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PHYSICOCHEMICAL PROPERTIES OF FLUOROTELOMER ALCOHOLS

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Abstract

Physicochemical properties such as vapor pressure and water solubility are necessary to determine environmental transport potential and environmental fate. Often these properties are estimated from models based on properties of chemically similar materials. Fluorinated compounds, however, are especially difficult to model since the properties of fluorinated compounds are quite different from their hydrocarbon analogues. Fluorotelomer Alcohols are also difficult to obtain in pure form since they are "products by process" which are a mixture of several compounds each differing by two carbon units and difficult to measure since many are solids at room temperature.

Introduction

The environmental fate of perfluorinated chemicals, such as fluorotelomer-based substances is of growing interest.[1-4] Fluorotelomer 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. Fluorotelomer Alcohols are of particular interest since they are expected to be among the possible compounds into which fluorotelomer-based surfactants and polymers may potentially transform in the environment.

Water Solubility of 8-2 Telomer B Alcohol $C_8F_{17}CH_2CH_2OH$

Temperature °C	Solubility ng/mL	Standard Dev. ng/mL	n
12	134	29	8
25	137	53	17
37	318	176	39
60	225	51	39

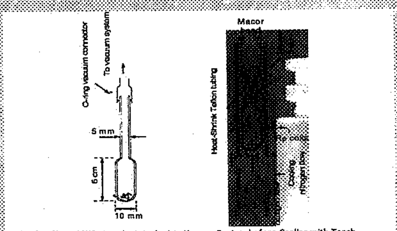
Vapor Pressure. Three techniques were used to measure the vapor pressure.

- **VP Method 1** *(reference 8)*
  - based on a dynamic measurement procedure developed by Scott
  - equilibrium temperature measured at a controlled pressure.
  - temperature varied from 80 to 200 C.
  - 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 %.
  - Apparatus
    - Mensor PCS400 pressure controller (San Marcos, TX)
    - Paroscientific 740 pressure transducer (Redmond, WA)
    - Hart Scientific stack base unit for temperature measurement (American Fork, UT).

- **VP Method 2** *(reference 9)*
  - based on the EPA OPPTS gas saturation method (used to obtain the vapor pressure of 8-2 Telomer B Alcohol at room temperature)
  - quantity of a substance transported by a known volume of a carrier gas is determined.
  - alcohol placed in a glass thermostated tube. Gas-chromatographic grade helium (99.999%) flowed over the solid 8-2 Telomer B alcohol.
  - flow controller from a Hewlett Packard (now Agilent, Little Falls, DE) model 5890 gas chromatograph
  - Due to the adsorptive properties of the alcohol, the vapor pressure was calculated from weight loss rather than from the weight of trapped material downstream
  - vapor pressure is calculated from the vapor density, W/V, by means of the equation $P/Pa = W/V \quad RT/M_r$ 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 the relative molecular mass
  - vapor pressure at 21 C was 3 Pa

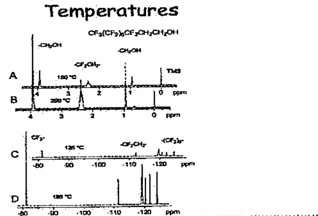
- **VP Method 3** *(references 10,11)*
- gas phase nuclear magnetic resonance
- method measures the vapor density at various temperatures relative to that of a much more volatile internal mass standard present in much smaller molar amounts of the order of 1 mol %
- vapor density is converted to vapor pressure using the ideal gas law or another appropriate equation of state.
- **Solubility methods 1 and 2**

  GC/ECD and GC/MSD determination of analyte in a closed, sealed, shaken container in the presence of excess sample

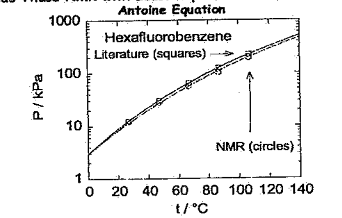


Left: Gas-Phase NMR Ampule Attached to Vacuum System before Sealing with Torch
Center: Sealed ampule attached via Teflon® sleeve to Matching 5 mm OD Glass Stub of Holding Tube. Tube rests firmly in a Macor® ceramic head that seals the heated compartment of commercial high-T NMR probe
Right: Ampule Assembly lowered into the magnet using a string and not spun

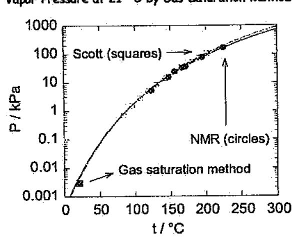
Proton and Fluorine Gas-Phase NMR Spectra of 8-2 Telomer B Alcohol at Different Temperatures



Comparison of Literature Vapor Pressures of Hexafluorobenzene with Vapor Pressures Obtained by Gas-Phase NMR with Least-Squares Fits Based on the Antoine Equation

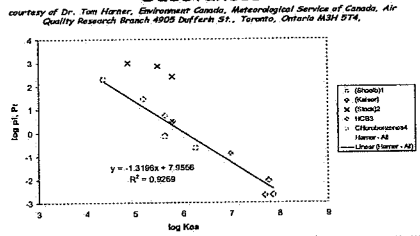


Vapor Pressure of 8-2 Telomer B alcohol by the Boiler Method with Least Squares fit using Antoine Equation. Also shown, Vapor Pressure at 21 °C by Gas Saturation Method

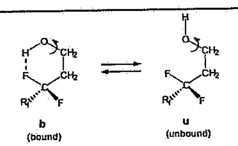


K_{oa} vs poL for Perfluoroalkylated Substances

courtesy of Dr. Tom Harner, Environment Canada, Meteorological Service of Canada, Air Quality Research Branch 4905 Dufferin St., Toronto, Ontario M3H 5T4,



Ab-initio Calculation of ΔE_{bond}



Species	H-bond energy (kcal/mol)
2-2 FTOH	1.6 kcal/mol
4-2 FTOH	1.6 kcal/mol

Conclusions: 1. The cyclic structure b has a weak H-bond.
2. There would be no significant change in the vapor pressure of the fluorotelomer alcohols due to bonding of type (b).

