

Forceless Spontaneous Delamination of High-Aspect Ratio Fluorohectorite into Monolayer Nanosheets in Chloroform

Kamonnart (Jaa) Imwiset,^a Volodymyr Dudko,^b Paul Markus,^c Georg Papastavrou,^c Josef Breu,^b and Makoto Ogawa^{a*}

^aSchool of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Engineering, Wangchan Valley, Rayong 21210, Thailand

^bDepartment of Chemistry and Bavarian Polymer Institute, University of Bayreuth, Bayreuth 95440, Germany

^cPhysical Chemistry II and Bavarian Polymer Institute, University of Bayreuth, Universitätsstr. 30, 95440, Bayreuth, Germany

Supporting Information

Content:

- Materials
- Preparation of sodium-fluorohectorite (Na-HEC)
- Preparation of dioctadecyldimethylammonium-fluorohectorite (2C18-HEC)
- Characterization of Na-HEC and 2C18-HEC
- Calculation of coefficient of variation (CV)
- Calculation of percentage exchange of 2C18 in resulting 2C18-HEC
- Screening for delamination by 1D dissolution
- Observing birefringence and structural colors from 2C18-HEC suspension
- Reflectance spectra of 2C18-HEC suspension
- Calculation of nanosheet separation from the reflectance spectra
- Small-angle X-ray scattering (SAXS) of 2C18-HEC suspension
- Atomic force microscopy (AFM) images of delaminated 2C18-HEC
- Preparation of restacked film of 2C18-HEC

Materials

Diocetadecyldimethylammonium bromide (2C18Br, >96%) was purchased from Chemos GmbH & Co. KG. *N*-methylpyrrolidone (>99%), toluene (>99.9%), acetonitrile (>99.8%), ethanol (>99.9%), tetrahydrofuran (99.9%), acetone (>99.5%), dichloromethane (>99.8%) were purchased from Merck. Pyridine (>99.5%) and chloroform (AR grade) were purchased from QRëC chemical Co., Ltd. Ethyl acetate (>99.8%) was purchased from Fisher scientific. Cyclohexane (99.5%), was purchased from TCI Co., Ltd.

Preparation of sodium-fluorohectorite (Na-HEC)

Sodium fluorohectorite (denoted as Na-HEC) was obtained by melt synthesis followed by long-term annealing according to a published procedure.³⁷ The material has a nominal composition of $[\text{Na}_{0.5}]^{\text{inter}}[\text{Mg}_{2.5}\text{Li}_{0.5}]^{\text{oct}}[\text{Si}_4]^{\text{tet}}\text{O}_{10}\text{F}_2$ with a cation exchange capacity (CEC) of 129 meq/100 g as determined by BaCl_2 -method (130 mequiv/100 g nominally).

Preparation of dioctadecyldimethylammonium-fluorohectorite (2C18-HEC)

Na-HEC was dispersed in a solution of 2C18Br (0.0125 M) in an ethanol/water mixture (ethanol/water ratio of 4:1) at a concentration of 0.532 wt%. The amount of added salt corresponded to 2.2 times of the CEC of Na-HEC. The mixture was magnetically stirred at room temperature for 1 day, and the cation exchange reaction was repeated twice to achieve quantitative ion exchange. The product was collected by centrifugation and washed with an ethanol/water mixture (ethanol/water ratio of 1:1). Finally, the product was dried at 60°C for 1 day.

Characterization of Na-HEC and 2C18-HEC

Before measurement, Na-HEC was equilibrated for 1 day at 43% relative humidity to convert it to the crystalline swollen monolayer hydrate. 2C18-HEC was dried at 100

°C for 1 hour and then cooled to room temperature in a desiccator to remove the last traces of water in the interlayer. X-ray diffraction patterns of Na-HEC and 2C18-HEC were measured in transmission mode applying a STOE STADI P powder diffractometer (Cu $K\alpha_1$ radiation, Ge monochromator, linear position-sensitive detector). The organic content of 2C18-HEC was analyzed by a PerkinElmer 2400 CHN equipped with a combustion tube filled with tungsten(VI)-oxide-granules operated at 1050°C. Sulfanilamide was used as the standard reference. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) applying a Zeiss 1530 equipped with a EDX INCA 400 unit (Oxford) were used to check for traces of Na^+ that would indicate incomplete ion exchange. For SEM/EDX analysis 2C18-HEC crystals was deposited on a carbon tape and sputtered with 10 nm carbon.

