J. Chem. Eng. Data **2009,** *54,* 405–410

Ternary Diffusion Coefficients of Cyclohexane + Toluene + Methanol by Taylor Dispersion Measurements at 298.15 K. Part 1. Toluene-Rich Area[†]

Thomas Grossmann and Jochen Winkelmann*

Institute of Physical Chemistry, University Halle−Wittenberg, Mühlpforte 1, D−06108 Halle, Germany

The concentration dependence of the mutual diffusion coefficients in the ternary liquid mixture cyclohexane + toluene + methanol is determined at 298.15 K by Taylor dispersion technique along two concentration paths of a constant toluene mole fraction of $x_2 = 0.40$ and $x_2 = 0.60$, respectively. The four elements of the matrix of mutual diffusion coefficients, the eigenvalues, and the determinant of the matrix are given.

Introduction

Mass transport by diffusion is a fundamental process that plays an important part in chemistry and chemical engineering in processes such as liquid extractions, solid extraction, distillation, and chemical reactions as well as biological systems. Different experimental methods are established to measure diffusion coefficients: diaphragm cell,[1−5] conductometric[6,7] and optical[8−12] (e.g., Gouy-, Rayleigh-, and holographic interferometry), and dynamic light scattering (DLS).[13−16] A fast and simple method compared with optical techniques, the Taylor dispersion technique is well established in the case of binary mixtures of organic compounds and of electrolyte solutions.[17−26] With this method, it is also possible to investigate diffusion processes in ternary systems.[27−34] However, the fact that in organic liquid systems one experimentally measurable quantity, the refractive index, has to be used to extract two eigenvalues or four elements of the matrix of ternary mutual diffusion coefficients demonstrates the considerably higher complexity of the ternary diffusion problem, and as a consequence, publications of ternary diffusion coefficients are rather rare.

In a systematic study on transport behavior in ternary mixtures with liquid−liquid phase separation, we performed interdiffusion or mutual diffusion coefficient measurements on the basis of Taylor's dispersion technique and compared these data with results from DLS measurements in the same system. Measurements were performed at 298.15 K in the system glycerol + acetone + water (GAW) in the acetone-rich[33] and water-rich regions[34] and along concentration paths in the vicinity of the critical solution point.[32] These mutual diffusion coefficient data were compared with DLS results,[16] and we found that none of the four elements of the diffusion coefficient matrix are related to the mass diffusion coefficient D_m of the DLS experiment. However, the lowest eigenvalue of the matrix coincides with D_m.[35] The other transport mode of the DLS experiment could be identified as thermodiffusion.

The aim of the present work is to continue this systematic study on diffusive transport to find out whether the results of the GAW system represent a more general behavior or whether they are specific to only that system. We determine diffusion coefficients in a ternary liquid mixture with a miscibility gap depending on the distance from the phase boundary. For a new model system, we chose mixtures of cyclohexane + toluene + methanol. Because ternary diffusion data from literature are

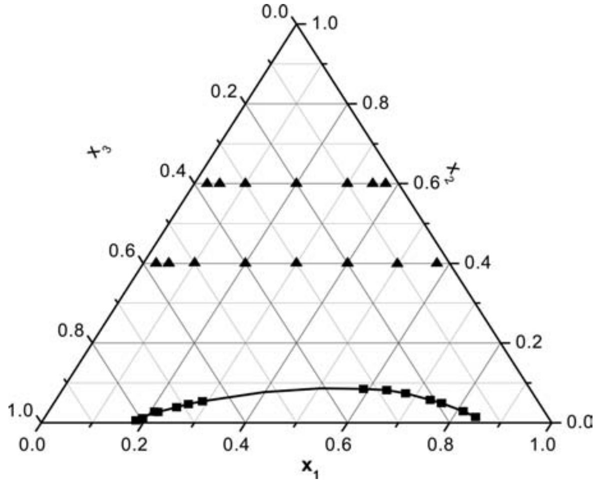

Figure 1. Liquid−Liquid phase diagram and range of concentration for the diffusion measurements in the system cyclohexane (1) + toluene (2) + methanol (3) at 298.15 K: ■, binodal curve; ▲, concentration of diffusion measurements.

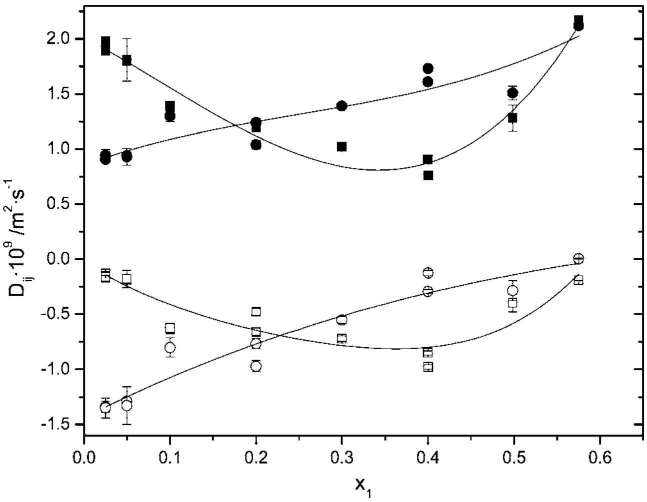

Figure 2. Mutual diffusion coefficients in the ternary system cyclohexane (1) + toluene (2) + methanol (3) versus mole fraction x_1 at 298.15 K and constant $x_2 = 0.40$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

---

* Corresponding author. E-mail: jochen.winkelmann@chemie.uni-halle.de. Fax: +49 345 55 27157. Tel: +49 345 55 25843.

