Supporting Information

GIANT MULTISTEP CRYSTALLINE VS. OSMOTIC SWELLING OF SYNTHETIC HECTORITE IN AQUEOUS ACETONITRILE

RAPHAEL KUNZ[1], SONJA AMSCHLER[1], ANDREAS EDENHARTER[1], LINA MAYR[1], SEBASTIAN HERLITZ[1], SABINE ROSENFELDT[1], AND JOSEF BREU[1,*]

[1] Department of Chemistry and Bavarian Polymer Institute, University of Bayreuth, 95447 Bayreuth, Germany

[*] Correspondence to J. Breu (E-mail: josef.breu@uni-bayreuth.de; Fax: (+49) 921-552788; Telephone: (+49) 921-552531)

1. SAXS pattern

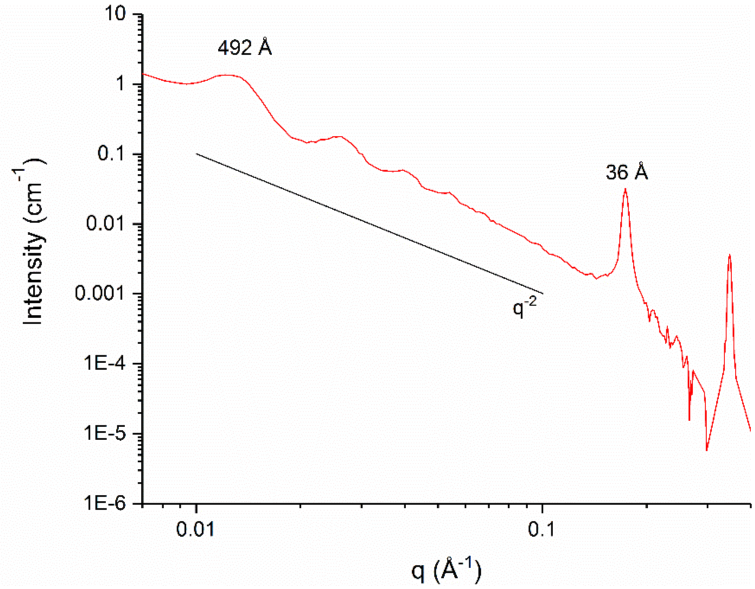

Figure S1: SAXS pattern of Na-hec in 68 vol % acetonitrile showing the coexistence of an osmotically swollen phase with 492 Å layer separation and a crystalline swollen phase with 36 Å basal spacing.

Obviously in this sample osmotic (regime two) and crystalline swelling coexist. Moreover, the layer separation (492 Å) of the osmotically swollen phase is clearly in the range of regime two. However, only few delaminated layers make up the nematic phase. The intensity of oscillations corresponding to the layer separation in the regime two is not only influenced by the particle number but also by the quality of coherence of adjacent layers. The volume ratios of two phases can consequently not be determined reliably, especially since the coherence in regime two is hampered by tilting and translational disorder, which in turn become more pronounced with increasing dilution.[i]

2. X-ray diffraction patterns

Please note: It is well known that the DECTRIS MYTHEN 1 K strip detector produces an assymetric peak shape at low angle side.

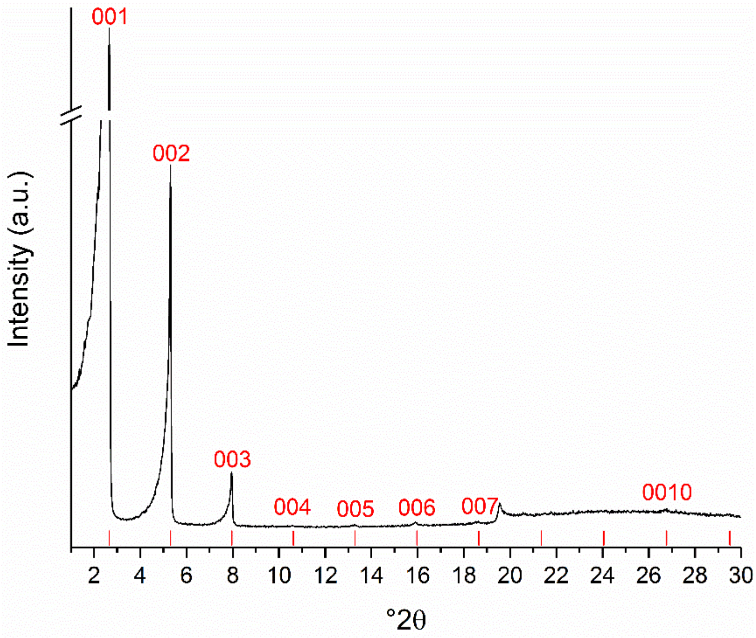

Figure S2: XRD pattern of Na-hec equilibrated in 71 vol % acetonitrile.

