and its acetic acid solvate, the interplanar spacings and visually estimated intensities were obtained from X-ray powder photographs but are omitted in order to save space.

Acknowledgment.—We wish to thank Dr. O. H. Emerson for the pure limonin and the limonin solvates, and Merle Ballantyne for the X-ray photographs.

Summary

Optical and crystallographic data are given for limonin, limonin monomethylene chloride solvate and limonin monoacetic acid solvate. Partial data are given for limonin hemimethylene chloride. The unit cell size, space group, and density are given for limonin and limonin monoacetic acid solvate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Surface Tensions and Refractive Indices of the Perfluoropentanes

BY GILSON H. ROHRBACK AND GEORGE H. CADY

Considerable interest has recently been shown in the physical properties of fluorocarbons for the testing and advancing of theories of the liquid state. It is known that the value of many of the properties related to the intermolecular forces are much lower than in the corresponding hydrocarbons, *viz.*, surface tension, viscosity, dispersion, etc. Careful measurements of such quantities for the perfluoropentanes should be of particular interest as these compounds are liquid at room temperature and are not as yet too complicated in structure for application to theory.

This research is a continuation of the program of the determination of physical properties of the perfluoropentanes; densities, melting points, transition temperatures and viscosities having been previously measured.[1]

Experimental

Indices.—Refractive indices were determined at 15° for the compounds n-C_5F_{12}, iso-C_5F_{12}, cyclo-C_5F_{10}, as well as for the two mono-hydrogen compounds n-C_5HF_{11}[1a] and cyclo-C_5HF_9. In order to obtain dispersion values, a wide range of wave lengths in the visible region was employed. Since the indices were too low to be measured by the refractometers available, a hollow prism containing the liquid to be studied was mounted in a spectroscope and the refractive index measured by the method of minimum angle of deviation. All readings were taken in a room cooled to 15°, each sample being allowed to stand for about one-half hour inside the prism, to which an airtight cap had been fitted, before measurements were commenced.

The magnitude of the angle of the prism was determined directly by measuring the angle of the reflected light from its inner faces. The value so determined was 60°06′. As a check on this value the n_D indices of water and carbon tetrachloride were determined using this prism. The comparison with the readings using an Abbe refractometer on the same samples as well as with literature values are as follows:

	Prism	Abbe	Literature	Temp., °C.
H_2O	1.3327	1.3326	1.3326[2]	24
CCl_4	1.4583	1.4582	1.4582[3]	24

Surface Tension.—The surface tension was measured by the capillary rise method. Due to its very small magnitude a capillary was chosen with a diameter of only 0.1614 mm. A uniform section of this tubing was selected by the usual method of observing the length of a mercury bead. An operating section of about 8 cm. was marked off with scribed markings and the tube was calibrated by observing the rise of pure water in the capillary. A total of ten determinations within the marked section gave an average rise of 18.43 cm. at 21.8°; the mean variation from this value being 0.014 cm. Using the expression $\gamma = 75.68 - 0.138t$[4] as a standard, the radius of the tube was calculated to be 0.0807 mm. Similar calculation using benzene as the reference liquid ($\gamma_{20°}$ = 28.80[5]) gave a value which was 0.25% higher, while direct measurements by a weighed mercury bead yielded a radius 0.3% lower. Therefore, because of the reliability of the water sample in both purity and surface tension value, the radius was taken to be 0.0807 mm.

After calibration the capillary was cut and fitted into the apparatus as pictured in Fig. 1. Since Richards and Coombs[6] had previously shown that the tube containing the main bulk of the liquid should be at least 3.3 cm. wide in order to make the liquid rise negligible, tube A was made 4.1 cm. in diameter; a loaded glass sinker was included to diminish the volume of liquid required. The capillary was well held into the smaller side tube by means of a tight fitting rubber sleeve which further permitted the capillary to be raised and lowered for measurements at various levels within the calibrated region. The top end of the capillary was vented back into the main chamber by means of a looped rubber tube which allowed easy vertical movement in the side-arm. The entire apparatus could be evacuated and filled by distillation.

After filling, the apparatus was mounted in a thermostat. The height of the liquid in the large tube of the apparatus and in the capillary was read by means of a cathetometer.

Four compounds were thus examined for capillary rise over varying temperature ranges from 0 to 45°, the upper value being determined in each case by the boiling point. In addition to the three perfluoropentanes, n-C_7F_{16}[6a] was also examined for comparison purposes.

Experimental Results

Indices.—The results of the several runs are recorded in tabular form in Table I with the plot of the same data given in Fig. 2.

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[1] L. L. Burger, Thesis, University of Washington, 1948.

[1a] Very probable H is on second carbon.

[2] L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. of Standards*, **20**, 419 (1938).

[3] E. Pohlaronini, *Bull. Soc. Chim. Belg.*, **36**, 533 (1927).

[4] W. D. Harkins, Chapter VI, A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, New York, N. Y., 1945.

[5] W. D. Harkins and F. L. Brown, THIS JOURNAL, **41**, 503 (1919).

