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Measurement of Diffusion Coefficients in Thermodynamically Nonideal Systems

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Accurate diffusion coefficient data are reported for highly nonideal binary mixtures. The mixtures consist of an alcohol (ethanol, 1-propanol, 1-butanol) dissolved in hexane, cyclohexane, carbon tetrachloride, or toluene. All measurements have been conducted over the whole concentration range at various temperatures, (25, 30, and 35) °C, by means of the Taylor dispersion technique. The uncertainty of the reported data is estimated to be within $3 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$.

Introduction

With the increasing use of the nonequilibrium model[1,2] in the design of chemical processes a thorough knowledge of many physical properties is required. One of the important transport coefficients is the diffusion coefficient since this type of mass transfer is often the rate-determining step. In contrast to other properties like viscosity or density, the number of reliable reported diffusion coefficients is limited, especially for highly nonideal binary mixtures. Therefore, diffusion coefficient measurements were conducted for several binary alcohol−solvent systems over the whole concentration range as a function of the temperature. The experimental setup used in this study is a Taylor dispersion unit, well-known for its accuracy and rapidity.[3−5]

Experimental Setup and Data Processing

In a Taylor dispersion experiment a pulse is rapidly injected into a fluid (eluent) of a different composition flowing slowly through a narrow capillary. Due to the superposition of a laminar flow profile (which pulls the pulse apart) and the radially induced molecular diffusion (which narrows the pulse), the pulse is dispersed. In the ideal case of a binary mixture does this lead to a Gaussian distribution. A mathematical description of the dispersion process and of the concentration profile at the end of the capillary was derived by Taylor.[6,7] The resulting expression was used within the data processing step. A formal derivation of the equation and the underlying assumptions may be found elsewhere.[8−11]

The experimental setup of a Taylor dispersion apparatus consists of standard HPLC equipment (see Figure 1). For details on the design of such an apparatus the reader is referred to the literature.[4,10,11] To prepare the eluent and injection solutions, a glass flask was placed on a balance (Mettler model A200, precision of 0.001 g), and the components were weighed in order of increasing volatility. The eluent was stored in a 500 mL glass flask while the samples were transferred from 10 mL glass flasks to clear crimp vials. All chemicals were obtained from Merck Eurolab (analytical grade) and used without further purification. During an experiment the helium purged eluent flowed through a membrane degasser to a quaternary dual piston pump (HP model 1050). The feed pump was connected to an autosampler (Spark Midas) equipped with a six-port sample injection valve (Rheodyne type 7739) and a sample loop volume of 20 μL. To avoid extra dispersion, dead volume connectors were used to connect the PEEK capillary directly to the injection valve. The 23.42 m long capillary with an inner diameter of $d = 0.53$ mm was helically coiled with a coiling diameter of $d_c = 0.8$ m. In this way the arrangement matches the assumption $d_c \gg d$ to avoid secondary flow in the capillary. Therefore, eqs 1−5 can be applied for further data processing. For temperature control, the capillary was placed in a water bath connected to a thermostat. The outlet of the capillary was linked to a differential refractometer (Waters model R-403) using dead volume connectors. Since only small composition differences were measured, the eluent was always taken as the reference fluid. Additionally, the refractometer cell was thermostated at a slightly higher temperature than the water bath of the capillary to reduce the noise in the detector signal. This was recorded by a PC, which also fully controlled the whole apparatus. Prior to carrying out measurements with a new eluent composition, the apparatus was initially purged with the new eluent mixture at a flow rate of 1 mL/min for about 10 min and afterward at the experimental flow rate of 0.15 mL/min for several hours. Typical residence times obtained at this flow rate are around 31 min.

A least-squares fitting strategy was applied for the data processing of the detector signals since the moment's method, an alternative procedure, was deemed less accurate.[4,12] Following the recommendation of Bollen,[10] the data processing was done in two steps. In the first step, data points that clearly belong to the baseline were selected from both sides of the peak, and a polynomial function (mostly of degree three) was then fitted to the selection. This function was then subtracted from the original peak to obtain a baseline corrected peak (i.e., to account for baseline drifting of the detector output). In the second step, a three-parameter form of Taylor's equation was then fitted

