Complications in the use of the Taylor Dispersion Method for ternary diffusion measurements: Methanol + Acetone + Water mixtures

Citation for published version (APA):

Ven - Lucassen, van de, I. M. J. J., Kemmere, M. F., & Kerkhof, P. J. A. M. (1997). Complications in the use of the Taylor Dispersion Method for ternary diffusion measurements: Methanol + Acetone + Water mixtures. *Journal of Solution Chemistry*, 26(12), 1145-1167. <https://doi.org/10.1023/A:1022929123165>

DOI:

[10.1023/A:1022929123165](https://doi.org/10.1023/A:1022929123165)

Document status and date:

Published: 01/01/1997

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Complications in the Use of the Taylor Dispersion Method for Ternary Diffusion Measurements: Methanol + Acetone + Water Mixtures

**I. M. J. J. van de Ven-Lucassen,* M. F. Kemmere, and
P. J. A. M. Kerkhof**

Received June 19, 1997; revised September 19, 1997

The Taylor dispersion technique is used to measure the ternary mutual diffusion coefficients of aqueous nonelectrolyte solutions at 25°C. The dispersion of the injected solutes is recorded by a differential refractometer and an ultraviolet-visible detector. The diffusion coefficients are calculated directly by fitting the theoretical dispersion equations to about six experimental curves simultaneously. If the ternary diffusion effects in the measured dispersion profiles are not confused by the inaccuracy of the experimental method or an unfavorable relative detector sensitivity, the diffusion coefficients are precise. For the system methanol + acetone + water, it is shown that the Taylor dispersion method is unsuitable for the determination of all the diffusion coefficients if the methanol mole fraction is less than 0.45 or the acetone mole fraction if more than 0.001.

KEY WORDS: Taylor dispersion; ternary diffusion coefficients; aqueous nonelectrolyte solutions; methanol; acetone.

1. INTRODUCTION

Diffusion coefficients in liquid systems can be measured by the Taylor dispersion method (TDM).⁽¹⁻⁵⁾ For binary systems this method is fast and convenient. The measured binary diffusion coefficients have an accuracy of 0.5–1.5%.⁽⁶⁾

The diffusion behavior in ternary or multicomponent systems, however, is more complicated. In a ternary system, *e.g.*, four Fick diffusion coefficients

Laboratory of Separation Processes and Transport Phenomena, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

have to be determined from the dispersion curves of two components. Ternary mutual diffusion coefficients were determined from Taylor dispersion profiles by Leaist *et al.* The three-component systems consisted of water + salt 1 + salt 2 or water + salt + organic solute. The diffusion coefficients were calculated from the temporal moments of the detector signal^(7,8) or by fitting the theoretical equation of the dispersion profile to the experimental curve.⁽⁸⁻¹⁴⁾ The main diffusion coefficients were more accurate than the cross-diffusion coefficients. The experimental curve was measured by a differential refractometer. Since changes in concentration of both solutes influence the detector signal, the concentrations of the two solutes were not measured independently. Therefore, the precision of the determination of the diffusion coefficients was dependent on the ratio R_1/R_2 of the refractive index increments per mole of solute 1 and solute 2. Independent measurement of the concentration profiles of the two solutes may increase the precision of the diffusion coefficients.

In this work the determination of ternary diffusion coefficients by the Taylor dispersion method is discussed for aqueous solutions of nonelectrolytes using a differential refractometer (RI-detector) as well as an ultraviolet-visible (UV-) detector.

2. THEORY OF THE TAYLOR DISPERSION METHOD

Diffusion in a three-component system is described by the coupled Fick equations

$$J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (1a)$$

$$J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (1b)$$

where J_i is the molar flux of component i , ∇C_i is the gradient of concentration of component i , D_{ii} is a main diffusion coefficient and D_{ij} a cross-diffusion coefficient. The ternary diffusion coefficients can be measured by the Taylor dispersion technique: A pulse of different concentrations C_1 and C_2 is injected into the ternary mixture (solvent) flowing slowly through a long capillary. The pulse spreads out because of the laminar velocity profile and molecular diffusion. The concentrations C_1 , C_2 at the end of the diffusion tube are given by the fundamental working equations of Price⁽¹⁵⁾

$$C_1 = \frac{A_1}{2\pi R^2} \frac{1}{\sqrt{\pi\sigma_1 t}} \exp\left\{-\frac{(t-\tau)^2 U^2}{4\sigma_1 t}\right\} + \frac{A_2}{2\pi R^2} \frac{1}{\sqrt{\pi\sigma_2 t}} \exp\left\{-\frac{(t-\tau)^2 U^2}{4\sigma_2 t}\right\} \quad (2a)$$

$$C_2 = \frac{A_3}{2\pi R^2} \frac{1}{\sqrt{\pi\sigma_1 t}} \exp\left\{-\frac{(t-\tau)^2 U^2}{4\sigma_1 t}\right\} + \frac{A_4}{2\pi R^2} \frac{1}{\sqrt{\pi\sigma_2 t}} \exp\left\{-\frac{(t-\tau)^2 U^2}{4\sigma_2 t}\right\} \quad (2b)$$

with

$$A_1 = \frac{\left\{D_{22} - \frac{1}{2}(D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}})\right\}M_1 - D_{12}M_2}{\sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}} \quad (2c)$$

$$A_2 = \frac{\left\{D_{22} - \frac{1}{2}(D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}})\right\}M_1 - D_{12}M_2}{-\sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}} \quad (2d)$$

$$A_3 = \frac{\left\{D_{11} - \frac{1}{2}(D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}})\right\}M_2 - D_{21}M_1}{\sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}} \quad (2e)$$

$$A_4 = \frac{\left\{D_{11} - \frac{1}{2}(D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}})\right\}M_2 - D_{21}M_1}{-\sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}} \quad (2f)$$

$$\sigma_1 = \frac{1}{2} \frac{R^2 U^2}{48} \frac{D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}}{D_{11}D_{22} - D_{12}D_{21}} \quad (2g)$$

$$\sigma_2 = \frac{1}{2} \frac{R^2 U^2}{48} \frac{D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}}{D_{11}D_{22} - D_{12}D_{21}} \quad (2h)$$

in which M_i represents the number of moles of component i in the injected pulse in excess of those in the same volume of the carrier stream: $M_1 = A_1 + A_2$ and $M_2 = A_3 + A_4$. C_i is the radially-averaged concentration at time t relative to the background concentration, τ is the mean residence time, R the internal radius of the diffusion tube and U the linear velocity averaged over the cross section.