[†] Part of the special issue "Robin H. Stokes Festschrift".

10.1021/je800444e CCC: $40.75

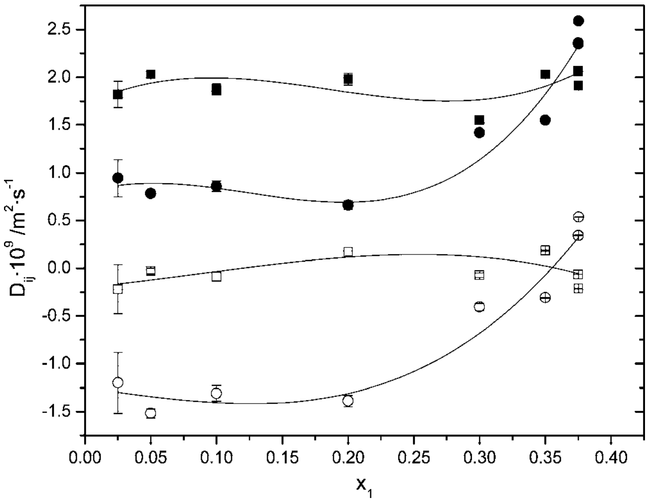

Figure 3. Mutual diffusion coefficients in the ternary system cyclohexane (1) + toluene (2) + methanol (3) versus mole fraction x_1 at 298.15 K and constant $x_2 = 0.60$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

rather scarce and experimental uncertainties are much higher than those in the binary case, we performed systematic diffusion measurements along two different concentration paths. In this work we performed measurements at concentrations with a constant toluene mole fraction of $x_2 = 0.40$ and $x_2 = 0.60$, respectively, and methanol was considered to be the reference component. The eigenvalues of the ternary diffusion matrix and the respective determinants were calculated to check the quality and internal consistency of the experimental data. These measurements will complete DLS experiments of the same system in the vicinity of the critical solution point by Ivanov and Winkelmann.[43]

Taylor dispersion method. In a ternary mixture, the diffusion processes are described by a coupled set of Fick's equations

$$\begin{aligned} J_1 &= -D_{11}\nabla c_1 - D_{12}\nabla c_2 \\ J_2 &= -D_{21}\nabla c_1 - D_{22}\nabla c_2 \end{aligned} \tag{1}$$

where J_i is the molar flux of component i in the volume-fixed frame of reference. The coefficients D_{ij} represent the elements of the mutual diffusion coefficient matrix. In the case of a ternary mixture, this relation describes two coupled mass fluxes, assuming the third component to be the reference. The Taylor dispersion method is a rapid and simple technique for determining mutual diffusion coefficients. A small volume of sample solution is injected into the laminar flow of a carrier stream of the same system at a slightly different concentration. At constant temperature, the liquid carrier flows with constant velocity through a capillary with an inner radius R. At the end of the capillary, a detector (e.g., differential refractometer, UV detector, conductometer, or other suitable flow-through detector) monitors the change in concentration. The injected square pulse develops into a parabolic velocity profile, and the radial concentration gradient causes a radial diffusion that changes the rectangular pulse shape into a Gaussian concentration profile

$$u(r) = 2\cdot\bar{u}\cdot\left[1-\left(\frac{r}{R}\right)^2\right] \tag{2}$$

where u is the velocity, $\bar{u}$ is the average velocity of the carrier flow, r is the radial coordinate, and R is the radius of the capillary.

The case of binary mixtures results in a differential equation that was solved by Taylor.[18]

To obtain the four diffusion coefficients D_{ik} of a ternary system, Price[27] solved the corresponding differential eq 3 for a ternary mixture that flows along z

$$\frac{\partial c_i}{\partial t} = \sum_{k=1}^{2} K_{ik}\cdot\frac{\partial^2 c_k}{\partial z^2} \tag{3}$$

with the dispersion coefficients as

$$K_{ii} = \frac{\bar{u}^2\cdot R^2}{48}\cdot\frac{D_{kk}}{D_{ii}\cdot D_{kk} - D_{ik}\cdot D_{ki}} \tag{4}$$

$$K_{ik} = -\frac{\bar{u}^2\cdot R^2}{48}\cdot\frac{D_{ik}}{D_{ii}\cdot D_{kk} - D_{ik}\cdot D_{ki}} \tag{5}$$

Here D_{kk} and D_{ik} denote the main and the corresponding cross diffusion coefficients, respectively.

