December 28, 2009

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Two polymeric ionic liquids (PIL) were synthesized and employed as sorbent coatings in solid-phase microextraction (SPME) for the selective extraction of CO_2. The two coatings, poly(1-vinyl-3-hexylimidazolium) bis[(trifluoromethyl)sulfonyl]imide [poly(VHIM-NTf$_2$)] and poly(1-vinyl-3-hexylimidazolium) taurate [poly(VHIM-taurate)], exhibited varied selectivity toward CO_2 due to functional groups within in the PIL that imparted different mechanisms of CO_2 capture. Extraction efficiencies were compared to those of two commercial SPME fibers [poly(dimethylsiloxane) (PDMS) and Carboxen−PDMS]. The poly(VHIM-NTf$_2$) PIL fiber exhibited comparable extraction efficiency at high CO_2 pressure compared to the Carboxen−PDMS fiber, even though the PIL-based fibers possessed much smaller film thicknesses. Calibration curves generated in pure CO_2 showed that the sensitivity of the poly(VHIM-NTf$_2$) coating was comparable to that of the Carboxen−PDMS fiber with both PIL-based fibers exhibiting larger linear ranges and higher extraction-to-extraction reproducibility. The storage ability for selected fibers was examined and revealed that the PIL-based coatings exhibited superior capability in retaining the CO_2 sorbate on the fiber under different storage conditions, particularly for the poly(VHIM-taurate) PIL which reversibly captures CO_2 as a carbamate salt.

An intense area of research today lies in the development of new methods and materials for the sequestration of CO_2. Global warming, due in large part to greenhouse gas emission from fossil fuel combustion, has attracted concerns from the scientific community, industry, and the general public. According to a report from the Energy Information Administration in 2005, approximately 28.2 billion metric tons of CO_2 has been released to the atmosphere due to the consumption and flaring of fossil fuels.[1] However, in the foreseeable future, fossil fuels will continue to be one of the primary global energy feedstock sources. Hence, it is no surprise that efforts have been devoted to developing technologies and materials that can effectively monitor and stabilize atmospheric CO_2 levels. Sensitive, selective, convenient, and reproducible methods are desired in order to perform sampling of CO_2. Moreover, materials with high affinity and selectivity for CO_2 need to be designed and coupled with the available sampling methods.

Due to its speed, simplicity, and ease of operation, solid-phase microextraction (SPME) has become a widely used extraction technique since its introduction by Pawliszyn and co-workers in the early 1990s.[2−4] SPME possesses many advantages over conventional sample preparation methods as it combines sampling and sample preparation into one step and can be readily automated and coupled with separation techniques such as gas chromatography (GC). SPME consists of a fiber support coated with a sorbent material that is exposed to the sample matrix by either headspace or direct-immersion sampling. Equilibration is subsequently established between the analytes and the fiber coating. When coupled with GC, the analytes are desorbed from the sorbent coating by thermal desorption in the injection port.

SPME has been demonstrated as a fast, accurate, and reproducible sampling method for airborne compounds. It has been reported that SPME can be utilized for the sampling of volatile chlorinated hydrocarbons,[5] volatile organic compounds (VOCs),[6] formaldehyde,[7] particulate matter,[8,9] hydrocarbons,[10,11] trimethylamine,[12] and hydrogen cyanide.[13] SPME can also be applied as a time-weighted average (TWA) sampler for gas-phase analytes by retracting the coated fiber a known distance into the needle housing during the sampling period.[14] Gas-phase compounds such as alkanes, primary alcohols, and methyl esters containing up to 22 carbons can be quantified by SPME during equilibration.[15] Special interfaces have been developed for SPME to allow for high-speed GC analysis of benzene, toluene, ethyl benzene, and xylene (BTEX),[16] sampling from inhaler-administered drug, spray insect

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repellent, and tailpipe diesel exhaust,[17] as well as nonequilibrium sampling and determination of airborne VOCs.[18] A major thrust of current SPME research involves the development of new sorbent coatings that are capable of expanding the range of analytes that can be selectively extracted. Our group is particularly interested in developing "task-specific" sorbent coatings based on polymeric ionic liquids (PILs) that exhibit high selectivity and high extraction efficiency for targeted analytes. With the growing interest in detecting and quantifying CO_2 in gas streams, our efforts have been focused on developing sorbent coatings suitable for its selective and sensitive detection.

Ionic liquids (ILs) are a class of nonmolecular ionic compounds that have melting points below 100 °C.[19] ILs have a number of significant advantages over traditional organic solvents; for example, many ILs possess very low vapor pressure at ambient temperature and exhibit high thermal stability. The physical and chemical properties of ILs, including viscosity and solubility with other solvents, can be tailored by altering the combination of cations and anions. In addition, functional groups can be introduced to either component to form task-specific ionic liquids (TSILs),[20] which are capable of interacting with analytes or substrates in specific ways. Due to their unique properties and versatility, ILs have been examined as extraction media for analytical microextractions.[21-26] Liu et al. first used IL-coated disposable SPME fibers for the analysis of BTEX in paints.[24] Alternative methods have been proposed to pursue smooth, thick, and stable IL-based coatings on SPME fibers using a Nafion membrane-supported IL coating,[25] IL coated on etched fused-silica fibers,[26] and IL impregnated in a cross-linked silicone elastomer.[27] Our group first utilized PILs as SPME sorbent coatings,[28,29] which resulted in enhanced thermal stability, high extraction-to-extraction reproducibility, and extended fiber lifetime. A logical progression of our work is to design sorbent coatings based on task-specific PILs that exhibit high extraction selectivities and efficiency for desired analyte(s) in addition to producing highly reproducible and long lifetime devices.

