Physicochemical Properties of 8-2 Fluorinated Telomer B Alcohol

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Physicochemical properties (vapor pressure, water solubility, gas-phase nuclear magnetic resonance) of 8-2 Telomer B alcohol, $CF_3(CF_2)_7CH_2CH_2OH$, were measured. Vapor pressures were measured in the temperature range from (21 to 200) °C by three different methods, including a novel method based on gas-phase NMR that requires only milligram quantities of substance. At 21 °C, the vapor pressure was 3 Pa; at 201.3 °C, the vapor pressure was 101.325 kPa (1 atm). Water solubility was measured at (12, 25, 37, and 60) °C in pure water. Solubility ranged from (134 to 318) μg/L.

Introduction

Fluorinated telomer B alcohols, including 8-2 Telomer B alcohol, $CF_3(CF_2)_7CH_2CH_2OH$, are used in the manufacture of fluorinated surfactants and fluorinated polymers. These substances provide unique surface modification properties in a wide variety of consumer products. Telomer B alcohols are of particular interest since they are expected to be among the possible compounds into which fluorinated surfactants and polymers may potentially transform in the environment.[1] To study more effectively their environmental fate, it is important to know their physicochemical properties.

The telomerization synthetic process yields a mixture of even-carbon telomers differing in their overall carbon chain length.[2,4] 8-2 Telomer B alcohol has eight perfluorinated carbon atoms attached to a $-CH_2CH_2OH$ group. The high level of fluorination in this compound gives it chemical and physical properties that are strikingly different from those of its hydrogen analogue and of analogous compounds of other halogens, where they exist.[3,4] Because of the high level of fluorination, 8-2 Telomer B alcohol tends to be absorbed into fluoropolymeric materials that can be part of the experimental apparatus, such as cap liners. Although it is a solid at room temperature, it easily sublimes from an open container at ambient temperature. It can also escape from an aqueous solution where no adsorptive substance is present, although its solubility is very low. These physical characteristics make it difficult to obtain reliable data, especially for aqueous systems.

Two basic physicochemical properties (vapor pressure and water solubility) were measured at conditions that are environmentally relevant. A novel methodology to measure its vapor density based on gas-phase NMR spectroscopy was brought to bear in addition to conventional measuring techniques.

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Experimental Section

Materials. The 8–2 Telomer B alcohol (CAS number 678-39-7; CAS name: 1-decanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,-10,10,10-heptadecafluoro) was obtained from Clariant (Germany) and was shown to be 99.2% pure via gas chromatography. The major impurity (0.8% by area) was tentatively identified as $C_7F_{15}CF=CHCH_2OH$ based on the mass spectral fragmentation pattern. Melting point (Clariant): 48–50 °C. All solutions were prepared in ultrapure water (17.6×10^6 Ω·cm).

Vapor Pressure. Three techniques were used to measure the vapor pressure. The first method was based on a dynamic measurement procedure developed by Scott,[5] where the equilibrium temperature is measured at a controlled pressure. Approximately 30 g of the 8-2 Telomer B alcohol were placed in a boiler. The pressure was held constant to 0.01% (0.01 kPa) and measured to an accuracy of 0.01%. The apparatus consisted of a Mensor PCS400 pressure controller (San Marcos, TX), a Paroscientific 740 pressure transducer (Redmond, WA), and a Hart Scientific stack base unit for temperature measurement (American Fork, UT). The temperature varied from (80 to 200) °C.

