1396 *J. Chem. Eng. Data* **2005,** *50,* 1396−1403

Ternary Diffusion Coefficients of Glycerol + Acetone + Water by Taylor Dispersion Measurements at 298.15 K

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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 along two concentration paths of constant water mole fractions of 0.468 and 0.420, ranging from the binary subsystem toward the phase boundary in the vicinity of the critical solution point. The eigenvalues of Fick's diffusion coefficient matrix are given, and the influence of the optical properties of the system on the diffusion coefficient determination is discussed. It was found that the determinant $|D|$ continuously declines on approaching the phase boundary.

Introduction

Diffusion is an important elementary process of mass transport in liquids and of mass transfer through fluid interfaces (e.g., in living cells and in technical extraction processes). Therefore, it is necessary 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.

To investigate diffusion phenomena, different experimental methods are established: diaphragm cell,[1−5] conductometric,[6,7] and optical[8−12] (e.g., Gouy, Rayleigh, and holographic interferometry and also dynamic light scattering for the measurement of mutual diffusion coefficients[13−15]).

As a fast and simple method, the Taylor dispersion technique is well established in the case of binary mixtures of organic compounds and of electrolyte solutions.[16−24] With this method, it is also possible to investigate diffusion processes in ternary systems.[25−28] The fact, however, that in organic liquid systems one experimentally measurable quantity has to be used to extract two eigenvalues or four elements of Fick's diffusion coefficient matrix demonstrates the considerably higher complexity of the ternary diffusion problem, and as a consequence, publications of ternary diffusion coefficients are rather rare.

The aim of our work was to study the behavior of the diffusion coefficients in a ternary liquid mixture with a miscibility gap depending on the distance from the phase boundary and in the vicinity of the critical solution point. As a model system, we chose mixtures of glycerol + acetone + water. This system was previously investigated by Pertler[33] and Rutten.[39] In his holographic interferometry measurements, 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. We decided to perform dynamic light scattering (DLS) measurements in the vicinity of the critical solution point,[29] and we found different transport modes. To identify the character of these transport processes, we want to compare the DLS results with measurements of the classical Fick's diffusion matrix.

The critical slowing down of the diffusional transport processes is investigated with respect to the dependency of the concentration along two paths of constant water content where water is considered to be the solvent. The two concentration paths were chosen in connection with the DLS experiments. Because of the high scattering intensities near the critical solution point of such a ternary system, overlapping areas exist in which both methods—the Taylor dispersion technique and DLS—can be applied. This will enable us to investigate mass transport phenomena in a crossover region from the homogeneous phase to areas near or close to the phase boundary.[29]

Because ternary diffusion data from the literature are rather scarce and experimental uncertainties are much higher than in the binary case, we performed systematic diffusion measurements along two different concentration paths from the binary subsystem to the phase boundary. The eigenvalues of Fick's matrix and the respective determinants were calculated to check the quality and internal consistency of the experimental data.

Taylor Dispersion Method

When describing mass transport, Fick[30] found the following relation for the diffusion process between two components

$$J = -D(\text{grad } c) \tag{1}$$

where J is the molar flux, grad c is the concentration gradient, and D is the diffusion coefficient.

In the case of a ternary mixture, this single relation transforms into a system of two coupled mass fluxes, assuming the third component to be the solvent. The Taylor dispersion method is a rapid and simple technique used to determine mutual diffusion coefficients. A small volume of sample solution is injected into the laminar flow of a carrier stream of the same mixture 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.,

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10.1021/je050082c CCC: $30.25

differential refractometer, UV detector, conductometer, or other suitable flow-through detectors) monitors the change in concentration. The injected square pulse develops into a parabolic velocity profile, and the radial concentration gradient causes radial diffusion that changes the rectangular pulse shape into a Gaussian concentration profile.

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

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.

In the case of binary mixtures, a differential equation results that was solved by Taylor[17] with some simplifying assumptions to describe the mass balance

$$\frac{\partial c_i}{\partial t} = K\frac{\partial^2 c_i}{\partial z^2} \tag{3}$$

with a transformed length coordinate z and the dispersion coefficient K as

$$K = \frac{\bar{u}^2 R^2}{48D} \tag{4}$$

$$z = x - \bar{u}t \tag{5}$$

where D is the mutual diffusion coefficient.

