The Purification and Physical Properties of 1-Hydropentadecafluoro-*n*-heptane

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Preparative scale gas-solid chromatography has been shown to be a feasible method of obtaining isomerically pure fluorocarbons and has been used to separate the *n*-isomer of 1-hydropentadecafluoroheptane from the four-component isomer mixture obtained by decarboxylation of perfluorooctanoic acid. The refractive index, density, coefficient of thermal expansion, vapor pressure in the region of one atmosphere, normal boiling point, latent heat of vaporization, and second virial coefficient of the pure material are reported.

THE PURIFICATION of fluorocarbons is difficult because of the similarity of the physical properties of the isomers. Of the methods which have been used previously, only fractional crystallization (*6*) appears to have been reasonably successful. Gas-liquid chromatography has been used with some success (*12*) but the low sample capacities and the relatively poor resolution obtained even with large columns are fairly serious drawbacks to the use of this method.

Martire (*10*) has discussed the application of solution theory to the choice of stationary phase for gas-liquid chromatography. By using the solubility parameter treatment (*7*) one can obtain the following relation for the corrected retention volumes V_R of a pair of compounds, 1 and 2:

$$\log(V_{R_1}/V_{R_2}) = \log(P_2^0/P_1^0) + [V_2(\delta_2 - \delta_L)^2 - V_1(\delta_1 - \delta_L)^2]/(2.303RT) \quad (1)$$

where P_1^0, P_2^0 are the vapor pressures of the compounds, V_1, V_2 are their molar volumes, and δ_1, δ_2, δ_L are the solubility parameters of the compounds 1 and 2 and of the stationary phase. For most separations the difference between the vapor pressures is the major factor in determining the relative retention volumes and a suitable stationary phase is one in which the two compounds form nearly ideal solutions—i.e., one for which δ_L is similar in value to δ_1 and δ_2. When the vapor pressures are very similar, as is the case with fluorocarbon isomers, it is necessary to rely on the activity coefficient differences represented by the second and third terms of Equation 1 to achieve a separation. For compounds with similar solubility parameters, the difference between the two terms in $(\delta_1 - \delta_L)$ and $(\delta_2 - \delta_L)$ can be made large only when δ_L is very different from δ_1 and δ_2—i.e., by choosing a stationary phase which is a poor solvent for the compounds to be separated. This, however, leads to a column of low capacity for which the actual values of the retention volumes are small so that very long columns must be used. These conclusions are borne out by the work of Reed (*12*) in which it was found that *n*-hexadecane is a more suitable stationary phase for separating fluorocarbon isomers than are the high molecular weight fluorinated compounds, but that a column of 55 foot × 0.5 inch was capable of handling only 0.05 ml. of material at a time.

An alternative, though at first sight unpromising, procedure was suggested by the work of Pope (*11*) who has shown that graphitised carbon blacks are selective stationary phases for the separation of both hydrocarbon and fluorocarbon isomers, although these columns again suffer from the defect for preparative purposes of having a low capacity.

Preliminary experiments with a 3 foot × ⅛ inch column packed with 60 to 85 mesh Spheron 6 (2700) suggested that, if the losses in efficiency normally experienced in scaling up could be minimized, reasonably successful separations of the *n*-isomer could be achieved using 1 foot × ⅝ inch bore column and sample sizes of up to 0.1 ml. Optimum operating conditions, as determined on the small scale columns, were 120° C. and flow rate of 32 cm.^{3} min.$^{-1}$ (500 cm.^{3} min.$^{-1}$ for the ⅝ inch column). Accordingly, a column 3 foot × ⅝ inch was constructed for use in a Beckman Megachrom preparative chromatograph. The extra length was included to allow for some loss of efficiency. The carbon for this column was sieved three times to ensure a uniform particle size on the column and was packed with a minimum of vibration to prevent the aggregates of carbon particles from breaking into finer particles. Nitrogen at 15 p.s.i. was passed through the column periodically during the packing and this assisted in giving maximum packing density without the use of excessive vibration. To improve the trapping capacity, the collecting trap shown in Figure 1 was used. This trap was attached to the apparatus with two short silicone-rubber sleeves and, after every four or five samples had been injected, was removed and attached to a simple vacuum line. The collected product was then transferred into a storage vessel by vacuum distillation.

Since the object was to separate the *n*-isomer which has a rather greater retention time than any of the three isomeric impurities, it was more economical in time to overload the column by injecting about 0.4 to 0.5 cm.^{3} of sample and to collect only the latter part of the *n*-isomer peak. Although this meant that some of the *n*-isomer was lost to the branched-chain sample in any given batch, the much greater throughput of material more than offset this loss. Typical analytical chromatograms of the impure mixture and of the purified material and a chromatogram of a preparative separation are shown in Figure 2. The final product was estimated from analytical chromatography to be better than 99.7 mole % pure. For the separation of the branch-chain isomers the authors are constructing a set of 6-foot columns so that the full capacity (eight 6-foot columns) of the Megachrom can be used. This should enable the separation of up to 3 to 4 cm.^{3} of material at a time.