The second procedure was based on the EPA OPPTS gas saturation method in which the quantity of a substance transported by a known volume of a carrier gas is determined.[6] This method is particularly suited for low vapor pressures and was used to obtain the vapor pressure of 8-2 Telomer B alcohol at room temperature. The alcohol was placed in a glass thermostated tube. Gas-chromatographic-grade helium (99.999%) flowed over the solid 8-2 Telomer B alcohol. The flow was controlled by a flow controller on a Hewlett-Packard (now Agilent, Little Falls, DE) model 5890 gas chromatograph. Because of the adsorptive properties of the alcohol, the vapor pressure was calculated from weight loss rather than from the weight of trapped material downstream. The vapor pressure is calculated from the vapor density, W/V, by means of the equation $P/Pa = (W/V)(RT/M_r)$ where P is the vapor pressure in Pa, W is the mass of transported substance in grams, V is the volume of saturated gas in cubic meters, R is the universal molar gas constant, T is the temperature in K, and M_r is
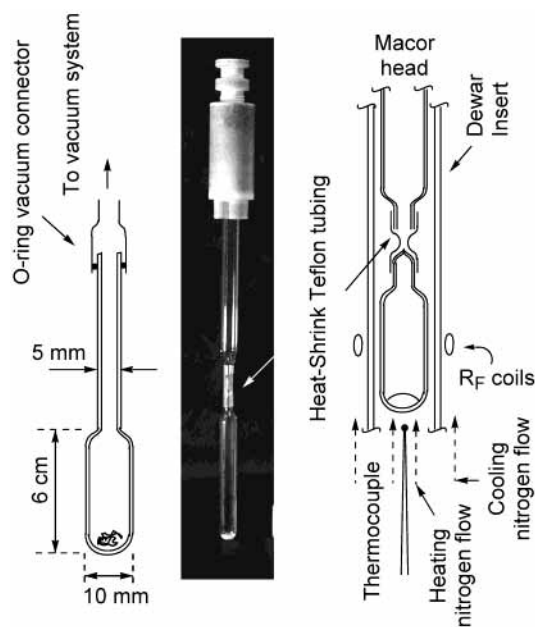
Figure 1. Diagram of the gas-phase NMR ampule attached to a vacuum system before being sealed off with a butane torch (left). Center: the sealed ampule attached by means of a short Teflon sleeve to a matching 5-mm o.d. glass stub of the holding tube. The latter rests firmly in a Macor ceramic head that seals the heated compartment of the commercial high-temperature NMR probe. The ampule assembly is lowered into the magnet using a string and is not spun. The amount of sample material is chosen so that the internal pressure after complete vaporization will not a exceed a safe limit (<1.5 atm).

the relative molecular mass. The vapor pressure at 21 °C was 3 Pa.

The third method is novel and is based on gas-phase NMR that has been used recently (with proton and fluorine detection) to study the kinetics of a variety of reactions of organic and fluoro-organic compounds in the vapor phase at temperatures up to 400 °C.[7−9] This method measures the vapor density at various temperatures relative to that of a much more volatile internal mass standard present in much smaller molar amounts of the order of 1 mol %. The vapor density is then converted to vapor pressure using the ideal gas law or another appropriate equation of state.

In short, a micromolar quantity of a substance is weighed into a glass ampule (Figure 1) made from a section of standard thin wall 10-mm outside diameter (o.d.) NMR tubing with a 5-mm o.d. extension to facilitate attachment to a vacuum system. The ampules are available from New Era Enterprises, Vineland, NJ. The internal volume (after sealing) is (4.2 ± 0.05) mL. The volume of the ampule is determined by filling the latter with water up to a marked level on the narrow extension tube at which the ampule is to be sealed. The weight of the water is determined using an analytical balance, and the volume is obtained therefrom. The ampules are kept in a vacuum oven at ∼110 °C prior to use. The quantity of substance is chosen so that at the temperature corresponding to the normal boiling point there remains a small pool of liquid at the bottom of the ampule. The length of the ampule was chosen so as to restrict the sample to the thermostated region of the probe and to minimize temperature gradients. An O-ring vacuum adapter is attached to the neck, and the ampule is transferred to a vacuum line equipped with a precision pressure transducer. After evacuation and degassing, a known micromolar amount (about 1 mol %) of volatile mass standard (tetramethylsilane, TMS, for proton detection or

hexafluoroethane, F116, for fluorine detection) is condensed from a bulb of known volume into the ampule by keeping the latter immersed in liquid nitrogen. After sealing the neck with a butane torch at the marked position, the ampule is attached to a sample holder by means of short piece of polytetrafluoroethylene sleeve (Figure 1), and the assembly is lowered into the high-temperature NMR probe (Nalorac Corporation, now part of Varian) so that only the vapor phase in the ampule is probed by the spectrometer. The temperature of the probe is increased until sufficient vapor pressure is established to allow detection and is stepped up from there in desired increments. Because of the low heat capacity of the loaded ampule, temperature equilibration takes place in less than 5 min. At each temperature, a spectrum is taken and the integrated intensities of the resonances of the protons or fluorines associated with the substance under study are compared, after normalization by the number of equivalent nuclei, with that of the volatile internal mass standard. Both TMS and F116 give rise to a single absorption appropriate for 12 equivalent protons and 6 equivalent fluorines, respectively. On the assumption that the amount of volatile mass standard adsorbed in the deliberately very small pool of liquid substance under study is a very small fraction of the total, the NMR intensity ratios yield the micromols of the substance in the vapor phase and therefore its vapor density, since the volume of the ampule is known. The pressure is then calculated on the basis of the ideal gas law.

