Measurement of Ternary Mutual Diffusion Coefficients from Ill-Conditioned Taylor Dispersion Profiles in Cases of Identical or Nearly Identical Eigenvalues of the Diffusion Coefficient Matrix[†]

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Taylor dispersion has gained popularity for the measurement of mutual diffusion coefficients (D_{ik}) for multicomponent solutions. In practice, however, the analysis of dispersion profiles, like the analysis of free-diffusion boundaries measured by optical interferometry, becomes ill-conditioned for solutes of similar diffusivities if the eigenvalues of the D_{ik} matrix differ by less than about (5 to 10) %. These numerical difficulties, well-known in studies of multiexponential decays with nearly identical decay constants, can produce large errors in measured D_{ik} coefficients and even rule out studies of important systems, including solutions of isomers, oligomers, polydisperse polymers, strongly associated solutes, and mixed electrolytes composed of ions of similar mobility. To investigate diffusion in these systems, equations are derived for the Taylor dispersion profiles produced by ternary mutual diffusion with equal eigenvalues. Using these equations, a simple least-squares procedure is developed to evaluate D_{ik} coefficients from equal-eigenvalue profiles. D_{ik} coefficients are reported from the analysis of severely ill-conditioned refractive-index profiles measured for aqueous solutions of 1-propanol + 2-propanol, 1-propanol + glycine, and mannitol + tetra(ethyleneglycol). In cases where the eigenvalues are not identical, but differ by several percent, the resulting errors in the D_{ik} coefficients are estimated to be small and similar in magnitude to the accuracy of the Taylor measurements.

Introduction

Mutual diffusion (also called chemical interdiffusion) provides mixing on the molecular level that is essential for a wide range of physical and chemical processes.[1–4] Important examples include chemical and electrochemical reactions, crystal growth and dissolution, gas absorption, sedimentation equilibrium, transport across membranes, cell metabolism, and the transmission of nerve impulses. In contrast to self-diffusion, which occurs without mass transport in systems of uniform chemical composition, mutual diffusion refers to the fluxes of solution components caused by composition differences and the resulting chemical potential gradient driving forces. Because mutual diffusion fluxes are coupled, mutual diffusion in a multicomponent solution of N solutes is described by N^2 mutual diffusion coefficients (D_{ik})

$$J_i = -\sum_{k=1}^{N} D_{ik}\nabla C_k \qquad i = 1, 2, 3, ..., N \tag{1}$$

This set of equations[5,6] reduces to Fick's well-known law $J = -D\nabla C$ for binary mutual diffusion in solutions of a single solute.

Taylor dispersion has gained popularity in recent years for the reliable and relatively convenient measurement of mutual diffusion in two-,[5–9] three-,[10–18] and four-component[19–22] solutions. The usual procedure is to inject small samples of solution into laminar carrier streams of solution flowing through a capillary tube. Mutual diffusion coefficients are calculated from the broadened distribution of the dispersed samples measured at the tube outlet by a detector, usually a high-precision differential refractometer fitted with a flow cell. Dispersion equipment is commercially available, inexpensive, and readily automated. Errors from convection, the traditional enemy of mutual diffusion measurements, are eliminated by confining diffusion within narrow-bore tubing.[23] This feature is especially important for studies of multicomponent solutions because coupled diffusion in these systems can produce density inversions and convection[23–26] in free solution columns, even if the lower solution is initially denser than the upper solution.

Though not widely appreciated, the analysis of multicomponent dispersion profiles,[27] like the analysis of free-diffusion boundaries measured by optical interferometry,[28–30] suffers from numerical ill conditioning for solutes of similar diffusivities when the eigenvalues ($D^{(i)}$) of the D_{ik} matrix differ by less than about 10 %. Related difficulties are well-known in studies of multiexponential decays with nearly identical time constants.[31,32] In practice, ill conditioning can produce large errors in the measured diffusion coefficients and even rule out studies of solutes with similar diffusivities. Systems prone to ill conditioning include solutions of isomers, oligomers, polydisperse polymers,[33,34] mixed surfactants[21,35] and other strongly associating solutes,[36] mixed electrolytes[27–29,37] composed of ions of similar mobilities (e.g., aqueous K^+, Cs^+, NH_3^+, Cl^-, I^-, Br^-, NO_3^- ions), and solutions near critical points.[35,38,39] As future work on multicomponent diffusion evolves into studies of systems with larger numbers of components and eigenvalues, the probability of ill conditioning will increase.

One strategy for reducing the effects of ill conditioning is to monitor dispersion profiles with two independent bulk-property detectors, such as a differential refractometer in series with a conductivity detector.[27] Alternatively, solute-specific detection

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may be used in cases where suitable absorption bands exist and appropriate detectors are available.[40–42] These detection methods hold considerable promise but are not yet generally applicable. Similar considerations apply to multicomponent diffusion measurements using magnetically stirred diaphragm cells.[43–46] This technique can be used to reduce errors from ill conditioning if chemical titration or another analytical procedure can be devised for the precise determination of individual solute concentrations. Unfortunately, despite considerable potential, multicomponent diaphragm-cell experiments are inconveniently long (days or weeks for measurements at a single composition) and rarely used.

