Ternary Diffusion Coefficients of Cyclohexane + Toluene + Methanol by Taylor Dispersion Measurements at 298.15 K. Part 2. Low Toluene Area Near the Binodal Curve[†]

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The concentration dependence of the mutual diffusion coefficients in the ternary liquid mixture cyclohexane (1) + toluene (2) + methanol (3) is determined at 298.15 K by the Taylor dispersion technique along three concentration paths of a constant toluene mole fraction of $x_2 = 0.05$, $x_2 = 0.10$, and $x_2 = 0.20$, ranging from the binary subsystems toward the liquid–liquid phase boundary of the ternary system. The four elements of the matrix of mutual diffusion coefficients, the corresponding eigenvalues, and the determinant of the matrix are given.

Introduction

Mass transport by diffusion is a fundamental process and plays an important part in chemistry and chemical engineering in processes like liquid extractions, solid extraction, distillation, chemical reactions but also in biological systems. Especially in the case of liquid–liquid extraction, the knowledge of the diffusion coefficients and of their behavior when approaching the phase boundary in a multicomponent system is essential for understanding mass transport rates and extraction kinetics.

In a systematic study on transport behavior in ternary mixtures with liquid–liquid phase separation, we performed diffusion coefficient measurements based on Taylor's dispersion technique[1−8] and compared these data with results from dynamic light scattering (DLS)[9−11] measurements in the same system. Measurements were performed at 298.15 K in the system glycerol + acetone + water (GAW).[12−14] These macroscopic mutual diffusion coefficients were compared with data from DLS experiments[11] that result from molecular transport processes caused by stochastic concentration fluctuations. The comparison should reveal whether different transport processes yield the same or similar transport coefficients.

The aim of the present work is to extend the systematic studies on the diffusion coefficients in a ternary liquid mixture with a miscibility gap and to find out whether the comparison to DLS experiments reveals a specific or a more general behavior. As a model system, we had chosen mixtures of cyclohexane + toluene + methanol. In a previous paper, hereafter referred to as part I,[15] we performed diffusion measurements at a set of concentrations of constant toluene mole fraction $x_2 = 0.60$ and $x_2 = 0.40$; in the present paper, we extended our measurements to regions with constant toluene concentration of $x_2 = 0.05$, 0.1, and 0.2, respectively. Again we choose methanol to be the reference. This will enable us to investigate mass transport phenomena in a region near or close to the phase boundary. These measurements are supported by first investigations on dynamic light scattering in the vicinity of the critical solution point of the ternary system.[16]

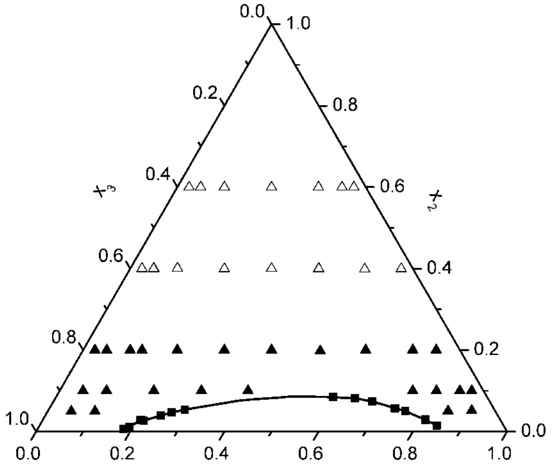

Figure 1. Liquid–liquid phase diagram and range of concentration for the diffusion measurements in the system cyclohexane (1) + toluene (2) + methanol (3) at 298.15 K: ■, binodal curve (Nagata[17]); ▲, paths of present measurements; Δ, previous measurements given in part I.[15]

Taylor Dispersion Method. In a ternary mixture, the diffusion processes are described by a coupled set of generalized Fick 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 matrix of mutual diffusion coefficients. This relation describes two coupled mass fluxes relative to that of the third component. In the Taylor dispersion experiment, a liquid carrier stream of a given concentration flows with constant velocity through a capillary with an inner radius R. A small sample volume with a slightly different composition is injected into the laminar carrier. At the end of the capillary, a differential refractometer is used to monitor the concentration change. The injected square pulse develops into a parabolic velocity profile changing the rectangular pulse shape into a Gaussian concentration profile. From the corresponding fluxes J_1 and J_2, there exist