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

$$J_1 = -D_{11}(\text{grad } c_1) - D_{12}(\text{grad } c_2)$$
$$J_2 = -D_{21}(\text{grad } c_1) - D_{22}(\text{grad } c_2)$$

where J_i is the molar flux of component i in the volume fixed frame of reference. To obtain the four diffusion coefficients D_{ik}, Price[25] solved the corresponding differential equation (eq 6) for a ternary mixture

$$\frac{\partial c_i}{\partial t} = \sum_{k=1}^{2} K_{ik}\frac{\partial^2 c_k}{\partial z^2} \tag{6}$$

with dispersion coefficients

$$K_{ii} = \frac{\bar{u}^2 R^2}{48}\frac{D_{kk}}{D_{ii}D_{kk} - D_{ik}D_{ki}} \tag{7}$$

$$K_{ik} = -\frac{\bar{u}^2 R^2}{48}\frac{D_{ik}}{D_{ii}D_{kk} - D_{ik}D_{ki}} \tag{8}$$

Here D_{kk} denotes the main and D_{ik} denotes the corresponding cross diffusion coefficients.

Solving the respective differential equations for the binary and for the ternary case leads to the final working equations that can be used to estimate the diffusion coefficients from the detector signal vs flow-time curve.

In the case of a binary mixture, the detector signal $S(t)$ is described by

$$S(t) = B_1 + B_2 t + B_3\frac{\sqrt{D}}{\sqrt{t}}\exp\left[-\frac{12D}{R^2}\frac{(t_R - t)^2}{t}\right] \tag{9}$$

where S denotes the detector output signal, t is the time, t_R is the retention time, and R is the inner radius of the capillary. B_1 and B_2 are baseline parameters. The peak height B_3 at t_R is given by

$$B_3 = \gamma\frac{2\sqrt{3}h}{\bar{u}R\sqrt{\pi}}$$
$$t_R = \frac{L}{\bar{u}} \tag{10}$$

where L is the length of the capillary, h is the length of the injected sample, and γ is the detector sensitivity.

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 where the diffusion coefficients can be extracted. After introducing a normalized peak signal $S_N(t)$ according to Leaist,[27] we obtain

$$S_N(t) = \sqrt{\frac{t_R}{t}}\sum_{i=1}^{2}\left[\frac{W_i}{W_1 + W_2}\exp\left(-\frac{12D_i}{R^2}\frac{(t - t_R)^2}{t}\right)\right] \tag{11}$$

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

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

$$W_2 = -\left[\left(D_{22} - \frac{R_2}{R_1}D_{21}\right)\alpha_1 + \left(D_{11} - \frac{R_1}{R_2}D_{12}\right)(1 - \alpha_1) - D_2\right]\sqrt{D_2} \tag{13}$$

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

$$D_1 = \frac{1}{2}\left[D_{11} + D_{22} + (D_{11} - D_{22})\sqrt{1 + \frac{4D_{12}D_{21}}{(D_{11} - D_{22})^2}}\right] \tag{14}$$

$$D_2 = \frac{1}{2}\left[D_{11} + D_{22} - (D_{11} - D_{22})\sqrt{1 + \frac{4D_{12}D_{21}}{(D_{11} - D_{22})^2}}\right] \tag{15}$$

and the parameter α_1 is given by

$$\alpha_1 = \frac{R_1\Delta c_1}{R_1\Delta c_1 + R_2\Delta c_2} \tag{16}$$

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

$$\Delta n = R_1\Delta c_1 + R_2\Delta c_2 \tag{17}$$

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

Finally, the following working equation results

$$S(t) = B_1 + B_2 t + B_3 S_N(t) \tag{18}$$

where $S(t)$ denotes the detector signal, B_1 and B_2 are the

Table 1. Diffusion Coefficients and Standard Deviations of Binary Mixtures of Glycerol (1) + Water (3), Acetone (2) + Water (3), and Glycerol (1) + Acetone (2) at 298.15 K

glycerol (1) + water (3)			acetone (2) + water (3)			glycerol (1) + acetone (2)		
x_1	10^9D/m^2 s^{-1}	$10^9\sigma$ /m^2 s^{-1}	x_2	10^9D/m^2 s^{-1}	$10^9\sigma$/m^2 s^{-1}	x_1	10^9D/m^2 s^{-1}	$10^9\sigma$/m^2 s^{-1}
0.0005	0.8684	0.0013	0.0018	1.2940	0.0047	0.0039	2.3726	0.0322
0.0007	0.8648	0.0010	0.0018	1.2384	0.0024	0.0107	2.1833	0.0612
0.0493	0.6501	0.0008	0.0041	1.2060	0.0013	0.0198	1.9229	0.0245
0.0509	0.6499	0.0011	0.0043	1.2259	0.0013	0.0286	1.5458	0.0099
0.0986	0.5129	0.0006	0.0045	1.2132	0.0010			
0.1012	0.4964	0.0007	0.0979	0.7544	0.0011			
0.1974	0.2981	0.0008	0.1061	0.7566	0.0007			
0.2018	0.2982	0.0015	0.2916	0.5956	0.0008			
0.2930	0.1602	0.0009	0.3068	0.5956	0.0011			
0.2930	0.1602	0.0008	0.4818	0.6152	0.0081			
0.3046	0.1509	0.0010	0.5161	0.8943	0.0021			
0.3894	0.0966	0.0004	0.5234	0.9048	0.0021			
0.3894	0.0959	0.0003	0.5375	0.9380	0.0023			
			0.6695	1.5651	0.0035			
			0.6698	1.6316	0.0050			
			0.7099	1.7530	0.0024			
			0.8547	3.4159	0.0182			
			0.9774	4.6505	0.0255			

