Supporting Information

Correlated diffusivities, solubilities, and hydrophobic interactions in ternary polydimethylsiloxane -water-tetrahydrofuran mixtures

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Self-diffusivities of THF in binary d-PDMS–THF mixtures as a function of polymer volume fraction

Due to the high viscosity of the d-PDMS, all samples were prepared on a mass basis for improved accuracy. To facilitate comparisons with data based on polymer volume fractions, self-diffusivities of THF in perdeuterated d-PDMS are plotted in Figure S1, as a function of d-PDMS volume fraction.

![Figure S1](image)

**Figure S1.** Self-diffusivities of THF in binary mixtures of perdeuterated d-PDMS, plotted as a function of d-PDMS volume fraction, as measured by $^1$H PFG NMR at 20 °C. The same data are shown in Figure 2 of the main manuscript and in Figure S2 below, as a function of THF mass fraction in d-PDMS.
As THF is a good solvent for PDMS, no evidence of aggregation was anticipated or observed at higher THF contents. This is consistent with an estimate for the overlap concentration \( c^* = \frac{3M_w}{4\pi N_A R_g^3} \),\(^3 \) where \( M_w \) is the polymer molecular weight, \( N_A \) is Avogadro’s number, the radius of gyration is given by \( R_g = \frac{ln^{1/2}}{6^{1/2}} \), and the literature value for segment length \( l = 5.6 \) Å. Using these values, the radius of gyration is estimated to be \( R_g = 4.2 \) nm for PDMS, leading to an estimated overlap concentration of \( c^* = 134 \) g/L, which corresponds to a PDMS mass fraction of 0.15, below which the PDMS chains can be considered non-interacting and dilute.

**Diffusion analyses of cross-linked polydimethylsiloxane-THF solutions**

For many PDMS applications, including membrane separations and microfluidics,\(^1 \) cross-linked polymer gels are used rather than non-cross-linked liquids, so diffusion of THF within cross-linked PDMS was also examined. THF self-diffusion coefficients (Figure S2) were measured, as a function of composition for binary mixtures of 20-50 wt% THF in cross-linked (non-deuterated) PDMS (blue triangles) and non-cross-linked deuterated \( d-\)PDMS. All of the measured THF self-diffusion coefficients exhibited an approximately linear quantitative dependence on THF mass fraction that was essentially identical for the cross-linked and non-cross-linked PDMS. Only the concentration range between 20 wt% and 50 wt% THF could be measured for the non-deuterated cross-linked PDMS samples, because radiation damping during the NMR measurement prevented resolution of THF \( ^1\)H NMR signals outside this composition range. Based on the technical specifications provided for the Sylgard\textsuperscript{TM} 184,\(^2 \) we estimate that there are approximately two functional branch points per polymer molecule. Assuming that all of the functional endgroups have reacted, we estimate a rough upper-bound for the cross-linking density to be about 1 cross-link for every 200 monomer sites. The actual value is probably significantly smaller than this value, and this is consistent with the observed liquid-like \( ^1\)H NMR spectra of the cross-linked samples. This low extent of cross-linking is consistent with the observed diffusivities not being significantly affected by the cross-linking. Much higher extents of cross-linking would likely have a larger effect on self-diffusion properties.
Figure S2. Self-diffusivities of THF in binary mixtures with cross-linked PDMS, plotted as a function of d-PDMS volume fraction, as measured by \(^1\)H PFG NMR under ambient conditions. The line shows the approximate trend for non-cross-linked PDMS, the data for which is shown in Figure 2 of the main text. The cross-linked data lie on approximately the same trend line, indicating that PDMS cross-linking does not have a strong effect on molecular self-diffusion of THF under these conditions. The uncertainties are approximately the size of the data points, except for 0.50 THF, where the error bar is slightly larger, as shown.