Calculation of coefficient of variation (CV)

The CV represents the standard deviation of the basal spacing and was derived from the individual reflection of the $00l$ -series of the crystalline 2C18-HEC powder (**Fig. S1**):

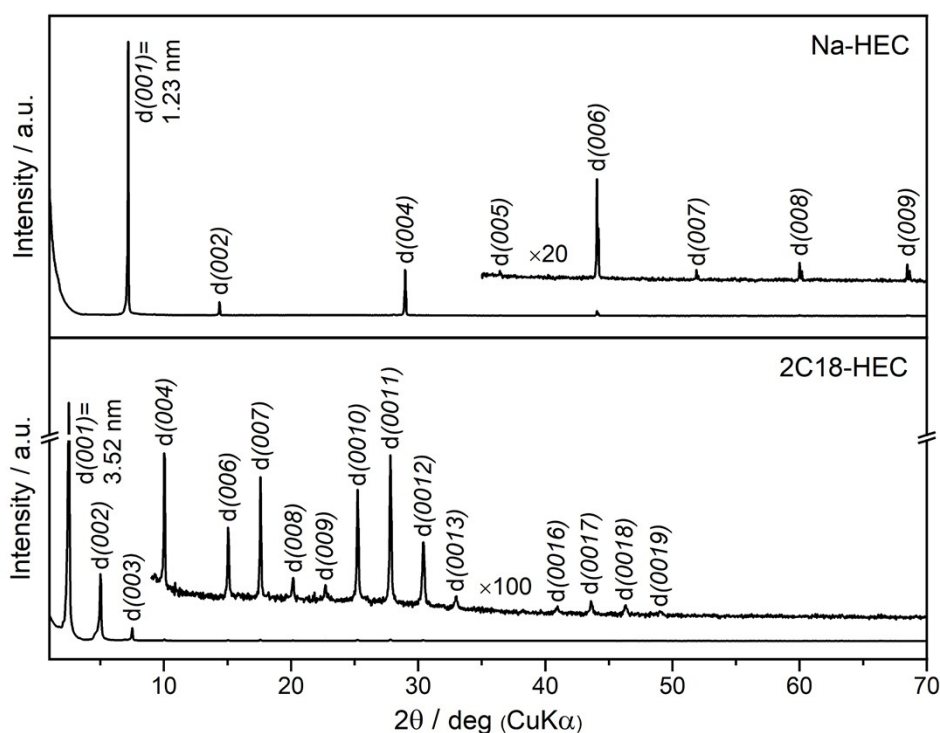


Fig. S1 XRD patterns of pristine Na-HEC and 2C18-HEC.

Table S1. Coefficient of variation (CV) of 2C18-HEC.

<i>l</i>	2 θ value	<i>d</i> -spacing (Å)	Calculated <i>d</i> ₀₀₁ values
1	2.5078	35.2094	1 × 35.2094 = 35.2094
2	5.0001	17.6760	2 × 17.6760 = 35.3521
3	7.5062	11.7933	3 × 11.7933 = 35.3800
4	10.0581	8.8212	4 × 8.8212 = 35.2848
6	15.1728	5.8862	6 × 5.8862 = 35.3169
7	17.7936	5.0414	7 × 5.0414 = 35.2897
8	20.4626	4.4068	8 × 4.4068 = 35.2542
10	25.8803	3.5295	10 × 3.5295 = 35.2947
11	28.7058	3.2075	11 × 3.2075 = 35.2823
12	31.5995	2.9402	12 × 2.9402 = 35.2824
Mean			35.2946
CV			0.13 %

Calculation of percentage exchange of 2C18 in resulting 2C18-HEC

The percentage of exchange was determined by CHN analysis. The amount of 2C18 in the product was calculated from the determined wt% of carbon in 2C18-HEC and the molar mass of carbon:

Molar weight of $[2\text{C}18_{0.5}]^{\text{inter}}[\text{Mg}_{2.5}\text{Li}_{0.5}]^{\text{oct}}[\text{Si}_4]^{\text{tet}}\text{O}_{10}\text{F}_2 = 609.65$ g/unit cell

% Molar weight = (molar weight of carbon / molar weight per unit cell) × 100

% Exchange = (%wt of carbon / % of molar weight of carbon) × 100

From CHN analysis, wt% of carbon in 2C18-HEC is 39.25%, corresponding to 104.95% exchange or 135 mequiv/100 g.

