Diffusion Coefficients of the Ternary System α-Cyclodextrin−Sodium Benzenesulfonate−Water at 25 °C: The Effect of Chemical Equilibrium and Complex Formation on the Diffusion Coefficients of a Ternary System

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Diffusion coefficients have been measured in the ternary system α-cyclodextrin−sodium benzenesulfonate−water at 25 °C. The higher mobility of the inclusion complex, compared to that of free cyclodextrin, proves that in the presence of binding complexes between solutes it is possible to measure positive cross diffusion coefficients. Previously only negative cross terms have been measured in systems containing cyclodextrin−ligand complexes. A discussion of the concentration dependence of the four diffusion coefficients and of the sign of cross terms is given.

Introduction

Studies of ternary diffusion have shown that solute−solute flow interactions, as measured by the cross-term diffusion coefficients, are generally significant not only for electrolyte solutions but also for systems containing nonelectrolytes. In some cases nonelectrolyte systems show large values of cross-term diffusion coefficients. Both positive and negative cross terms have been found.

Focusing our attention on the cross terms, we note the wide range of behavior found in the following selection of previous experimental investigations. The succinic acid−urea−water system shows both D_{ij} ($i \neq j$) negative and reasonably large.[1] The sodium dodecyl sulfate (SDS)−*n*-butanol−water system, at a surfactant concentration above the cmc, has positive cross coefficients.[2] On the other hand, the SDS−*n*-hexanol−water system has positive and negative cross terms, and the SDS−*n*-octanol−water system has D_{12} generally negative and D_{21} always positive.[2] The α-cyclodextrin(CD)−L-phenylalanine−water,[3] α-CD−norleucine−water,[4] and α-CD−*n*-butylurea−water systems[5] show negative D_{21} terms and almost negligible D_{12} terms. The ternary system chloroform−water−acetic acid shows positive cross-term diffusion coefficients whose values increase as the concentrations approach the critical mixing point.[6−8] Similar results were found for the system poly-(vinylidene fluoride)−water-*N*,*N*-dimethylformamide.[9]

The presence of one or both negative cross terms was, in general, attributed to the presence of chemical equilibria between solutes,[6,10] while positive cross terms could be due to short-range interactions between solutes or to *salting-out* effects that would increase the solute activities.[6,9]

This wide variety of behaviors suggests a need for a more accurate insight into the contribution of cross-term diffusion coefficients to the transport process in ternary solution. As far as we know, such a discussion is still lacking in the literature.

We plan to discuss here the case of association complexes between solutes. A set of diffusion runs on the α-cyclodextrin (CD)−sodium benzenesulfonate (NaBS)−water system is presented to support our discussion.

Theoretical Background

In a ternary system, the flows of solute 1 and solute 2 through the solvent (component 0) are described by a set of phenomenological equations as follows:

$$-J_1 = D_{11} \, \text{grad} \, C_1 + D_{12} \, \text{grad} \, C_2 \qquad (1a)$$

$$-J_2 = D_{21} \, \text{grad} \, C_1 + D_{22} \, \text{grad} \, C_2 \qquad (1b)$$

where J_i is the flow of solute i, C_i its concentration, D_{ii} its main-term diffusion coefficient, and D_{ij} ($i \neq j$) its cross-term diffusion coefficient.

Irreversible thermodynamics imposes some restrictions on the matrix of the D_{ij} coefficients:[8] (a) the trace of the matrix must be positive,

$$\sum_i D_{ii} > 0 \qquad (2)$$

(b) the determinant must be positive or zero,

$$|D_{ij}| \geq 0 \qquad (3)$$

For ternary systems these conditions reduce to

$$D_{11} + D_{22} > 0 \qquad (4)$$

and

$$D_{11}D_{22} - D_{12}D_{21} \geq 0 \qquad (5)$$

Furthermore, in dilute solution of component i, the following relation holds:

$$\lim_{C_i \to 0} D_{ij} = 0 \quad (i \neq j) \qquad (6)$$

This limitation is due to the evidence that in the absence of component i its flow must vanish. For solutions of hydrolyzing solutes, such as $Na_2CO_3(1)−NaOH(2)$−water, large positive values of D_{21} were found as $C_2 \to 0$.[11] In this case, however, even in the absence of added NaOH this component is always present due to the hydrolysis process.

At high solute concentrations, the magnitude of D_{12} or D_{21} may exceed the magnitude of one or both main-terms diffusion coefficients.[7,8,12]

The reason for nonzero cross-term diffusion coefficients in concentrated solution can be attributed either to the different volumes of particles that interchange their position by the diffusion process or to interactions among the solute species.

