Supporting information for – Crystal templating through liquid–liquid phase separation

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Temperature-composition phase diagrams

In order to estimate the mutual solubilities of the mixtures under consideration, we use a simple activity approach. The molar Gibbs free energy G of the solution is divided into ideal G^{id} and excess G^{ex} contributions

$$G = G^{id} + G^{ex}. \tag{1}$$

The ideal mixing contribution is given by

$$G^{id} = x_1\mu_1^0 + x_2\mu_2^0 + x_1 RT\ln x_1 + x_2 RT\ln x_2 \ , \tag{2}$$

where x_i is the mole fraction of component i, μ_i^0 is the chemical potential of pure component i, R is the ideal gas constant, and T is the absolute temperature of the system.

In order to model the nonidealities of the solution, we use the three-suffix Margules model

$$\frac{G^{ex}}{RT} = \left[A + B\left(x_1 - x_2\right)\right]x_1 x_2 \ , \tag{3}$$

where A and B are fit parameters that relate to the interactions between the components of the solution. The corresponding expressions for the activity coefficient are

$$\begin{aligned} \ln\gamma_1 &= \left(A+3B\right)x_2^2 - 4Bx_2^3 \\ \ln\gamma_2 &= \left(A-3B\right)x_1^2 + 4Bx_1^3 \end{aligned} \tag{4}$$

The parameters A and B of the model are chosen to have a temperature dependence of the form

$$A = A_0 + \frac{A_1}{RT}, B = B_0 + \frac{B_1}{RT} \tag{5}$$

where A_0, A_1, B_0, and B_1 are parameters that are adjusted in order to fit available thermodynamic data (*e.g.*, solubilities).

For the hexane (1) – nitrobenzene (2) systems, the parameters of the excess free energy model were fit to liquid–liquid equilibria data.[1,2] The best-fit values were found to be $A_0 = -3.157$, $A_1 = 12.53$ kJ mol^{-1}, $B_0 = -2.139$, and $B_1 = 5.760$ kJ mol^{-1}. A comparison of the fit of the two-term Margules model to the experimental data is shown in Fig. SI 1. Samples were made at **0.1%, 1%, and 10% nitrobenzene in hexane by volume** corresponding to **0.127 mol%, 1.27 mol%, and 12.7 mol%**. At these mole fractions, we predict liquid–liquid equilibria at 184.0, 225.9, and 277.6 K.

For the trans-1,2-dichloroethene (1) – water (2) systems, the parameters of the excess free energy model were fit to the solubility data[3] and chromatography measurements of the infinite dilution activity coefficients (for both water in dichloroethene and dichloroethene in water).[4-6] The optimal values were found to be $A_0 = 3.096$, $A_1 = 8.079$ kJ mol^{-1}, $B_0 = -6.227$, and $B_1 = 13.46$ kJ mol^{-1}. The trans-DCE samples as obtained from by Sigma-Aldrich have a water content of 80 ppm (4.3 10^{-3} mole fraction). At this mole fraction, we predict a liquid–liquid equilibrium at 238 K.

