Supplementary Information

Intensified Recovery of Switchable Hydrophilicity Solvents in Flow

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S1. Chemical Properties

Chemicals were used as received without further purification. Toluene (99%) was purchased from Sigma Aldrich and 1,3,5-trimethoxybenzene (99%) was purchased from Acros Organics. Carbon dioxide (CO_2, research 5.0 grade) and nitrogen (N_2, ultrahigh purity 5.0 grade) were purchased from Airgas. Deionized water was produced in house using PURELAB Flex system (Elga LabWater). Amines used as switchable hydrophilicity solvents were purged with argon and stored under inert atmosphere: 2-(dibutylamino)ethanol (DBAE, 99%, TCI America), 2-(diisopropylamino)ethanol (DIPAE, 99%, Sigma-Aldrich), *N*,*N*-dimethylhexylamine (DMHA, 99%, Alfa Aesar Chemical), and *N*,*N*-dimethylcyclohexylamine (DMCA, 98%, TCI America). Properties of the chemicals used in this work are listed in **Table S1**.

Table S1. Molecular weight, density, and boiling point of the chemicals used in this work.

Chemical	Molecular Weight [g/mol]	Density [g/ml] at 25℃	Boiling Point [℃]
Toluene	92.1	0.867	110.6
Water	18.02	0.998	100.0
DBAE **1**	173.3	0.86	229-230
DIPAE **2**	145.24	0.826	187-192
DMHA **3**	129.24	0.744	146-150
DMCA **4**	127.23	0.849	158-159