As pointed out before, large and positive D_{ij} ($i \neq j$) were found in systems where the solutes tend to *salt out*.[7,9] The D_{ij} magnitude increases when moving toward a critical mixing point where the equality in eq 5 holds. This condition corresponds to a zero diffusion coefficient in the binary systems at the critical mixing point and was verified by some of us for the chloroform−water−acetic acid system.[7,13]

On the other hand, large negative cross-term diffusion coefficients have been interpreted in terms of large attractive interactions between solutes. In the presence of a system where a chemical equilibrium occurs according to the equation

$$A + B = C \qquad (7)$$

only two solute components are present and the diffusion process is described by eqs 1; however, three diffusing species are present in solution, and the flow equations should be written

$$-J_1^* = D_{11}^* \text{ grad } C_1^* + D_{12}^* \text{ grad } C_2^* + D_{13}^* \text{ grad } C_3^* \quad (8a)$$

$$-J_2^* = D_{21}^* \text{ grad } C_1^* + D_{22}^* \text{ grad } C_2^* + D_{23}^* \text{ grad } C_3^* \quad (8b)$$

$$-J_3^* = D_{31}^* \text{ grad } C_1^* + D_{32}^* \text{ grad } C_2^* + D_{33}^* \text{ grad } C_3^* \quad (8c)$$

where we number species A, B, C as 1, 2, 3, respectively, and the * index refers to the diffusion coefficients, flows, and concentrations of the actual species present in solution.

If the solute concentrations are not too high, the cross terms in eqs 8 can be ignored. However, if species B and C are electrolytes, terms D_{23}^* and D_{32}^* cannot be ignored because interactions among all ions are present even in very dilute solutions. With these assumptions it is possible to relate the experimental D_{ij} to the D_{ij}^*, C_i, and the equilibrium constant according to the following equations:[1,3,14]

$$D_{11} = 0.5\{(D_{11}^* - D_{32}^* + D_{33}^*) + (D_{11}^* - D_{33}^* + D_{32}^*)[1 - K(C_2 - C_1)]R\} \quad (9a)$$

$$D_{12} = 0.5\{(D_{33}^* - D_{11}^* + D_{32}^*) + (D_{11}^* - D_{33}^* + D_{32}^*)[1 - K(C_2 + C_1)]R\} \quad (9b)$$

$$D_{21} = 0.5\{(D_{33}^* - D_{22}^* - D_{32}^* + D_{23}^*) + (D_{22}^* - D_{33}^* + D_{32}^* - D_{23}^*)[1 - K(C_2 - C_1)]R\} \quad (9c)$$

$$D_{22} = 0.5\{(D_{33}^* + D_{22}^* + D_{32}^* + D_{23}^*) + (D_{22}^* - D_{33}^* + D_{32}^* - D_{23}^*)[1 + K(C_2 - C_1)]R\} \quad (9d)$$

where

$$R = \{[1 + K(C_2 - C_1)]^2 + 4KC_1\}^{-0.5} \qquad (10a)$$

and

$$K = C_3^* / (C_1^* C_2^*) \qquad (10b)$$

is the equilibrium constant. In eqs 9 species B and C are assumed to have a common counterion, numbered 4, so that

the electroneutrality condition is fulfilled by the relation $J_4^* = J_2^* + J_3^* = J_2$.

The limiting values with concentration can be easily obtained from eqs 9:

(a) At fixed C_2

For $C_1 \rightarrow 0$

$$D_{11} = 0.5\left[D_{33}^* + D_{11}^* + (D_{11}^* - D_{33}^*)\frac{(1 - KC_2)}{(1 + KC_2)}\right];$$
$$D_{12} = 0 \quad (11a)$$

$$D_{21} = 0.5\left[D_{33}^* - D_{22}^* + D_{23}^* + (D_{22}^* - D_{33}^* - D_{23}^*)\frac{(1 - KC_2)}{(1 + KC_2)}\right];$$
$$D_{22} = D_{22}^* \quad (11b)$$

$$D_{32}^* = 0 \qquad (11c)$$

For $C_1 \rightarrow \infty$ $D_{11} = D_{11}^*$; $D_{12} = D_{33}^* - D_{11}^*$; $D_{21} = 0$;
$$D_{22} = D_{33}^* + D_{23}^* \quad (11d)$$

(b) At fixed C_1

For $C_2 \rightarrow 0$ $D_{22}^* = D_{11}^*$;

$$D_{12} = 0.5\left[D_{33}^* - D_{11}^* + (D_{11}^* - D_{33}^*)\frac{(1 - KC_1)}{(1 + KC_1)}\right] \quad (12a)$$

$$D_{21} = 0 \quad D_{22}^* = 0.5\left[D_{33}^* + D_{22}^* + (D_{22}^* - D_{33}^*)\frac{(1 - KC_1)}{(1 + KC_1)}\right] \quad (12b)$$

$$D_{23}^* = D_{32}^* = 0 \qquad (12c)$$

For $C_2 \rightarrow \infty$ $D_{11} = D_{33}^* - D_{32}^*$; $D_{12} = 0$;
$$D_{21} = D_{33}^* - D_{22}^* + D_{23}^* - D_{32}^*; \quad D_{22} = D_{22}^* + D_{32}^* \quad (12d)$$

