

Supporting Information for

**Development and Validation of Diffusive Gradients in Thin-Films for
in Situ Monitoring of Ionic Liquids in Waters**

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Number of Pages: 17

Number of Tables: 6

Number of Figures: 5

Contents:

Chemicals, Reagents, and Materials	3
Instrumental Analysis.....	4
MS Conditions	4
Treatment Protocol of Water Samples	5
Quality Assurance and Quality Control.	6
Table S1. Basic information of target IILs in this study.	7
Table S2. Characteristics of three candidates for binding resins in this work.	8
Table S3. MRM conditions for target compounds.....	9
Table S4. Instrument detection limits (IDL) and method detection limits (MDL _{DGT}) of target IILs for DGT samples.	10
Table S5. Spiked recoveries and method detection limits (MDL _{SPE}) of target IILs for SPE samples.	11
Table S6. Water quality parameters in the collected river water.	12
Figure S1. Adsorption percentages (%) of target IILs by 6 membrane filters, i.e., polyethenesulfone (PES), polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), hydrophilic polypropylene (GHP), nylon, and polyacrylamide diffusive gels (PA).	13
Figure S2. Comparison of adsorption of HLB, WCX and MCX gels for target IILs at pH = 6 (A) and pH =9 (B), respectively..	14
Figure S3. Adsorption capacity of target IILs by MCX gels.	15
Figure S4. Elution recoveries (%) of target IILs from MCX gels by different elution solvents.....	16
Figure S5. Measured free dissolved concentrations of IILs at different DGT deployment times (0, 1, 2, 3 days) in a 20 L of river water spiked with 400 µg IILs..	17

Chemicals, Reagents, and Materials

Target IILs (> 98% purity, Table S1), sodium chloride, hydrochloric acid, formic acid and ammonium hydroxide (3 25% in water) were purchased from Aladdin Reagent Inc. (Shanghai, China). Methanol (HPLC grade) and acetonitrile (HPLC grade) were supplied by Merck (Germany). Sorbents including hydrophobic-lipophilic balance (HLB), mixed-mode cationic exchange (MCX), and weak cationic exchange (WCX) were all purchased from Green Union Science Instrument CO., LTD (Jiangsu, China). The sorbents were copiously washed with MQ water (Elga, France) to remove salts and then conditioned with methanol followed by MQ water before use. DOM isolates (humic acid) were obtained from the International Humic Substance Society (IHSS, <http://www.ihss.gatech.edu>). DGT pistons and gel cross-linker were obtained from Version Environ. Tech. Co. Ltd (Nanjing, China). The filter membranes used were all purchased from Chuang-wei Filtration Equipment Factory (Haining, China).

Instrumental Analysis

The instrument analysis was performed on an ultra-performance liquid chromatography (UPLC ACUITY, Waters, Milford, MA, USA) coupled to a triple quadrupole tandem mass spectrometer (Xevo TQS, Waters, Milford, MA, USA) equipped with an electrospray ionization interface (ESI) source. An ACUITY UPLC BEH C18 (2.1mm × 50mm, 1.7 mm) column was used. The mobile phases were (A) 0.1% formic acid in MQ water and (B) methanol with a flow speed of 0.3 mL/min. The gradient procedure was optimized at: 0–0.5 min, 10% B, then increase to 100% B within 2.5 min, hold for 1 min, after that decrease to the initial condition (10% B) within 0.1 min. Finally, 0.9 min of post-run ensured re-equilibration of the column before the next injection. The injection volume was 5 µL and the column temperature was set at 40 °C. 1-butyl-2,3-dimethylimidazolium chloride (C5mim) was used as an internal standard for quantification.

MS Conditions

Ionization: ESI+, Capillary voltage: 3.0 kV; Sampling cone: 40 V; Source offset: 80 V; Source temperature: 120 °C; Desolvation gas temperature: 500 °C; Desolvation gas: 800 L/hr; Cone gas: 150 L/h; Collision gas: 0.17 mL/min; Nebuliser gas: 7 bar. Other MS conditions are summarized in Table S2.

