Vapor Pressures of Perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic Acids

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A dynamic method was used to determine the vapor pressures of perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic acids. Measurements were made over the temperature range from (59.25 to 190.80) °C for perfluorooctanoic acid, from (99.63 to 203.12) °C for perfluorononanoic acid, from (129.56 to 218.88) °C for perfluorodecanoic acid, from (112.04 to 237.65) °C for perfluoroundecanoic acid, and from (127.58 to 247.36) °C for perfluorododecanoic acid. Pressures ranged from (0.128 to 96.50) kPa for perfluorooctanoic acid, from (1.12 to 99.97) kPa for perfluorononanoic acid, from (3.129 to 99. 97) kPa for perfluorodecanoic acid, from (0.616 to 99.97) kPa for perfluoroundecanoic acid, and from (0.856 to 99.96) kPa for perfluorododecanoic acid. A sealed vial experiment demonstrated that perfluorooctanoic acid sublimes at room temperature.

Introduction

Reliable physical property data are required for efficient chemical engineering design as well as for modeling environmental transport of perfluorocarboxylic acids. Physical property data for perfluorocarboxylic acids are scarce in the literature. No vapor pressure data exist. In this work, the vapor pressures of 8 through 12 carbon perfluorocarboxylic acids over the temperature range from (59.25 to 247.36) °C at 5 °C intervals are reported.

Salts of perfluorocarboxylic acids, especially perfluoronoanoic and perfluorooctanoic acids, are commonly used as processing aids in the production of fluoropolymers.[1] Perfluorocarboxylic acids and perfluorosulfonic acids have been reported in human blood[2−4] and in tissues of animals in a wide variety of locations.[5,6] Recent work[7] reported quantifiable levels of perfluorinated carboxylic acids in polar bears in both the Western and Eastern Arctic in Canada. To understand how these materials move through the environment and their potential for long-range transport, it is necessary to know their fundamental physical properties. Both water solubility and vapor pressure are important parameters to consider when assessing potential for long-range transport. Vapor pressure is indicative of the ability of a substance to partition into in the gas phase (to air) in the absence of sorption. Long-range transport via air as can occur when a substance is in the gas phase or sorbed to a particle or water in the atmosphere. For very water-soluble materials that are not present in air, it would take on the order of decades for inland-produced materials to reach remote locations such as the Arctic through transport in rivers and seas.[8] Perfluoroocarboxylic acids are generally very efficient surfactants.[9] They dramatically lower the surface tension of aqueous solutions and move rapidly to the air−water interface. As such, vapor pressure plays an important role in predicting their transport and disposition in the environment.

Experimental Section

Materials. Perfluorooctanoic acid (99 %) ($C_8HF_{15}O_2$, CAS Registry No. 335-67-1) was obtained from Daikin Industries, Ltd. (Osaka, Japan). The three following acids were obtained from Oakwood Products (West Columbia, SC): perfluorononanoic acid (99 %) ($C_9HF_{17}O_2$, CAS Registry No. 375-951, catalog no. 002263); perfluoroundecanoic acid (99 %) ($C_{11}HF_{21}O_2$, CAS Registry No. 2058-94-8, catalog no. 002265); and perfluorododecanoic acid (99 %) ($C_{12}HF_{23}O_2$, CAS Registry No. 307-55-1, catalog no. 002266). Perfluorodecanoic acid (99.9 %) ($C_{10}HF_{19}O_2$, CAS Registry No. 335-76-2, catalog no. 177741) was obtained from Sigma-Aldrich.

Vapor Pressure Measurements. The vapor pressure measurement is based on a dynamic measurement procedure developed by Scott (the Scott method) wherein the equilibrium temperature is measured at a controlled pressure.[10] A schematic diagram of the apparatus is given in Figure 1. Approximately 30 g of the acid was placed in a round-bottom flask 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 60 to 250 °C (± 0.0001 °C).

Sublimation. A solid sample of perfluorooctanoic acid was placed in an individual glass sample bottle, capped with a lid, shaken, and stored at room temperature to assess the potential for sublimation at room temperature. After 9 months, the vial was removed from storage and visually evaluated.