In the work reported here, prompted by the challenge of measuring diffusion for ill-conditioned systems, equations are derived for the dispersion profiles produced by ternary mutual diffusion

$$J_1(\text{solute } 1) = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \qquad (2)$$

$$J_2(\text{solute } 2) = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \qquad (3)$$

with equal eigenvalues of the D_{ik} matrix. These equations are used to develop a simple least-squares procedure for the evaluation of mutual diffusion coefficients from changes in the refractive index measured across equal-eigenvalue dispersion profiles.

Ternary mutual diffusion with equal eigenvalues can be arranged, in principle, for solutions of two solutes with identical limiting diffusion coefficients, $D°$. Provided the solutes are nonionic and nonassociating, solute–solute interactions will be negligible for sufficiently dilute solutions. Cross-coefficients D_{12} and D_{21} will vanish for these solutions, and main coefficients D_{11} and D_{22} will equal their limiting values. Under these conditions, the eigenvalues of the D_{ik} matrix will be identical and equal to $D°$. Conveniently, the limiting diffusion coefficients of aqueous mannitol[47] and aqueous tetra(ethyleneglycol)[48] determined by Gouy interferometry ($0.666_4 \cdot 10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}$ and $0.666 \cdot 10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}$, respectively, at 25 °C) are identical within the high precision of the measurements (about 0.3 %). Accordingly, the procedure for measuring equal-eigenvalue ternary mutual diffusion coefficients developed in this paper is tested for dispersion profiles measured for dilute aqueous mannitol + tetra(ethyleneglycol) solutions. Additional data are reported from the analysis of severely ill-conditioned profiles for ternary aqueous solutions of 1-propanol + glycine and 1-propanol + 2-propanol. The dispersion profiles for these solutions resisted all attempts at analysis using conventional methods developed previously for systems with distinct eigenvalues of the D_{ik} matrix.

The proposed evaluation of D_{ik} coefficients from ill-conditioned dispersion profiles is based on the assumption of equal eigenvalues of the D_{ik} matrix. This assumption will lead to systematic errors in the measured D_{ik} coefficients when the analysis is applied to systems with eigenvalues that are not identical but are too close to be resolved. A procedure for estimating these errors suggests they are small (about $\pm 0.01 \cdot 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$) and similar in magnitude to the accuracy of Taylor dispersion measurements.

Experimental Section

A metering pump maintained a steady flow of carrier solution through a Teflon dispersion tube (length 3000 cm, inner radius 0.0390_7 cm). The tube was coiled in the form of a helix of radius 40 cm and held at 25.0 °C in a thermostat. Solution samples containing (0.01 to 0.05) $\text{mol}\cdot\text{dm}^{-3}$ excess solute relative to the carrier stream were injected at the tube inlet through a six-port valve fitted with a 0.020 cm^3 loop. A differential refractometer high-performance liquid chromatography (HPLC) detector (Agilent model 1100) monitored the dispersion profiles at the tube outlet. The refractometer output voltage was measured at timed intervals using a digital voltmeter. Flow rates were adjusted to give retention times of about $1.5 \cdot 10^4$ s. The solutions used for the dispersion measurements were prepared by dissolving weighed amounts of reagent-grade solutes (purity > 99 %) in distilled, deionized water in volumetric flasks. Tetra(ethyleneglycol) and the propanols were purchased from Sigma. The mannitol and glycine were BDH Analar products.

Binary Diffusion. A few diffusion measurements were made on binary aqueous solutions of the solutes. In these experiments, samples of solution containing solute at concentration $C_\infty + \Delta C$ were injected into laminar carrier solutions of composition C_∞. At time t after an injection, the concentration of dispersed solute flowing through the detector cell at the tube outlet is[5–9]

$$C(t) = C_\infty + \frac{2\Delta C \Delta V}{r^3 u}\sqrt{\frac{3D}{\pi^3 t}}\exp\left(-\frac{12D(t - t_R)^2}{r^2 t}\right) \qquad (4)$$

Equation 4 is valid for liquid solutions with D values on the order of $10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}$ and negligible diffusion along the axis of the dispersion tube ($D^2 \ll u^2 r^2/48$). ΔV is the volume of the injected solution sample, r is the inner radius of the tube, and $t_R = L/u$ is the retention time for samples flowing at mean speed u in a dispersion tube of length L. The initial concentration differences were kept sufficiently small to ensure that the changes in the detector signal $V(t)$ would be proportional to the changes in solute concentration across the dispersion profiles, $V(t) - V_\infty = R[C(t) - C_\infty]$, where $R = dV/dC$ is the detector sensitivity. Adding the linear baseline $V_\infty + V_1 t$ to allow for small drifts in the detector signal gives the working expression

$$V(t) = V_\infty + V_1 t + \Delta V_{\max}\sqrt{\frac{t_R}{t}}\ \exp\left(-\frac{12D(t - t_R)^2}{r^2 t}\right) \qquad (5)$$

for the measured dispersion profile. $\Delta V_{\max} = R[C(t_R) - C_\infty]$ is the peak height relative to the baseline. Binary mutual diffusion coefficients D were evaluated by fitting eq 5 to measured detector signals, treating D, t_R, $\Delta V_{\max}$, V_∞, and V_1 as adjustable least-squares parameters. The estimated accuracy of the D values is (1 to 2) %.

