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Ternary Diffusion Coefficients of Glycerol + Acetone + Water by Taylor Dispersion Measurements at 298.15 K. 3. Water-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 along two concentration paths of a constant water mole fraction of $x_3 = 0.60$ and 0.80, respectively. The eigenvalues of Fick's diffusion coefficient matrix are given. The present paper is a continuation of part 1 with measurements along concentration paths in the vicinity of the critical solution point and of part 2 in the acetone-rich region.

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 provide systematic diffusion coefficient measurements as a function of concentration and especially their behavior in multicomponent systems with a liquid−liquid phase separation.

As a fast and simple method, the Taylor dispersion technique is well-established in the case of binary and ternary liquid mixtures.[1−8] 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. As a consequence, publications of ternary diffusion coefficients are rather rare.

The aim of our work is to perform a systematic study of the behavior of diffusion coefficients in a ternary liquid mixture with a miscibility gap depending on the distance from the phase boundary. As a model system we chose mixtures of glycerol + acetone + water. In the first part of this study (hereafter called part 1),[7] we measured Fick's diffusion coefficients at two concentration paths of constant water mole fraction $x_3 = 0.420$ and 0.486, ranging from the limit of 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.[9,10] In the second part of this study (part 2),[8] we reported diffusion coefficients in the acetone-rich region of the ternary system at three concentration paths of constant water mole fraction $x_3 = 0.10$, 0.20, and 0.30, respectively. The aim of the present study (part 3) is to complete the systematic investigation by measuring the diffusion coefficients D_{ij} at two concentration paths in the water-rich region. The two concentration paths were chosen at constant water mole fraction $x_3 = 0.60$ and 0.80, respectively, ranging from the limit of the binary subsystem toward increasing concentration of glycerol. Parts of the ternary system were previously investigated in a small acetone-rich region by Pertler[11] and in the water-rich region by Rutten.[12]

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 identical to those described in parts 1[7] and 2.[8] In all Taylor dispersion experiments, the carrier flows through a stainless steel capillary of 11.50 m length and an effective radius of 260.65 μm with a velocity of 4 $\text{mL}\cdot\text{h}^{-1}$. The injected sample volume was 20 μL. As a detector, we used a differential refractometer (Wiss. Gerätebau Herbert Knauer) with a baseline noise of $2 \cdot 10^{-8}$ RUI. Both detector and capillary were kept at constant temperature of (298.15 ± 0.1) K. The refractometer signal was recorded at time intervals of 1 s, and 1000 to 2000 data points were taken to characterize one peak. Densities of the solution were measured with a vibrating-tube density meter (Anton Paar DAS 48) with a standard deviation of $1 \cdot 10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$ and temperature control of ± 0.01 K. To prepare the solutions for diffusion, density, and refractive index measurements, an analytical balance was used that allows mass determination accurate to ± 0.00001 g.

As reported earlier,[7,8] a small sample of composition ($c_1 + \Delta c_1$, $c_2 + \Delta c_2$) is injected 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 $S_N(t)$, we obtain

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

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

$$W_1 = \left[\left(D_{22} - \frac{R_2}{R_1} D_{21} \right) \alpha_1 + \left(D_{11} - \frac{R_1}{R_2} D_{12} \right) (1 - \alpha_1) - D_1 \right] \sqrt{D_1} \tag{2}$$

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$$W_2 = -\left[\left(D_{22} - \frac{R_2}{R_1}D_{21}\right)\alpha_1 + \left(D_{11} - \frac{R_1}{R_2}D_{12}\right)(1 - \alpha_1) - D_2\right]\sqrt{D_2} \quad (3)$$

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

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

and the parameter α_1 is given by

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

Altogether eight peaks of four different injected samples were fitted simultaneously by a Marquardt−Levenberg nonlinear least-squares regression method to obtain the diffusion coefficients D_{11}, D_{12}, D_{21}, and D_{22}.

Results and Discussion

Experimental data in the range between the subsystem acetone + water at one end and the other end of the concentration paths could not be found in literature to proof and to compare our results. Figure 1 shows the liquid−liquid phase diagram of the ternary system. The binodal curve at 298.15 K together with the plait point is given. Krishna et al.[13] determined the plait point at 298.15 K to be found at $x_1 = 0.1477$, $x_2 = 0.4163$, and $x_3 = 0.4360$.