The sum of the main diffusion coefficients is positive: $D_{11} + D_{22} > 0$. Further conditions for the diffusion coefficients are $D_{11}D_{22} - D_{12}D_{21} > 0$ and $(D_{11} - D_{22})^2 + 4D_{12}D_{21} > 0$.^(16,17,18)

The assumptions made in the derivation of the working equations are similar to those of the binary dispersion technique⁽⁶⁾ with an effective diffusion coefficient D_{eff} .⁽¹⁵⁾ By comparing Toor's method,⁽¹⁷⁾ used in the derivation

of Price's equations, with Taylor's derivation of the binary equation,^(2,3) D_{eff} can be described with the eigenvalues of the D_{ij} matrix

$$D_{\text{eff}} = \frac{2(D_{11}D_{22} - D_{12}D_{21})}{D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}} \quad (3)$$

The effective diffusion coefficient is of the same order of magnitude as the main diffusion coefficients and is used in the equations that provide the criteria for the operating conditions (*e.g.*, calculation of the flow rate).^(6,15)

The calculation of the Fick diffusion coefficients may be complicated due to their mutual dependence. In a solvent-fixed situation, in which diffusion causes no bulk motion of the liquid, the following relation can be derived⁽¹⁹⁾

$$(D_{12})_s \mu_{11} - (D_{11})_s \mu_{12} = (D_{21})_s \mu_{22} - (D_{22})_s \mu_{21} \quad (4a)$$

where $\mu_{ij} = (\partial \mu_i / \partial C_j)_{T,p,C_{k \neq 0,j}}$ is the molar chemical potential and $(D_{ij})_s$ is the solvent-fixed diffusion coefficient. For volume-fixed diffusion coefficients a similar relation has been derived by Dunlop.⁽²⁰⁾ Transformation of the volume-fixed diffusion coefficients D_{ij} , measured by the Taylor dispersion method, to the solvent-fixed diffusion coefficients is possible by⁽²¹⁾

$$(D_{ij})_s = D_{ij} + \frac{C_i}{C_0 \bar{V}_0} \sum_{k=1}^{n-1} \bar{V}_k D_{kj} \quad (i, j = 1, \dots, n-1) \quad (4b)$$

where C_i is the molar concentration and $\bar{V}_i$ the partial molar volume of component i . The subscript 0 refers to the solvent.

Near infinite dilution $(D_{ij})_s$ is equal to D_{ij} . For low concentrations of the solute components, and even in relatively concentrated solutions, the solvent-fixed- and the volume-fixed diffusion coefficients may differ only by 1–5%.⁽²¹⁾ Furthermore, the thermodynamic, molar concentration-based matrix $(\Gamma_c)_{ij}$ can be simplified to⁽²²⁾

$$(\Gamma_c)_{ij} = \delta_{ij} + C_i \frac{\partial \ln \gamma_i}{\partial C_j} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} = \Gamma_{ij} = \frac{x_i}{RT} \mu_{ij} \quad (5)$$

in which δ_{ij} is the Kronecker delta, γ_i the activity coefficient of component i defined by convention I ,⁽²³⁾ and Γ_{ij} the thermodynamic mole fraction-based matrix. Combination of Eqs. (4, 5) leads to

$$D_{21} = \left(\frac{x_2}{x_1} D_{12} \Gamma_{11} - \frac{x_2}{x_1} D_{11} \Gamma_{12} + D_{22} \Gamma_{21} \right) / \Gamma_{22} \quad (6)$$

Eq. (6) is valid at low concentrations of the solute components and provides good estimates at higher concentrations.

The working equations of Price, Eq. (2) simplify for very low concentrations of the solute components. If the concentration of component 2 tends to zero (tracer), we have $D_{21} \approx 0$,⁽²⁴⁾ and Eqs. (2a,2b) become, respectively

$$C_1 = \frac{-\frac{D_{12}}{D_{11} - D_{22}} M_2}{2\pi R^2} \frac{1}{\sqrt{\pi \frac{R^2 U^2}{48 D_{22}} t}} \exp\left\{-\frac{(t - \tau)^2}{4 \frac{R^2}{48 D_{22}} t}\right\} + \frac{M_1 + \frac{D_{12}}{D_{11} - D_{22}} M_2}{2\pi R^2} \frac{1}{\sqrt{\pi \frac{R^2 U^2}{48 D_{11}} t}} \exp\left\{-\frac{(t - \tau)^2}{4 \frac{R^2}{48 D_{11}} t}\right\} \quad (7a)$$

$$C_2 = \frac{M_2}{2\pi R^2} \frac{1}{\sqrt{\pi \frac{R^2 U^2}{48 D_{22}} t}} \exp\left\{-\frac{(t - \tau)^2}{4 \frac{R^2}{48 D_{22}} t}\right\} \quad (7b)$$

The concentration curve of component 2 is a single Gaussian and is independent of the injected amount of component 1. Similar equations can be derived if component 1 tends to zero (component 1 is tracer), *i.e.*, $D_{12} \approx 0$. If both components tend to zero, C_1 and C_2 are both single Gaussians: The concentration curve of component 1 is not influenced by the injected amount of component 2 and *vice versa*.

When the concentration is measured, the relation between the detector signal $s(t)$ and the concentration *vs.* time curves, Eq. (2), is assumed to be

$$s(t) = w_1 C_1 + w_2 C_2 + a + bt + \varepsilon(t) \quad (8)$$

in which w_i is the detector sensitivity for component i , a and b compensate for the detector drift (which is assumed to be linear in time), and $\varepsilon(t)$ is noise. The signal is sampled with a sample interval of $\Delta t_i = 0.98s$: $y_i = s(t_i)$.

Diffusion coefficients can be calculated from the measured dispersion peaks in two different ways: Calculation from the temporal moments^(7,8); fitting of the theoretical Eq. (2), combined with Eq. (8), to the experimental curve.⁽⁸⁻¹⁴⁾ In this work only fitting procedures with the diffusion coefficients as fitting parameters will be used. In these fitting procedures a discrete signal without drift is required: $y_i = y_i^* - (a + bt_i)$. For the calculation of a and b , regions of the detected signal, where the concentration is negligible, are visually marked in our software as baseline. Through these regions of the signal the drift is fitted and subtracted from the signal.

3. FITTING PROCEDURES

Fitting of the theoretical equations to the experimental curves can be done in several different ways:

- fitting to a single curve
- simultaneously fitting of two or more curves (with different injection concentrations) from one detector
- simultaneously fitting of two or more curves from two different detectors (different detector sensitivities).

