

Ionic Guest in Ionic Host: Ionosilica Ionogel Composites *via* Ionic Liquid Confinement in Ionosilica Supports

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Experimental section

Chemicals

3-Aminopropyltrimethoxysilane 97%, 3-chloropropyltrimethoxysilane 97% and N,N-Diisopropylethylamine 99% were purchased from ABCR. Formic acid (p.a.) was purchased from VWR and the ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide >99% was purchased from Iolitec. All reagents were used as received.

Materials Synthesis

Tris(3-(trimethoxysilyl) propyl) amine (TTA) was synthesized following adapted previously described protocols: a mixture of 170 mL (1.0 mol) of 3-aminopropyltrimethoxysilane, 450 mL (2.5 mol) of 3-chloropropyltrimethoxysilane and 494 mL (3.0 mol) of N,N-diisopropylethylamine was heated (160°C) and stirred under argon for 72 hours. After cooling at room temperature, salts were eliminated by filtration and the oily residue was distilled under vacuum (Bp= 165 °C at 0.1 mmHg) giving rise to TTA compound as a colorless viscous liquid with 80% yield.

Apparatus and Procedures

Infrared Spectroscopy FTIR spectra were recorded on a PerkinElmer 100 FT spectrometer.

Thermogravimetric Analysis TGA experiments were performed on a TA Instruments Q50 apparatus. The samples were heated under an air stream from 25 to 1000 °C with a heating rate of 10 °C/min.

¹H solid state Nuclear Magnetic Resonance NMR spectra were recorded at $\nu_0(^1\text{H}) \equiv 600.1$ MHz on a VARIAN VNMR 600 spectrometer fitted with a Varian T3 MAS probe using 3.2 mm ZrO₂ rotors. The measurements were carried out at a temperature of 20 °C with a one pulse sequence

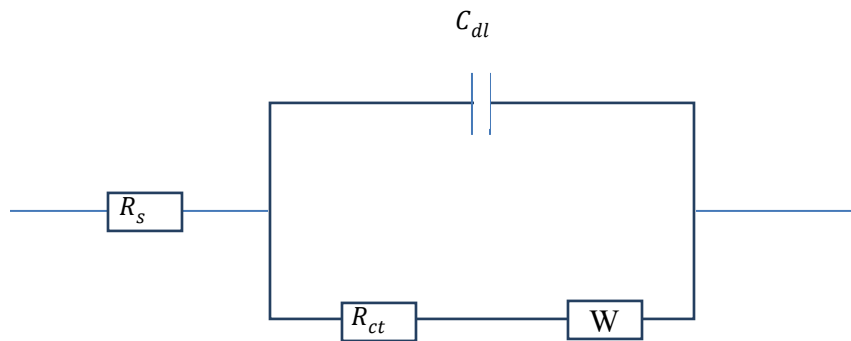
(OP), a $\pi/2$ pulse of 4 μs and a recycling delay of 10 s. The samples were static or rotated at a MAS frequency $\nu_{MAS} = 24$ kHz. The chemical shift value was calibrated using Adamantane as a secondary reference (peak at 1.8 ppm). The acquisition window is 100 kHz and no line broadening has been applied. ^1H spectrum fitting has been achieved using pseudo-Voigt functions, with equivalent Gaussian and Lorentzian contributions, in the freely accessible *DmFit* software. [Massiot, D.; Fayon, F.; Capron, M.; King, I.; Calvé, S. L.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR Spectra. *Magn. Reson. Chem.* 2002, 40, 70-76. , <http://nmr.cemhti.cnrs-orleans.fr/Dmfit/>]