PHYSICAL PROPERTIES OF *n*-$C_7F_{15}H$

Refractive Index. the refractive index of the *n*-$C_7F_{15}H$ and of the isomer mixture obtained directly from the decarboxylation of perfluorooctanoic acid were measured with an Abbe refractometer equipped for low refractive index measurements. The values obtained are shown in Table I.

Density and Coefficient of Thermal Expansion. Densities were measured in a single-stem pycnometer of about 8.5-ml.

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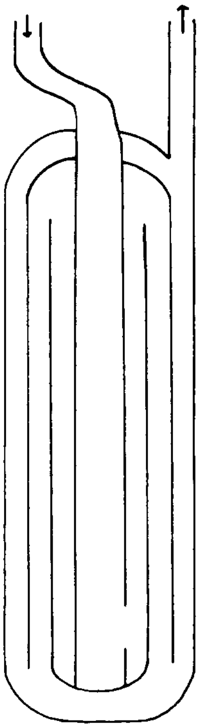

Figure 1. Collection trap

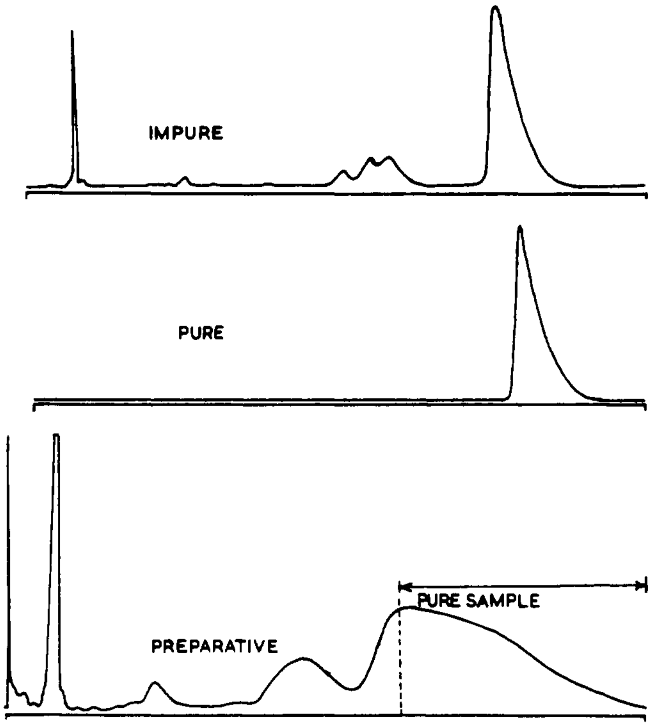

Figure 2. Analytical and preparative chromatograms

capacity with a capillary stem of about 2-mm. bore, and a calibration line about one-third of the way up the stem. The volume of the pycnometer to the calibration mark and the volume per unit length of the stem were calibrated at 25° C. with distilled water for which a density of 0.997075 gram ml.$^{-1}$ was assumed. All weighings were carried out on a Mettler Type B6 balance and were corrected for air buoyancy. The height of the meniscus above the calibration mark was measured with the pycnometer fully immersed in a thermostat maintained to ±0.005° C. These measurements were made with a cathetometer which could be read to ±0.02 mm. Temperatures were measured with a laboratory calibrated thermometer which is believed to be accurate to ±0.01° C. Calibration figures at temperatures other than 25° C. were calculated using the coefficient of cubical expansion of borosilicate glass. The mean of five calibrations was used in the density measurements. Corrections were applied for the difference in shape of the water meniscus and that of the fluorocarbon, assuming the meniscus to be the cap of a sphere. Densities were measured in duplicate using different masses of fluorocarbon in the pycnometer. The duplicate measurements always agreed to within ±0.00002 gram ml.$^{-2}$ and are believed to be accurate to ±0.00005 gram ml.$^{-1}$. The values obtained are shown in Table II. The density at 25° C. is somewhat lower than that measured in this laboratory (1.72395) (*8*) and in other laboratories (1.7278, 1.720) (*1, 2*) for the isomer mixture and just slightly lower than than that quoted by Konecny and Deal (*9*). This lower value for the *n*-isomer is consistent with the variation in density among the isomers of fully-fluorinated materials reported in the literature (*5*).

The coefficient of thermal expansion, $(dV/dT)_P/V$, was determined from the density measurements assuming it to be constant over the temperature range studied. From these data the coefficient of thermal expansion is estimated to be $(1.47 \pm 0.01) \times 10^{-3}$ deg.$^{-1}$.