Screening for delamination by 1D dissolution

Since successful 1D dissolution can be spotted visually through a significant increase in dispersion viscosity compared to the examined solvent and by the presence of birefringence under polarized light, which attributes to the liquid

crystalline phase, preliminary test for the swelling behavior of 2C18-HEC in various organic solvents can be done quickly. Before the swelling tests, 2C18-HEC was heated to 100°C for 1 hour to remove any remaining water. For this 2C18-HEC (3 mg) was dispersed in organic solvents (0.5 ml), and the suspensions were prepared by gentle shaking applying an over-head shaker at 50 rpm at room temperature for 1 day. Visual inspections of the 2C18-HEC suspensions in various organic solvents were conducted immediately after shaking. The dielectric constants of the examined solvents and appearance of 2C18-HEC suspensions in the examined solvents are summarized in the table as shown below.

Table S2. Dielectric constant of the examined solvents along with the appearance of 2C18-HEC in these solvents.

Solvent	Dielectric constant (ϵ)	Swelling of 2C18-HEC
Acetonitrile	^a 36.64 (20 °C)	Sediment
N-Methylpyrrolidone	^a 32 (20 °C)	Sediment
Ethanol	^a 24.6 (20 °C)	Sediment
Acetone	^a 21.01 (20 °C)	Sediment
Pyridine	^a 12.3 (25 °C)	Sediment
Dichloromethane	^b 8.93 (25 °C)	Sediment
Tetrahydrofuran	^a 7.52 (20 °C)	Sediment
Ethyl acetate	^b 6.02 (25 °C)	Sediment
Chloroform	^a 4.81 (20 °C)	Gel
Toluene	^a 2.38 (25 °C)	Sediment
Cyclohexane	^a 2.02 (20 °C)	Sediment

^a<https://organicchemistrydata.org/solvents/>

^b<https://macro.lsu.edu/howto/solvents/Dielectric%20Constant%20.htm>

Observing birefringence and structural colors from 2C18-HEC suspension

The 2C18-HEC suspension in chloroform (0.42 vol% or 1.32 wt%) was prepared by gentle shaking applying a replicating shaker at 200 rpm at room temperature

for 1 day (or an over-head shaker at 50 rpm at room temperature for 3 days). To assess birefringence, the suspension was placed between two crossed polarizers. For the investigation of structural colors, the suspension was placed in front of a black background in a darkroom. The structural colors of the suspension were observed in various containers: a 1 cm diameter borosilicate vial and quartz cuvettes with light paths of 1 cm and 2 mm. For 2C18-HEC in 2 mm quartz cuvette, the appearance of the suspension was observed at various angles (**Fig. S2**): tilting a cuvette (a) 0° and (b) 10° in the vertical direction, with the camera positioned 30° horizontally away from the LED light source, and (c) tilting a cuvette 0° in the vertical direction and the camera positioned 60° horizontally away from the LED light source. The photos of the suspension were taken using a Canon EOS RP with a Canon RF 24-105mm f/4-7.1 IS STM Lens.