Let us first discuss the correlation between the D_{ij} and the D_{ii}^*, as shown by eqs 9, if species B and C are not electrolytes. In this case the cross terms D_{23}^* and D_{32}^* can be ignored, so that, in principle, it is possible to have three cases for the D_{ii}^* values:

(1) $$D_{22}^* > D_{11}^* > D_{33}^*$$

(2) $$D_{22}^* > D_{33}^* > D_{11}^*$$

(3) $$D_{33}^* > D_{22}^* > D_{11}^*$$

In general, the diffusivity of the complex is lower than those of both parent components (case 1). As a consequence, both cross diffusion terms D_{ij} ($i \neq j$) are expected to be negative with the limiting condition 6. This was recently found to be true for systems containing α-cyclodextrin (component 1) and various ligands (components 2). Negative D_{21} terms were found, although, since $D_{11}^* \cong D_{33}^*$ in these cases, the D_{12} cross terms were found negligible.[3−5]

The physical reason for the presence of negative cross terms, as pointed out by Kim,[1] is that in a ternary system where two solutes chemically react to form a complex the concentration gradient of one component (j) also causes a concentration gradient contribution of complex 3 in the same direction. At total constant concentration of the other component (i), the concentration gradient of species 3 causes the formation of a

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concentration gradient of *free* component i with an opposite sign [it must be remembered that $grad(C_3^*) = -grad(C_i^*)$]. If the mobilities of the A and B species are larger than that of the complex C (species 3), there will be a net transport of component i against the concentration gradient of the first component (j), thereby producing negative cross-term diffusion coefficients.

However, in his discussion, Kim ignored case 2. If D_{33}^* is intermediate between D_{11}^* and D_{22}^*, D_{21} is still expected to be negative while D_{12} should be positive. The physical reason for D_{21} being negative is the same as discussed before. On the other hand, if component 1 is at constant total concentration, the amount of component 1 carried by the faster diffusion of species 3 is larger than that due to the countercurrent diffusion of *free* component 1. Therefore a positive D_{12} should be found.

Case 3 leads to both positive cross diffusion coefficients. This last case is, most likely, only speculative since it is quite difficult to conceive of a complex with a diffusivity higher than that of both parent components.

Actually, the appearance of concentration gradients due to a binding equilibrium is general. Consequently our discussion is not limited to a 1 to 1 equilibrium, but can be applied to any association equilibrium.

With regards to the main diffusion coefficients, since grad $C_j = grad\ C_j^* + grad\ C_3^*$, the comparison of eqs 1 and 8 (with the assumption that $D_{ij}^* = 0$ for $i \neq j$) shows that the D_{jj} are always intermediate between D_{jj}^* and D_{33}^*. Accordingly, for case 1, D_{jj} is lower than both D_{11}^* and D_{22}^*; for case 2, D_{jj} is smaller than D_{22}^* but larger than D_{11}^*; and for case 3, D_{jj} should be larger than both D_{11}^* and D_{22}^*.

The presence of electrolyte species makes the previous discussion somewhat arbitrary. Equations 9 require the presence of the cross terms D_{23}^* and D_{32}^* because the diffusion of the three ions is not independent.[15] However, if the cross terms are not too large, the previous discussion still holds.

Case 1 is the most common and obvious. Case 2 can be obtained using as component B (eq 7) a salt with an ion that can be bound by component A. In this case, due to the electroneutrality condition, the free counterion speeds up the complex ion so that the complex C may diffuse faster than component A.

We succeeded in measuring diffusion coefficients on a ternary system corresponding to case 2, namely, an aqueous solution of α-cyclodextrin (1) and sodium benzenesulfonate (2). In this case, since the complex is an anion, its diffusion is accelerated by the free Na$^+$ counterions to preserve electroneutrality.

Experimental Section

Materials. α-CD and benzenesulfonic acid sodium salt (NaBS) were purchased from Sigma and used without further purification. The water content of air-equilibrated α-CD, determined with the same procedure described elsewhere, was found to be 9.50%.[3] The molar masses used for α-CD, C$_6$H$_5$-SO$_3$Na, and water were 972.9, 180.15, and 18.016 g mol^{-1}, respectively. All solutions were prepared by weight with doubly distilled water.

Density Measurements. The density of each solution used in a diffusion run was measured with an Anton Paar DMA 602 densimeter. The temperature of the density meter was regulated at 25.00 ± 0.01 °C and calibrated with air and water, whose density was assumed to be 0.997 044 kg dm^{-3}.