^{13}C and ^{29}Si solid state NMR spectra were recorded at $\nu_0(^{13}\text{C}) \equiv 75.5$ MHz and $\nu_0(^{29}\text{Si}) \equiv 59.6$ MHz on a VARIAN VNMR 300 spectrometer fitted with Varian MAS probes using ZrO_2 rotors. ^{13}C solid state NMR spectra have been acquired using CP-MAS with ^1H decoupling in 3.2 mm rotors spun at $\nu_{MAS} = 12$ kHz with a proton $\pi/2$ pulse of 5 μs , a contact time of 1 ms and a recycle delay of 3s. Adamantane has been used as a secondary reference (left peak at 38.5 ppm). ^{29}Si spectra have been acquired using both CP-MAS and OP. CP-MAS spectra have been recorded in 3.2 mm rotors spun at $\nu_{MAS} = 6$ kHz with a proton $\pi/2$ pulse of 5 μs , a contact time of 5 ms and a recycle delay of 3 s. OP spectra have been recorded in 7.5 mm rotors spun at $\nu_{MAS} = 5$ kHz with a $\pi/6$ pulse of 2 μs and a recycle delay of 60 s giving quantitative information on the siloxane condensation degree. $\text{Q}_8\text{M}_8^{\text{H}}$ (octakis (dimethylsiloxy)octasilsesquioxane) has been used as a secondary reference (left peak at -2.25 ppm). The number of scans was in the range 1000–3000 for ^{29}Si OP and CP-MAS spectra, and of 2000–4000 for ^{13}C CP-MAS spectra.

Raman spectra were recorded using a Xplora Horiba spectrometer. The samples were excited using a 473 nm laser (P= 25 mW, 1200 grooves) through a “x100” objective. 2 acquisitions of 30 s were recorded under optimized focus conditions.

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a BioLogic VSP-300 potentiostat and the EC-Lab software. The samples were ground, placed in a two-electrode Swagelok cell (stainless steel cell with Teflon seal), pressed down between the two cylindrical electrodes and placed in an oven at 30°C. EIS measurements were performed over the frequency range 1 Hz - 7 MHz with an amplitude of 200 mV (50 points collected per decade). The

ionic conductivity, σ , was calculated using the formula $\sigma = \frac{L}{RS}$, where L is the thickness of the sample, S is the geometric surface area of the sample (which corresponds to the contact area between the powdered sample and the cylindrical electrode), and R is the bulk resistance. R was determined by fitting the Nyquist diagram to an equivalent electrical circuit model, using the EC-Lab software. Randles cell equivalent circuits with mixed kinetic and charge-transfer control were used as models.



R_s : Solution resistance

R_{ct} : Charge transfer resistance

C_{dl} : Double layer capacitance

W: Warburg diffusion element

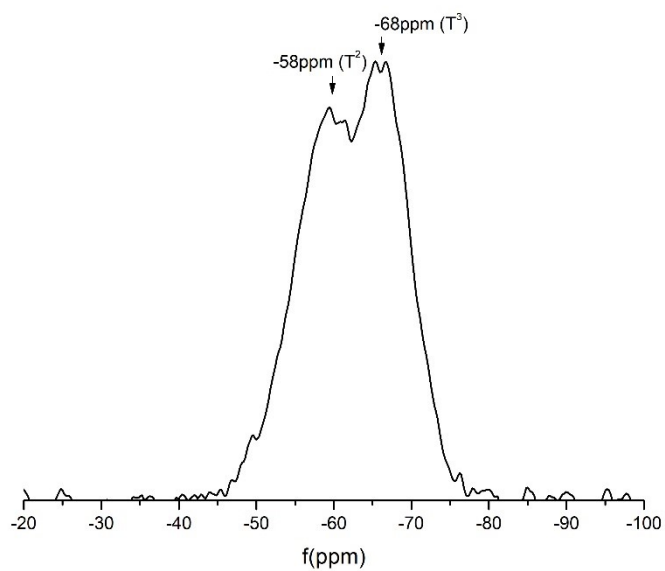


Figure S1: Solid-state ^{29}Si OP-NMR spectrum of TS_6^{LL} .