In this work, PIL-based sorbent coatings were used for the determination of CO_2 using SPME. The structures of these PILs, namely, poly(1-vinyl-3-hexylimidazolium) bis[(trifluoromethyl)-sulfonyl]imide [poly(VHIM-NTf$_2$)] and poly(1-vinyl-3-hexylimidazolium) taurate [poly(VHIM-taurate)], were carefully tailored to enhance CO_2 solubility. SPME fibers were coated with neat PILs as well as mixtures with desired weight percentage of

these two PILs. For comparison, two commercially available SPME fibers, namely, poly(dimethylsiloxane) (PDMS) (film thickness of 7 μm) and Carboxen−PDMS (film thickness of 75 μm), were included in this study. The sensitivity, linearity, and linear range of these sorbent coatings were determined from calibration curves generated in pure CO_2 and CO_2 spiked with a known amount of air. The storage capability under different storage conditions was examined for selected fibers, revealing that PIL-based sorbent coatings provided superior abilities in retaining CO_2 compared to the commercial carboxen fiber. Although SPME is widely used for the determination of airborne organic contaminants, no report to our knowledge has demonstrated the application of SPME in the direct analysis of CO_2.

EXPERIMENTAL SECTION

Materials. The synthesis of all IL monomers and polymers involved the use of vinyl imidazole, 1-bromohexane, 2,2′-azo-bis(isobutyronitrile) (AIBN), and taurine, which were purchased from Sigma-Aldrich (St. Louis, MO). Lithium bis[(trifluoromethyl)sulfonyl]imide was obtained from SynQuest Laboratories (Alachua, FL). Deuterated chloroform and dimethyl sulfoxide were obtained from Cambridge Isotope Laboratories (Andover, MA). Deionized water (18.2 MΩ/cm) was obtained from a Milli-Q water-purification system (Millipore, Bedford, MA). Ethyl acetate, chloroform, 2-propanol, hexane, acetone, methanol, methylene chloride, and sodium hydroxide were obtained from Fisher Scientific (Fairlawn, NJ). Propane and microflame brazing torches were purchased from Sigma-Aldrich. Amberlite IRA-400(OH) anion-exchange resin was also obtained from Sigma-Aldrich.

All laboratory-made SPME devices were constructed using a 5 μL syringe purchased from Hamilton (Reno, NV) and 0.05 mm i.d. fused-silica capillary obtained from Supelco (Bellefonte, PA). Commercial SPME fibers of PDMS (film thickness of 7 μm) and Carboxen−PDMS (film thickness of 75 μm) were obtained from Supelco. A fiber holder purchased from the same manufacturer was used for manual injection of the commercial fibers. All commercial fibers were conditioned in the inlet according to the instructions provided by the manufacturer. Gas sampling bulbs (250 mL) with thermogreen LB-1 cylindrical septa were obtained from Supelco and were used in all extraction studies. A manometer pressure/vacuum gauge (0 to ±30 psi), obtained from Fisher Scientific, was used to record the pressure of the system.

Methods. *Synthesis of IL Monomers and Polymers.* The IL monomers were synthesized using a slight modification of a previously published procedure,[28] as shown in Figure 1. Briefly, 1-vinyl-3-hexylimidazolium bromide (VHIM-Br) was produced by mixing 1-vinylimidazole with an equimolar amount of 1-bromo-hexane in 2-propanol. The mixture was then allowed to react at 60 °C under constant stirring for 24 h. After removal of 2-propanol under vacuum, the product was dissolved in a small amount of Milli-Q water and then extracted with ethyl acetate five times to remove any unreacted starting materials. Ethyl acetate was then removed, and the product was collected and dried in a vacuum oven. The purity of the VHIM-Br was confirmed by ^{1}H NMR before polymerization or metathesis anion exchange.

To obtain poly(VHIM-NTf$_2$), polymerization of VHIM-Br was carried out by free radical polymerization following the proce-

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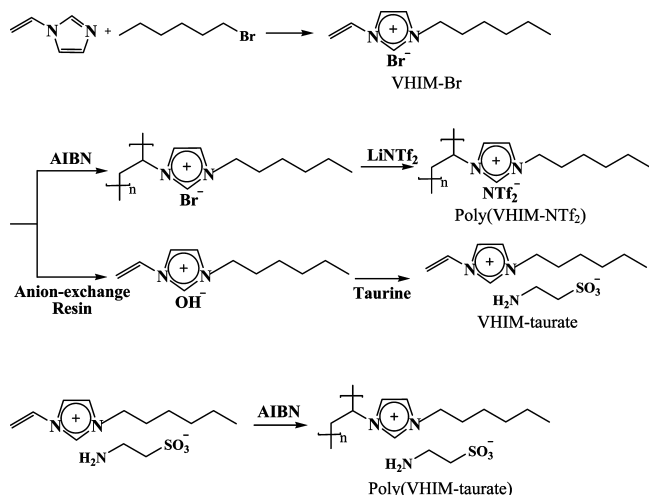(29) Meng, Y.; Pino, V.; Anderson, J. L. *Anal. Chem.* **2009**, *81*, 7107–7112.