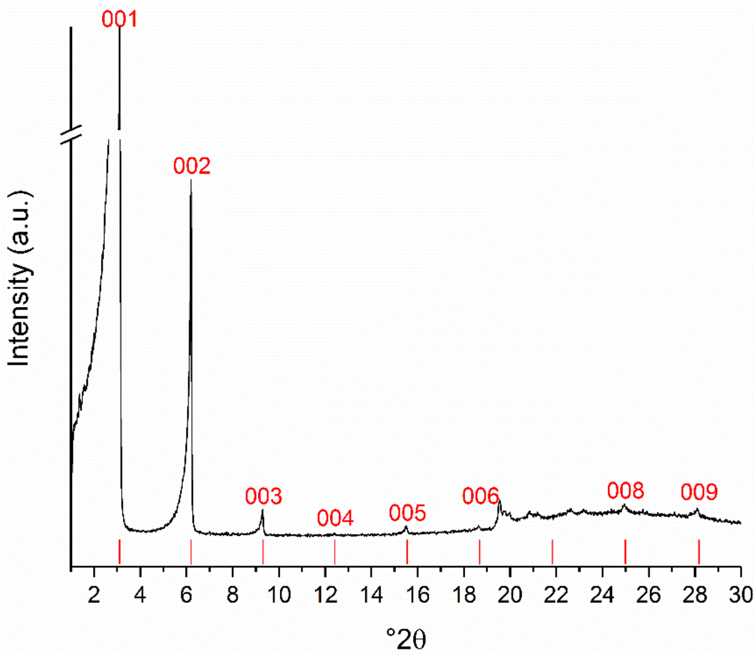

Figure S3: XRD pattern of Na-hec equilibrated in 78 vol % acetonitrile.

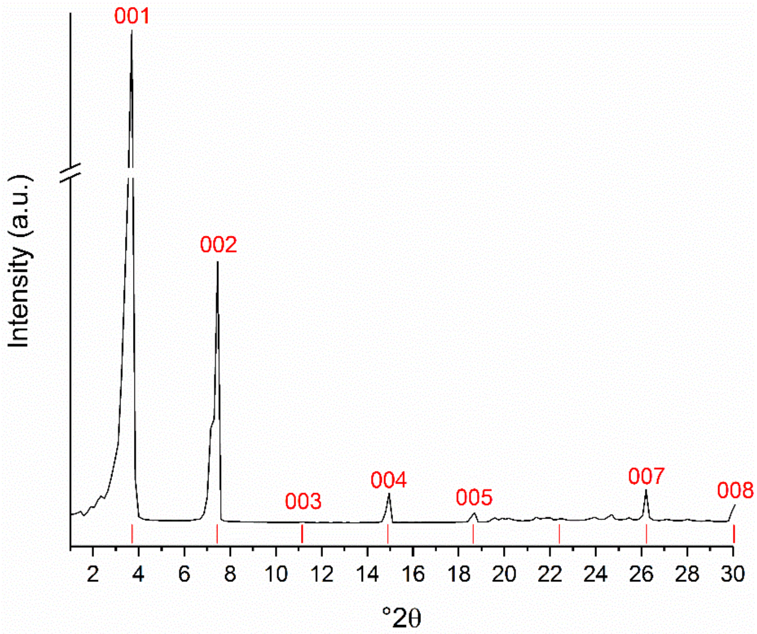

Figure S4: XRD pattern of Na-hec equilibrated in 84 vol % acetonitrile.