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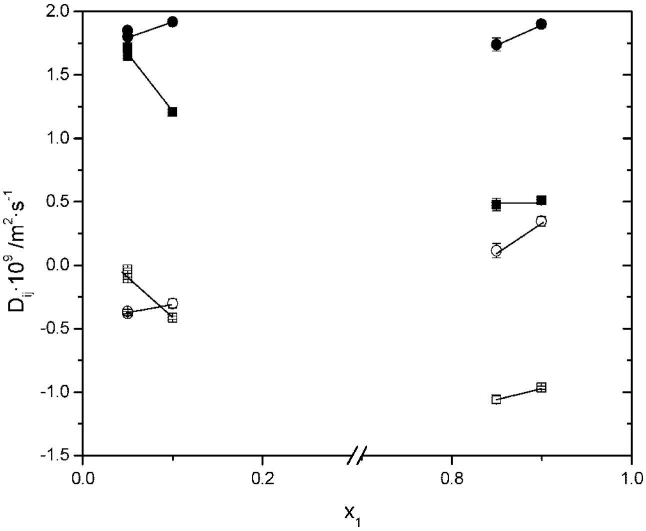

Figure 2. Mutual diffusion coefficients in the ternary system cyclohexane (1) + toluene (2) + methanol (3) versus mole fraction x_1 at 298.15 K and constant toluene mole fraction $x_2 = 0.050$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

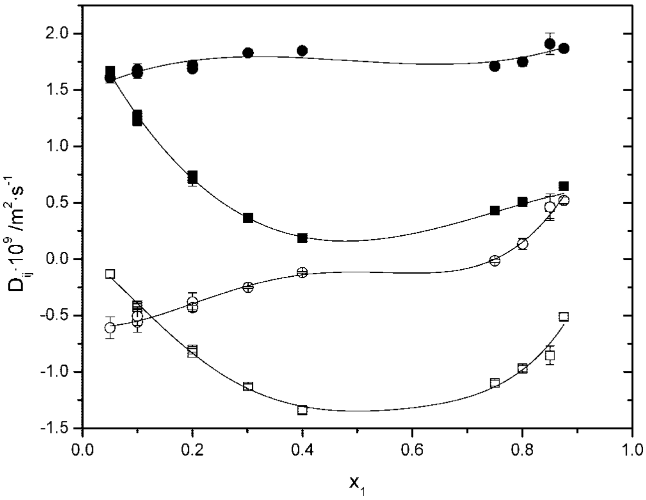

Figure 3. Mutual diffusion coefficients in the ternary system cyclohexane (1) + toluene (2) + methanol (3) versus mole fraction x_1 at 298.15 K and constant toluene mole fraction $x_2 = 0.10$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

two overlapping profiles from where the diffusion coefficients can be extracted. We obtain a normalized peak signal $S_N(t)$ according to Leaist[6]

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

with the normalized weights W_i of the two exponentials. These weights are given by

$$W_i = \left[\left(D_{22} - \frac{R_2}{R_1} \cdot D_{21} \right) \cdot \alpha_1 + \left(D_{11} - \frac{R_1}{R_2} \cdot D_{12} \right) \cdot (1 - \alpha_1) - D_i \right] \cdot \sqrt{D_i} \tag{3}$$

where D_i are the eigenvalues of the matrix of the ternary diffusion coefficients

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

and the parameter α_1 is given by

$$\alpha_1 = \frac{R_1 \cdot \Delta c_1}{R_1 \cdot \Delta c_1 + R_2 \cdot \Delta c_2} \tag{5}$$

To calculate the parameters α_1, a linear dependency of refractive index−concentration change is assumed supposing small concentration jumps between sample and carrier composition

$$\Delta n = R_1 \cdot \Delta c_1 + R_2 \cdot \Delta c_2 \tag{6}$$

The R_i are the concentration derivatives of the refractive index at the carrier composition. They account for the optical properties of the mixture, and their ratio contributes substantially to the accuracy of a Taylor measurement in a given system.

