SUPPLEMENTARY DATA

Interferometric diffusion data

Experimental data on individual diffusion experiments performed using the Gosting diffusiometer are reported below for the PEG-water binary system and for the PEG -DEG-water ternary system (see Tables S1-S8).

A typical diffusion experiment using the Gosting diffusiometer starts from preparing a sharp boundary (using a peristaltic pump) between two uniform solutions of slightly different solute concentrations located inside a vertical channel with inside width a. In our case, we have: $a = 2.5057$ cm. The light source used for generating the Rayleigh interference pattern is a He-Ne Uniphase laser with wavelength $\lambda = 543.5$ nm. A cell holder is located inside a water bath. The temperature of the bath was regulated at 25.00±0.001 ºC. The cell holder has the function to support a Tiselius cell, where diffusion occurs, and a mask, which consists of a double window. Here the laser beam is splitted into two parts: one going through the diffusion channel of the Tiselius cell and one passing through the water bath (reference channel). A pair of two cylinder lenses focuses the diffusion channel onto the detector, where the Rayleigh interference pattern is observed and recorded. Rayleigh fringes shift horizontally as the refractive index, n, inside the diffusion channel changes with vertical height. This gives direct information about refractive index versus vertical position. The difference in refractive index, Δn, between the two solutions is related to the total number of interference fringes J by $\Delta n = J\lambda / a$.[25,50]

Each interferometric diffusion experiment requires the preparation of a pair of solutions with different composition. PEG and DEG are denoted with the labels "1" and "2" respectively. For each solution pair associated, their average molar concentration, $\overline{C}_1$ and $\overline{C}_2$, and the corresponding difference, ΔC_1 and ΔC_2 are reported. To obtain the four ternary diffusion coefficients, $(D_{ij})_V$, at least four experiments were performed at the same mean composition, $(\overline{C}_1, \overline{C}_2)$, but with different values of ΔC_1 and ΔC_2. These concentration differences define the number of fringes of a given experiment by: $J = R_1\,\Delta C_1 + R_2\,\Delta C_2$, where $R_i = (a/\lambda)(\partial n/\partial C_i)_{C_j, i\neq j}$. For our ternary system, the values: $R_1 = 124000$ cm^3 mol^{-1} and $R_2 = 530$ cm^3 mol^{-1} were determined fitting the experimental values of J. In Tables S3-8, six sets of ternary experiments are reported. In Tables S1-8, the following experimental parameters are also reported: densities of bottom and top solutions, d_{top} and d_{bot}; the measured number of interference fringes, J_{measd}; the number of interference fringes, J_{calcd}, calculated using $R_1\Delta C_1 + R_2\Delta C_2$, and the measured reduced-height-area ratio, D_A.[25,50]

The four ternary diffusion coefficients are determined by applying a well-established nonlinear least-squares method to the data of Rayleigh fringe positions.[51] Since diffusion experiments on binary PEG-water systems show a small polydispersity, accurate polydispersity corrections on fringe positions have been applied as described in ref 52 in details.

Table S1. Binary diffusion experiment data for PEG-water at 298.15 K

expt	1
$\overline{C}_1$ (mM)	0.2500
ΔC_1 (mM)	0.4454
d_{bot} (g cm^{-3})	0.998587
d_{top} (g cm^{-3})	0.997092
J_{measd}	54.970
D_A (10^{-9} m^2 s^{-1})	0.06116

Table S2. Binary diffusion experiment data for DEG-water at 298.15 K

expt	1	2	3	4	5	6	7
$\overline{C}_2$ (M)	0.1000	0.2000	0.3000	0.5001	0.9997	1.9937	3.9301
ΔC_2 (M)	0.0931	0.0930	0.0930	0.0931	0.0931	0.0931	0.0914
d_{bot} (g cm^{-3})	0.998953	1.000396	1.001657	1.004837	1.012143	1.026868	1.055142
d_{top} (g cm^{-3})	0.997629	0.999156	1.000558	1.003485	1.010752	1.025373	1.053854
J_{measd}	48.731	49.001	49.014	49.205	49.672	50.062	48.812
D_A (10^{-9} m^2 s^{-1})	0.8871	0.8761	0.8646	0.8431	0.7934	0.6988	0.5225