Treatment Protocol of Water Samples





1000 mL of water samples were collected and pre-filtered through a 0.7 μm GF/F fiber to eliminate the particulate matter. The filtered water samples were then adjusted to $\text{pH} = 8$ with $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH. The extraction was performed using CNWBOND MCX SPE cartridges (500 mg, 6 mL) with flow rate of $2\text{--}3 \text{ mL}\cdot\text{min}^{-1}$ under vacuum. The cartridges were conditioned with 6 mL of methanol and 6 mL of alkaline water ($\text{pH} = 8$). Prior to the elution of the analytes with $5 \times 2 \text{ mL}$ of 2% formic acid-methanol, the cartridges were washed with 6 mL of 5% ammonium hydroxide and sequentially dried for 120 min. Finally, the extracts were evaporated to near dryness under a gentle stream of nitrogen at $50 \text{ }^\circ\text{C}$ and reconstituted with 1 mL of initial mobile phases for UPLC-MS/MS analysis. Each sample was extracted in triplicate.

Quality Assurance and Quality Control.

Instrumental detection limits (IDL) of these IILs were estimated to be 0.02–0.09 $\mu\text{g}\cdot\text{L}^{-1}$ (Table S4), based on the signal/noise ratio (S/N) = 3. Method detection limits for DGT samples (MDL_{DGT}) were calculated from the IDLs, the concentration factors (CF) and the absolute recovery. For grab samples, the MDLs were calculated as three times the mean absolute standard deviation (SD) of seven replicates at the spiked concentration of 10 ng L^{-1} ($n = 7$). The MDLs of these IILs ranged from 4 ng L^{-1} to 29 ng L^{-1} for DGT samples (Table S4) and from 6.2 ng L^{-1} to 14 ng L^{-1} for grab samples (Table S5), respectively. Accuracy and precision of the SPE method were evaluated by treating and analyzing three replicates at the spiked concentration of 25 and 250 ng L^{-1} , respectively ($n = 3$). Except C2mim and C12mim, the mean spiked recoveries for the other IILs were 82–101% with the relative standard deviations (RSD) less than 19% (Table S5).

Three blank DGT devices were kept throughout the laboratory tests as well as the field applications and analyzed along with the exposed samples. No IIL was detected in any procedural blanks and field blanks. The DGT-measured concentrations presented in this study were all corrected by the corresponding elution efficiencies.

Table S1. Basic information of target IILs in this study.

No.	Compound	CAS Number	Abbr.	Formula	MW	Structure
1	1-ethyl-3-methylimidazolium Chloride	65039-09-0	C2mim	C ₆ H ₁₁ N ₂ Cl	146.62	
2	1-butyl-3-methylimidazolium chloride	79917-90-1	C4mim	C ₈ H ₁₅ N ₂ Cl	174.67	
3	1-hexyl-3-methylimidazolium chloride	171058-17-6	C6mim	C ₁₀ H ₁₉ N ₂ Cl	202.72	
4	1-octyl-3-methylimidazolium chloride	64697-40-1	C8mim	C ₁₂ H ₂₃ N ₂ Cl	230.78	
5	1-decyl-3-methylimidazolium chloride	171058-18-7	C10mim	C ₁₄ H ₂₇ N ₂ Cl	258.83	
6	1-dodecyl-3-methylimidazolium chloride	114569-84-5	C12mim	C ₁₆ H ₃₁ N ₂ Cl	286.88	
7	1-butyl-2,3-dimethylimidazolium chloride ^a	98892-75-2	C5mim	C ₉ H ₁₇ N ₂ Cl	188.70	

^a used as internal standard

Table S2. Characteristics of three candidates for binding resins in this work.