[6] T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

[6a] This sample of perfluoro-n-heptane was generously furnished by R. D. Fowler, Johns Hopkins University. It was redistilled through an 82-plate column, only the middle cut being used in this research.

TABLE I

REFRACTIVE INDICES OF THE FLUOROPENTANES AT 15°

	Hα λ = 6563 Å.	NaD 5893	Hg 5779	Hg 5461	Hg 4916	Hg 4861	Hg 4358	Hg 4047
n-C_5F_{12}	1.2409	1.2411	1.2412	1.2420		1.2430	1.2437	
	1.2406	1.2415		1.2416		1.2428		
Iso-C_5F_{12}	1.2470	1.2475	1.2477	1.2484	1.2492	1.2494	1.2505	
	1.2467			1.2483		1.2489		
Cyclo-C_5F_{10}	1.2574	1.2582		1.2586	1.2597	1.2595	1.2610	1.2620
	1.2577	1.2583		1.2590				
n-C_5HF_{11}	1.2520	1.2525		1.2531	1.2540	1.2543		
Cyclo-C_5HF_9	1.2717	1.2725		1.2732	1.2743	1.2742		

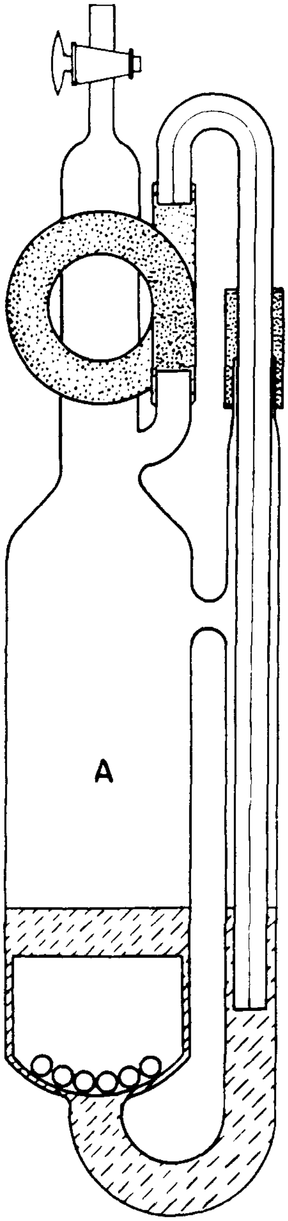

Fig. 1.

In Table II are given the index values from the smoothed curves for the sodium-D line. From these are calculated the molar refraction MR_D of the completely fluorinated compounds as well as the value of the atomic refraction of fluorine using the value for carbon equal to 2.418. Dispersion values are also listed between the wave lengths of 6563 and 4861 Å.

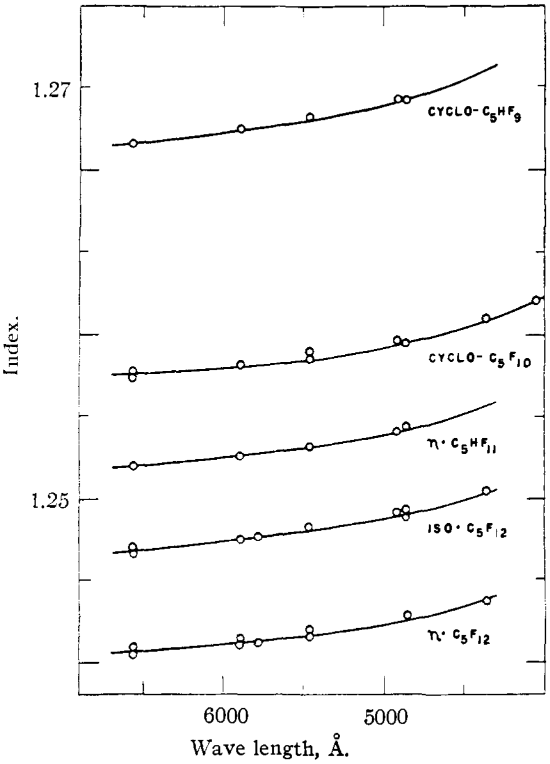

Fig. 2.—Refractive index of fluoropentanes at 15°.

TABLE II

	n^{15}_D	MR_D	Atomic refraction of fluorine	Dispersion Hβ − Hα
n-C_5F_{12}	1.2412	26.87	1.23	0.0019
Iso-C_5F_{12}	1.2474	26.80	1.23	.0022
Cyclo-C_5F_{10}	1.2581	24.50	1.24	.0019
n-C_5HF_{11}	1.2525			.0023
Cyclo-C_5HF_9	1.2723			.0025

It is seen that both the magnitude of the refractive index and its variation with wave length are low in comparison to other liquids. For example, iso-C_5H_{12}[7] has a sodium-D index of 1.3580 at 15° and its dispersion ($H_\beta - H_\alpha$) is 0.00619. It is also interesting to note that the index of perfluoro-*n*-pentane is lower than that of the perfluoroisopentane, a situation just opposite to the usual order of molecular properties of the hydrocarbons.[8]

Surface Tension.—The surface tensions for the four compounds examined are listed in Table III together with the value for $\gamma_{20°}$ taken from the smoothed curves. The plot of these values is shown in Fig. 3.

