# THE VISCOSITY OF SOME FLUOROCARBONS IN THE VAPOUR PHASE

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Measurements have been made of the temperature coefficients of viscosity of the vapours of tetrafluoro-ethylene, hexafluoro-ethane, perfluoro-n-pentane and perfluoro-n-hexane. For all of these vapours the temperature coefficients of viscosity are smaller than those for the corresponding hydrocarbons. This has been interpreted in terms of the intermolecular forces between fluorocarbon molecules which change steeply with the distance between molecular centres.

A class of compounds which has attracted considerable attention in the last few years is the fully fluorinated hydrocarbons or perfluorocarbons. These compounds are of particular interest because of their high thermal stability and chemical inertness. A number of their physical properties have been measured; these include density, refractive index, vapour pressure, critical constants and a wide range of properties in binary liquid solutions.<sup>1,2</sup>

Few measurements of the vapour viscosity have been made for the larger fluorocarbons,<sup>3</sup> and no values of the temperature coefficients of viscosity are available. The latter quantity can be used to help to understand the intermolecular forces arising between these molecules and consequently some of the other physical properties.

We have previously made measurements of the temperature coefficient of viscosity for carbon tetrafluoride; we now report measurements for tetrafluoroethylene, hexafluoro-ethane, perfluoro-n-pentane and perfluoro-n-hexane and compare their behaviour with that of the corresponding hydrocarbons.

#### EXPERIMENTAL

Measurements of viscosity for perfluoro-ethane, perfluoro-ethylene and perfluoro-npentane have been made in the apparatus previously described by McCoubrey and Singh.<sup>4</sup> Measurements for perfluoro-n-hexane have been made in an apparatus similar to that described by McCoubrey, McCrea and Ubbelohde.<sup>5</sup> In this the saturated vapour from a liquid reservoir at a measured pressure transpires through a pre-heater and capillary to vacuum, and the drop in liquid level is measured. The present apparatus differs from that previously described in that the spiral pressure gauge used to measure the driving pressure has been replaced by a mercury manometer, used also as a vacuum cut-off, and that the pre-heater and capillary are contained in a vapour-jacketed thermostat.

#### MATERIALS

TETRAFLUORO-ETHYLENE.—This was prepared from  $CF_2BrCF_2Br$  (kindly given to us by I.C.I. Plastics Division) by dropping this into a mixture of zinc powder in ethyl alcohol with vigorous stirring. The evolved gas passed through a water condenser and a salt+ice trap and was collected in a liquid-oxygen trap. Several distillations *in vacuo* were carried out and the gas was finally vaporized into the apparatus from a bath at the temperature of solid  $CO_2$  in order to minimize the non-volatile impurities.

HEXAFLUORO-ETHANE.—A small cylinder of this was kindly supplied by I.C.I. General Chemicals; this gas was used without further chemical purification.

PERFLUORO-n-PENTANE.—This was prepared by the fluorination of n-pentane in a cobalt-trifluoride reactor. The washed and dried sample was fractionated and a sample

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boiling between 27.5 and 29.6°C was taken, there being no good plateau of separation. A mass-spectrometer analysis of this sample showed it to contain 5-10 % of a mono-hydro-fluorocarbon. We are indebted to Prof. M. Stacey for facilities to carry out the preparation of this compound.

PERFLUORO-n-HEXANE.—A sample of this compound was kindly given to us by I.C.I. General Chemicals Division. The boiling point was found to be  $56.7^{\circ}$ C at 749.3 mm Hg compared with a value interpolated from the literature<sup>2</sup> at this pressure of  $56.73^{\circ}$ C. Nuclear magnetic resonance spectra (kindly measured by Dr. L. Pratt) showed there to be about 5 % total impurity of which not more than 3 % was material containing a hydrogen atom.

The viscosity of CF<sub>4</sub> is about 15 % greater than that of CHF<sub>3</sub>, mainly due to the molecular-weight difference of 26 %. For mixtures of mono-hydro-fluorocarbons and perfluorocarbons of C<sub>5</sub> or C<sub>6</sub> chain length the viscosities of the components are not expected to differ by more than 3-4 % and the error in the viscosities of the perfluorocarbons recorded above due to hydro bodies should not exceed 1 %.

PROCEDURE.-All materials were de-gassed and distilled in vacuum before use.

#### RESULTS

Viscosities corrected for slip are given in table 1. Calculation procedures for deriving viscosities have previously been given.<sup>4,5</sup>

$C_2F_4$		$C_2F_6$	
T,⁰K	$\eta  imes 10^6$ poises	<i>T</i> ,°K	$\eta  imes 10^6$ poises
291.7	142.7	290.8	141.5
298.2	149.3	325-2	156.0
308.2	152.5	354-2	168.5
326.1	161.8	363-3	169.6
355.4	174.2	377.3	175.8
388.4	183.5	404.7	186-2
414·7	194.8	429.1	196.4
453 <b>·</b> 2	209.1	455-5	204.5
n-C5F12		n-C6F14	
T,⁰K	$\eta  imes 10^6$ poises	T,⁰K	$\eta  imes 10^6$ poises
296	110	310	112
339	124	329	117
379	137	405	140
420	150	457	155
445	156		
471	166		

## DISCUSSION

The temperature coefficients of viscosity for these four fluorocarbons are small, e.g.