Furthermore, all these procedures are able to fit

- D_{11} , D_{22} , D_{21} (4-parameter fit); residence time τ calculated,⁽⁶⁾ detector sensitivities calculated from the peak areas.
- D_{11} , D_{22} , D_{12} (3-parameter fit); D_{21} is calculated during the iterative process using Eq. (6), residence time τ , and detector sensitivities calculated as above.
- 4- or 3-parameter fit + residence time τ
- 4- or 3-parameter fit + residence time τ + detector sensitivities w_1 and w_2 .
- Combinations of these procedures and other fitting procedures are possible.^(7,8)

The fitting procedures were developed in two test series. First, an ideal detector signal was calculated by means of Eq. (2). The values of the parameters used are listed in Table I. This ideal signal was processed by fitting procedures based on the least-squares approximation between the experimental data points (=ideal signal) and the points calculated. These fitting procedures were written in the SAS for Windows package (version 6.08/6.10, © SAS Institute Inc.), using the Gauss-Newton method as well as the Marquardt method. D_{11} , D_{22} , D_{12} (τ , w_1 and w_2) were fitting parameters. D_{21} was always

Table I. Parameters of Ideal Signals Series I

D_{11} (10^{-9} m ² ·s ⁻¹)	1.30	M_1 (10^{-3} mol)	0.14
D_{22} (10^{-9} m ² ·s ⁻¹)	0.80	M_2 (10^{-3} mol)	-0.14
D_{12} (10^{-9} m ² ·s ⁻¹)	-0.02	τ (s)	12000
D_{21} (10^{-9} m ² ·s ⁻¹)	-0.01 ^a	U (10^{-3} m·s ⁻¹)	0.002
(calc. acc. Eq. 6)	-0.0045 ^b	$w_{1,RI}$ (RIU·m ³ ·mol ⁻¹)	1; 300; 600
Γ_{11}	0.9	$w_{1,UV}$ (AU·m ³ ·mol ⁻¹)	0.015
Γ_{22}	0.9	$w_{2,RI}$ (RIU·m ³ ·mol ⁻¹)	1; 200; 400
Γ_{12}	-0.01	$w_{2,UV}$ (AU·m ³ ·mol ⁻¹)	—
Γ_{21}	-0.005	noise (%)	0.5; 1; 5; 20

^a $x_2/x_1 = 1$

^b $x_2/x_1 = 0.015$

calculated using Eq. (6). The detector sensitivities and the mole fraction ratio x_2/x_1 were varied. Two curves with different values of the detector sensitivities were simultaneously fitted, simulating different detectors. The influence of noise was tested by superposition of randomly generated noise on the signal (0.5%, 1%, 5%, 20%). The Marquardt method yields the best results. In some cases it is difficult to achieve convergence depending on the ratio of the detector sensitivities and the mole fraction ratio. The accuracy of the diffusion coefficients is good. The cross coefficients are of poorer precision than the main coefficients. The values of the residence time and the detector sensitivities (if fitted) are very accurate. Noise of less than 1% causes no problems in the calculation of the diffusion coefficients.

The developed fitting procedures were tested on experimental curves of the systems acetone + ethyl benzene + water and glucose + acetone + water. Simultaneously fitting of two or more curves with different injection concentrations showed an increase of precision and a decrease of convergence difficulties. Disadvantages of the procedures were the long calculation times. Another problem was the determination of accurate activity coefficients, needed in calculating D_{21} according to Eq. (6). Reduction of the calculation times was achieved by dividing the ternary systems into three types, resulting in a reduction of the necessary fitting parameters and a simplification of the working equations for two types:

1. solvent(0) + tracer(1) + tracer(2): fitting parameters D_{11} and D_{22} ; $D_{12} = 0$, $D_{21} = 0$.
2. solvent(0) + solute(1) + tracer(2): fitting parameters D_{11} , D_{22} , and D_{12} ; $D_{21} = 0$.
3. solvent(0) + solute(1) + solute(2): fitting parameters D_{11} , D_{22} , D_{12} , and D_{21} .

Use of the thermodynamic Eq. (6), *i.e.*, knowledge of the activity coefficients, is only necessary for type 3. For each type a fitting procedure was developed, using Marquardt's method.

Ideal signals were calculated for each type of ternary system. Parameters were chosen to simulate a real ternary system like water(0) + methanol(1) + acetone(2) (Table IIa). The UV-detector measured the concentration of component 2 by absorbance changes, the RI-detector measured changes in concentration (by refractive-index) of component 1 as well as component 2. Results of the testing of the fitting procedures are listed in Table IIb.

From the UV-signals of type 1 and type 2, D_{22} can be calculated by means of Eq. (7b). This calculation is fast and very accurate. At least two RI-signals of type 1 have to be simultaneously fitted to calculate the diffusion coefficients D_{11} and D_{22} [Eq. (7b) and the analog for C_1]. The accuracy is high. The RI-signals of type 2 were used to calculate the diffusion coefficients

Table IIa. Parameters of Ideal Signals, Series IIa, IIb^a

Common Parameters								
	w_1	w_2						
$w_{i,RI-det.}$	1000	5000			$\tau_{RI-det.}$	10100		
$w_{i,UV-det.}$	0	0.015			$\tau_{UV-det.}$	9750		
U	2.354							
R [10^{-3} m]	0.520							
Series IIa								
signal code	2a	2b	2c	2d	2e	2f		
M_1	5.7	5.2	4.9	4.5	4	3.5		
M_2	3.6	4.7	1.2	2.4	3.6	4.8		
	type 1		type 2		type 3			
			$(x_2/x_1 = 2.43 \cdot 10^{-11})$		$(x_2/x_1 = 0.27)$			
D_{11}	1.560		1.498		1.494			
D_{22}	1.300		1.372		1.331			
D_{12}	0		-0.214		-0.387			
D_{21}	0		0		-0.108			
Γ_{11}	1		0.9453		0.9067			
Γ_{22}	1		1		0.8750			
Γ_{12}	0		-0.1158		-0.1956			
Γ_{21}	0		0		-0.0588			
Series IIb type 3 ($x_2/x_1 = 1.0$)								
signal code	2g	2h	2i	2j	2k	2l	2m	2n
M_1	-5.7	-5.7	0.010	0.010	5.7	5.7	5.7	5.7
M_2	5.7	0.010	-5.7	5.7	5.7	-5.7	-1.0	-0.010
D_{11}		1.668		Γ_{11}		0.9478		
D_{22}		1.136		Γ_{22}		0.6628		
D_{12}		-0.298		Γ_{12}		-0.1348		
D_{21}		-0.372		Γ_{21}		-0.1664		

^aUnits as in Table I.

D_{11} , D_{22} , and D_{12} [Eqs. (7a,7b)]. The accuracy of D_{12} is less than that of D_{11} and D_{22} . D_{12} is strongly correlated with D_{22} . The determination of the diffusion coefficients of type 3 was more difficult [Eq. (2)]. In series IIa the UV-signals achieved convergence with accurate values of the diffusion coefficient. The RI-signals, however, showed no convergence. In series IIb convergence was achieved by simultaneously fitting 6 RI-signals, provided that the starting values of the fitting parameters were close to the real values. The accuracy was dependent on the combinations of signals used.

