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Articles

Ternary Diffusion Coefficients of Glycerol + Acetone + Water by Taylor Dispersion Measurements at 298.15 K. 2. Acetone-Rich Region

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The concentration dependence of the mutual diffusion coefficients in the ternary liquid mixture glycerol + acetone + water is determined at 298.15 K by the Taylor dispersion technique. As a continuation of previous measurements, we selected three concentration paths of a constant water mole fraction of $x_3 = 0.1$, 0.2, and 0.3, respectively, ranging from the limit of the binary subsystem toward the phase boundary in the ternary system. The eigenvalues and the determinant of Fick's diffusion coefficient matrix are given.

Introduction

Diffusion is an important elementary process of mass transport in liquids and of mass transfer through fluid interfaces. Therefore, it is of theoretical and engineering importance to know the diffusion coefficients as a function of concentration and especially their behavior when approaching the phase boundary in multicomponent systems with a liquid−liquid phase separation.

As a fast and simple method, the Taylor dispersion technique is recommended for measurements in binary mixtures,[1−7] and it can be easily extended to investigate diffusion processes in ternary systems.[8−11] The aim of our work was to perform a systematic experimental study of the diffusional transport behavior in a ternary liquid mixture with a miscibility gap. As a model system, we chose mixtures of glycerol + acetone + water. In the first part of our study (hereafter called part 1),[11] we reported Fick's diffusion coefficient matrix at two concentration paths of constant water mole fraction $x_3 = 0.420$ and 0.486, ranging from the binary subsystem toward the phase boundary in the vicinity of the plait point. These measurements were supported by dynamic light scattering (DLS) investigations in the overlapping concentration region close to the critical solution point.[12,13] There we found that DLS measurements give a mass diffusion transport mode that coincides with one of the eigenvalues of Fick's matrix but not with any of the diffusion coefficients itself. This system was previously investigated by Pertler[14] using holographic interferometry. Pertler found that, approaching the phase boundary, the two main elements of the 2 × 2 matrix of Fick's diffusion coefficients should coincide whereas the off-diagonal elements approach zero.

In the present paper (part 2), we continue the systematic study by measuring diffusion coefficients at three different concentration paths in the acetone-rich region. The concentrations are chosen at a constant water mole fraction of $x_3 = 0.1$, 0.2, and 0.3, respectively, ranging from the limit of the binary subsystem toward the phase boundary. The slowing down of the diffusional transport processes is investigated along three paths. This will enable us to investigate mass transport phenomena in a region from the homogeneous phase to areas near or close to the phase boundary.

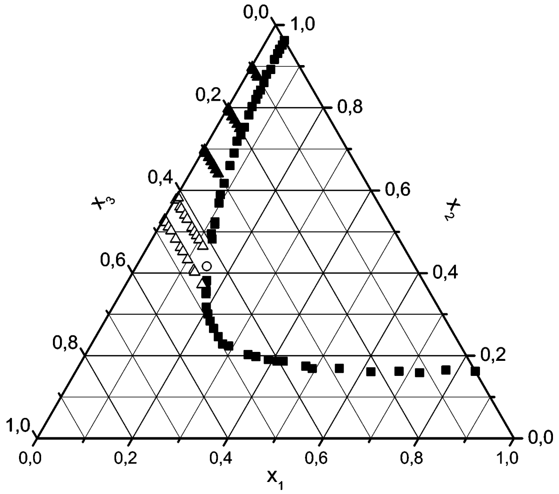

Figure 1. Liquid−liquid phase diagram and concentration path of the diffusion measurements in the system glycerol + acetone + water at 298.15 K: ■, binodal curve; ▲, paths of measurements; △, paths of previous diffusion measurements (part 1); ○, plait point.

