes a link between the hydrodynamic radius of an equivalent spherical particle, R_h , and its tracer diffusion coefficient, D_T^0 ,

$$D_T^0 = k_B T / (6\pi\eta^0 R_h) \quad (4)$$

Thus, the hydrodynamic radii of alginate anion for two different temperatures were estimated from this equation, which assumes that the particles are perfectly spherical and are solely subject to solvent friction (Table 2).

This relation can only be considered as an approximated one, (mainly arising from the fact that the structure of both the solute kinetic species and the solvent are disregarded). However, since sodium alginate is relatively large compared to water molecules, it can be used to derive some valuable information on the relation between alginate size, shape, and tracer-diffusion coefficient at infinitesimal concentration.

4. Conclusions

It was possible to determine experimental limiting mutual diffusion coefficients at infinitesimal concentrations of alginate at 25°C and 37°C , using the Taylor technique.

From these data, we have estimated the limiting ionic conductivities, the hydrodynamic radii of alginate ion and the limiting diffusion coefficients (tracer and mutual), permitting us to provide the usefulness of the transport data to model the diffusion for *in vivo* applications.

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