Figure 1. Schematic demonstrating the synthesis of the task-specific polymeric ionic liquids used for the selective capture of CO_2.

dures described elsewhere.[30] Briefly, 5.0 g of purified VHIM-Br was dissolved in 30 mL of chloroform. Then, 0.1 g ($\sim$2%) of the free radical initiator AIBN was introduced, and the solution refluxed for 3 h under N_2 protection. Chloroform was then removed under vacuum, and the product was dried in a vacuum oven. The polymerization step was proven to be complete by the disappearance of the peaks that represent the vinyl group in the ^{1}H NMR. The polymerization was repeated when necessary. The obtained poly(1-vinyl-3-hexylimidazolium) bromide was dissolved in Milli-Q water, and an equimolar amount of lithium bis[(trifluoromethyl)sulfonyl]imide was introduced to perform metathesis anion exchange. This solution was stirred overnight, and the resulting PIL precipitate, poly(VHIM-NTf₂), was collected and washed with three aliquots of water and then dried under vacuum at 70 °C for 2 days.

The synthesis of poly(VHIM-taurate) involved exchanging the counteranion of VHIM-Br to hydroxide by passing the monomer through a column packed with anion-exchange resin in the hydroxide ion form, following a method by Fukumoto et al. that was used to synthesize amino acid-based ILs.[31] Specifically, 100 mL of the regenerated anion-exchange resin was packed into a 50 cm × 2 cm column followed by flushing an excess amount of 5 M NaOH to ensure the resin was entirely in the hydroxide ion form. This was verified by adding silver nitrate to a collected fraction of the eluent. White silver bromide precipitate formed when bromide ions persisted in the solution. Nitric acid was used to avoid the potential interference of silver oxide, which is a dark precipitate and can be dissolved by introducing nitric acid. After regenerating the resin, VHIM-Br was dissolved in water and passed through the anion-exchange column at an appropriate flow rate. The IL eluent was kept in aqueous solution due to its limited stability. An acid−base titration was used to determine the concentration of 1-vinyl-3-hexylimidazolium hydroxide (VHIM-OH) in the aqueous solution. The final step was a neutralization reaction between VHIM-OH and taurine. An equimolar amount of taurine was dissolved in water and added into an aqueous solution of

VHIM-OH dropwise to avoid intense reaction. The reaction was stirred and allowed to stand overnight. Water was then removed by rotary evaporation, and the product dried under vacuum for 48 h. Polymerization was performed using the aforementioned conditions to yield poly(VHIM-taurate). ^{1}H NMR spectra for VHIM-Br, VHIM-taurate, and poly(VHIM-taurate) are included in the Supporting Information.

Preparation of PIL-Coated SPME Fibers. Laboratory-made SPME devices were constructed following the previously published procedure by our group.[28] A microflame torch was used to seal the end of the capillary followed by removing the polyimide polymer from the last 1.0 cm segment of the fiber by a high-temperature flame. The fiber was then washed with methanol, hexane, acetone, and dichloromethane, followed by a 10 min conditioning step in the GC injection port at 250 °C. Coating solutions were prepared by mixing the PIL in chloroform at a ratio of 9:1 (v/v). Binary PIL mixtures containing poly(VHIM-NTf₂) and poly(VHIM-taurate) were mixed in chloroform at the desired weight percentage of each component. The coating solution was shaken for 5 min to ensure that the two PILs were homogeneously mixed. The pretreated SPME fiber was dipped into the PIL coating solution, held for approximately 20 s, and then removed from the coating solution. The coated fibers were allowed to dry in air for 10 min and then conditioned in the GC injection port for 10 min at 250 °C for the poly(VHIM-NTf₂) coating and 180 °C for all other remaining PIL coatings. The film thickness of the PIL-based coatings was estimated by scanning electron microscopy.

Extraction of CO_2. All extractions were performed in a 250 mL gas sampling bulb at 14 °C. A schematic describing the extraction apparatus used in this study is shown in Figure 2. With the regulator closed, valve 1 and valve 2 were opened, and the entire system evacuated via vacuum pump until the pressure reading from the pressure gauge was constant. Valve 1 was closed to isolate the system from the atmosphere and the initial pressure was recorded from the pressure gauge. The regulator was opened to introduce a desired amount of CO_2 into the sample bulb. The reading from the pressure gauge was recorded as the final pressure when the pressure reached a constant value. Valve 2 was closed and the SPME syringe injected into the sample bulb through the septum, and the fiber exposed to the gas sample for a desired length of time. The fiber was withdrawn into the syringe, and the syringe was removed from the sampling bulb. The captured CO_2 was released from the SPME fiber by high-temperature desorption in the GC injection port. The obtained CO_2 peak area was normalized by ΔP (final pressure − initial pressure).