Solving the respective differential equations for the ternary case leads to the final working equations, which can be used to estimate the diffusion coefficients from the detector signal versus flow time curve.

In the case of ternary mixtures, we inject a small sample of composition $c_1 + \Delta c_1$, $c_2 + \Delta c_2$ into a laminar flow of a carrier with c_1, c_2. From the corresponding fluxes J_1 and J_2, there exist two overlapping profiles from which the diffusion coefficients can be extracted. After introducing a normalized peak signal $S_N(t)$ according to Leaist,[29] we obtain

$$S_N(t) = \sqrt{\frac{t_R}{t}}\cdot\sum_{i=1}^{2}\left[\frac{W_i}{W_1+W_2}\cdot\exp\left(-\frac{12\cdot D_i}{R^2}\cdot\frac{(t-t_R)^2}{t}\right)\right] \tag{6}$$

with W_i as the normalized weight of the two exponential terms. These weights are given by

$$W_1 = \left[\left(D_{22} - \frac{R_2}{R_1}\cdot D_{21}\right)\cdot\alpha_1 + \left(D_{11} - \frac{R_1}{R_2}\cdot D_{12}\right)\cdot(1-\alpha_1) - D_1\right]\cdot\sqrt{D_1} \tag{7}$$

$$W_2 = -\left[\left(D_{22} - \frac{R_2}{R_1}\cdot D_{21}\right)\cdot\alpha_1 + \left(D_{11} - \frac{R_1}{R_2}\cdot D_{12}\right)\cdot(1-\alpha_1) - D_2\right]\cdot\sqrt{D_2} \tag{8}$$

where D_i is the eigenvalue of the matrix of the ternary diffusion coefficients

$$D_1 = \frac{1}{2}\cdot\left[D_{11} + D_{22} + (D_{11} - D_{22})\cdot\sqrt{1 + \frac{4\cdot D_{12}\cdot D_{21}}{(D_{11}-D_{22})^2}}\right] \tag{9}$$

$$D_2 = \frac{1}{2}\cdot\left[D_{11} + D_{22} - (D_{11} - D_{22})\cdot\sqrt{1 + \frac{4\cdot D_{12}\cdot D_{21}}{(D_{11}-D_{22})^2}}\right] \tag{10}$$

and the parameter α_1 is given by

$$\alpha_1 = \frac{R_1\cdot\Delta c_1}{R_1\cdot\Delta c_1 + R_2\cdot\Delta c_2} \tag{11}$$

For calculating the parameter α_1, a linear dependency of refractive index concentration change is assumed, supposing small concentration jumps between sample and carrier composition

$$\Delta n = R_1\cdot\Delta c_1 + R_2\cdot\Delta c_2 \tag{12}$$

R_i is the concentration derivative of the refractive index at the carrier composition. It accounts for the optical properties

Table 1. Diffusion Coefficients and Their Standard Deviations of the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K with x_2 = 0.40

x_1	x_2	$\frac{10^9(D_{11})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9\sigma}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{12})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{21})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{22})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$
0.0249	0.4000	1.8877	0.0108	−0.1294	0.0183	−1.3369	0.0534	0.9066	0.0292
0.0250	0.4000	1.9762	0.0252	−0.1617	0.0429	−1.3528	0.0906	0.9421	0.0532
0.0499	0.4003	1.8024	0.0000	−0.1935	0.0000	−1.2928	0.0000	0.9395	0.0000
0.0500	0.4000	1.8076	0.1937	−0.1805	0.0789	−1.3256	0.1724	0.9294	0.0754
0.1002	0.4011	1.3869	0.0461	−0.6269	0.0476	−0.8017	0.0862	1.2987	0.0497
0.2000	0.4000	1.0422	0.0392	−0.6601	0.0324	−0.7663	0.0467	1.2390	0.0354
0.2000	0.4000	1.2030	0.0413	−0.4793	0.0328	−0.9731	0.0510	1.0449	0.0376
0.3000	0.4002	1.0188	0.0372	−0.7215	0.0253	−0.5520	0.0316	1.3864	0.0220
0.4000	0.4000	0.9044	0.0206	−0.8509	0.0188	−0.2933	0.0189	1.6087	0.0162
0.4004	0.4000	0.7603	0.0316	−0.9798	0.0192	−0.1251	0.0245	1.7330	0.0160
0.4987	0.3988	1.2764	0.1194	−0.3980	0.0785	−0.2857	0.0919	1.5137	0.0628
0.5752	0.3998	2.1682	0.0034	−0.1914	0.0011	0.0031	0.0013	2.1194	0.0020