### $(\eta_{450\,^{\circ}\text{K}} - \eta_{300\,^{\circ}\text{K}})/\eta_{300\,^{\circ}\text{K}}$

is about 10-20 % smaller than that for the corresponding hydrocarbons.6

For purposes of interpolation and for numerical comparisons we have fitted the viscosity data to the Lennard-Jones 12:6-potential form.<sup>7</sup> The parameters of fit are given below; these are  $\varepsilon/k$ , the potential energy at the equilibrium distance of separation divided by Boltzmann's constant, and  $\sigma$  the low-velocity collision diameter (table 2).

These values may be compared with those for the corresponding hydrocarbons <sup>7</sup> which are C<sub>2</sub>H<sub>4</sub> ( $\epsilon/k = 205^{\circ}$ K,  $\sigma = 4.23$  Å); C<sub>2</sub>H<sub>6</sub> ( $\epsilon/k = 230^{\circ}$ K,  $\sigma = 4.42$  Å); C<sub>5</sub>H<sub>12</sub> ( $\epsilon/k = 345^{\circ}$ K,  $\sigma = 5.77$  Å); *n*-C<sub>6</sub>H<sub>14</sub> ( $\epsilon/k = 413^{\circ}$ K,  $\sigma = 5.91$  Å).

TABLE 1

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For the fluorocarbons no serious physical significance can be attached to these parameters. It has previously been shown that even for a simple fluorocarbon such as CF<sub>4</sub>, a potential function with higher indices of attraction and repulsion, viz.,  $\phi(r) = A/r^{28} - B/r^7$  is a considerably better approximation to the intermolecular potential between molecular centres.<sup>8</sup>

Although the 28:7-potential has been shown to be less satisfactory in correlating viscosity and virial coefficients for  $CF_4$  than the 12:6-potential, nevertheless it gives a more realistic value of the collision diameter for this compound and correlates the properties better for the other quasi-spherical molecules. For this reason it is probably a more realistic two-parameter potential for  $CF_4$ , the inadequacies arising principally from the use of any two-parameter form for the interactions of such complexity.

TABLE 2					
compound	<i>ε</i> / <b>k</b> , °K	σ, Å			
$C_2F_4$	152	5.12			
$C_2F_6$	163	5.56			
$n-C_5F_{12}$	195	7.36			
n-C6F14	160	8.05			

In the same way for the larger fluorocarbons containing a number of peripheral atoms which act as force centres, relative movements of the carbon centres of the two molecules would be expected to produce steeper intermolecular effects than those between two hydrocarbons in which the peripheral atoms have relatively little interaction with one another. Evidence to support this view comes from the plots of the reduced vapour pressure or reduced virial coefficients against reduced temperature, in which fluorocarbons show much greater deviations from the 12: 6-curves than hydrocarbons of the same shape. In addition, the ratios of the  $\sigma^3$  from the 12: 6-potential given in table 2 for fluorocarbons/hydrocarbons are considerably larger than the ratios of the measured critical volumes.

It seems clear that the small temperature coefficients of viscosity for the fluorocarbons are not due to small values of the intermolecular potential energy at equilibrium separation as indicated by table 2, but derive from the fact that the attraction and repulsion potentials between molecular centres of the fluorocarbons fall off more rapidly with distance than those for the inert gases or for the hydrocarbons.

No two-parameter potential would be adequate to explain the behaviour of perfluoro-n-pentane of perfluoro-n-hexane. However, the 28:7-potential which was found to be suitable for CF<sub>4</sub> should give a reasonable approximation to the behaviour of tetrafluoro-ethylene and hexafluoro-ethane. The present viscosity data for these compounds have been fitted to this potential using collision integrals previously calculated <sup>9</sup> and the parameters are:  $C_2F_4(\epsilon/k = 289^\circ K, \sigma = 4.69 \text{ Å})$ ;  $C_2F_6(\epsilon/k = 334^\circ K, \sigma = 5.01 \text{ Å})$ . From these values of  $\sigma$ , it is possible to derive the equilibrium separations  $R^* = (4)^{1/21}\sigma$  for the 28:7-potential. These are 5.00 Å for  $C_2F_4$  and 5.35 Å for  $C_2F_6$ . These may be compared with the values of  $R^*$  from the 12:6-potential for  $C_2H_4$  of 4.74 Å and for  $C_2H_6$  of 4.95 Å. This indicates that the real equilibrium separations for the fluorocarbons are probably not much larger than those for the corresponding hydrocarbons. The differences in the above values of  $R^*$  can be accounted for by the difference in the C—H and C—F bond lengths. This suggests that the value walls radius of fluorine may not be much greater than that for hydrogen.

The fact that the  $\epsilon/k$  values on the 28:7-potential for C<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> are larger than those for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> on the 12:6-potential suggests that when proper account is taken of the difference in the repulsion and attraction indices the potential

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energies at their respective equilibrium separations are larger for the fluorocarbons than for the hydrocarbons (the approximation of a spherically symmetrical twoparameter potential being used for each type of molecule). However, the intermolecular potential energy between two hydrocarbons at a fixed distance may be larger than that between two fluorocarbons of the same carbon number at the same distance of separation, due to the more rapid decrease of the potential energy with distance between molecular centres for the fluorocarbons.

The comparatively low values of the boiling points and critical temperatures for the fluorocarbons, particularly from  $C_4$  upwards, may probably be explained in a similar way. These low values do not represent small values of the effective potential energies at equilibrium separations, but reflect the fact that the total potential energy of the liquid depends also upon the indices of attraction and repulsion of the intermolecular potential. Thus for the fluorocarbons, this potential energy will fall off rapidly for small displacements of the molecules from the equilibrium separations.

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