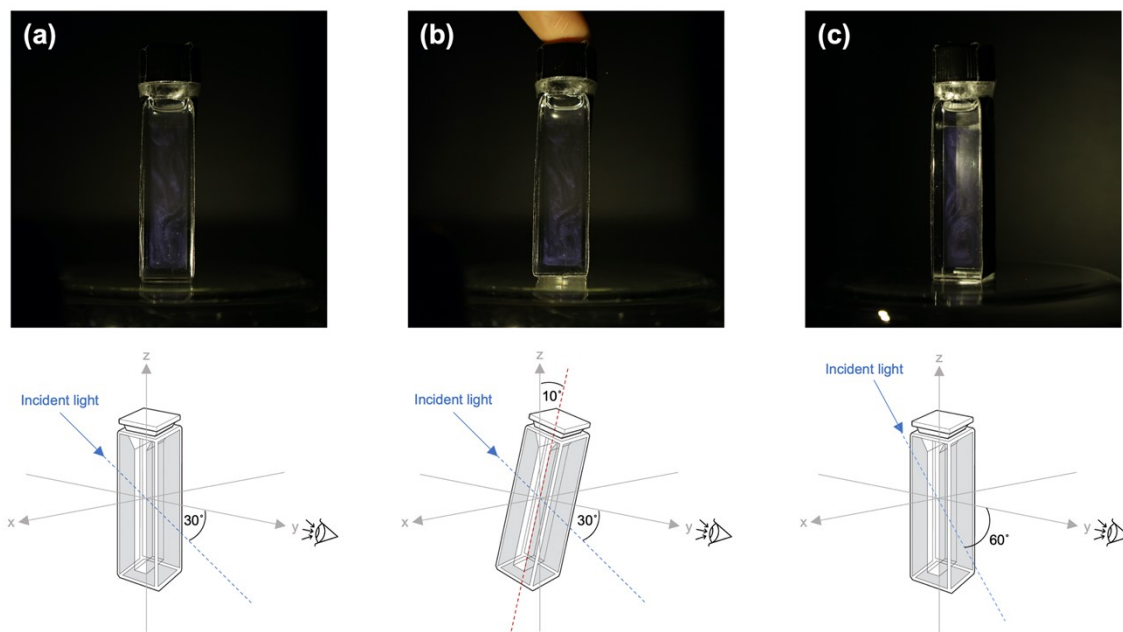


Fig. S2 2C18-HEC suspension in a 2 mm quartz cuvette at the following angles: tilting a cuvette (a) 0° and (b) 10° in the vertical direction, with the camera positioned 30° horizontally away from the LED light source, and (c) tilting a cuvette 0° in the vertical direction and the camera positioned 60° horizontally away from the LED light source.

Reflectance spectra of 2C18-HEC suspension

The normalized reflectance of 2C18-HEC suspensions in chloroform (0.42 vol% or 1.32 wt%) were measured applying a PerkinElmer Lamda 1050. Spectralon® served as white diffuse reflectance standard to calibrate the spectrometer. The suspension, filled into a 1 mm quartz cuvette, was vertically positioned and connected to the integrating sphere, perpendicular to the UV-Vis spectrometer's incoming light. A black, light-absorbing background was placed behind the cuvette to prevent reflection of transmitted light. To investigate angle-dependent reflectivity, the suspension was examined by tilting the cuvette by 10° in the vertical direction. These measurements were taken immediately after filling the suspension in the cuvette.

This result revealed a reflection at 420 nm (**Fig. S3**), corresponding well to the purple hue observed in the 2 mm path light cuvette (**Fig. S2**). The reflectivity of the 2C18-HEC suspension at different angles indicated that there was no angle-dependent change of the wavelength of reflectivity when altering the angle of incident light (**Fig. S3**). This is in line with our visual observation of 2C18-HEC suspensions inside the narrow slit of a 2 mm quartz cuvette, where the position of incident light was changed (**Fig. S2**). Based on Bragg-Snell's law, the nanosheet separation in the nematic domains (d) at this concentration as calculated from the reflectance peak at 420 nm corresponded to 435 nm (violet) for the second-order colour ($m = 2$). Fine-tuning the structural colour could be achieved by adjusting the nanosheet separation, which, in turn, is controlled by the concentration of 2C18-HEC in chloroform—a factor that deserves further exploration.

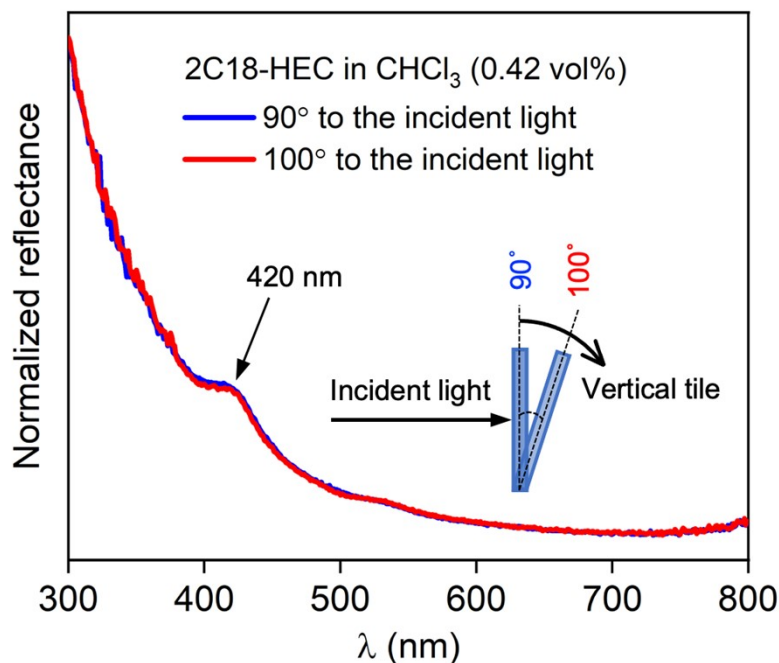


Fig. S3 Normalized reflectance of the 2C18-HEC in chloroform (0.42 vol%) in a 1 mm path cuvette at 90° and 100° to the UV-vis spectrometer's incoming light.