baseline parameters, B_3 is the peak height relative to the baseline, and S_N is the normalized detector signal as given by eq 11.

Experimental Section

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

In all Taylor dispersion experiments, the flow velocity of the carrier, 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. As the detector, we used a differential refractometer (Wissenschaftlicher Gerätebau, Dr. Ing. Herbert Knauer, GmbH) with a baseline noise of 2×10^{-8} RUI. The detector and the capillary were kept at a constant temperature of (298.15 ± 0.1) K. The refractometer signal was recorded at a time intervals of 1 s. The instrumental setup is analogous to the apparatus described in ref 31. About 1000 to 2000 data points were taken into account to characterize 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 1×10^{-5} g cm^{-3} and temperature control of ±0.01 K. For the determination of the refractive index differences, a differential refractometer (Shimadzu Corporation model RID 10A) with a baseline noise of 0.25×10^{-8} RUI was used. To prepare the solutions for the diffusion, density, and refractive index measurements, an analytical balance was used that allows mass determination accurate to ±0.00001 g.

The procedure to determine the ternary diffusion coefficients was derived from Leaist.[28] 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 and also the starting values for t_R and B_3 were calculated in this peak separation. Altogether, eight peaks of four different injection samples were fitted simultaneously with the fitting parameters D_{11}, D_{12}, D_{21}, and D_{22}, retention time t_R, and peak height B_3. Furthermore, the concentration derivatives of refractive indexes R_1 and R_2 were determined after measuring the refractive index differences with a differential refractometer and the densities with a density meter. As the nonlinear least-squares regression method, we applied the Marquardt−Levenberg algorithm derived from ref 32. From the uncertainties in temperature and composition and from an estimated uncertainty in the refractive index determination of 5×10^{-5}, we find an overall uncertainty in the diffusion coefficients of 1.6%.

Results and Discussion

Binary Systems. In a systematic investigation of the transport behavior in ternary systems, we had performed measurements of mutual diffusion coefficients in the binary subsytems glycerol + water, glycerol + acetone, and water + acetone. To calculate the diffusion coefficients of binary mixtures, the parameters were obtained by fitting eq 9 to the detector output signal $S(t)$ using a Marquardt−Levenberg algorithm. We find the parameters B_1, B_2 and B_3, the retention time t_R, and the mutual diffusion coefficient D. Two injections with different concentrations were applied four times at one respective carrier concentration. The results of our diffusion measurements in the three binary subsystems are represented in Table 1, where the mutual diffusion coefficients and their respective standard deviations are given.

Mutual diffusion coefficients of glycerol + acetone mixtures were measured by Pertler[33] by holographic interferometry. These values should be of higher accuracy than the Taylor measured coefficients. Data of holographic interferometry are available for the glycerol + water system by Ternstroem et al.[34] and also coefficients from Nishijima et al.[35] measured by an interferometric microdiffusion method. Garner et al.[36] and Marinin et al.[37] used a Jamin-type interferometer and a polarization interferometric method, respectively. In Figure 1, we compare our experimental results for two subsystems with these literature data. In the subsystem glycerol + acetone, where only a small homogeneous area is available for measurements, our results agree very well with those of Pertler.[33] In the subsystem glycerol + water, our data are in good agreement with those of refs 35 and 36, whereas values published in refs 34 and 37 show larger deviations. Results for the subsystem water + acetone are shown in Figure 2 in good agreement with data obtained some years ago in our laboratory by Taylor dispersion[31] and with values measured by Tyn et al.[38] using a diaphragm-cell method.