For the binary systems, a set of solutions were prepared in the molality range 0–0.95 mol kg^{-1}. The experimental densities

TABLE 1: Density of the Binary System Na Benzenesulfonate−Water at 25 °C[a]

m (mol kg^{-1})	d (kg dm^{-3})	m (mol kg^{-1})	d (kg dm^{-3})
0.000 00	0.997 044	0.500 02	1.033 281
0.050 01	1.000 872	0.549 97	1.036 633
0.100 00	1.004 678	0.599 99	1.039 971
0.149 98	1.008 419	0.650 03	1.043 270
0.199 99	1.012 085	0.699 98	1.046 624
0.250 01	1.015 732	0.749 97	1.049 805
0.299 99	1.019 611	0.799 99	1.053 109
0.349 97	1.022 915	0.850 00	1.056 163
0.400 00	1.026 390	0.900 04	1.059 700
0.450 01	1.029 874	0.950 03	1.061 882

[a] The last three data were not used for computing eq 13.

TABLE 2: Diffusion Data of the Binary System Na Benzenesulfonate−Water at 25 °C[a]

C (mol dm^{-3})	ΔC (mol dm^{-3})	J_m	$D \times 10^5$ (cm^2 s^{-1})
0.01988	0.02979	32.94	1.0173
0.02974	0.05948	61.63	1.0158
0.04950	0.05895	68.75	1.0056
0.07411	0.05895	66.50	0.9977
0.09857	0.05907	66.55	0.9865
0.14281	0.05561	68.28	0.9730
0.19462	0.05917	64.80	0.9680
0.24296	0.05688	65.25	0.9593
0.28952	0.05526	65.27	0.9549

[a] C, average concentration of each diffusion run; ΔC, concentration difference between bottom and top solutions; J_m, total number of Gouy fringes; in terms of refractive index difference, Δn, between bottom and top solutions at the He−Ne laser red light ($\lambda = 632.8$ nm), $J_m = 3.951 \times 10^6 \Delta n$. D, diffusion coefficients.

are given in Table 1; the following equation fits the data:

$$d/\text{kg dm}^{-3} = 0.997044\ (\pm 0.00002) + 0.07676\ (\pm 0.0001)m - 0.008648\ (\pm 0.0002)\ m^2 \quad (13)$$

This equation was then used to compute the molar concentration of the solutions.

The following equation, obtained with the method of least-squares,

$$d = \bar{d} + H_1(C_1 - \bar{C}_1) + H_2(C_2 - \bar{C}_2) \quad (14)$$

fits the experimental density data of the ternary systems. $\bar{C}_i/$ mol dm^{-3} is the mean concentration of component i in the ternary diffusion runs and $\bar{d}$ the density of solution at the mean concentration of the diffusion experiments. H_i are the differential concentration increments of the density. The values of the parameters $\bar{d}$, H_1, and H_2 are listed in Table 3.

Diffusion Experiments. The experiments were performed with a Gouy diffusiometer,[16] which has been automated to scan Gouy patterns and to record the fringe positions during the experiment. The bath temperature was regulated at 25.00 ± 0.01 °C. A single channel cell was used, and the initial boundary was formed with the siphoning technique. The light source was a Unifas PHASE 0.8 mW neon−helium laser operating at 632.8 nm.

Analysis of Data. Fringe position data for each experiment were analyzed with a series of computer programs described in the literature.[17−20] The relevant data for discussing diffusion results are collected in Table 2 for the binary system NaBS− water and in Table 3 for the ternary systems.

TABLE 3: Diffusion Data of the Ternary System α-Cyclodextrin(1)−Sodium Benzenesulfonate(2) − Water at 25 °C[a]

$\bar{C}_1 = 0.009\ 87$ mol dm^{-3} $\bar{C}_2 = 0.019\ 74$ mol dm^{-3} $d = 1.002\ 094 \pm 0.000\ 014$ g cm^{-3}					$\bar{C}_1 = 0.019\ 61$ mol dm^{-3} $\bar{C}_2 = 0.019\ 59$ mol dm^{-3} $d = 1.005\ 484 \pm 0.000\ 015$ g cm^{-3}				
ΔC_1 (mol dm^{-3})	ΔC_2 (mol dm^{-3})	J_m	$D_A \times 10^5$ (cm^2 s^{-1})	$Q_o \times 10^4$	ΔC_1 (mol dm^{-3})	ΔC_2 (mol dm^{-3})	J_m	$D_A \times 10^5$ (cm^2 s^{-1})	$Q_o \times 10^4$
0.00004	0.03652	38.98	1.0205	−33.1	−0.00008	0.03626	38.59	1.0667	-85.5
0.00139	0.03153	41.56	0.7900	103.5	0.00169	0.03623	48.45	0.7861	90.0
0.00570	0.00780	39.70	0.4013	69.2	0.00347	0.02712	47.99	0.6134	163.5
0.00640	0.00356	38.66	0.3621	13.3	0.00703	0.00869	47.52	0.3961	83.3