Taylor Dispersion Method

In a ternary mixture the diffusion processes are described by a coupled set of Fick's equations:

$$J_1 = -D_{11}\,\mathrm{grad}\,c_1 - D_{12}\,\mathrm{grad}\,c_2$$

$$J_2 = -D_{21}\,\mathrm{grad}\,c_1 - D_{22}\,\mathrm{grad}\,c_2 \qquad (1)$$

where J_i is the molar flux of component i in the volume-fixed frame of reference. To perform a diffusion experiment, a small sample of composition ($c_1 + \Delta c_1$, $c_2 + \Delta c_2$) is injected into a

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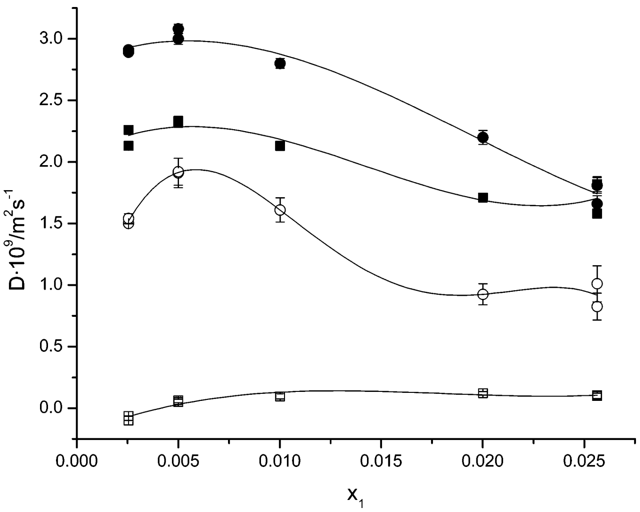

Figure 2. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.1$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

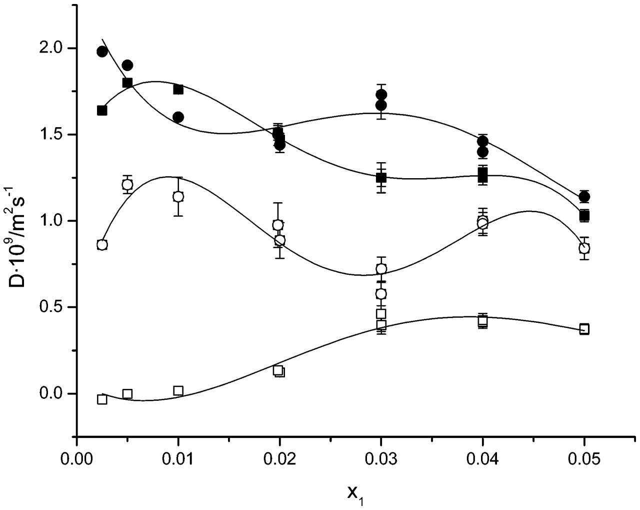

Figure 3. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.2$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

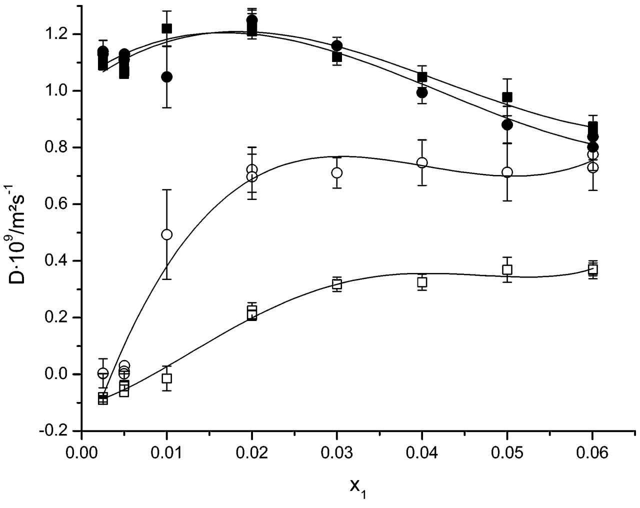

Figure 4. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.3$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

laminar flow of a carrier with constant composition (c_1, c_2). From the corresponding fluxes J_1 and J_2 in a laminar flow, two overlapping profiles were formed from which the diffusion coefficients can be extracted. After introducing a normalized peak signal $S_N(t)$ according to Leaist,[10] we obtainwith the W_i

