Liquid Viscosity of Halocarbons

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The liquid viscosity of seven halocarbons has been measured at saturated conditions over a pressure range of 0.1 to 20 bars. The compounds cover the series CHX_3 and CH_2X_2, where X is F or Cl.

LIQUID VISCOSITY is one of the fundamental properties of a fluid and is of considerable value in formulating and testing various theories of liquid behavior. These data are also important in the computation of heat transfer and fluid flow.

The compounds in the series CH_2X_2 and CHX_3, where X is either F or Cl, have several members which are of considerable industrial importance. Many of these fluids are used in heat transfer processes involving vaporization and condensation, so that knowledge of the liquid viscosity at saturated conditions is most useful.

The saturated liquid viscosities of the seven compounds making up the series CH_2X_2 and CHX_3 have been measured over a pressure range of 0.1 to 20 bars.

APPARATUS

Because of the wide pressure range covered in this study, a sealed system was desirable. A review of the literature gave many different techniques, but a capillary type viscometer was chosen for accuracy and simplicity of operation. The design (Figure 1) in general follows that of Edwards and Bonilla (*6*), but with several significant modifications. The basic design was changed to an Ubbelohde suspended level type.

The unit was fabricated from heavy-walled glass tubing and was capable of standing pressures up to 20 bars.

Trumpet-shaped capillary ends were used to minimize energy losses. In addition, the instrument was designed with a capillary length-to-radius ratio of better than 200. This is large enough to make any end effects negligible, as compared to the pressure drop within the capillary.

Reynolds numbers for the study ranged from approximately 50 to 700, well below the critical value of 2300 which represents the transition from laminar to turbulent flow.

The viscometer was thermostated in a stirred liquid bath with a uniformity and control of 0.02° C or better.

Temperature measurements were made by a platinum resistance thermometer, using techniques previously reported (*11*). The accuracy of the measurements was ±0.01° C.

The efflux time was measured by a Standard Model S-10 electric stopwatch. The accuracy was checked against time signals from the National Bureau of Standards. In the efflux time intervals measured, the accuracy was better than 1 part in 5000.

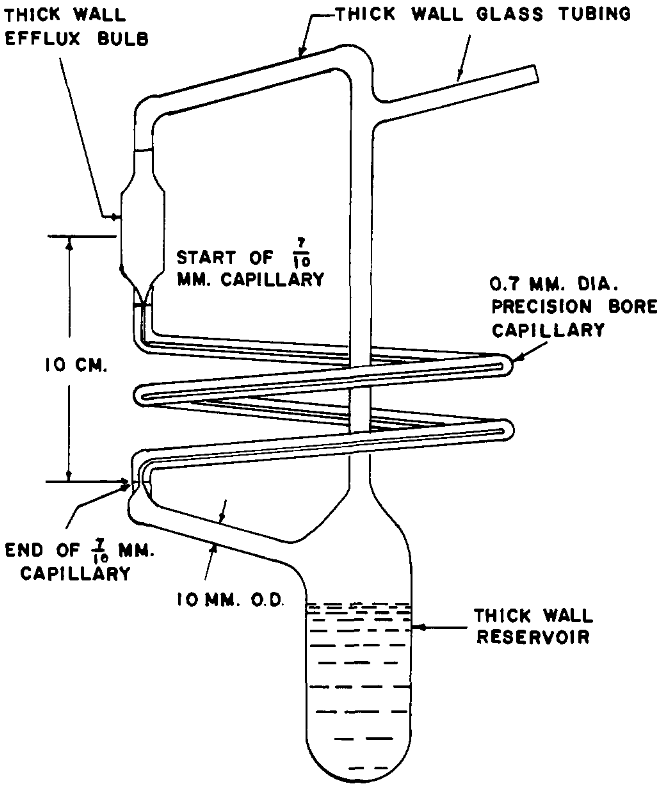

Figure 1. Modified suspended level viscometer

CALIBRATION OF VISCOMETER

The viscometer constants C and E for the equation

$$\nu = \eta/\rho = Ct - E/t^2 \tag{1}$$

were determined by calibration with diethyl ether (Baker and Adamson reagent grade). The viscosity, η, of the ether was taken from the literature (*8*).

Evaluation of C and E is also possible using Equations 2 and 3, if the indicated viscometer parameters are known with acceptable precision. However, as pointed out by Cannon (*4*), it is better to determine E by calibration, inasmuch as its value also depends on the degree of tapering of the trumpet-shaped capillary ends.