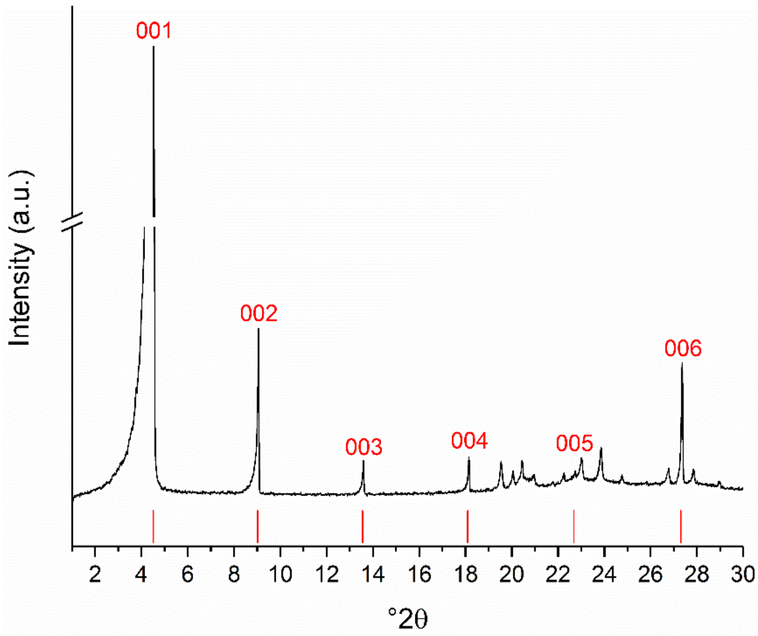

Figure S5: XRD pattern of Na-hec equilibrated in 90 vol % acetonitrile.

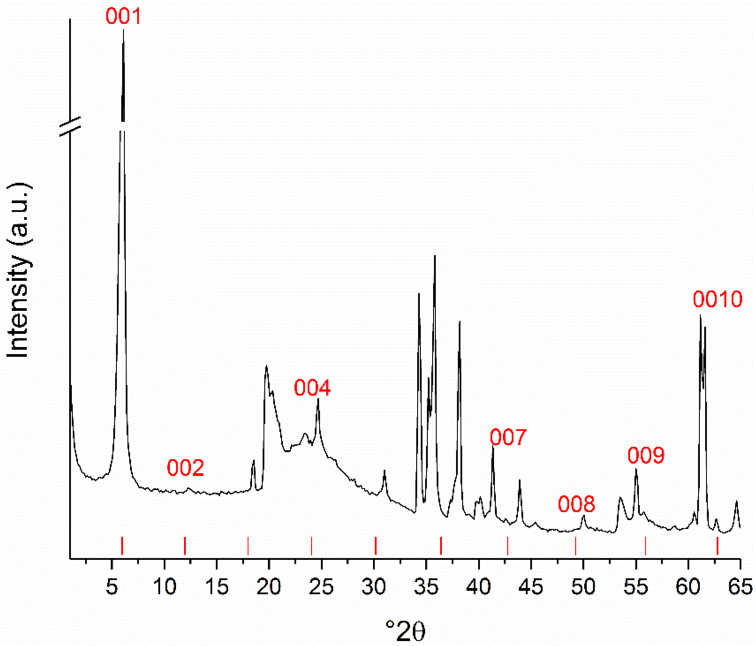

Figure S6: XRD pattern of Na-hec equilibrated in 100 vol % acetonitrile.

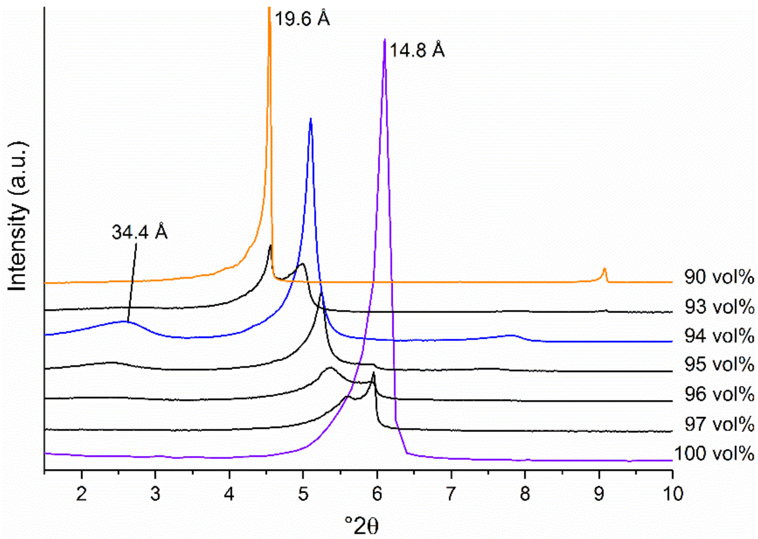

Figure S7: Low angle region of the XRD patterns of Na-hec swollen with various acetonitrile:water mixtures between 90 and 100 vol % acetonitrile. Only at 94 vol % actonitrile equal weights of the two distinct interlayer spaces are achieved leading to a rational *00l*-series of the ordered interstratification going along with the most intense superstructure reflection at 34.4 Å.