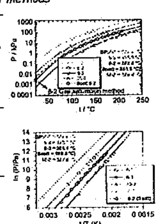
Vapor Pressure of Select Telomer Alcohols by Gas-Phase NMR Spectroscopy

Comparison with other methods

TABLE 1. Extrapolated vapor pressures at 25 °C of select fluorinated telomer alcohols.

FTOH	Extrapolated[a] vapor pressure[c] Mabury et al. (Pa)	Extrapolated[b] vapor pressure Gas-phase NMR (Pa)	Extrapolated[a] Vapor pressure Gas-phase NMR (Pa)	Extrapolated[b] vapor pressure Scott method Kaiser et al. (Pa)
4:2	992 (7.4 Torr)	217 (1.6 Torr)	250 (1.9 Torr)	
6:2	713 (5.4 Torr)	18 (0.14 Torr)	46 (0.3 Torr)	
8:2	254 (1.9 Torr)	4 (0.03 Torr)	16 (0.12 Torr)	7 (3[d])
10:2	144 (1.1 Torr)	1 (0.008 Torr)	3 (0.02 Torr)	
1-decanol		0.7 (0.005 Torr)	3 (0.02 Torr)	

[a] Extrapolated using linear fit of ln(P/Pa) vs. 1/T /K plot (Mabury et al.).
[b] Extrapolated using least-squares fit of Antoine equation to data: $\log_{10}(P/kPa) = a - b/(c + t/°C)$.
[c] Determined using the boiling-point method.
[d] Measured by gas saturation method (Kaiser et al.). Reference 12



Results & Discussions

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.

- a least-squares fit of the data, including the low temperature measurement by the gas saturation method, was obtained using the Antoine equation

  $\log_{10}(P/kPa) = a - b/(c + t/°C)$ (Figure 2) with the parameters a = 6.457, b = 1623, and c = 163.3
- boiling 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 might be expected since it is several orders of magnitude smaller than the boiler data at substantially higher temperatures).

Water Solubility. The solubility in water at 12 °C is 134 ppb (29 ppb) (134 g/L); 137 ppb (53 ppb) at 25° C; 318 ppb (176 ppb) at 37° C, and 225 ppb (51 ppb) at 60 °C.

Varying pH from 3 to 11 had little or no impact on the solubility measurement.

References

1. Hekster, Floris M.; Laane, Remi W. P. M.; de Voogt, Pim. *Reviews of Environmental Contamination and Toxicology* (2003), 179 99-121.
2. Schultz, Melissa M.; Barofsky, Douglas F.; Field, Jennifer A., *Environmental Engineering Science* (2003), 20(5), 487-501.
3. Dimitrov, S.; Kamenska, V.; Walker, J. d.; Windle, W.; Purdy, R.; Lewis, M.; Mekenyan, O., *SAR and QSAR in Environmental Research* (2004), 15(1), 69-82.
4. Stock, Naomi L.; Lau, Fiona K.; Ellis, David A.; Martin, Jonathan W.; Muir, Derek C. G.; Mabury, Scott A., *Environmental Science and Technology* (2004), 38(4), 991-996.
5. Kissa, E. *Fluorinated Surfactants and Repellents*; Marcel Dekker, Inc.: New York, 2001, p. 37.
6. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, Interscience Publishers: New York, 1966
7. Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds. *Organofluorine Chemistry. Principles and Commercial Applications*. Plenum Press: New York, 1994.
8. Scott, L. Determination of Activity Coefficients by Accurate Measurement of Boiling Point Diagram. Fluid Phase Equilibria 1986, 26, 149-163.
9. United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (7101), OPPTS 830.7950, Vapor Pressure, August 1996, p. 13, Gas Saturation Method.
10. Shtarov, A. B.; Krusic, P. J.; Smart, B. E.; Dolbier, W. R. Jr. Bimolecular Kinetic Studies with High-Temperature Gas-Phase 19F NMR: Cycloaddition Reactions of Fluoroolefins. J. Am. Chem. Soc. 2001, 123, 9956-9962.
11. Krusic, P. J.; Roe, D. C.; Smart, B. E. Kinetics of Hexafluoropropylene Oxide Pyrolysis Studied by Gas-Phase NMR. Kinetic Measurements Made Easy. Israel J. Chem. 1999, 39, 117-123.
12. Kaiser, Mary A., Cobranchi, Daryl P., Kao, Chien-Ping Chai, Krusic, Paul J., Marchione, Alexander A. and Buck, Robert C., Physicochemical properties of 8-2 Fluorinated Telomer B Alcohol, J. Chem. Engr. Data, in press.
13. Naomi L. Stock, David A. Ellis, Lisa Deleebeeck, Derek C. G. Muir, and Scott A. Mabury, Vapor Pressures of the Fluorinated Telomer Alcohols-Limitations of Estimation Methods Environ. Sci. Technol.; 2004; 38(6) pp 1693 - 1699