

Surprisingly Selective Sulfate Extraction by a Simple Monofunctional Di(imino)guanidinium Micelle-Forming Anion Receptor

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Supplemental Information

General

All reagents and solvents were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded using a Bruker 400 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm, with the residual internal CHCl₃ (δ 7.26 and 77.16, respectively) being used as the standard.

Synthesis of 3,7-dimethyl-1-iodooctane. 3,7-Dimethyl-1-octanol (32.34 g, 204 mmol), triphenylphosphine (64.30 g, 245 mmol) and imidazole (20.86 g, 306 mmol) were added to a two-necked 1 L round bottom flask. To the reaction mixture was added 500 mL of 1,2-dichloromethane. The reaction mixture was stirred using mechanical stirring and cooled to 0° C prior to the addition of iodine (67.42 g, 265 mmol). The iodine was added slowly over the course of three hours using a solid addition funnel. Ice was periodically added to the ice bath to keep the temperature of the reaction around 0° C. As the iodine was added, the color of the reaction

solution turned yellow, and the color would disappear as the iodine was consumed. During the course of the reaction, as the concentration of triphenylphosphine oxide built up, a white solid began to precipitate from solution. When a majority of the iodine had been added to the reaction mixture, the color of the reaction changed from colorless to brown. Once all the iodine had been added, the reaction was allowed to stir and come to room temperature for 4 h, whereupon 200 mL of a 10% solution of $\text{Na}_2\text{S}_2\text{O}_3\text{aq}$ was added to the reaction mixture to neutralize the residual iodine in solution. Within 10 min the reaction changed from dark brown suspension to clear colorless solution. Once the reaction mixture became clear and colorless, the mixture was poured into a 1 L separatory funnel, and the organic layer was collected and the dichloromethane removed under reduced pressure. After the dichloromethane was removed, the 400 mL of hexanes was added to the oil in the flask; upon addition of the hexanes the dissolved triphenylphosphine oxide precipitated out of the oil/hexanes mixture. The desired product was obtained by passing the solution containing the suspension through a silica gel plug. The product was eluted off of the silica gel using pure hexanes. The hexanes were removed under reduced pressure, and pure 3,7-dimethyl-1-iodooctane was obtained. Yield: >99% (54.84 g). ^1H NMR (400 MHz, CDCl_3) δ 3.221 (2H, m), 1.855 (1H, t), 1.640 (2H, quint), 1.525 (1H, s), 1.270 (3H, s), 1.131 (3H, s), 0.857 (9H, s). ^{13}C NMR (100 MHz, CDCl_3) δ 41.02, 39.22, 36.52, 33.89, 27.96, 24.57, 22.77, 22.68, 18.83, 5.14.

Synthesis of 3,4-bis(3,7-dimethyloctyl)oxybenzaldehyde. 3,7-Dimethyl-1-iodooctane (16.69 g, 62.23 mmol) and 3,4-dihydroxybenzaldehyde (3.91 g, 28.29 mmol) were combined in a 500 mL round bottom flask. Acetone (250 mL) was added to the reaction mixture, and the reagents were

stirred at room temperature for 30 min prior to the addition of K_2CO_3 (15.63 g, 113.2 mmol). After the addition of the K_2CO_3 was complete, the reaction mixture was heated to reflux (70 °C) for 12 h or overnight. After 12 h, the reaction mixture was allowed to cool to room temperature and then filtered through a Büchner funnel to remove the unreacted K_2CO_3 and KI formed during the reaction. The solvent was then removed under reduced pressure from the filtrate, resulting in a suspension containing a yellow oil. To this suspension was first added DI water to dissolve the salts; then hexanes was added to dissolve the oil. The mixture was poured into a 500 mL separatory funnel, the aqueous layer was removed, and then the organic layer was washed with brine prior to drying with Na_2SO_4 . The hexanes were removed under reduced pressure, leaving a yellow oil, which was placed on a silica gel column to obtain the pure compound. To purify the compounds using column chromatography, an eluant consisting of hexanes and ethyl acetate was used. A solvent gradient was used to improve the separation of the desired compound from the impurities. The desired product 3,4-bis(3,7-dimethyloctyl)oxy)benzaldehyde was obtained with a yield of 82.0% (9.72 g). 1H NMR (400 MHz, $CDCl_3$) δ 9.970 (1H, s), 7.387 (1H, d), 7.365 (1H, s), 6.929 (1H, d), 4.076 (4H, quint), 1.882 (2H, quint), 1.657 (4H, m), 1.526 (2H, br), 1.318 (6H, quint), 1.148 (6H, quint), 0.931 (6, d), 0.843 (12H, d). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.92, 154.58, 149.40, 129.83, 126.67, 111.53, 110.53, 67.41, 67.37, 39.21, 37.30, 37.28, 35.98, 35.85, 29.94, 29.93, 29.91, 29.89, 27.97, 24.72, 22.72, 22.62, 19.71, 19.68. Elemental analysis: Anal. Calcd for $C_{27}H_{46}O_3$: C, 77.46; H, 11.08. Found: C, 77.74; H, 10.91.