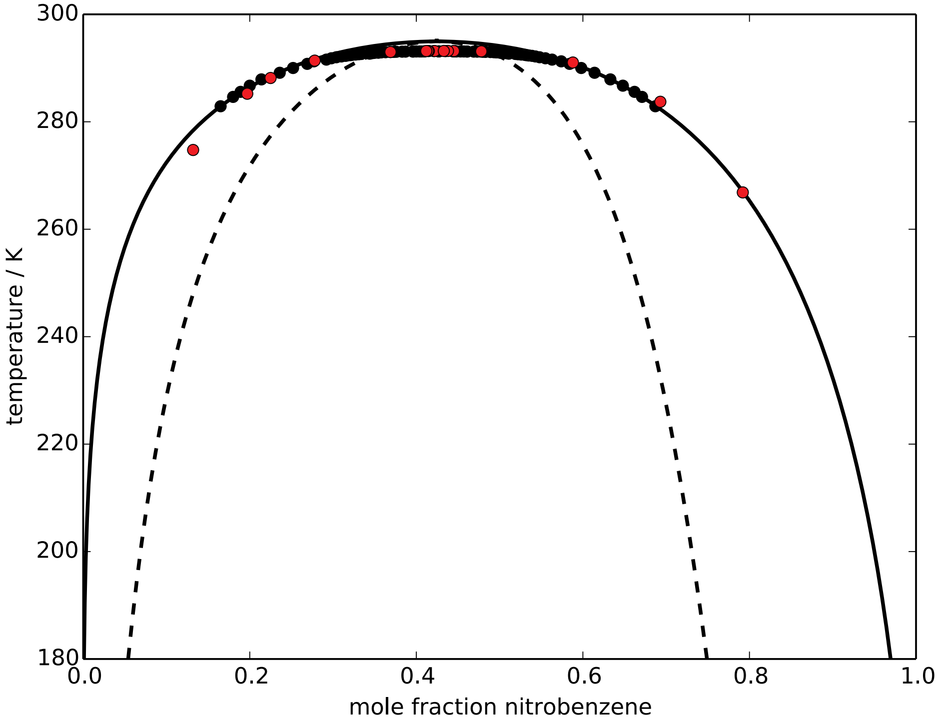

Fig. SI 1. *Temperature-composition phase diagram for mixtures of nitrobenzene and hexane. Symbols are the measurements in Refs.* [1,2]*. Dashed line is the estimated spinodal.*

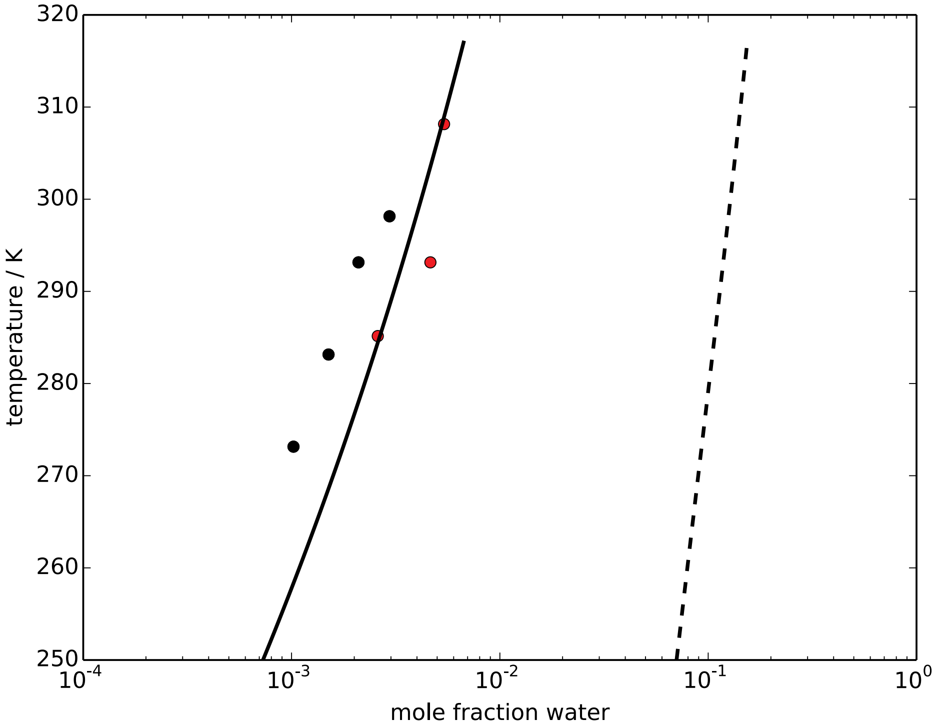

Fig. SI 2. *Partial temperature-composition phase diagram for mixtures of water in trans-1,2-dichloroethylene. Symbols are the measurements in Refs.* [3-6] *Dashed line is the estimated spinodal based on limited solubility data.*

Fluff in other liquids

Fluff-like water crystals have been observed in other nonpolar liquids as well. Shown here are results in carbon disulfide (see Fig. SI 3) and cis-1,2-dichloroethylene (cis-DCE, see Fig. SI 4). Both liquids were purchased from Sigma Aldrich and used as supplied.