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[1] Deceased.

$$C = \frac{\pi g (D/2)^4}{8LV} (X_1 - X_2) \qquad (2)$$

$$E = \frac{1.66 V^{3/2}}{L(CD)^{1/2}} \qquad (3)$$

To test the reliability of the calibration, including a surface tension correction, the viscosity of absolute ethanol was measured and compared to the results published by the National Bureau of Standards (*3*). The ethanol densities were obtained from the same source (*3*). The experimental results are shown in Table I. Table II shows a comparison of our data with the National Bureau of Standards data. The values in both cases are calculated from four-constant equations derived from our experimental results and from the NBS published data.

The diethyl ether and ethanol showed no impurities, with a detection limit of approximately 0.01%.

Table I. Effect of Surface Tension Correction on Ethanol Viscosity

°C	η^a	η^b
0.10	1.787	1.781
16.11	1.290	1.293
37.97	0.860	0.863
59.23	0.600	0.602
78.27	0.447	0.448

[a] Data without surface tension correction. [b] Surface tension correction applied.

Table II. Viscosity of Ethanol

T = °C	η, Centipoises Present	η, Centipoises NBS	Difference
0.00	1.785	1.780	+0.005
5.00	1.611	1.614	−0.003
10.00	1.456	1.464	−0.008
15.00	1.321	1.329	−0.008
20.00	1.200	1.208	−0.008
25.00	1.092	1.099	−0.007
30.00	0.996	1.001	−0.005
35.00	0.910	0.913	−0.003
40.00	0.833	0.835	−0.002
45.00	0.763	0.764	−0.001
50.00	0.701	0.701	0.000
55.00	0.645	0.644	+0.001
60.00	0.595	0.593	+0.002
65.00	0.549	0.548	+0.001
70.00	0.508	0.507	+0.001
75.00	0.470	0.470	0.000

Table III. Halocarbons Studied

Compounds	Normal Boiling Point, °C
$CHCl_3$	+61.2
$CHCl_2F$	+8.9
$CHClF_2$	−40.8
CHF_3	−82.1
CH_2Cl_2	+40.1
CH_2ClF	−9.1
CH_2F_2	−51.7

SAMPLES

The halocarbons studied are shown in Table III. All samples were distilled from over phosphorus pentoxide and then analyzed by gas chromatography. The results showed a purity of 99.90 mole % or better. This drying procedure was necessary, since even small amounts of moisture would precipitate out at low temperatures as ice or hydrate crystals, causing erratic efflux times.

PROCEDURE

The viscometer was carefully cleaned and evacuated to a pressure of 10^{-4} torr. The sample was distilled into the viscometer, condensing with liquid nitrogen. Standard vacuum techniques were used for this procedure. The glass side arm connecting the viscometer to the vacuum system was then sealed off.

The viscometer was mounted in a rotating holder such that the unit could be inverted to fill the upper chamber, then righted to begin the run. The mounting returned the viscometer to the identical vertical position each time.

After thermal equilibration, as determined by the consistency of the efflux time, at least five sets of efflux times were measured by visual observation of the meniscus. The

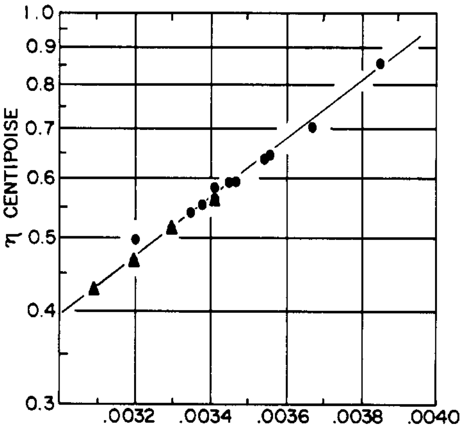

Figure 2. Liquid viscosity of $CHCl_3$

● (8)

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Table IV. Constants for Viscosity Equations

$\text{Log } \eta = A + B/T + CT + DT^2$

Compound	A	B	C	D	Standard Deviation	99% Confidence Limits
$CHCl_3$	−3.72086	592.281	0.00747539	-8.54583×10^{-6}	0.00225	±0.0022
$CHCl_2F$	−1.75347	333.553	0.000783465	-1.092225×10^{-6}	0.00065	±0.00064
$CHClF_2$	−5.40057	556.320	0.0162973	-2.31479×10^{-5}	0.00127	±0.0015
CHF_3	−5.31765	434.527	0.0203424	-3.69802×10^{-5}	0.00100	±0.0014
CH_2Cl_2	−2.67174	469.701	0.00349359	-3.70069×10^{-6}	0.00280	±0.0024
CH_2ClF	−2.31373	370.934	24.1356×10^{-4}	-2.91742×10^{-6}	0.00136	±0.0015
CH_2F_2	−5.35949	550.807	0.0172998	-2.80974×10^{-5}	0.000493	±0.0005