Table 2. Diffusion Coefficients and Their Standard Deviations of the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K with x_2 = 0.60

x_1	x_2	$\frac{10^9(D_{11})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9\sigma}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{12})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{21})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_{22})}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(\sigma)}{\mathrm{m^2 \cdot s^{-1}}}$
0.0250	0.6000	1.8228	0.1370	−0.2189	0.2562	−1.1996	0.3178	0.9444	0.1935
0.0500	0.6000	2.0342	0.0435	−0.0280	0.0309	−1.5196	0.0489	0.7825	0.0301
0.1000	0.5999	1.8709	0.0577	−0.0879	0.0496	−1.3143	0.0843	0.8583	0.0547
0.2000	0.6000	1.9795	0.0608	0.1703	0.0470	−1.3901	0.0589	0.6614	0.0441
0.3000	0.6000	1.5469	0.0276	−0.0716	0.0223	−0.4054	0.0383	1.4186	0.0231
0.3500	0.6000	2.0296	0.0000	0.1855	0.0000	−0.3092	0.0000	1.5503	0.0000
0.3500	0.6000	2.0254	0.0068	0.1847	0.0065	−0.3092	0.0044	1.5473	0.0029
0.3750	0.6000	2.0602	0.0056	−0.0628	0.0010	0.3420	0.0015	2.3539	0.0065
0.3750	0.6000	2.0679	0.0106	−0.0612	0.0012	0.3444	0.0026	2.3584	0.0100
0.3752	0.5998	1.9139	0.0009	−0.2108	0.0006	0.5361	0.0005	2.5864	0.0003

of the mixture, and its ratio substantially contributes to the accuracy of a Taylor measurement in a given system. There is an alternative numerical procedure for the evaluation of eq 6 proposed by Ko, Chang, and Li.[42] They rearrange the coefficient W_i and parametrize it in terms of D_i. Therefore, they first obtain the eigenvalues and calculate the diffusion coefficients by inverting eqs 9 and 10.

Experimental Section

For our measurements, the following substances from Acros Organics (Fischer Scientific GmbH, Schwerte, Germany) were used: cyclohexane, toluene, and methanol (all HPLC grade). The chemicals were dried on molecular sieves (Wolfen Zeosorb 4A).

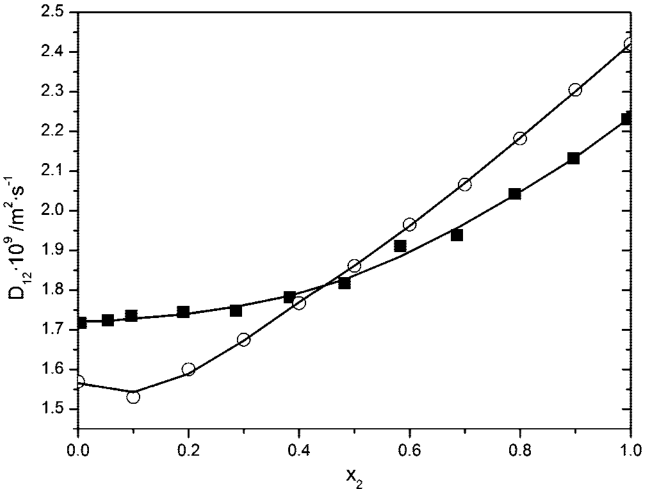

Figure 4. Mutual diffusion coefficient D_{12} in the binary system cyclohexane (1) + toluene (2) versus mole fraction x_2 at 298.15 K: ■, data from Thiel;[39] ○, data from Sanni et al.[40]

Table 3. Determinant |*D*| and Eigenvalues D_1 and D_2 with x_2 = 0.40

x_1	x_2	$10^9\lvert D\rvert$	$\frac{10^9(D_1)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_2)}{\mathrm{m^2 \cdot s^{-1}}}$
0.0249	0.4000	1.5385	2.0403	0.7540
0.0250	0.4000	1.6432	2.1564	0.7620
0.0499	0.4003	1.4432	2.0315	0.7104
0.0500	0.4000	1.4407	2.0258	0.7112
0.1002	0.4011	1.2986	2.0531	0.6325
0.2000	0.4000	0.7855	1.8586	0.4226
0.2000	0.4000	0.7906	1.8115	0.4365
0.3000	0.4002	1.0141	1.8599	0.5453
0.4000	0.4000	1.2053	1.8678	0.6453
0.4004	0.4000	1.1950	1.8459	0.6474
0.4987	0.3988	1.8184	1.7525	1.0376
0.5752	0.3998	4.5958	2.1445	2.1431

Table 4. Determinant |*D*| and Eigenvalues D_1 and D_2 with x_2 = 0.60

x_1	x_2	$10^9\lvert D\rvert$	$\frac{10^9(D_1)}{\mathrm{m^2 \cdot s^{-1}}}$	$\frac{10^9(D_2)}{\mathrm{m^2 \cdot s^{-1}}}$
0.0250	0.6000	1.4588	2.0585	0.7087
0.0500	0.6000	1.5493	2.0673	0.7494
0.1000	0.5999	1.4902	1.9744	0.7548
0.2000	0.6000	1.5460	1.7650	0.8759
0.3000	0.6000	2.1654	1.6648	1.3007
0.3500	0.6000	3.2039	1.7986	1.7814
0.3500	0.6000	3.1911	1.7883	1.7844
0.3750	0.6000	4.8709	2.2153	2.1988
0.3750	0.6000	4.8979	2.2153	2.2109
0.3752	0.5998	5.0632	2.2551	2.2452

In all Taylor dispersion experiments, the flow velocity of the carrier, which is generated by a linear pulse-free HPLC pump, was 4 mL·h^{-1}. The capillary, made from stainless steel, had a length of 11.50 m and an effective radius of 260.65 μm. The pump was connected to a commercial six-port valve with a sample loop volume of 20 μL. For a detector, we used a differential refractometer (Wissenschaftlicher Gerätebau Dr. Ing.