Table S3. Ternary diffusion experimental data for 0.25 mM PEG-0.10 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2500	0.2500	0.2501	0.2500
$\overline{C}_2$ (M)	0.1000	0.1000	0.1000	0.1000
ΔC_1 (mM)	0.0000	0.0000	0.4455	0.4454
ΔC_2 (M)	0.0931	0.0931	0.0000	0.0000
d_{bot} (g cm^{-3})	0.999830	0.999930	1.000015	0.999983
d_{top} (g cm^{-3})	0.998621	0.998583	0.998529	0.998557
J_{measd}	48.784	48.813	55.081	55.077
J_{calcd}	48.792	48.805	55.067	55.091
D_A (10^{-9} m^2 s^{-1})	0.9073	0.9069	0.06085	0.06087

Table S4. Ternary diffusion experimental data for 0.25 mM PEG-0.20 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2500	0.2500	0.2500	0.2500
$\overline{C}_2$ (M)	0.2000	0.2000	0.2000	0.2000
ΔC_1 (mM)	0.0000	0.0000	0.4454	0.4454
ΔC_2 (M)	0.0931	0.0931	0.0000	0.0000
d_{bot} (g cm^{-3})	1.001386	1.001388	1.001449	1.001451
d_{top} (g cm^{-3})	0.999976	0.999976	0.999978	0.999980
J_{measd}	48.917	48.925	55.264	55.322
J_{calcd}	48.921	48.921	55.293	55.293
D_A (10^{-9} m^2 s^{-1})	0.8970	0.8970	0.06100	0.06100

Table S5. Ternary diffusion experimental data for 0.25 mM PEG-0.50 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2500	0.2500	0.2500	0.2500
$\overline{C}_2$ (M)	0.5001	0.5001	0.5000	0.5001
ΔC_1 (mM)	0.0000	0.0000	0.4454	0.4454
ΔC_2 (M)	0.09307	0.09307	0.0001	0.0000
d_{bot} (g cm^{-3})	1.005655	1.005657	1.005668	1.005765
d_{top} (g cm^{-3})	1.004339	1.004337	1.004156	1.004283
J_{measd}	49.233	49.282	55.227	55.364
J_{calcd}	49.257	49.258	55.296	55.295
D_A (10^{-9} m^2 s^{-1})	0.8655	0.8655	0.05941	0.05940

Table S6. Ternary diffusion experimental data for 0.25 mM PEG-1.00 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2499	0.2499	0.2499	0.2499
$\overline{C}_2$ (M)	0.9997	0.9997	0.9997	0.9997
ΔC_1 (mM)	0.0000	0.0000	0.4452	0.4452
ΔC_2 (M)	0.0931	0.0930	0.0001	0.0001
d_{bot} (g cm^{-3})	1.012997	1.012919	1.013042	1.013042
d_{top} (g cm^{-3})	1.011638	1.011625	1.011521	1.011521
J_{measd}	49.514	49.695	55.701	55.667
J_{calcd}	49.623	49.587	55.684	55.684
D_A (10^{-9} m^2 s^{-1})	0.8139	0.8141	0.05803	0.05803

Table S7. Ternary diffusion experimental data for 0.25 mM PEG-1.99 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2492	0.2492	0.2493	0.2492
$\overline{C}_2$ (M)	1.9934	1.9938	1.9939	1.9939
ΔC_1 (mM)	0.0001	0.0000	0.4514	0.4514
ΔC_2 (M)	0.0935	0.0930	-0.0097	-0.0098
d_{bot} (g cm^{-3})	1.027650	1.027706	1.027750	1.027726
d_{top} (g cm^{-3})	1.025951	1.026246	1.026359	1.026359
J_{measd}	50.081	49.943	51.323	51.325
J_{calcd}	50.136	49.887	51.339	51.310
D_A (10^{-9} m^2 s^{-1})	0.7147	0.7152	0.04753	0.04750

Table S8. Ternary diffusion experimental data for 0.25 mM PEG-3.93 M DEG-water at 298.15 K

expt	1	2	3	4
$\overline{C}_1$ (mM)	0.2456	0.2456	0.2456	0.2456
$\overline{C}_2$ (M)	3.9297	3.9297	3.9300	3.9297
ΔC_1 (mM)	0.0000	0.0000	0.4361	0.4361
ΔC_2 (M)	0.0915	0.0915	-0.0194	-0.0195
d_{bot} (g cm^{-3})	1.055874	1.055876	1.055847	1.055777
d_{top} (g cm^{-3})	1.054555	1.054553	1.054707	1.054654
J_{measd}	48.786	48.866	43.001	42.840
J_{calcd}	48.830	48.821	42.897	42.943
D_A (10^{-9} m^2 s^{-1})	0.5317	0.5318	0.03414	0.03420