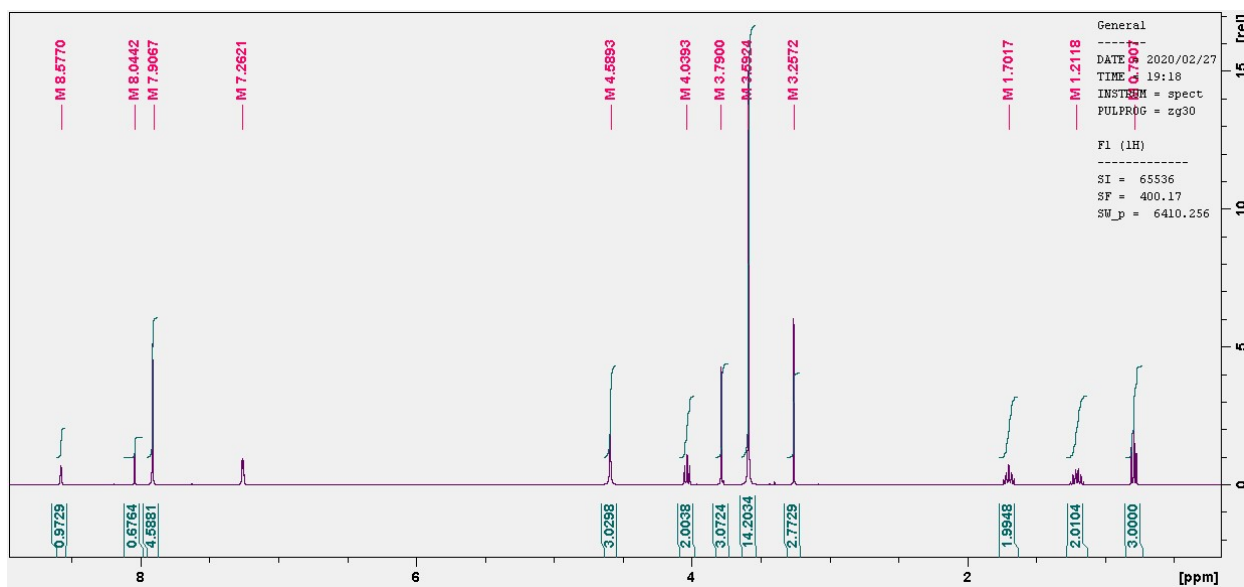


Figure S2: ^1H NMR spectrum of the supernatant liquid of the TS_3^{LL} .



Figure S3: photograph of TS_6 monolith after drying.

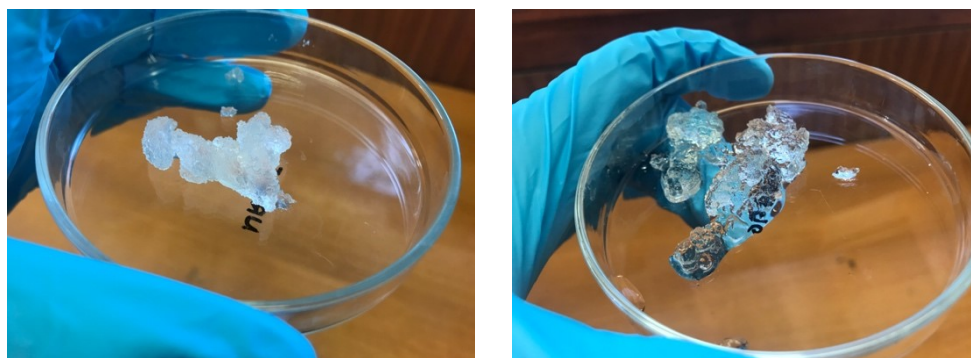


Figure S4: photographs of the silica-based ionogels containing respectively 1 mL (left) and 6 mL (right) of IL.

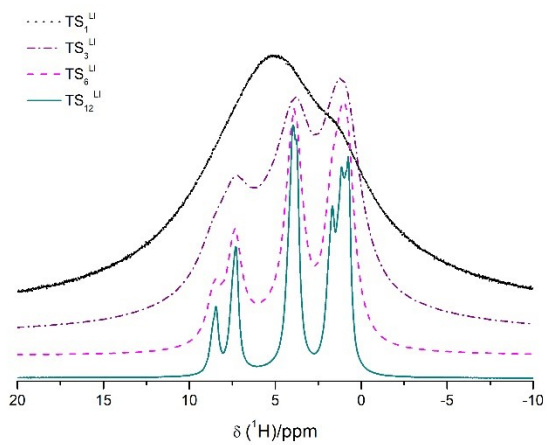
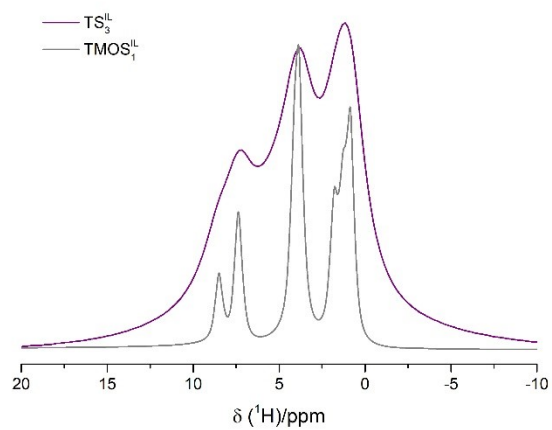
a**b**