Ternary System Glycerol (1) + Acetone (2) + Water (3). Experimental data in the range between the subsystem

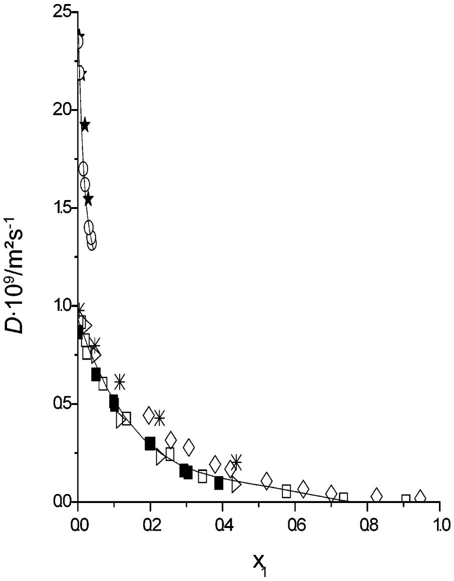

Figure 1. Mutual diffusion coefficients in the binary subsystems glycerol (1) + water: *,[34] right-facing triangle,[35] □,[36] ◇,[37] ■, this work; glycerol (1) + acetone: ★, this work, ○,[33] (limited by the phase boundary).

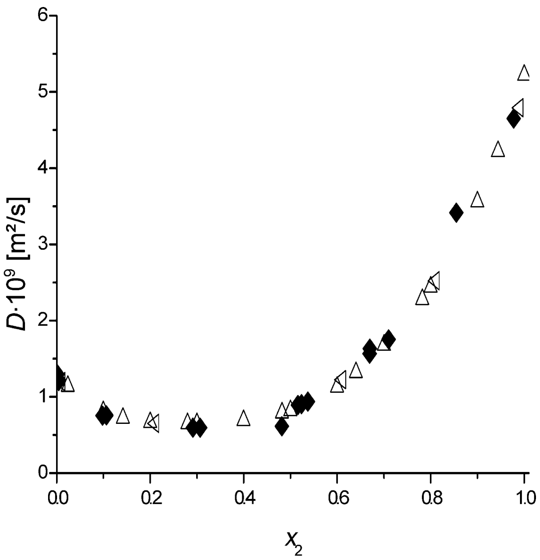

Figure 2. Mutual diffusion coefficients in the binary subsystem water + acetone (2): ♦, this work, left-facing triangle,[31] △.[38]

acetone + water and the phase boundary could not be found in the literature to prove and compare our results. Only Pertler[33] and Rutten[39] published some diffusion coefficients on the acetone-rich side and the water-rich side, respectively, of the ternary system. Figure 3 shows the liquid−liquid phase diagram. The binodal curve at 298.15 K together with the plait point is given. Krishna et al.[40] determined the plait point at 298.15 K to be at $x_1 = 0.1477$, $x_2 = 0.4163$, and $x_3 = 0.4360$. For the Taylor dispersion measurements, we selected two sets with constant water content on both sides of the plait point. In Figure 3, we show the concentration paths of the sets of measurements with $x_3 = 0.420$ and 0.468, beginning at the binary subsystem and ending at the phase boundary in the close vicinity of the plait point.

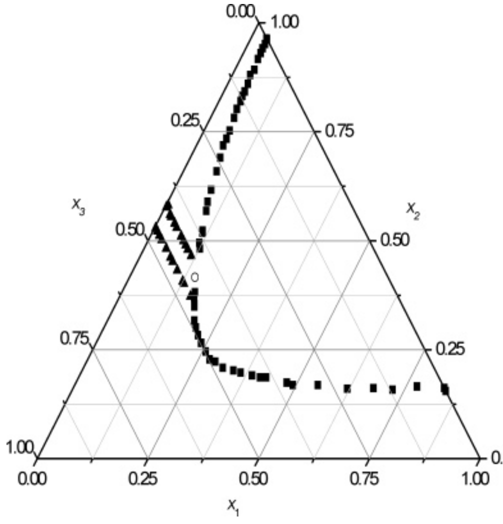

Figure 3. Liquid−liquid phase diagram and concentration paths of the diffusion measurements in the system glycerol (1) + acetone (2) + water (3) at 298.15 K: ■, binodal curve; ▲, paths of measurements; ○, plait point.

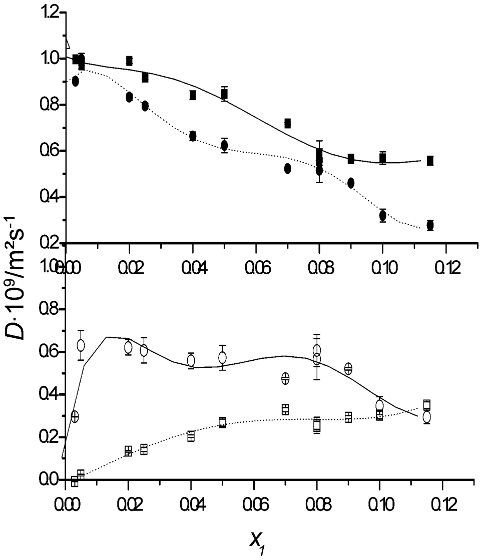

Figure 4. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.4200$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.The Δ shows D of the binary subsystem acetone−water.