Retention times are typically long enough to ensure that $(t - t_R)^2/t$ and $(t - t_R)^2/t_R$ are nearly identical across typical dispersion profiles. Under these conditions, binary dispersion profiles closely resemble Gaussian peaks centered on time t_R with variance $\sigma^2 = r^2 t_R/24D$.

Ternary Dispersion Profiles: Distinct Eigenvalues. Ternary dispersion profiles are generated by introducing samples of solution containing solutes at concentrations $C_{1\infty} + \Delta C_1$ and $C_{2\infty} + \Delta C_2$ into carrier streams of composition $C_{1\infty}$ and $C_{2\infty}$. In this section, the equations describing ternary profiles in cases of distinct eigenvalues ($D^{(1)} \neq D^{(2)}$) of the D_{ik} matrix

$$D^{(1)} = \frac{D_{11} + D_{22} + (D_{11} - D_{22})\sqrt{1 + [4D_{12}D_{21}/(D_{11} - D_{22})^2]}}{2} \qquad (6)$$

$$D^{(2)} = \frac{D_{11} + D_{22} - (D_{11} - D_{22})\sqrt{1 + [4D_{12}D_{21}/(D_{11} - D_{22})^2]}}{2} \qquad (7)$$

are briefly summarized. These equations are used in the following section to derive expressions for dispersion profiles produced by diffusion with equal eigenvalues.

For ternary solutions with distinct eigenvalues, Price[10] derived

$$C_1(t) = C_{1\infty} + \frac{2\Delta V}{r^3 u}\sqrt{\frac{3}{\pi^3 t}}[A_{11}\sqrt{D^{(1)}}\exp(-D^{(1)}\eta) + A_{12}\sqrt{D^{(2)}}\exp(-D^{(2)}\eta)] \tag{8}$$

$$C_2(t) = C_{2\infty} + \frac{2\Delta V}{r^3 u}\sqrt{\frac{3}{\pi^3 t}}[A_{21}\sqrt{D^{(1)}}\exp(-D^{(1)}\eta) + A_{22}\sqrt{D^{(2)}}\exp(-D^{(2)}\eta)] \tag{9}$$

for the concentration profiles at the outlet of the dispersion tube at time t after the injection. η is an abbreviation for $12(t - t_R)^2/r^2t$ and the A_{ik} coefficients are defined as follows

$$A_{11} = \frac{(D_{22} - D^{(1)})\Delta C_1 - D_{12}\Delta C_2}{D^{(2)} - D^{(1)}} \tag{10}$$

$$A_{12} = \frac{(D_{22} - D^{(2)})\Delta C_1 - D_{12}\Delta C_2}{D^{(1)} - D^{(2)}} \tag{11}$$

$$A_{21} = \frac{(D_{11} - D^{(1)})\Delta C_2 - D_{21}\Delta C_1}{D^{(2)} - D^{(1)}} \tag{12}$$

$$A_{22} = \frac{(D_{11} - D^{(2)})\Delta C_2 - D_{21}\Delta C_1}{D^{(1)} - D^{(2)}} \tag{13}$$

Using $R_1 = (\partial V/\partial C_1)_{C2}$ and $R_2 = (\partial V/\partial C_2)_{C1}$ to denote the detector sensitivities for the solutes gives

$$V(t) = V_\infty + V_1 t + R_1[C_1(t) - C_{1\infty}] + R_2[C_2(t) - C_{2\infty}] \tag{14}$$

for the detector signal. Substituting the expressions for $C_1(t)$ and $C_2(t)$ into eq 14 and including the linear baseline terms leads to the working equation

$$V(t) = V_\infty + V_1 t + \Delta V_{\max}\sqrt{\frac{t_R}{t}}[W_1\exp(-D^{(1)}\eta) + (1 - W_1)\exp(-D^{(2)}\eta)] \qquad (D^{(1)} \neq (D)^{(2)}) \tag{15}$$

for the detector signal. The normalized weights W_1 and $1 - W_1$ of the exponential terms are given by

$$W_1 = \frac{(R_1A_{11} + R_2A_{21})\sqrt{D^{(1)}}}{(R_1A_{11} + R_2A_{21})\sqrt{D^{(1)}} + (R_1A_{12} + R_2A_{22})\sqrt{D^{(2)}}} \tag{16}$$

In this case (distinct eigenvalues), the detector signals for ternary diffusion resembles two superimposed Gaussian curves centered on time t_R with variances $r^2t_R/24D^{(1)}$ and $r^2t_R/24D^{(2)}$.

Direct D_{11}−D_{12}−D_{21}−D_{22} Fitting Procedure. Ternary dispersion profiles were first analyzed by fitting eq 15 to the measured detector signals, treating D_{11}, D_{12}, D_{21}, and D_{22} as adjustable least-squares parameters. Additional fitting parameters for each profile included the retention time t_R, peak height $\Delta V_{\max}$, and the baseline parameters V_∞ and V_1. Details of this procedure can be found in ref 11.