Figure S5: (a) ¹H NMR MAS spectra of ground TS_x^{IL} monoliths under static conditions, (b) ¹H NMR MAS spectra of ground TS_3^{IL} and $TMOS_1^{IL}$ monoliths under static conditions.

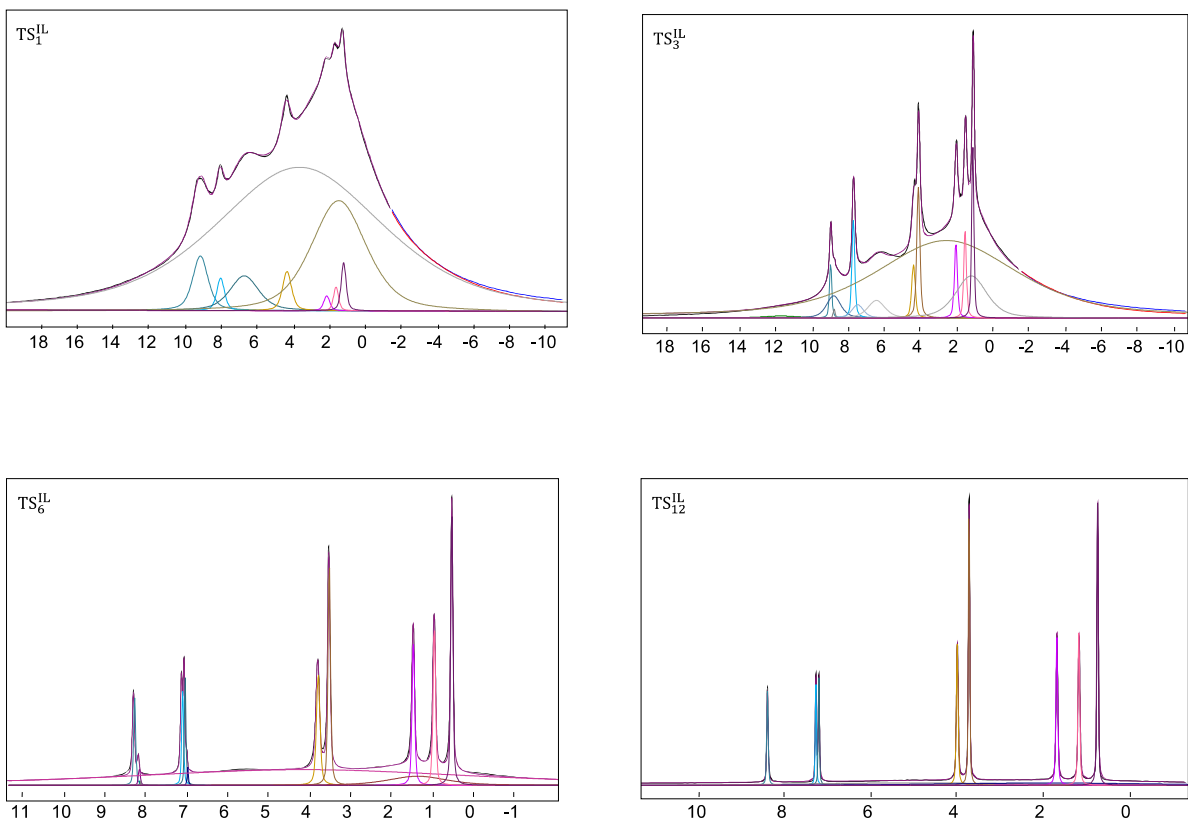


Figure S6: Resulting fits of the ^1H NMR MAS spectra of ground TS_x^L monoliths ($\nu_{\text{MAS}} = 24$ kHz). Full model and individual lines are shown. See the Table below for details.

