

Electronic Supplementary Information

Sorption kinetics and mechanical properties of hydrogel nanocomposite thin films

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Methods. Preparation of mixed (3-aminopropyl)trimethoxysilan (APS) / *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammoniumchloride-functionalised (TMAPS) silica nanoparticles. The mix-modified particles were prepared according to ref. 23, centrifuged at 11000 rpm for 30 minutes, dried at 100 °C for 4h, and redispersed in water by ultrasonic vibration for 2h. The lab made dispersion are designated as **1a** (unfunctionalised), **1a_{0.2}** ($\chi_{\text{APS}}=0.2$), **1a_{0.4}** ($\chi_{\text{APS}}=0.4$) and **1a_{0.6}** ($\chi_{\text{APS}}=0.6$) where χ_{APS} is the molar fraction of (3-aminopropyl)trimethoxysilan (APS) in the silane mixture ($\chi_{\text{APS}} = n_{\text{APS}}/(n_{\text{APS}} + n_{\text{TMAPS}})$). The Bindzil dispersions **1b** are designated accordingly.²³

Table S1. Diameters of the mixed APS/TMAPS functionalised silica nanoparticles

Source	1a	1b
χ_{APS}		
0.2	20 ± 8 nm ^a	34 ± 29 nm ^a
0.4	26 ± 12 nm ^a	34 ± 34 nm ^a
0.6	35 ± 21 nm ^a	117 ± 44 nm ^a

^aThe size interval is calculated from the peak width at half height.

Synthesis of NCO-terminated six-armed star copolymers ($M_n = 12000$ g/mol). The synthesis is described in ref. 24. The polymers are stored in a glove box until further usage. Estimation of chain length of the star polymer arms was done by ChemBio3D Ultra 11.0.

Aminosilylation of Si-wafer. The wafers were activated with UV/ozon for 12 minutes. Aminosilylation was done in a solution of 0.3 ml *N*-[3-(trimethoxysilyl)propyl]ethylenediamine in 50 ml dry toluene for 2h. After rinsing several times with dry toluene, the wafers were stored in dry toluene until further usage.

Spin coating was done on a Convac 1001 S at 3000 rpm for 90s. Aminosilylated wafers were dried in nitrogen stream before the solution was placed. Contact angle measurements

were performed at Krüss Contact Angle Measuring System G2 by the sessile drop method with water. Contact angle measurements with water by the captive bubble method were done on a Krüss G-23.

Atomic force microscopy (AFM) was performed with a Nanoscope III (Digital Instruments) microscope. Investigations in the tapping mode were carried out with Si-cantilevers with a spring constant of approx. 50 N/m and at a tapping frequency around 350 kHz. Images were edited with Nanoscope software (v5.12r5).

Determination of layer thickness was done by ellipsometry in the wave length range of 400 – 900 nm at an azimuthal angle of 15 °. Each sample was measured at three different positions and a standard deviation of the average value was calculated.

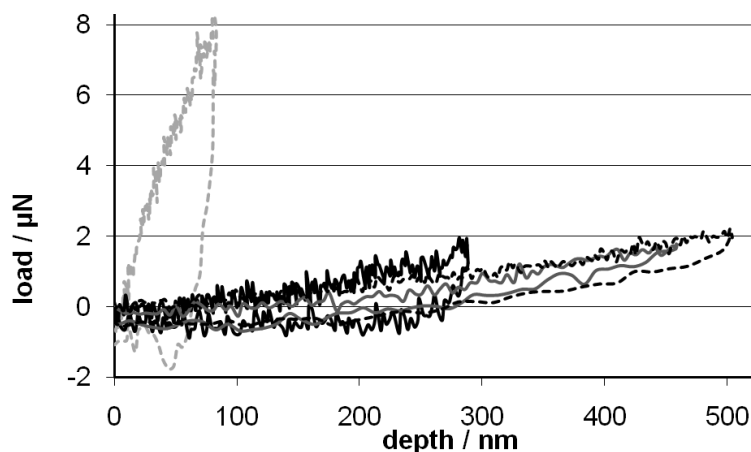


Figure S1. Nanoindenter-measurements of the pure gel (grey line), a gel with **1b** (grey dashed line), a gel with **1b_{0.4}** (black line) and a gel with PEI (black dashed line).