Table SI1. *Melting temperatures of organic liquids used.*

	T_m (° C)	T_m (K)
trans-1,2-dichloroethylene	-50	223
cis-1,2-dichloroethylene	-80	192
carbon disulfide	–111.6	161
nitrobenzene	5.7	278.7
hexane	-95	178

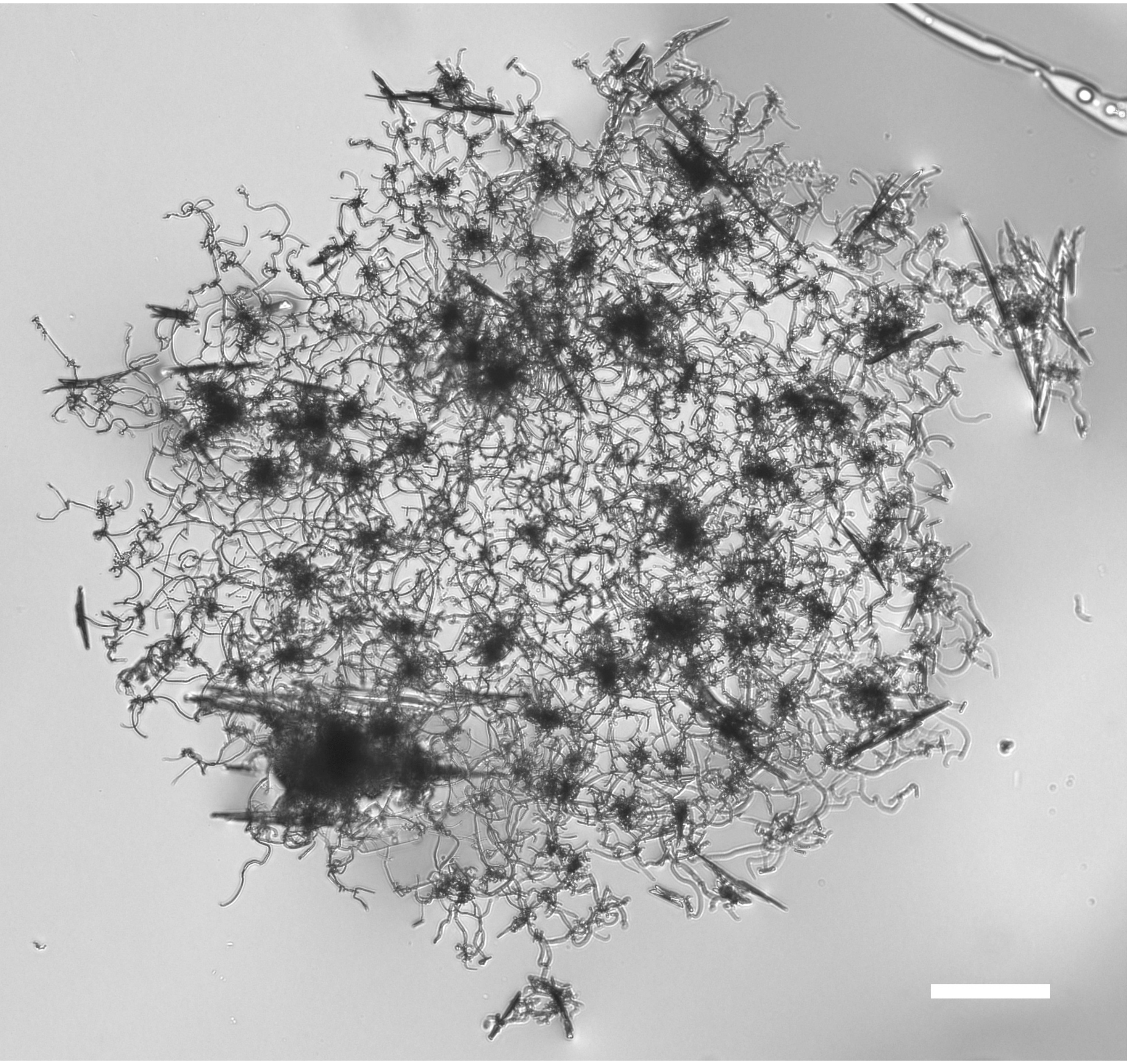

Fig. SI 3. *The formation of fluff-like water crystals observed in CS_2 after cooling to about 258 K at 0.5 K/min. The concentration of water was about 15% by volume. Scale bar 50 μm.*