Calibration curves were generated under two different conditions to perform a quantitative study of CO_2 extraction efficiency. This involved exposing the SPME fiber to the sample bulb containing pure CO_2 at a given pressure, as well as performing extractions in the sample bulb containing a fixed amount of air with varied concentrations of CO_2. For the latter condition, vacuum was first applied to the entire extraction system, followed by introducing air into the sample bulb up to a pressure of 70 kPa. CO_2 was subsequently injected into the sampling bulb to increase the total pressure (i.e., 75, 80, 85

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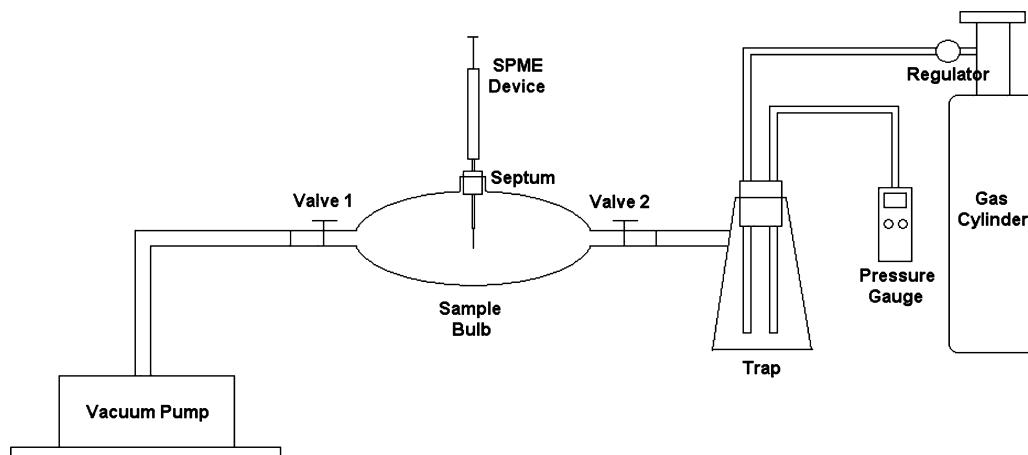
Figure 2. Apparatus of SPME setup used to perform extraction of CO_2.

kPa, etc.). In each case, the partial pressure of CO_2 was known (i.e., 5, 10, 15 kPa, etc.).

Gas Chromatographic Separation. All separations were conducted using an Agilent Technologies 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA). The GC was equipped with thermal conductivity and flame ionization detectors coupled in series. All separations were performed using a Carboxen 1010 PLOT capillary column (30 m × 0.32 mm i.d.) purchased from Supelco. The following temperature program was used for the separation of CO_2: initial temperature of 35 °C held for 10 min and then increased to 225 °C employing a ramp of 12 °C/min. Helium was used as the carrier gas with a flow rate of 1 mL/min. The inlet temperature was maintained at 250 °C for PDMS, Carboxen−PDMS, and poly(VHIM-NTf$_2$) PIL fibers and 180 °C for the remaining fibers. An inlet desorption time of 2 min was used for all fibers. Splitless injection was used, and a purge flow to split vent of 20.0 mL/min at 0.10 min was applied. The thermal conductivity detector was held at 250 °C using a reference flow of 20.0 mL/min and a makeup flow of helium at 7.0 mL/min. Agilent Chemstation software was used for data acquisition.

RESULTS AND DISCUSSION

Design of PIL-Based Sorbent Coatings. In this study, two different PIL-based SPME fiber coatings were designed, synthesized, and evaluated for the purpose of selective capture of CO_2. The polymeric imidazolium cation was chosen due to its high thermal stability as well as the tendency of these materials to form smooth and homogeneous coatings.[28] It has been shown previously that for unfunctionalized ILs, the nature of the counteranion exhibits a more dominant effect on overall CO_2 solubility.[32] The poly(VHIM-NTf$_2$) PIL was chosen as it contains the bis[(trifluoromethyl)sulfonyl]imide (NTf$_2^-$) anion and ILs consisting of this anion often exhibit high thermal stability and higher CO_2 solubility. Another PIL, poly(VHIM-taurate), was chosen as it contains a primary amine in its counteranion. The mechanism of CO_2 capture by the poly-(VHIM-taurate) PIL coating is believed to be largely dominated by the reversible formation of a carbamate salt. Task-specific ILs of this class were first introduced by Davis and co-
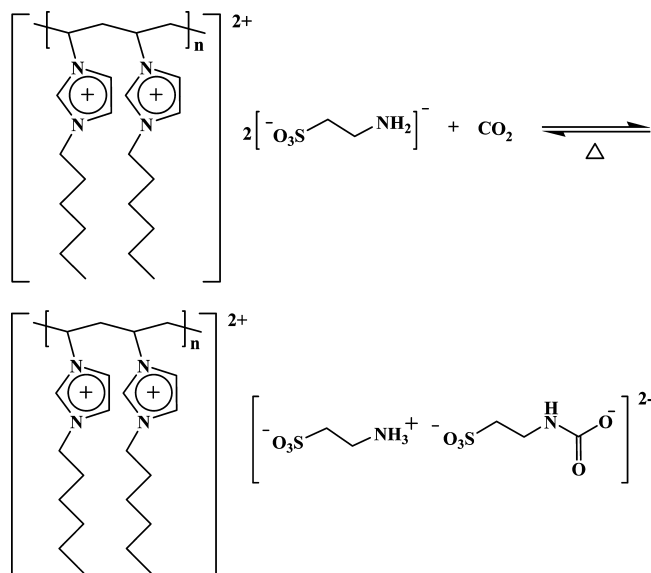