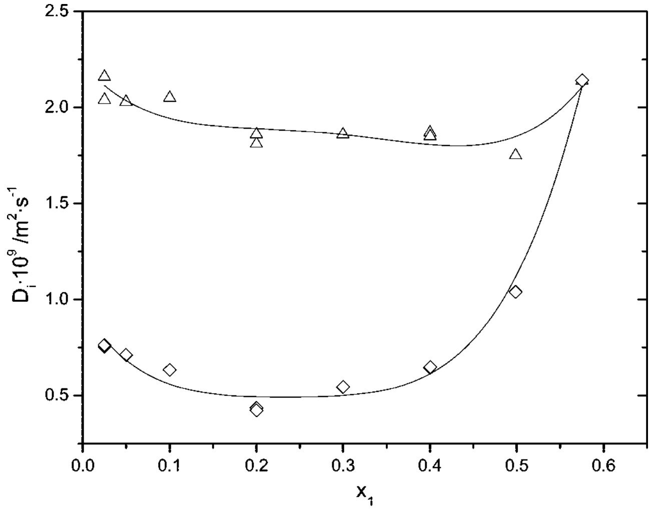

Figure 5. Calculated eigenvalues D_i of the matrix of mutual diffusion coefficients versus mole fraction x_1 of cyclohexane at constant mole fraction $x_2 = 0.40$: △, D_1; ◇, D_2.

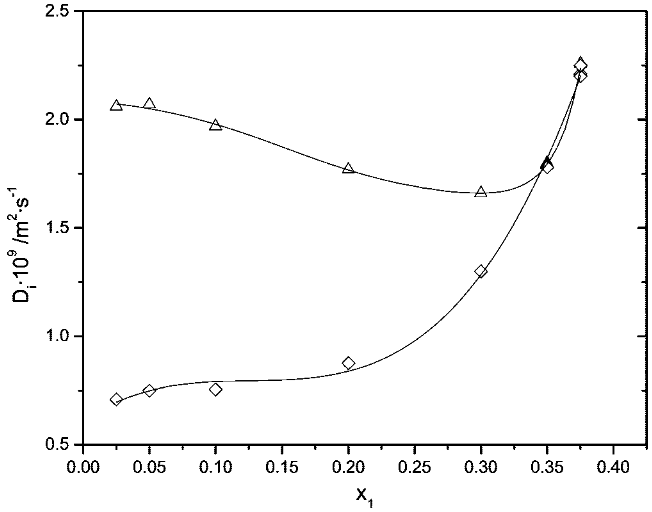

Figure 6. Calculated eigenvalues D_i of the matrix of mutual diffusion coefficients versus mole fraction x_1 of cyclohexane at constant mole fraction $x_2 = 0.60$: △, D_1; ◇, D_2.

Herbert Knauer GmbH) with a baseline noise of $2 \cdot 10^{-8}$ refractive index units (RUI). The detector and the capillary were kept at constant temperature of (298.15 ± 0.1) K. The refractometer signal was recorded at time intervals of 1 s. The instrumental setup is analogous to the apparatus described in ref 32. About 1000 to 2000 data points were taken into account for the characterization of one peak.

The densities of the solution were measured with a vibrating-tube density meter (Anton Paar GmbH, model DAS 48) with a standard deviation of $1 \cdot 10^{-5}$ g·cm^{-3} and internal temperature control of ± 0.01 K. For the determination of the refractive index differences, a differential refractometer (Shimadzu, model RID 10A) with a baseline noise of $0.25 \cdot 10^{-8}$ RUI was used. To prepare the solutions for the diffusion, density, and refractive index measurements, we used an analytical balance that allowed mass determination accurate to ± 0.00001 g.

Data Evaluation Procedure. The procedure to determine the ternary diffusion coefficients was adopted from Leaist and Hao.[30] To increase the reliability of our data evaluation, we performed four runs with different Δc_i, that is, with different values of α_1, and analyzed the corresponding signal profiles in a common nonlinear least-squares (NLSQ) procedure. This procedure results in a model with a high number of nonlinear parameters; most of them are specific to the experiment (baseline, amplitudes), and only four are the diffusion coefficients.

$$S(t) = B_1 + B_2 \cdot t + B_3 \cdot S_N(t) \qquad (13)$$

We reduced the number of nonlinear parameters by separately evaluating some of the linear parameters. In a preliminary step, we separated the single peaks from the complete data set of one measurement. The baseline parameters B_1 and B_2 as well as the starting values for retention time t_R and B_3 were calculated in this peak separation. Altogether, eight peaks of four different injection samples were simultaneously fit with the fitting parameters D_{11}, D_{12}, D_{21}, and D_{22} and the retention time t_R and peak height B_3. Furthermore, the concentration derivatives of refractive indices R_1 and R_2 were determined after the refractive index differences were measured with a differential refractometer and the densities were measured with a vibrating-tube density meter. We applied a modified Marquardt–Levenberg algorithm derived from ref 36 as the NLSQ regression method.