$D^{(1)}$−$D^{(2)}$−a−b Fitting Procedure. The eigenvalues and the A_{ik} coefficients in the expression for the detector signal are cumbersome functions of the D_{ik} coefficients. To simplify the analysis of ternary dispersion profiles (and the corresponding analysis of free-diffusion profiles[28,29] in Gouy and Rayleigh interferometric experiments), it is customary to define the a and b parameters[12]

$$a = \frac{D_{11} - D^{(1)} - (R_1/R_2)D_{12}}{D^{(2)} - D^{(1)}} \tag{17}$$

$$b = \frac{D_{22} - D_{11} + (R_2/R_1)D_{21} - (R_1/R_2)D_{12}}{D^{(2)} - D^{(1)}} \tag{18}$$

Using α_1 to denote the fraction of the initial refractive difference contributed by solute 1

$$\alpha_1 = \frac{R_1\Delta C_1}{R_1\Delta C_1 + R_2\Delta C_2} \tag{19}$$

gives

$$W_1 = \frac{(a + b\alpha_1)\sqrt{D^{(1)}}}{(a + b\alpha_1)\sqrt{D^{(1)}} + (1 - a - b\alpha_1)\sqrt{D^{(2)}}} \tag{20}$$

If ill conditioning is not severe, the eigenvalues $D^{(1)}$ and $D^{(2)}$ and the a and b parameters can be reliably evaluated by using nonlinear least-squares to fit eq 15 to dispersion profiles measured for two or more different values of α_1, such as $\alpha_1 = 0$ (initial gradient in solute 2) and $\alpha_1 = 1$ (initial gradient in solute 1). The four ternary mutual coefficients are calculated from $D^{(1)}$, $D^{(2)}$, a, and b as follows[12]

$$D_{11} = D_1 + \frac{a(1 - a - b)}{b}(D^{(1)} - D^{(2)}) \tag{21}$$

$$D_{12} = \frac{R_2}{R_1}\frac{a(1 - a)}{b}(D^{(1)} - D^{(2)}) \tag{22}$$

$$D_{21} = \frac{R_1}{R_2}\frac{(a + b)(1 - a - b)}{b}(D^{(2)} - D^{(1)}) \tag{23}$$

$$D_{22} = D_2 + \frac{a(1 - a - b)}{b}(D^{(2)} - D^{(1)}) \tag{24}$$

The ratio R_1/R_2 of the detector sensitivity to the solutes is conveniently evaluated by taking the ratio of peak areas generated per mole of excess solute 1 and 2 injected into the carrier solution.

Ternary Dispersion Profiles: Equal Eigenvalues. To derive the equations for dispersion profiles in cases of equal eigenvalues of the D_{ik} matrix, it is convenient to define the mean eigenvalue

$$\bar{D} = \frac{D^{(1)} + D^{(2)}}{2} \tag{25}$$

and the eigenvalue difference

$$\Delta D = \frac{D^{(2)} - D^{(1)}}{2} \tag{26}$$

Substituting the expressions for $\bar{D}$ and ΔD into eqs 8 and 9 for distinct-eigenvalue profiles gives

$$C_1(t) = C_{1\infty} + \frac{2}{r^3 u}\sqrt{\frac{3}{\pi^3 t}}(A_{11}\sqrt{\bar{D} - \Delta D} \times \exp[-(\bar{D} - \Delta D)\eta] + A_{12}\sqrt{\bar{D} + \Delta D}\exp[-(\bar{D} + \Delta D)\eta]) \tag{27}$$

$$C_2(t) = C_{2\infty} + \frac{2}{r^3 u}\sqrt{\frac{3}{\pi^3 t}}(A_{21}\sqrt{\bar{D} - \Delta D} \times \exp[-(\bar{D} - \Delta D)\eta] + A_{22}\sqrt{\bar{D} + \Delta D}\exp[-(\bar{D} + \Delta D)\eta]) \tag{28}$$

Noting that the A_{ik} coefficients are inversely proportional to ΔD and taking the limit $\Delta D \rightarrow 0$ gives the equal-eigenvalue concentration profiles

$$C_1(t) = C_{1\infty} + \frac{2\Delta V}{r^3 u}\sqrt{\frac{3\bar{D}}{\pi^3 t}}\Bigg[\Delta C_1 + \frac{(D_{11} - D_{22})\Delta C_1 + 2D_{12}\Delta C_2}{2\bar{D}}\left(\frac{1}{2} - \bar{D}\eta\right)\Bigg]\exp(-\bar{D}\eta) \tag{29}$$

$$C_2(t) = C_{2\infty} + \frac{2\Delta V}{r^3 u}\sqrt{\frac{3\bar{D}}{\pi^3 t}}\Bigg[\Delta C_2 + \frac{(D_{22} - D_{11})\Delta C_2 + 2D_{21}\Delta C_1}{2\bar{D}}\left(\frac{1}{2} - \bar{D}\eta\right)\Bigg]\exp(-\bar{D}\eta) \tag{30}$$