The results of the Taylor dispersion measurements for the two sets are shown in Figures 4 and 5. In both cases, the right-hand side of the diagram represents the phase boundary of the ternary system. When approaching the limit of the binary subsystem, the cross diffusion coefficients go toward zero, whereas the main coefficients seem to reach the limit of the binary diffusion coefficient. On the other end of the concentration path, which ends in the phase boundary near the critical solution point, the main diffusion coefficients decrease, but they still differ considerably. According to the results of Pertler,[33] we expected that at the phase boundary we will find only a single coefficient because of the beginning of cluster formation, but from our data, there is no sign of a collapse of both main diffusion coefficients into a single point. Probably the expected behavior is only realized 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, 50 data sets were created from each injection and modified by superimposing 1% artificial Gaussian-distributed noise.[32] Then, the peak profiles with the artificial noise were subjected to the same fitting procedure as the original profiles. The diffusion

Table 2. Diffusion Coefficients and Standard Deviations (Calculated by Adding 1% Artificial Noise to the Detector Signal) of the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K with $x_3 = 0.42$

x_1	x_2	$10^9 D_{11}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{12}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{21}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{22}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$
0.0030	0.5770	0.9977	0.0404	−0.0077	0.0093	0.2962	0.1511	0.9022	0.1456
0.0049	0.5819	0.9703	0.0096	0.0221	0.0043	0.6299	0.0945	0.9978	0.0421
0.0200	0.5600	0.9904	0.0031	0.1348	0.0012	0.6213	0.0094	0.8335	0.0037
0.0250	0.5550	0.9181	0.0020	0.1423	0.0003	0.6070	0.0074	0.7948	0.0013
0.0400	0.5400	0.8423	0.0017	0.2047	0.0012	0.5579	0.0049	0.6639	0.0032
0.0500	0.5300	0.8465	0.0019	0.2684	0.0012	0.5725	0.0050	0.6238	0.0029
0.0700	0.5100	0.7181	0.0006	0.3289	0.0003	0.4751	0.0011	0.5238	0.0007
0.0800	0.5000	0.5568	0.0010	0.2502	0.0008	0.6066	0.0030	0.5577	0.0020
0.0800	0.5000	0.5902	0.0011	0.2603	0.0007	0.5661	0.0034	0.5166	0.0021
0.0900	0.4901	0.5656	0.0004	0.2942	0.0003	0.5211	0.0009	0.4608	0.0005
0.1000	0.4800	0.5684	0.0011	0.3046	0.0007	0.3476	0.0016	0.3195	0.0010
0.1150	0.4650	0.5567	0.0005	0.3505	0.0003	0.2949	0.0005	0.2772	0.0004

Table 3. Diffusion Coefficients and Standard Deviations (Calculated by Adding 1% Artificial Noise to the Detector Signal) of the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K with $x_3 = 0.468'$

x_1	x_2	$10^9 D_{11}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{12}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{21}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$	$10^9 D_{22}$ / $m^2\ s^{-1}$	$10^9\sigma$ / $m^2\ s^{-1}$
0.0030	0.5290	0.8904	0.0080	0.0113	0.0102	-0.0609	0.0476	0.8378	0.0666
0.0100	0.5220	0.9134	0.0039	0.0507	0.0019	0.4952	0.0225	0.7709	0.0111
0.0200	0.5119	0.8858	0.0032	0.1254	0.0016	0.3691	0.0111	0.6692	0.0055
0.0200	0.5119	0.9045	0.0035	0.1197	0.0017	0.4000	0.0139	0.6821	0.0066
0.0300	0.5020	0.8708	0.0016	0.1357	0.0008	0.4801	0.0060	0.5957	0.0031
0.0500	0.4820	0.7047	0.0008	0.1810	0.0002	0.5891	0.0028	0.5786	0.0010
0.0700	0.4620	0.5472	0.0008	0.1852	0.0004	0.5349	0.0028	0.5019	0.0017
0.0800	0.4520	0.5787	0.0008	0.2325	0.0005	0.4724	0.0019	0.4466	0.0012
0.1000	0.4320	0.4950	0.0008	0.2306	0.0005	0.4839	0.0016	0.4025	0.0010
0.1000	0.4320	0.4901	0.0006	0.2267	0.0004	0.4585	0.0016	0.3991	0.0010
0.1250	0.4070	0.4847	0.0005	0.2788	0.0004	0.3037	0.0009	0.2719	0.0006
0.1300	0.4020	0.4020	0.0004	0.2269	0.0003	0.4067	0.0009	0.3310	0.0006
0.1600	0.3720	0.4221	0.0007	0.2801	0.0005	0.2464	0.0006	0.2129	0.0005

coefficients, obtained in this way, were the source used to calculate the respective standard deviation σ of the experimental data. These diffusion coefficients as shown in Figures 4 and 5 together with their standard deviations are given in Tables 2 and 3, respectively.