Figure 3. Schematic illustrating the reversible reactive capture of CO_2 by the poly(VHIM-taurate) PIL. For simplicity, two imidazolium cations and taurate anions from the linear polymer backbone are represented.

workers.[33,34] As shown in Figure 3, CO_2 can be extracted and sequestered in the sorbent coating through the reaction of CO_2 with two amine groups of the PIL, followed by thermally desorbing CO_2 in the GC injection port resulting in regeneration of the PIL. By carefully tailoring the structures of the PILs as well as incorporating various functional groups to the cation or anion, the selectivity of sorbent coatings for CO_2 can be optimized.

Initial SPME studies utilizing these sorbent coatings revealed impressive extraction efficiencies of CO_2 at various pressures. To investigate the extraction performance of these PILs, the morphology of the poly(VHIM-taurate) coating was examined by scanning electron microscopy (SEM). As shown in Figure 4A, the poly(VHIM-taurate) PIL produced an even and smooth surface when coated on the fused-silica support. After exposure

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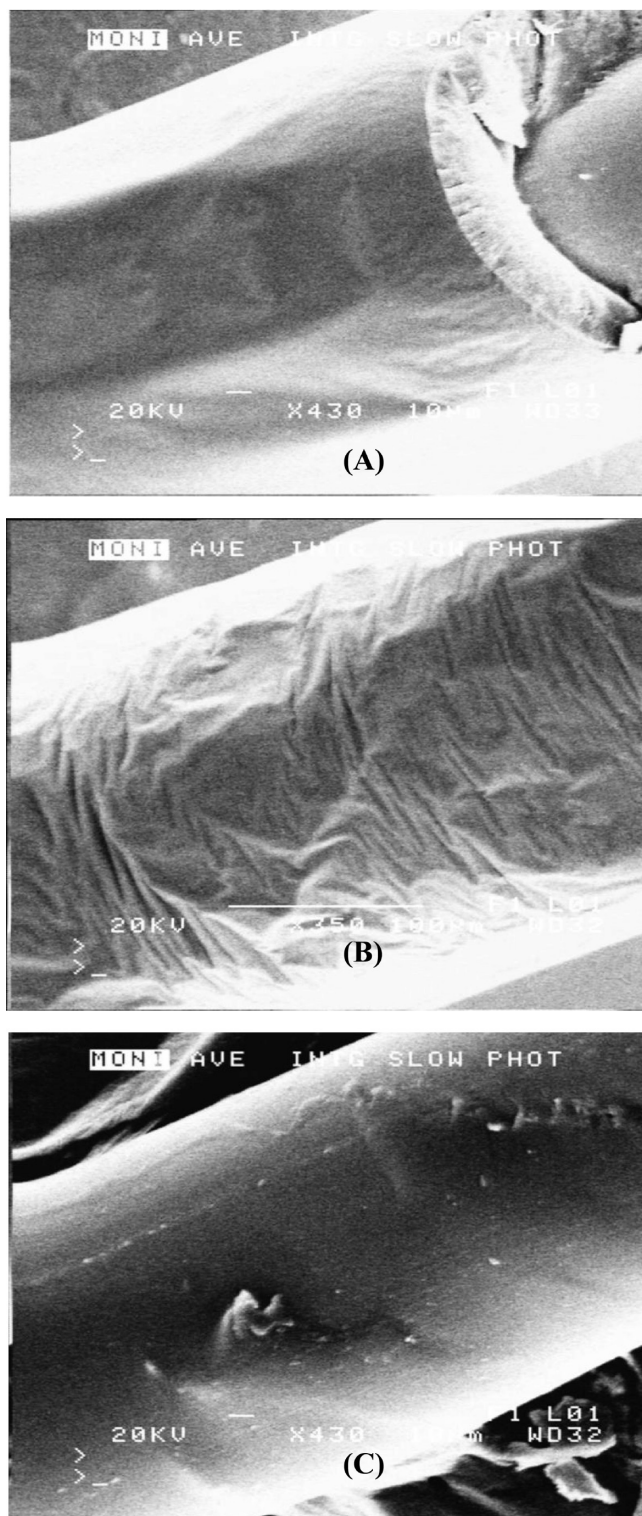
Figure 4. Scanning electron micrographs of a SPME fiber coated with the poly(VHIM-taurate) PIL: (A) before exposure to CO_2, (B) after exposure to CO_2, and (C) after thermal desorption of CO_2.