Properties	HLB	MCX	WCX
Polymer Type	PS-DVB	PS-DVB	PS-DVB
Functionality	N-Vinyl-2-pyrrolidone (NVP)	Sulfonic acid	Carboxylic acid
Ionic form	H	Na	No data
Surface area (m ² /g)	830	600	500-700
particle size (μm)	30	50	40-50
Appearance	White powder	Little yellow powder	White powder

Table S3. MRM conditions for target compounds

Compound	Retention time (min)	Parent ion (m/z)	Cone Voltage (V)	Daughter ion (m/z)	Collision Energy (eV)
C2mim	0.51	111.1	26	43.0	18
				83.1	5
C4mim	1.04	139.1	14	57.1	16
				83.1	5
C6mim	2.07	167.2	40	43.0	16
				83.0	18
C8mim	2.64	195.2	40	57.1	20
				83.1	18
C10mim	3.05	223.2	46	57.1	30
				83.1	24
C12mim	3.39	251.2	38	57.1	30
				83.1	24
C5mim	1.33	153.2	26	97.1	20

Table S4. Instrument detection limits (IDL) and method detection limits (MDL_{DGT}) of target IILs for DGT samples.

Compound	IDL (ng/mL) ^a	Concentration factor (CF) ^b	MDL_{DGT} (ng/L) ^c
C2mim	0.05	5.2	12
C4mim	0.09	3.0	29
C6mim	0.03	4.4	7
C8mim	0.02	4.6	4
C10mim	0.09	4.2	19
C12mim	0.02	1.2	17

^a IDL was calculated from the low level of standards with $S/N > 3$.

^b $CF = \frac{D_e At}{V \Delta g}$, where V is the volume of eluent (10 mL) after 7-day deployment in the laboratory under 25 °C.

^c $MDL_{DGT} = \frac{IDL}{R \cdot CF}$, where R is the absolute recovery for DGT samples.

Table S5. Spiked recoveries and method detection limits (MDL_{SPE}) of target IILs for SPE samples.

Compound	Recovery, % (mean \pm SD, $n = 3$)		MDL_{SPE} (ng/L) ^a
	Spiked 25 ng/L	Spiked 250 ng/L	
C2mim	62 \pm 1.4	34 \pm 1.5	13
C4mim	83 \pm 9.4	82 \pm 7.0	6.5
C6mim	94 \pm 15	93 \pm 2.5	8.2
C8mim	91 \pm 11	101 \pm 5.6	6.2
C10mim	91 \pm 19	98 \pm 5.4	11
C12mim	57 \pm 9.7	35 \pm 7.8	14

^a $MDL_{SPE} = 3.14 \times SD$, where SD is the mean absolute standard deviation of the seven spiked replicates at the concentration level of 10 ng/L ($n = 7$).

Table S6. Water quality parameters in the collected river water.

	<i>DOC</i> (mg/L)	<i>DO</i> (mg/L)	pH	<i>ORP</i> (mV)	σ (μ S/cm)	Temperature ($^{\circ}$ C)
River water	8.134	2.01	7.8	139.7	228.1	25.2 \pm 0.3

DO: Dissolved Oxygen.

ORP: Oxidation-Reduction Potential.

σ : Conductivity.