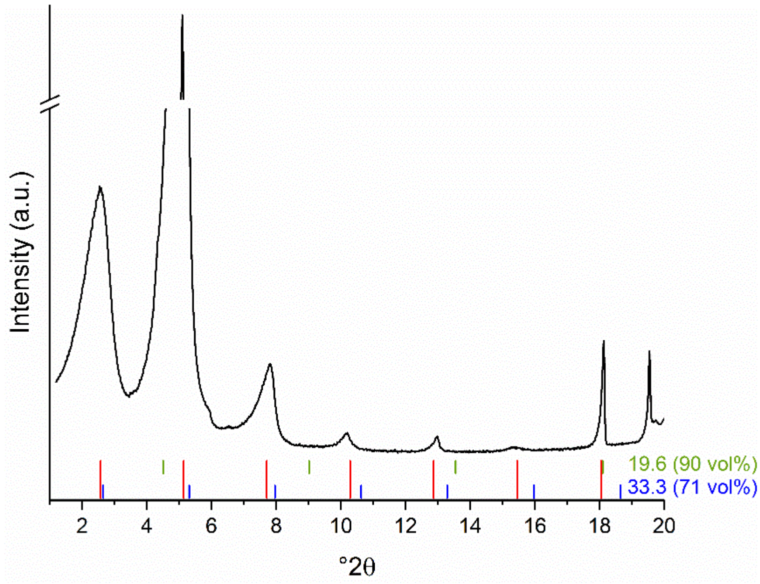

Figure S8: Low angle region of the XRD pattern of the ordered interstratification of Na-hec in 94 vol % acetonitrile. The diffraction pattern of the ordered interstratification cannot be explained by a superposition of the patterns of 33.3 Å tactoids with 71 vol% acetonitrile and 19.6 Å tactoids with 90 vol% acetonitrile.

3. Derivation of water:acetonitrile ratio adsorbed

Starting with the water content of the supernatant after equilibration as determined by KF titration the adsorption capacities for water and acetonitrile can be derived when assuming that the molar volumes/densities of acetonitrile and water in the solvent mixture and being adsorbed in the interlayer are the same. Furthermore, the corrugation of the 2:1 silicate layers is neglected which is anyhow counterbalanced by neglecting the interlayer space occupied by the interlayer cations (Na^+).

The volume of the swelling medium adsorbed into the interlayer space can be calculated by multiplying the *ab*-unit cell area of Na-hec (a = 5.2401(10) Å, b = 9.0942(10) Å, Z = 2)[ii] with the interlayer height. The latter corresponds to the basal spacing subtracted by the thickness of the silicate layer (9.6 Å).[iii] This interlayer volume per unit cell can then be transformed into the total interlayer volume by deviding the amount of Na-hec in the dispersion by the molecular weight of Na-hec per formula unit (M_w = 386.06 gmol^{-1}).

Table S1: Derivation of water:acetonitrile adsorbed.

swelling medium	**71 vol %**	**78 vol %**	**84 vol %**	**90 vol %**	**94 vol %**
• acetonitrile weight /g	2.769	3.042	3.276	3.510	3.205
≙ acetonitrile volume /m^3	3.52E-6	3.87E-6	4.17E-6	4.47E-6	4.08E-6
• water weight /g	1.445	1.098	0.798	0.499	0.260
≙ water volume /m^3	1.45E-6	1.10E-6	8.00E-7	5.01E-7	2.60E-7
volume of swelling medium /m^3	4.90E-6	4.91E-6	4.93E-6	4.94E-6	4.34E-6
Na-hec weight /g	1.316	1.335	1.358	1.320	1.155
⇒ number of unit cells	1.03E21	1.04E21	1.06E21	1.03E21	9.01E20
basal reflection /Å	33.3	28.5	23.8	19.6	34.4
⇒ interlayer height /Å	23.7	18.9	14.2	10.0	15.2 / 2
interlayer volume per unit cell /m^3	1.13E-27	8.99E-28	6.76E-28	4.76E-28	3.62E-28
× number of unit cells					
⇒ total interlayer volume /m^3	1.16E-6	9.36E-7	7.15E-7	4.90E-7	3.26E-7
remaining volume supernatant / m^3	3.74E-6	3.98E-6	4.21E-6	4.45E-6	4.01E-6
water content of supernatant (KF) /wt %	28.55	20.27	14.35	9.93	6.25
⇒ water content supernatant /mol %	46.79	36.68	27.63	20.07	13.19
⇒ water volume supernatant /m^3	8.83E-7	6.70E-7	4.94E-7	3.57E-7	2.00E-7
⇒ water volume in interlayer /m^3	5.66E-7	4.32E-7	3.06E-7	1.44E-7	6.01E-8
⇒ acetonitrile volume supernatant /m^3	2.90E-6	3.34E-6	3.74E-6	4.11E-6	3.81E-6
⇒ acetonitrile volume in interlayer /m^3	6.20E-7	5.29E-7	4.28E-7	3.59E-7	2.69E-7
water adsorption capacity /mmolg^{-1}	23.8	17.9	12.5	6.0	2.9
acetonitrile adsorption capacity /mmolg^{-1}	9.0	7.6	6.0	5.2	4.5
water:acetonitrile ratio adsorbed	**2.6**	**2.4**	**2.1**	**1.2**	**0.6**