In general, the accuracy was improved by the use of τ , w_1 and w_2 as fitting parameters. The thermodynamic Eq. (6) was only used to obtain a starting value of D_{21} . The determination of the diffusion coefficients from the concentration vs. time curves of the Taylor dispersion method is only

Table IIb. Results of Testing Fitting Procedures. Inaccuracy (%) of the Diffusion Coefficients, Residence Time, and Detector Sensitivities, Dependent on the Number of Signals Simultaneously Fitted^a

Series IIa											
	type 1					type 2				type 3	
	1 RI	2 RI	6 RI	1 UV	6 UV	1 RI	6 RI	1 UV	6 UV	6 RI	6 UV
D_{11}	—	<0.1	<0.03	—	—	—	<0.1	—	—	no. conv.	<0.06
D_{22}	—	<0.03	<0.009	<0.004	<0.002	—	<0.1	<5	<0.002		<0.5
D_{12}						—	<4	—	—		<1
D_{21}											<0.8
τ							0.00005				
w_1							0.02				
w_2							0.004				
N. B. Eq. (6) not needed						Eq. (6) not applicable (zero values)				$w_1 = 0$ and Eq. (6) used	
Series IIb type 3 (two different combinations of 6 RI-signals)											
	6 RI (comb. 1)			6 RI (comb. 2)							
D_{11}	0.04			0.08							
D_{22}	0.1			0.2							
D_{12}	0.4			0.7							
D_{21}	2			3							
w_1	1			3							
N.B. Strong correlation between D_{12} and w_1, w_2 . Accuracy of the results calculated with use of Eq. (6) poorer than without Eq. (6).											

^aUnits as in Table I.

possible under certain conditions, dependent on the ratios M_1/M_2 and w_1/w_2 , the values of the diffusion coefficients and the noise level.

The fitting procedure, in which RI-signals and UV-signals of the same injections were simultaneously fitted, was compared with the procedure, in which the result of the UV-fittings (D_{22}) was used as a fixed value in the RI-fittings. The first method was rather complicated owing to the different values of the residence time τ , and the accuracy was poorer. Moreover, in many real systems it is not possible to get two independent detector signals from one injection. Very often only RI-signals are available.

Therefore, the simultaneous fitting of the UV- and RI-signals (or two other independent detector signals) will not be discussed further in this work.

4. EXPERIMENTAL

The apparatus used differs slightly from that discussed earlier for binary systems.⁽⁶⁾ A UV-detector and two extra diffusion tubes were added to the

original binary set-up. The equipment for the measurement of diffusion coefficients in ternary liquid systems is shown schematically in Figure 1.

Deionized water filtered through a Milli-Q water purification system (Millipore, resistivity 18 M Ω -cm) was used. Analytical grade methanol (purity $\geq 99.8\%$, water $< 0.05\%$), ethanol (purity $\geq 99.8\%$, water $< 0.2\%$), acetone (purity $\geq 99.5\%$, water $< 0.2\%$), D (+)-glucose anhydrous (purity $\geq 99.0\%$, water $< 0.2\%$) and ethyl benzene (purity $\geq 99\%$) were obtained from Merck and used without further purification. All experiments were performed at 25°C. The determination of the mean residence time was very accurate in both the binary experiments and the ternary experiments (inaccuracy $< 0.01\%$).

Solutions were prepared by mass and degassed by sparging with helium. Injection solutions were made by volumetric mixing of the degassed solvents. To prevent bubbles from disturbing the flow, an in-line degasser (Separations DG1300) was installed. The HPLC-pump (type LKB2150), which maintained a steady flow, was connected to an autosampler (Spark Marathon) with a fixed-volume sample loop of 20 μ L. Zero dead volume fittings were used to connect the diffusion tube with the autosampler and the UV-detector and a short capillary tube between the UV and RI detectors. Several diffusion tubes were installed: stainless steel tubes (i.d. 1.041 mm) of various lengths (10, 15, 25, 50 m) and PEEK (polyether ether ketone) tubes (i.d. 1.04 mm) of two lengths (15, 25 m). The internal radii of the tubes were determined in several ways: by gravimetry and residence time measurements as well as by calibration with diffusion measurements of the systems methanol + water (whole concentration range), ethanol + water, acetone + water.

The eluted peaks were detected with a UV-detector (Applied Biosystems 785A) and subsequently by a differential refractometer (Shodex SE61). The UV-detector was installed between the capillary tube and the RI detector of the original binary set-up. For the conversion of the analog output signal of the UV-detector a hardware interface device (Strawberry-Tree Mini16 ADC) was installed in the personal computer. The software for data acquisition and

Fig. 1. Experimental setup for measurement of diffusion coefficients in ternary liquid systems: SV, selection valve; D, degasser; A, autosampler; UV, ultraviolet-visible detector; RI, refractive index detector.

controlling the equipment as well as the data processing software package were adequately extended.

The procedure for the measurement of diffusion coefficients in binary systems is described in detail by Van de Ven-Lucassen *et al.*⁽⁶⁾ Before starting an experiment the system was flushed for at least six h at the flow rate of the diffusion experiment to attain a stable, linear baseline in each detector. The flow velocity was set in accordance with the conditions of Section 2 (typically $0.12 \text{ cm}^3\text{-min}^{-1}$). Diffusion samples were injected every 1.5–2 h. The extended original software package was used to apply a baseline correction to each experimental curve. Binary fits were done for dispersion peaks obtained from $M_2 = 0$ or $M_1 = 0$ injections: the mean residence time τ , the binary diffusion coefficient (D_{11} or D_{22}) and the peak area were calculated. The detector sensitivity (w_1 or w_2) was determined from the peak area and the injected amount. These values could be used as starting values for the fitting parameters in the ternary procedures.

5. RESULTS AND DISCUSSION

Diffusion coefficients were measured for the ternary systems acetone + ethyl benzene + water, glucose + acetone + water, and methanol + acetone + water. Preliminary measurements were done for the binary systems methanol + water, ethanol + water, acetone + water, glucose + water, ethylbenzene + water.

5.1. Binary Systems

Experiments with the binary systems methanol + water, ethanol + water, acetone + water, and glucose + water, were performed to show that the detector response was linear with concentration and to study the influence of the concentration of the injected sample on the measurement of the diffusion coefficients. In these experiments the stainless steel tubes as well as the PEEK tubes were used. For each binary system a minimum difference in concentration between injection solution and solvent was necessary to obtain an accurate experimental curve as a result of detector noise. This minimum difference was dependent on the binary system and the detector used. Above a certain concentration difference the calculated diffusion coefficients started to increase, probably due to secondary flow effects. This maximum concentration difference was independent on the detector used. For both detectors the response was linear over a much wider range of concentration differences. The maximum concentration difference was 5 vol% for methanol + water, 4 vol% for ethanol + water, 6 vol% for acetone + water (UV and RI detectors), and 3 wt% for glucose + water. For the RI and UV detectors and

for both types of capillary tubes, the calculated diffusion coefficients were not significantly different. Moreover, the values of the binary diffusion coefficients, measured with the ternary set-up, were within the uncertainty of the measurements with the original binary set-up.⁽⁶⁾ Injections of solutions that were denser or less dense than the solvent did not influence the measured diffusion coefficients. The inaccuracy of the results was lower for the PEEK tubes (PEEK: 0.5%; stainless steel: 1.5%). For the system acetone + water the UV detector was more accurate (uncertainty UV: 0.3%; RI: 0.5%).

