[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Viscosity of Hydrogen Fluoride

BY J. H. SIMONS AND RICHARD D. DRESDNER

It is well known by all who have used and handled hydrogen fluoride that it is a material of high fluidity. The increasing amount of work employing this substance makes it desirable to have quantitative measurements of its viscosity. To date there are no measurements of this property recorded in the literature. We have succeeded in making measurements of pure hydrogen fluoride, commercial hydrogen fluoride, and hydrogen fluoride containing a small percentage of ethyl alcohol over the range of temperatures from approximately −70 to above 0°. Hydrogen fluoride has a viscosity not greatly different from that of ethyl ether at the same temperature and small amounts of impurities such as water and ethyl alcohol tend to increase the viscosity very considerably.

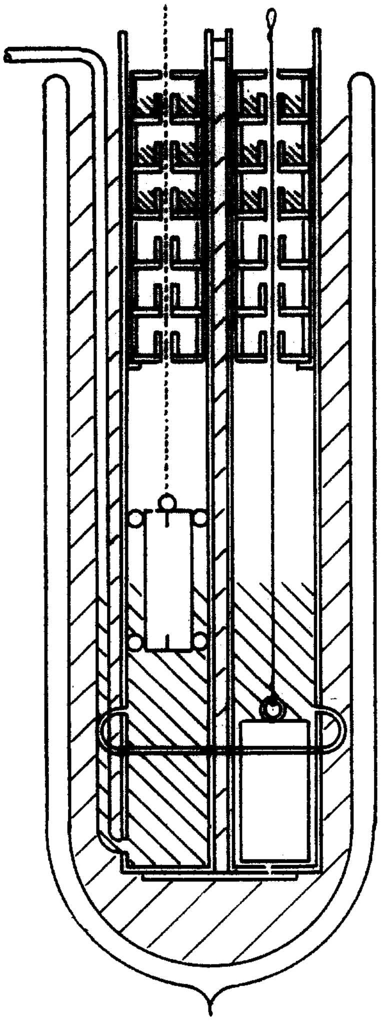

Fig. 1.—Copper viscometer.

Method.—The usual laboratory viscometer is not suitable for use with hydrogen fluoride due to its reaction with glass. Its strong deliquescence, its high volatility, and its corrosive action on many metals in the presence of air are additional factors which necessitate the design of a viscometer for making the measurements.

The principle employed was the measurement of the rate of flow of the liquid through a length of capillary tubing. The viscometer consisted of two copper tubes connected by a piece of capillary tubing. In one tube was a metal bob of density greater than that of hydrogen fluoride fastened to a wire which extended through the top of the tube. Raising this wire to above the liquid level created a liquid head between the two tubes and initiated the flow of the liquid through the capillary. In the other tube a light float made of sheet metal was suspended in the liquid by a fine gold chain which fastened to the arm of a small analytical balance. As the liquid level fell in this tube, the float would descend. This was indicated by the pointer of the analytical balance, and the rate of descent could be determined by the rate of motion of this pointer.

Apparatus.—A diagram of the viscometer is shown in Fig. 1. It consisted of two copper tubes 2.5 cm. in diameter and 30 cm. long. These were tacked together, by means of solder, top and bottom by pieces of copper sheet. The capillary had a bore of about 0.75 mm. and was about 12 cm. long. The ends were silver soldered into the copper tubes about 6 cm. from the bottom. A copper tube for the entrance of the liquid was silver soldered to the bottom of one of the main tubes. This had a diameter of about 6 mm. In order to prevent the entrance of water and the exit of hydrogen fluoride, the main tubes were provided with a set of 6 circular trays. These were made by silver soldering a piece of sheet copper to the end of a piece of copper tubing which fitted loosely into the main tube. A small tube about 4 mm. in diameter was silver soldered concentrically on this copper sheet. The larger tube was cut about 1 cm. long and the smaller was shorter. The hole in the center of the sheet provided a passageway for the wire or chain. A stop in the main tube was provided 17.7 cm. from the bottom to support the lowest tray. The remaining five rested one on top of the other. These trays provided both a tortuous path for gas diffusion and, by placing anhydrous calcium chloride on the upper ones, a means of preventing the entrance of water. The bob was made of a piece of copper tubing 2 cm. in diameter and 4.5 cm. long with silver-soldered end-plates. Its volume was approximately 15 cc. The float was made of copper foil, silver soldered into the shape of a cylinder 1 cm. in diameter and about 4 cm. long. A gold chain, about 26 cm. long, was silver soldered to the center of the top, and a pin hole was provided in the top to allow for pressure differences. Loops of no. 28 gage wire were silver soldered to the float to provide guides. There were four of these equally placed near the top of the float and another four near the bottom. This viscometer fitted conveniently into the usual one-quart size wide-mouthed laboratory Dewar vessels.