of this PIL-coated fiber to CO_2, the coating underwent a distinct morphology change presumably due to the dramatic increase in viscosity of the PIL (see Figure 4B). Previous studies have also observed a pronounced increase in viscosity, and occasionally solidification, for similar classes of ILs.[34,35] When the complexed
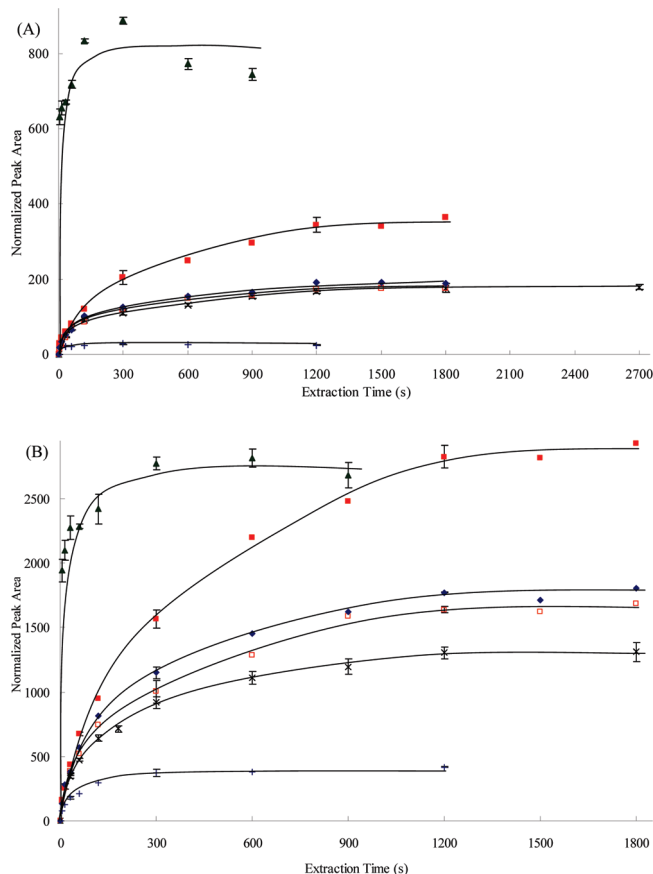
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Figure 5. Sorption−time profiles under two different CO_2 pressures, (A) CO_2 pressure = 12 kPa and (B) CO_2 pressure = 112 kPa, obtained for four PIL-based (∼10 μm) and two commercial fiber coatings: (▲) carboxen (75 μm), (■) poly(VHIM-NTf$_2$), (◆) poly(VHIM-NTf$_2$) (85%)/poly(VHIM-taurate) (15%), (□) poly(VHIM-NTf$_2$) (50%)/poly(VHIM-taurate) (50%), (×) poly(VHIM-taurate), (+) PDMS (7 μm).

CO_2 was desorbed from the fiber in the GC injector, the morphology of the sorbent coating returned to its original state, as shown in Figure 4C.

Sorption−Time Profiles. The effect of the extraction time on the amount of CO_2 extracted by the fiber coating was investigated by plotting the CO_2 peak area versus the extraction time for four different PIL-based fibers including: neat poly-(VHIM-taurate), neat poly(VHIM-NTf$_2$), 50% poly(VHIM-taurate)/50% poly(VHIM-NTf$_2$) (w/w), and 15% poly(VHIM-taurate)/85% poly(VHIM-NTf$_2$) (w/w). Sorption−time profiles were generated under two different CO_2 pressures (i.e., 12 and 112 kPa), which represent two different CO_2 concentration levels. Triplicate extractions were performed at selected time intervals to examine the reproducibility of the fiber coatings.

As shown in Figure 5, parts A and B, sorbent coatings consisting of neat poly(VHIM-NTf$_2$) and PIL binary mixtures reached equilibration in 20 min under both CO_2 pressures. However, the neat poly(VHIM-taurate) sorbent coating did not achieve equilibration until 30 min under a CO_2 pressure of 112 kPa. Under low CO_2 pressure (12 kPa), the poly(VHIM-NTf$_2$) fiber exhibited higher extraction efficiency compared to the poly(VHIM-taurate) fiber and two binary PIL-coated fibers, which all exhibited similar extraction efficiencies. However, when the CO_2 pressure was increased to 112 kPa, the extraction

Table 1. Reproducibility of Four Task-Specific PIL-Based Fibers and Two Commercial Fibers

sorbent coating	% RSD at low CO_2 pressure (12 kPa)[a]	% RSD at high CO_2 pressure (112 kPa)[a]
poly(VHIM-taurate)	6.8	5.9
poly(VHIM-NTf$_2$)	5.3	6.5
poly(VHIM-NTf$_2$) (85%)/ poly(VHIM-taurate) (15%)	3.6	4.5
poly(VHIM-NTf$_2$) (50%)/ poly(VHIM-taurate) (50%)	7.2	4.7
carboxen	9.0	7.4
PDMS	8.7	10.0

[a] Relative standard deviation was determined after performing eight successive extractions at the equilibration time of the sorbent coatings.