$$\text{Weight to volumen fraction: } V_p = \frac{w_p}{w_p + (1 - w_p) \frac{\rho_p}{\rho_m}} \quad (\text{Ref. 26})$$

$$\text{The rule of mixtures (ROM) upper limit: } E_c = E_p V_p + E_m V_m \quad (\text{Ref. 26})$$

$$\text{The rule of mixtures lower limit: } E_c = \frac{E_m E_p}{V_m E_p + V_p E_m} \quad (\text{Ref. 24})$$

Density of silica: 2.3 g/cm³ (N. M. Dimitrijevic, A. Henglein, D. Meisel, *J. Phys. Chem. B* **1999**, *103*, 7073)

Mechanical properties of silica particles: $H_p = 2.4 \pm 0.4$ GPa, $E_p = 68.9 \pm 9.6$ GPa (M. Zou, D. Yang, *Tribology Letters* **2006**, *22*, 189-196)

	Particles 1a	Particles 1b	Matrix	Composite 1a	Composite 1b
Density	2,3	2,3	1,2		
Hardness	2,40E+09	2,40E+09	2,00E+06	5,60E+06	4,90E+07
Modulus	6,89E+10	6,89E+10	1,10E+07	2,70E+07	1,35E+09
Weight-Fr	0,25	0,25	0,75		
Vol.-Fr	0,148	0,148	0,852		
			upper H (ROM)	3,57E+08	3,57E+08
			lower H (ROM)	2,35E+06	2,35E+06
			upper E (ROM)	1,02E+10	1,02E+10
			lower E (ROM)	1,29E+07	1,29E+07
			βH	1,10E-02	1,33E-01
			βE	1,73E-03	1,32E-01

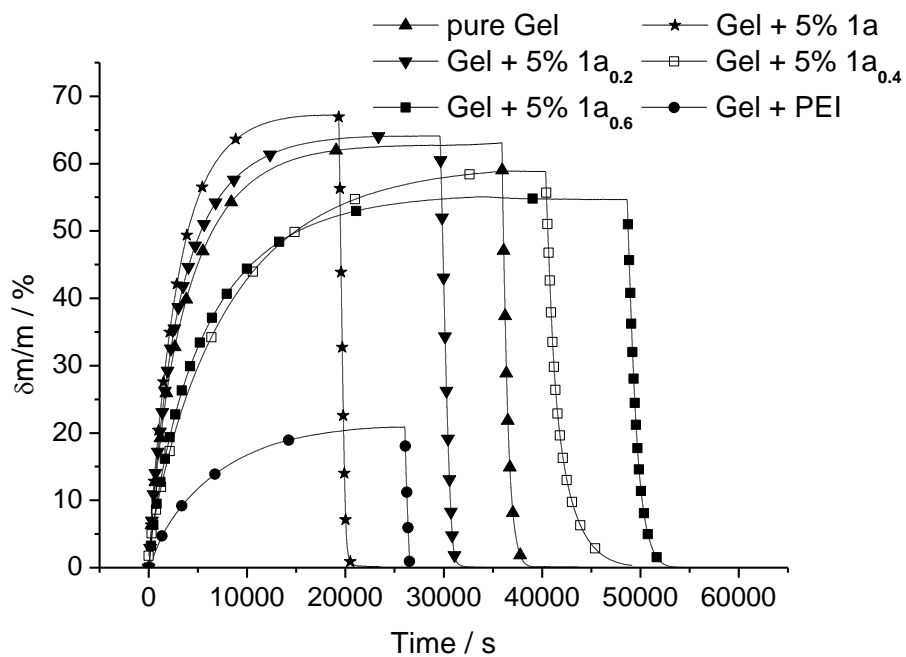


Figure S2. Sorption curves of bulk gels for **1a** and reference samples at 25 °C