S2. Experimental Setup

The intensified extraction and recovery of SHSs in the developed modular flow chemistry platform was conducted with the following steps: (i) Toluene and SHS mixture solutions were prepared with pre-determined concentrations. The organic phase (toluene+SHS) and DI water were then loaded separately on syringe pumps (Harvard Apparatus, PHD Ultra) using two 10-ml glass syringes (SGE). Sudan red dye (Sigma Aldrich) and blue food dye were added to each organic and aqueous phase for demonstration purposes only (**Fig. S1**). (ii) A segmented flow of organic (*i.e.*, toluene/SHS mixture) and aqueous phases were formed with a Y-junction (Idex Health & Science) and introduced to the inner annulus of the tube-in-tube flow reactor, constructed with a gas-permeable tubular membrane (Teflon AF 2400, outer diameter (o.d.): 0.04" and inner diameter (i.d.): 0.032", Biogeneral) placed inside a fluorinated ethylene propylene (FEP) tubing (o.d.: 0.125" and i.d.:0.0625", Idex Health & Science). Detailed assembly steps of the tube-in-tube flow reactor using off-the-shelf and commercially available components are described in Han *et al.*.[1] (iii) The facile delivery of carbon dioxide (CO_2) from the outer annulus to the segmented flow (toluene/SHS and DI water) flowing through the inner annulus of the tube-in-tube flow reactor, resulted in accelerated protonation and extraction of SHS from the organic phase to the aqueous phase. The liquid (inner annulus) and gas (outer annulus) pressures were controlled using a digital gas back pressure regulator (BPR, Alicat Scientific, PC series) and a liquid BPR (Equilibar, ZF-series), respectively. (iv) The effluent of the SHS extraction flow reactor was collected in a septa vial (Fisher Scientific). The aqueous phase (blue) from the collection vial was then continuously fed to the second tube-in-tube flow reactor via a syringe-free pump (Valco, M6). In the SHS recovery reactor, nitrogen (N_2) was flowing through the outer annulus. The pressures for both the liquid and gas phases were controlled in a similar manner to the extraction reactor. The BPR and the outlet of the gas stream of the recovery flow reactor were connected to a custom-made stainless steel pressurized reservoir, preventing any condensation of water flowing through the gas BPR. The recovery flow reactor was placed into a custom-machined aluminum plate and heated with four cartridge heaters (WATLOW) and a PID temperature controller (Omega). (v) At the same time, the organic phase (red) in the intermediate collection vial was withdrawn by a syringe pump with the same flowrate as the aqueous phase, to maintain the same organic to aqueous volume ratio in the collection vial to ensure the equilibrium composition of the effluent. (vi) The recovered SHS and remaining aqueous phase were collected into a vial and sampled for analysis using gas chromatography.
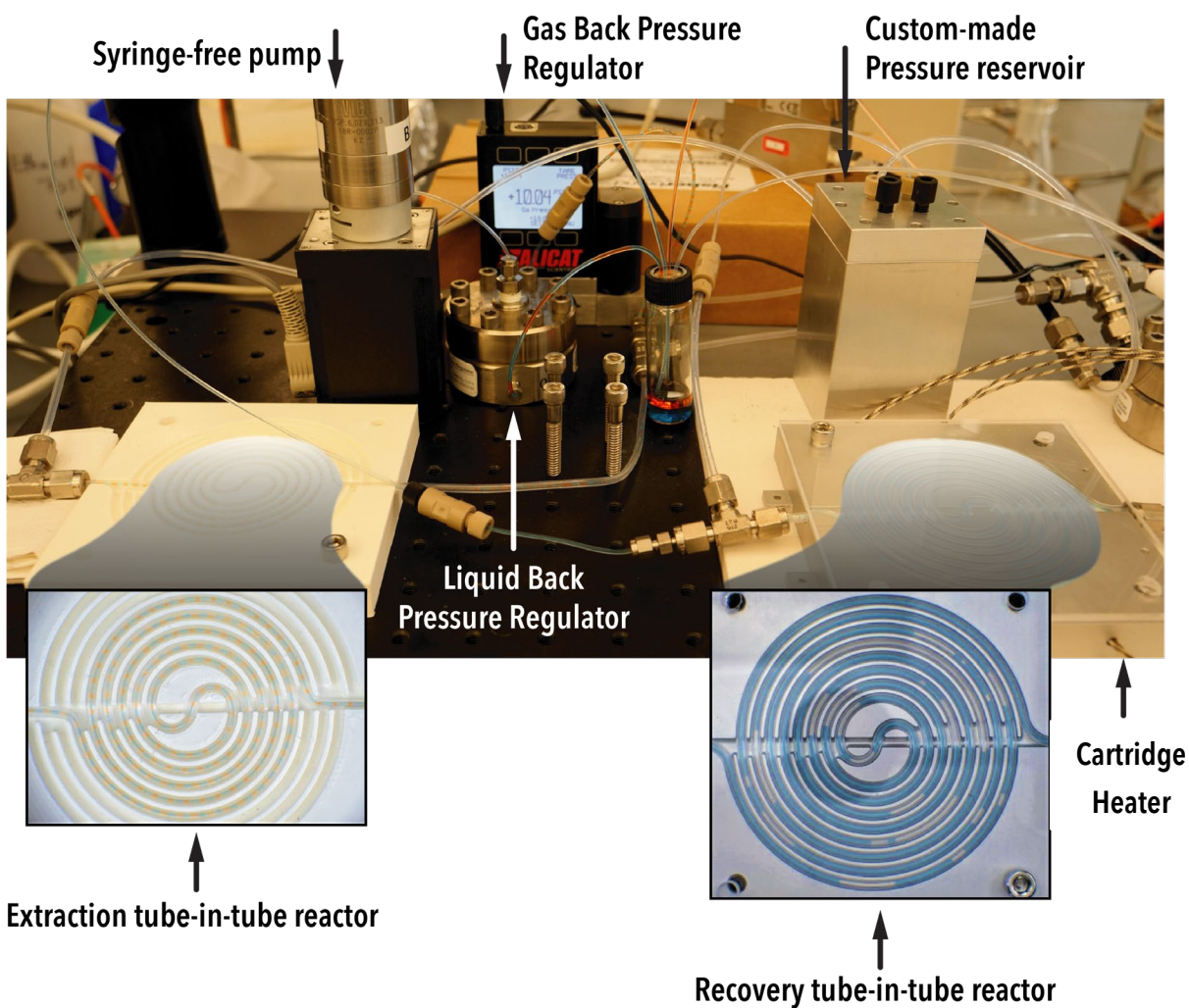
Syringe-free pump