Experimental Section

The experimental procedure is the same as described in part I.[15] The substances cyclohexane, toluene, and methanol (all HPLC grade) from ACROS-ORGANICS (Fischer Scientific GmbH Schwerte Germany) were used. They were dried over molecular sieves (Wolfen Zeosorb 4 A) to remove traces of water and filtered before use.

In all Taylor dispersion experiments, the flow velocity of the carrier was 4 mL·h^{-1}, and the sample volume was 20 μL. The stainless steel capillary had a length of (11.50 ± 0.002) m and an effective radius of 260.65 μm, determined from measurements of a binary reference system. The differential refractometer (Wissenschaftlicher Gerätebau Dr. Ing. Herbert Knauer GmbH) had a baseline noise of $\pm 1 \cdot 10^{-8}$ refractive index units (RUI). The detector and the capillary were kept at constant temperature of (298.15 ± 0.01) K by a Julabo FP 40 thermostat and external Pt-100 sensor. The instrumental setup is analogous to the apparatus described in ref 12. About 1000 to 2000 data points with an interval of 1 s were taken into account to characterize one peak. All solutions were prepared using an analytical balance with an uncertainty of ± 0.00001 g. The densities were measured

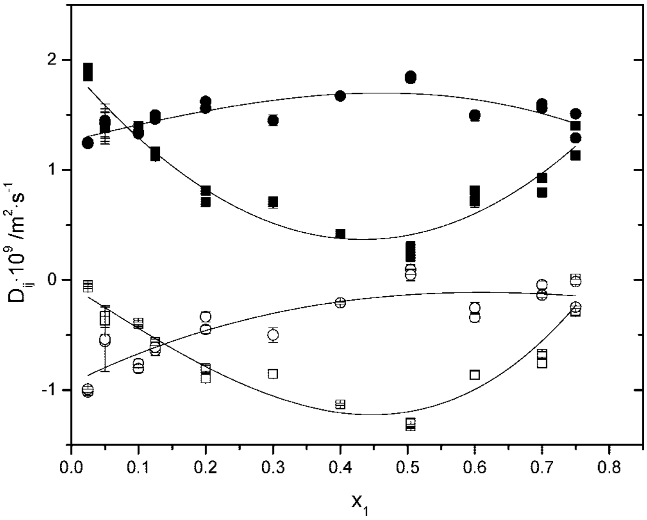

Figure 4. Mutual diffusion coefficients in the ternary system cyclohexane (1) + toluene (2) + methanol (3) versus mole fraction x_1 at 298.15 K and constant toluene mole fraction $x_2 = 0.20$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

Table 1. Diffusion Coefficients D_{ij} and Their Standard Deviations σ in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K with $x_2 = 0.050$

x_1	x_2	10^9D_{11}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{12}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{21}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{22}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$
0.0501	0.0497	1.6508	0.0063	−0.1010	0.0085	−0.3813	0.0163	1.8047	0.0104
0.1001	0.0499	1.2113	0.0136	−0.4131	0.0133	−0.3024	0.0365	1.9176	0.0163
0.0500	0.0500	1.7210	0.0075	−0.0310	0.0091	−0.3640	0.0180	1.8549	0.0112
0.8498	0.0502	0.4780	0.0497	−1.0562	0.0303	0.1146	0.0567	1.7433	0.0511
0.8995	0.0518	0.5114	0.0319	−0.9649	0.0127	0.3461	0.0376	1.9006	0.0271

Table 2. Diffusion Coefficients D_{ij} and Their Standard Deviations σ in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K with $x_2 = 0.10$