The corresponding detector signal, obtained using eq 14, is

$$V(t) = V_\infty + V_1 t + \Delta V_{\max}\sqrt{\frac{t_R}{t}}\left[1 - \frac{2E + 4F\alpha_1}{4\bar{D} + E + 2F\alpha_1}\bar{D}\eta\right] \times \exp(-\bar{D}\eta) \qquad (D^{(1)} = D^{(2)} = \bar{D}) \tag{31}$$

where E and F are abbreviations for

$$E = D_{22} - D_{11} + 2\frac{R_1}{R_2}D_{12} \tag{32}$$

$$F = D_{11} - D_{22} - \frac{R_1}{R_2}D_{12} + \frac{R_2}{R_1}D_{21} \tag{33}$$

In general, the detector signal produced by equal-eignevalue ternary diffusion consists of a Gaussian peak of variance $\sigma^2 = r^2 t_R/24\bar{D}$ superimposed on a Gaussian peak of variance σ^2 multiplied by $(t - t_R)^2$. If cross-coefficient D_{12} or D_{21} is zero, then $D_{11} = D_{22} = \bar{D}$, and $E = F = 0$; the detector signal simplifies to a single Gaussian peak of variance σ^2.

***$\bar{D}$−E−F* Fitting Procedure.** Nonlinear least-squares procedures may be used to evaluate $\bar{D}$, E, and F by fitting eq 31 to dispersion profiles measured for initial conditions corresponding to two or more different values of α_1. The D_{ik} coefficients can then be evaluated from

$$D_{11} = \bar{D} - \frac{E(E + 2F)}{4F} \tag{34}$$

$$D_{12} = -\frac{R_2}{R_1}\frac{E^2}{4F} \tag{35}$$

$$D_{21} = \frac{R_1}{R_2}\frac{(E + 2F)^2}{4F} \tag{36}$$

$$D_{22} = \bar{D} + \frac{E(E + 2F)}{4F} \tag{37}$$

These relations for the four D_{ik} coefficients follow from eqs 25, 32, and 33 and the requirement

$$(D_{11} - D_{12})^2 + 4D_{12}D_{21} = 0 \qquad (D^{(1)} = D^{(2)}) \tag{38}$$

for equal eigenvalues.

The procedure for the measurement of the D_{ik} coefficients was checked by calculating simulated dispersion profiles from eq 31 for known values of D_{ik}. Appropriate random errors in $V(t)$ were included with standard deviations of about 0.5 % of $\Delta V_{\max}$. The D_{ik} values recovered by least-squares analysis of the profiles agreed with the values used in the simulations within $\pm\ 0.01 \cdot 10^{-5}$ cm$^2 \cdot$s^{-1}, the estimated uncertainty of the results.

Table 1. Binary Mutual Diffusion Coefficients[a] for Aqueous Solutions at 25 °C

solute	C mol·dm^{-3}	D (this work) 10^{-5} cm^2·s^{-1}	D (literature) 10^{-5} cm^2·s^{-1}
mannitol	0.0040	0.661 ± 0.005	0.666_4[47]
tetra(ethyleneglycol)	0.0040	0.658 ± 0.006	0.666[48]
glycine	0.0100	1.049 ± 0.012	1.059[49]
1-propanol	0.0100	1.055 ± 0.002	1.06[50,51]
2-propanol	0.0100	1.032 ± 0.009	1.03[51]

[a] Uncertainties are quoted at the 95 % confidence interval.

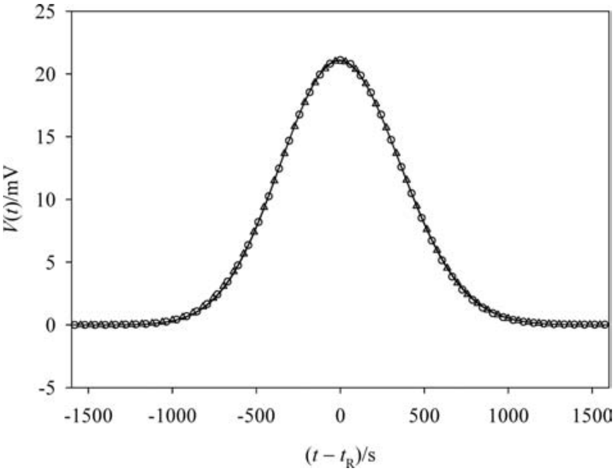

Figure 1. Dispersion profiles measured for a 0.00200 mol·dm^{-3} mannitol (1) + 0.00200 mol·dm^{-3} tetra(ethyleneglycol) (2) carrier stream: ○, initial mannitol gradient ($\alpha_1 = 1.00$, $\Delta C_1 = 0.0177$ mol·dm^{-3}, $\Delta C_2 = 0.0000$ mol·dm^{-3}); △, initial tetra(ethyleneglycol) gradient ($\alpha_1 = 0.00$, $\Delta C_1 = 0.0000$ mol·dm^{-3}, $\Delta C_2 = 0.0200$ mol·dm^{-3}). The initial concentration differences have been adjusted to give peaks of equal height. For clarity, only every fifth data point is plotted.