Materials.—The pure hydrogen fluoride was made by the method described by Simons.[1] It was condensed into a small receiver containing a metal valve in the lower outlet and was allowed to run into the viscometer from this outlet. The commercial hydrogen fluoride was obtained from an ordinary 100-pound cylinder. The ethyl alcohol in the ethyl alcohol solution was an industrial product of absolute grade which had an index of refraction of 1.3621 at 20°. This corresponds to a mixture of 98.75% alcohol and 1.25% water. The ethyl ether used for the calibration was dried over sodium and then distilled. A fraction boiling

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[1] J. H. Simons, THIS JOURNAL, 46, 2179 (1924).

TABLE I

RECORD OF EXPERIMENTS

t is temperature in degrees centigrade. s is efflux time in seconds.

Commercial HF				Pure HF				Ethyl ether				Pure HF and alcohol	
Expt. 1		Expt. 2		Expt. 1		Expt. 2		Expt. 1		Expt. 2		Expt. 1	
t	s	t	s	t	s	t	s	t	s	t	s	t	s
−70.3	199.2	−58.6	172.3	−72.8	184.4	−66.8	170.0	−70.0	198.8	−68.2	196.0	−73.6	300 (?)
−62.7	180.0	−47.4	152.0	−68.3	170.0	−60.2	153.1	−62.0	179.5	−58.7	171.6	−64.9	216.2
−52.7	160.0	−44.0	146.7	−64.6	163.3	−56.9	143.7	−54.1	166.2	−55.3	170.0	−61.3	207.1
−45.6	148.3	−39.4	140.3	−60.8	155.7	−43.3	127.5	−44.1	152.1	−50.1	164.7	−52.5	189.1
−40.9	140.1	−30.7	127.7	−57.5	147.5	−35.7	118.2	−38.9	147.3	−41.7	150.5	−44.3	170.0
−37.5	137.5	−19.7	117.5	−54.4	144.0	−27.6	111.6	−33.2	141.0	−35.3	141.0	−38.3	157.6
−34.4	131.9	−13.7	113.7	−48.8	133.3	−11.8	97.1	−27.1	137.4	−25.7	134.2	−31.7	151.6
−32.1	130.0	− 9.3	109.4	−44.9	129.1			−21.7	131.4	−19.2	128.2	−29.1	147.5
−28.0	127.5	− 6.7	105.8	−39.7	126.3			−13.2	126.5	−17.8	126.1	−21.5	142.1
−23.3	122.2	− 4.0	104.6	−31.2	112.9			− 7.7	122.0	−12.6	123.4	−14.7	137.7
−18.7	118.0	+ 1.9	103.6	−23.0	105.3			− 2.6	120.2	− 2.6	119.5	−10.3	133.2
−14.9	116.3			−13.6	99.9			+ 1.6	118.2			− 3.5	129.0
												+ 3.9	126.0

TABLE II

VISCOSITY OF HYDROGEN FLUORIDE

t is in degrees centigrade. C is the corresponding viscosity in centistokes. ρ is the corresponding density in grams/cc η is the corresponding viscosity in centipoise.