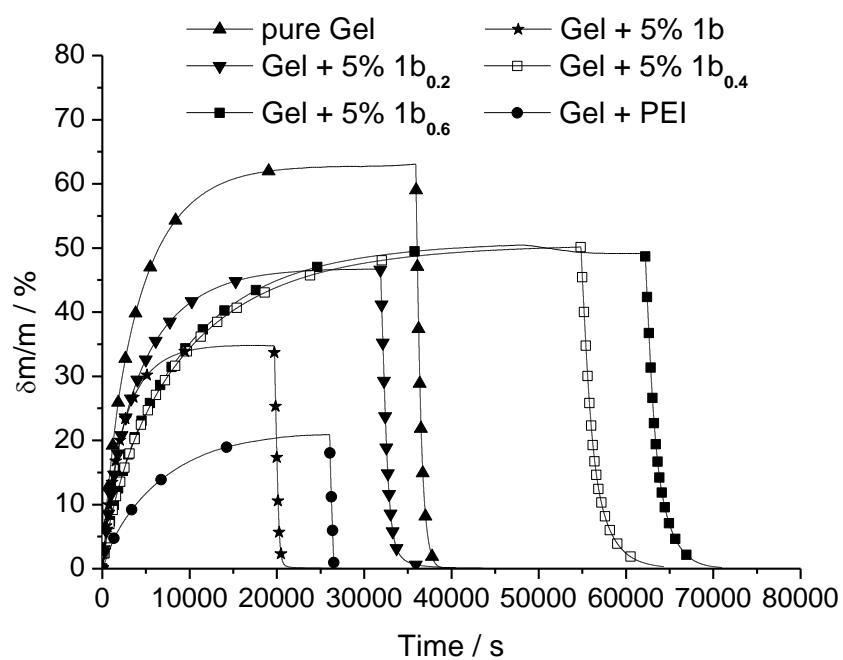


Figure S3. Sorption curves of bulk gels for **1b** and reference samples at 25 °C

Rate constants k are determined by plotting $-\ln(1-\alpha)$ versus the sorption time t

$\alpha = (m_t - m_{t=0}) / (m_{\max} - m_{t=0})$ with m_t being the weight of the sample at time t , $m_{t=0}$ the mass of the sample at $t=0$, and m_{\max} the weight of the sample at equilibrium

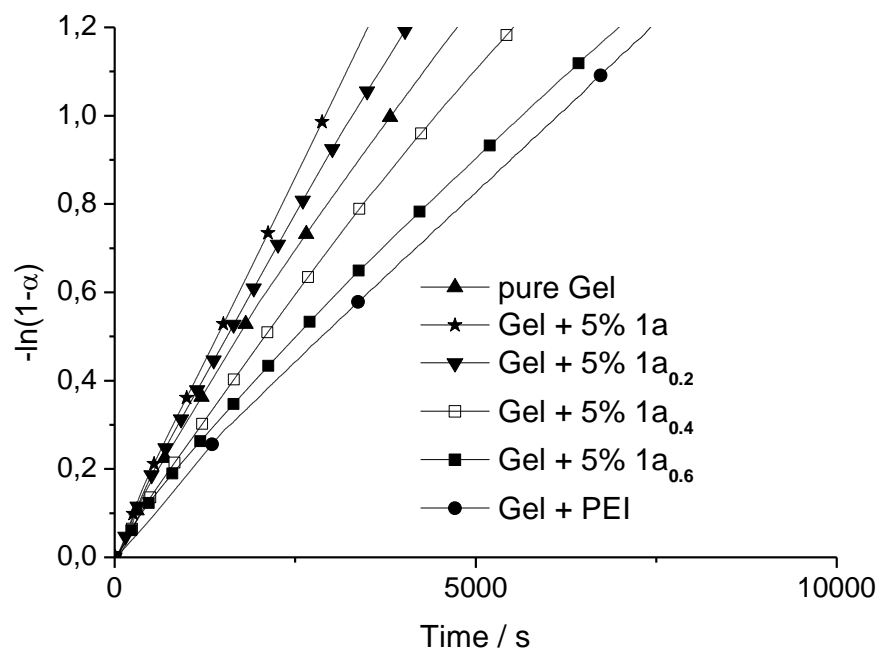


Figure S4. Linear determination of sorption coefficients for **1a** and references at 25 °C