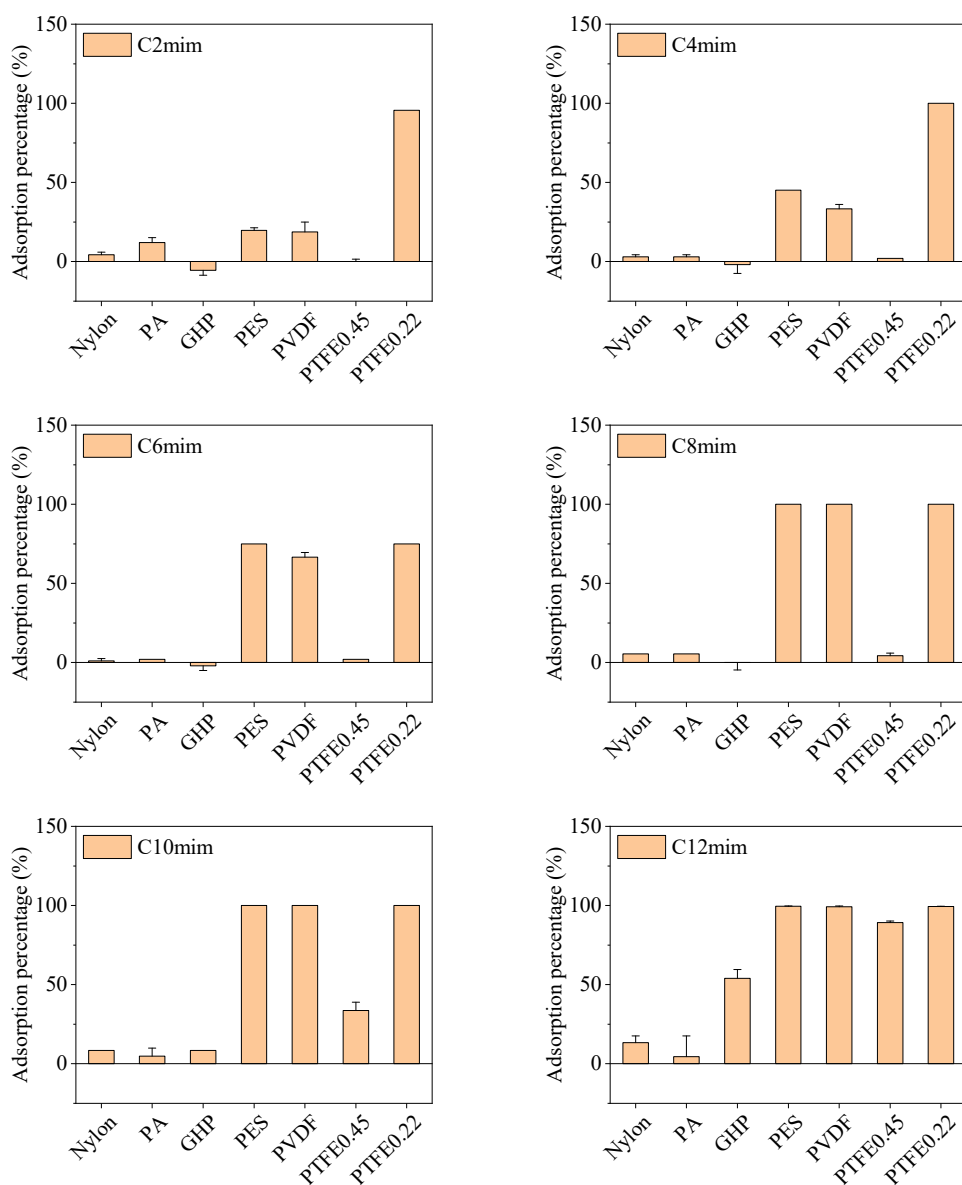


Figure S1. Adsorption percentages (%) of target IILs by 6 membrane filters, i.e., polyethenesulfone (PES), polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), hydrophilic polypropylene (GHP), nylon, and polyacrylamide diffusive gels (PA). PTFE membranes with different pore sizes (0.22 and 0.45 μm) were test. Other membrane filters used had a 0.45 μm pore diameter. Error bars represent 1 standard deviation (SD, $n = 3$).

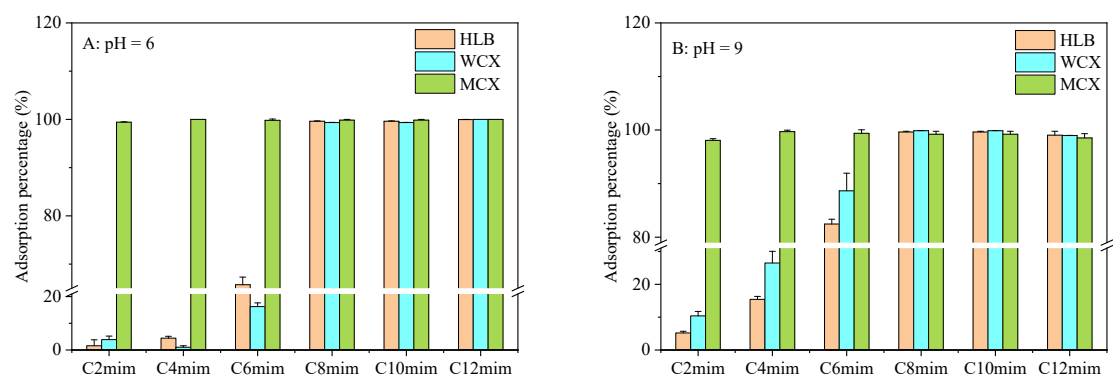


Figure S2. Comparison of adsorption of HLB, WCX and MCX gels for target IILs at pH = 6 (A) and pH =9 (B), respectively. The ionic strength was maintained at 0.01 mol/L NaCl. Error bars represent 1 standard deviation (SD, $n = 3$).