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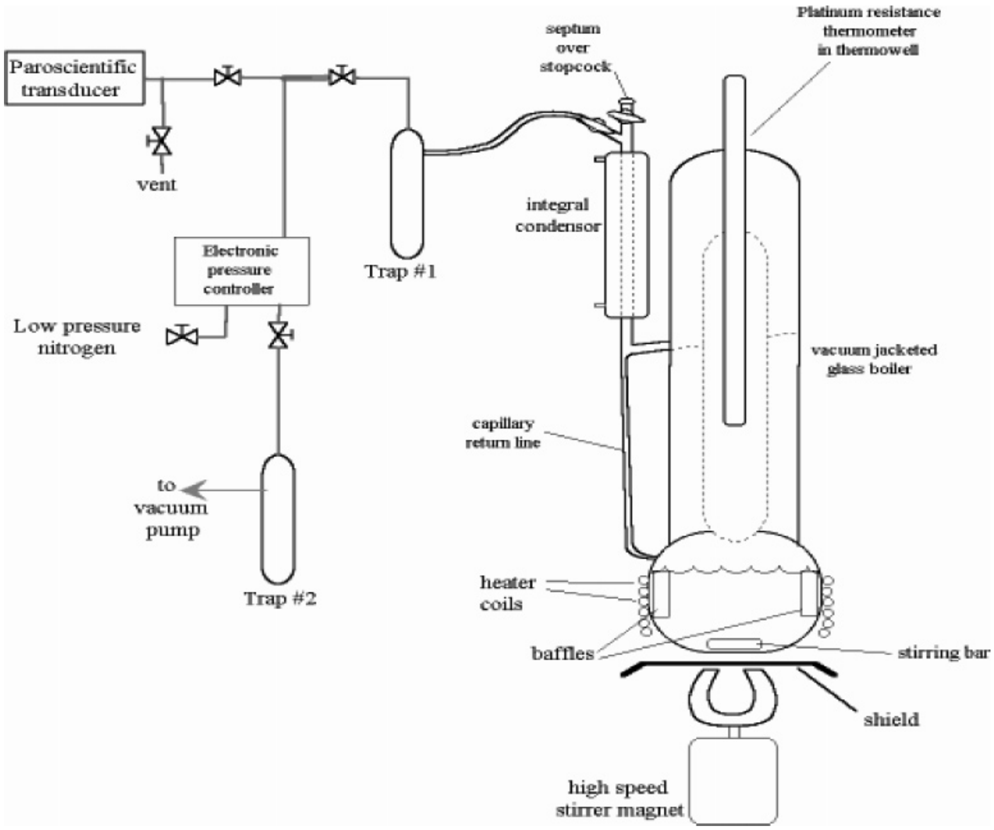

Figure 1. Schematic diagram of the vapor pressure apparatus.

Table 1. Vapor Pressure at Various Temperatures

perfluorooctanoic		perfluorononanoic		perfluorodecanoic		perfluoroundecanoic		perfluorodecanoic	
t/°C	*P*/kPa	*t*/°C	*P*/kPa	*t*/°C	*P*/kPa	*t*/°C	*P*/kPa	*t*/°C	*P*/kPa
59.25	0.128	99.63	1.12	129.56	3.129	112.04	0.616	127.58	0.856
62.37	0.168	109.54	2.02	133.09	3.749	120.63	1.062	140.57	1.819
66.60	0.231	117.66	3.12	140.93	5.541	129.54	1.752	148.95	2.854
72.60	0.361	128.55	5.54	152.20	9.331	139.14	2.785	149.60	2.985
79.00	0.581	139.77	9.33	163.68	15.18	139.26	2.789	160.12	4.848
86.60	0.960	150.71	15.19	173.97	22.77	149.22	4.513	172.48	8.290
94.90	1.602	159.70	22.77	187.50	37.23	158.32	6.925	184.79	13.81
103.94	2.690	172.96	37.25	202.93	62.05	172.02	12.44	197.44	22.07
114.00	4.591	187.93	62.07	218.88	99.97	186.77	20.70	210.51	34.48
124.40	7.691	202.98	99.97			200.68	34.49	225.70	55.15
136.11	13.07	203.12	99.97			202.09	34.48	247.36	99.96
148.60	22.16					218.29	58.60		
162.20	37.25					218.64	58.60		
177.80	63.98					236.68	96.51		
190.80	96.50					237.65	99.97		