In our previous measurements of diffusion coefficients in this ternary system at 298.15 K, we determined D_{ij} at three concentration paths with a constant water mole fraction of $x_3 = 0.10$, 0.20, and 0.30, respectively (part 2) and at two concentration paths with $x_3 = 0.420$ and 0.486 (part 1). All measurements range from the limit of the binary subsystem at $x_1 = 0.0$ toward the phase boundary. These concentration paths are shown in Figure 1 together with those of the present measurements. These present measurements at concentration paths of $x_3 = 0.60$ and 0.80 will complete our study. It provides diffusion coefficient data over the whole concentration range of this ternary system, limited only by the increasing viscosity of the solutions with increasing content of glycerol.

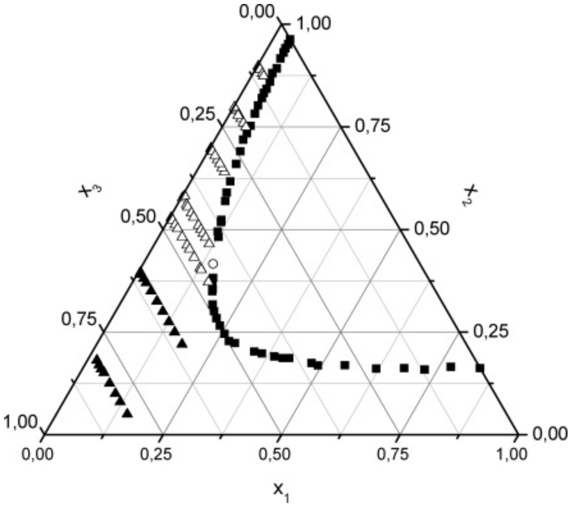

Figure 1. Liquid−liquid phase diagram and concentration path of the diffusion measurements in the system glycerol + acetone + water at 298.15 K: ■, binodal curve; ▲, paths of present measurements; △, paths of previous diffusion measurements (parts 1 and 2); ○, plait point.

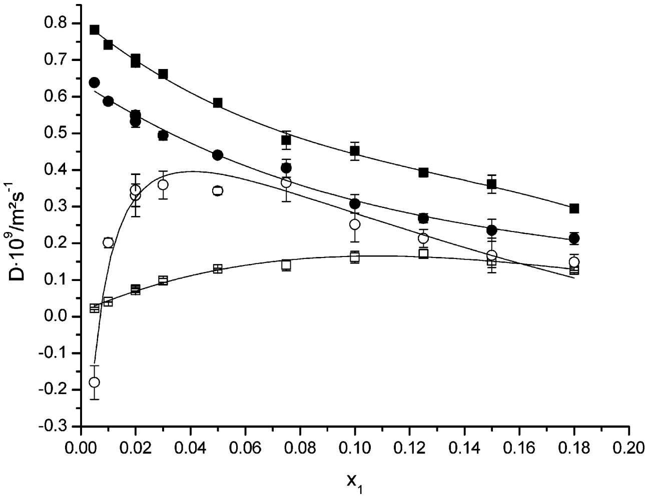

Figure 2. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.60$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

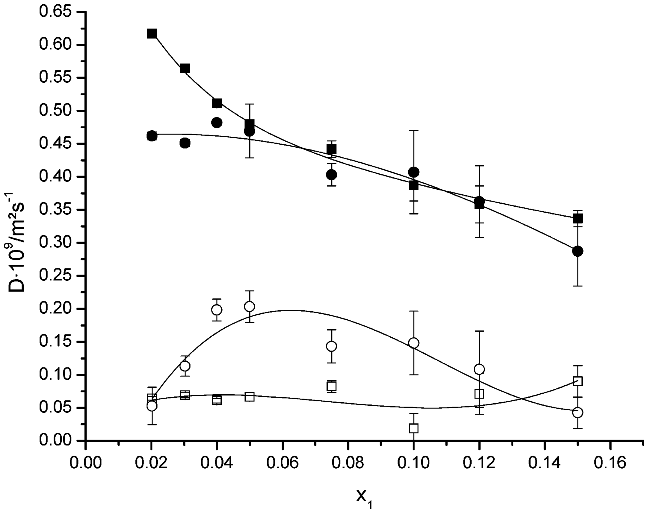

Figure 3. Mutual diffusion coefficients in the ternary system glycerol + acetone + water at 298.15 K and $x_3 = 0.80$: ■, D_{11}; ●, D_{22}; □, D_{12}; ○, D_{21}.