$R_1 = 5476.6 \pm 37.2$ dm^3 mol^{-1}
$R_2 = 1068.1 \pm 6.6$ dm^3 mol^{-1}
$H_1 = 0.3669 \pm 0.0069$ kg mol^{-1}
$H_2 = 0.0725 \pm 0.0012$ kg mol^{-1}

$D_{11} = 0.3497 \pm 0.0010 \times 10^{-5}$ cm^2 s^{-1}
$D_{12} = 0.0050 \pm 0.0004 \times 10^{-5}$ cm^2 s^{-1}
$D_{21} = -0.1767 \pm 0.0070 \times 10^{-5}$ cm^2 s^{-1}
$D_{22} = 0.9706 \pm 0.0040 \times 10^{-5}$ cm^2 s^{-1}

$R_1 = 5387.8 \pm 23.4$ dm^3 mol^{-1}
$R_2 = 1080.8 \pm 3.5$ dm^3 mol^{-1}
$H_1 = 0.3359 \pm 0.0060$ kg mol^{-1}
$H_2 = 0.0714 \pm 0.0012$ kg mol^{-1}

$D_{11} = 0.3371 \pm 0.0021 \times 10^{-5}$ cm^2 s^{-1}
$D_{12} = 0.0086 \pm 0.0004 \times 10^{-5}$ cm^2 s^{-1}
$D_{21} = -0.1111 \pm 0.0171 \times 10^{-5}$ cm^2 s^{-1}
$D_{22} = 0.9446 \pm 0.0061 \times 10^{-5}$ cm^2 s^{-1}

$\bar{C}_1 = 0.048\ 03$ mol dm^{-3} $\bar{C}_2 = 0.019\ 19$ mol dm^{-3}
$d = 1.015\ 719 \pm 0.000\ 014$ g cm^{-3}

ΔC_1 (mol dm^{-3})	ΔC_2 (mol dm^{-3})	J_m	$D_A \times 10^5$ (cm^2 s^{-1})	$Q_o \times 10^4$
0.001 35	0.031 94	39.42	0.8174	18.9
0.003 15	0.024 00	41.51	0.6003	132.9
0.006 05	0.007 91	41.41	0.3807	80.1

$R_1 = 5538.5 \pm 9.2$ dm^3 mol^{-1}
$R_2 = 1000.9 \pm 1.6$ dm^3 mol^{-1}
$H_1 = 0.3603 \pm 0.0055$ kg mol^{-1}
$H_2 = 0.0748 \pm 0.0014$ kg mol^{-1}

$D_{11} = 0.3221 \pm 0.0029 \times 10^{-5}$ cm^2 s^{-1}
$D_{12} = 0.0321 \pm 0.0004 \times 10^{-5}$ cm^2 s^{-1}
$D_{21} = -0.0908 \pm 0.0089 \times 10^{-5}$ cm^2 s^{-1}
$D_{22} = 0.8509 \pm 0.0089 \times 10^{-5}$ cm^2 s^{-1}

[a] ΔC_i, concentration difference of component i between bottom and top solutions. J_m, number of Gouy fringes (see Table 2 for correlation with refractive index). D_A, maximum height/area ratio (apparent diffusion coefficient). Q_o, area under the fringe deviation graph.[17] R_i, refractive index increments of concentration in terms of fringe numbers. H_i, density increments of concentration, eq 14.
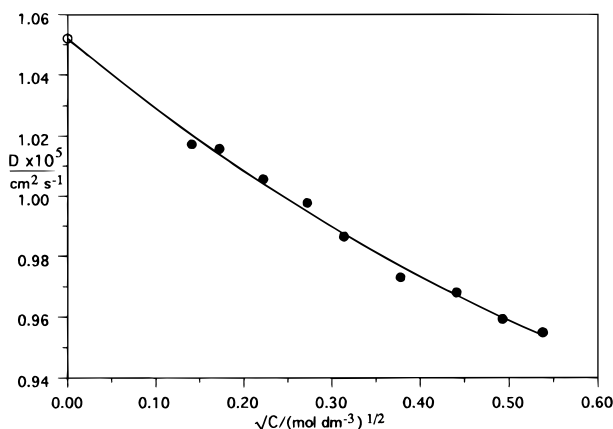
Figure 1. Diffusion coefficients of sodium benzenesulfonate in aqueous solution at 25 °C.