Figure 6 gives the refractive index versus concentration in the binary system acetone + water. Both of our concentration paths (x_2 = 0.580 and 0.532) are in a region where the slope of n_D over x is rather small, which results in larger uncertainties in the R_i entering eq 16 for the calculation of the parameter α and the ratio used in eqs 12 and 13.

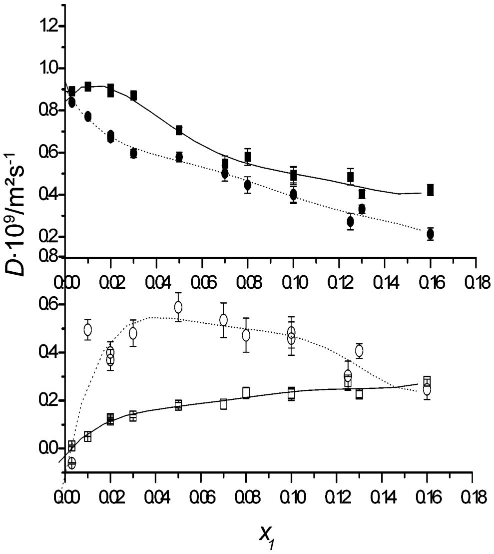

Figure 5. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and x_3 = 0.4680: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}. The △ shows D of the binary subsystem acetone−water.

The relative scatter of the four diffusion coefficients D_{ij} is mostly caused by the small ${}^{dn}/_{dc}$ values for the chosen water/acetone ratios. Surprisingly, the eigenvalues D_1 and D_2, which we calculated from eqs 14 and 15 and also their ratio D_1/D_2, are more homogeneous and show a much better internal consistency, as seen in Figures 7 and 8. Having the diffusion coefficients of Fick's matrix, we can calculate its determinant $|D|$

$$|D| = D_{11}D_{22} - D_{12}D_{21}$$

The corresponding numerical data of the eigenvalues for both concentration paths and the respective determinants

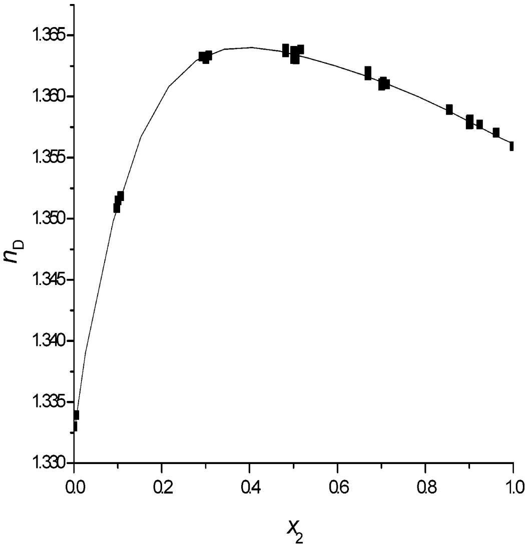

Figure 6. Refractive index versus concentration of the binary mixture acetone (2) + water at 298.15 K.

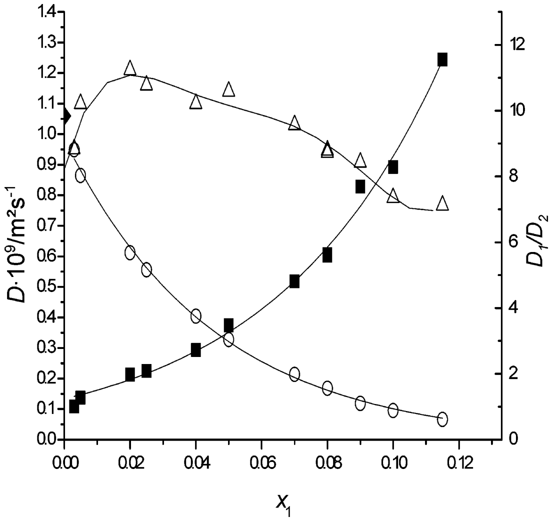

Figure 7. Calculated eigenvalues of the diffusion coefficient matrix △, D_1; ◊, D_2; and their ratio ■, D_1/D_2 at x_3 = 0.4200.

