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Quaternary Diffusion Coefficients of β -Cyclodextrin + KCl + Caffeine + Water at 298.15 K Using a Taylor Dispersion Method

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A Taylor dispersion method was used to measure quaternary diffusion coefficients (D_{11} , D_{22} , D_{33} , D_{12} , D_{13} , D_{21} , D_{23} , D_{31} and D_{32}) of the four-component system β -cyclodextrin + KCl + caffeine + water at 298.15 K at carrier concentrations from (0.002 to 0.010) mol·dm⁻³ for each solute with an inaccuracy of \pm (1 to 2) %. These diffusion coefficients were measured in order to obtain a better understanding of the structure of these systems, e.g., for reliable and safe delivery of precise dosages of medical drugs.

Introduction

The development of controlled-release systems for reliable and safe delivery of precise dosages of drugs continues to be an active area of research. Important results have been obtained by manipulating the rates of diffusion of the carrier–drug complexes. In those systems, cyclodextrins (CDs) are among the most important carriers, and they are useful functional excipients. These cyclic oligosaccharides with a hydrophobic cavity have been widely used to enhance solubility, chemical stability, and bioavailability of poorly soluble drugs.^{1–3} Among them we find caffeine, a stimulant drug acting on the central nervous system, muscles (including the cardiac muscle), and kidneys, that has been used in a wide range of pharmaceutical preparations. Having in mind that most physiological intra- and extracellular physiological fluids have a significant presence of ions (e.g., K⁺ and Cl⁻), we consider it important to study the influence of electrolytes on the diffusion of controlled-release systems (e.g., β -CD + caffeine) in aqueous media.

While numerous studies have been devoted to the structural aspects of these systems involving cyclodextrins and different drugs in aqueous solutions,^{2–4} few have taken into account the multicomponent diffusion work on aqueous cyclodextrin solutions and the alteration of these properties as a result of the presence of different substrates in these solutions.^{5–12} As far as the authors are aware after a careful literature search, no data for quaternary systems involving β -CD, caffeine, and potassium chloride entities are available in the literature. The purpose of this work was to study the diffusion behavior (i.e., to find the diffusion coefficients D_{11} , D_{22} , D_{33} , D_{12} , D_{13} , D_{21} , D_{23} , D_{31} , and D_{32}) for the β -CD + KCl + caffeine system in aqueous solutions at carrier concentrations of (0.002, 0.005, 0.008, and 0.010) mol·dm⁻³ for each solute at 298.15 K using a Taylor dispersion technique. These data were compared with the previously reported diffusion coefficients for the binary systems β -CD, caffeine, and potassium chloride in aqueous solutions.^{5,6,13,14}

Experimental Section

Reagents and Solutions. Caffeine (Sigma, pro analysi, > 0.985 in mass fraction), β -CD (Sigma, with a water mass fraction of 0.131), and potassium chloride (Sigma, pro analysi, > 0.995 in mass fraction) were used as received. The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using doubly distilled water. The solutions were freshly prepared and deaerated for about 30 min before each set of runs.

Equipment and Procedure. The theory of the Taylor dispersion technique is well-described in the literature,^{15–21} so only some relevant points concerning the use of this method for the experimental determination of quaternary diffusion coefficients are described here.

Diffusion in an aqueous quaternary system [which, for brevity, we will indicate as ijk (not including the solvent, component 0)] is described by the diffusion equations (eqs 1 to 3):

$$-J_1 = {}^{123}(D_{11})_v \frac{\partial c_1}{\partial x} + {}^{123}(D_{12})_v \frac{\partial c_2}{\partial x} + {}^{123}(D_{13})_v \frac{\partial c_3}{\partial x} \quad (1)$$

$$-J_2 = {}^{123}(D_{21})_v \frac{\partial c_1}{\partial x} + {}^{123}(D_{22})_v \frac{\partial c_2}{\partial x} + {}^{123}(D_{23})_v \frac{\partial c_3}{\partial x} \quad (2)$$

$$-J_3 = {}^{123}(D_{31})_v \frac{\partial c_1}{\partial x} + {}^{123}(D_{32})_v \frac{\partial c_2}{\partial x} + {}^{123}(D_{33})_v \frac{\partial c_3}{\partial x} \quad (3)$$

where J_i represents the molar flux of solute i in the volume-fixed frame and the ${}^{ijk}D_{ij}$ are the quaternary diffusion coefficients. The main diffusion coefficients ${}^{123}D_{ii}$ (i.e., ${}^{123}D_{11}$, ${}^{123}D_{22}$, and ${}^{123}D_{33}$) give the flux of solute i produced by its own concentration gradient. The cross-diffusion coefficients ${}^{123}D_{ij}$ (i.e., ${}^{123}D_{12}$, ${}^{123}D_{13}$, ${}^{123}D_{21}$, ${}^{123}D_{23}$, ${}^{123}D_{31}$, and ${}^{123}D_{32}$) give the coupled flux of solute i driven by a concentration gradient in another solute j .