Synthesis of DIG•Cl. 3,4-Bis(3,7-dimethyloctyl)oxy)benzaldehyde (5.620 g, 13.42 mmol) and diaminoguanidine hydrochloride (0.803 g, 6.39 mmol) were combined in a 100 mL round bottom

flask. Anhydrous ethanol (50 mL) was added to the reaction mixture, and the flask was then sealed with a rubber septum and heated to 65° C for 24 h. After 24 h, the reaction mixture was allowed to cool to room temperature, and then the ethanol was removed under reduced pressure, leaving a red oil behind. The product was obtained using column chromatography. The red colored oil was loaded onto a silica gel column using a solvent consisting of CHCl₃ and 10% MeOH. DIG•Cl was obtained as a yellow/amber wax. Yield of 84.4% (5.001 g). ¹H NMR (400 MHz, CDCl₃) δ 8.549 (2H, bs), 7.947 (2H, d), 7.206 (2H, s), 6.962 (2H, d), 6.683 (2H, d), 3.995 (8H, d), 1.810 (4H, m), 1.619 (4H, bs), 1.506 (8H, m), 1.271 (12H, m), 1.125 (12H, q), 0.891 (12H, q), 0.835 (24H, dd). ¹³C NMR (100 MHz, CDCl₃) δ 152.86, 151.72, 149.27, 125.45, 122.67, 112.22, 110.57, 67.56, 67.25, 39.23, 37.46, 37.43, 37.38, 37.36, 36.22, 36.06, 29.93, 29.88, 27.95, 24.72, 24.70, 22.69, 22.60, 19.65, 16.64. Elemental analysis: Anal. Calcd for C₅₅H₉₆N₅O₄Cl: C, 71.21; H, 10.44; N, 7.56. Found: C, 71.63; H, 10.32; N, 7.57.

Sulfate Separations

The methods and procedures used to test the effectiveness of the DIG•Cl and the A336•Cl for removing sulfate from the aqueous phase, as the same as those described in prior literature.^{S1-S2} Extraction of sulfate by 5 mM (just under the solubility limit of 6 mM) Aliquat 336 in Isopar L from an aqueous solution containing 10 mM NaCl and 0.1 mM Na₂SO₄ were unsuccessful due to the formation of a white precipitate that formed at the interface of the organic and aqueous layers. From the mass balance of the total counts of ³⁵SO₄ in both organic and aqueous phases, it was determined that ≥50% of the total counts were absent from solution and assumed to be present in the precipitate. Due to the large percentage of missing counts, we were unable to accurately determine the distribution ratio of sulfate for Aliquat 336 in Isopar L.