To obtain information on possible errors during the fitting procedure and on the influence of different experimental quantities on the final result, we created 20 data sets from each injection and modified them by superimposing 1 % artificial Gaussian-distributed noise. Also, the concentrations and the refraction index differences were perturbed with 1 % and 5 % noise, respectively. Then, the resulting data sets were subjected to the same fitting procedure as that of the original data sets. The diffusion coefficients obtained this way are considered to be the basis for the calculation of the respective standard deviation σ of the experimental data.

Results and Discussion

Figure 1 shows the liquid–liquid phase diagram of the ternary system cyclohexane (1) + toluene (2) + methanol (3). The miscibility gap is rather small; binodal curve data at 298.15 K have been published by Nagata.[37] For the systematic Taylor dispersion measurements, we selected two concentration ranges with constant toluene content. The third component, methanol, is considered to be the reference. In Figure 1, we show the concentration paths of the two sets of measurements with $x_2 = 0.40$ and $x_2 = 0.60$, respectively. The results of the Taylor dispersion measurements for the two sets are shown in Figures

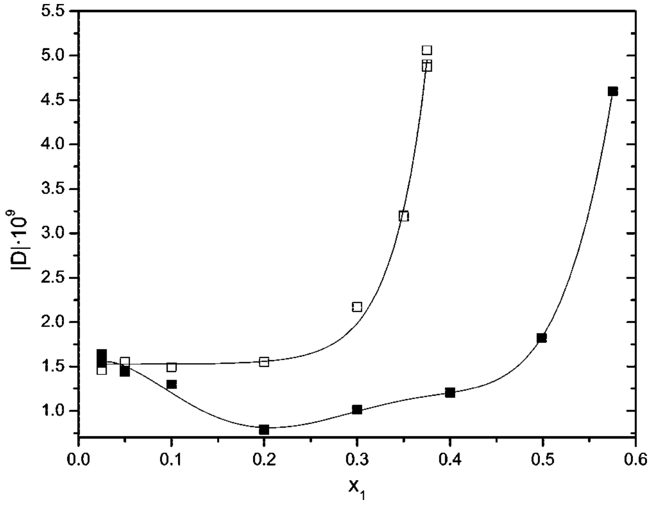

Figure 7. Determinant of the diffusion coefficient matrix versus cyclohexane mole fraction x_1 at constant toluene mole fraction: ■, at $x_2 = 0.40$; □, at $x_2 = 0.60$.

2 and 3. As described above, the diffusion coefficient D_{ij} of each concentration were obtained by NLSQ fitting of a set of at least four different runs with a constant carrier and different values of α_1 in the sample plugs. They are shown in Figures 2 and 3 for $x_2 = 0.40$ and 0.60, respectively; the numerical value of D_{ij} together with its standard deviation are given in Tables 1 and 2, respectively.

If we assume that $x_1 \rightarrow 0.0$, then we approach the binary mixture toluene + methanol with traces of cyclohexane. In this limit, D_{11} becomes the tracer diffusion coefficient of cyclohexane in the binary mixture toluene + methanol, whereas D_{22} becomes the mutual diffusion coefficient of the binary system. The extrapolated values of D_{22} within their experimental uncertainties for both toluene concentrations are slightly smaller than the data reported by Shemilt and Nagarajan[41] for 298.15 K. No data were found for the tracer diffusion coefficient for a comparison. The cross coefficient D_{12} tends to disappear in the limit $x_1 \rightarrow 0.0$, and D_{21} shows negative values. This behavior is found for $x_2 \rightarrow 0.40$ in Figure 2, whereas for $x_2 = 0.60$ in Figure 3, the experimental scatter is rather high on this side so that we can state only a tendency of D to approach the limiting values.

In the other limit, $x_3 \rightarrow 0.0$, where we have traces of methanol in a binary mixture cyclohexane + toluene, our choice of the reference component does not allow a similar interpretation. The available experimental data for the mutual diffusion coefficient in this binary subsystem differ considerably, as shown in Figure 4. Here our data of Thiel[39] are compared with those of Sanni et al.[40] At toluene mole fractions $x_2 = 0.40$ to 0.50, there is a rather good agreement, but at lower and higher concentrations, large differences are observed.

The corresponding numerical data of the eigenvalues for both sets of measurements with constant toluene concentration and the respective determinants are given in Tables 3 and 4. The eigenvalues are plotted in Figures 4 and 5. Their concentration dependency looks much smoother than that of the individual coefficients. Figure 6 shows the determinants $|D|$ versus the mole fraction x_1 of both concentration sets.