NMR spectra were obtained with a Varian INOVA spectrometer operating at 399.973 kHz with a wide-bore Oxford cryomagnet. The high-temperature 10-mm probe and variable temperature (VT) controller have an upper temperature rating of 400 °C and were purchased from Nalorac Corporation. Since ^{19}F spin-rotation relaxation is very efficient in the gas phase, 50 ms recycle delays were appropriate and permitted rapid signal averaging (e.g., 32 transients in much less than 1 min). Proton spin-rotation relaxation is less efficient, and a single pulses was used. In general, the NMR lines are broader in the gas phase than in solution, particularly for fluorines, and magnetic field homogeneity is less critical than for solution NMR; consequently, no field lock was used, and the ampule was not spun.

Thermal losses in the probe necessarily lead to sample temperatures that are lower than the VT controller set point. The internal temperature was measured with a thin thermocouple positioned in the center of a dummy ampule, identical to those used for the actual vapor density measurements except for a small hole at the end of the 5-mm stub to allow entry to the thermocouple. A temperature calibration curve was obtained by measuring over a broad temperature range the internal temperatures in the dummy ampule, positioned in the probe exactly as the actual samples, and comparing them to the controller set temperatures. The internal temperature depends on the flow rates of the nitrogen gas, whose temperature is being regulated by the VT controller, and on that used for cooling of the peripheral space around the probe dewar. For the flow rates used in this work, $t_{corrected}/°C = t_{controller}/°C − 0.000128(t_{controller}/°C)^2$.

Three test ampules were prepared in a nitrogen glovebox containing, respectively, 23.2 mg (50 μmol), 45.5 mg (98 μmol), and 96.2 mg (207 μmol) of 8-2 Telomer B alcohol to which 1 μmol of TMS was transferred using vacuum techniques. ^{1}H NMR spectra were acquired at progressively higher temperatures (starting at 125 °C) until it became

evident that no additional material entered the vapor phase with an increase in temperature (the point of complete vaporization). Although 8-2 Telomer B contains both protons and fluorines, proton detection was chosen since TMS gives a much narrower line (for twelve equivalent protons) than F116 (for six equivalent fluorines), which can be integrated more accurately.

The vapor density of hexafluorobenzene was also measured, and the derived vapor pressure (ideal gas law) was compared with literature data to validate the methodology. A gas-phase NMR ampule was loaded with 39 μL (337 μmol) hexafluorobenzene (Aldrich, 99%) and 5 μmol perfluoroethane. ^{19}F NMR spectra were acquired at temperatures from 300 K to 380 K. The relative integrated intensities of the perfluoroethane and hexafluorobenzene resonances were used to calculate the concentration of hexafluorobenzene in the vapor phase at each temperature. The vapor pressure was calculated in each case using the ideal gas law with $V = 0.0042$ L.

Water Solubility. Water solubility was determined at (12, 25, 37, and 60) °C by two methods. In the first, excess alcohol was placed in 2-mL gas chromatographic sample vials and ultrapure water (conductivity of 17.6×10^6 Ω·cm) was added to fill the vials completely. After sealing with caps using silicone rubber septa, the vials were shaken at constant temperature on a shaker table. The alcohol concentration was measured at various time intervals in the aqueous phase by gas chromatography with mass spectrometric detection (electron impact, EI, detection, m/z = 463) to obtain a steady value. In the second method, approximately 100 mg of the alcohol was added to a standard glass gas chromatography vial. The vial was coated with excess alcohol by placing the open vial on a warm surface to melt the alcohol and to condense the vapors onto the cooler upper surfaces of the vial. It was then removed from the warm surface and allowed to come to room temperature. Ultrapure water (conductivity of 17.6 $\times 10^6$ Ω·cm) was added so that no headspace was available. A cap with a silicone rubber septum was used for sealing. The vial was placed on a thermostated shaker table at the temperature of interest, and it was shaken at approximately 100 rpm for 4 days to make sure that equilibration took place. Samples were removed periodically to a temperature-controlled chromatographic autosampler tray, and the alcohol was determined by gas chromatography coupled with mass spectrometry (GC/MS). The second method is faster than the first and gives the same result.