x_1	x_2	10^9D_{11}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{12}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{21}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{22}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$
0.0500	0.1000	1.6650	0.0419	−0.1297	0.0333	−0.6107	0.0973	1.6137	0.0464
0.1000	0.1000	1.2279	0.0452	−0.4109	0.0286	−0.5065	0.0829	1.6533	0.0481
0.1000	0.1000	1.2697	0.0497	−0.4275	0.0318	−0.5586	0.0893	1.6809	0.0522
0.2000	0.1000	0.7109	0.0639	−0.8329	0.0379	−0.3812	0.0832	1.7217	0.0382
0.2000	0.1000	0.7443	0.0030	−0.8015	0.0242	−0.4306	0.0196	1.6903	0.0138
0.3014	0.1002	0.3658	0.0024	−1.1264	0.0236	−0.2511	0.0083	1.8299	0.0051
0.4000	0.1001	0.1873	0.0077	−1.3407	0.0331	−0.1192	0.0062	1.8470	0.0058
0.7498	0.1002	0.4298	0.0087	−1.1037	0.0248	−0.0145	0.0124	1.7114	0.0140
0.8004	0.0999	0.5100	0.0419	−0.9691	0.0256	0.1338	0.0489	1.7546	0.0366
0.8502	0.0999	0.4584	0.0991	−0.8536	0.0837	0.4615	0.1181	1.9088	0.0946
0.8753	0.0999	0.6468	0.0320	−0.5113	0.0316	0.5199	0.0309	1.8709	0.0256

Table 3. Diffusion Coefficients D_{ij} and Their Standard Deviations σ in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at 298.15 K with $x_2 = 0.20$

x_1	x_2	10^9D_{11}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{12}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{21}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$	10^9D_{22}/$\mathrm{m^2\cdot s^{-1}}$	$10^9\sigma$/$\mathrm{m^2\cdot s^{-1}}$
0.0250	0.2000	1.8474	0.0246	−0.0713	0.0073	−0.9937	0.0257	1.2547	0.0123
0.0250	0.2000	1.9285	0.0229	−0.0487	0.0074	−1.0212	0.0275	1.2402	0.0131
0.0500	0.2000	1.3889	0.1298	−0.3311	0.1004	−0.5612	0.2767	1.4164	0.1349
0.0500	0.2000	1.3759	0.1453	−0.3711	0.1230	−0.5397	0.2960	1.4511	0.1507
0.1000	0.2000	1.3473	0.0128	−0.4039	0.0213	−0.7602	0.0383	1.3416	0.0228
0.1000	0.2000	1.3957	0.0146	−0.3895	0.0190	−0.8072	0.0342	1.3265	0.0208
0.1250	0.2000	1.1240	0.0253	−0.5676	0.0281	−0.6428	0.0457	1.4596	0.0220
0.1250	0.2000	1.1702	0.0302	−0.6071	0.0325	−0.6136	0.0472	1.4965	0.0245
0.2000	0.2000	0.7070	0.0307	−0.8980	0.0394	−0.3369	0.0460	1.6177	0.0314
0.2000	0.2000	0.8092	0.0220	−0.8062	0.0270	−0.4523	0.0340	1.5598	0.0209
0.3000	0.2000	0.7052	0.0493	−0.8562	0.0396	−0.5016	0.0666	1.4498	0.0495
0.4000	0.2000	0.4186	0.0162	−1.1315	0.0097	−0.2092	0.0096	1.6705	0.0049
0.5046	0.1981	0.2140	0.0477	−1.3349	0.0189	0.0924	0.0461	1.8516	0.0258
0.5046	0.1981	0.2948	0.0516	−1.3014	0.0335	0.0442	0.0518	1.8337	0.0366
0.6000	0.2000	0.7157	0.0554	−0.8632	0.0389	−0.2556	0.0525	1.4946	0.0420
0.6000	0.2000	0.8114	0.0401	−0.8655	0.0334	−0.3423	0.0422	1.4966	0.0351
0.6999	0.2000	0.9259	0.0227	−0.6760	0.0242	−0.1404	0.0205	1.5603	0.0163
0.6999	0.2000	0.7949	0.0401	−0.7597	0.0355	−0.0464	0.0353	1.6046	0.0261
0.7500	0.2000	1.4024	0.0141	0.0121	0.0040	−0.2488	0.0114	1.2925	0.0060
0.7500	0.2000	1.1348	0.0268	−0.2928	0.0262	−0.0166	0.0230	1.5073	0.0205

Table 4. Determinant |D| and Eigenvalues D_1 and D_2 in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at $x_2 = 0.050$

x_1	x_2	10^9|D|	10^9D_1/$\mathrm{m^2\cdot s^{-1}}$	10^9D_2/$\mathrm{m^2\cdot s^{-1}}$
0.0500	0.0500	3.1810	1.9135	1.6624
0.0501	0.0497	2.9407	1.9386	1.5169
0.1001	0.0499	2.1979	2.0641	1.0648
0.8498	0.0502	0.9544	1.6391	0.5823
0.8995	0.0518	1.3059	1.5914	0.8206

with a vibrating-tube density meter (Anton Paar GmbH model DAS 48) with a standard deviation of ± $1\cdot10^{-5}$ $\mathrm{g\cdot cm^{-3}}$ and internal temperature control of ± 0.01 K.