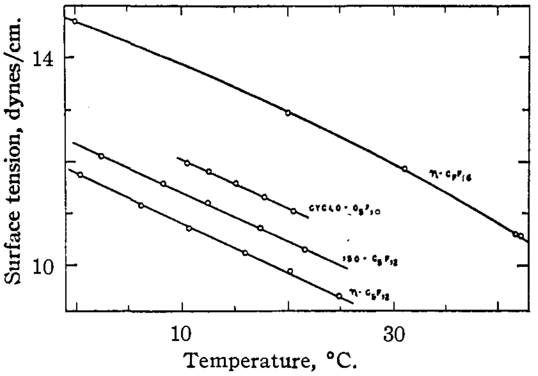

Fig. 3

TABLE III

SURFACE TENSION (DYNES/CM.)

n-C_5F_{12}	Iso-C_5F_{12}	Cyclo-C_5F_{10}	*n*-C_7F_{16}
0.40°—11.73	2.43°—12.11	10.5°—11.99	42.2° —10.57
6.23°—11.16	8.2° —11.59	12.5°—11.82	41.7° —10.60
10.67°—10.72	12.44°—11.21	15.1°—11.59	31.05°—11.86
15.95°—10.25	17.43°—10.72	17.8°—11.32	20.0° —12.96
20.16°— 9.90	21.6° —10.31	20.5°—11.04	0.0° —14.69
24.95°— 9.42			
$\gamma_{20°}$ = 9.87	$\gamma_{20°}$ = 10.48	$\gamma_{20°}$ = 11.09	$\gamma_{20°}$ = 12.96[a]

[a] R. D. Fowler, *et al.*, obtained a value of γ_{20} = 13.6 for perfluoro-*n*-heptane using a du Noüy interfacial tensiometer; R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 375 (1947).

The values for the surface tensions of the fluoropentanes are seen to be lower than any yet reported for compounds normally liquid at room temperature. Again the peculiarity of this molecular property being lower in the normal than in the iso-fluorocarbon is noted.

Acknowledgment.—This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

Summary

The refractive indices over a wide range of wave lengths have been measured at 15° for the compounds: *n*-C_5F_{12}, iso-C_5F_{12}, cyclo-C_5F_{10}, *n*-C_5HF_{11} and cyclo-C_5HF_9. Both magnitude of the indices and dispersion were found to be very low.

The surface tensions of the perfluoropentanes as well as of *n*-C_7F_{16} were measured over a temperature range between 0 and 40°. The value for *n*-C_5F_{12} is lower than any previously reported for a compound normally liquid at that temperature.

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(7) J. Timmermans and F. Martin, *J. Chim. Phys.*, **23**, 747 (1926).

(8) Burger (*cf.* ref. 1) also found that the boiling point, the density and the viscosity of *n*-C_5F_{12} were lower than those of iso-C_5F_{12}.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Thermodynamics of the System KHF_2–KF–HF, Including Heat Capacities and Entropies of KHF_2 and KF. The Nature of the Hydrogen Bond in KHF_2[1]

BY EDGAR F. WESTRUM, JR.,[2] AND KENNETH S. PITZER

This investigation was undertaken to determine whether the proton in the F–H–F⁻ ion is located in a single potential minimum midway between the fluoride ions or is unsymmetrically placed as in the O–H–O case in ice,[3] etc. The method initially adopted included measurements of the heat capacity from 14° to 500° K. of KF(s) and KHF_2(s). From these data and the statistically calculated entropy of HF(g) the change in entropy can be calculated for the reaction

$$KHF_2(s) = KF(s) + HF(g)$$

This was to be compared with the entropy change from direct heat and equilibrium measurements. If the two results agree, then KHF_2 must have taken on a perfectly ordered structure at low temperatures. However, if the F–H–F⁻ ion is not symmetrical, one expects either a disordered structure at low temperatures or a transition of some sort where the disorder sets in on heating.

In addition, there are the infrared spectral data of Ketelaar[4] and values of the dielectric constant obtained by us which help in making the conclusions definite.

Experimental

Preparation and Purity of KHF_2.—The crystalline potassium hydrogen fluoride for the calorimetric work was prepared by slowly adding anhydrous potassium carbonate to aqueous hydrofluoric acid; both reagents were "Chemically Pure." The only stated contaminants were maxima of 0.001% H_2SiF_6 in the acid and 0.02% of sodium

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(1) These results are abstracted from the Ph.D. Dissertation of E. F. Westrum, Jr., University of California, 1944, except for the dissociation pressures of KHF_2 measured by E. F. Westrum, Jr., in 1946 and the dielectric constant measured by K. S. Pitzer in 1948.

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(3) L. Pauling, THIS JOURNAL, **57**, 2680 (1935); W. F. Giauque and J. W. Stout, *ibid.*, **58**, 1144 (1936).

(4) J. A. A. Ketelaar, *Rec. trav. chim.*, **60**, 523 (1941).