For the mutual diffusion coefficient matrix, the choice of the reference component is arbitrary, but a better choice would have been to use toluene as a reference. To transform numerical values of diffusion coefficients within a ternary system by interchanging the order of components (e.g., toluene as reference instead of methanol), two ways are possible: (i) calculating the α_1, α_2, R_1, and R_2 values with x_3 set as the mole fraction of toluene instead of methanol and applying the fitting procedure or (ii) transforming the methanol-based diffusion coefficients into toluene-based diffusion coefficients by using the partial molecular volumes as described by Vitagliano.[38] The results are in very good accordance.

Conclusions

In a systematic study of the mass transport behavior in ternary liquid mixtures with a liquid−liquid phase separation, Taylor dispersion measurements of mutual diffusion coefficients were performed along two concentration paths at constant toluene concentration in the system cyclohexane + toluene + methanol.

Literature Cited

(1) Kosanovich, G. M.; Cullinan, H. T., Jr. Experimental design for the determination of coefficients in coupled non-symetric first order systems: the multicomponent diaphragm cell. *Can. J. Chem. Eng.* **1971**, *49*, 753–757.

(2) Rai, G. P.; Cullinan, H. T. Diffusion coefficients of quaternary liquid system acetone−benzene−carbon tetrachloride−*n*-hexane at 25°. *J. Chem. Eng. Data* **1973**, *18*, 213–214.

(3) Leaist, D. G. Diaphragm-cell studies of diffusion in the four-component system hydrochloric acid−sodium chloride−sodium iodide−water. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 829–839.

(4) Noulty, R. A.; Leaist, D. G. Quaternary diffusion in aqueous potassium chloride−potassium dihydrogen phosphate−phosphoric acid mixtures. *J. Phys. Chem.* **1987**, *91*, 1655–1658.

(5) Leaist, D. G. Bidirectional coupled diffusion of glycine driven by pH gradients. *Ber. Bunsen−Ges.* **1987**, *91*, 1059–1064.

(6) Leaist, D. G. Moments analysis of restricted ternary diffusion. Sodium sulfite−sodium hydroxide−water. *Can. J. Chem.* **1985**, *63*, 2933–2939.

(7) Leaist, D. G.; Noulty, R. A. An eigenvalue method for determination of multicomponent diffusion coefficients. Application to sodium hydroxide + sodium chloride + water mixtures. *Can. J. Chem.* **1985**, *63*, 476–482.

(8) Fujita, H.; Gosting, L. J. A. New procedure for calculating the four diffusion coefficients of three component systems from Gouy diffusiometer data. *J. Am. Chem. Soc.* **1960**, *64*, 1256–1263.

(9) Edwards, O. W.; Dunn, R. L.; Hatfield, J. D.; Huffman, E. O.; Elmore, K. L. Diffusion at 25 °C of solutions in the system phosphoric acid−monocalcium phosphate−water. *J. Phys. Chem.* **1966**, *70*, 217–226.

(10) Revzin, A. New procedure for calculating the four diffusion coefficients for ternary systems from Gouy optical data. Application to data for the system potassium bromide−hydrobromic acid−water. *J. Phys. Chem.* **1972**, *76*, 3419–3429.

(11) Miller, D. G. A method for obtaining multicomponent diffusion coefficients directly from Rayleigh and Gouy fringe position data. *J. Phys. Chem.* **1988**, *92*, 4222–4226.

(12) Albright, J. G.; Sherrill, B. C. Methods for the analysis of ternary free-diffusion processes by the Rayleigh optical interferometric method. *J. Solution Chem.* **1979**, *8*, 201–215.

(13) Müller, O.; Winkelmann, J. Comparision of critical properties in binary and ternary liquid mixtures using light scattering techniques. *Phys. Rev. E* **1999**, *59*, 2026–2038.

(14) Will, S.; Leipertz, A. Mutual diffusion coefficient and dynamic viscosity near the critical consolute point probed by dynamic light scattering. *Int. J. Thermophys.* **1999**, *20*, 791–803.

(15) Fiedel, H. W.; Schweiger, G.; Lucas, K. Mutual diffusion coefficients of the systems bromobenzene + acetonitrile, bromobenzene + hexane, and bromobenzene + ethanol. *J. Chem. Eng. Data* **1991**, *36*, 169–170.

(16) Ivanov, D. A.; Winkelmann, J. Static and dynamic light scattering measurements near the critical solution point of a ternary liquid mixture. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3490–3499.

(17) Taylor, G. Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. London* **1953**, *A219*, 186–203.

(18) Taylor, G. Conditions under which the dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. Roy. Soc. London* **1954**, *A225*, 473–477.

(19) Aris, R. On a dispersion of a solute in a fluid flowing through a tube. *Proc. Roy. Soc. London* **1956**, *A235*, 67–77.

(20) Pratt, K. C.; Wakeham, W. A. Mutual diffusion coefficient of ethanol−water mixtures. Determination by a rapid new method. *Proc. Roy. Soc. London* **1974**, *A333*, 393–406.

(21) Pratt, K. C.; Wakeham, W. A. Mutual diffusion coefficient for binary mixtures of water and the isomers of propanol. *Proc. Roy. Soc. London* **1975**, *A342*, 401–419.