The gas chromatograph was a Hewlett-Packard (now Agilent, Little Falls, DE) model 5890 with a mass-selective detector in the EI mode (70 eV) with a 5-min delay. Ions 463.0, 131.0, 95.0, 69.0, and 31.0 were monitored. The separation occurred in a sixty meter by 250 μm (1.00-μm film thickness) Restek RTX 200 (Bellefonte, PA) trifluoropropylmethylpolysiloxane column. A 1-μL splitless injection was used (225 °C, no pumping, quiescent), and the sample was taken 10.0 mm above the normal position (further from the bottom of the vial) to ensure that no particulates were introduced into the chromatographic system from the solution. The initial oven temperature was set at 80 °C for one minute and was increased at 20 °C/min to 300 °C, where it was held for 10 minutes. The limit of detection was approximately 20 ppb, and the limit of quantitation approximately 50 ppb.

Results and Discussion

Vapor Pressure. The vapor pressure of the 8-2 Telomer B alcohol varies from 3 Pa at 21 °C to 101 kPa at 201 °C.
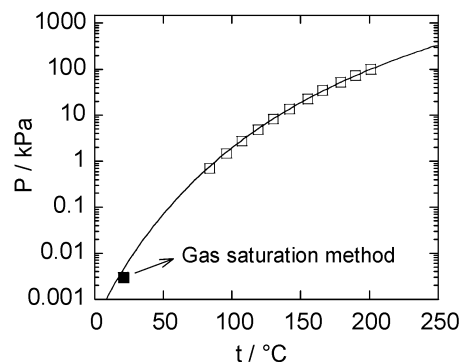

Figure 2. Vapor pressures of 8-2 Telomer alcohol obtained by the Scott method with the least-squares fit using the Antoine equation. Also shown is the vapor pressure at 21 °C obtained by the gas saturation method.

Table 1. Vapor Pressures of Telomer 8-2 Alcohol

temperature	vapor Pressure		
t/°C	P/Pa	P/Torr	method
21	3	0.022	gas-saturation method
84	708	5	Scott method
96	1465	11	Scott method
107	2774	21	Scott method
119	4910	37	Scott method
124	5100	38.3	NMR spectroscopy
130	8284	62	Scott method
142	13798	103	Scott method
148	15267	115	NMR spectroscopy
155	22752	171	Scott method
157	23400	176	NMR spectroscopy
166	34449	258	Scott method
167	32000	240	NMR spectroscopy
172	35667	268	NMR spectroscopy
179	51667	388	Scott method
190	72339	543	Scott method
195	75750	568	NMR spectroscopy
201	100607	755	Scott method
225	162100	1220	NMR spectroscopy

Table 2. Water Solubility of Telomer 8-2 Alcohol at Autogenous pH

temperature t/°C	solubility S/ng·mL^{-1}	std dev σ/ng·mL^{-1}	n
12	134	29	8
25	137	53	17
37	318	176	10
60	225	51	10

Table 3. Water Solubility of Telomer 8-2 Alcohol at Various pHs at 12 °C

pH	solubility S/ng·mL^{-1}	std dev σ/ng·mL^{-1}	n
3[a]	227	109	6
autogenous pH = 5.8	104	57	6
11[b]	74	29	5

[a] Adjusted with H_3PO_4. [b] Adjusted with NaOH.

The results from the single measurement taken at 21 °C with the gas saturation method and from the eleven measurements taken at higher temperatures by the Scott method are shown in Figure 2 on a logarithmic scale. Table 3 shows the individual experimental data points. An excellent least-squares fit of the data, including the low-temperature measurement by the gas saturation method, was obtained using the Antoine equation, $\log(P/\text{kPa}) = a - b/(c + t/°\text{C})$ (Figure 2) with the parameters $a = 6.457$, $b = 1623$, and $c = 163.3$. Convergence to these values was independent of the starting parameters of the fit. A boiling
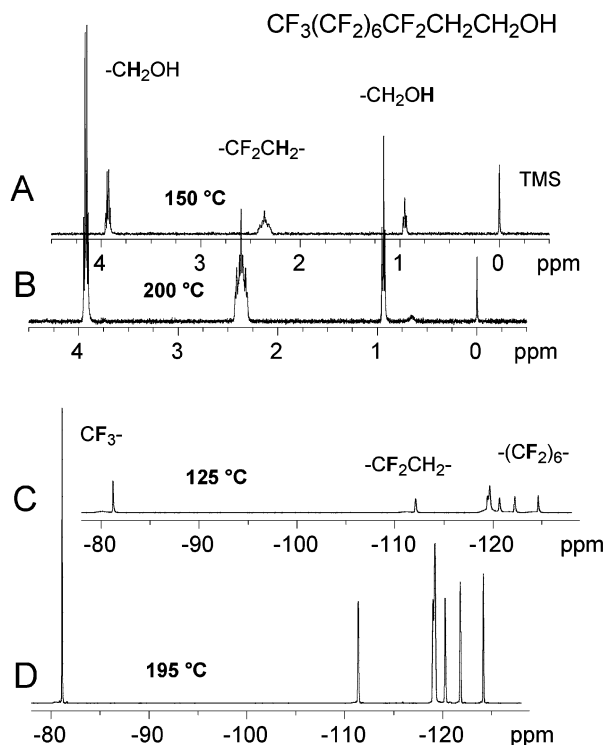
CF$_3$(CF$_2$)$_6$CF$_2$CH$_2$CH$_2$OH