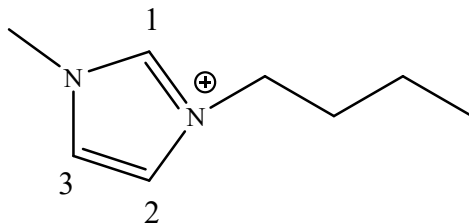


Table S1: Data obtained via Dmfit of the ^1H solid-state MAS NMR spectra of ground TS_x^{IL} monoliths ($\nu_{\text{MAS}} = 24$ kHz).

	Amplitude	$\delta(^1\text{H})$	FWHM	Assignment
		(ppm)	(ppm)	
TS_{12}^{IL}				
#1	107.19	8.48	0.039	H1
#2	122.33	7.35	0.03	H2
#3	121.94	7.28	0.03	H3
#4	2.36	5.01	7.14	
#5	161.12	4.06	0.05	$\text{CH}_2\text{-N}$
#6	314.88	3.78	0.04	$\text{CH}_3\text{-N}$
#7	2.36	1.94	6.10	
#8	169.79	1.74	0.05	$(\text{CH}_2)\text{CH}_2(\text{CH}_2)$
#9	171.84	1.22	0.05	$\text{CH}_2\text{-CH}_3$
#10	321.00	0.79	0.04	CH_3
TS_6^{IL}				
#1	41.39	8.55	0.06	H1*
#2	7.47	8.44	0.05	H1*
#3	3.29	8.43	0.02	H1*
#4	3.13	8.41	0.01	H1*
#5	45.78	7.38	0.05	H2*

#6	52.61	7.32	0.04	H2, H3*
#7	9.07	7.26	0.04	H3*
#8	7.27	4.44	9.75	
#9	52.49	4.07	0.11	CH ₂ -N
#10	104.29	3.80	0.072	CH ₃ -N
#11	68.24	1.74	0.07	(CH ₂)CH ₂ (CH ₂)
#12	4.38	1.64	1.66	
#13	74.35	1.23	0.07	CH ₂ -CH ₃
#14	131.71	0.80	0.06	CH ₃
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TS_3^{IL}				
#1	55.48	8.65	0.15	H1
#2	23.50	8.48	0.92	
#3	9.68	8.45	0.12	
#4	103.47	7.4	0.19	H2, H3
#5	12.91	7.16	0.75	
#6	17.65	6.13	1.11	
#7	55.32	4.09	0.23	CH ₂ -N
#8	139.22	3.82	0.21	CH ₃ -N
#9	82.45	2.27	9.04	
#10	77.91	1.76	0.20	(CH ₂)CH ₂ (CH ₂)
#11	92.84	1.25	0.17	CH ₂ -CH ₃
#12	44.31	0.91	2.02	
#13	183.14	0.83	0.15	CH ₃
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TS_1^{IL}				
#1	21.53	8.57	0.97	
#2	13.09	7.47	0.49	H1, H2, H3
#3	13.22	6.2	1.82	

#4	15.62	3.9	0.58	CH ₂ -N/CH ₃ -N
#5	54.88	3.23	10.72	
#6	6.17	1.77	0.38	(CH ₂)CH ₂ (CH ₂)
#7	9.43	1.27	0.32	CH ₂ -CH ₃
#8	42.17	1.12	3.52	
#9	18.49	0.86	0.32	CH ₃
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<i>TMOS</i> ₁ ^{IL}				
#1	19817.55	8.43	0.08	H1
#2	22756.81	7.34	0.08	H2
#3	21917.91	7.27	0.06	H3
#4	1017.83	5.66	0.10	
#5	24911.85	4.07	0.08	CH ₂ -N
#6	46799.98	3.79	0.11	CH ₃ -N
#7	8458.99	3.78	0.11	
#8	29127.12	1.75	0.09	(CH ₂)CH ₂ (CH ₂)
#9	29822.38	1.24	4.24	CH ₂ -CH ₃
#10	54811.64	0.8	0.47	CH ₃

*Observation of a splitting that may be due to J couplings with ¹⁴N nuclei. However, we considered the FWHM of the signals presenting no ambiguity.