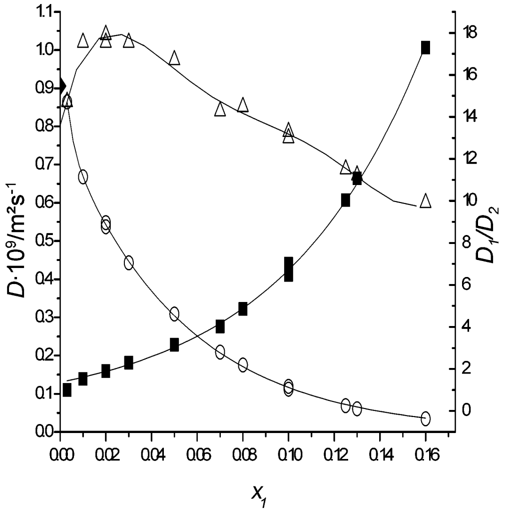

Figure 8. Calculated eigenvalues of the diffusion coefficient matrix, △, D_1; ◊, D_2; and their ratio ■, D_1/D_2 at x_3 = 0.4680.

Table 4. Determinant |*D*| and Eigenvalues D_1 and D_2 with x_3 = 0.42'

x_1	x_2	$10^9\|D\|$	10^9D_1/m² s⁻¹	10^9D_2/m² s⁻¹
0.0030	0.5770	0.9023	0.9506	0.9493
0.0049	0.5819	0.9542	1.1027	0.8653
0.0200	0.5600	0.7417	1.2118	0.6121
0.0250	0.5550	0.6434	1.1568	0.5562
0.0400	0.5400	0.4450	1.1026	0.4036
0.0500	0.5300	0.3743	1.1426	0.3276
0.0700	0.5100	0.2199	1.0280	0.2139
0.0800	0.5000	0.1588	0.9469	0.1677
0.0800	0.5000	0.1575	0.9390	0.1678
0.0900	0.4901	0.1074	0.9082	0.1182
0.1000	0.4800	0.0757	0.7924	0.0956
0.1150	0.4650	0.0509	0.7675	0.0664

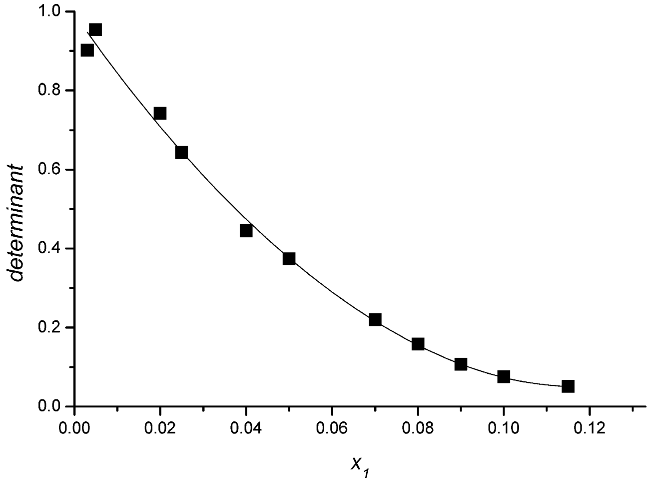

Figure 9. Determinant of the diffusion coefficient matrix at x_3 = 0.42.

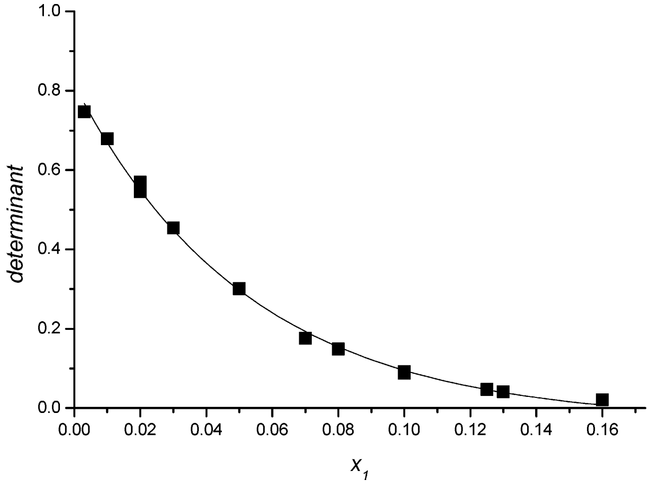

Figure 10. Determinant of the diffusion coefficient matrix at x_{water} = 0.4680.