Commercial HF		Pure HF			Alcohol and pure HF	Ethyl ether Calibration of viscometer		
t	C	C	ρ	η	C	t	s	C
−68.75	0.893	0.780	1.1696	0.914	...	−67.5	192.5	0.873
−62.5	.797	.668	1.1560	.772	0.983	−60.0	177.5	.787
−56.25	.720	.585	1.1394	.666	.878	−52.5	165.0	.710
−50.0	.645	.507	1.1231	.570	.788	−45.0	154.5	.643
−43.75	.579	.450	1.1072	.498	.720	−37.5	145.8	.584
−37.5	.525	.397	1.0914	.434	.668	−30.0	138.7	.532
−31.25	.472	.360	1.0761	.387	.615	−22.5	132.3	.488
−25.0	.420	.330	1.0606	.350	.575	−15.0	127.0	.449
−18.75	.377	.306	1.0471	.320	.533	− 7.5	122.5	.417
−12.5	.353	.285	1.0308	.296	.499	− 0	117.7	.389
− 6.25	.330	.270	1.0163	.274	.470	+ 7.5	115.0	.365
− 0	.310	.256	1.0020	.256	.447	+ 1.5	112.2	.343
+ 6.25		.243	.9879	.240	...	+19.0[a]	210.3	.983

[a] Special point with water.

between 35 and 36° was used. The ethyl alcohol solution was made by adding hydrogen fluoride to a weighed amount of alcohol. This solution is estimated to contain hydrogen fluoride, ethyl alcohol and water in the mole per cents. of 93.4, 6.1 and 0.5, respectively.

Procedure.—The analytical balance was supported on a three-legged table with a leveling screw on each leg. Holes through the floor of the balance and the top of the table enabled the chain from the float to be attached below the center of one balance pan. The viscometer was supported in a vertical position below the balance with the chain on the float attached to the balance. The float was then counter-balanced and the positions adjusted until it moved freely but with the float and its support slightly heavier than the counter-balance. The viscometer was then surrounded with a Dewar vessel and was cooled with a dry-ice–acetone bath. The liquid was introduced from its container until the float balanced at its highest position. Leveling screws on the balance table were then adjusted to set the balance pointer at the zero point of a special scale of about thirty divisions which had been made to replace the regular balance scale. The temperature was determined by means of a thermocouple fastened to the viscometer and read with the laboratory potentiometer. The liquid displacing bob in the second tube of the viscometer was then raised. This lowered the liquid level in that tube approximately 3.3 cm., and the liquid flow through the capillary began. At the time when the pointer had moved 1 mm., the stopwatch was started and it was stopped when it had moved through an additional 5 mm. As the pointer moved 31 mm. for the complete displacement, the ratio of the amount of the displacement used for measurement and the total was 5 divided by 31. After measurement was made, the bob was again lowered, the liquid allowed to return to its original condition, and the temperature allowed to rise to that desired for the new measurement. The operation was then repeated. Due to the increase in volume of the liquid with the rise in temperature, the position of the balance had to be adjusted for each measurement in order that the pointer start at the same zero mark.

The viscometer was calibrated using the same procedure with ethyl ether. The viscosity was determined over the same temperature range in a modified Ostwald instrument patterned after the design of Dr. M. R. Cannon, of this College, for liquids in this viscosity range. As the viscometer was calibrated with a liquid of approximately the same viscosity as that of the hydrogen fluoride, the instrument provided a relative and not an absolute measurement, and serious instrumental errors could not be involved.

Results.—The record of the measurements is shown in Table I and reproduced in Fig. 2. The deviation of the points from a smooth curve of

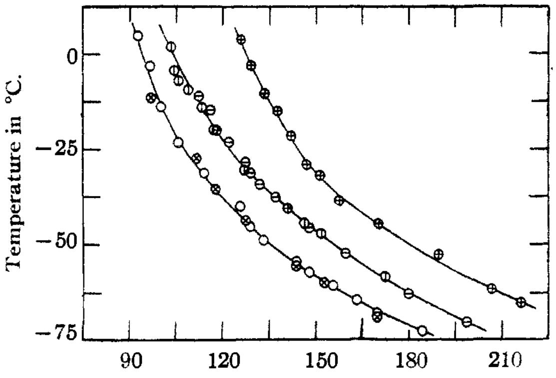

Fig. 2.—Time–temperature data: O, pure HF, exp. 1; ⊗, pure HF, exp. 2; ⊖, commercial HF, exp. 1; ⦶, commercial HF, exp. 2; ⊕, alcohol–HF solution.

