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Influence of fructose on the diffusion of potassium hydrogen phosphate in aqueous solutions at 25 °C

Luis M.P. Verissimo [a,b], Joana M.M. Teigão [a], M. Luísa Ramos [a], Hugh D. Burrows [a], Miguel A. Esteso [b], Ana C.F. Ribeiro [a,*]

[a] Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[b] U.D. Química Física, Facultad de Farmacia, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain

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ABSTRACT

Diffusion coefficients have been measured at 25 °C for potassium hydrogen phosphate (K_2HPO_4, 0.101 mol kg^{-1}) in aqueous solutions containing various concentrations of fructose from (0.001 to 0.101) mol kg^{-1}, using a conductimetric cell (the Lobo cell) coupled to an automatic data acquisition system. Significant effects of fructose were observed on the diffusion of K_2HPO_4 in these mixtures, which are attributed to the interaction between HPO_4^{2-} anion (or other protonated forms) and fructose. Support for this comes from ^{1}H and ^{13}C NMR spectroscopy, which are compatible with binding between the anomeric forms of D-fructose and the HPO_4^{2-} anion.

1. Introduction

Carbohydrates are the most abundant biological molecules [1], and are widely distributed in nature. They can be isolated from plants, animals, bacteria and fungi as molecules of low molar mass, oligosaccharides or as polymers. They are also building units of natural products, complex carbohydrates, molecules in which carbohydrates appear covalently bound to proteins, lipids or a glycon (alkaloids, steroids, etc.). The knowledge of the qualitative and quantitative distribution of these compounds in materials, especially those related with food chain and human health, is extremely important because the carbohydrates are one of the main food constituents and they are involved in food authenticity, nutritional characteristics (as flavour and sensory) and are frequently responsible for some biological activity. Moreover, they are involved in all metabolisms of living organisms, in the storage and transport of energy, and are present as structural components.

Monosaccharides, are chiral polyhydroxy carbonyl compounds, and of particular relevance. These often exist in cyclic hemiacetal form, as pyranoses or furanoses, which can often be isolated in pure form. However, acyclic isomers have also been detected as very minor components in solution, where they coexist in equilibrium with the cyclic forms. Fructose is a monosaccharide found *in natura* in fruits and honey. However, exponential growth in the use of high fructose corn syrup (HFCS) as a sweetener in processed foods, appeared on the focus of recent scientific literature as a main cause of both the obesity epidemics and a growing number of fructose-correlated diseases and conditions [2–10].

In aqueous solution, free ketoses may exist as four forms: α_p, β_p, α_f and βf, which interconvert through the acyclic form. The β anomers prevail for D-fructose (Scheme 1), and only traces of α_f are observed. The α_p and the acyclic forms are not detected. The main structural difference between pyranose and furanose anomers is at C(6)H_2. D-Fructose dissolves in water and reaches the equilibrium state, which depends on temperature. In D_2O, at 20 °C, the anomeric composition is 75% of β-D-fructopyranose, 21% of α-D-fructofuranose, and 4% of β-D-fructofuranose [11].

We have previously reported transport properties of aqueous solutions of fructose alone [12] and in the presence of calcium chloride [13], copper (II) chloride [14] and ammonium vanadate [15]. There are indications in this last case of oxidation of the carbohydrate and reduction of vanadium(V).

Phosphates are critical for human life, and they fulfill important roles e.g. ATP/ADP energy management or pH buffering. Mobility of phosphates in and around cells is critical and changes in this parameter can seriously compromise health.

Systems containing fructose and phosphates have significant biological, technological and environmental relevance, and can either be chemically bound, as in fructose phosphates [16], or

* Corresponding author.
E-mail address: anacfrib@ci.uc.pt (A.C.F. Ribeiro).

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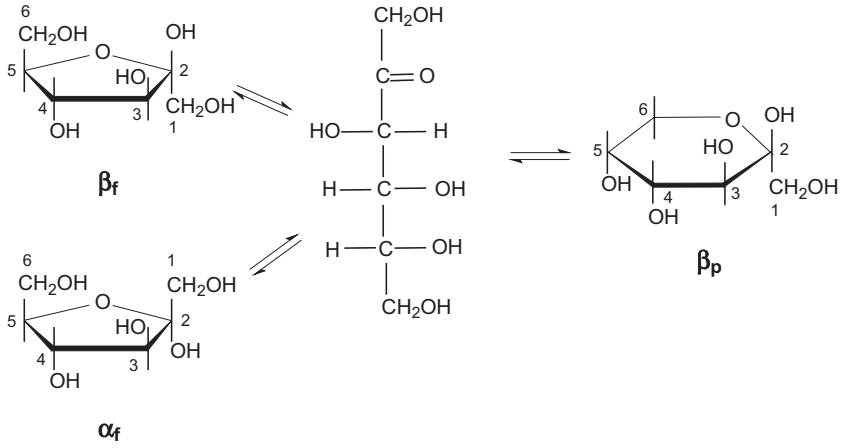

Scheme 1. Representation of different forms of fructose.

associated through noncovalent interactions, such as hydrogen bonds [17]. In fact, this carbohydrate is an important component in formulations for pharmaceutical, food, and biomedical applications. We have been particularly interested in extending our studies on the multicomponent transport behaviour of aqueous solutions of fructose to the characterization of the diffusion of systems containing K_2HPO_4 and fructose, since these studies may lead to a better understanding of the physical chemistry underlining the diffusion phenomena of these two species in human biological systems.