(22) Alizadeh, A.; Nieto de Castro, C. A.; Wakeham, W. A. The theory of the Taylor dispersion technique for liquid diffusivity measurements. *Int. J. Thermophys.* **1980**, *1*, 243–284.

(23) Alizadeh, A. A.; Wakeham, W. A. Mutual diffusion coefficients for binary mixtures of normal alkanes. *Int. J. Thermophys.* **1982**, *3*, 307–323.

(24) Matthews, M. A.; Rodden, J. B.; Akgerman, A. High-temperature diffusion of hydrogen, carbon monoxide, and carbon dioxide in liquid *n*-heptane, *n*-dodecane, and *n*-hexadecane. *J. Chem. Eng. Data* **1987**, *32*, 319–322.

(25) Harris, K. R.; Goscinska, T.; Lam, N. L. Mutual diffusion coefficients for the systems water−ethanol and water−propan-1-ol at 25 °C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1969–1974.

(26) Chang, L.-C.; Lin, T.-I.; Li, M.-H. Mutual diffusion coefficients of some aqueous alkanolamines solutions. *J. Chem. Eng. Data* **2005**, *50*, 77–84.

(27) Price, W. E. Theory of the Taylor dispersion technique for three-component-system diffusion measurements. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2431–2439.

(28) Leaist, D. G. Determination of ternary diffusion coefficients by the Taylor dispersion method. *J. Phys. Chem.* **1990**, *94*, 5180–5183.

(29) Leaist, D. G. Ternary diffusion coefficients of 18-crown-6 ether−potassium chloride−water by direct least-squares analysis of Taylor dispersion measurements. *J. Chem. Soc., Faraday Trans. 1* **1991**, *87*, 597–601.

(30) Leaist, D. G.; Hao, L. Gravitational stability of Taylor dispersion profiles. Revised diffusion coefficients for barium chloride−potassium chloride−water. *J. Phys. Chem.* **1993**, *97*, 1464–1469.

(31) Leaist, D. G.; Abdu, S. M. Ternary mutual diffusion coefficients and critical micelle concentrations of aqueous sodium dodecyl sulfate + lithium dodecyl sulfate solutions at 25 °C. *J. Chem. Eng. Data* **2001**, *46*, 922–926.

(32) Grossmann, T.; Winkelmann, J. Ternary diffusion coefficients of glycerol + acetone + water by Taylor dispersion measurements at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1396–1403.

(33) Grossmann, T.; Winkelmann, J. Ternary diffusion coefficients of glycerol + acetone + water by Taylor dispersion measurements at 298.15 K. 2. Acetone-rich region. *J. Chem. Eng. Data* **2007**, *52*, 336–340.

(34) Grossmann, T.; Winkelmann, J. Ternary diffusion coefficients of glycerol + acetone + water by Taylor dispersion measurements at 298.15 K. 3. Water-rich region. *J. Chem. Eng. Data* **2007**, *52*, 341–344.

(35) Ivanov, D. A.; Grossmann, T.; Winkelmann, J. Comparison of ternary diffusion coefficients obtained from dynamic light scattering and Taylor dispersion. *Fluid Phase Equilib.* **2005**, *228−229*, 283–291.

(36) Press, W. H.; Flammery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes in Pascal: The Art of Scientific Computing*; Cambridge University Press: New York, 1990.

(37) Nagata, I. Liquid−liquid equilibria for four ternary systems containing methanol and cyclohexane. *Fluid Phase Equilib.* **1984**, *18*, 83–92.

(38) Vitagliano, V. Some phenomenological and thermodynamic aspects of diffusion in multicomponent systems. *Pure Appl. Chem.* **1981**, *63*, 1441–1448.

(39) Thiel, P. Ph.D. Thesis, Halle-Wittenberg University, 1995.

(40) Sanni, S. A.; Fell, C. J. D.; Hutchison, H. P. Diffusion coefficients and densities for binary organic liquid mixture. *J. Chem. Eng. Data* **1971**, *16*, 424–427.

(41) Shemilt, L. W.; Nagarajan, R. Liquid diffusivities for the system methanol−toluene. *Can. J. Chem.* **1967**, *45*, 1143–1148.

(42) Ko, C. C., Chang, W. H., Li, M. H. Ternary diffusion coefficients of monoethanolamine and *N*-methyldiethanolamine in aqueous solutions. J. Chin. Inst. Chem. Eng., in press.

(43) Ivanov, D. A.; Winkelmann, J. Measurement of diffusion in ternary liquid misture by light scattering technique and comparison with Taylor dispersion data Int. J. Thermophys. [Online] **2007**, DOI: 10.1007/s10765−007−0298−4.

Received for review June 19, 2008. Accepted October 6, 2008. We acknowledge the financial support of the Deutsche Forschungsgemeinschaft, Schwerpunktprogramm: “Nichtgleichgewichtsprozesse in Flüssig-Flüssig-Systemen” (Az. Wi 1081/10-4).

JE800444E