Figure 3. Proton and fluorine gas-phase NMR spectra of 8-2 Telomer alcohol at different temperatures.

Figure 4. Comparison of the vapor pressures of 8-2 Telomer alcohol obtained by the Scott method, by the gas-saturation method (at 21 °C), and by gas-phase NMR with least-squares fits using the Antoine equation.

point of 201.3 °C was extracted (vapor pressure at 101.325 kPa). Excluding the gas saturation value from the data to be fitted has no effect on the resulting Antoine parameters, as expected by the fact that it is several orders of magnitude smaller than the Scott data at substantially higher temperatures. It is reassuring, therefore, keeping in mind the difficulties in extrapolating exponential behavior far from the range of the measurements, that the gas saturation point (3 Pa, 0.023 Torr at 21 °C) falls so close to the extrapolated value based on the Antoine equation (7 Pa at 21 °C).

Figure 2A shows the proton NMR spectrum of the vapor phase at 150 °C in an ampule loaded with 96.2 mg (207 μmol) 8-2 Telomer B alcohol and 1 μmol TMS: there are three absorptions with their spin−spin interaction splittings for the three chemically distinct protons of 8-2 Telomer B alcohol as well as a single absorption for TMS. TMS at 150 °C is well above its boiling point of 27 °C. As the temperature is raised, the intensity of the 8-2 Telomer B alcohol resonances increases relative to that of TMS as more of the 8-2 Telomer B alcohol vaporizes (Figure 3B). Complete vaporization of the 8-2 Telomer B alcohol can be recognized when the intensities of the 8-2 Telomer B alcohol proton resonances stop growing with an increase in temperature. The number of micromols of 8-2 Telomer B alcohol in the vapor phase at each temperature can be easily obtained by comparing the integrated intensities of the 8-2 Telomer B alcohol resonances with that of TMS. The integrated intensities must, of course, be normalized for the number of equivalent protons giving rise to each resonance (2 for CH$_2$ protons, 1 for OH protons, and 12 for TMS protons).

The fluorine resonances of 8-2 Telomer B alcohol behave similarly as shown in parts C and D of Figure 3: they also grow in intensity as the temperature is increased until all 8-2 Telomer B alcohol has entered the vapor phase. Their integrated intensities can be compared with those of added hexafluoroethane (F116, 1.5 mol %, six equivalent fluo-
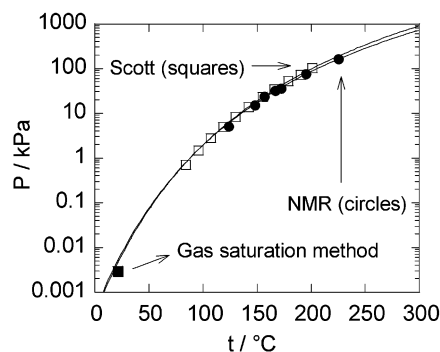
rines, bp = −78 °C, resonance not shown in parts C and D of Figure 3) to obtain the micromoles of 8-2 Telomer B alcohol in the vapor phase at each temperature. The broader lines characteristic for fluorines in the vapor phase reduce the accuracy of integration compared to proton detection. Accordingly, the quantitative treatment to yield vapor pressure was carried out using proton detection.