An aqueous quaternary system ijk has three corresponding aqueous ternary systems ij , ik , and jk and three corresponding aqueous binary systems i , j , and k . The main quaternary diffusion coefficient ${}^{ijk}D_{ii}$ can then be compared with the two ternary values ${}^{ij}D_{ii}$ and ${}^{ik}D_{ii}$ and the binary value D_i ; similar comparisons apply for the other two main terms ${}^{ijk}D_{ij}$ and ${}^{ijk}D_{kk}$. The quaternary cross-diffusion coefficient ${}^{ijk}D_{ij}$ can be compared with only one ternary diffusion coefficient ${}^{ij}D_{ij}$; this is also true for all of the other cross

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Table 1. Quaternary Diffusion Coefficients $^{123}D_{11}$, $^{123}D_{22}$, $^{123}D_{33}$, $^{123}D_{12}$, $^{123}D_{13}$, $^{123}D_{21}$, $^{123}D_{23}$, and $^{123}D_{31}$ for Aqueous β -CD (1) + KCl (2) + Caffeine (3) Solutions and the Corresponding Standard Deviations S_D at 298.15 K at Various Concentrations $c = c_1 = c_2 = c_3$

	$c/\text{mol}\cdot\text{dm}^{-3}$			
	0.002	0.005	0.008	0.010
$(^{123}D_{11} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	0.322 ± 0.025	0.320 ± 0.005	0.317 ± 0.020	0.311 ± 0.020
$(^{123}D_{12} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	-0.028 ± 0.006	-0.025 ± 0.008	-0.025 ± 0.012	-0.034 ± 0.012
$(^{123}D_{13} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	-0.002 ± 0.017	0.020 ± 0.009	0.010 ± 0.040	0.055 ± 0.040
$(^{123}D_{21} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	0.505 ± 0.013	0.210 ± 0.017	0.082 ± 0.031	-0.052 ± 0.031
$(^{123}D_{22} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	1.911 ± 0.036	1.882 ± 0.080	1.730 ± 0.030	1.518 ± 0.030
$(^{123}D_{23} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	-0.121 ± 0.042	-0.101 ± 0.050	-0.081 ± 0.030	-0.104 ± 0.030
$(^{123}D_{31} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	-0.007 ± 0.053	0.004 ± 0.076	0.007 ± 0.015	0.057 ± 0.015
$(^{123}D_{32} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	-0.030 ± 0.040	0.001 ± 0.073	0.090 ± 0.026	0.141 ± 0.026
$(^{123}D_{33} \pm S_D)/(10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1})$	0.797 ± 0.073	0.770 ± 0.029	0.768 ± 0.012	0.748 ± 0.012

Table 2. Ternary Diffusion Coefficients $^{23}D_{22}$, $^{23}D_{23}$, $^{23}D_{32}$, and $^{23}D_{33}$ for Aqueous KCl (2) + Caffeine (3) Solutions and the Respective Standard Deviations S_D at 298.15 K

c_2	c_3	$^{23}D_{22} \pm S_D$	$^{23}D_{23} \pm S_D$	$^{23}D_{32} \pm S_D$	$^{23}D_{33} \pm S_D$
$\text{mol}\cdot\text{dm}^{-3}$	$\text{mol}\cdot\text{dm}^{-3}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$
0.002	0.002	1.955 ± 0.045	-0.165 ± 0.040	-0.056 ± 0.012	0.806 ± 0.014
0.005	0.005	1.903 ± 0.028	-0.120 ± 0.024	-0.124 ± 0.009	0.781 ± 0.020
0.010	0.010	1.844 ± 0.031	0.104 ± 0.027	-0.402 ± 0.009	0.688 ± 0.015