Injections of dilute ethyl benzene (0.01–5.5 vol.%) into pure water showed tailing in the measured concentration against time curves due to adsorption at the wall of the PEEK tube. If ethyl benzene was present in the solvent (0.01 vol% ethyl benzene in water) no tailing was observed. Although it is possible to calculate a diffusion coefficient from an asymmetric peak by means of a capacity factor k (in this case $k = 2$),⁽²⁵⁾ tailing was avoided in the subsequent experiments. The dispersion profiles of high injection concentrations of ethyl benzene (5 vol%) were non-Gaussian and irreproducible, because of demixing in the injection vials, due to the very low solubility of ethyl benzene in water.⁽²⁶⁾ Therefore, only injection concentrations < 2 vol% could be used.

The binary experiments led to the selection of the PEEK capillary for the ternary experiments. For all experiments the concentration difference between injection solution and solvent was chosen well below the maxima of the binary systems, which appeared to agree with a value of the Grashof number < 100 as mentioned by Ananthakrishnan *et al.*⁽²⁷⁾ [$Gr = d^3 \cdot g \cdot (\Delta\rho/\rho)/\nu^2$ in which d is the tube diameter, g the gravity constant, $\Delta\rho$ the density difference between injection solution, and solvent, ρ the density and ν the kinematic viscosity of the solvent.].

5.2 Ternary Systems

5.2.1. Acetone(1) + Ethyl Benzene (2) + Water (0)

Ethyl benzene was used at infinite dilution: $D_{21} = 0$. The value of D_{12} , estimated with Eq. (6) was $-7 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ with $D_{11} = 1.3 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (acetone in water⁽²⁸⁾) and $D_{22} = 7.9 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (ethyl benzene in water) and a thermodynamic matrix Γ_{ij} estimated from the UNIQUAC model^(16,29,30) with parameters from Rutten⁽³¹⁾ and Macedo and Rasmussen.⁽³²⁾ The flow rate was 0.10–0.11 $\text{cm}^3 \cdot \text{min}^{-1}$. Acetone was detected at a wavelength of 266 nm, ethyl benzene at 215 nm. The RI detector response was the summation of the acetone and ethyl benzene refractive-index differences between peak and solvent. For each solvent, three to six experiments with at least ten different injections were performed, in each experiment 3 to 9 RI-peaks of

Table III. Diffusion Coefficients at 25°C for the Acetone(1) + Ethyl benzene(2) + Water(0): System^a

	Acetone	Ethyl benzene	
		0 [vol%]	0.01 [vol%]
	0 [vol%]		
D_{11}		1.297±0.004	1.30±0.01
D_{22}		0.775 ^{b,c} /0.673 ^{b,c} ±0.01/0.006	0.83/0.78±0.01/0.01
D_{12}		—	—
		$D_{11} = 1.30$ (Ref.28)	
	0.2 [vol%]		
D_{11}			1.30±0.01
D_{22}		0.787±0.004	
D_{12}		0.002 ^c ±0.004	
	0.4 [vol%]		
D_{11}			1.296±0.005
			D_{11} fixed value 1.300:
D_{22}			0.758±0.046
D_{12}			0.005±0.003

^aUnits as in Table I.^bTailing.^cUnreliable.

different injection concentrations were simultaneously fitted and at least three different combinations of peaks. Results are shown in Table III.

The cross diffusion coefficient D_{12} is very imprecise owing to the strong correlation between D_{12} and D_{22} : 0.4% deviation in the value of D_{22} causes 40% deviation in D_{12} , D_{11} fixed (deviation $D_{11} = 0.8\%$: deviation $D_{12} = 0.4\%$, D_{22} fixed). Another cause of the inaccuracy of D_{12} was the relative RI detector sensitivity w_1/w_2 of 4500/600. At this ratio of w_1/w_2 the ternary effects were best detected if $M_1 \ll M_2$ [Eqs. (7,8)]. If the ternary peak was compared with a summation of two binary peaks (*i.e.*, $D_{12} = 0$), the maximum difference between the two curves was $\pm 2\%$ for a cross-diffusion coefficient D_{12} of $\pm 5 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ (Fig. 2, curves 1 and 2). The same difference could be caused by an inaccuracy of 2% in the determination of the injected amounts M_1 and M_2 (Fig. 2, curves 3 and 4). Noise can mask these differences.

5.2.2. Glucose(1) + Acetone(2) + Water(0)

Glucose (5 wt%, $\chi_1 = 0.0052$) ($\chi_1 = 0.0052$ and acetone (0.2 vol%, $x_2 = 0.0005$) were dissolved in pure water. The flow rate was $0.09 \text{ cm}^3 \cdot \text{min}^{-1}$. In this mixture the cross diffusion coefficient D_{21} was zero (acetone tracer component). The estimated value of D_{12} is $3 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ with $D_{11} = 6.7 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (glucose in water) and $D_{22} = 1.3 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (acetone

Fig. 2. Acetone(1) + ethylbenzene(2) + water(0) at 25°C. Influence of the cross-diffusion coefficient and injection amount on the deviation of the detected "ternary" signal compared to the "binary-sum" signal. $\text{Dev. sign./sign.max.} = (\text{ternary signal}(t_i) - \text{binary-sum signal}(t_i)) / \text{binary-sum signal}(t_{\text{max}} = \tau)$. Parameters of the binary-sum signal: $D_{11} = 1.30 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$; $D_{22} = 7 \times 9.10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$; $D_{12} = 0$; $D_{21} = 0$; $w_1/w_2 = 4500/600$; $M_1 = 1.00 \times 10^{-10} \text{ mol}$; $M_2 = 7.00 \times 10^{-6} \text{ mol}$. Curve 1: $D_{12} = 5.0 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$; Curve 2: $D_{12} = -7.0 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$; Curve 3: $M_2 = 7.14 \times 10^{-6} \text{ mol}$; Curve 4: $M_2 = 6.86 \times 10^{-6} \text{ mol}$.

in water) and a thermodynamic matrix Γ_{ij} estimated from the UNIQUAC model^(16,29,30) with parameters from Rutter⁽³¹⁾ and Reid *et al.*⁽³³⁾ The dispersion of acetone was measured by the UV detector at 266 nm. The RI detector response was the summation of the glucose and acetone refractive index differences between eluted peak and solvent. Four experiments were performed with 9 to 12 different injections, in each experiment six RI peaks were simultaneously fitted in at least three different combinations of peaks. Within the experimental precision all experiments gave identical results for the main diffusion coefficients: $D_{11} = 0.652 (\pm 0.0004) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ and $D_{22} = 1.167 (\pm 0.003) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. The accuracy of D_{11} is good compared with the literature: $D_{11} = 0.673 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (0.39 wt% glucose).⁽²⁶⁾ The calculation of the cross diffusion coefficient was very imprecise: $D_{12} = 1.0 (\pm 0.2) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. D_{12} was strongly correlated with D_{22} . In these experiments the ratio w_1/w_2 was 850/6000. From the RI curves, D_{12} could not be calculated accurately. The maximum difference between the ternary peak and the sum of two binary peaks (*i.e.*, $D_{12} = 0$), caused by an inaccuracy of 1% in the injected amounts M_1 and M_2 was much larger than that caused by a cross coefficient of $5 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, independent of the injected amounts M_1 and M_2 (Table IV). Noise masks these differences.