Gas Back Pressure Regulator

Custom-made Pressure reservoir

Liquid Back Pressure Regulator

Cartridge Heater

Extraction tube-in-tube reactor

Recovery tube-in-tube reactor

Fig. S1 Photo of the developed modular flow chemistry platform with two in-series tube-in-tube flow reactors for intensified continuous extraction and recovery of SHSs. The tube-in-tube flow reactor on the left (white PLA) is utilized for extraction of SHSs, introducing CO_2 to toluene/SHS (red) and water (blue) two-phase flow in the inner annulus. The tube-in-tube flow reactor on the right (machined aluminum plate) is utilized for accelerated recovery of SHS, providing N_2 to the aqueous phase containing the protonated SHS (blue) flowing through the inner annulus. As the recovery of the SHS proceeds in the second tube-in-tube flow reactor, the flow becomes two phases with regenerated SHS (clear) and remaining aqueous phase (blue).

S3. Gas Chromatography (GC) Analysis

For each GC analysis, 10 µL of the calibration or post-regeneration samples were diluted with 1 mL of 0.01 M solution of 1,3,5 trimethoxybenzene in 1,4 dioxane in a GC vial. Complete dissolution of the protonated SHS sample in dioxane occurred without salt precipitation. 1 µL of GC mixture was injected into a Shimadzu GCMS-2010 with a Zebron ZB-5MSi column (30m × 0.25mm × 0.25µm).

GC method: 3 min at 35°C then ramp at 20°C /min to 260°C. The injection port temperature was maintained at 240°C. Calibrations were performed on the peak area ratio of $A_{amine}/A_{1,3,5\ trimethoxybenzene}$ for the four amines as shown in **Fig.**

Fig. S2 GC calibration graphs for calculating aqueous SHS solution after recovery with (A) DBAE, (B) DIPAE, (C) DMHA, and (D) DMCA. The red point in (A) is CO_2-saturated DI water without any amine.

S2. No side products were formed during the in-flow SHS regeneration process (analyzed by GC-MS). The red data point in **Fig. S2A** illustrates saturated CO_2 concentration in DI water without any amine. Triplicate samples of the same target concentration were prepared and analyzed. The combined error was calculated to be 0.83% (0.0075M). This error was applied to other GC measurements with equation S1 shown below,

$$\%\ Error = \pm \frac{0.0075M}{C_{SHS,recovery}}$$
(Equation S1)

where $C_{SHS,recovery}$ is the concentration of the regenerated SHS in the aqueous phase after the recovery.