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

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

$$W_1 = \left[\left(D_{22} - \frac{R_2}{R_1} \cdot D_{21} \right) \alpha_1 + \left(D_{11} - \frac{R_1}{R_2} D_{12} \right)(1 - \alpha_1) - D_1 \right] \sqrt{D_1} \quad (3)$$

$$W_2 = -\left[\left(D_{22} - \frac{R_2}{R_1} D_{21} \right) \alpha_1 + \left(D_{11} - \frac{R_1}{R_2} D_{12} \right)(1 - \alpha_1) - D_2 \right] \sqrt{D_2} \quad (4)$$

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

$$D_{1,2} = \frac{1}{2} \left[D_{11} + D_{22} \pm (D_{11} - D_{22}) \sqrt{1 + \frac{4D_{12}D_{21}}{(D_{11} - D_{22})^2}} \right] \quad (5)$$

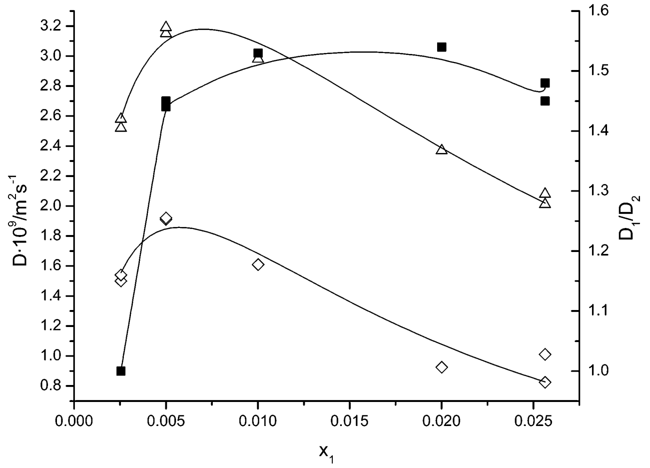

Figure 5. Calculated eigenvalues of the diffusion coefficient matrix (△, D_1; ◇, D_2) and their ratio (■, D_1/D_2) at $x_3 = 0.1$.

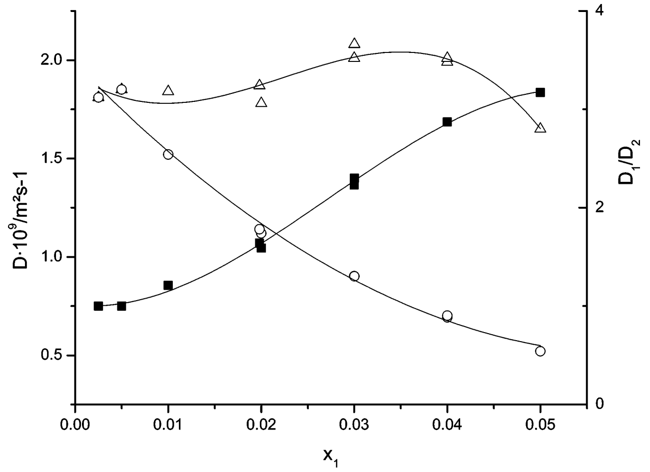

Figure 6. Calculated eigenvalues of the diffusion coefficient matrix (△, D_1; ◇, D_2) and their ratio (■, D_1/D_2) at $x_3 = 0.2$.