Table IV. Deviation [%] in the Dispersion Peak for the Glucose(1) + Acetone(2) + Water(0) System^a

Injected amount		as a result of an inaccuracy of				compared with $D_{12} = 0$, if	
M_1 [10 ⁻³ mol]	M_2 [10 ⁻³ mol]	1% in M_1	2% in M_1	1% in M_2	2% in M_2	$D_{12} = 0.05$ [10 ⁻⁹ m ² -s ⁻¹]	$D_{12} = 0.1$ [10 ⁻⁹ m ² -s ⁻¹]
-0.140	0.020	2.8	5.7	3.8	7.7	1.3	2.7
-0.140	0.010	3.1	6.2	2.1	4.2	0.73	1.5
-0.140	-0.0005	1	1.9	0.03	0.07	0.011	0.023
-0.050	0.010	1.1	2.2	2.1	4.4	0.75	1.5

^aUnits as in Table I.**5.2.3. Methanol(1) + Acetone(2) + Water(0)**

This ternary system was extensively tested. For the calculation of the density of solutions, prepared by mass, equations of the form

$$\rho_{ij} = \sum_m A_m x_{i,b}^m \quad (9)$$

and

$$\rho_{ijk} = (\rho_{ij})^{x_{ij}}(\rho_{jk})^{x_{jk}}(\rho_{ik})^{x_{ik}} \quad (10)$$

were used, in which $x_{i,b}$ is the mole fraction of component i in the binary system of components i and j , x_i the mole fraction of component i in the ternary system of components i , j , and k ; $x_{i,b} = x_i/(x_i + x_j)$ and $x_{ij} = (x_i + x_j)/2$. ρ_{ij} is the density of the binary system of components i and j at composition $x_{i,b}$, and ρ_{ijk} is the density of the ternary system. Similar equations were used for the viscosity of the solutions. These equations were fitted to the experimental values of Noda *et al.*⁽³⁴⁾ The values of the constants A_m are given in Tables Va and Vb. The mean relative deviation of the calculated value vs. the experimental value was 0.006 for the density and 0.05 for the viscosity of the ternary system. The injected amounts of components 1 and 2, M_1 and M_2 , were calculated from the sample volume and the density

Table Va. Constants of Eq. (9) for Calculation of the Density of the Methanol(1) + Acetone(2) + Water(0) System.^a

comp.i	comp.j	A_0	A_1	A_2	A_3	A_4
methanol	water	996.887	-275.817	152.202	-162.454	75.793
acetone	water	996.880	-399.668	260.633	-73.227	
methanol	acetone	784.713	13.886	-12.194	19.387	-19.070

^aUnits, kg-cm⁻³.

Table Vb. Constants of Eq. (9) for Calculation of the Viscosity of the Methanol(1) + Acetone(2) + Water(0) System^a

comp.i	comp.j	A_0	A_1	A_2	A_3	A_4	A_5
methanol	water	0.8803	5.8337	-11.7715	1.4854	10.1519	-5.8959
acetone	water	0.8901	8.3422	-41.1046	72.4864	-57.5002	17.2709
methanol	acetone	0.3850	0.3530	-1.5645	3.5076	-3.2706	1.2790

^aUnits mPa-s.

equations with an inaccuracy of $\pm 2\%$. The elements of the thermodynamic matrix Γ_{ij} were estimated from the multicomponent form of the UNIQUAC model^(16,29,30); parameters used are listed in Table Vc.⁽³⁵⁾

Preliminary type 1 experiments (see fitting procedures) were performed with pure water and very dilute solutions of methanol ($x_1 = 0.002$) and acetone ($x_2 = 0.001$) as solvents, and injection solutions of 20 different concentrations ($Gr < 100$). The flow rate was $0.12 \text{ cm}^3\text{-min}^{-1}$. Methanol was detected by the UV detector at 266 nm. Both detectors were linear with concentration according to Eq. (8). No adsorption at the wall was observed. The calculated diffusion coefficients D_{11} and D_{22} were independent of the injected amounts. Simultaneous injection of both components or separate injection did not influence the values of the calculated diffusion coefficients. Results are listed in Tables VIa and VIb, type 1.

Next, experiments were performed for the ternary system of type 2: methanol(1) + acetone(2) + water(0). Binary mixtures of methanol + water were used as solvents. The flow rate was $0.12 \text{ cm}^3\text{-min}^{-1}$. Injection solutions were prepared in vials to give four different values of M_1 with $M_2 = 0$, 4 different values of M_2 with $M_1 = 0$, and 6 to 12 different combinations of M_1 and M_2 ; the methanol-solely and acetone-solely injections were made twice. To minimize the inaccuracy, only one injection was made from each vial. From the methanol injections the binary diffusion coefficient D_{11} was calculated. The binary diffusion coefficient D_{22} was calculated from the UV signals and was independent of the injected amounts of methanol and acetone. Comparison of the binary diffusion coefficients with the literature^(6,36) showed good agreement (Fig. 3). The ternary diffusion coefficients D_{11} , D_{22} , and D_{12}

Table Vc. UNIQUAC-Parameters of the Methanol(1) + Acetone(2) + Water(0) System

i	comp.	r	q	q'	A_{i0}	A_{i1}	A_{i2}
0	water	0.92	1.4	1	0	-259.596	-155.31
1	methanol	1.43	1.43	0.96	402.77	0	-119.144
2	acetone	2.5735	2.336	2.336	733.82	429.104	0

Table VIa. Diffusion Coefficients and Detector Sensitivity Ratio at 25°C for the System Methanol(1) + Acetone(2) + Water(0)^a

x_1	x_2	Separate Fit				Simultaneous Fit					
		w_1/w_2	$D_{11\text{-RI}}$	$D_{22\text{-RI}}$	$D_{22\text{-UV}}$	w_1/w_2	D_{11}	D_{22}	D_{12}	$D_{12,f}$	D_{21}
type 1											
0.000	0.000	0.17	1.566	1.299	1.295	0.15	1.649	1.301			
0.000	0.001		1.575	1.292	1.288	0.19	1.658	1.301			
0.002	0.000	0.19	1.568	1.291	1.287	0.22	1.579	1.293			
type 2											
0.000	0.000		1.566		1.295	0.15					
0.041	0.000		1.405		1.158	0.18	1.404	1.174	-0.013	0.080	
0.086	0.000		1.276		1.051	0.17	1.320	1.139	-0.486	0.089	
0.207	0.000		1.047		0.950	0.21	1.168	0.940	-0.169	-0.259	
0.299	0.000		0.941		1.000	0.03				0.012	
0.411	0.000		0.964		1.119	-0.20	0.971	1.117	-0.485	-0.471	
0.478	0.000		1.018		1.205	-0.46	1.020	1.263	-0.300	-0.413	
0.553	0.000		1.144		1.362	-1.59	1.145	1.360	-0.436	-0.439	
0.641	0.000		1.294		1.565	-34.52	1.296	1.563	-0.475	-0.475	
0.747	0.000		1.576		1.875	1.77	1.557	1.879	-0.548	-0.524	
0.878	0.000		1.805		2.344	0.96	1.788	2.299	-0.892	-0.909	
1.000	0.000		2.172		3.014	-5.13 ^b	2.36 ^b	2.56 ^b			
type 3											
0.092	0.025					0.14	1.093	0.914	-0.149		-0.119
0.624	0.229					0.89	2.230	2.000	-0.229		-0.189
0.198	0.010					0.09	0.868	0.913	-0.086		-0.039
						^c	0.887	0.882	-0.073		-0.031
0.196	0.020					0.07	0.867	0.930	-0.085		-0.028