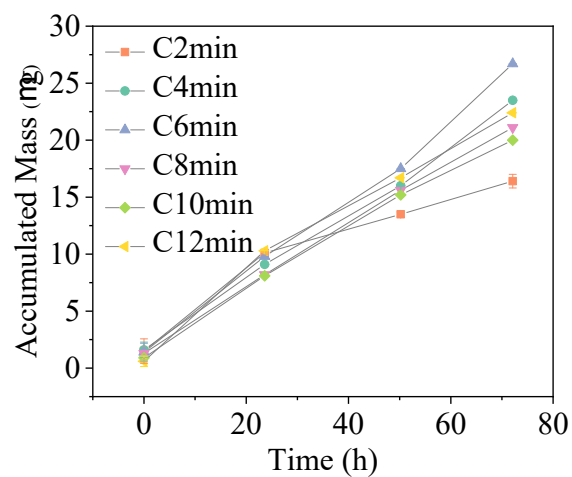


Figure S3. Adsorption capacity of target IILs by MCX gels. The ionic strength was maintained at 0.01 mol/L NaCl. Error bars represent 1 standard deviation (SD, $n = 3$).

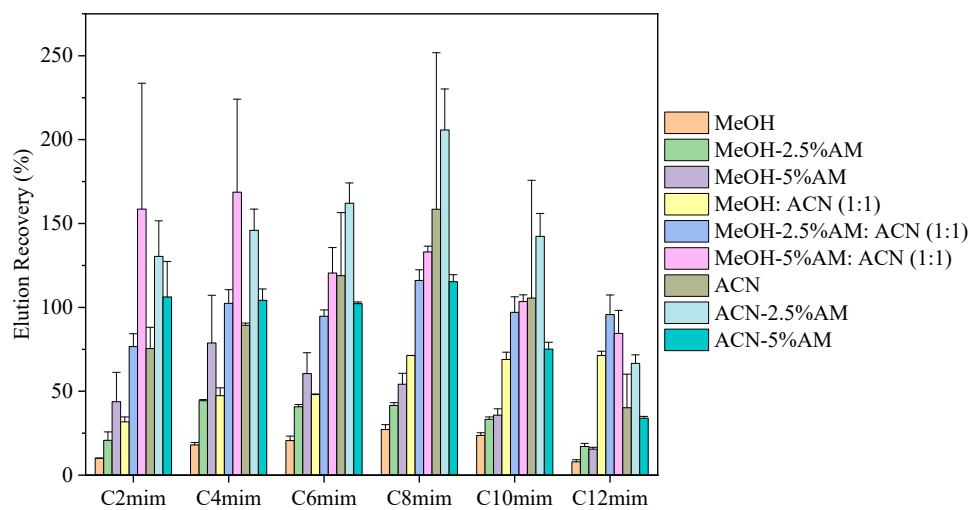


Figure S4. Elution recoveries (%) of target IILs from MCX gels by different elution solvents. Error bars represent 1 standard deviation (SD, $n = 3$). MeOH: methanol; ACN: acetonitrile; AM: ammonium hydroxide.

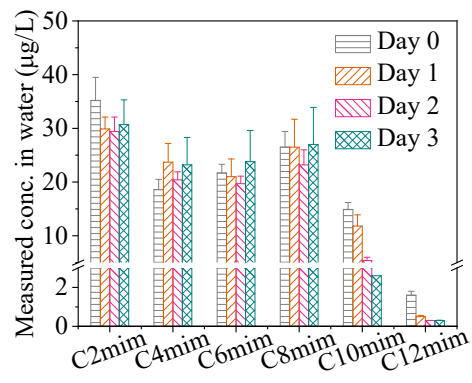


Figure S5. Measured free dissolved concentrations of IILs at different DGT deployment times (0, 1, 2, 3 days) in a 20 L of river water spiked with 400 µg IILs. Error bars represent 1 standard deviation (SD, $n = 3$).