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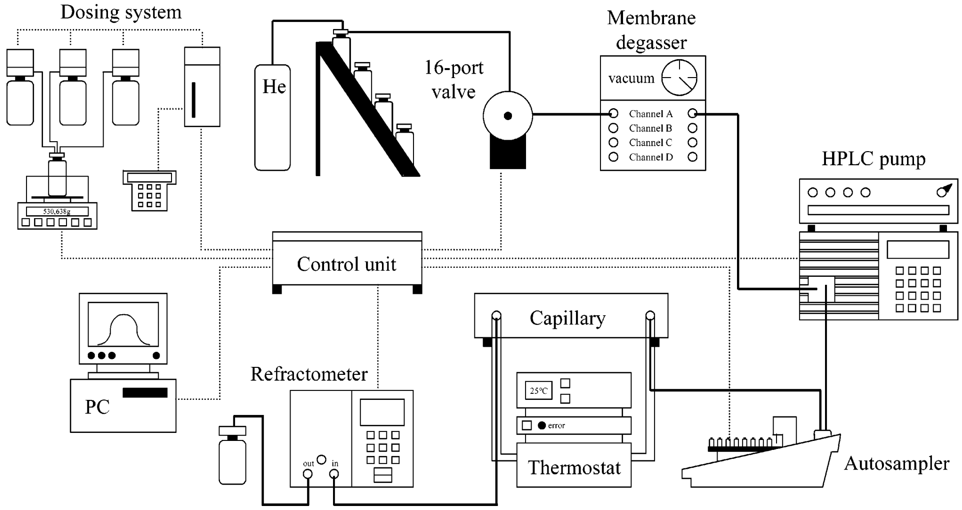

Figure 1. Experimental setup of the Taylor dispersion unit.

to the corrected peak as was also mentioned by other researchers:[4,11]

$$\Delta y_1(t) = \frac{P_1}{\sqrt{P_2 t}} \exp\left(-\frac{L^2(1 - t/P_3)^2}{4P_2 t}\right) \tag{1}$$

Here, Δy_1 denotes the computed value of the detector signal, t is the time and L is the length of the capillary while the three parameters are defined by

$$P_1 = \frac{2s_1 n_1^{\mathrm{E}}}{\pi d^2 \sqrt{\pi}} \tag{2}$$

$$P_2 = \frac{u_{\mathrm{av}}^2 d^2}{192D} \tag{3}$$

$$P_3 = \frac{L}{u_{\mathrm{av}}} \tag{4}$$

with s_1 as the detector linearity, n_1^{E} as the excess number of tracer moles in the pulse, d as the inner diameter of the capillary, and u_{av} as the cross-section averaged velocity of the eluent. As may be seen from their definition, the parameters P_2 and P_3 represent the dispersion coefficient and the residence time, respectively. The defining eqs 3 and 4 of these parameters also serve to compute the desired diffusion coefficient from

$$D = \frac{L^2 d^2}{192 P_2 P_3^{\,2}} \tag{5}$$

The estimated uncertainty in x is 0.01, in t it equals 1 s, and it amounts to $3 \cdot 10^{-11}$ m²·s⁻¹ in D.

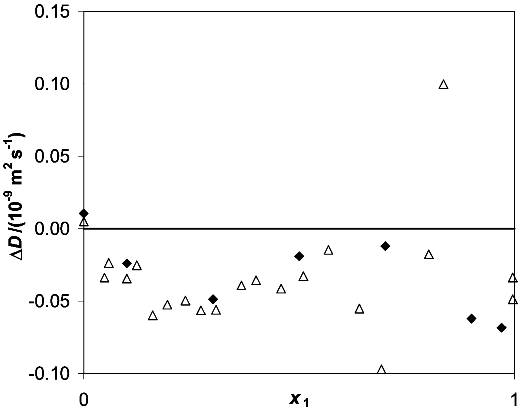

Figure 2. Differences ΔD between experimental data and orthogonal polynomial function[5] for the mixture methanol (1) + water (2) at 25 °C: ◆, this work; △, Ven-Lucassen et al.[4]