The diffusion coefficients of the binary system are shown in Figure 1. They have been fitted by the equation

$$D \times 10^5/\text{cm}^2\ \text{s}^{-1} = 1.052\ (\pm 0.006) - 0.237\ (\pm 0.041)\ \sqrt{C} + 0.102\ (\pm 0.060)C \quad (15)$$

The limiting diffusion coefficient of the BS$^-$ ion, $D^\circ_{BS^-}$ can be evaluated from the intercept of eq 15 using the Nernst−Hartley equation and assuming as limiting mobility for the sodium ion the literature value $D^\circ_{Na^+} \times 10^5 = 1.334$ cm^2 s^{-1}:[21]

$$D^\circ_{BS^-} \times 10^5/\text{cm}^2\ \text{s}^{-1} = \frac{1.052 \times 1.334}{(2 \times 1.334 - 1.052)} = 0.868 \quad (16a)$$

From eqs 15 and 16a an approximate diffusion coefficient of BS$^-$ ion at the concentration of our diffusion runs, $C_2 \cong 0.0195$ mol dm^{-3}, can be obtained:

$$D_{BS^-} \times 10^5/\text{cm}^2\ \text{s}^{-1} \cong \frac{1.021 \times 1.253}{(2 \times 1.253 - 1.021)} = 0.861 \quad (16b)$$

where the diffusion coefficient of the sodium ion was computed from the experimental diffusion coefficients of NaCl at 25 °C[21] using literature transference numbers[22] to separate the Na$^+$ ion contribution from that of the Cl$^-$ ion according to the Nernst−Hartley equation:

$$D_{Na^+} \times 10^5/\text{cm}^2\ \text{s}^{-1} = 1.334 - 0.779C_2^{1/2} + 1.635C_2 - 1.789C_2^{3/2} + 0.989C_2^2 - 0.2148C_2^{5/2} \quad (17)$$

Discussion

This paper has provided experimental diffusion data for dilute aqueous solutions of a nonelectrolyte α-CD (component 1) and an electrolyte NaBS (component 2); these components form a complex. A qualitative description of the behavior of D_{ij}'s at the three mean concentrations explored clarifies the result reported in Table 3.

In terms of independent components, Table 3 shows that the cross-term diffusion coefficients have opposite sign and cannot be ignored. In agreement with our previous discussion, this indicates that even in systems with large interactions between solutes, as well as in the presence of a complex, the D_{ij}'s ($i \neq j$) do not necessarily have to be negative.[23]

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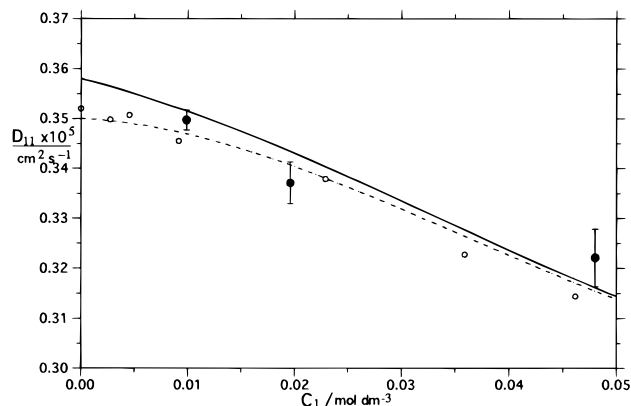*J. Phys. Chem. B, Vol. 102, No. 25, 1998* **5027**

Figure 2. Main diffusion coefficient of α-cyclodextrin in the ternary system: (●) experimental data, (○) diffusion coefficient of α-cyclodextrin in the binary aqueous solution,[26] (---) values computed using the Nernst−Hartley eqs 18, (—) values computed choosing empirical values for the D_{ij}^* coefficients to minimize eq 22.
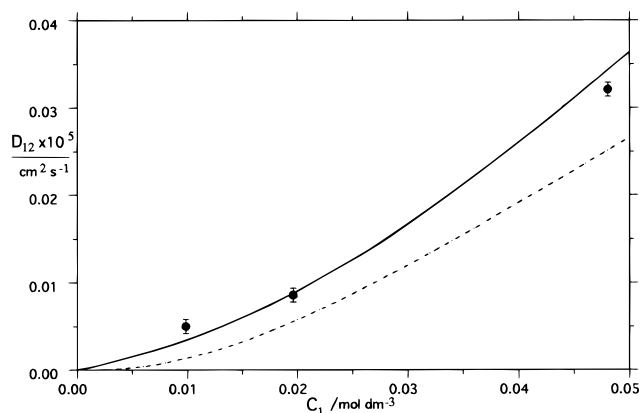

Figure 3. Cross diffusion coefficient of α-cyclodextrin in the ternary system: (●) experimental data, (---) values computed using the Nernst−Hartley eqs 18, (—) values computed choosing empirical values for the D_{ij}^* coefficients to minimize eq 22.