Table 2. Figures of Merit of Calibration Curves for Two Task-Specific PIL-Based Fibers and One Commercial Fiber in Pure CO_2[a]

sorbent coating	slope ± error	S_{yx}[b]	linear range (kPa)	R
carboxen	28.71 ± 1.7	119.3	1.5−75	0.990
poly(VHIM-NTf$_2$)	23.28 ± 0.4	54.63	1.5−125	0.999
poly(VHIM-taurate)	12.30 ± 0.4	49.62	1.5−125	0.996

[a] Extraction time: 5 min for the carboxen fiber, 20 min for the poly(VHIM-NTf$_2$) fiber, and 30 min for the poly(VHIM-taurate) fiber. [b] Standard deviation of the regression.

Table 3. Figures of Merit of Calibration Curves for Two Task-Specific PIL-Based Fibers and One Commercial Fiber in CO_2 Spiked with Air (70 kPa)[a]

sorbent coating	slope ± error	S_{yx}[b]	linear range (kPa CO_2)	R
carboxen	13.31 ± 0.3	15.70	5−50	0.997
poly(VHIM-NTf$_2$)	5.25 ± 0.2	6.87	15−50	0.995
poly(VHIM-taurate)	4.76 ± 0.2	6.46	15−50	0.995

[a] Extraction time: 5 min for the carboxen fiber, 20 min for the poly(VHIM-NTf$_2$) fiber, and 30 min for the poly(VHIM-taurate) fiber. [b] Standard deviation of the regression.

efficiency of the neat poly(VHIM-NTf$_2$) PIL was distinctly higher than that of the 15% poly(VHIM-taurate)/85% poly-(VHIM-NTf$_2$) fiber, followed by the 50% poly(VHIM-taurate)/ 50% poly(VHIM-NTf$_2$) coating and the neat poly(VHIM-taurate) coating.

For comparison purposes, sorption profiles of two commercial SPME sorbent coatings, namely, PDMS and Carboxen−PDMS (carboxen), were also generated. It can be observed that equilibration was reached within approximately 5 min for both coatings under the two different CO_2 pressures. The PDMS fiber provided the lowest extraction efficiency among all of the evaluated coatings in this study. The carboxen fiber, which possessed a film thickness of 75 μm and a highly porous surface, exhibited the highest extraction efficiency under both CO_2 pressures. In comparison to the carboxen fiber, the poly(VHIM-NTf$_2$) fiber, with an approximate film thickness of 10 μm, produced an extraction efficiency approximately 45% of that of the carboxen fiber under a CO_2 pressure of 12 kPa, whereas a comparable extraction efficiency was attained under a CO_2 pressure of 112 kPa. In the case of the poly(VHIM-taurate) fiber, the extraction efficiency was nearly 22% of that of the carboxen fiber at 12 kPa and increased to nearly 45% when the CO_2 pressure was increased to 112 kPa. It should be emphasized that both of the neat PIL-coated fibers possessed film thicknesses of approximately 10 μm, resulting in a much smaller volume of the sorbent phase compared to that of the carboxen fiber. These results clearly indicate that comparable, if not higher, extraction efficiencies could be attained with these sorbent coatings if similar film thicknesses were employed.

Analytical Performance. The sorbent coatings and the extraction method were evaluated by examining the analytical performance in terms of reproducibility and figures of merit of calibration curves including sensitivity, standard deviation of the regression, linear range, and correlation coefficients. The reproducibility was examined by studying six different coatings at their equilibration times under CO_2 pressures of 12 and 112 kPa. As shown in Table 1, relative standard deviation (RSD) values of the PIL-based fibers ranged from 3.6% to 7.2% and were significantly lower than those of the commercial fibers which ranged from 7.4% to 10.0%.

Calibration curves were obtained for the carboxen, poly(VHIM-NTf$_2$), and poly(VHIM-taurate) fibers at their equilibration times. Table 2 includes the figures of merit of the calibration curves generated in a sampling bulb containing pure CO_2 with a pressure ranging from 1.5 to 125 kPa. The poly(VHIM-NTf$_2$) fiber exhibited similar sensitivity to the carboxen fiber, despite the fact that the film thickness of the poly(VHIM-NTf$_2$) coating is approximately 15% that of the carboxen coating. Both PIL fibers exhibited lower standard deviations of the regression line and wider linear ranges compared to the carboxen fiber.

To evaluate the capability of the sorbent coatings to selectively extract CO_2 in a mixed gas matrix, a preliminary study was performed by carrying out extractions in CO_2 spiked with 70 kPa of air at the equilibration time of the sorbent coatings. With a fixed pressure of air, an increased amount of CO_2 was introduced into the sample bulb resulting in an increased total pressure. The mole fraction of CO_2 ranged from 0.067 to 0.417. The figures of merit from the obtained calibration curves are listed in Table 3. As expected, the sensitivity of all fibers for CO_2 decreased in the mixed gas matrix. The poly(VHIM-taurate) fiber provided comparable sensitivity to the poly(VHIM-NTf$_2$) fiber, whereas the carboxen fiber exhibited higher sensitivity and larger linear range than the PIL-based fibers. The standard deviations of the regression and correlation coefficients were comparable for all fibers. Again, due to the fact that the PIL-based fibers possess film thicknesses of approximately 10 μm, it is expected that enhanced sensitivity would be achieved if a thicker PIL sorbent coating was used.