^aUnits as in Table I.^bInaccurate.^c $w_{2,UV} = 0.00032 \text{ [AU}\cdot\text{m}^3\cdot\text{mol}^{-1}\text{]}$

were calculated by simultaneously fitting 6 RI peaks, each with a different value of M_1 and M_2 . Starting values were the results of the binary fits and $D_{12} = 0$ or D_{12} estimated using Eq. (6). The values of the main diffusion coefficients, obtained from six different groups of six peaks, agreed well within the precision of the fitting procedure, except for the cross diffusion coefficient at low methanol mole fractions. The precision of the ratio of the detector sensitivities w_1/w_2 was more dependent on the chosen combination of dispersion peaks. For systems at low mole fractions of methanol (x_1 below 0.4 to 0.5) D_{12} was very imprecise. The fitting procedures for the experiment at methanol mole fraction 0.3 did not converge. At this mole fraction the main diffusion coefficients, and the eigenvalues of the diffusion coefficient matrix, are nearly identical, and it is difficult to determine the ternary diffusion

Table VIb. Imprecision (%) of Diffusion Coefficients and Detector Sensitivity Ratio at 25°C for the Methanol(1) + Acetone(2) + Water(0) System

x_1	x_2	separate fit				simultaneous fit					
		w_1/w_2	D_{11-RI}	D_{22-RI}	D_{22-UV}	w_1/w_2	D_{11}	D_{22}	D_{12}	$D_{12,f}$	D_{21}
type 1											
0.000	0.000	6.9	0.5	0.3	0.1	0.7	1.3	0.4			
0.000	0.001			1.0	0.4	1.6	2.7	0.9			
0.002	0.000	26	0.03	0.1	0.2	1.0	1.6	0.7			
type 2											
0.000	0.000		0.5		0.1	0.7					
0.041	0.000		0.1		0.2	0.2	0.4	1.1	145	7.7	
0.086	0.000		0.6		0.3	0.2	0.5	0.7	23	6.7	
0.207	0.000		2.5		0.2	3.1	6.2	7.9	542	24	
						73	3.4	1.1	75	58	
0.299	0.000		2.9		0.2	0.2				9.2	
0.411	0.000		0.5		0.1	0.3	0.6	0.9	22	1.0	
0.478	0.000		0.1		0.2	0.3	0.4	0.9	17	0.8	
0.553	0.000		1.1		0.2	0.2	0.2	0.6	8.8	0.3	
0.641	0.000		0.8		0.2	2.2	0.1	0.3	3.4	0.1	
0.747	0.000		0.7		0.5	0.1	0.1	0.5	5.2	0.2	
0.878	0.000		0.9		0.2	0.7	0.6	2.0	12	0.4	
1.000	0.000		1.2		0.1	-81 ^a	11 ^a	176 ^a			
type 3											
0.092	0.025					92	0.4	5.4	15		8.5
0.624	0.229					14	5.4	3.8	55		39
0.198	0.010					254	0.6	8.5	95		17
						0.2 ^b	0.3	8.5	129		9.2
0.196	0.020					65	0.6	11	120		17

^ainaccurate.^b $w_{2,UV} = 0.00032$ [AU-m³-mol⁻¹].

coefficient by any method.⁽³⁷⁾ The cross diffusion coefficient D_{12} was also calculated with fixed values of D_{11} , the binary RI diffusion coefficient, and D_{22} , the binary UV diffusion coefficient. However, in this case the value of D_{12} was more dependent on the chosen combination of fitted peaks and the fixed value of D_{22} , caused by the strong correlation between D_{12} and D_{22} . Results are shown in Tables VIa and VIb, type 2 and Fig. 3. It was impossible to calculate the cross diffusion coefficient D_{12} with even moderate imprecision from the measured dispersion peaks for a mole fraction of methanol less than about 0.5. This was caused by an unfavorable combination of the relative detector sensitivity and the values of the diffusion coefficients as can be seen in Figs. 4a and 4b. For $x_1 < 0.45$ the ternary effects were masked by the experimental inaccuracy.

Fig. 3. Ternary diffusion coefficients of the system methanol(1) + acetone(2) + water(0) at 25°C and $x_2 = 0$. $\square$, D_{11} -RI; $\diamond$, D_{22} -UV; $\triangle$, D_{12} -fixed; $\times$, D_{11} -tern.; $+$, D_{22} -tern.; $*$, D_{12} -tern.; $\circ$, D_{11} (Ref. 6); $-$, D_{22} (Ref. 36).

From the ternary experiments of type 3 with high acetone concentrations only RI signals were available, except for the experiment with $x_2 = 0.01$; in this case the UV signals measured at a wavelength of 208 nm (a minimum in the UV spectrum of acetone) appeared to be linear with concentration. The experimental procedure was similar to the type 2 procedure. Starting values for the fitting procedure were values close to the binary D_{11} and the "binary" D_{22} calculated from the methanol-solely and acetone-solely injections, or calculated from a type 1 fitting procedure of two or more peaks simultaneously. The cross diffusion coefficients were estimated using Eq. (6). Results are shown in Tables VIa and IVb, type 3. The precision of the calculated diffusion coefficients, especially of the cross coefficients, was low and dependent on the chosen combination of peaks as well as the starting values of the fitting parameters. Moreover, there were severe convergence problems, caused by the strong correlation between the diffusion coefficients. The influence of the imprecision of the experimental procedure (determination of the injected amounts

Fig. 4. (a) Relative detector sensitivity and diffusion coefficients of the system methanol(1) + acetone(2) + water(0) at 25°C and $x_2 = 0$. $\diamond$, $\text{abs}(w_1/w_2)$; $\square$, $\text{abs}(D_{11}/D_{22})$; $\triangle$, $\text{abs}(D_{12}/D_{22})$. (b) Minimum measurable value of D_{12}/D_{22} for the system methanol(1) + acetone(2) + water(0) at 25°C and $x_2 = 0$. —, $\text{abs}(D_{12}/D_{22}) = 0.5$; ---, $\text{abs}(D_{12}/D_{22}) = 0.3$; ·····, $\text{abs}(D_{12}/D_{22}) = 0.2$; -·-·-·-, $\text{abs}(D_{12}/D_{22}) = 0.1$; -·-·-·-, $\text{abs}(D_{12}/D_{22}) = 0.05$.

and the relative detector sensitivity) on the measured dispersion profiles was much stronger than the ternary diffusion effects (Fig. 5). Therefore, the RI detector was not suited for the measurement of this ternary system.