Vapor Pressure, Boiling Point, and Latent Heat of Vaporization. The vapor pressure in the region about the normal boiling point was determined using a modification of Simmons' (*14*) apparatus which requires less than 1 ml. of material. In this apparatus, the liquid whose boiling point is to be measured is confined over mercury in one arm of a U-tube immersed in a heating bath. The other end of the U-tube is open to the atmosphere. The boiling point is taken as the temperature at which the two mercury levels become equal. By inserting an adjustable electrical contact into the open arm of the U-tube, the apparatus was made to act also as a thermoregulator maintaining the bath temperature, and hence the vapor pressure, constant at any desired value within a few degrees either side of the boiling point. When equilibrium had been reached for each setting of the probe, the temperature of the bath and the mercury heights in the two limbs of the apparatus were measured.

Table I. Refractive Index vs. Temperature

Sample	Temp., ° C.	n_d
Mixed isomers	20	1.2712
Mixed isomers	25	1.2691
n-Isomer	20	1.2722
n-Isomer	25	1.2702

Table II. Density of *n*-$C_7F_{15}H$

	Temp., ° C.			
	19.97	25.00	30.00	35.00
Density, gram ml.$^{-1}$	1.72853	1.71578	1.70342	1.69048

Table III. Vapor Pressure of 1-Hydropentadecafluoro-*n*-heptane

	Temp., ° K.							
	365.41	366.57	366.96	367.56	368.26	368.56	368.96	369.69
Pressure/mm. of Hg	696.63	719.75	728.71	742.06	757.59	765.20	773.71	788.60

Temperatures were measured with a laboratory-calibrated thermometer accurate to ±0.01° C. and the mercury heights were measured with a cathetometer which could be read to ±0.02 mm. Atmospheric pressure was measured with a standard Fortin barometer located near the apparatus. Pressure measurements were corrected for scale and mercury temperatures and for the head of liquid above the merury in the closed limb of the apparatus and are believed to be accurate to ±0.1 mm. of Hg. With this apparatus there is some uncertainty about the relation between the bath temperature and that of the liquid in the apparatus since the temperature control appeared to be of the order of ±0.01° C. Simultaneous measurements at various stages of the control cycle gave sets of values of T and P which were consistent within ±0.1 mm. of Hg and ±0.05° C.

Prior to measuring the vapor pressure, the liquid was degassed by heating to a temperature a few degrees higher than the boiling point with excess mercury in the open arm of the U-tube. The bubble of air which formed above the liquid was then forced out of the apparatus when the mercury-sealed stopper at the top of the closed limb was eased slightly. This process was repeated until no further gas was evolved. Traces of air in the apparatus would give systematically high values for the vapor pressure and consequently a low value for the boiling point. Trial measurements with cyclohexane indicated that any effects due to imperfect degassing do not cause an error in the boiling point of more than 0.05° C.

Vapor pressures determined in this way are shown in Table III. The normal boiling point interpolated from these data, 95.20° C., is believed to be accurate to ±0.05° C. This value is somewhat higher than that quoted by other workers [94.7 to 95° C. (*1*); 94 to 95° C. at 751 mm. of Hg (*13*)] although it is in fairly good agreement with the value (95° C. at 751 mm. of Hg) quoted by Konecny and Deal (*9*) whose density value also agrees better with our determination than do the measurements of other workers. By using our estimates of dP/dT, we calculate that Konecny and Deal's boiling point corresponds to a value of 95.4° C. at 760 mm. of Hg. Using the slope of the plot of log P *vs.* $1/T$ for the above data determined by the method of least squares, $[\mathrm{d}\ln P/\mathrm{d}(1/T)] = -1733$ deg., a value of the second virial coefficient at 95.20° C. interpolated from the data in Table IV (−1985 cm.^{3} mole^{-1}), and a molar volume of the liquid extrapolated from the density measurements (239 cm.^{3} mole^{-1}), the latent heat of vaporization was calculated from the relation

Table IV. Second Virial Coefficients of n-$C_7F_{15}H$

	Temp., ° C.					
	50.00	53.30	73.45	106.84	125.55	158.40
$-B$/cm.^{3} mole^{-1}	2990	2890	2372	1813	1568	1243.

$$\Delta H = -\left\{\frac{\mathrm{d}\ln P}{\mathrm{d}(1/T)}\right\}\left\{R + \frac{(B - V_1)P}{T}\right\}$$

The value obtained in this way was 7346 cal. mole^{-1} with an estimated uncertainty of ±75 cal. mole^{-1}.

Second Virial Coefficients. The second virial coefficients for the normal isomer for the equation of state (*3, 4*)

$$PV = nRT[1 + B(n/V)]$$

are shown in Table IV.

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