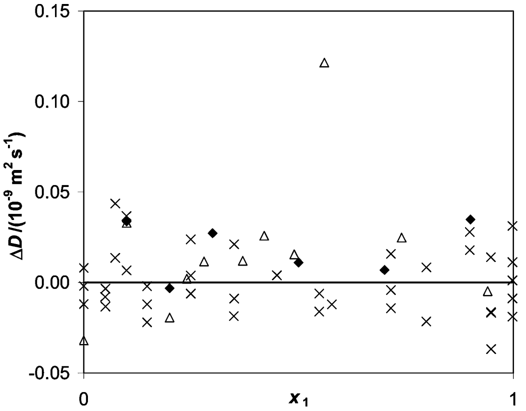

Figure 3. Differences ΔD between experimental data and orthogonal polynomial function[5] for the mixture ethanol (1) + water (2) at 25 °C: ◆, this work; △, Ven-Lucassen et al.;[4] ×, Harris et al.[5]

Results

The Taylor dispersion apparatus was tested at (25.0 ± 0.1) °C using the mixtures methanol + water and ethanol + water. Figures 2 and 3 present the deviations between the measurements of this work and an orthogonal polynomial function determined by Harris et al.[5] to test their data against those of other authors. Additionally, results of other researchers are depicted for comparison. The average deviation of the validation experiments is ± $3 \cdot 10^{-11}$ m²·s⁻¹, which is in agreement with the accuracy for this type of setup and type of systems reported by other researchers.[3−5] The measured diffusion coefficients as well as the computed differences are summarized in Table 1. The tabulated D values are averages of at least three replicate measurements.

Diffusion coefficients of several alcohol + solvent systems were measured. In addition to the concentration dependence, the influence of the chain length of the alcohol component as well as the effect of temperature on the diffusion coefficients were considered. In total, nine different binary mixtures at temperatures from (25 to 35) °C

Table 1. Diffusion Coefficients *D* of Alcohol (1) + Water (2) Mixtures[a]

		$D/(10^{-9}\ m^2 \cdot s^{-1})$ and $\Delta D/(10^{-9}\ m^2 \cdot s^{-1})$ at x_1								
	t/°C	0.0	0.1	0.2	0.3	0.5	0.7	0.9	0.97	1.0
MeOH	25	1.57	1.22		0.95	1.03	1.37	1.87	2.05	
		(0.01)	(−0.02)		(−0.05)	(−0.02)	(−0.01)	(−0.06)	(−0.07)	
EtOH	25		0.70	0.41	0.38	0.51	0.76	1.08		
			(0.03)	(0.0)	(0.03)	(0.01)	(0.01)	(0.03)		

[a] Deviations ΔD from orthogonal polynomial function[5] given in parentheses.

Table 2. Diffusion Coefficients *D* of Alcohol (1) + Carbon Tetrachloride (2) Mixtures

		$D/(10^{-9}\ m^2 \cdot s^{-1})$ at x_1								
	t/°C	0.0	0.03	0.1	0.3	0.5	0.7	0.9	0.97	1.0
EtOH	25	1.90	1.06	0.82	0.64	0.73	0.99	1.32	1.43	1.47
	30	2.15	1.60	0.99	0.83	0.87	1.14	1.45	1.56	1.61
	35	2.24	1.80	1.10	0.95	0.99	1.28	1.60	1.76	1.82
1-PrOH	25	1.61	0.83	0.61	0.39	0.46	0.66	0.83	0.91	0.95
1-BuOH	25	1.47	0.7	0.50	0.29	0.32	0.54	0.65	0.69	0.72
	35	1.74	0.93	0.71	0.52	0.56	0.65	0.80	0.89	0.94

Table 3. Diffusion Coefficients *D* of Alcohol (1) + Toluene (2) Mixtures

		$D/(10^{-9}\ m^2 \cdot s^{-1})$ at x_1								
	t/°C	0.0	0.03	0.1	0.3	0.5	0.7	0.9	0.97	1.0
EtOH	25	3.12	2.94	2.41	1.22	0.98	1.16	1.55	1.70	1.74
	35	3.61	3.40	2.90	1.70	1.35	1.59	1.89	2.04	2.11
1-PrOH	25	2.67	2.37	1.81	1.00	0.85	1.01	1.28	1.40	1.46

Table 4. Diffusion Coefficients *D* of Alcohol (1) + Hexane Mixtures

		$D/(10^{-9}\ m^2 \cdot s^{-1})$ at x_1								
	t/°C	0.0	0.03	0.1	0.3	0.5	0.7	0.9	0.97	1.0
EtOH	25	5.74	4.07	2.41	1.54	1.30	1.30	1.43	1.54	1.60
1-PrOH	25	5.20	3.37	2.17	1.38	1.15	1.08	1.09	1.03	1.02

