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Melting Point and Aqueous Solubility Determination of 2*H*-Hexadecafluoro-2-decenoic Acid ($C_{10}F_{16}H_2O_2$)

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Two physical properties of the fluorinated carboxylic acid, 2*H*-hexadecafluoro-2-decenoic acid ($C_{10}F_{16}H_2O_2$), were investigated in this study: melting point and solubility. Melting point data were ascertained on a traditional melting point apparatus and a differential scanning calorimeter (DSC), while solubility data were obtained using an LC−MS/MS system. A melting point of 105 ± 1 °C and an aqueous solubility of 64 ± 5 ng/μL at ambient temperatures were observed.

Introduction

Trace quantities of fluoropolymer processing aids (FPAs) and their degradation byproducts have been found in numerous places in the environment, resulting in recent concerns regarding their effects on the environment and human health.[1−4] Their documented thermal and chemical stability,[5−10] while industrially useful, can be problematic because it may result in prolonged lifetimes in eco- and biosystems.[2] Such concerns have prompted the need for the physical and chemical characterization of these materials and their degradation byproducts in an effort to understand and predict their transport behavior.[11,12] The degradation of perfluoroalkylethanol FPAs (also called fluorotelomer alcohols) to corresponding carboxylic acids has been demonstrated in a number of studies. These include smog chamber studies,[1] rat metabolism studies,[4] and microbial sewage sludge decomposition studies.[13] This investigation focuses on determining key physical properties of one of these acid decomposition products, 2*H*-hexadecafluoro-2-decenoic acid ($C_{10}F_{16}H_2O_2$), which may play a significant role in the understanding of the environmental transport mechanism of these types of materials. We have determined melting points on neat and annealed material as well as the solubility of this material in water at ambient conditions.

Experimental Section

Chemicals. The fluorinated carboxylic acid (FCA) sample was obtained from the E. I. DuPont de Nemours Company. All solvents obtained from Fisher Scientific (King of Prussia, PA) and J. T. Baker (Phillipsburg, NJ) were HPLC grade. A Barnstead (Corning) MP-12A Mega-Pure glass still was used to purify in-house deionized water.

Melting Points. A Thomas Hoover Uni-Melt 6406-H capillary melting point apparatus from Arthur H. Thomas Company (Philadelphia, PA) was utilized to determine the melting point of the FCA. In addition to determining the melting point of the original sample, samples were annealed, cooled, and then reheated to investigate thermal history and crystallization patterns. A Mettler Toledo differential scanning calorimeter (model DSC821) was also used to find the melting and freezing points and thermal behavior. Samples were held isothermally for 1 min at 80 °C, heated to 140 °C and cooled to 80 °C twice, and then reheated to 140 °C, at a rate of 5 °C/min. An indium standard was used to validate instrument calibration.

Liquid Chromatography−Mass Spectrometry Optimization and Analysis. The concentrations of fluorinated carboxylic acid in standards and samples were determined by liquid chromatography with tandem mass spectrometry (LC−MS/MS). Chromatographic separations were performed with a Cohesive Technologies (Franklin, MA) Aria TLX system equipped with an Agilent (Wilmington, DE) model 1100 binary HPLC pump and a CTC (Zwingen, Switzerland) autosampler under the control of Aria software version 1.4.1. The system was configured for direct injections from the autosampler to an HPLC column, which was connected to an atmospheric pressure ionization source (heated nebulizer) of an API 365 (Applied Biosystems/Sciex, Foster City, CA) triple−quadrupole mass spectrometer (MS/MS) under the control of Analyst 1.4.1 software. While infusing a standard solution (1000 ng/mL) of FCA using a series 74900 (Cole-Palmer, Vernon Hills, IL), the software Quantitative Optimization routine was used to tune quadrupole potentials for negative-ion multiple-reaction monitoring (MRM) for the precursor ion to product ion transition of 457.5 to 392.7 (*m*/*z*). Optimized potentials, source temperature, and gas flows (as shown in Table 1) were programmed into an Analyst data acquisition method, which was used to selectively and quantitatively monitor the presence of the acid during HPLC separations. A mobile-phase blend of 75 % acetonitrile, 25 % water, and 0.2 % formic acid was pumped at a flow rate of 0.5 mL/min to achieve isocratic elution of FCA from 10 μL sample injections through a Supelco (Bellefonte, PA) Ascentis C-18 column (4.6 × 50 mm packed with 3 μm particles). Duplicate injections were made for each standard and each sample.

In order to determine the linear working range of the LC−MS/MS assay, a series of working standards in the range of 10−700 ng/μL was prepared from a stock standard of 1000 ng/μL of FCA in HPLC-grade methanol.