Table 1. Diffusion Coefficients and Standard Deviations of the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K at Constant Water Content $x_3 = 0.1$

x_1	x_2	$10^9 D_{11}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{12}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{21}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{22}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$
0.0025	0.8974	2.2632	0.0148	−0.0635	0.0020	1.5449	0.0393	2.8898	0.0042
0.0025	0.8974	2.1333	0.0009	−0.1008	0.0001	1.4961	0.0018	2.9099	0.0005
0.0050	0.8950	2.3166	0.0395	0.0629	0.0182	1.9136	0.1190	3.0040	0.0460
0.0050	0.8950	2.3296	0.0401	0.0512	0.0197	1.9187	0.1091	3.0777	0.0385
0.0100	0.8900	2.1267	0.0350	0.0962	0.0208	1.6109	0.0973	2.8022	0.0393
0.0200	0.8799	1.7057	0.0244	0.1211	0.0150	0.9246	0.0850	2.2010	0.0564
0.0256	0.8742	1.5833	0.0382	0.1001	0.0224	0.8252	0.1090	1.8140	0.0628
0.0256	0.8742	1.8237	0.0605	0.1057	0.0299	1.0066	0.1467	1.6605	0.0637

Table 2. Diffusion Coefficients and Standard Deviations of the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K at Constant Water Content $x_3 = 0.2$

x_1	x_2	$10^9 D_{11}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{12}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{21}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{22}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$
0.0025	0.7975	1.6387	0.0000	−0.0329	0.0000	0.8606	0.0000	1.9754	0.0000
0.0050	0.7949	1.8031	0.0100	−0.0020	0.0004	1.2091	0.0528	1.9017	0.0028
0.0100	0.7900	1.7552	0.0163	0.0173	0.0094	1.1434	0.1133	1.5990	0.0172
0.0198	0.7782	1.5078	0.0424	0.1364	0.0234	0.9751	0.1293	1.4961	0.0626
0.0200	0.7800	1.4679	0.0362	0.1231	0.0210	0.8874	0.1034	1.4369	0.0438
0.0300	0.7700	1.2406	0.0466	0.3121	0.0407	0.7231	0.0926	1.5260	0.0617
0.0400	0.7600	1.2803	0.0421	0.4149	0.0366	1.0047	0.0718	1.4004	0.0396
0.0400	0.7600	1.2504	0.0424	0.4251	0.0395	0.9820	0.0671	1.4624	0.0405
0.0500	0.7499	1.0299	0.0347	0.3742	0.0311	0.8415	0.0643	1.1380	0.0347

Table 3. Diffusion Coefficients and Standard Deviations of the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K at Constant Water Content $x_3 = 0.3$

x_1	x_2	$10^9 D_{11}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{12}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{21}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 D_{22}$ / $\mathrm{m^2 \cdot s^{-1}}$	$10^9 \sigma$ / $\mathrm{m^2 \cdot s^{-1}}$
0.0025	0.6975	1.1118	0.0005	−0.0807	0.0019	0.0024	0.0004	1.1397	0.0033
0.0025	0.6975	1.0905	0.0154	−0.0911	0.0063	0.0036	0.0511	1.1268	0.0489
0.0050	0.6946	1.0903	0.0000	−0.0427	0.0000	0.0022	0.0000	1.1095	0.0000
0.0050	0.6946	1.0588	0.0000	−0.0634	0.0000	0.0102	0.0000	1.1096	0.0000
0.0050	0.6946	1.0661	0.0000	−0.0380	0.0000	0.0302	0.0000	1.1339	0.0000
0.0100	0.6900	1.2240	0.0631	−0.0149	0.0432	0.4934	0.1578	1.0523	0.1088
0.0200	0.6800	1.2385	0.0333	0.2254	0.0281	0.7221	0.0791	1.2499	0.0414
0.0200	0.6800	1.2088	0.0258	0.2086	0.0183	0.6967	0.0797	1.2454	0.0351
0.0300	0.6700	1.1158	0.0290	0.3181	0.0250	0.7112	0.0534	1.1623	0.0298
0.0400	0.6600	1.0538	0.0387	0.3252	0.0286	0.7472	0.0805	0.9938	0.0391
0.0500	0.6500	0.9776	0.0648	0.3695	0.0440	0.7131	0.1011	0.8813	0.0648
0.0601	0.6399	0.8723	0.0414	0.3695	0.0324	0.7288	0.0807	0.8021	0.0449
0.0601	0.6399	0.8625	0.0272	0.3707	0.0226	0.7763	0.0574	0.8382	0.0322