S4. Mass Loss in Flow

The Teflon AF-2400 membrane used in the tube-in-tube flow reactor, in addition to high permeability for CO_2 and N_2, can also permeate water vapor to the outer annulus of the recovery flow reactor. In order to calculate the mass loss due to water evaporation in the recovery flow reactor, the mass of 1 mL sample before recovery was compared to the mass of the collected sample by injecting 1 mL into the flow reactor after reaching a steady state. The higher the temperature and/or the residence time in the recovery flow reactor, the higher the mass loss of water. The maximum mass loss at 60 °C, due to water evaporation, was 9% at a 60 min residence time (**Fig. S3A and S3B**). By increasing the operating pressure, the mass loss of water decreased from 7% at the atmospheric pressure to 5% at 30 psig (**Fig. S3C**). Although increasing the pressure is not favorable from the energy consumption perspective, it can be utilized in the SHS recovery process when water mass loss is not desirable.
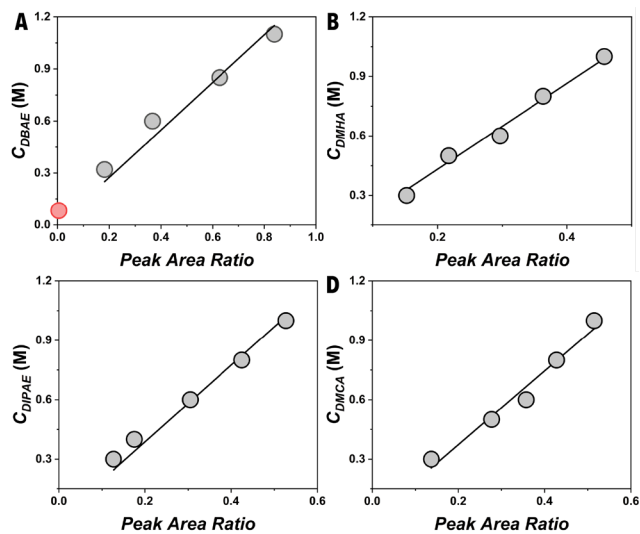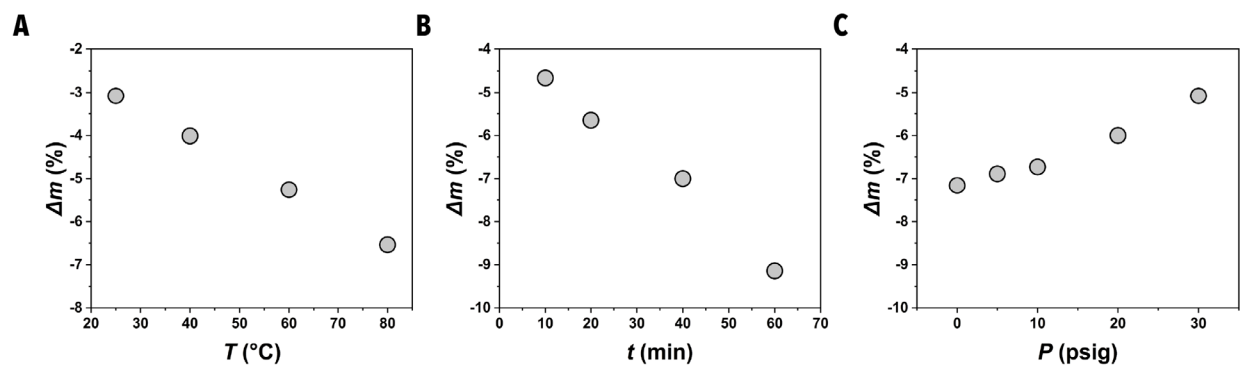
Fig. S3 Mass loss due to water evaporation in the heated tube-in-tube flow reactor. (A) Mass loss by varying temperature in the SHS recovery process. Experimental conditions: C_{DBAE} = 1 M, P = 30 psig, t = 20 min. (B) Mass loss by varying residence time in the SHS recovery process. Experimental conditions: C_{DBAE} = 1 M, P = 30 psig, T = 60 °C. (C) Mass loss by varying pressure in the SHS recovery process. Experimental conditions: C_{DBAE} = 1 M, t = 10 min, T = 60 °C.

S5. DBAE Recovery in Batch

To compare the performance of the developed flow chemistry platform for intensified regeneration of the SHSs, a batch recovery experiment was conducted under a similar reaction. 1 M of the protonated DBAE in water was prepared using the in-flow protonation reactor. Then, 10 ml of the prepared solution was placed into a 16 mL septa vial (Thermo Scientific) and the vial was connected to two FEP tubing; one was connected to a digital N_2 mass flow controller (Alicat Scientific, Model MC series) and the other tubing was connected to a digital N_2 back pressure regulator (Bronkhorst, EL-PRESS series). A pressurized vessel was connected in between the vial and the back pressure regulator to prevent any liquid from flowing into the back pressure regulator. The temperature of the reactor vial was controlled by immersing the vial in an oil bath placed on a hot stir plate. The oil bath was stirred and heated to 60°C. The vial was immersed into the heated oil bath after the temperature reached a steady state, and bubbling started simultaneously. For accurate GC analysis of the batch SHS recovery experiment, for every sample point, 0.5 ml of the aqueous phase was taken from the bottom of the vial. After waiting 30 min for the separation of the two phases (regenerated amines and aqueous solution), the solution was sampled for GC analysis as described above.

S6. References

1.   S. Han, M. A. Kashfipour, M. Ramezani and M. Abolhasani, *Chem. Commun.*, 2020, **56**, 10593-10606.