For the solubility determination, weighed quantities of acid were added to disposable glass centrifuge tubes containing

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Table 1. API 365 MS/MS Data Acquisition Method Parameters[a]

Q1 mass	457.5 amu
Q3 mass	392.7 amu
dwell time	200 ms
declustering potential	−5.00 V
focusing potential	−90.00 V
entrance potential	−2.50 V
collision cell entrance potential	−25.00 V
collision energy	−20.00 V
collision cell exit potential	−20.00 V
heated nebulizer (APCI) temperature	400 °C
nebulizer gas	10.00 L/min
nebulizer current	−5.00 μA
curtain gas	10.00 L/min
collision activated dissociation gas	5.00 L/min

[a] Scan type: MRM negative polarity, unit resolution for Q1 and Q3.

known volumes of distilled−deionized water, such that some solid remained undissolved. Samples were mixed on a Vortex mixer initially for 2 min and then were allowed to sit at room temperature (22 °C) for a minimum of 24 h. Prior to analysis, each sample was vortex-mixed for 1 min and then centrifuged for 20 min to separate the saturated solution from any solid particles. Glass disposable pipettes were used to transfer samples and standards into 2-mL glass autosampler vials with the silicone side of septa facing the solution.

A preliminary analysis was performed on a single saturated solution in order to determine the approximate solubility and the optimum range for standards. Five replicates were used for the actual solubility determination experiment. Since the supernatant matrix (water) was different from the LC elution solvent, three of the samples were diluted with acetonitrile to check for chromatographic differences that might affect the solubility determination.

Quality control blanks of water, methanol, acetonitrile, and LC eluent were run to check for interferences. In addition, all solubility test samples and standards were analyzed in duplicate.

Results and Discussion

Melting Point. The initial melting point range for nine replicate samples of 2*H*-hexadecafluoro-2- decenoic acid that was obtained with the Hoover melting point apparatus was (96 to 106) °C. After subsequent cooling and reheating, the solid remelted over a tighter range, (103 to 105) °C. Multiple reheats generally yielded much tighter and more reproducible melting point ranges.

The DSC was also utilized to find the melting point and to observe the effects of annealing. Recycle scans show a narrowing of the peak of the endotherm after the first cycle, but subsequent reheats maintained a constant peak width as can be seen in Figure 1. This behavior corroborates the observed melting point data range reduction that was described above for the reheated solids melting point determinations. This effect is commonly observed once a sample has been exposed to a consistent thermal history. In addition, rearrangement of the crystals into a more favorable mode can yield similar results.[14] Melting points of (105.4, 104.5, and 104.5) °C were observed for the first, second, and third heating cycles, respectively, using the differential scanning calorimeter. Hysteresis was observed in the solidification process, resulting in a solidification temperature lower than the melting point, as seen in the exotherm of Figure 1. Since the Hoover melting point determination is subject to human error in visualizing the point at which melting occurs, we are reporting the DSC melting point average, 105 ± 1 °C, as the melting point.

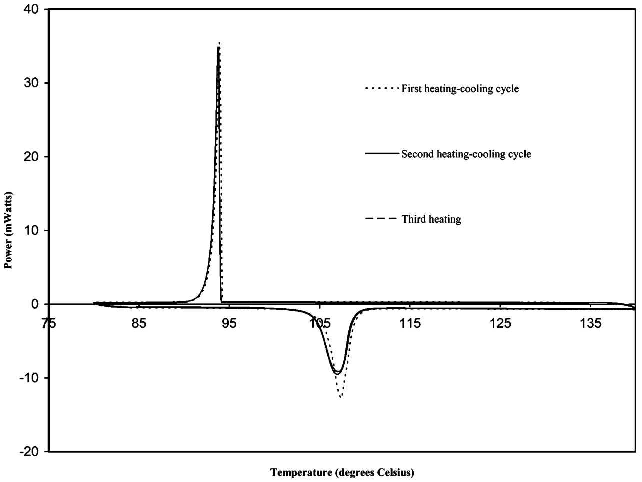

Figure 1. DSC thermal curve for 2*H*-perfluoro-2-decenoic acid showing two complete heating and cooling cycles.

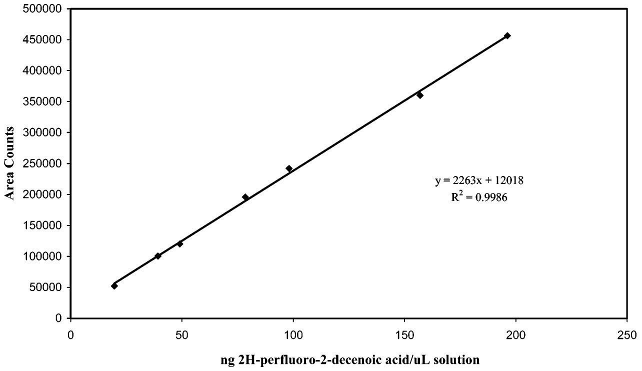

Figure 2. Calibration curve for 2*H*-perfluoro-2-decenoic acid.