and the parameter α_1 is given by

$$\alpha_1 = \frac{R_1 \Delta c_1}{R_1 \Delta c_1 + R_2 \Delta c_2} \tag{6}$$

The R_i are the concentration derivatives of the refractive index at the carrier composition.[11]

Experimental Section

For our measurements the following substances were used: acetone (ECD tested) with a purity of 99.9 % and a water content < 0.2 % and glycerol (ACS reagent) with a purity of 99.5 and a water content < 0.5 %, both from ACROS-ORGANICS (Fischer Scientific GmbH Schwerte Germany). The chemicals were applied without further purification. The water was deionized and distilled.

The experimental setup is identically the same as described in ref 11. In all Taylor dispersion experiments the carrier flow velocity was 4 mL·h^{-1}, and the capillary had a length of 11.50 m with an effective radius of 260.65 μm. As a detecting unit, a differential refractometer with a baseline noise of $2 \cdot 10^{-8}$ RUI was applied. Both the detector and capillary were kept at a constant temperature of (298.15 ± 0.1) K. The refractometer signal was recorded at time intervals of 1 s with 1000 to 2000 data points taken into account to characterize one peak.

The densities of the solution were measured with a vibrating-tube density meter (Anton Paar DAS 48) with a standard deviation of $1 \cdot 10^{-5}$ g·cm^{-3} and temperature control of ± 0.01 K. To prepare solutions for the measurement of diffusion coefficients, an analytical balance was used that allows mass determination accurate to ± 0.00001 g.

The experimental procedure follows the same path as described in ref 11. Altogether eight peaks of four different injected samples were fitted simultaneously by a Marquardt−Levenberg nonlinear least-squares regression method to obtain the D_{11}, D_{12}, D_{21}, and D_{22} values.

Results and Discussion

Experimental data in the range between the subsystem acetone + water at one end and the phase boundary at the other end of the concentration path could not be found in literature to proof and to compare our results. Only Pertler[14] published some diffusion coefficients on the acetone-rich side of the ternary system. Figure 1 presents the liquid−liquid phase diagram, where the binodal curve at 298.15 K together with the plait point is shown. Krishna et al.[15] determined the plait point at

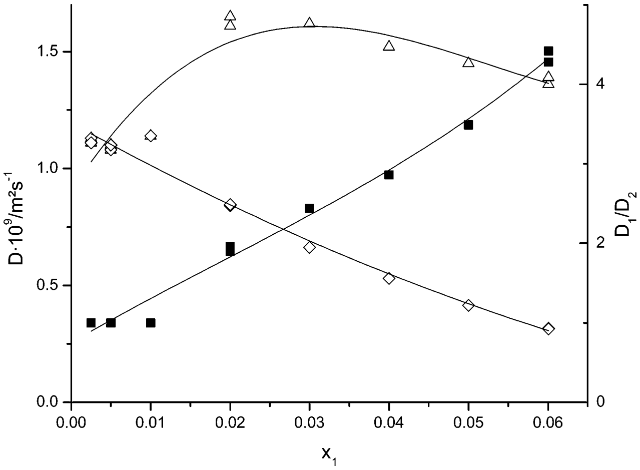

Figure 7. Calculated eigenvalues of the diffusion coefficient matrix (△, D_1; ◇, D_2) and their ratio (■, D_1/D_2) at $x_3 = 0.3$