Calculation of $\frac{m_2 \mu_{22}^{(m)}}{RT}$ for the DEG-H_2O binary system at 298.15 K

According to the Van Laar equation applied to the DEG-H_2O binary system, we have:

$$\frac{\mu_0 - \mu_0^*}{RT} = \ln x_0 + \frac{A}{\left(1 + \frac{A x_0}{B x_2}\right)^2}$$

$$\frac{\mu_2 - \mu_2^*}{RT} = \ln x_2 + \frac{B}{\left(1 + \frac{B x_2}{A x_0}\right)^2}$$

where μ_i^* (with $i = 0, 2$) is the chemical potential of pure component i and x_i is its mole fraction in the binary mixture. For the DEG-water system at 298.15 K, the following values were taken from ref 40:

$$A = -0.348$$
$$B = -0.90$$

If we insert $x_2 = m_2 / (m_2 + 1000 / M_0)$ in the expression for μ_2 and then differentiate μ_2 with respect to m_2, we obtain:

$$\frac{m_2 \mu_{22}^{(m)}}{RT} = 1 - \frac{2M_0}{1000} \frac{B^2}{A} \frac{m_2}{\left(1 + \frac{M_0}{1000} \frac{B}{A} m_2\right)^3} - \frac{m_2}{m_2 + 1000 / M_0}$$

By applying this equation to the experimental m_2, we obtain the following values of $m_2 \mu_{22}^{(m)} / RT$:

C_2 (M))	m_2 (mol kg^{-1})	$m_2 \mu_{22}^{(m)} / RT$
0.1000	0.1017	1.0066
0.2000	0.2053	1.0130
0.5000	0.5281	1.0317
0.9997	1.1093	1.0604
1.9938	2.4602	1.1066
3.9298	6.2054	1.1424

Calculation of $\frac{m_1 \mu_{11}^{(m)}}{RT}$ for the PEG-H_2O binary system at 298.15 K

We start from the virial expression of the water thermodynamic activity taken from ref 54:

$$\frac{\mu_0 - \mu_0^*}{RT} = -V_0^* \, c_1 \left(\frac{1}{M_1} + A c_1 + B c_1^{\,2} \right)$$

where $c_1 = C_1 M_1$ is the mass/volume concentration, μ_0^* and V_0^* are the chemical potential and molar volume of pure water respectively, and the values

$$M_1 = 20729 \, \mathrm{g \, mol^{-1}}$$
$$A = 1.67 \times 10^{-3} \, \mathrm{mol \, cm^3 \, g^{-2}}$$
$$B = 1.96 \times 10^{-2} \, \mathrm{mol \, cm^6 \, g^{-3}}$$

were taken from Table 3 of ref x. The virial expression can be rewritten in terms of PEG molar concentration:

$$\frac{\mu_0 - \mu_0^*}{RT} = -V_0^* \, C_1 \left(1 + A' C_1 + B' C_1^{\,2} \right)$$

where $A' \equiv A M_1^{\,2} = 7.18 \times 10^2 \, \mathrm{M^{-1}}$ and $B' \equiv B M_1^{\,3} = 1.75 \times 10^5 \, \mathrm{M^{-2}}$.

To obtain the expression of the PEG chemical potential, we differentiate μ_0 and use the Gibbs-Duhem equation at constant temperature and pressure:

$$d\mu_1 = -\frac{C_0}{C_1} d\mu_0 = \frac{V_0^* C_0}{C_1} \left(1 + 2A' C_1 + 3B' C_1^{\,2} \right) dC_1$$

We therefore obtain:

$$\frac{C_1 \mu_{11}^{(c)}}{RT} = \left(1 - \bar{V}_1 C_1 \right) \left(1 + 2A' C_1 + 3B' C_1^{\,2} \right)$$

If we apply eq 4a to the PEG-H_2O binary system, we finally obtain:

$$\frac{m_1 \mu_{11}^{(m)}}{RT} = (1 - C_1 \bar{V}_1) \frac{C_1 \mu_{11}^{(c)}}{RT} = \left(1 - \bar{V}_1 C_1 \right)^2 \left(1 + 2A' C_1 + 3B' C_1^{\,2} \right)$$

At $C_1 = 0.25 \, \mathrm{mM}$, we obtain: $m_1 \mu_{11}^{(m)} / RT = 1.38$.