Results

Binary Solutions. Binary mutual diffusion coefficients were measured for aqueous solutions of mannitol, tetra(ethyleneglycol), glycine, 1-propanol, and 2-propanol. Four to six replicate injections were made into each carrier solution. The average value of D for each composition is listed in Table 1. Good agreement is obtained with the D values interpolated from previously reported Gouy[47–49] and Taylor data.[50,51]

Aqueous Mannitol (1) + Tetra(ethyleneglycol) (2) Solutions. Dispersion profiles were measured for aqueous mannitol (C_1) + tetra(ethyleneglycol) (C_2) carrier solutions containing 0.00400 mol·dm^{-3} total solute at five different C_1:C_2 ratios. Figure 1 shows the profiles generated by injecting excess mannitol ($\alpha_1 = 1$) or excess tetra(ethyleneglycol) ($\alpha_1 = 0$) into a 0.00200 mol·dm^{-3} mannitol + 0.00200 mol·dm^{-3} tetra(ethyleneglycol) carrier solution. The two profiles are virtually superimposable, illustrating the nearly identical eigenvalues of the D_{ik} matrix for this system.

Not surprisingly, the analysis of the mannitol + tetra(ethyleneglycol) profiles using conventional techniques developed for distinct-eigenvalue diffusion was unsuccessful. The $D^{(1)}$−$D^{(2)}$−a−b fitting procedure, for example, failed to converge. Because the a and b fitting parameters are inversely proportional to the eigenvalue difference $D^{(1)} - D^{(2)}$ and therefore diverge in the limit of equal eigenvalues, the changes in these parameters remained large and erratic during the least-squares iterations. The more direct D_{11}−D_{12}−D_{21}−D_{22} fitting procedure does not employ a and b parameters, but it too failed to converge. During the parameter iterations, moreover, both fitting procedures incorrectly indicated complex eigenvalues of the D_{ik} matrix

Table 2. $\bar{D}$, E, and F Parameters from the Least-Squares Analysis of Dispersion Profiles[a]

C_1 / $\mathrm{mol \cdot dm^{-3}}$	C_2 / $\mathrm{mol \cdot dm^{-3}}$	D / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	E / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	F / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$
		Aqueous Mannitol (1) + Tetra(ethyleneglycol) (2)[b]		
0.0000	0.0040	0.655 ± 0.002	0.006 ± 0.004	0.008 ± 0.002
0.0010	0.0030	0.662 ± 0.004	0.003 ± 0.006	0.006 ± 0.003
0.0020	0.0020	0.662 ± 0.004	−0.002 ± 0.003	0.012 ± 0.006
0.0030	0.0010	0.661 ± 0.005	0.004 ± 0.010	0.009 ± 0.003
0.0040	0.0000	0.658 ± 0.005	−0.004 ± 0.002	0.010 ± 0.006
		Aqueous 1-Propanol (1) + Glycine Glycol (2)[c]		
0.0000	0.0100	1.051 ± 0.003	−0.012 ± 0.010	0.020 ± 0.007
0.0025	0.0075	1.056 ± 0.003	−0.009 ± 0.015	0.006 ± 0.003
0.0050	0.0050	1.059 ± 0.003	−0.022 ± 0.002	0.007 ± 0.002
0.0075	0.0025	1.060 ± 0.003	−0.011 ± 0.013	0.006 ± 0.014
0.0100	0.0000	1.054 ± 0.003	0.002 ± 0.005	−0.004 ± 0.002
		Aqueous 1-Propanol (1) + 2-Propanol (2)[d]		
0.0000	0.0100	1.048 ± 0.009	−0.029 ± 0.007	0.021 ± 0.005
0.0025	0.0075	1.052 ± 0.012	−0.048 ± 0.015	0.025 ± 0.006
0.0050	0.0050	1.047 ± 0.011	−0.036 ± 0.017	0.031 ± 0.010
0.0075	0.0025	1.041 ± 0.006	−0.032 ± 0.011	0.037 ± 0.011
0.0100	0.0000	1.044 ± 0.009	−0.028 ± 0.018	0.024 ± 0.003

[a] Uncertainties are quoted at the 95 % confidence interval. [b] $R_2/R_1 = 0.886 \pm 0.005$. [c] $R_2/R_1 = 2.76 \pm 0.01$. [d] $R_2/R_1 = 0.961 \pm 0.003$.

Table 3. Ternary Mutual Diffusion Coefficients at 25 °C[a]