Because only a refractive index detector could be used for the in-line detection of the component concentrations of the system methanol(1) + acetone(2) + water(0) (for acetone concentrations above 1 vol%), the type 3 ternary diffusion measurements of this system could not be performed by the Taylor dispersion method.

Fig. 5. Influence of the inaccuracy of the diffusion coefficients, injection amount, detector sensitivity, and residence time on the deviation in the peak maximum ($t = \tau$) of the detected ternary signal compared to the ideal ternary signal, calculated by Eq. (2) Parameters of the ideal ternary signal: $D_{11} = 1.10 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$; $D_{22} = 9.1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$; $D_{12} = -1.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$; $D_{21} = -1.2 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$; $w_1/w_2 = 0.14$; $M_1 = 8.00 \times 10^{-6} \text{ mol}$; $M_2 = 1.00 \times 10^{-6} \text{ mol}$; $\tau = 10110 \text{ s}$. — Δ —, D_{12} ; — $\diamond$ —, D_{21} ; — $\square$ —, D_{11} ; — $\circ$ —, D_{22} ; — $\times$ —, M_1 ; — $+$ —, M_2 ; — $\bullet$ —, w_1/w_2 ; — $\blacksquare$ —, τ .

6. CONCLUSIONS

The Taylor dispersion method is an accurate and convenient technique for measuring diffusion coefficients in binary systems. In ternary systems the calculation of the main and cross diffusion coefficients from the measured dispersion profiles is only possible under certain conditions depending on the ratio of the injected amounts M_1/M_2 , the relative detector sensitivity w_1/w_2 , the values of the diffusion coefficients and the noise level. The measurement of accurate dispersion profiles of the components is often hindered by an unfavorable relative sensitivity of the in-line detector used. For moderate cross-diffusion coefficients the imprecision of the experimental procedure can mask the ternary diffusion effects in the dispersion profiles and the diffusion coefficients may not be calculated correctly. This is shown for the system methanol + acetone + water. If the methanol mole fraction is less than 0.45 or the acetone mole fraction is more than 0.001, the only usable refractive index detector is unsuitable for measuring the dispersion profiles accurately enough to determine the main diffusion coefficients as well as the cross-diffusion coefficients. Another experimental technique, such as the diaphragm cell method, has to be used.

ACKNOWLEDGMENTS

We thank F.G. Kieviet and A.J.P.M. Staring for their technical support, G.D. Mooiweer for advice on the calculations and Stichting Scheikundig Onderzoek in Nederland for financial support.

REFERENCES

1. C. Erkey and A. Akgerman, in *Measurement of the transport properties of fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds., (Blackwell Scientific Publications, Oxford, U.K., 1991) Chap. 9, p. 251.
2. G. Taylor, *Proc. Roy. Soc. Lond. A* **219**, 186 (1953).
3. G. Taylor, *Proc. Roy. Soc. Lond. A* **225**, 473 (1954).
4. R. Aris, *Proc. Roy. Soc. Lond. A* **235**, 67 (1956).
5. A. Alizadeh, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophysics* **1**, 243 (1980).
6. I. M. J. J. Van de Ven-Lucassen, F. G. Kieviet, and P. J. A. M. Kerkhof, *J. Chem. Eng. Data* **40**, 407 (1995).
7. D. G. Leaist, *J. Phys. Chem.* **94**, 5180 (1990).
8. D. G. Leaist, L. Hao, and R. Ibrahimov, *J. Chem. Soc. Faraday Trans.* **89**, 515 (1993).
9. D. G. Leaist, *J. Solution Chem.* **20**, 175 (1991).
10. D. G. Leaist, *J. Chem. Soc., Faraday Trans. I* **87**, 597 (1991).
11. Z. Deng and D. G. Leaist, *Can. J. Chem.* **69**, 1548 (1991).
12. Z. Deng and D. G. Leaist, *J. Solution Chem.* **21**, 15 (1992).
13. D. G. Leaist and L. Hao, *J. Phys. Chem.* **97**, 1464 (1993).
14. D. G. Leaist and L. Hao, *J. Phys. Chem.* **98**, 4702 (1994).
15. W. E. Price, *J. Chem. Soc., Faraday Trans. I* **84**, 2431 (1988).
16. R. Taylor and R. Krishna, *Multicomponent Mass Transfer* (Wiley, New York, 1993).
17. H. L. Toor, *A. I. Ch. E. Journal* **10**, 448 (1964).
18. D. G. Miller, V. Vitagliano, and R. Sartorio, *J. Phys. Chem.* **90**, 1509 (1986).
19. L. Onsager, *Ann. N. Y. Acad. Sci.* **46**, 241 (1945).
20. P. J. Dunlop, *J. Phys. Chem.* **68**, 26 (1964).
21. R. P. Wendt, *J. Phys. Chem.* **69**, 1227 (1965).
22. P. J. A. M. Kerkhof, *Chem. Eng. J.* **64**, 319 (1996), app. D.
23. I. N. Levine, *Physical Chemistry*, 4th edn. (McGraw-Hill, New York, 1995) chap. 10.
24. P. J. Dunlop, *J. Phys. Chem.* **69**, 4276 (1965).
25. W. Loh, C. A. Tonegutti, and P. L. O. Volpe, *J. Chem. Soc. Faraday Trans.* **89**, 113 (1993).
26. R. C. Weast, *Handbook of Chemistry and Physics*, 52nd edn. (CRC Press, 1971–1972).
27. V. Ananthakrishnan, W. N. Gill and A. J. Barduhn, *A. I. Ch. E. Journal* **11**, 1063 (1965).
28. M. T. Tyn and W. F. Calus, *J. Chem. Eng. Data* **20**, 310 (1975).
29. D. S. Abrams and J. M. Prausnitz, *A. I. Ch. E. Journal* **21**, 116 (1975).
30. T. F. Anderson and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* **17**, 552 (1978).
31. Ph. W. M. Rutten, *Diffusion in Liquids*, Dissertation (Delft University Press, Delft, 1992).
32. E. A. Macedo and P. Rasmussen, *Liquid-Liquid Equilibrium Data Collection. Suppl. Chemistry Data Series V*, (Dechema, Frankfurt am Main, 1979) Part 3, p. 402.
33. R. C. Reid, J. M. Prausnitz, and B. Poling, *The Properties of Gases and Liquids* 4th edn. (McGraw-Hill, New York, 1987).
34. K. Noda, M. Ohashi, and K. Ishida, *J. Chem. Eng. Data* **27**, 326 (1982).

35. J. Gmehling, U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection. Aqueous-Organic Systems. Suppl. 1, Chemistry Data Series I*, (Dechema, Frankfurt am Main, 1981) part 1a.
36. A. Alimadadian and C. Ph. Colver, *Can. J. Chem. Eng.* **54**, 208 (1976).
37. D. G. Miller, J. G. Albright, R. Mathew, C. M. Lee, J. A. Rard, and L. B. Eppstein, *J. Phys. Chem.* **97**, 3885 (1993).