Table 5. Determinant |*D*| and Eigenvalues D_1 and D_2 with x_3 = 0.468

x_1	x_2	$10^9\|D\|$	10^9D_1/m² s⁻¹	10^9D_2/m² s⁻¹
0.0030	0.5290	0.7467	0.8646	0.8636
0.0100	0.5220	0.6790	1.0159	0.6684
0.0200	0.5119	0.5465	1.0184	0.5366
0.0200	0.5119	0.5691	1.0388	0.5478
0.0300	0.5020	0.4535	1.0232	0.4433
0.0500	0.4820	0.3011	0.9742	0.3091
0.0700	0.4620	0.1755	0.8401	0.2089
0.0800	0.4520	0.1486	0.8505	0.1747
0.1000	0.4320	0.0877	0.7860	0.1115
0.1000	0.4320	0.0917	0.7703	0.1190
0.1250	0.4070	0.0471	0.6881	0.0685
0.1300	0.4020	0.0408	0.6723	0.0607
0.1600	0.3720	0.0208	0.6003	0.0347

are given in Tables 4 and 5. The diffusion coefficients scatter much more than both eigenvalues D_1 and D_2 and the determinant, calculated from these coefficients. The smooth graphs in Figures 7 to 10 imply that one can use these data for a critical evaluation and for a consistency test of experimental results. The continuous decline of the determinant |*D*|, which occurs when approaching the critical solution point, is predicted and discussed in detail by Vitagliano et al.[42] It is verified by our experimental results of diffusion coefficients in the ternary system glycerol−acetone−water. Figures 9 and 10 show the smooth decline of the determinant |*D*| for both concentration paths.

To get more information on the influence of the measured differences of refractive indices on the calculated diffusion coefficients, 5% Gaussian distributed noise was added to the Δ*n* values 20 times for each data set, and the fitting procedure was repeated to calculate the standard deviations σ of the coefficients. The results are represented by the error bars in Figures 4 and 5. The large influence of accuracy of the Δ*n* values is also demonstrated in Table 6, which gives an example for diffusion coefficients, calculated

Table 6. Comparison of Ternary Diffusion Coefficients, Eigenvalues, and Determinants Calculated by Using Different Sources of Refractive Index Differences with $x_3 = 0.486'$

	x_1	$10^9 D_{11}$ / $m^2 s^{-1}$	$10^9 D_{12}$ / $m^2 s^{-1}$	$10^9 D_{21}$ / $m^2 s^{-1}$	$10^9 D_{22}$ / $m^2 s^{-1}$	$10^9 \lvert D \rvert$	$10^9 D_1$ / $m^2 s^{-1}$	$10^9 D_2$ / $m^2 s^{-1}$
standard refractometer	0.05	0.7632	0.2276	0.4162	0.5164	0.2994	0.9714	0.3082
differential. refractometer	0.05	0.7047	0.1810	0.5891	0.5786	0.3011	0.9742	0.3091
difference/%		7.6650	20.4845	41.5425	12.0449	0.5678	0.2882	0.2920

two different ways, based on the same concentration profile. On one hand, we used Δn values, estimated by a standard Abbe-type refractometer, and on other hand, we applied a high-precision differential refractometer. The difference in the respective eigenvalues and determinants is less than 1%, in contrast to the large differences found for the diffusion coefficients. This underlines the importance of measuring the refractive indices with extremely high accuracy. It was not difficult to find suitable starting values for the fitting procedure in the bulk of the ternary system, but when approaching the binary boundary, the sensitivity to starting values was much higher. An explanation could be the dependence of refractive indices on concentration as shown in Figure 6.

Another important influence was found in the size of the concentration differences in the injected samples, relative to the carrier composition. If these concentration steps are too large, then simultaneous fitting of the peaks becomes difficult or even impossible, especially in concentration areas with a strong dependence of the diffusion coefficients on concentration. Differences, chosen too small, result in concentration profiles of the injected peaks that are not accurately measurable because of the limited sensitivity of the detector. It demands some experience to choose a suitable sample composition for injection. A detailed discussion of these problems is given by van de Ven-Lucassen et al.[41]

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 two concentration paths in the vicinity of the plait point in the system glycerol + acetone + water. The critical slowing down of diffusion is investigated with respect to the dependency of the concentration along a path of constant water content with water as the solvent, but the expected collapse of the two main diffusion coefficients into a single point near the phase boundary could not be observed.

Because of the weak refractive index−concentration dependency of the chosen water−acetone ratio in the model system, the accuracy of the estimated diffusion coefficients is not always satisfactory. The eigenvalues and the determinant of the matrix of diffusion coefficients are not strongly 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 as a test of their internal consistency.

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Received for review March 3, 2005. Accepted April 21, 2005. We gratefully acknowledge the financial support of the Deutsche Forschungsgemein-schaft, Schwerpunktprogramm: “Nichtgleichgewichtsprozesse in Flüssig-flüssig-Systemen“, Az. Wi 1081 /10-3.

JE050082C