Table V. Viscosity of Halocarbons

Temperature, °C	Density, G/Cc	Centipoises Observed	Centipoises Calculated
	$CHCl_3$		
−63.07	1.6436	1.9615	1.9576
−48.72	1.6166	1.4600	1.4637
−35.19	1.5915	1.1538	1.1563
−20.60	1.5645	0.9278	0.9272
−8.81	1.5427	0.7931	0.7918
4.18	1.5187	0.6779	0.6771
16.36	1.4959	0.5939	0.5927
31.58	1.4670	0.5093	0.5095
46.27	1.4385	0.4450	0.4459
61.26	1.4087	0.3922	0.3930
80.05	1.3699	0.3397	0.3390
	$CHCl_2F$		
−65.37	1.5698	0.9280	0.9279
−50.73	1.5377	0.7347	0.7352
−36.19	1.5063	0.6008	0.6005
−22.41	1.4757	0.5066	0.5065
−9.81	1.4479	0.4405	0.4403
3.66	1.4169	0.3841	0.3843
18.03	1.3828	0.3367	0.3370
32.88	1.3470	0.2978	0.2978
46.45	1.3127	0.2687	0.2685
60.49	1.2761	0.2434	0.2433
73.56	1.2410	0.2232	0.2233
	$CHClF_2$		
−72.49	1.4966	0.5128	0.5130
−57.74	1.4598	0.4161	0.4155
−43.10	1.4201	0.3477	0.3482
−28.25	1.3766	0.2967	0.2978
−15.41	1.3364	0.2654	0.2634
−2.08	1.2920	0.2329	0.2337
12.39	1.2411	0.2058	0.2061
25.97	1.1904	0.1834	0.1833
	CHF_3		
−83.32	1.4432	0.3166	0.3165
−72.30	1.4056	0.2750	0.2753
−60.51	1.3616	0.2397	0.2395
−49.12	1.3144	0.2106	0.2105
−37.26	1.2597	0.1840	0.1842
Temperature, °C.	Density, G/Cc	Centipoises Observed	Centipoises Calculated
	CHF_3		
−26.39	1.2033	0.1627	0.1626
−16.22	1.1395	0.1442	0.1442
	CH_2Cl_2		
−64.77	1.4792	1.4157	1.4113
−51.26	1.4557	1.0867	1.0916
−23.51	1.4063	0.7090	0.7101
−7.34	1.3767	0.5793	0.5787
4.11	1.3554	0.5093	0.5087
15.30	1.3344	0.4548	0.4534
27.61	1.3110	0.4043	0.4036
40.06	1.2870	0.3619	0.3623
55.07	1.2577	0.3208	0.3216
70.07	1.2280	0.2877	0.2883
85.01	1.1980	0.2608	0.2608
100.78	1.1659	0.2366	0.2362
	CH_2ClF		
−80.95	1.4462	0.9383	0.9383
−62.22	1.3924	0.6671	0.6670
−47.27	1.3659	0.5293	0.5306
−32.12	1.3297	0.4364	0.4340
−17.76	1.2946	0.3662	0.3671
−2.49	1.2561	0.3127	0.3135
11.01	1.2210	0.2768	0.2766
26.60	1.1790	0.2431	0.2427
41.40	1.1374	0.2167	0.2168
	CH_2F_2		
−72.87	1.7628	0.5353	0.5351
−61.79	1.6776	0.4438	0.4444
−50.27	1.5887	0.3735	0.3731
−43.80	1.5385	0.3407	0.3403
−39.43	1.5045	0.3206	0.3204
−28.40	1.4184	0.2766	0.2767
−26.38	1.4025	0.2688	0.2696
−14.15	1.3062	0.2310	0.2307
−2.11	1.2104	0.1984	0.1984
14.16	1.0793	0.1617	0.1617

times varied from about 100 to 1000 seconds, depending on the compound and temperature. Five efflux times were measured for each temperature and had to agree to ±0.1 second or the set was discarded.