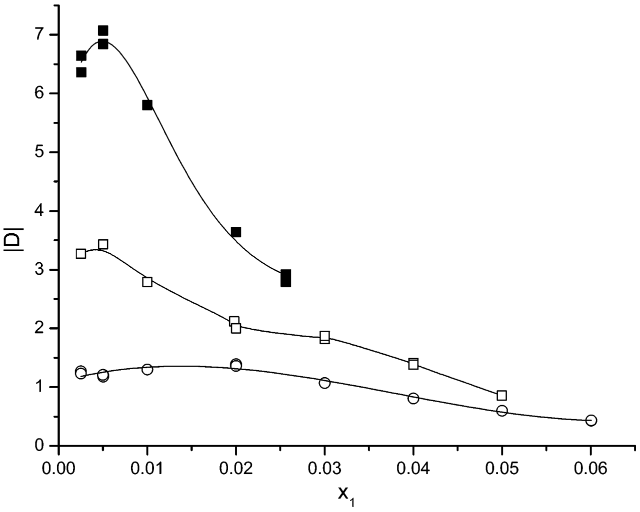

Figure 8. Determinant of the diffusion coefficient matrix: ■, at $x_3 = 0.1$; □, at $x_3 = 0.2$; ○, at $x_3 = 0.3$.

298.15 K to be found at $x_1 = 0.1477$, $x_2 = 0.4163$, and $x_3 = 0.4360$. In part 1, we measured two concentration paths at constant water content of $x_3 = 0.420$ and 0.468, which were on both sides of the plait point concentration and rather close to it. These concentration paths are shown in Figure 1 together with the present data. In our present Taylor dispersion measurements (part 2), we selected three sets with constant water content of $x_3 = 0.1$, 0.2, and 0.3, beginning at the binary subsystem and ending at the phase boundary.

The results of the Taylor dispersion measurements for the three concentration sets are shown in Figures 2 to 4. The four diffusion coefficients D_{ij} of Fick's matrix were obtained by direct fitting of eq 2 together with eqs 3 and 4 to our experimental data pool. The corresponding eigenvalues D_1 and D_2 are derived from these D_{ij} values according to eq 5. Figure 2 presents D_{ij} at a water content of $x_3 = 0.10$. We found that both main values D_{11} and D_{22} differ at low glycerol concentrations and seem to coincide close to the phase boundary. When approaching the limit of the binary subsystem at $x_1 = 0.0$ the cross coefficients tend toward zero. On the other side of the concentration path, which ends in the phase boundary, the main diffusion coefficients decrease but they still differ considerably. This trend continues for the other two sets with $x_3 = 0.20$ (Figure 3) and $x_3 = 0.30$ (Figure 4). The main diffusion coefficients become smaller and their curves approach each other and seem very close at $x_3 = 0.3$ for all three sets. Only at $x_3 = 0.30$ (Figure 4), we found that they approach zero at the limit of the binary subsystem. At the phase boundary, the differences remain large and come down to zero only in the vicinity of the critical solution point, as shown in part 1.

Table 4. Determinant |*D*| and Eigenvalues D_1 and D_2 for the Concentration Path at $x_3 = 0.1$

x_1	x_2	$10^9 \lvert D \rvert$	$\frac{10^9 D_1}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_2}{m^2 \cdot s^{-1}}$
0.0025	0.8974	6.6384	2.5792	2.5738
0.0025	0.8974	6.3583	2.5245	2.5187
0.0050	0.8950	6.8385	3.1487	2.1719
0.0050	0.8950	7.0714	3.1917	2.2155
0.0100	0.8900	5.8045	2.9831	1.9458
0.0200	0.8799	3.6421	2.3696	1.5370
0.0256	0.8742	2.7894	2.0082	1.3890
0.0256	0.8742	2.9218	2.0783	1.4059