Calculation of nanosheet separation from the reflectance spectra

Based on the Bragg-Snell's law, constructive interference of white light from individual nanosheets is described as $2d(n^2 - \sin^2\theta)^{1/2} = m\lambda$; where d represents the nanosheet separation or interlayer spacing, n is the effective refractive index, θ is the angle between the nanosheet plane and the observer's point of view, m is the order of Bragg-Snell reflection, and λ stands for the wavelength of the light reflected by the Bragg mirror for a given d and θ . The effective refractive index can be expressed as $n = (n_1^2\Phi_1 + n_2^2\Phi_2)^{1/2}$, where n_1 and n_2 are refractive indices and Φ_1 and Φ_2 are volume fractions of 2C18-HEC and chloroform. Considering that chloroform was the major component of the suspension (>99.9%), we assumed that the effective refractive index is $n \approx n_{\text{CHCl}_3} = 1.44$ at 20 °C. Using the derived Bragg-Snell's equation, $d = \frac{1}{2} m\lambda(n^2 - 1)^{1/2}$, the nanosheet separation in the nematic domains (d) may be calculated from the reflectance peak at 420 nm (**Fig. S3**). The calculated d -

spacing was 438 nm for the second order color ($m = 2$).

$$d = \frac{1}{2} m \lambda (n^2 - 1)^{1/2} = \frac{1}{2} (2)(420)((1.44)^2 - 1)^{1/2} = 435 \text{ nm}$$

Small-angle X-ray scattering of 2C18-HEC suspension

SAXS data were collected using an SAXS instrument installed at the BL19B2 beamline in SPring-8 (Hyogo, Japan). The X-ray energy was 18 keV, with a sample-to-detector distance of 3 m. Employing a two-dimensional detector, the PILATUS 2M, it covered the scattering vector range, $q = 0.06\text{--}3.2 \text{ nm}^{-1}$. The 2C18-HEC suspensions (6 vol%, 4 vol%, 3 vol%, and 2 vol%) were prepared by adding a certain amount of 2C18-HEC in chloroform (300 μl) followed by magnetically stirring at $\sim 200\text{--}300 \text{ rpm}$, depending on the viscosity of the suspension, for 30 minutes. The 2C18-HEC suspensions were filled into quartz capillaries (WJM-Glas Müller GmbH, outer diameter = 2 mm, and wall thickness = 0.01 mm) using a disposable syringe (1 ml) and a needle (diameter = 0.6 mm and length = 5.5 cm). The quartz capillary filled with 2C18-HEC suspensions were sealed using epoxy resin (Araldite). Before the measurement, the quartz capillaries were centrifuged for $\sim 45,000\text{--}55,000 \text{ rpm}$ for $\sim 1\text{--}3 \text{ minutes}$, depending on the viscosity of the suspension to remove bubbles in the suspension. For SAXS measurement, the exposure times were set as 60 s for 6 vol%, 4 vol%, and 3 vol% of 2C18-HEC suspension, and 30 s for 2 vol%.

The separation of nanosheets in the nematic domains ($d(001)$) of the 2C18-HEC suspensions for the variable volume fractions (ϕ) of 2C18-HEC were calculated from the peaks observed in the SAXS patterns in the table as shown below.

The expected separation of adjacent nanosheets ($d(001)$ from volume fraction (nm) in **Table S3**) in a homogeneously swollen gel can be calculated *via* the volume fraction ϕ using the thickness of a single lamella D , where m (g) and ρ

(cm³/g) are mass and density, respectively. The density of HEC is 2.73 g/cm³, and the density of CHCl₃ is 1.49 g/cm³.

$$\phi = (m_{\text{HEC}} / \rho_{\text{HEC}}) / ((m_{\text{HEC}} / \rho_{\text{HEC}}) + (m_{\text{CHCl}_3} / \rho_{\text{CHCl}_3}))$$

$$d = D / \phi$$

Table S3. Component of 2C18-HEC suspension in chloroform, volume fraction of gel, $d(001)$ from the volume fraction of the gel, and $d(001)$ obtained from SAXS.