C_1 / $\mathrm{mol \cdot dm^{-3}}$	C_2 / $\mathrm{mol \cdot dm^{-3}}$	D_{11} / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	D_{12} / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	D_{21} / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	D_{22} / $10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$
		Aqueous Mannitol (1) + Tetra(ethyleneglycol) (2)			
0.0000	0.0040	0.653 ± 0.004	−0.001 ± 0.002	0.015 ± 0.009	0.659 ± 0.002
0.0010	0.0030	0.660 ± 0.008	−0.001 ± 0.001	0.011 ± 0.010	0.664 ± 0.002
0.0020	0.0020	0.662 ± 0.003	0.000 ± 0.002	0.011 ± 0.003	0.660 ± 0.006
0.0030	0.0010	0.659 ± 0.013	−0.001 ± 0.002	0.015 ± 0.018	0.665 ± 0.002
0.0040	0.0000	0.660 ± 0.005	0.000 ± 0.002	0.007 ± 0.005	0.657 ± 0.006
		Aqueous 1-Propanol (1) + Glycine (2)			
0.0000	0.0100	1.055 ± 0.004	−0.006 ± 0.006	0.003 ± 0.001	1.047 ± 0.006
0.0025	0.0075	1.053 ± 0.008	−0.016 ± 0.042	0.001 ± 0.003	1.057 ± 0.016
0.0050	0.0050	1.054 ± 0.003	−0.040 ± 0.013	0.001 ± 0.001	1.065 ± 0.006
0.0075	0.0025	1.059 ± 0.013	−0.017 ± 0.028	0.000 ± 0.001	1.060 ± 0.012
0.0100	0.0000	1.054 ± 0.005	0.002 ± 0.003	−0.010 ± 0.001	1.055 ± 0.003
		Aqueous 1-Propanol (1) + 2-Propanol (2)			
0.0000	0.0100	1.051 ± 0.003	−0.011 ± 0.008	0.003 ± 0.004	1.044 ± 0.012
0.0025	0.0075	1.053 ± 0.005	−0.022 ± 0.019	0.001 ± 0.002	1.052 ± 0.021
0.0050	0.0050	1.054 ± 0.012	−0.011 ± 0.007	0.006 ± 0.004	1.040 ± 0.010
0.0075	0.0025	1.050 ± 0.005	−0.007 ± 0.003	0.012 ± 0.005	1.032 ± 0.008
0.0100	0.0000	1.050 ± 0.003	−0.008 ± 0.014	0.004 ± 0.002	1.038 ± 0.015

[a] Uncertainties are quoted at the 95 % confidence interval.

characteristic of oscillating dispersion profiles. Previously developed peak-width[32] and moments[13] analysis procedures gave similar erroneous results. The second law of thermodynamics and the Onsager reciprocal relation can be used to show that the eigenvalues of the D_{ik} matrix are positive real numbers.[35,38,39,52,53] This requirement places the constraint $(D_{11} - D_{22})^2 + 4D_{12}D_{21} \geq 0$ on ternary mutual diffusion coefficients, whereas equal eigenvalues require $(D_{11} - D_{22})^2 + 4D_{12}D_{21} = 0$. Systems with equal or nearly equal eigenvalues are therefore “teetering on the brink” of physically impossible complex eigenvalues. During the analysis of dispersion profiles for these systems, small errors in the calculated D_{ik} coefficients can easily produce negative values of $(D_{11} - D_{22})^2 + 4D_{12}D_{21}$ and complex values of the calculated eigenvalues of the D_{ik} matrix.

Equation 31 for equal-eigenvalue diffusion was successfully fitted to the mannitol−tetra(ethyleneglycol) profiles. Table 2 gives the average values of the $\bar{D}$, E, and F fitting parameters obtained from four to six replicate pairs of peaks at each composition. The corresponding D_{ik} coefficients calculated from eqs 21 to 24 are listed in Table 3. The results appear to be reasonable. Cross-coefficients D_{12} and D_{21}, for example, are very small relative to the main coefficients, as expected for dilute solutions of nonionic solutes. Also, the values of main coefficients D_{11} and D_{22} are consistent with the limiting binary mutual diffusion coefficients reported previously for aqueous mannitol[47] and tetra(ethyleneglycol).[48]

Aqueous 1-Propanol (1) + Glycine (2) Solutions. Dispersion profiles for this system were measured for carrier solutions containing 0.0100 $\mathrm{mol \cdot dm^{-3}}$ total solute at five different C_1:C_2 ratios. Limiting binary mutual diffusion coefficients reported previously for aqueous 1-propanol[50,51] and aqueous glycine[49] are identical within the accuracy of the measurements (0.5 % for Gouy interferometry and (1 to 2) % for Taylor dispersion). The resulting severe ill conditioning ruled out analysis of the profiles by the $D^{(1)}{-}D^{(2)}{-}a{-}b$ and $D_{11}{-}D_{12}{-}D_{21}{-}D_{22}$ fitting procedures. The $\bar{D}{-}E{-}F$ fitting procedure converged successfully for the 1-propanol + glycine profiles. The results obtained are summarized in Tables 2 and 3.

Aqueous 1-Propanol (1) + 2-Propanol (2) Solutions. Ternary mutual diffusion coefficients for dilute aqueous 1-propanol (1) + 2-propanol (2) solutions were measured at the compositions given in Tables 2 and 3. The limiting binary mutual diffusion coefficient of aqueous 1-propanol is about 3 % larger than that for aqueous 2-propanol, suggesting that the eigenvalue $D^{(1)}$ might be a few percent larger than $D^{(2)}$ for the ternary 1-propanol (1) + 2-propanol (2) solutions. Once again, however, the eigenvalue difference was too small to be detected by the $D^{(1)}-D^{(2)}-a-b$ or $D_{11}-D_{12}-D_{21}-D_{22}$ fitting procedures. The D_{ik} coefficients determined by the $\bar{D}-E-F$ fitting procedure are listed in Table 3.