Table 5. Determinant |*D*| and Eigenvalues D_1 and D_2 for the Concentration Path at $x_3 = 0.2$

x_1	x_2	$10^9 \lvert D \rvert$	$\frac{10^9 D_1}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_2}{m^2 \cdot s^{-1}}$
0.0025	0.7975	3.2655	1.8087	1.8054
0.0050	0.7949	3.4315	1.8534	1.8515
0.0100	0.7900	2.7868	1.8382	1.5161
0.0198	0.7782	2.1229	1.8667	1.1373
0.0200	0.7800	2.0000	1.7832	1.1216
0.0300	0.7700	1.6674	1.8793	0.8872
0.0400	0.7600	1.3761	1.9888	0.6919
0.0400	0.7600	1.4112	2.0111	0.7017
0.0500	0.7499	0.8572	1.6477	0.5202

Table 6. Determinant |*D*| and Eigenvalues D_1 and D_2 for the Concentration Path at $x_3 = 0.3$

			$10^9 D_1$	$10^9 D_2$
0.0025	0.6975	1.2673	1.1262	1.1253
0.0025	0.6975	1.2292	1.1091	1.1082
0.0050	0.6946	1.2098	1.1002	1.0996
0.0050	0.6946	1.1755	1.0847	1.0837
0.0050	0.6946	1.2100	1.1006	1.0994
0.0100	0.6900	1.2954	1.1391	1.1372
0.0200	0.6800	1.3853	1.6477	0.8408
0.0200	0.6800	1.3602	1.6087	0.8455
0.0300	0.6700	1.0707	1.6152	0.6629
0.0400	0.6600	0.8043	1.5177	0.5300
0.0500	0.6500	0.5981	1.4450	0.4139
0.0601	0.6399	0.4304	1.3573	0.3171
0.0601	0.6399	0.4351	1.3869	0.3137

According to the results of Pertler,[14] we should expect that at the phase boundary we will find only a single diffusion coefficient because of the beginning of a cluster formation. But from our data there is no clear sign for a collapse of both main diffusion coefficients into one single point. Probably the expected behavior is only observed very close to the phase boundary or in the metastable area between the binodal and spinodal curve.

To obtain information on possible errors during the fitting procedure and on the influence of different experimental quantities on the final result, 20 data sets were created from each injection and modified by superimposing 1 % artificial Gaussian-distributed noise. Both the concentrations and the refraction index differences were corrupted with 1 % and 5 % noise, too. Then the resulting data sets were subject to the same fitting procedure as the original ones. The diffusion coefficients, obtained this way, were the source to calculate the respective standard deviation σ of the experimental data. The numerical values of these diffusion coefficients together with their standard deviations are given in Tables 1 to 3, respectively.

The corresponding numerical data of the eigenvalues for both concentration paths and the respective determinants are given in Tables 4 to 6. The diffusion coefficients scatter much more then both the eigenvalues D_1 and D_2 and the determinant. The smooth graphs in Figures 5 to 7 imply that one could use these data for a critical evaluation and for a consistency test of experimental results. Especially the measurements at $x_3 = 0.2$, which gave rather scattered diffusion coefficients (see Figure 3) resulted in smooth graphs of the eigenvalues and determinant in Figure 6. As shown in Figure 8, for all three concentration paths the determinants decline continuously when approaching the phase boundary.

Conclusions

In a systematic study of the mass transport behavior in ternary liquid mixtures with a liquid−liquid phase separation Taylor dispersion measurements of Fick's diffusion coefficients were performed along three concentration paths in direction to the phase boundary at constant water concentration in the system glycerol + acetone + water. Thus, we provide diffusion coefficient data in regions of engineering interest.

Because of the strong nonlinear refractive index concentration dependency of the binary system water + acetone, the accuracy of the estimated diffusion coefficients is not always satisfactory. The eigenvalues and the determinant of the matrix of diffusion coefficients seem to be much less influenced by the optical properties of the system. They show rather smooth and continuous trends in their dependency on concentration. Therefore, they can be used for a critical evaluation of experimental measurements and to test for their internal consistency.

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