The present work combines an NMR spectral study of the species present in solution with the experimental determination of diffusion coefficients for a system containing K_2HPO_4 and fructose at 25 °C, using an open-ended capillary cell developed by Lobo [18–25]. Significant effects on these data were observed in the presence of the fructose, suggesting interaction between this carbohydrate and K_2HPO_4.

2. Experimental

2.1. Materials

The solutes used in this study, K_2HPO_4 (*Riedel-de Häen*, mass fraction purity > 0.99) and D-fructose (*Baker*, mass fraction purity 0.99) (Table 1), were used as received. Solutions for the mutual diffusion measurements were prepared in calibrated volumetric flasks using ultrapure water (*Millipore*, 18.2 MΩ cm^{-1} at 25 °C). For the NMR measurements, D-fructose 0.089 mol kg^1, alone, pH* 7.2 (pH* of dissolution) and in the presence of K_2HPO_4, 0.089 mol kg^1, pH* 9.0 (pH of mixing), were prepared in D_2O (mass fraction purity 0.999, Aldrich). The pH* value quoted is the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers [26]. The ^1H and ^{13}C spectra were obtained on a Bruker Avance III 500 spectrometer. The methyl signal of *tert*-butyl alcohol was used as internal reference δ = (1.3 and 31.2)10^{-6} for ^1H and ^{13}C, respectively. All solutions were freshly prepared before each experiment. The solutions (concentrations in molality, as is usually defined, moles of solute per kg of water) were freshly prepared and de-aerated for about 30 min before each set of runs.

Table 1
Sample description.

Chemical name	Source	Purity
K_2HPO_4	*Riedel-de Häen*	Mass fraction > 0.99 (as stated by the supplier)
D (−) Fructose	*Baker*	Mass fraction > 0.99 (as stated by the supplier)

2.2. Mutual diffusion coefficients, D, measured by the open-ended conductimetric capillary cell

The open-ended capillary cell employed, which has previously been used to obtain mutual diffusion coefficients for a wide variety of electrolytes, has been described in detail in previous papers [18,19,27]. Fig. 1 shows a schematic representation of the open-ended capillary cell. This apparatus is essentially the same as previously reported [18,19,27]. It consists basically of two vertical capillaries, each closed at one end by a platinum electrode, and positioned one above the other with the open ends separated by a distance of about 14 mm. The upper and lower tubes, initially filled with solutions of concentrations 0.75 $\bar{m}$ and 1.25 $\bar{m}$, respectively, are surrounded with a solution of concentration $\bar{m}$ of electrolyte. We prepared aqueous solutions of concentration $\bar{m}$ = 0.1 mol kg^{-1} of K_2HPO_4 and various concentrations of fructose (*i.e.*, 0.001 mol kg^{-1}, 0.005 mol kg^{-1}, 0.010 mol kg^{-1},

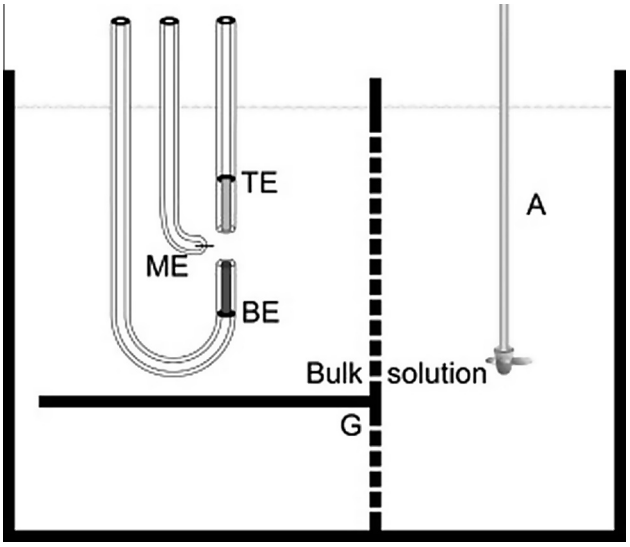

Figure 1. Schematic representation of the Lobo's open-ended capillaries conductimetric cell. TE and BE are the top and the bottom Pt-electrodes, respectively; ME is the medium Pt-electrode; G is a grid-bulkhead (in perspex); and A is a glass stirrer [18,19].