Optimization of API-MS/MS Conditions. The precursor ion to product ion transition of (457.5 to 392.7) *m*/*z* that was observed and utilized in the optimization and subsequent solubility study results from a likely loss of CO_2 and HF, which is consistent with the molecular structure ($C_{10}F_{16}H_2O_2$) and literature spectral results.[15]

Solubility Determination Using Quantitative HPLC−MS/MS Analysis Results. A seven-point standard calibration curve of 2*H*-hexadecafluoro-2-decenoic acid in methanol gave a linearity correlation coefficient of greater than 0.999 in the (20 to 200) ng/μL region. This range of standards was chosen after determining that the solubility of the acid was in the <100 ng/μL concentration range in the scouting solubility experiment.

When compared to these standards, the saturated water samples from five separate saturated solutions contained a concentration of (64 ± 5) ng/μL of the acid at the 95 % confidence level. Dilutions (50:50 water/acetonitrile) of the saturated solutions were also run; the solubility values that were calculated from these determinations showed no significant difference when compared to those that were obtained with the original aqueous supernatant. Water and mobile phase blanks (methanol and 25:75:0.2 water/acetonitrile/formic acid) showed no acid presence and no noticeable carryover from previous injections.

A calibration curve for methanol standards and a sample chromatogram for a standard are shown in Figures 2 and 3, respectively. In addition, a sample chromatogram of a saturated aqueous solution is shown in Figure 4. The total area under both the shoulder peak and main peak in the chromatograms for the solubility test samples was used to compute the solubility. The shoulder peak appeared in each of the saturated solutions

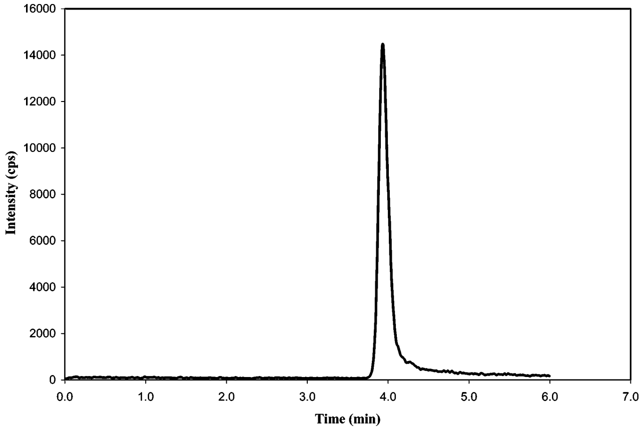

Figure 3. Sample chromatogram of 50 ng of 2*H*-perfluoro-2-decenoic acid/μL in methanol.

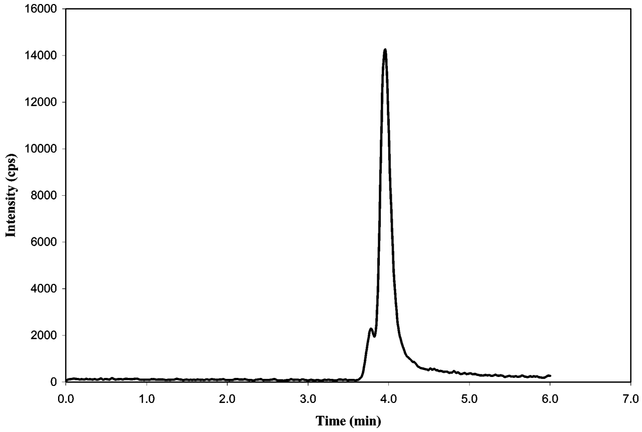

Figure 4. Chromatogram of a saturated aqueous solution of 2*H*-perfluoro-2-decenoic acid.

as well as in acetonitrile dilutions of the saturated aqueous samples, but never in the methanol standards. The solubility test samples were further analyzed using several different chromatographic solvent conditions (isocratic and gradient elution using water:methanol and water:acetonitrile) and different columns (C-8 and C-18 stationary phases) indicating that the shoulder peak is not likely to be an artifact. The mass spectrum of the shoulder and the main peak in Figure 4 were found to be identical. The identity and origin of the shoulder peak [(1 to 5) % of total peak area] is still under investigation.

Conclusions

Characterization of 2*H*-hexadecafluoro-2-decenoic acid ($C_{10}F_{16}H_2O_2$) was accomplished using melting point techniques and LC−MS/MS. The melting point was found to be (105 ± 1) °C, and the solubility was found to be (64 ± 5) ng/μL. These physicochemical data can serve as a component in understanding the behavior and subsequently the degradation mechanism of these materials in order to explain transport of fluorocarbons in the environment.

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