Data Evaluation Procedure

The procedure to determine the ternary diffusion coefficients was adopted from Leaist and Hao.[7] To increase the reliability of our data evaluation, we performed four runs with different Δc_i and analyzed the corresponding signal profiles. This procedure results in a model with a large number of parameters. Most of them are specific to the experimental conditions like baseline and amplitudes, and only four of them are the diffusion coefficients. The signal reads

$$S(t) = B_1 + B_2\cdot t + B_3\cdot S_N(t) \tag{7}$$

We reduced the number of parameters as described in part I.[15] Altogether, eight peaks of four different injection samples

Table 5. Determinant |D| and Eigenvalues D_1 and D_2 in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at $x_2 = 0.10$

x_1	x_2	10^9|D|	10^9D_1/$\mathrm{m^2\cdot s^{-1}}$	10^9D_2/$\mathrm{m^2\cdot s^{-1}}$
0.0500	0.1000	2.6076	1.9220	1.3567
0.1000	0.1000	1.8219	1.9439	0.9373
0.1000	0.1000	1.8953	2.0054	0.9451
0.2000	0.1000	0.9065	1.9732	0.4594
0.2000	0.1000	0.9130	1.9715	0.4631
0.3014	0.1002	0.3866	2.0027	0.1931
0.4000	0.1001	0.1862	1.9383	0.0960
0.7498	0.1002	0.7197	1.7238	0.4175
0.8004	0.0999	1.0245	1.6399	0.6248
0.8502	0.0999	1.2690	1.5470	0.8203
0.8753	0.0999	1.4759	1.5886	0.9290

Table 6. Determinant |*D*| and Eigenvalues D_1 and D_2 in the Ternary System Cyclohexane (1) + Toluene (2) + Methanol (3) at $x_2 = 0.20$

x_1	x_2	$10^9\|D\|$	$10^9 D_1/\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_2/\mathrm{m^2 \cdot s^{-1}}$
0.0250	0.2000	2.2470	1.9494	1.1527
0.0250	0.2000	2.3419	1.9944	1.1742
0.0500	0.2000	1.7814	1.8339	0.9714
0.0500	0.2000	1.7963	1.8626	0.9644
0.1000	0.2000	1.5004	1.8985	0.7903
0.1000	0.2000	1.5370	1.9228	0.7993
0.1250	0.2000	1.2757	1.9187	0.6649
0.1250	0.2000	1.3786	1.9651	0.7015
0.2000	0.2000	0.8411	1.8763	0.4483
0.2000	0.2000	0.8976	1.8955	0.4736
0.3000	0.2000	0.5929	1.8312	0.3238
0.4000	0.2000	0.4625	1.8374	0.2517
0.5046	0.1981	0.5195	1.7724	0.2931
0.5046	0.1981	0.5981	1.7954	0.3332
0.6000	0.2000	0.8491	1.7153	0.4950
0.6000	0.2000	0.9181	1.7972	0.5108
0.6999	0.2000	1.3498	1.6853	0.8009
0.6999	0.2000	1.2403	1.6460	0.7535
0.7500	0.2000	1.8155	1.3483	1.3466
0.7500	0.2000	1.7056	1.5199	1.1222

