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SUPPLEMENTARY INFORMATION

Two distinct mechanisms upon absorption of volatile organic compounds into Siloxane Polymers

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Fit of the absorption and desorption curves

The manuscript describes the fit of the absorption and desorption curves to equations that describe the diffusion of the gases into siloxane polymers. Equation (4) of the main manuscript can be written as

$$X(t)_{absorption} = \sum_{i=1}^{K} X_i \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D_i \pi^2 (t-t_0)}{4d^2} \right) \right] \text{* MERGEFORMAT S(1)}$$

And the corresponding desorption curve is

$$X(t)_{desorption} = \sum_{i=1}^{K} X_{0i} \left[\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 D_i \pi^2 (t-t_0)}{4d^2} \right) \right] \text{* MERGEFORMAT S(2)}$$

In the manuscript it is argued that a biexponential fit (K=2) is adequate for most curves and accordingly two diffusion constants D_i are given for each process, i.e. for absorption and desorption. While the quality of the residuals provides a good indicator for the adequacy of the fit, a more careful analysis is required to ensure that the data are neither "overfitted" nor "underfitted".

Figure S1 shows the absorption and desorption curve following exposure of a PDMS film to 200 Pa m-xylene and nitrogen. The three functions with K=1 (blue), K=2 (red) and K=3 (green) all provide excellent fits with a correlation coefficient $R^2 > 0.98$. The fit and residuals for the K=2 and 3 are nearly identical, indicating that fitting the data to three distinct rates is not improving the fit quality over the b-exponential model.

The adequacy of the bi-exponential fit is further supported by the analysis of the co-variance matrix.

Table S1 lists the results from the fit using the Levenberg-Marquardt algorithm (implemented through *Microcal Origin 6.0*). The uncertainties are determined in this algorithm from the covariance matrix and clearly indicate that a third exponential function overfits the data.

The fit also indicates that two exponential functions give only a modest improvement of the coefficient of determination compared to fits with a single exponential function. We nevertheless believe that a second term improves the fit quality, because both of the two additional fit parameters may be obtained with low uncertainties, i.e. their covariance terms are low.

A similar analysis was carried out for absorption and desorption curves of the other analytes, except where indicated in the text. Note that the uncertainties given in Table 3 of the main text arise from the distribution of values obtained in at least five different absorption and desorption experiments. The reproducibility of the kinetics between runs gave uncertainties of several 10%, which is much larger than the uncertainties arising from the fits to each of the curves.

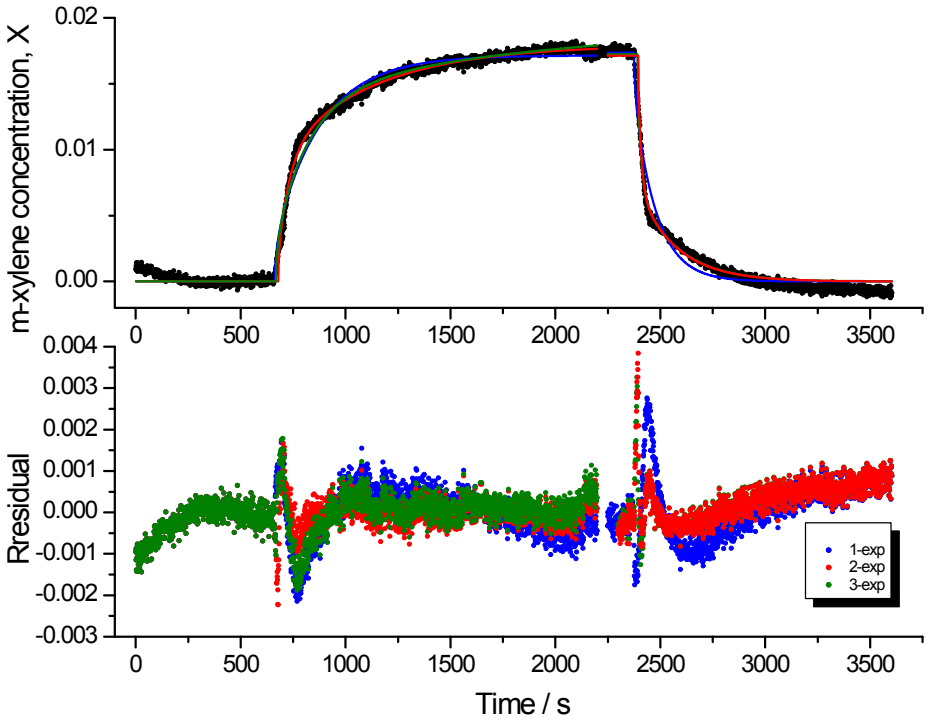

Figure S1: Absorption and desorption of m-xylene at 200 Pa into a PDMS polymer film akin to Fig 4 of the main text. The fits to K = 1, 2 and 3 independent diffusion processes according to equations * MERGEFORMAT S(1) and * MERGEFORMAT S(2) are given in blue, red and green respectively.

Table S1: Fit parameters of equations * MERGEFORMAT S(1) and * MERGEFORMAT S(2). and associated uncertainties obtained using a Levenberg-Marquardt fit to the data in Fig S1

Absorption	Value (K=3)	uncertainty	Value (K=2)	uncertainty	Value (K=1)	uncertainty
X_1	0.00597	73%	0.00785	2%	0.01714	*0.12%*
X_2	0.00654	14%	0.01013	1%	0	
X_3	0.00593	76%	0		0	
D_1	1.05	59%	4.453	4%	1.18991	*0.80%*
D_2	5.34	12%	0.569	3%		
D_3	0.336	82%				
t_0	680.9855	0.06%	678.9988	0%	663.245	*0.09%*
R^2	0.9974		0.9975		0.9942	
Desorption						
X_{01}	0.00874	5%	0.00863	2%	0.01736	0.35%
X_{02}	0.00724	12673%	0.0085	2%	0	
X_{03}	0.00128	71663%	0		0	
D_1	15.02	14%	17.91873	12%	2.48851	1.24%
D_2	1.38	696%	1.4331	3%		
D_3	1.54	3941%				
t_0	2391.961	0.08%	2395.802	0.03%	2375.659	0.03%
R^2	0.990		0.989		0.983	