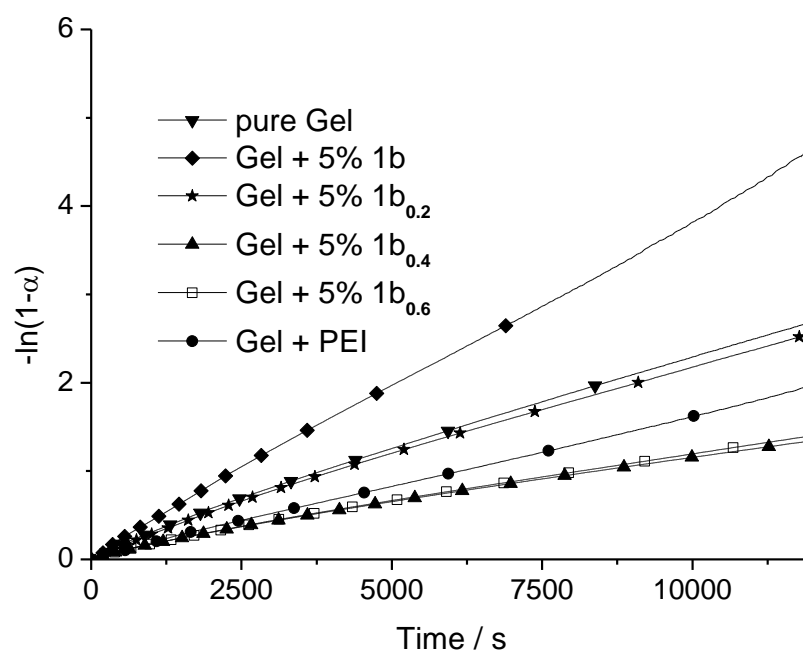


Figure S5. Linear determination of sorption coefficients for **1b** and references at 25 °C

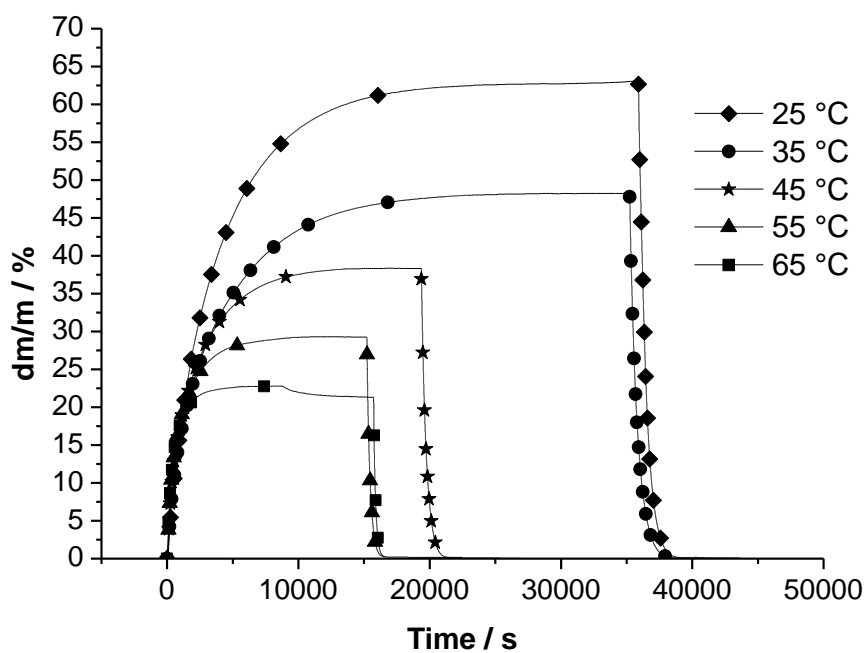


Figure S6. Temperature dependent sorption curves of the pure gel

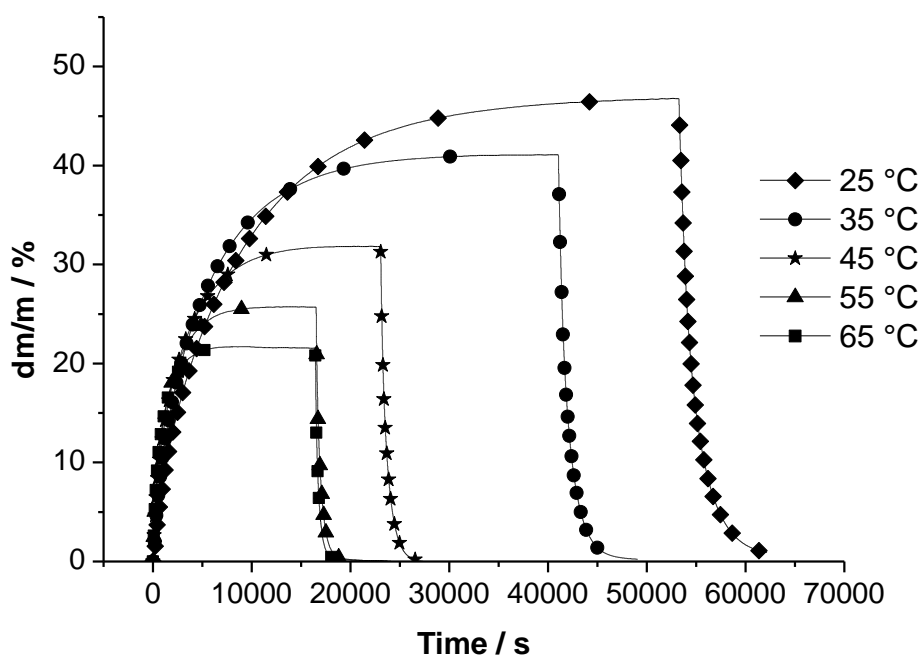


Figure S7. Temperature dependent sorption curves of the pure gel with **1a**.