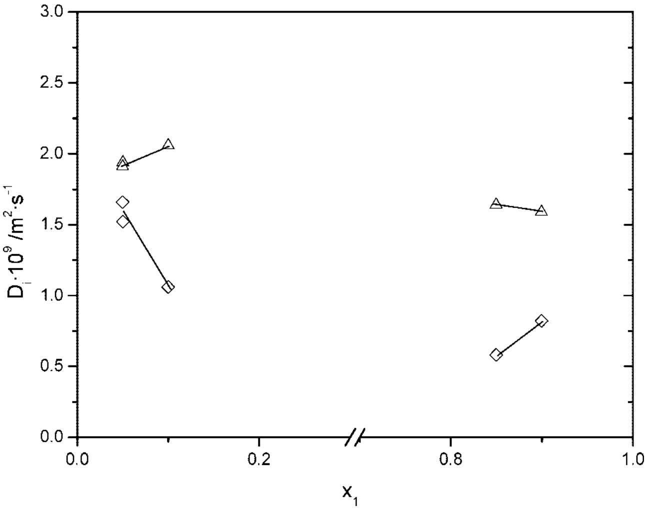

Figure 5. Calculated eigenvalues D_i of the matrix of mutual diffusion coefficients versus mole fraction x_1 of cyclohexane at constant toluene mole fraction $x_2 = 0.050$: △, D_1; ◇, D_2.

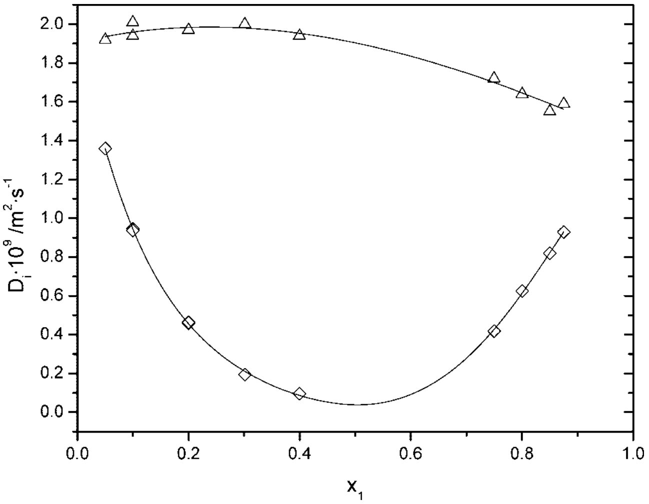

Figure 6. Calculated eigenvalues D_i of the matrix of mutual diffusion coefficients versus mole fraction x_1 of cyclohexane at constant toluene mole fraction $x_2 = 0.10$: △, D_1; ◇, D_2.

were simultaneously fitted to obtain the D_{11}, D_{12}, D_{21}, and D_{22}..

To simulate possible errors during the fitting procedure and the influence of experimental conditions on the final result, 20 data sets were created from each injection and modified by superimposing 1 % artificial Gaussian-distributed noise. Also, the concentrations and the refraction index differences were perturbed by superimposing 1 % and 5 % noise, respectively, on the experimental data. Then, these modified data sets were subject to the same fitting procedure as the original data. The diffusion coefficients, obtained this way, were taken to calculate 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, and binodal curve data at 298.15 K have been published by Nagata.[17] The previous diffusion measurements in the toluene-rich area (part I) are shown as triangles. For the systematic Taylor dispersion measurements, presented here, we selected three sets of experiments along concentrations of constant toluene mole fraction $x_2 = 0.050$, 0.10, and 0.20, respectively. In all cases, the third component methanol is considered to be the reference.

The results of the Taylor dispersion measurements for the three sets are shown in Figures 2 to 4. As described above, the diffusion coefficients 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 Figure 2 for $x_2 = 0.050$, in Figure 3 for $x_2 = 0.10$, and in Figure 4 for $x_2 = 0.20$. The numerical values of D_{ij} together with their standard deviations are given in Tables 1, 2, and 3, respectively.

The corresponding numerical data of the eigenvalues were obtained from the elements of the diffusion coefficient matrix by evaluating eq 4. The resulting data for the three toluene mole fractions and the respective determinants are given in Tables 4, 5, and 6. The eigenvalues are plotted in Figures 5, 6, and 7. Except for the values at $x_2 = 0.050$, their concentration dependency looks much smoother than that of the individual elements of the mutual diffusion coefficient matrix. As discussed in part I,[15] in the limit $x_1 => 0.0$, we approach the binary mixture toluene + methanol where D_{11} becomes the tracer diffusion coefficient of cyclohexane in the binary mixture, whereas D_{22} approaches the mutual diffusion coefficient of the binary system. In the other limit, $x_3 => 0.0$, our choice of methanol as the reference component does not allow a similar interpretation. A comparison of binary mutual diffusion coefficient data of Sanni et al.[18] with those of Thiel[19] reveals rather large differences between both sets.