The D_{21} coefficients decrease in absolute value by increasing C_1 concentration, whereas the D_{12} increase by increasing C_1 (see Figures 3 and 4). This means that at low concentration of CD its gradient produces a counterflow of NaBS, while at high concentration of CD this effect tends to become negligible, in agreement with eq 11d.

In other words, at low CD concentration, if there is a gradient in CD and no gradient in NaBS concentration, the negative sign of D_{21} means (as previously discussed) a net transport of NaBS "uphill" toward the higher concentration of CD, where the concentration of uncomplexed component 2 is lower.

On the other hand, the positive and increasing value of D_{12} with CD concentration supports our previous explanation, namely, that the faster transport of component 1 bound to the complex overwhelms the slower backward transport of free component 1.

Both main diffusion coefficients decrease with the CD concentration. D_{11} has the tendency to be larger than its corresponding value in the binary system (see Figure 2). This is reasonable because D_{11} arises from the contribution of the slower uncomplexed CD and the faster complex CD−C$_6$H$_5$-SO$_3^-$ trailed by the Na$^+$ counterion. On the other hand, D_{22} (see Figure 3) is lower than its corresponding value in the binary system ($D_2 = 1.021 \times 10^{-5}$ cm^2 s^{-1}), because the C$_6$H$_5$SO$_3^-$ in the complex form is slower than the free BS$^-$.

An approach to treat diffusion in similar systems was explicitly discussed in the past.[24,25] The treatment was applied

to the I$_2$, NaI, water system,[25] which is quite similar to ours; however, this treatment does not seem proper in our case. We do not have information on the activity, conductivity, and transport numbers of sodium benzenesulfonate solutions; for this reason a correct treatment of diffusion[15] would require in our case too many arbitrary assumptions.

Approximate expressions for the four D_{ij}^* ($i, j = 2, 3$) in the case of two electrolyte solutes with a common ion are obtained using the Nernst−Hartley equation extended to a ternary system.[15] If we define the diffusion coefficients of individual ions, in our case, as D_{BS^-}, D_{CDBS^-}, and D_{Na^+}, the extended Nernst−Hartley equations can be written as follows:

$$D_{22}^* = (D_{\text{BS}^-}) + \left(\frac{C_2^*}{C_2}\right)\frac{(D_{\text{BS}^-})(D_{\text{Na}^+}) - (D_{\text{BS}^-})^2}{\Lambda^\circ} \quad (18\text{a})$$

$$D_{23}^* = \left(\frac{C_2^*}{C_2}\right)\frac{(D_{\text{BS}^-})(D_{\text{Na}^+}) - (D_{\text{BS}^-})(D_{\text{CDBS}^-})}{\Lambda^\circ} \quad (18\text{b})$$

$$D_{32}^* = \left(\frac{C_3^*}{C_2}\right)\frac{(D_{\text{CDBS}^-})(D_{\text{Na}^+}) - (D_{\text{BS}^-})(D_{\text{CDBS}^-})}{\Lambda^\circ} \quad (18\text{c})$$

$$D_{33}^* = (D_{\text{CDBS}^-}) + \left(\frac{C_3^*}{C_2}\right)\frac{(D_{\text{CDBS}^-})(D_{\text{Na}^+}) - (D_{\text{CDBS}^-})^2}{\Lambda^\circ} \quad (18\text{d})$$

where

$$\Lambda^\circ = \left(\frac{C_2^*}{C_2}\right)(D_{\text{BS}^-}) + \left(\frac{C_3^*}{C_2}\right)(D_{\text{CDBS}^-}) + (D_{\text{Na}^+}) \quad (19)$$

Some assumptions were made to compute the individual ions' diffusion coefficients in order to obtain the best possible agreement with the experimental data. The following expressions were used:

$$D_{\text{Na}^+} \times 10^5/\text{cm}^2 \text{ s}^{-1} = 1.253(1 - 0.7C_1) \quad (20\text{a})$$

$$D_{\text{BS}^-} \times 10^5/\text{cm}^2 \text{ s}^{-1} = 0.861(1 - 0.7C_1) \quad (20\text{b})$$

$$D_{\text{CDBS}}/\text{cm}^2 \text{ s}^{-1} = 0.98D_{11}^* \quad (20\text{c})$$

The term D_{11}^* was assumed equal to the diffusion coefficient of CD in the binary aqueous solution at concentration C$_1$:[26]

$$D_{11}^* \times 10^5/\text{cm}^2 \text{ s}^{-1} = 0.3516 - 0.355C_1 - 18.031C_1^2 + 178.51C_1^3 \quad (21)$$

K was measured using the competion of the *p*-nitrophenol dye for the α-CD inclusion site;[27] its value was found to be $K = 13 \pm 2$ dm^3 mol^{-1}.

The D_{ij} values were then computed according to eqs 9; however, they were not found in good agreement with the experimental data, although their trend with C_1 concentration was as expected (see Figures 2−5, dotted lines).