Since the internal volume of the ampules is known as (4.2 ± 0.05) mL as well as the number of micromols of telomer in the vapor phase, the vapor pressure at each temperature can be calculated using the ideal gas law. The averaged calculated vapor pressures derived by proton gas-phase NMR using three differently loaded ampules, containing 23.2 mg (50 μmol), 45.5 mg (98 μmol), and 96.2 mg (207 μmol) 8-2 Telomer B alcohol, respectively, are shown on a logarithmic scale in Figure 4 together with the vapor pressures obtained by the gas saturation and the Scott methods, already shown in Figure 2. The Antoine equation was used again to fit the data. The agreement is remarkably good for a method that measures vapor density rather than vapor pressure. The distribution of the mass standard between the liquid and the vapor phase is probably insignificant considering (a) the large disparity in the volume of the condensed phase (miniscule liquid pool at the bottom of the ampule) compared to the free space above it and (b) the large difference in boiling points between the substance being studied and the mass standards. From the calculated curve, one obtains a boiling point (temperature at which $P = 101.325$ kPa) for the 8-2 Telomer B alcohol of 206.3 °C from the NMR data that is 5 °C higher than that similarly extracted from the data obtained by the Scott method (201.3 °C). It is again reassuring that the extrapolated value of the vapor pressure at 21 °C based on the fit of the NMR vapor pressures to the Antoine equation is in very good agreement with the experimental value obtained by the gas saturation method (Figure 4).

Since the vapor pressures of 8-2 Telomer B alcohol in the vicinity of room temperature are important to environmental issues, an alternative extrapolation was considered based on a plot of $\ln(P)$ vs $1/T$ (Figure 5). Careful scrutiny shows a slight downword curvature of both the Scott-method and the NMR-method points in this type of plot, indicating that they cannot be well represented by a straight line. The extrapolated value at 21 °C based on a least-squares linear fit of the Scott data in this plot is slightly higher (15 Pa) then the value obtained at the same temperature by the Antoine equation (7 Pa).

Additional validation of the gas-phase NMR methodology was obtained with hexafluorobenzene, the vapor pressure of which is well known. In this case, the ampule was loaded
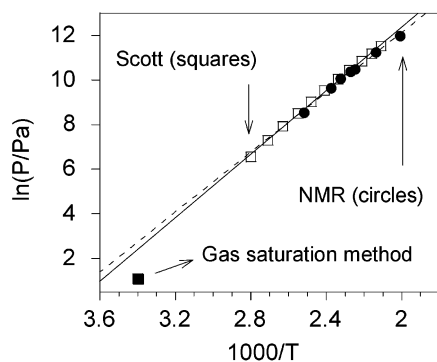
Figure 5. Vapor pressures of 8-2 Telomer alcohol obtained by the Scott method, by the gas-saturation method (at 21 °C), and by gas-phase NMR with linear least-squares fits.
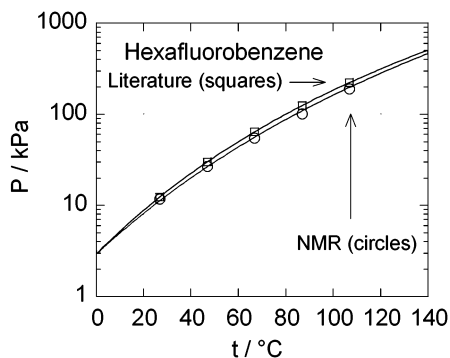

Figure 6. Comparison of literature vapor pressures of hexafluorobenzene with vapor pressures obtained by gas-phase NMR with least-squares fits based on the Antoine equation.

with 30 μL (337 μmol) of hexafluorobenzene and 5 μmol of perfluoroethane as internal mass standards. The vapor pressures obtained by the gas-phase NMR method (using the ideal gas law) are compared with literature data[10] in Figure 6 that also shows the least-squares fits based on the Antoine equation for both sets of data. Here the NMR method gives systematically somewhat lower vapor pressures that tend to merge, however, with the literature values at lower temperatures. The literature data yield a boiling point of 80.3 °C, whereas the gas-phase NMR data yield a boiling point that is 4.0 °C higher. It should be noted, however, that the broader line widths of the fluorine NMR resonances in the gas phase compared to proton resonances lead to less accurate integrated intensities. The primary value of the gas-phase NMR method in the case of the 8-2 Telomer B alcohol is that it confirms the correctness of the results obtained by the conventional Scott method used in this work. An important advantage of the new method is that it uses about 3 orders of magnitude less material than conventional methods for vapor pressure measurements.

Water Solubility. The solubility in water at 12 °C is 134 ppb ($\pm$29 ppb) (134 μg/L), 137 ppb ($\pm$53 ppb) at 25 °C, 318 ppb ($\pm$176 ppb) at 37 °C, and 225 ppb ($\pm$ 51 ppb) at 60 °C. Varying pH from 3 to 11 had little or no impact on the solubility measurement. Table 2 shows the solubility as a function of temperature. Table 3 shows the solubility at pH 3.0, 5.8, and 11 at 12 °C.

Acknowledgment

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