Table 3. Ternary Diffusion Coefficients $^{12}D_{11}$, $^{12}D_{12}$, $^{12}D_{21}$, and $^{12}D_{22}$ for Aqueous β -CD (1) + KCl (2) Solutions and the Respective Standard Deviations S_D at 298.15 K

c_1	c_2	$^{12}D_{11} \pm S_D$	$^{12}D_{12} \pm S_D$	$^{12}D_{21} \pm S_D$	$^{12}D_{22} \pm S_D$
$\text{mol}\cdot\text{dm}^{-3}$	$\text{mol}\cdot\text{dm}^{-3}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$	$>10^{-9}\cdot\text{m}^2\cdot\text{s}^{-1}$
0.002	0.002	0.324 ± 0.036	-0.068 ± 0.010	-0.242 ± 0.028	1.959 ± 0.045
0.005	0.005	0.317 ± 0.032	-0.088 ± 0.037	-0.196 ± 0.059	1.937 ± 0.044
0.010	0.010	0.313 ± 0.012	-0.119 ± 0.051	-0.059 ± 0.041	1.925 ± 0.034

terms. Comparison of the diffusion coefficients of system ijk with those of systems ij , ik , and jk provides information about the effect of adding each solute to the other two. Comparison of the diffusion coefficients of system ijk with those of the systems i , j , and k provides information about the effect of adding each pair of solutes to the remaining one.

Extensions of the Taylor technique have been used to measure quaternary mutual diffusion coefficients $^{ijk}(D_{ij})$ for multicomponent solutions. These coefficients $^{ijk}(D_{ij})$, defined by eqs 1 to 3, were evaluated by fitting the quaternary dispersion equation (eq 4):

$$V(t) = V_0 + V_1 t + K \sum_{i=1}^3 R_i [c_i(t) - \bar{c}_i] \quad (4)$$

where V is the detector signal, $K = dV/dn$ is the sensitivity of the detector, n is the refractive index (or another property), $R_i = dn/d\bar{c}_i$ measures the change in the detected property per unit change in the concentration of solute, and $c_i(t) - \bar{c}_i$ represents the dispersion solute average concentration, given by

$$c_i(t) - \bar{c}_i = \frac{2\Delta v}{\pi r^3 u} \left(\frac{3}{\pi t} \right)^{1/2} \sum_{k=1}^3 \sum_{p=1}^3 A_{ik} B_{kp} \Delta C_p D_k^{1/2} \times \exp[-12D_k(t - t_R)^2/r^2 t] \quad (5)$$

where the D_k are the eigenvalues of the matrix \mathbf{D} of quaternary diffusion coefficients, the columns of matrix \mathbf{A} are the independent eigenvectors of \mathbf{D} , and matrix \mathbf{B} is the inverse of \mathbf{A} . The quantity $V_0 + V_1 t$ in eq 4 is often included in practice to allow for small drifts in the detector signal.

In these experiments, small volumes ΔV of solution having composition $\bar{c}_1 + \Delta\bar{c}_1$, $\bar{c}_2 + \Delta\bar{c}_2$, and $\bar{c}_3 + \Delta\bar{c}_3$ are injected into carrier solutions of composition \bar{c}_1 , \bar{c}_2 , and \bar{c}_3 at time $t = 0$.

Results and Discussion

The average diffusion coefficient values for the quaternary system β -CD (1) + KCl (2) + caffeine (3) + water at 298.15

K ($^{123}D_{11}$, $^{123}D_{22}$, $^{123}D_{33}$, $^{123}D_{12}$, $^{123}D_{13}$, $^{123}D_{21}$, $^{123}D_{23}$, $^{123}D_{31}$, and $^{123}D_{32}$) are summarized in Table 1. These results are averages of at least six experiments. Good reproducibility was observed, as seen by the small standard deviations of the mean, S_D [experimental uncertainties of (1 to 2) %].

These results are compared with those obtained for binary systems at the same temperature using the same technique, that is, D_1 for β -CD,⁵ D_2 for potassium chloride,¹⁴ and D_3 for caffeine^{6,13} in aqueous solutions.

The main coefficients $^{123}D_{11}$, $^{123}D_{22}$, and $^{123}D_{33}$ give the molar fluxes of the β -CD (1), potassium chloride (2), and caffeine (3) components driven by their own concentration gradients (Table 1). It can be seen that these coefficients decrease with increasing concentration and that $^{123}D_{11}$ is very close to the diffusion coefficient D_1 of β -CD in pure water (in general, these differences are close to the uncertainties of the measurements). This behavior can be explained by the fact that β -CD is a nonelectrolyte and consequently is not expected to interact with other components in dilute solutions ($c \leq 0.010$ M). Also, the same argument can be used to explain the zero values for the cross-coefficients $^{123}D_{13}$, $^{123}D_{12}$, and $^{123}D_{31}$ within experimental error. That is, there are no coupled flows of β -CD produced by gradients in caffeine and KCl, respectively, and no coupled flow of caffeine produced by a gradient in β -CD. We can consider that the gradients in KCl do not produce appreciable coupled flows of the other components (nonelectrolytes or weak electrolytes) because the K^+ and Cl^- ions have similar mobilities and consequently the electric field generated during the diffusion of KCl is relatively small.