Karl Fischer Titrations

The uptake of water by the DIG•Cl in Isopar L was determined by Karl Fischer (KF) titrations performed on a Metrohm 831 KF Coulometer equipped with a Metrohm 860 KF Thermoprep. The latter is used to evaporate the water in sealed sample vials containing pre-contacted samples and to push the liberated water into the titration cell. The Thermoprep was employed due to concerns that the imine bonds present in the DIG may react with the SO₂ and I₂ present in the anode solution, interfering with the measurement. Hydranal-Coulomat AG-H was used as the anode solution to enhance the dissolution of the Isopar L (C-12 average hydrocarbon), allowing for an accurate measurement and determination of water concentration in the DIG•Cl/Isopar L samples. The DIG•Cl samples were contacted with water in equal volumes for one hour at 25 ± 0.2 °C on a rotating wheel set at 60 rpm. After one hour, the samples were centrifuged, and the organic layer was removed via pipette and placed into pre-weighed sealable vials for KF titrations using the KF Thermoprep. The samples were run in duplicate. Results are shown in Figure S1, comparing pre-contacted DIG•Cl solutions with post-contacted DIG•Cl solutions. The KF titrations revealed that precontacted DIG•Cl contains an appreciable amount of water, presumably from the reagents as well as solution preparation. On contact with water, the DIG•Cl solutions take up an additional two waters to give an equilibrium ratio of 2.5/1 water/DIG•Cl.

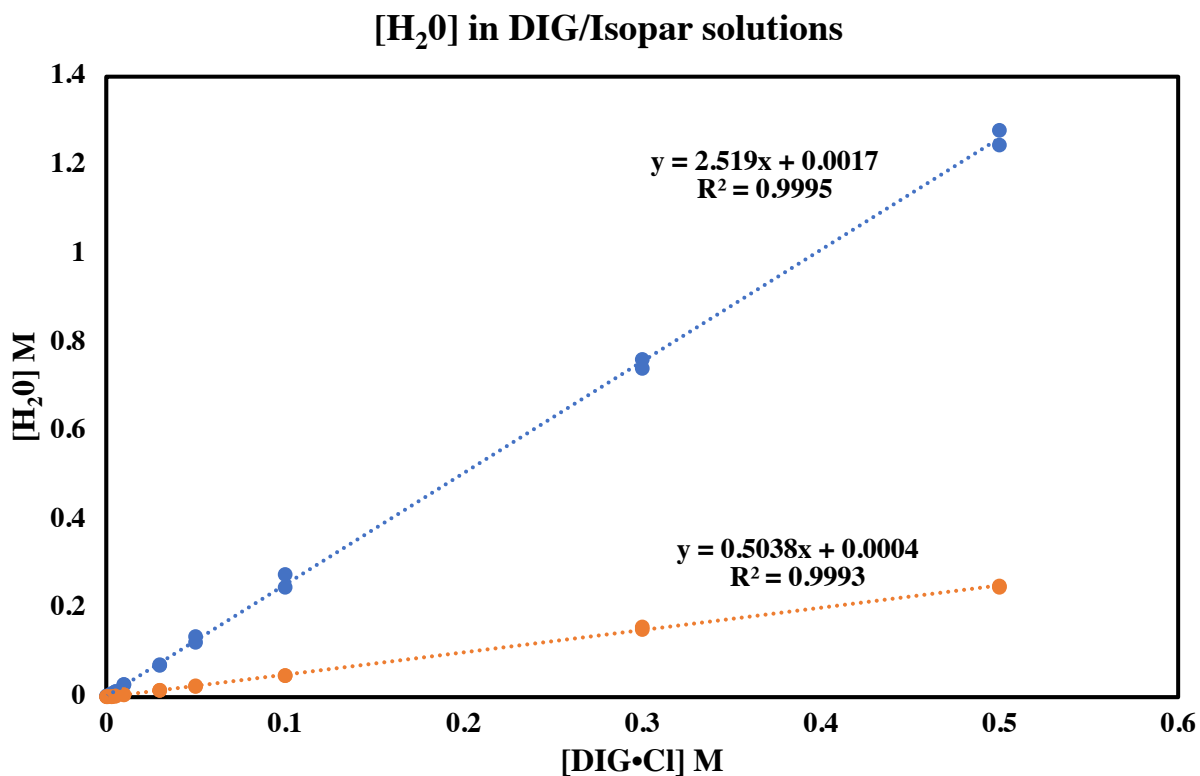


Figure S1. Results from KF titrations comparing the concentration of DIG•Cl (M) to the concentration of water in the organic solvent pre- and post mixing with water. The pre-mixed DIG•Cl solutions in Isopar L are shown above in the figure in orange with a slope of 0.5, indicating a half a water per receptor. The concentrations of water in the pre-contacted and post contacted DIG•Cl solutions in Isopar L are denoted in orange and blue, respectively.

