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Diffusion coefficients of β-cyclodextrin sulfated sodium salt in aqueous solutions

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ABSTRACT

The Taylor dispersion technique has been used for measuring mutual diffusion coefficients of β-cyclodextrin sulfated sodium salt ($NaSO_3\beta CD$) at temperatures (298.15 and 310.15) K and at finite concentrations. These studies have been complemented by density and viscosity measurements. From these experimental results, the hydrodynamic radius R_h, and its dependence on the viscosity, diffusion coefficient at infinitesimal concentration, D^0, ion conductivity of $NaSO_3\beta CD$ and the thermodynamic factor, F_T, have been estimated, permitting us to have a better understanding of the structure of the aqueous system containing $NaSO_3\beta CD$.

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1. Introduction

Cyclodextrins (CDs) are among the most important carriers and useful functional excipients. They are cyclic oligosaccharides composed, in the more common forms, of six to eight α-1,4-linked α-D-glucopyranose units (α-, β- and γ-cyclodextrin). They have a truncated cone structure with a hydrophilic external surface and a relatively non-polar cavity [1–3] because of the primary (on the narrow side of the cone) and secondary hydroxyl groups of the glucose units point to the external part of the structure.

CDs form inclusion complexes with a wide variety of ions and molecules. Due to this ability, the most common pharmaceutical application of cyclodextrins is to increase the solubility of poorly soluble drugs and to engineer slow-release delivery systems for drug molecules (*e.g.* [2,4,5]). In addition, aqueous solutions of CDs have also become important systems in fundamental and other applied research due to their wide range of applications [6–9]. However, while numerous studies have been devoted to the structural aspects of these systems involving cyclodextrins and different drugs in aqueous solutions (*e.g.* [1–3]), multicomponent mutual diffusion data for these systems are practically nonexistent (*e.g.* [10–25]). Moreover, their transport behaviour under different conditions relevant to physiological conditions are still poorly understood, even though this is a prerequisite to obtain systems with safer and effective anaesthetic formulations. Thus, this has provided the impetus for the present study of the diffusion of one cyclodextrin in aqueous solutions. As far as the authors know, no data on mutual diffusion coefficients of β-cyclodextrin sulfated sodium salt ($NaSO_3\beta CD$) have been published.

In the present work, the densities, viscosities and the binary diffusion coefficients, *D*, using the Taylor technique, for aqueous solutions of $NaSO_3\beta CD$ at $T = (298.15$ and $310.15)$ K were measured. From these results, we have estimated some thermodynamic and structural parameters, contributing this new information to a better understanding of the transport behaviour of this carrier in aqueous solution at different concentrations and to contribute to the design of better matrices and appropriate conditions for the release and uptake of different drugs (see scheme 1).

2. Experimental

2.1. Materials

The β-cyclodextrin sulfated sodium salt ($NaSO_3\beta CD$) was used as received without further purification (table 1). Nevertheless,

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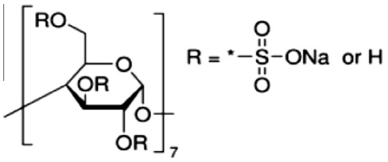

SCHEME 1. Structure of β-cyclodextrin sulfated sodium salt (see table 1).

its water content (7 mass per cent by Karl Fischer) and purity (mass fraction > 0.99 by HPLC-UV, $\lambda = 254$ nm) were checked and these values taken into account to calculate the concentration of the solutions used in this study. The 'work solutions', prepared by using Millipore-Q water, were freshly prepared and de-aerated for about 30 min before use. The uncertainty concerning their compositions was always less than ±0.1%.

2.2. Apparatus and procedures

2.2.1. Density measurements

The densities of $NaSO_3\beta CD$ aqueous solutions at $T = (298.15$ and $310.15)$ K were determined with an Anton Paar DMA5000 M densimeter (precision of $1 \cdot 10^{-6}\ g \cdot cm^{-3}$ and accuracy of $5 \cdot 10^{-6}\ g \cdot cm^{-3}$ in the range of (0–90) °C for temperature within ±0.005 K and (0–1.0) MPa pressure). The uncertainty of the results obtained is estimated to be less than 0.001%.