Figure 8 shows the determinants |*D*| versus cyclohexane mole fraction x_1 of all three concentration sets. The determinant |*D*| shows a continuous decline, when approaching the phase boundary. It ends at the phase boundary for the concentration path $x_2 = 0.050$. For $x_2 = 0.10$, the determinant becomes almost zero when the concentration path is very close to the miscibility gap, and it shows a minimum, less pronounced, for $x_2 = 0.20$. As observed already in part I, it was not difficult to find suitable starting values for the NLSQ fitting procedure in the bulk of the ternary system, but when approaching the binary subsystems, the sensitivity with respect to starting values was much higher. This behavior results in a larger scatter of the data in these concentration regions.

When we compare the macroscopic mutual diffusion coefficient measurements with corresponding DLS experiments of

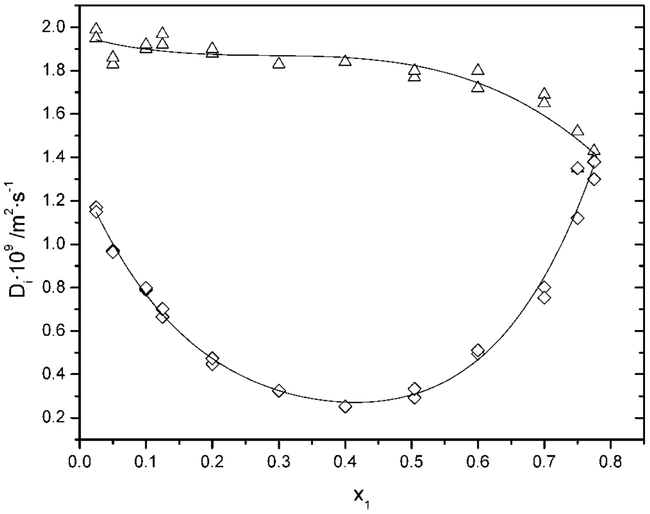

Figure 7. Calculated eigenvalues D_i of the matrix of mutual diffusion coefficients versus mole fraction x_1 of cyclohexane at constant toluene mole fraction $x_2 = 0.20$: △, D_1; ◇, D_2.

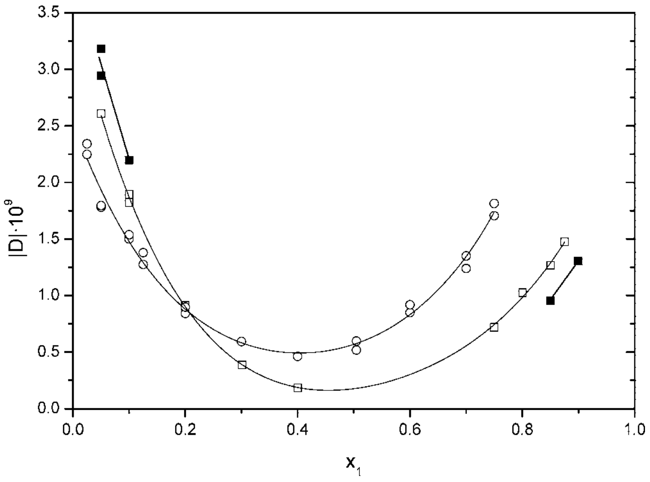

Figure 8. Determinant of the diffusion coefficient matrix versus cyclohexane mole fraction x_1 at constant toluene mole fraction: ■ at $x_2 = 0.050$; □ at $x_2 = 0.10$; ○ at $x_2 = 0.20$.

