Electronic Supplementary Information for:

Multicomponent diffusion coefficients from microfluidics using Raman microspectroscopy

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S1 Pure component data

Table S1 Used chemicals with supplier and purity

	supplier	description	purity in %
cyclohexane	VWR	Spectronorm	99.7
toluene	VWR	Spectronorm	99.8
methanol	VWR	Spectronorm	99.9
acetone	Merck Millipore	Uvasol	99.9
1-propanol	Merck	LiChrosolv	99.8
1-chlorobutane	Merck	LiChrosolv	99.8
heptane	Bernd Kraft	p.a.	99

Table S2 Molar volumes of pure components

	V_i^0 in $m^3\,mol^{-1}$	reference
cylohexane	108.8×10^{-6}	[1]
toluene	106.9×10^{-6}	[2]
1-propanol	75.17×10^{-6}	[3]
1-chlorobutane	105.2×10^{-6}	[4]
heptane	147.4×10^{-6}	[5]

S2 Reparameterization for the estimation procedure of ternary diffusion coefficients

For ternary mixtures, the following constraints impose positive definiteness of the diffusion coefficient $\boldsymbol{D}^V$:[6]

$$D_{11} + D_{22} > 0 \tag{S1}$$

$$D_{11}D_{22} - D_{12}D_{21} > 0 \tag{S2}$$

$$(D_{11} - D_{22})^2 + 4D_{12}D_{21} > 0 \tag{S3}$$

In practice, many solvers employ infeasible path strategies and allow violations of constraints during the iterations. We employed the reparameterization proposed by Bardow *et al.*:[7]

$$\theta_1 = D_1^\dagger,\ \theta_2 = D_2^\dagger,\ \theta_3 = D_{11} - D_{22},\ \text{and}\ \theta_4 = D_{12}\ . \tag{S4}$$

The inverse transformation is performed according to

$$D_{11} = \frac{\theta_1 + \theta_2 + \theta_3}{2},\ D_{22} = \frac{\theta_1 + \theta_2 - \theta_3}{2},\ D_{21} = \frac{(\theta_1 - \theta_2)^2 - \theta_3^2}{4\theta_4},\ \text{and}\ D_{12} = \theta_4. \tag{S5}$$

With simple constraints on θ_1 and θ_2, the constraints (S1) - (S3) are trivially satisfied.[7] In practical applications, division by the unknown parameter θ_4 to compute D_{21} does not lead to numerical difficulties in our experience.

S3 Cyclohexane + toluene

The influence of the temperature inaccuracy on the diffusion coefficient is expected to be in the same order of magnitude as the standard deviation $\sigma(D)$ based on the correlation

$$D(T) = D(T_0)\,\frac{T}{T_0}\,\frac{\eta_{AB}(x, T_o)}{\eta_{AB}(x, T)} \tag{S6}$$

between the diffusion coefficient D, absolute temperature T and viscosity η.[8] The index 0 indicates the reference conditions. For a temperature accuracy of $\pm 0.5\,\mathrm{K}$, a relative error of the diffusion coefficient of $0.8\,\%$ is expected according to the temperature correlation (S6) and the viscosities of cyclohexane + toluene listed in Table S3.

Table S3 Expected influence of temperature on the diffusion coefficient and the viscosity of cyclohexane + toluene at $x_{\mathrm{cyclohexane}} = 0.6$. Viscosities were interpolated based on the data published by Silva *et al.*[9] The diffusion coefficient at $25\,^{\circ}\mathrm{C}$ was published by Sanni *et al.*[10]

T in $^{\circ}\mathrm{C}$	η in mPa s	D in $10^{-9}\,\mathrm{m^2\,s^{-1}}$	comment on D
24.5	0.635	1.753	eq. S6
25	0.631	1.767	Reference[10]
25.5	0.627	1.781	eq. S6

S4 1-Propanol + 1-chlorobutane + heptane

Table S4 Composition of the experiments with 1-propanol + 1-chlorobutane + heptane in $\mathrm{mol\,\%}$

		series A		series B	
	$\bar{x}$	x_{left}	x_{right}	x_{left}	x_{right}
1-propanol	33.3	35.8	30.8	35.8	30.8
1-chlorobutane	33.3	35.8	30.8	30.8	35.8
heptane	33.3	28.4	38.4	33.4	33.4

Table S5 Measured diffusion coefficient for 1-propanol + 1-chlorobutane + heptane at $x_{\text{1-propanol}} = x_{\text{1-chlorobutane}} = 33.3\,\mathrm{mol\,\%}$ and $25\ ^{\circ}\mathrm{C}$ by microfluidic experiment in this work with standard deviation $\sigma(\boldsymbol{D}^{V})$ from repeated experiments in comparison to Käshammer *et al.*[11]. The quality of fit for the diffusion coefficient is given as $\mathrm{RMSE_{fit}}$.

	D_{11}	D_{12}	D_{21}	D_{22}	$\mathrm{RMSE_{fit}}$
		in $1 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$			in $\mathrm{mol\,\%}$
$n_{\mathrm{exp}} = 1$[a]	0.746 ± 0.202	-0.552 ± 0.474	0.423 ± 0.120	2.571 ± 0.263	0.29
$n_{\mathrm{exp}} = 2$[b]	0.998 ± 0.025	-0.279 ± 0.044	0.311 ± 0.027	2.521 ± 0.050	0.29
$n_{\mathrm{exp}} = 9$[c]	1.017	-0.236	0.310	2.516	0.29
literature	1.033 ± 0.016	-0.174 ± 0.025	0.255 ± 0.012	2.463 ± 0.017	

[a] estimated from nine separate experiments

[b] estimated from all combinations of two experiments, one from series A and series B each

[c] estimated from all experiments simultaneously, four from series A and five from series B each. No standard deviations from repeated experiments are available, but standard deviations are expected to be less than for $n_{\mathrm{exp}} = 2$ as more data was used.

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