Vol %	Component		Volume fraction ϕ	$d(001)$ from volume fraction (nm)	$d(00l)$ from SAXS (nm)		
	2C18-HEC	CHCl ₃			$d(001)$	$d(002)$	$d(003)$
2	28.5 mg	3 μ l	0.0196	51.0	55.3	27.5	N.A.
3	42.8 mg	3 μ l	0.0291	34.3	34.1	16.7	N.A.
4	57.1 mg	3 μ l	0.0385	26.0	25.9	12.7	8.5
6	85.6 mg	3 μ l	0.0566	17.7	18.5	9.3	6.1

Atomic force microscopy (AFM) images of delaminated 2C18-HEC

The AFM images were processed with NanoScope Analysis 1.80 (Bruker Nano Inc.). The topography was flattened by subtracting the first-order polynomial background using a threshold to exclude platelets from flattening. Platelet heights were determined by means of the “step tool” as implemented in the NanoScope Analysis software. The sample was prepared by slow evaporation of a few drops of a very diluted suspension in chloroform (~ 20 mg l⁻¹) on a Silicon wafer at ambient temperature.

Preparation of restacked film of 2C18-HEC

The restacked film of 2C18-HEC by depositing 200 μ l of a 2C18-HEC suspension in chloroform (10 mg ml⁻¹ or 0.21 vol%) onto borosilicate glass (15 x 15 mm). Subsequently, the film was dried under ambient conditions for 12 hours. The XRD patterns of restacked film indicated the formation of a 2C18-HEC film with

a well-ordered structure (**Fig. S4**). The basal spacing of the restacked film was measured at 3.75 nm (CV = 0.78%), which closely resembles that of pristine 2C18-HEC before delamination by 1D dissolution. The restacking of 2C18-HEC was conducted to achieve a highly ordered monodomain film through the evaporation of chloroform.

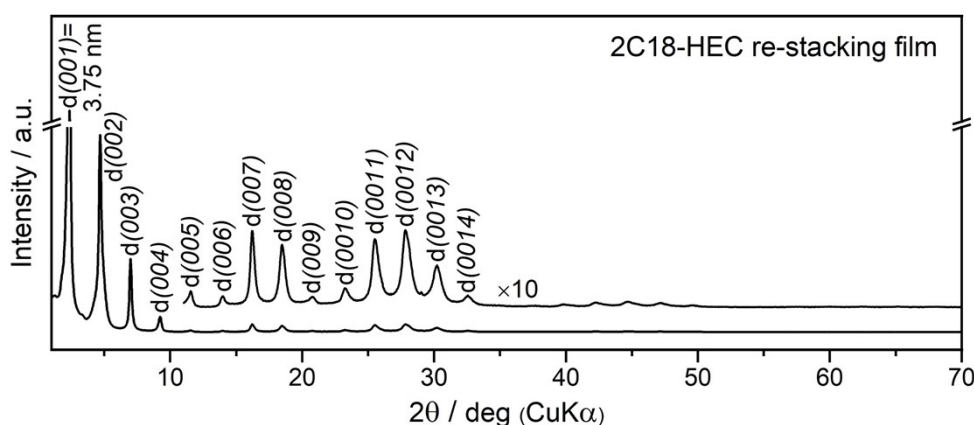


Figure S4. XRD patterns of restacking film of 2C18-HEC.

Table S4. Coefficient of variation (CV) of 2C18-HEC re-stacking film.

l	2θ value	d -spacing (Å)	Calculated d_{00l} values
1	2.353	37.5476	$1 \times 37.5476 = 37.5476$
2	4.658	18.8671	$2 \times 18.8671 = 37.7342$
3	6.991	12.6445	$3 \times 12.6445 = 37.9336$
4	9.222	9.5784	$4 \times 9.5784 = 38.3138$
5	11.528	7.6685	$5 \times 7.6685 = 38.3427$
6	13.955	6.3426	$6 \times 6.3426 = 38.0554$
7	16.209	4.8013	$7 \times 4.8013 = 38.2432$
8	18.474	4.2714	$8 \times 4.2714 = 38.4107$
10	20.790	3.8205	$10 \times 3.8205 = 38.4424$
11	23.252	3.4910	$11 \times 3.4910 = 38.4012$
12	25.514	3.2041	$12 \times 3.2041 = 38.4497$
Mean			38.17329
CV			0.78 %