In contrast, the main diffusion coefficient $^{123}D_{33}$ is slightly larger than the binary diffusion coefficient of aqueous caffeine, D_3 , and $^{123}D_{22}$ is in general less than the binary diffusion coefficient of aqueous KCl, D_2 ; moreover, the $^{123}D_{23}$, $^{123}D_{21}$, and $^{123}D_{32}$ values are different from zero. The larger $^{123}D_{21}$ values can be interpreted in terms of the presence of the possible interactions between β -CD and KCl components for very dilute solutions (e.g., 1:1 complexes). Support for these phenomena also comes from various thermodynamic studies.^{22,23} The D_{32} values illustrate a significant association

between the caffeine and potassium chloride species, but only in solutions with concentrations of $0.01 \text{ mol} \cdot \text{dm}^{-3}$. That behavior can be explained on the basis that some potassium chloride species can be present in solution as eventual inclusion complexes of β -CD. If caffeine is added, amounts of caffeine can be transported as 1:1 complexes, as shown by the respective binding constant $K_{\text{complex(KCl-CAF)}} = 5.08 \cdot 10^3 \text{ dm}^3 \cdot \text{mol}^{-1}$ at 298.15 K .²⁴ Having in mind that $^{123}D_{21}/^{123}D_{11}$ gives the number of moles of potassium chloride cotransported per mole of β -CD driven by its own concentration gradient, we can consider that at the compositions used, 1 mol of diffusing β -CD cotransports at most 1.4 mol of potassium chloride. From the $^{123}D_{23}/^{123}D_{33}$ values at the same compositions, we can expect that 1 mol of diffusing of caffeine countertransports at most 0.13 mol of KCl. From the $^{123}D_{31}/^{123}D_{22}$ values at the same compositions, we can expect that 1 mol of diffusing potassium chloride cotransports 0.09 mol of caffeine. In conclusion, it is not possible to accurately know the reasons for the behavior of these coefficients over the range of studied concentrations, as we would desire. However, we could say that what eventually can be more important for some areas of interest (e.g., pharmaceutical applications) is the experimental thermodynamic behavior of the involved species rather than the complex question of the interpretation of these data (such as the nature of their internal binding forces).

These results can also be compared with those obtained for ternary systems at the same temperature using the same technique, that is, for β -CD (1) + caffeine (3),⁶ KCl (2) + caffeine (3) (Table 2), and β -CD (1) + KCl (2) (Table 3) in aqueous solutions. The comparisons between the quaternary and ternary diffusion coefficients for β -CD and caffeine (i.e., $^{123}D_{11}$ with $^{13}D_{11}$, $^{123}D_{33}$ with $^{13}D_{33}$, $^{123}D_{13}$ with $^{13}D_{13}$, and $^{123}D_{31}$ and $^{13}D_{31}$) confirm the idea that there is not inclusion of the caffeine into the β -CD cavity and that they are an eventual presence of weak interactions between β -CD and caffeine and between β -CD and KCl. In fact, within experimental error, the $^{123}D_{11}$ values coincide with the $^{13}D_{11}$, $^{12}D_{11}$, and D_1 values, while $^{13}D_{13}$ and $^{13}D_{31}$ are also almost zero. In regard to the $^{123}D_{33}$ values, they are a little larger than the $^{13}D_{33}$ and D_3 values, the latter ones being very similar. The $^{123}D_{22}$ values are in general smaller than the ternary diffusion coefficients $^{12}D_{22}$, and the $^{123}D_{12}$ and $^{123}D_{21}$ values are different from zero.

Conclusions

The Taylor dispersion method can provide values of the diffusion coefficients of a four-component liquid. For the quaternary system β -CD (1) + KCl (2) + caffeine (3) + water, since the cross-coefficients $^{123}D_{23}$, $^{123}D_{21}$, and $^{123}D_{32}$ are different from zero at finite concentrations and the main coefficients $^{123}D_{22}$ and $^{123}D_{33}$ are not identical to the binary and ternary diffusion coefficients of aqueous KCl and β -CD, respectively, we may conclude that at finite concentrations in this quaternary system there are solute interactions that affect the diffusion of the present components.

The diffusion coefficients measured for aqueous solutions of this quaternary system provide transport data necessary to model the diffusion in pharmaceutical applications.

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