Sorbate Storage Capacity. The capability of sorbent coatings to retain extracted analyte(s) during storage is an important parameter to consider when designing new coating materials. To determine the storage capacity of the task-specific PIL-based coatings, extractions were carried out at the equilibration time for each fiber at room temperature. Three storage conditions were examined in this study. Following extraction, the SPME fiber was retracted into the syringe and left uncapped for 1 min. In addition, the syringe was capped with a thermored septum for 1 and 10 min following extraction. When the storage time had elapsed, the
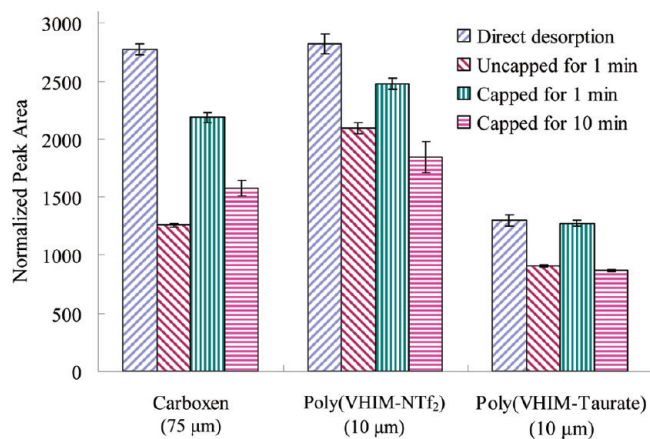
Figure 6. Comparison of the amount of CO_2 sorbate retained in two PIL-based fibers and the carboxen fiber under various storage conditions.

fiber was immediately desorbed in the GC injection port to determine the amount of CO_2 that was retained in the coating.

As shown in Figure 6, a significant amount of CO_2 was lost for all fibers when a sampled SPME fiber was withdrawn into the syringe needle and left uncapped at room temperature for 1 min. In comparison to direct desorption, an average of 54.7% of the captured CO_2 was lost from the carboxen fiber under this storage condition. The task-specific PIL-based fibers exhibited an enhanced ability to retain the extracted CO_2 as 25.9% of the captured CO_2 was lost from the poly(VHIM-NTf$_2$) fiber and 30.6% of the CO_2 was lost from the poly(VHIM-taurate) fiber. Using a septum to seal the tip of the syringe needle for 1 min prior to desorption appears to have imparted improved stability of CO_2 within the sorbent coating. Approximately 21.2% of the captured CO_2 was lost from the carboxen fiber after capping for 1 min, whereas only 12.4% and 2.2% of the captured CO_2 was lost under the same condition for the poly(VHIM-NTf$_2$) and poly(VHIM-taurate) fibers, respectively. When a sampled carboxen fiber was sealed for 10 min after CO_2 extraction, 43.1% of the captured CO_2 escaped from the fiber coating. For the PIL-based sorbent coatings, 34.7% of captured CO_2 was lost from the poly(VHIM-NTf$_2$) fiber, whereas 33.0% was lost from the poly(VHIM-taurate) fiber. These results indicate that the task-specific PIL coatings exhibit distinct advantages in their storage capabilities compared to the carboxen coating. Despite its lower extraction efficiency compared to the poly(VHIM-NTf$_2$) fiber, the poly(VHIM-taurate) fiber was capable of retaining more CO_2 after short periods of storage. This is likely due to the fact that the CO_2 is chemically captured by the sorbent coating, whereas the poly(VHIM-NTf$_2$) and carboxen coatings retain the CO_2 via physical sorption.

CONCLUSIONS

Polymeric ionic liquids have proven to be a useful class of sorbent coatings for SPME due to their unique physicochemical properties. For the first time, the structures of two PILs were carefully tailored to incorporate specific functional groups to serve as task-specific PIL sorbent coatings that exhibit high extraction efficiencies and selectivities for CO_2. The PIL sorbent coatings are capable of undergoing two different types of mechanisms responsible for capturing the CO_2 sorbate, namely, physical sorption by the poly(VHIM-NTf$_2$) coating and carbamate formation by the poly(VHIM-taurate) coating. The PIL-based coatings exhibited impressive extraction efficiencies of CO_2 as well as exceptional extraction-to-extraction reproducibility. In comparison to the commercial carboxen SPME fiber, similar extraction efficiency of CO_2 was achieved using the poly(VHIM-NTf$_2$) PIL fiber at high CO_2 pressure, despite the fact that the carboxen fiber possessed a much larger film thickness. The poly(VHIM-taurate) sorbent coating exhibited enhanced storage capacity of CO_2 on the fiber compared to the poly(VHIM-NTf$_2$) and carboxen coatings, most likely due to the ability of the task-specific PIL-based sorbent coating to chemically react and sequester CO_2 within the coating.

Future studies involving these sorbent coatings will focus on examining the effect of humidity and temperature on the extraction efficiency of CO_2. To further investigate the advantages of employing task-specific PILs that capture CO_2 by two different mechanisms, the performance of the coatings will be examined in a mixed gas matrix. The results from this work indicate the promise that PIL-based SPME coatings possess in developing task-specific microextractions that result in high extraction efficiencies, high selectivities, and low detection limits.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.