The results of the Taylor dispersion measurements for the two concentration sets are shown in Figures 2 and 3. When approaching the limit of the binary subsystem, the cross diffusion coefficients tend toward zero. On the concentration path of $x_3 = 0.8$ at $x_1 < 0.02$, it was not possible to obtain significant reliable results.

The four diffusion coefficients D_{ij} of Fick's matrix were obtained by direct fitting of eq 1 together with eqs 2 and 3 to our experimental Taylor dispersion peaks. The corresponding eigenvalues D_1 and D_2 are derived from these D_{ij} values according to eq 4. A direct fit of the raw data to find D_i was not successful. Figure 2 shows Fick's diffusion coefficients D_{ij} along the concentration path at $x_3 = 0.60$. We observed that both main values D_{11} and D_{22} have an almost constant difference with the same concentration dependence. At $x_3 = 0.80$, as shown in Figure 3, this situation changes and within their experimental uncertainty, both diffusion coefficients become rather similar. The cross coefficients, however, show a different behavior. The coefficient D_{12} slightly increases with increasing mole fraction of glycerol at $x_3 = 0.60$, very similar to the results at $x_3 = 0.486$ and 0.420 (part 1).[7] At $x_3 = 0.80$, the D_{12} remains almost

Table 1. Diffusion Coefficients and Standard Deviations in the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K with Constant Water Content $x_3 = 0.60$

x_1	x_2	$\frac{10^9 D_{11}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{12}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{21}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{22}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$
0.0050	0.3949	0.7819	0.0025	0.0218	0.0034	−0.1795	0.0462	0.6382	0.0044
0.0100	0.3900	0.7425	0.0009	0.0403	0.0005	0.2007	0.0132	0.5865	0.0094
0.0200	0.3800	0.7008	0.0089	0.0719	0.0066	0.3305	0.0576	0.5322	0.0156
0.0200	0.3800	0.7026	0.0047	0.0748	0.0040	0.3308	0.0313	0.5473	0.0101
0.0200	0.3800	0.6918	0.0070	0.0714	0.0052	0.3453	0.0443	0.5503	0.0122
0.0300	0.3700	0.6615	0.0087	0.0982	0.0052	0.3594	0.0382	0.4943	0.0116
0.0500	0.3500	0.5829	0.0025	0.1295	0.0023	0.3427	0.0101	0.4397	0.0045
0.0750	0.3250	0.4808	0.0248	0.1402	0.0150	0.3646	0.0512	0.4054	0.0241
0.1000	0.3000	0.4513	0.0251	0.1618	0.0160	0.2512	0.0475	0.3075	0.0255
0.1250	0.2750	0.3929	0.0119	0.1713	0.0125	0.2133	0.0246	0.2678	0.0120
0.1500	0.2500	0.3613	0.0250	0.1523	0.0186	0.1673	0.0473	0.2352	0.0298
0.1800	0.2200	0.2938	0.0094	0.1271	0.0074	0.1483	0.0216	0.2127	0.0162

Table 2. Diffusion Coefficients and Standard Deviations in the Ternary System Glycerol (1) + Acetone (2) + Water (3) at 298.15 K with Constant Water Content $x_3 = 0.80$

x_1	x_2	$\frac{10^9 D_{11}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{12}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{21}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_{22}}{m^2 \cdot s^{-1}}$	$\frac{10^9 \sigma}{m^2 \cdot s^{-1}}$
0.0202	0.1808	0.6168	0.0058	0.0639	0.0028	0.0527	0.0282	0.4624	0.0059
0.0303	0.1704	0.5640	0.0046	0.0686	0.0037	0.1132	0.0155	0.4507	0.0056
0.0400	0.1600	0.5114	0.0049	0.0607	0.0035	0.1985	0.0166	0.4824	0.0045
0.0499	0.1512	0.4796	0.0059	0.0664	0.0064	0.2032	0.0239	0.4692	0.0408
0.0750	0.1250	0.4423	0.0124	0.0823	0.0091	0.1432	0.0252	0.4029	0.0167
0.1000	0.1000	0.3868	0.0237	0.0184	0.0225	0.1477	0.0483	0.4073	0.0632
0.1200	0.0800	0.3583	0.0283	0.0711	0.0312	0.1082	0.0577	0.3618	0.0547
0.1500	0.0500	0.3365	0.0122	0.0901	0.0236	0.0423	0.0235	0.2873	0.0526