Interactions between symmetric PDMS thin films

In SFA measurements of force-distance curves, values for the force \(F\) are typically scaled with respect to the radius of the curved interacting surface \(R\), which allows results obtained from other techniques to be compared. The scaled force \(F/R\) can be used to calculate the interaction energy by using the Derjaguin approximation, \(W = F/2\pi R\), and was measured during both approaches and separations of the surfaces, as a function of the film-film separation distance \(d\). Typical force-distance curves exhibit repulsive forces as \(F/R > 0\) and attractive forces as \(F/R < 0\), as functions of the separation distance \(d\) between the surface films. As shown in Figure S3, the interactions between two PDMS films are fully attractive on both approach and separation. During approach, the surfaces jump-in from a large distance \(D_j = 22\) nm to a hardwall distance \(D_H = 13\) nm, which corresponds to the combined thickness of the two PDMS films. The attractive force is clearly longer-ranged than the van der Waals forces for this system, as shown by the red
curve. During separation of the two surfaces, a very large adhesion energy of $W_0 = 85 \text{ mJ/m}^2$ was measured, a value very close to the expected thermodynamic adhesion for two PDMS surfaces, i.e., $W_0 = 2\gamma = 88 \text{ mJ/m}^2$. This force run is representative for the PDMS-PDMS system in water.

![Figure S3](image-url)

**Figure S3.** Interaction forces between two PDMS thin films in 1 mM NaCl aqueous solution at pH 3 and room temperature, as measured using the surface forces apparatus. The blue curve represents the maximum hydrophobic interaction using Equation 1 in the text, with $H_y = 1$, $\gamma = 44 \text{ mJ/m}^2$, and $D_H = 1 \text{ nm}$. The van der Waals forces according to Equations S2 and S3 below are shown for comparison as the red curve.

The interactions between PDMS films in aqueous solutions and aqueous-organic liquids mixtures can be described quantitatively by the total interaction energy $W_{\text{tot}}$, which consists of contributions from both hydrophobic and van der Waals interactions, $W_{\text{tot}} = W_H + W_{\text{vdW}}$, with the van der Waals interaction energy $W_{\text{vdW}}$ calculated, as described below. The fit to the force data (Figure S3) establishes that the overall interaction potential is quantitatively well-described with $H_y = 1$, capturing both the long range attraction ($d > 10 \text{ nm}$) and adhesion when the two films are in molecular contact ($d = 0$).

As shown above and in the main text of the manuscript, the interactions between the PDMS films are attractive during both approach and separation, with the main contribution arising from hydrophobic interactions. However, van der Waals interactions are always present between surfaces, and in this case the main contribution from van der Waals forces arises between the two
PDMS films. The PDMS films are sufficiently thick that the van der Waals force between the underlying mica and gold can be effectively ignored. The van der Waals interaction energy per unit area, $W_{vdW}$, between two PDMS films depends on the Hamaker constant of PDMS interacting with PDMS across water, $A_{131}$, and the separation distance $D$ between the films, as shown in Equation S2:3

$$W_{vdW} = -\frac{A_{131}}{12\pi D^2}$$

(S2)

The Hamaker constant was calculated by using the following equation, as described in detail in reference.4 Equation S3 comes from Lifshitz theory and is used to calculate the Hamaker constant for the symmetric case of two identical phases 1 interacting across medium 3:

$$A_{131} = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 - \varepsilon_3} \right)^2 + \frac{3h\nu}{16\sqrt{2}} \left( \frac{n_1^2 - n_3^2}{n_1^2 + n_3^2} \right)^{3/2}$$

(S3)

In this case, the subscript 1 corresponds to PDMS, while subscript 3 corresponds to water. Using well-known values for the refractive indices and dielectric constants for PDMS and water, the Hamaker constant for PDMS films interacting across pure water, $A_{131} = 4 \times 10^{-21}$ J. Tabulated data for the concentration dependent refractive indices and dielectric constants in water-THF mixtures were used to calculate the Hamaker constant for each composition. The van der Waals adhesion was estimated using Equation S2 and the Hamaker constant for each composition, at a cut-off distance of $D = 0.165$ nm. The line labelled “VDW” in Figure 4 (main manuscript text) corresponds to the van der Waals adhesion calculated in this way.

References


2. Flowers, G.; Switzer, S. T. Background material properties of selected silicone potting compounds and raw materials for their substitutes; Mason and Hanger-Silas Mason Co., Inc.: Amarillo, Texas (USA), 1978.