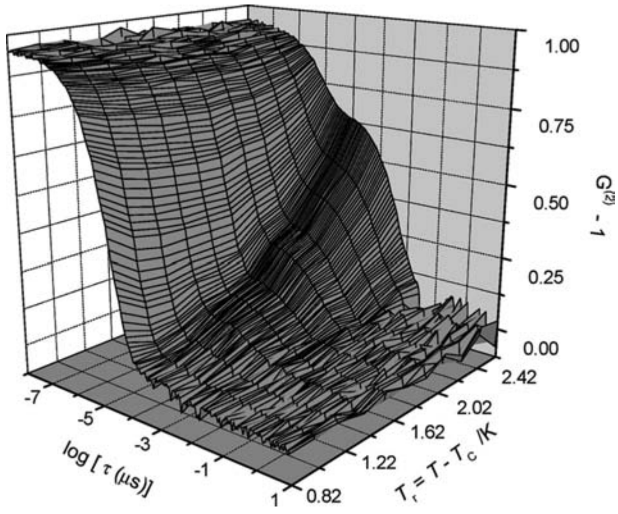

Figure 9. Intensity autocorrelation function versus temperature difference $T_r = T - T_c$ and lag time τ from dynamic light scattering experiments of a near critical concentration in the system cyclohexane (1) + toluene (2) + methanol (3).

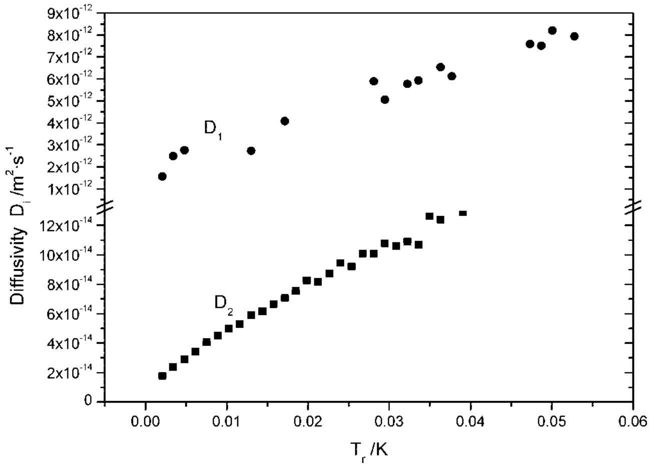

Figure 10. Diffusivities D_i in the system cyclohexane (1) + toluene (2) + methanol (3) as obtained from dynamic light scattering. Thermodiffusion mode D_1 and mass diffusion mode D_2 versus temperature difference $T_r = T - T_c$.

molecular mass transport caused by concentration fluctuations along the phase boundary in the vicinity of the critical solution point, we observed a behavior of the transport processes, very similar to that of the system glycerol + acetone + water.[11,16] In that system, we found that neither one of the four mutual diffusion coefficients was related to the mass diffusion coefficient D_m of the DLS experiment. However, the lowest eigenvalue of the matrix of the macroscopic diffusion coefficients coincides with the mass diffusion coefficient D_m.[20] The other transport mode of the DLS experiment could be identified as thermodiffusion.

We performed similar DLS experiments on the present system to find out whether the existence of two transport modes in DLS measurements could be verified in another ternary mixture. A temperature scan of DLS measurements over a rather large range of $T_r = T - T_c$ revealed that at least two independent transport modes appear in the intensity autocorrelation function (ACF) $G^{(2)}(\tau)$ of the dynamic light scattering, which is the primary experimental information. Figure 9 shows this ACF $G^{(2)}(\tau) - 1$ over a range of $0.8\ \text{K} \leq T_r \leq 2.50\ \text{K}$ with two clearly separated exponentially decaying transport modes. The numerical evaluation of the data resulted in two diffusivities, as shown in Figure 10. Here the fast mode D_1 behaves like thermodiffusion. It tends toward a final value when approaching the critical temperature. The slow mode D_2, however, shows the typical slowing down of a mass diffusion mode. It tends toward zero for decreasing T_r. Unfortunately, we do not yet have measurements in an overlapping concentration region as in the case of the GAW system. So we only conjecture that the mass diffusion mode might coincide with one of the eigenvalues of the Fick diffusion matrix.

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 three concentration paths in direction to the phase boundary at constant toluene concentration in the system cyclohexane + toluene + methanol.

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