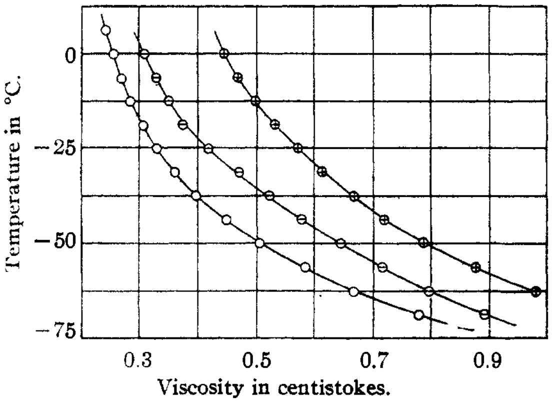

Fig. 3.—Time–temperature data: O, pure HF; ⊖, commercial HF; ⊕, alcohol–HF solution.

Fig. 2 is a measure of the reproducibility of the measurements. The calibration of the viscometer is shown in Table II with all points taken with ether except the last one which was with water. The viscosities in centistokes as calculated from the above measurements are shown in Table II and reproduced in Fig. 3. The density of pure hydrogen fluoride is known from Simons and Bouknight[2] ($\rho = 1.0020 - 2.2625 \times 10^{-3}t + 3.125 \times 10^{-6}t^2$), so that the viscosity of pure hydrogen fluoride can be calculated in centipoises ($\eta = C\rho$).

Summary

The viscosity of hydrogen fluoride has been determined on the temperature range from −70 to approximately +10° by means of a viscometer designed specifically for this purpose. The viscosity is low, approximately the same as ethyl ether in the same temperature range, and it is very remarkably raised by small amounts of certain impurities.

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(2) J. H. Simons and J. W. Bouknight, THIS JOURNAL, **54**, 129 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

Pure and Mixed Monolayers of Dilauryl Maleate and Fumarate[1,2]

BY J. L. SHERESHEFSKY AND A. A. WALL

Langmuir,[3] Adam[4] and Rideal[5] have shown that the presence of a double bond and its stereochemical configuration, *i. e.*, whether it is *cis-* or *trans-*, influence many of the properties of monolayers, including among others limiting area, surface potential and temperature of expansion. In these studies, however, the double bond and its isomerism were connected with the hydrocarbon chains of the molecules, which as it is now well established constitute the external part of films. The influence of the double bond in its geometrical configurations when located in the head group, *i. e.*, the part of the film which interacts with the underlying liquid, is not known. Surface potentials and stability are two important properties of films which must be closely related to the nature of the head group. It was therefore considered of interest to study the properties of monolayers formed by the dilauryl esters of maleic and fumaric acids, since in these and similar molecules the head groups of the monolayers formed by them will consist of geometric isomers.

Experimental

The film balance used in this investigation was of the type developed at the Colloid Science Laboratory,[6] Cambridge University. A Pyrex baking dish of the dimensions 12 × 8 × 2 inches served as the tray, the float was made of mica, and the movable barriers were made of window glass strips. The balance was enclosed by a wooden case to protect it from dust, and was operated by external controls. The sensitivity of the balance was 0.1 dyne per cm. per degree.

The monolayers were prepared by spreading measured quantities of the substances dissolved in purified Eastman Kodak Co. ligroin, b. p. 60–80°, with the aid of a micrometric syringe,[7] of which one division of the micrometer delivered 0.0002 cc. of solution. The substrate in all cases consisted of 0.01 N hydrochloric acid solutions.

The measurements at temperatures lower than room

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(1) Data taken from Master's thesis submitted by Arthur A. Wall.

(2) Presented before the Colloid Chemistry Division at the Buffalo meeting of the American Chemical Society, Sept. 7–11, 1942.

(3) Irving Langmuir, THIS JOURNAL, **39**, 1848 (1917).

(4) N. K. Adam, *Proc. Roy. Soc.* (London), **A101**, 516 (1922); N. K. Adam and J. W. W. Dyer, *ibid.*, **106**, 694 (1924); N. K. Adam and G. Jessup, *ibid.*, **112**, 362 (1926).

(5) A. H. Hughes and E. K. Rideal, *ibid.*, **A140**, 253 (1933); G. Gee and E. K. Rideal, *ibid.*, **153**, 116 (1935).

(6) C. G. Lyons and E. K. Rideal, *ibid.*, **A124**, 344 (1929).

(7) Burroughs Welcome Co., New York.