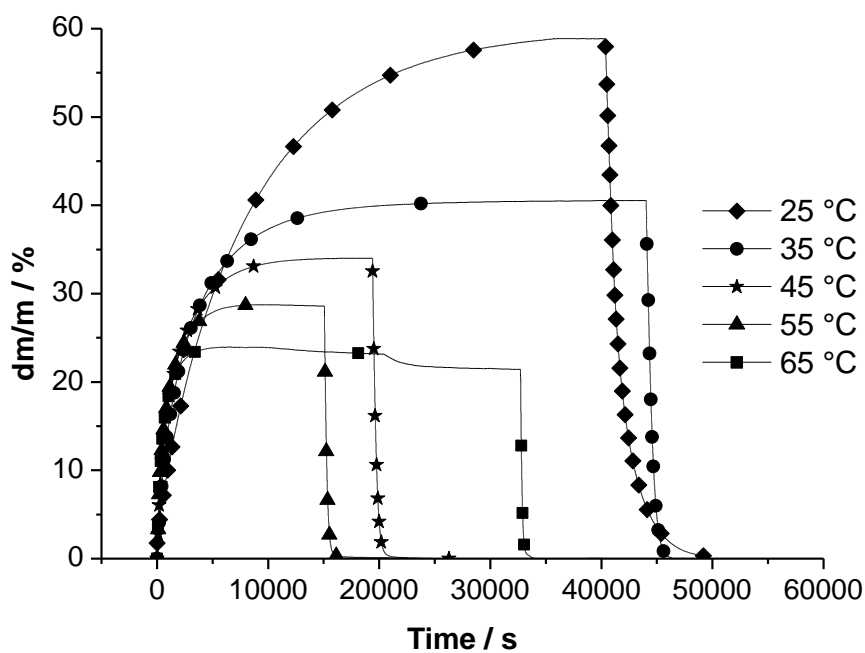


Figure S8. Temperature dependent sorption curves of the pure gel with **1a**_{0.4}.

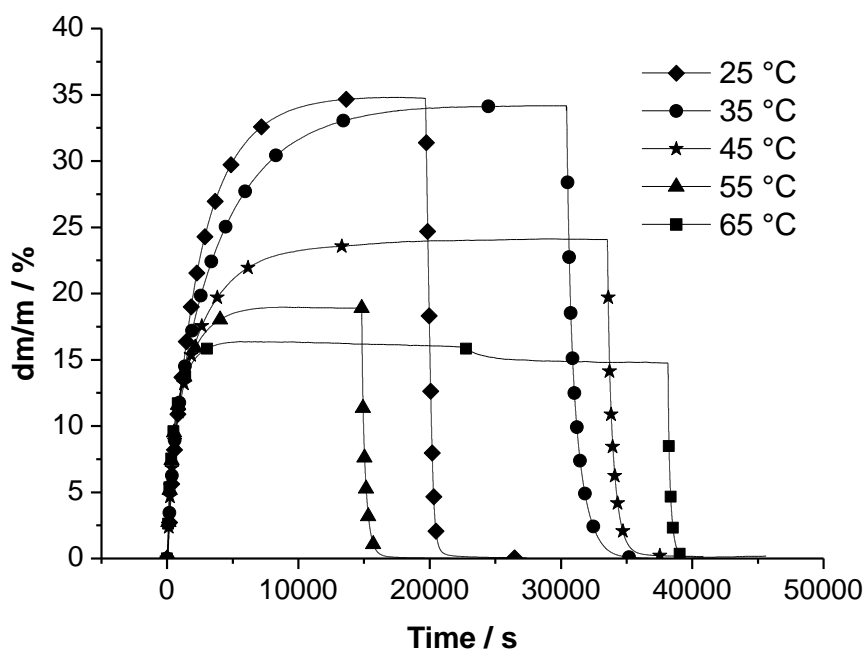


Figure S9. Temperature dependent sorption curves of the pure gel with **1b**.

