1. Introduction

Alginates are polysaccharides characterized by a wide variety of industrial applications including food, pharmaceuticals and biomedicals [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 (NaC6H7O6, 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 ºC and 37 ºC. From these diffusion coefficients at infinitesimal concentration, the hydrodynamic radius and the limiting ionic conductivity of the unit of sodium alginate (NaC6H7O6), 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 ± 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 theodolytes and appropriate mirrors capable of focusing the capillary tube ends very accurately. This technique gave a tube length of 3.2799 (± 0.0001) x 103 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 (± 0.00003) cm. At the start of each run, a 6-port Teflon injection valve (Rheodyne, model 5020) was used to introduce 0.063 cm3 of solution into the laminar carrier stream of slightly different composition. A flow rate of 0.23 cm3 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 x 103 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 $V(t) = V_0 + V_1 t + V_{max} (t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2 t]$ (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 Nersnt-Hartley equation The limiting mutual diffusion coefficient at infinitesimal concentration D_0 values for different molecular weights, were estimated by extrapolating experimental data to $c \circledR 0$ (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 ºC and T = 37 ºC c /(g dm-3) D ± a)/(10-9 m2 s-1) D ± a)/(10-9 m2 s-1) 0.0010 0.0030 0.0050 0.0075 0.0100 0.599 ± 0.021 0.580 ± 0.018 0.566 ± 0.012 0.543 ± 0.002 0.521 ± 0.010 0.835 ± 0.020 0.820 ± 0.018 0.811 ± 0.012 0.796 ± 0.002 0.781 ± 0.010 D_0 = 0.607 x 10-9 m2 s-1 b) $D_\square$ = 0.840 x 10-9 m2 s-1 b) aD is the mean diffusion coefficient value from 4-6 experiments andis 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 ºC and 37 ºC, D_{T0}, can be estimated through the Nernst equation (equation 2) [7-9] (2) where $l_{0alginate}$ 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], (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 l_{0c} and l_{0a} 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 50.51×10^{-4} m2 mol−1 for 25 ºC and 63.94×10^{-4} m2 mol−1 for 37 ºC [8], we obtained $l_0$alginate equal to 14.72×10^{-4} S.m2 mol−1 and 39.10×10^{-4} S.m2 mol−1, respectively. From these values, the corresponding limiting tracer diffusion coefficients, D_{T0}, were estimated and shown in Table 2. Table 2 - Hydrodynamic radius, R_h, of sodium alginate, limiting ionic conductivity, $l_0$alginate, tracer diffusion coefficients, D_{T0}, and limiting mutual diffusion coefficients, D_0, at T = 25 ºC and T = 37 ºC

T/ºC	$l_0$alginate/ (10^{-4} m2 mol-1 S)	R_h/(nm)	D_0/ (10^{-9} m2 s-1)	D_{T0}/ (10^{-9} m2 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 ºC and 37 ºC, 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 h_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_{T0}, $D_{T0} = k_BT/(6ph_0R_h,)$ (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 ºC and 37 ºC, 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.