Small-angle X-Ray Scattering

SAXS data was acquired at the Center for Nanophase Materials Sciences (CNMS) in Oak Ridge National Laboratory on an Anton Paar SAXSess mc2. The scattered beam was recorded on a CCD detector (PI-SCX, Roper) with a pixel resolution of 2084 × 2084 and pixel dimensions of 24 × 24 μm². The data collection time was 20 min. For the measurements, X-rays were generated at 40 kV/50 mA at a beam wavelength of $\lambda = 1.541 \text{ \AA}$ (Cu K α radiation). The generated X-ray beam was

slit-collimated using Kratky camera giving rise to a beam size of 18 mm (length) x 0.5 mm (width), and the collected SAXS data were desKeummeared and expressed as intensity versus q , where $q = (4\pi \sin \theta)/\lambda$ after subtraction of detector dark current and background scattering.

GIFT Method

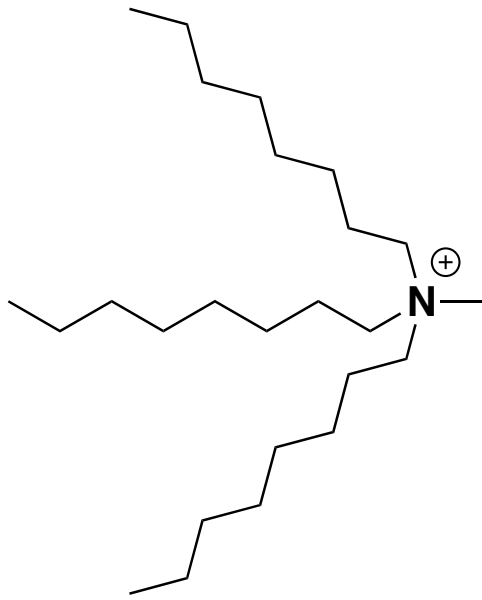
The GIFT method^{S3-S5} was used to obtain real-space $p(r)$ functions from background subtracted scattering data. GIFT interprets the globular particle system, $I(q) = nP(q)S(q)$, where $P(q)$ is the average form factor, $S(q)$ is the average structure factor, and n is the number of particles per unit volume in the solution. $P(q)$ is the Fourier transformation of its real space counterpart, $p(r)$, described by:

$$P(q) = 4\pi \int_0^{\infty} p(r) \frac{\sin qr}{qr} dr \quad (2)$$

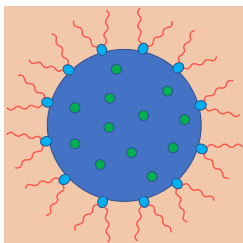
To calculate $p(r)$, the inverse Fourier transformation (IFT) of an experimental $P(q)$ is computed. In concentrated interacting systems, the structure factor must be modeled and subtracted from the scattering data, $I(q)$, to give $P(q)$, before calculating $p(r)$. The selection of the appropriate structure factor model is essential to achieving coherent $p(r)$ functions from GIFT. The model selected in the present study was the Percus-Yevick (PY) closure relation.⁴ This has been shown to closely approximate the interaction effects $S(q)$ of concentrated reverse micelles in SAXS studies from numerous solvent extraction systems.^{S6-S18}

The PY closure relation approximates the structure factor for concentrated systems by modelling the 'excluded volume effect' for globular particles. This is achieved by solving the Ornstein–Zernicke equation, where the hard-sphere potential is zero if the particles do not overlap, and