Table 2. Constants of the Antoine Equation ln (*p*/kPa) = *A* + *B*/(*t*/°C + *C*)

	temp range/K	*A*	*B*	*C*
perfluorooctanoic	332.4 to 463.95	14.72793	−3387.980	142.690
perfluorononanoic	372.78 to 476.27	15.01941	−3564.853	139.380
perfluordecanoic	402.71 to 492.03	14.24952	−3258.902	119.009
perfluoroundecanoic	385.19 to 509.83	13.94980	−3339.461	119.482
perfluorododecanoic	400.73 to 520.51	13.46482	−3040.089	

Results

The temperature-dependent vapor pressure of the acids is reported in Table 1. The temperature-dependent vapor pressure data are fitted with the Antoine equation[11]:

$$\ln(p/\mathrm{kPa}) = A + B/(t/°\mathrm{C} + C)$$

where p is pressure, t is temperature (°C), and A, B, and C are the Antoine constants. These constants are presented in Table 2. All coefficients of determination (r^2) were greater than 0.9998.

After nine months, the solid crystalline material was observed on the cap and around the sides near the top of

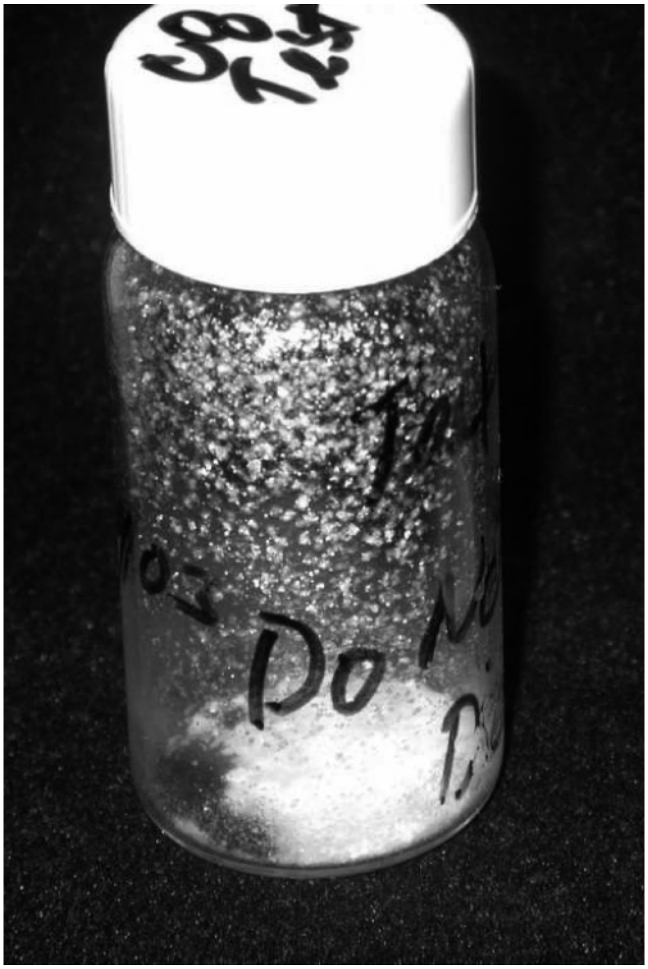

Figure 2. Evidence of sublimation of perfluorooctanoic acid.

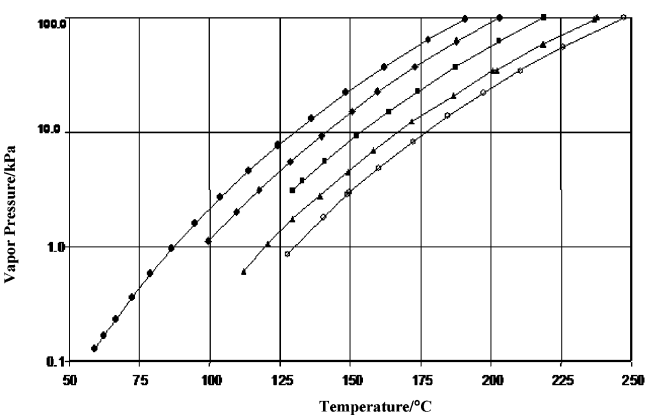

Figure 3. Vapor pressure (kPa) of ●, C8; ◆, C9; ■, C10; ▲, C11; and ○, C12 acids.

the sample bottle for perfluorooctanoic acid (Figure 2). These results indicate that these substances sublime at room temperature. Figure 3 shows the vapor pressure of C8, C9, C10, C11, and C12 acids.

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