A better agreement with the set of experimental data was obtained applying a phenomenological treatment with the inclusion of the two cross terms, D_{23}^* and D_{32}^*, treated as adjusting parameters.

The following values were chosen for the D_{ij}^* coefficients: D_{11}^* was taken from eq 21, $D_{22}^* = 1.021 \times 10^{-5}$, $D_{33}^* = 0.38 \times$
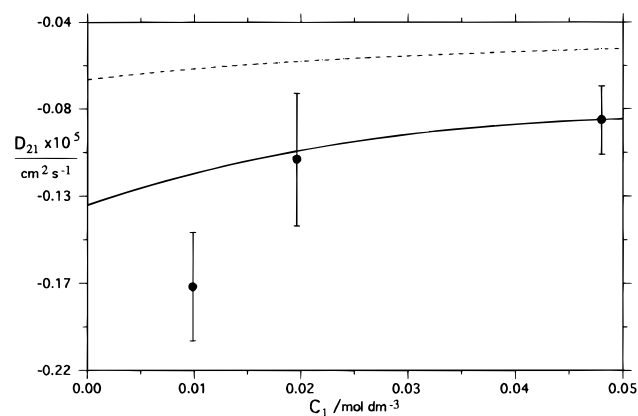
Figure 4. Cross diffusion coefficient of sodium benzenesulfonate in the ternary system: (●) experimental data, (---) values computed using the Nernst–Hartley eqs 18, (—) values computed choosing empirical values for the D_{ij}^* coefficients to minimize eq 22.
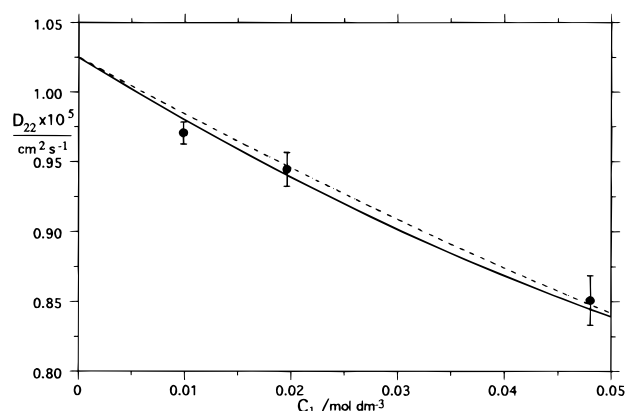

Figure 5. Main diffusion coefficient of sodium benzenesulfonate in the ternary system: (●) experimental data, (---) values computed using the Nernst–Hartley eqs 18, (—) values computed choosing empirical values for the D_{ij}^* coefficients to minimize eq 22.

10^{-5}, $D_{23}^* = 0.05 \times 10^{-5}$, $D_{32}^* = 0.7 \times 10^{-5}C_1$, cm^2 s^{-1}. These values gave a minimum for the expression

$$\sum_{3 \text{ runs}} \left\{ \sum_{i,j} [(D_{ij})_{\text{calc}} - (D_{ij})_{\text{exp}}]^2 \right\} \tag{22}$$

The comparison between experimental and computed values is shown in Figures 2–5; the standard deviations shown in these figures are twice those given in Table 3. The agreement with the experimental data is quite good. The worst agreement is obtained with the set of D_{21} coefficients; these coefficients also show the largest standard deviation. However, it must be pointed out that in ternary systems a poor accuracy of D_{21} coefficients has been always found when the mobility of component 2 is larger than that of component 1.[3,4,12,28]

Some comments can be made about these D_{ij}^* values. The main terms D_{11}^* and D_{22}^* are in agreement with the values found in the corresponding binary aqueous solutions; D_{33}^* is larger than D_{11}^* as expected. The cross terms D_{23}^* and D_{32}^* were found both positive, in agreement with eqs 18b and 18c since the

diffusion coefficient of the sodium ion is larger than the diffusion coefficients of both benzenesulfonate and complex 3 ions. According to eq 18b, at constant C_2 concentration, D_{23}^* should not change much, so that the constant value that fits the experimental data is reasonable. On the other hand, D_{32}^* must approach zero as $C_3^* \rightarrow 0$, namely, as $C_1 \rightarrow 0$. The linear relation found for D_{32}^* is in line with this evidence. Furthermore, the larger value of D_{23}^* with respect to D_{32}^* is also predicted by eqs 18b and 18c when C_2^* is larger than C_3^*, as in our case.

Finally, let us point out that, in our discussion, the viscosity of solutions was ignored. Although viscosity and diffusion can often be related, a correlation between these two properties is very difficult to explicate. The commonly used Stokes–Einstein equation is valid only at infinite dilution with large solute molecules in a solvent of small molecules. So we preferred to avoid any speculation involving the solution viscosity.

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