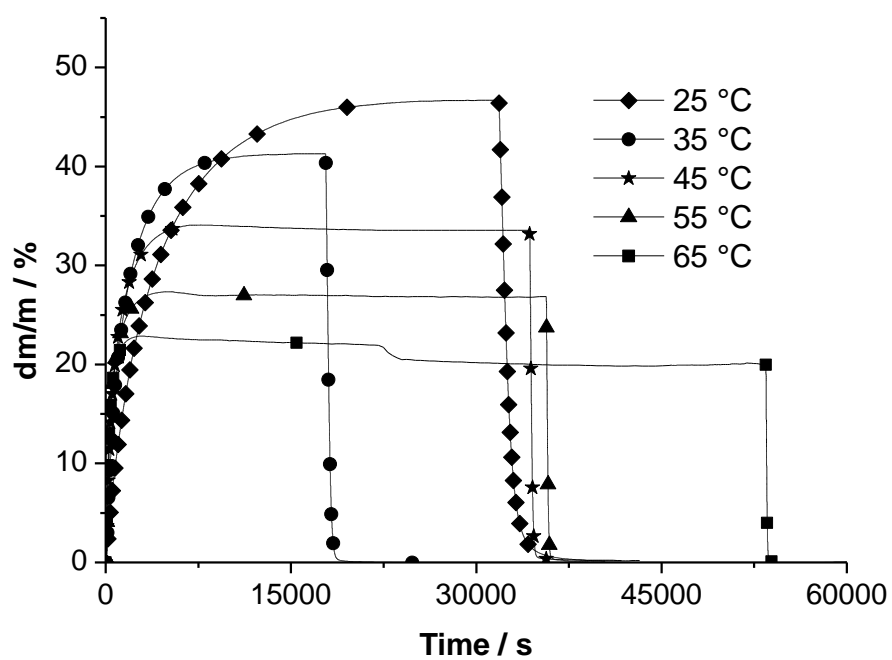


Figure S10. Temperature dependent sorption curves of the pure gel with **1b_{0.4}**.

Activation Energies were determined by using Figs. S6–S9 to calculate the rate constants at different temperatures, which were then used to construct an Arrhenius plot.

Thermodynamic data were obtained by calculating the equilibrium constant $K = [c_\infty]/[c_0]$,

where c_∞ is the moisture concentration at equilibrium and c_0 the concentration at $t=0$. ΔH and

ΔS are obtained from $\Delta G = \Delta H - T\Delta S = RT \ln K$ by plotting $\ln K$ vs. T^{-1} (Figure S11).

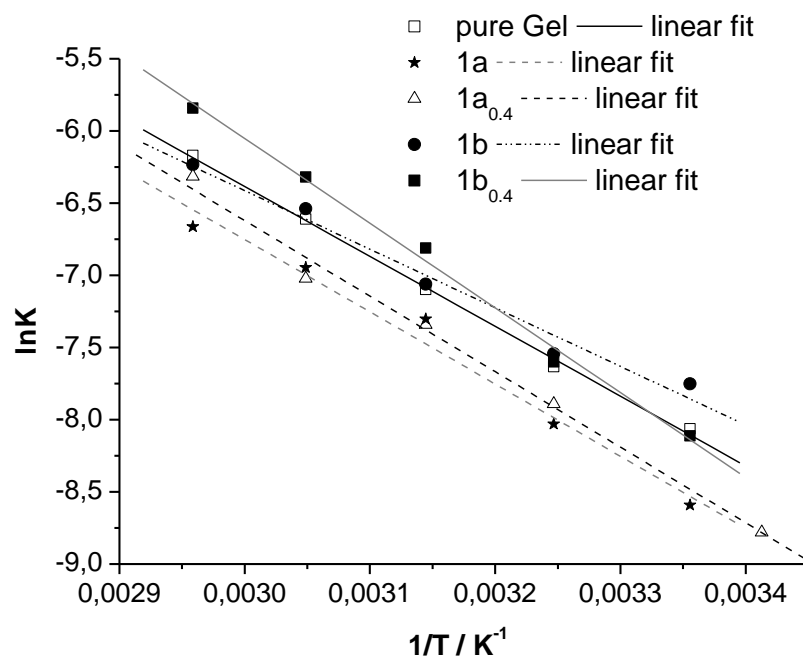


Figure S11. Linear determination of sorption energy and $\ln k_{0\text{sorp}}$.