Table 5. Diffusion Coefficients *D* of Alcohol (1) + Cyclohexane (2) Mixtures

		$D/(10^{-9}\ m^2 \cdot s^{-1})$ at x_1								
	t/°C	0.0	0.03	0.1	0.3	0.5	0.7	0.9	0.97	1.0
EtOH	25		0.99	0.77	0.43	0.46	0.73	1.23	1.41	
1-PrOH	25		0.83	0.66	0.39	0.42	0.65	1.00	1.15	

were studied over the whole concentration range. For the alcohol, ethanol (EtOH), 1-propanol (1-PrOH), and 1-butanol (1-BuOH) were chosen while for the solvent hexane, cyclohexane, toluene, and carbon tetrachloride were taken. Tables 2 to 5 provide a summary of the experimental results. Again, only the average *D* values are reported. The mole fractions given in the tables always refer to the alcohol component.

Figure 4 shows the *D* values for the ethanol + carbon tetrachloride system at various temperatures. The results of holographic interferometry measurements by Sanchez and Oftadeh[13] are also depicted. The lines presented serve only as a visual aid. As can be seen from the graph the findings of this work and of the research by Sanchez and Oftadeh[13] are in excellent agreement. This graph also reveals a strong concentration dependence of the *D* values, and as expected from theory, they are also strongly related to the temperature. With increasing temperature, the mobility of the molecules is enhanced due to a decrease in the liquid viscosity.

The influence of the molecular chain length on the diffusion coefficient has also been investigated as the results in Figure 5 show. Here, the diffusion coefficients of alcohol + carbon tetrachloride mixtures are presented at 25 °C. As is evident from the graph, an increase in the chain length causes a decrease in the diffusion coefficient. This behavior, which lowers the *D* values from ethanol to 1-butanol, can be explained by the lower mobility of the larger alcohol molecules.

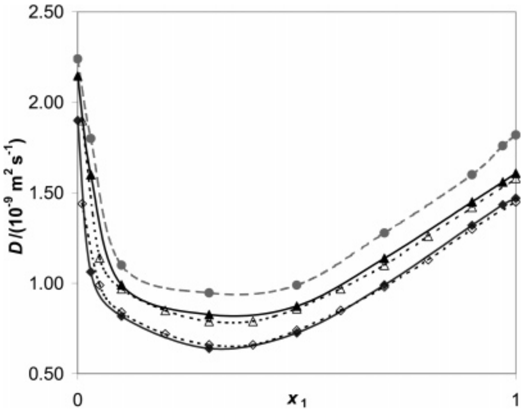

Figure 4. Diffusion coefficients *D* of ethanol (1) + carbon tetrachloride (2) mixtures: ◆, this work 25 °C; ▲, this work 30 °C; ●, this work 35 °C; ◇, Sanchez and Oftadeh[13] 25 °C; △, Sanchez and Oftadeh[13] 30 °C.

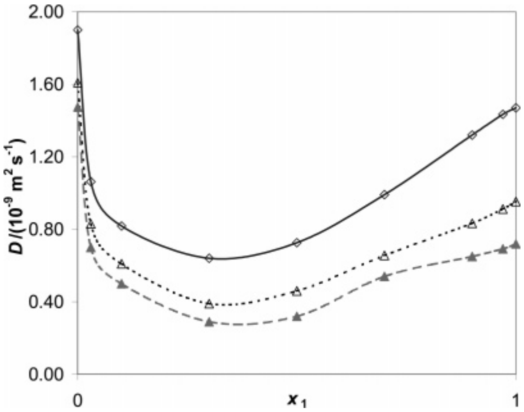

Figure 5. Diffusion coefficients *D* of alcohol (1) + carbon tetrachloride (2) mixtures at 25 °C: ◇, ethanol; △, 1-propanol; ▲, 1-butanol.

Summary

In this work a fully automated Taylor dispersion apparatus was used to determine diffusion coefficients of nine binary alcohol−solvent mixtures. As expected for thermodynamically nonideal mixtures, the reported data points show a strong concentration dependence. Additionally, the *D* values are also a strong function of temperature. The uncertainty of the reported data is estimated to be within $3 \cdot 10^{-11}\ m^2 \cdot s^{-1}$.

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