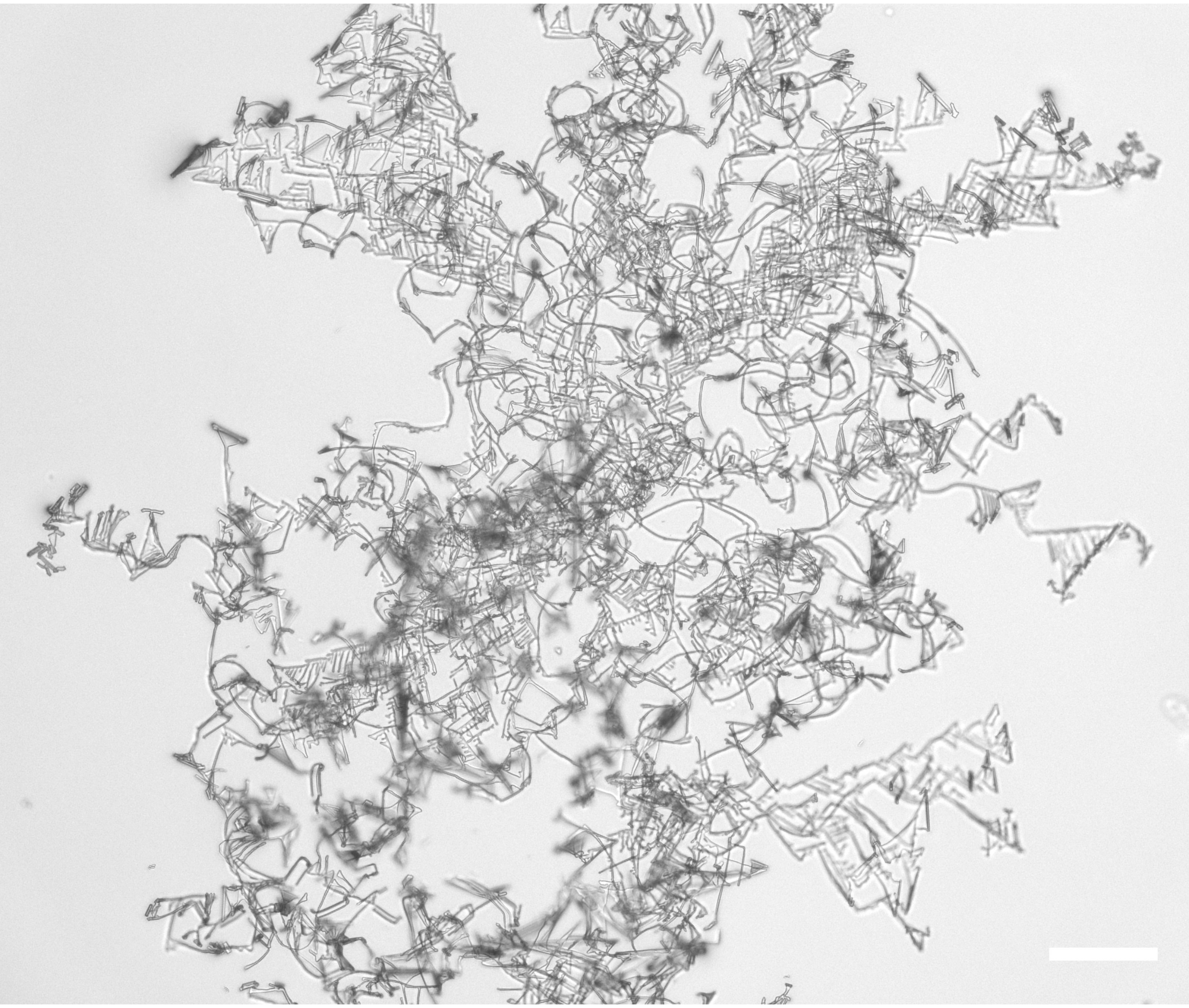

Fig. SI 4. *The formation of fluff-like water crystals observed in cis-1,2-dichloroethylene (cis-DCE) after cooling to 228 K at 15 K/min. Scale bar 50 µm.*