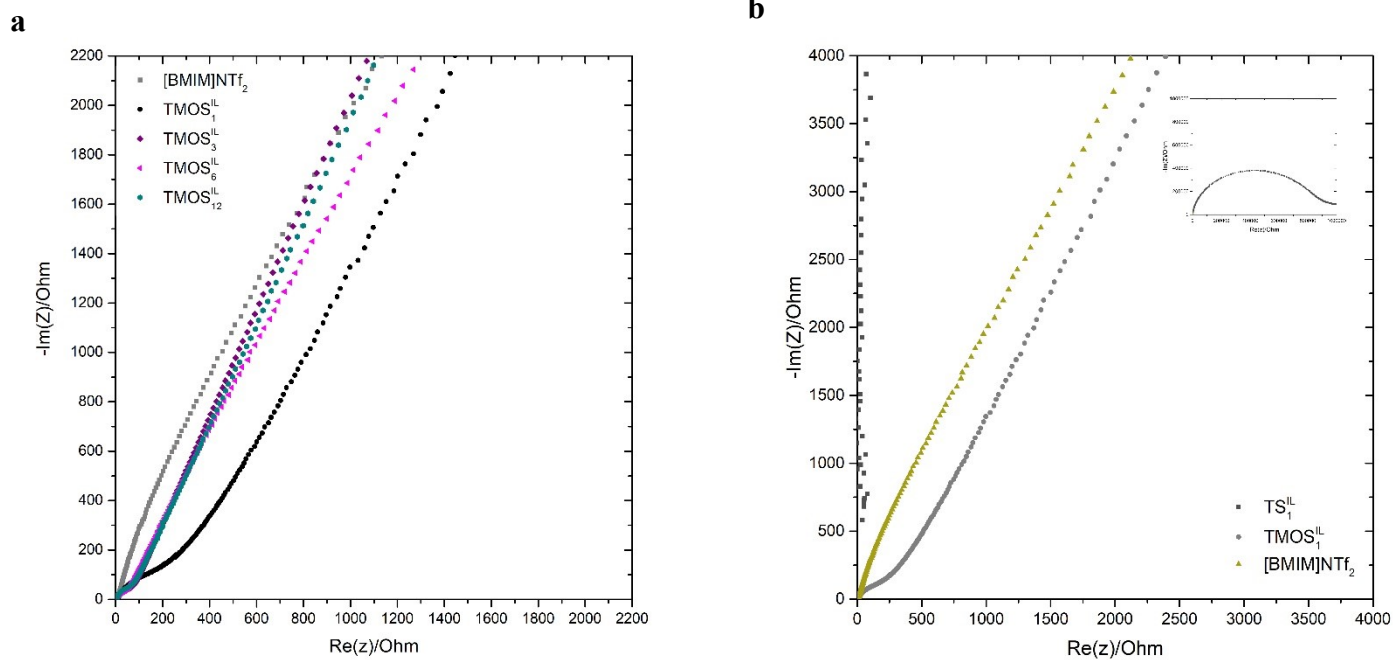


Figure S7: (a) Nyquist plots obtained for the different silica-based *ionogels* samples using electrochemical impedance spectroscopy (EIS), (b) Nyquist plots of TS_1^{LL} , $TMOS_1^{LL}$ and $[BMIM]NTf_2$.

Table S2: Data calculated based on Nyquist plots fitting using adapted equivalent circuits.

	Resistance	Thickness	Thickness	Surface	Conductivity
	(Ohm)	(m)	(m)	(m^2)	($S.m^{-1}$)
TS	1400000	0.087	0.0054	0.000113097	3.41 E-05
TS_{1}^{IL}	879000	0.0831	0.0015	0.000113097	1.50 E-05
TS_{3}^{IL}	128000	0.0858	0.0042	0.000113097	2.9 E-04
TS_{6}^{IL}	1450	0.0862	0.0046	0.000113097	0.028
TS_{12}^{IL}	88	0.0848	0.0032	0.000113097	0.322
$TMOS_{1}^{IL}$	85	0.0852	0.0036	0.000113097	0.374