amounts up to 10%, to a saturated aqueous solution of acrylonitrile will cause the separation of an acrylonitrile phase.

LITERATURE CITED

(1) American Cyanamid Co., Synthetic Organic Chemicals Dept., "Chemistry of Acrylonitrile," *Cyanamid's Nitrogen Chemicals Digest* **5**, (1951).

(2) Booth, H. S., Everson, H. E., *Ind. Eng. Chem.* **40**, 1491 (1948).

(3) McBain, M. E. L., Hutchinson, E., "Solubilization and Related Phenomena," Chap. 6, Academic Press, New York, 1955.

(4) Vaughn, T. H., Nutting, E. G., Jr., *Ind. Eng. Chem., Anal. Ed.* **14**, 454 (1942).

Received for review May 18, 1956. Accepted August 25, 1956.

Mention of trade names does not imply endorsement by the Department of Agriculture over similar competitive products.

Viscosities of Fluorinated Methyl Bromides and Chlorides

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In studying the chemical reactions of the fluorinated methyl chlorides and bromides with sodium vapor, it was necessary to obtain the viscosities of these halides. Very few data on the viscosities of these compounds are recorded; the values that exist have been obtained by independent measurements and provide no opportunity for internal comparison or consistency.

EXPERIMENTAL

The fluorinated chloro compounds were obtained from the Kinetic Chemicals Division, E. I. du Pont de Nemours & Co. Methyl chloride and bromide were Eastman Kodak white label products. The fluorinated bromo compounds were all synthesized by using the Hunsdiecker degradation of the silver or sodium salt of the corresponding carboxylic acid by bromine. All compounds were distilled several times on a low temperature fractionating column and only the middle fractions of constant boiling range were employed. Mass spectral patterns were obtained for all compounds and showed the absence of appreciable impurities.

The coefficient of viscosity was determined by allowing the specimen gas to flow from a 2-liter bulb through a uniform glass capillary at room temperature into an evacuated borosilicate glass trap refrigerated by liquid nitrogen. The initial and final pressures in the bulb were measured, as well as the elapsed time. The collected condensate was transferred to a tared evacuated gas bulb and weighed. Samples were 100 to 300 mg. and required collection times were 1 to 3 hours. The pressures in the large bulb were 2 to 15 cm. and no correction for slip was necessary. Three to seven determinations were made on each sample. The maximum error was in the weighing, which had a precision within 1%.

RESULTS

The procedure was calibrated using methyl chloride, for which the value of the absolute viscosity of Benning and Markwood (*1*) was adopted. All measurements were adjusted to 25 ° C., using temperature coefficients of 0.3 and 0.6 micropoise per degree for the chlorides and bromides, respectively, based on the methyl compounds. These corrections were of the order of magnitude of the probable error of a single measurement. The results are given in Table I, with literature values.

Table I. Viscosities and Molecular Diameters of Gases

Compound	η, Exptl. (25 °C.),[a] Micropoises	η Lit. (25 °C.), Micropoises	Diameter, A.
CH_3Cl	[107.9 (0.1)]	107.9 (*1*)	5.55
CFH_2Cl	113.1 (0.7)	...	5.85
CF_2HCl	...	129.2 (*1*)	5.81
CF_3Cl	139.6 (0.7)	...	5.85
CH_3Br	134.8 (0.1)	135.2 (2)	5.81
CFH_2Br	129.1 (0.4)	...	6.20
CF_2HBr	140.4 (0.1)	...	6.18
CF_3Br	151.2 (0.2)	...	6.15

[a] Probable error of average given in parentheses.

DISCUSSION

The coefficient of viscosity increases gradually with increase in the number of fluorine atoms in the molecule for the chlorides, although a minimum occurs in the bromide series. This may be considered a consequence of the relative increase in molecular mass and molecular diameter, on passing down the two series.

In view of the general lack of transport quantities of gases, one or more of these quantities must often be estimated. When insufficient data are available for correlations based on structural features, the kinetic theory of gases is often used. However, even in the latter case, a structural parameter, such as a collision diameter, is necessary. The collision diameter of each of these molecules was calculated from the viscosity coefficient on the basis of the hard, elastic sphere approximation (Table I). Substitution of one fluorine atom in the molecule results in an increase in diameter, and successive substitutions of fluorine cause no further increment. This behavior is consistent with the view of the simple, hard sphere model.

ACKNOWLEDGMENT

The authors thank G. H. Cady for his cooperation and the Kinetic Chemicals Division of the Du Pont Co. for its generous gift. This work was supported by the Office of Naval Research.

LITERATURE CITED

(1) Benning, A. F., Markwood, W. H., *Refrig. Eng.* **37**, 243 (1939).

(2) Titani, T., *Bull. Chem. Soc. Japan* **5**, 99 (1930).

Received for review September 8, 1956. Accepted February 4, 1957.