Table 3. Determinant $|D|$ and Eigenvalues D_1 and D_2 for the Concentration Path at $x_3 = 0.60$

x_1	x_2	$10^9 \lvert D \rvert$	$\frac{10^9 D_1}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_2}{m^2 \cdot s^{-1}}$
0.0050	0.3949	0.5029	0.7453	0.6747
0.0100	0.3900	0.4274	0.7835	0.5455
0.0200	0.3800	0.3492	0.7922	0.4408
0.0200	0.3800	0.3598	0.8003	0.4496
0.0200	0.3800	0.3560	0.7933	0.4488
0.0300	0.3700	0.2917	0.7836	0.3723
0.0500	0.3500	0.2119	0.7338	0.2888
0.0750	0.3250	0.1438	0.6723	0.2139
0.1000	0.3000	0.0981	0.5935	0.1653
0.1250	0.2750	0.0687	0.5315	0.1292
0.1500	0.2500	0.0595	0.4699	0.1266
0.1800	0.2200	0.0437	0.3965	0.1101

Table 4. Determinant $|D|$ and Eigenvalues D_1 and D_2 for the Concentration Path at $x_3 = 0.80$

x_1	x_2	$10^9 \lvert D \rvert$	$\frac{10^9 D_1}{m^2 \cdot s^{-1}}$	$\frac{10^9 D_2}{m^2 \cdot s^{-1}}$
0.0202	0.1808	0.2819	0.6362	0.4431
0.0303	0.1704	0.2465	0.6122	0.4026
0.0400	0.1600	0.2347	0.6076	0.3862
0.0499	0.1512	0.2116	0.5907	0.3582
0.0750	0.1250	0.1664	0.5330	0.3123
0.1000	0.1000	0.1472	0.4993	0.2947
0.1200	0.0800	0.1219	0.4478	0.2723
0.1500	0.0500	0.0929	0.3783	0.2454

constant. On the other hand, the cross coefficient D_{21} passes through a maximum at low glycerol concentrations. This trend was observed already in part 1,[7] and with increasing water content the D_{ij} values become smaller and the maximum seems to disappear.

To derive information on possible errors during the fitting procedure and on different experimental influences on the final result, data sets were created from each injection and modified by superimposing 1 % artificial Gaussian-distributed noise, as described in refs 7 and 8. The resulting data sets were subject to the same fitting procedure as the original ones; they served as a source to calculate the respective standard deviation σ of the experimental data. The numerical data for these diffusion coefficients together with their standard deviations are given in Tables 1 and 2, respectively.

The corresponding numerical data of the eigenvalues for both concentration paths and the respective determinants are given in Tables 3 and 4. The values of the diffusion coefficients scatter much more as compared to both the eigenvalues D_1 and D_2 and the determinant, which were calculated from these coefficients. At a water content of $x_3 = 0.60$ both eigenvalues differ considerably from each other as shown in Figure 4. The overall behavior is similar to the situation in part 1[7] with a slight maximum of D_2 at low glycerol concentrations. With increasing water content at $x_3 = 0.80$ (Figure 5) the difference between D_1 and D_2 becomes smaller. Unfortunately, we were not able to obtain reliable experimental data at $x_1 \leq 0.02$ so that we have no information on the behavior of the eigenvalues at high water and low glycerol concentrations.

The smooth graphs in Figures 4 and 5 imply that one can use these data for a critical evaluation and for a consistency

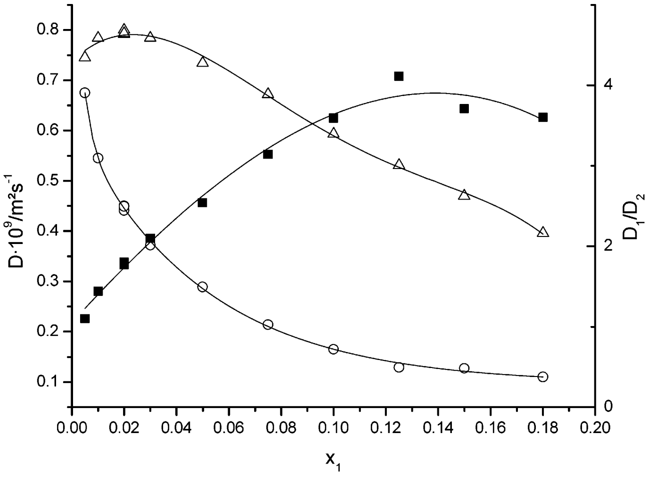

Figure 4. Calculated eigenvalues of the diffusion coefficient matrix (△, D_1; ○, D_2) and their ratio (■, D_1/D_2) at $x_3 = 0.60$.