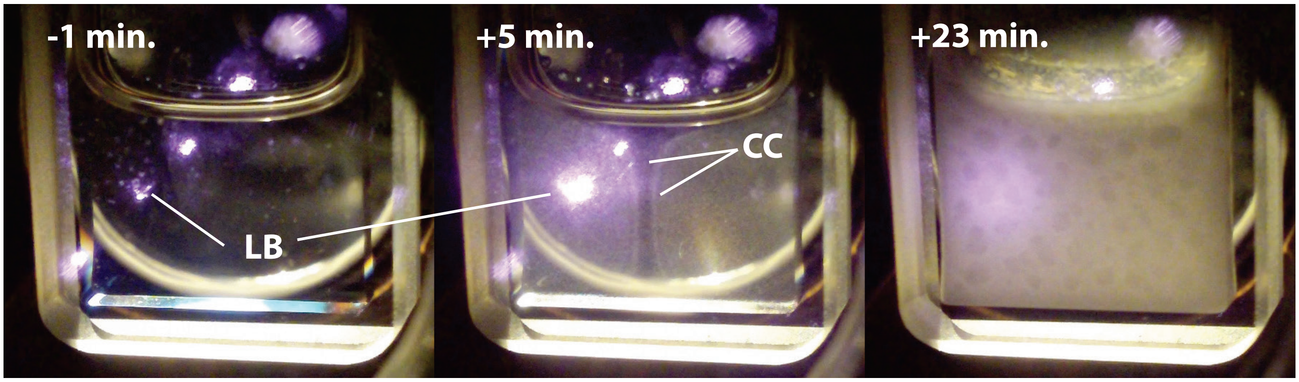

Fig. SI 5. *Dark-field time lapse of fluff formation in trans-DCE taking place in a 2 mm × 1 cm cuvette. LB: Laser beam; CC: convection current. The fluff appears a few minutes after cooling to 218 K and can be seen by the scattering of the laser beam. The trans-DCE phase is supercooled and freezes after about 20 minutes.*

Viscosity trans-DCE

The viscosity of trans-DCE was measured over the accessible range of -10 to 30° C using a Cambridge Viscosity Viscolab 3000 viscometer (see Fig. SI 6 and Table SI2) and over this very limited range was found to be Arrhenius with an activation energy of $E_A = 0.13$ kJ mol^{-1}.[7]

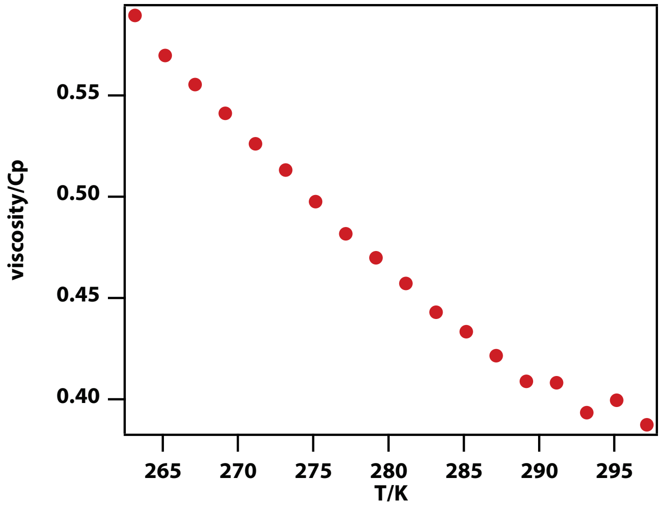

Fig. SI 6. *Measured temperature-dependent viscosity of trans-DCE.*

T/K	η/cP
263.15	0.5895
265.15	0.5697
267.15	0.55535
269.15	0.5412
271.15	0.52615
273.15	0.5132
275.15	0.4976
277.15	0.48165
279.15	0.46985
281.15	0.4572
283.15	0.44295
285.15	0.4333
287.15	0.4215
289.15	0.4088
291.15	0.4082
293.15	0.3934
295.15	0.3995
297.15	0.3874

Table SI2. *Temperature-dependent viscosity of trans-DCE*

References

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