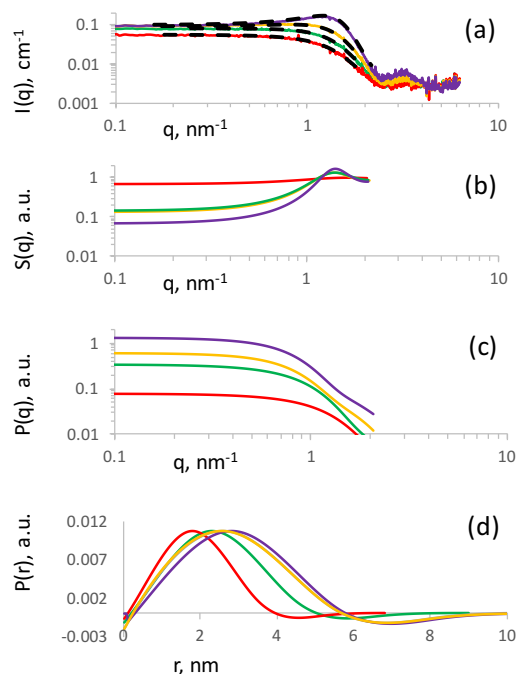
infinity if they do. This model depends on radius and volume fraction of particles, providing additional information on phase structure and aggregation, and includes a modification to approximate polydispersity. A detailed discussion of the PY closure relation model in the GIFT treatment of SAXS data was given in a review article by Otto Glatter.⁵³



Aliquat 336



Sketch of a reverse micelle. Polar core (blue) is sensitive to SAXS, and is made up from the DIG headgroups, chloride and water.



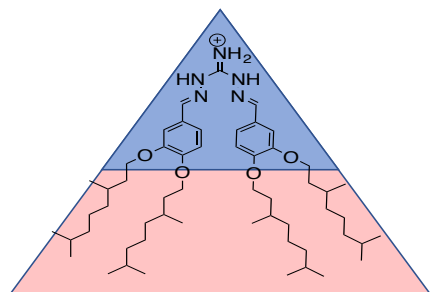
(a) Background subtracted SAXS data showing hard-sphere model fits (dashed black) to data. (b) Structure factors calculated using GIFT. (c) Form factors calculated using GIFT. (d) PDDF from form factors calculated using GIFT.

Using the particle dimensions given by GIFT, we can calculate the aggregation number of DIG•Cl molecules per inverted micelle. Only the core of the inverted micelle is sensitive to SAXS, and this is made up from water, chloride, and guanidinium extractant ‘head-groups’. We can calculate the molecular volume of the imino(guanidinium) headgroup by subtracting the molecular volume of the alkyl chains (estimated using the method given by Tanford)^{S19} from the molecular volume of DIG. Knowing the concentration and molecular volumes of both water and DIG•Cl headgroups in the system, as well as the size of the inverted micelle cores, we can then calculate the DIG•Cl aggregation number.

Molecular volume DIG•Cl: 1 g DIG•Cl was dissolved in 1.3 mL of Isopar. An increase in volume of 1.2 mL was observed, translating to a molecular volume of 1905 A³ /molecule DIG•Cl in Isopar L. Using the equation from Tanford,⁵¹⁹ the four DIG•Cl alkyl chains have a molecular volume of 1103 A³/molecule DIG•Cl. Therefore, the polar 'headgroup' of DIG•Cl has a molecular volume of 802 A³ /molecule DIG•Cl. This value was used to calculate aggregation number.

Comparing sphere radius from GIFT with sphere radius from hard sphere model.

[DIG] (M)	sphere radius (nm)	
	PY HS	GIFT
0.05	1.88(0.11)	1.77
0.1	1.92(0.06)	1.8
0.2	1.82(0.03)	2.22
0.5	2.03(0.003)	2.3



Amphiphilic conformation of DIG⁺ showing hydrophilic portion in blue and lipophilic portion in pink. This conformation would be unfavorable in the gas phase. However, this would be expected in a biphasic oil-water solution system, where solvation interactions would hold DIG at the oil-water interface with tail-groups in the oil and headgroup in the water. Likewise, this conformation would allow DIG•Cl to form reverse micelles.

Single crystal X-ray diffraction. Single crystals of (DIG)₂(SO₄)(H₂O)(DMSO) were obtained by slow evaporation of an aqueous/DMSO solution. The structure was solved by direct methods and refined on F^2 using the SHELXTL software package (Bruker AXS, Inc., Madison, WI, 1997). Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. Crystallographic details can be found in the supporting cif file submitted with the manuscript.

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