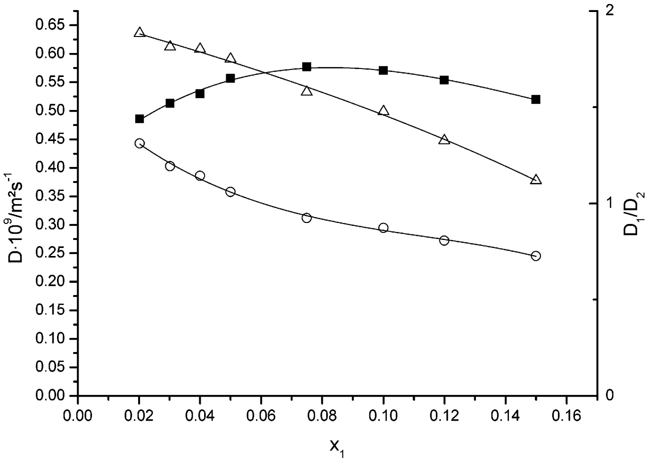

Figure 5. Calculated eigenvalues of the diffusion coefficient matrix (△, D_1; ○, D_2) and their ratio (■, D_1/D_2) at $x_3 = 0.80$.

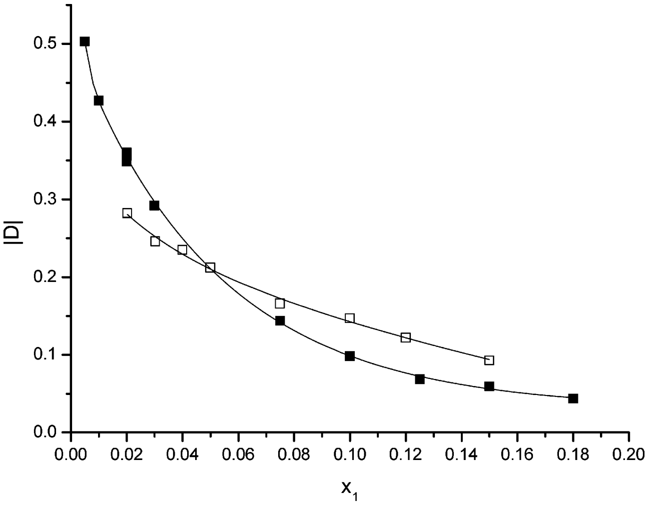

Figure 6. Determinant of the diffusion coefficient matrix: ■, $x_3 = 0.60$; □, $x_3 = 0.80$.

test of experimental results. The determinant $|D|$ shows a continuous decline when approaching the phase boundary (Figure 6).

In the bulk of the ternary system, it was not difficult to find suitable starting parameters for the nonlinear fitting procedure, but when approaching the limit of the binary subsystem, the sensitivity to starting values became much higher, which might result from the strong nonlinear dependence of refractive indices on concentration as described in ref 7.

Conclusions

In the last part of our systematic study of the mass transport behavior in ternary liquid mixtures with a liquid−liquid phase separation, the Taylor dispersion measurements of Fick's diffusion coefficients were performed along two concentration paths in direction to the phase boundary at constant water concentration in the system glycerol + acetone + water. Because of the above-mentioned 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, however, 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 test for their internal consistency.

Literature Cited

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

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

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

(4) 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.

(5) 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.

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

(7) 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* (4), 1396−1403.

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

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

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

(11) Pertler, M. Die Mehrkomponenten-Diffusion in nicht vollständig mischbaren Flüssigkeiten. Ph.D. Thesis, TU München, 1996.

(12) Rutten, P. W. M. Diffusion in liquids. Ph.D. Thesis, Delft University, 1992.

(13) Krishna, R.; Low, C. Y.; Newsham, D. M. T.; Olivera-Fuentes, C. G.; Paybarah, A. Liquid−liquid equilibrium in the system glycerol-water-acetone at 25 °C. *Fluid Phase Equilib.* **1989**, *45*, 115−120.

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