Acetonitrile:water weight ratios can be interconverted into volume ratios by applying the known density variations with composition (Fig. S9).[iv] The composition of the supernatant was determined by KF titration. From this together with the not-adsorbed volume of the solvent mixture, the individual adsorption capacities for acetonitrile and water, respectively, can be derived and the selectivity, expressed as water:acetonitrile ratio adsorbed, follows.

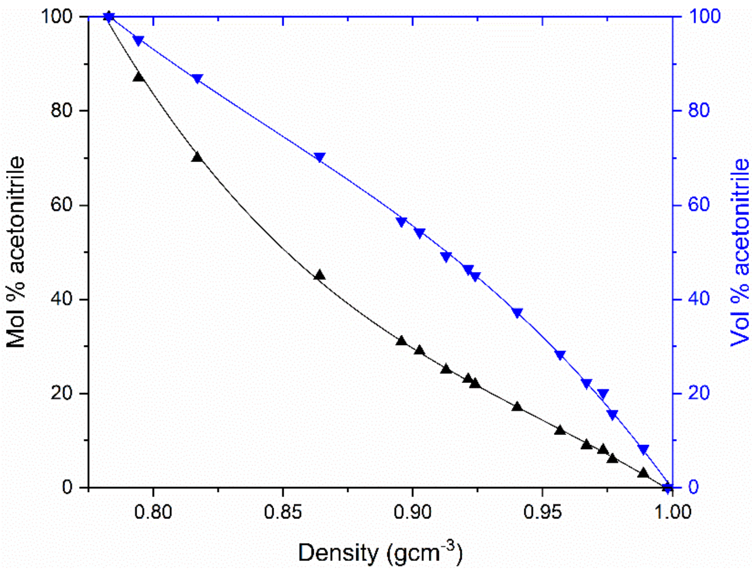

Figure S9: Experimentally determined densities of various acetonitrile water mixtures based on mol % and vol % acetonitrile and their fitting curve over the entire area.[iv]

4. Calculation of the arithmetic mean of the adsorption capacity in 94 vol % acetonitrile

Based on the basal reflection of the 100 vol % sample, the interlayer height was calculated to be 5.2 Å. Applying the assumptions from chapter 2.3, the acetonitrile adsorption capacity can be determined to be 3.7 mmolg^{-1}. Therefore, the arithmetic mean of the 90 and 100 vol % samples, representing an ordered interstratification with equal weight, is calculated to be (5.2 mmolg^{-1} + 3.7 mmolg^{-1}) / 2 = 4.5 mmolg^{-1} acetonitrile and (6.0 mmolg^{-1} + 0 mmolg^{-1}) / 2 = 3.0 mmolg^{-1} water.

[i] S. Rosenfeldt, M. Stöter, M. Schlenk, T. Martin, R.Q. Albuquerque, S. Förster, J. Breu, Langmuir **2016**, *32*, 10582-10588

[ii] J. Breu, W. Seidl, A. Stoll, Z. Anorg. Allg. Chem. 2003, 629, 503-515.

[iii] M. Stöter, B. Biersack, N. Reimer, M. Herling, N. Stock, R. Schobert, J. Breu, Chem. Mater. **2014**, *26*, 5412-5419.

[iv] A. M. Nikitin, A. P. Lyubartsev, J. Comput. Chem. **2007**, *28*, 2020-2026.