2.2.2. Viscosity measurements

Viscosity measurements of these solutions were determined with an Ostwald type viscometer, calibrated from water, immersed into a water-thermostat bath which temperature was controlled within ±0.02 K by using a digital thermometer. The arithmetic mean value of four flow times for each solution was taken to calculate such viscosity values. The measurement of the efflux time was carried out with a stopwatch with a resolution of 0.2 s. The uncertainty of the results obtained is estimated to be less than 1%.

2.2.3. Diffusion measurements

The Taylor dispersion is well described in the literature and consequently only some important points concerning the use of this method for the experimental determination of binary diffusion coefficients are described here [26–32].

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 (length 3279.9 cm, inner radius $r = 0.0557$ 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 $0.23\ cm^3 \cdot min^{-1}$ (corresponding to 3.5 rotations per minute of the peristaltic pump head) was used and controlled by a metering pump (Gilson model Miniplus 3) to give retention times of about $8 \cdot 10^3$ s. The dispersion tube and the injection valve were kept at $T = (298.15$ and $303.15)$ K (±0.01 K) in an air thermostat.

TABLE 1
Provenance and mass fraction purity of the materials studied.

Chemical name	Source	CAS number	Water content	Mass fraction purity
β-Cyclodextrin – sulfated sodium salt	Sigma–Aldrich [a]	37191-69-8	7%	>0.99[b]

[a] β-Cyclodextrin, sulfated sodium salt; General catalog, 389,153 [Online]; Sigma–Aldrich Co. LLC: St. Louis, Missouri, (2013), www.sigmaaldrich.com/catalog/product/aldrich/389153 (accessed July 01, 2014). β-Cyclodextrin, sulfated sodium salt extent of labelling: 12–15 mol per mol β-CD.The formula weight can be stated as 1135 + 102*n*, where *n* = degree of substitution. The value of 1135 is for the molecule without substitutions. The 102*n* corresponds to the *R* groups and how many are substituted on the ring.

[b] The mass fraction purity is on the water-free basis.

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

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

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.

The concentrations of the injected solutions $(\bar{c} + \Delta c)$ and of the carrier solutions $(\bar{c})$ differed by $\pm 10.0\ g \cdot dm^{-3}$ or less. Solutions of different composition were injected into each carrier solution to confirm that the measured diffusion coefficients were independent of the initial concentration difference and therefore represented the differential value of D at the carrier-stream composition. The uncertainty of the results obtained is estimated to be (1–2)%.

3. Results and discussion

3.1. Concentration dependence of density, viscosity and mutual diffusion coefficient, D, at finite concentrations

The experimental density and viscosity values of $NaSO_3\beta CD$ aqueous solutions at $T = (298.15$ and $310.15)$ K are collected in table 2. The values for density were linearly fitted by using a least-squares regression method to obtain their dependence with concentration (table 3). Both sets of data present a parallel behaviour being the values found for ρ^0 in good agreement with those for water in the literature [37,38].

The analysis of the dependence of the viscosity on the concentration was evaluated by fitting the values of relative viscosity, η_r, (table 4) to the Jones–Dole equation as follows,

$$\eta_r = 1 + A\,c^{1/2} + Bc, \qquad (2)$$

where for this study c is express in ($g_{(NaSO3\beta CD)}$ per kg of solution, and A and B are empirical terms that permit to provide useful information. While the A coefficient has been related to the solute–solute interactions taking place in the solution, the B term has been found to depend upon solute–solvent interactions. In this work, from the A values almost zero and the low positive B values (table 4), we can consider, as an approach, that the interactions between $NaSO_3\beta CD$ and water are the predominant ones.

Table 5 gives the average experimental values for the mutual diffusion coefficient, D, for each carrier solution determined from 4 to 5 profiles generated by injecting samples that were more or less concentrated than the carrier solution. Good reproducibility was, in general, observed, within ±2%.

The concentration dependence of the measured diffusion coefficients, D, can be represented by the polynomial equation:

$$D = a_0 + a_1 c + a_2 c^2, \qquad (3)$$

where the coefficients a_0 to a_2 are fitting parameters. The least-squares values of these coefficients are listed in table 6. Also, the goodness of the fit (obtained with a confidence interval of 98%) can be assessed by the excellent correlation coefficients, R^2, and the low percent standard deviation (1%).

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