The analysis of ill-conditioned diffusion developed in this paper is based on the assumption of equal eigenvalues of the D_{ik} matrix. In practice, however, it is more likely to encounter systems with eigenvalues that are not identical but too close together to resolve. It would therefore be useful to estimate the possible errors in the D_{ik} coefficients when the $\bar{D}-E-F$ analysis is applied to systems with "nearly identical" eigenvalues. For this purpose, a series of numerical simulations were performed by using eq 15 to calculate dispersion profiles for trial D'_{ik} values with small but unresolvable eigenvalue differences ($< 0.05 \cdot 10^{-5}$ $\text{cm}^2 \cdot \text{s}^{-1}$). The simulated profiles were analyzed by the $\bar{D}-E-F$ fitting procedure, allowing detailed comparisons to be made between the "measured" D_{ik} values (assuming equal eigenvalues) and the "true" D'_{ik} values (small eigenvalue differences). The errors $\delta D_{ik} = D_{ik} - D'_{ik}$ in the diffusion coefficients caused by the assumption of equal eigenvalues were found to be small, typically ± $(0.01 \text{ to } 0.02) \cdot 10^{-5}$ $\text{cm}^2 \cdot \text{s}^{-1}$, which is similar in magnitude to the accuracy of the Taylor method.

The simulations revealed that the apparent diffusion coefficients obtained by injecting excess solute 1 ($\Delta C_2 = 0$)

$$D_{11} + \frac{R_2}{R_1}D_{21} = D'_{11} + \frac{R_2}{R_1}D'_{21} = D_{1\text{app}} \qquad (39)$$

or excess solute 2 ($\Delta C_1 = 0$)

$$D_{22} + \frac{R_1}{R_2}D_{12} = D'_{22} + \frac{R_1}{R_2}D'_{12} = D_{2\text{app}} \qquad (40)$$

were identical for both sets of D_{ik} and D'_{ik} coefficients. Also, $\bar{D}$ for the equal-eigenvalue matrix was accurately approximated by the R_i-weighted average of $D'^{(1)}$ and $D'^{(2)}$.

$$\bar{D} = \frac{D_{11} + D_{22}}{2} = \frac{R_1 D'^{(1)} + R_2 D'^{(2)}}{R_1 + R_2} \qquad (41)$$

Given a set of D_{ik} coefficients determined by the $\bar{D}-E-F$ fitting procedure, the four relations provided by eqs 39 to 41 and a trial value of the eigenvalue differences $D'^{(1)} - D'^{(2)}$ can be used to calculate the four D'_{ik} coefficients and the corresponding errors $\delta D_{ik} = D_{ik} - D'_{ik}$ caused by the assumption of equal eigenvalues. The results of these calculations are illustrated for $0.0050 \text{ mol} \cdot \text{dm}^{-3}$ 1-propanol + $0.0050 \text{ mol} \cdot \text{dm}^{-3}$ 2-propanol in Figure 2. For $D'^{(2)} - D'^{(1)} = -0.03 \cdot 10^{-5}$ $\text{cm}^2 \cdot \text{s}^{-1}$ suggested by the limiting binary mutual diffusion coefficients of 1-propanol and 2-propanol, the corresponding errors in the fitted diffusion coefficients are less than $0.01 \cdot 10^{-5}$ $\text{cm}^2 \cdot \text{s}^{-1}$.

Conclusions

Taylor dispersion with refractive-index detection can be used to measure ternary mutual diffusion coefficients in cases of identical or nearly identical eigenvalues of the D_{ik} matrix. The evaluation of diffusion coefficients for these systems is difficult or impossible using traditional methods based on the assumption of distinct eigenvalues because the equations used in the analysis become numerically ill-conditioned. Equations derived for equal-eigenvalue Taylor dispersion profiles break the ill conditioning and allow ternary diffusion coefficients to be measured for electrolyte or nonelectrolyte solutes using simple refractive-index detection, without resorting to more elaborate experimental procedures, such as dual detectors or solute-specific spectroscopic detection. The proposed analysis removes a significant impediment to the measurement of diffusion in solutions of solutes of similar diffusivity.

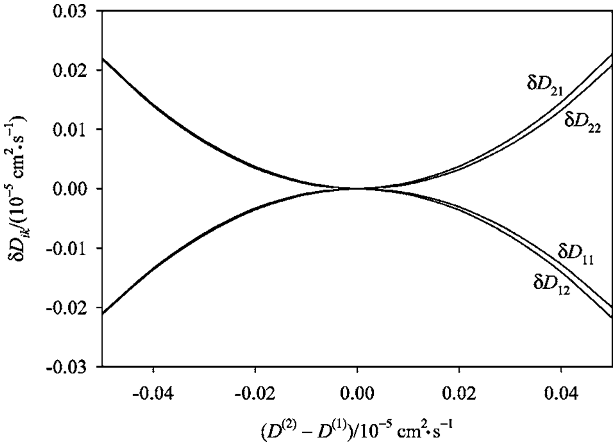

Figure 2. Errors in the ternary mutual diffusion coefficients determined for $0.0050 \text{ mol} \cdot \text{dm}^{-3}$ 1-propanol + $0.0050 \text{ mol} \cdot \text{dm}^{-3}$ 2-propanol solutions for different assumed eigenvalue differences.

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