The calculation of the viscosity followed the procedure described in the section on calibration. A correction was required because of the differential driving head, ΔH, between calibrating fluid and the liquid being measured. This was accomplished by using the capillary rise relationship (*4*).

$$\Delta H = 2/g \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \left(\frac{\gamma_1}{\rho_1} - \frac{\gamma_2}{\rho_2}\right) \qquad (4)$$

From Equation 2 we know $C = K\ (X_1 - X_2)$ where K is a function only of the viscometer, but $(X_1 - X_2)$ is a function both of the liquid properties and the viscometer design. By calibration with water and diethyl ether, two slightly different values of C are obtained ($C_{H_2O} = 0.001890$ and $C_{ether} = 0.001860$), thus permitting evaluation of ΔH for these two liquids. Substitution into Equation 4 permits the estimation of $(1/r_1 - 1/r_2)$, which was assumed to be constant and independent of the liquid being studied. These assumptions are justified, inasmuch as the correction applied to the data is almost three orders of magnitude less than the measurement itself.

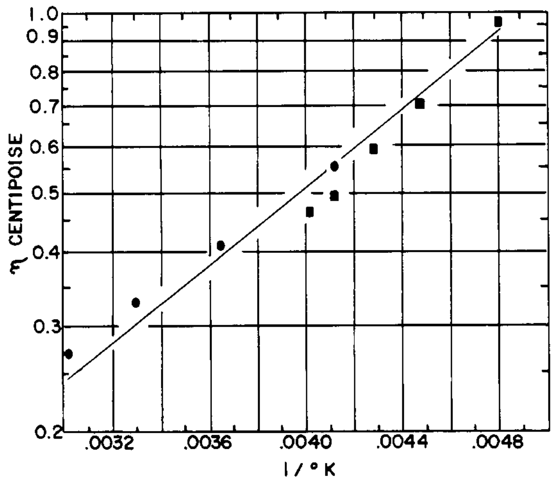

Figure 3. Liquid viscosity of $CHCl_2F$

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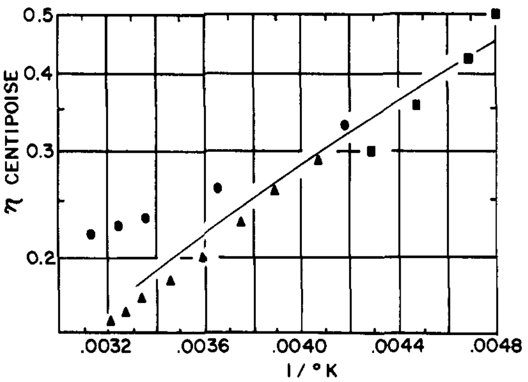

Figure 4. Liquid viscosity of $CHClF_2$

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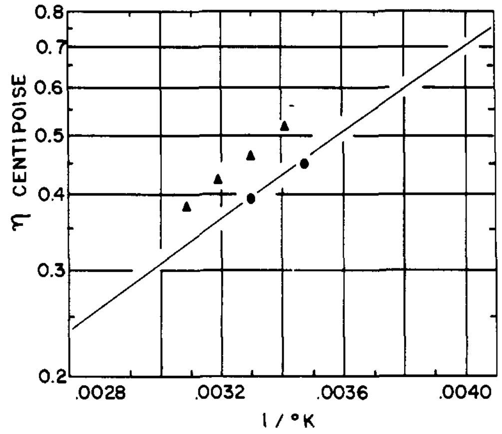

Figure 5. Liquid viscosity of CH_2Cl_2

● (*12*)

▲ (*5*)

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With a value for $(1/r_1 - 1/r_2)$, Equation 4 may be used to determine the ΔH between diethyl ether and the liquid under investigation. Equation 2, combined with a value for ΔH, makes possible the estimation of a small correction in C in each case.

The surface tensions required for the foregoing were obtained from the parachor expression:

$$\text{Parachor} = \frac{\text{mol. wt.}}{\text{density}} \gamma^{1/4} \quad (5)$$

The density data for $CHCl_3$(*8*), $CHFCl_2$(*1*), CHF_2Cl(*1*), CHF_3(*1*), and CH_2F_2(*10*) were taken from the literature. For CH_2ClF and CH_2Cl_2 it was experimentally measured, using techniques previously reported (*11*).

The viscosity data were fitted to a four-constant equation of the form:

$$\log \eta = A + B/T + CT + DT^2, \text{ where } T = {}^\circ\text{K}$$

The constants for the various liquids are given in Table IV. The fit of the data is shown in Table V, along with the standard deviation and 99% confidence limits.

COMPARISON OF DATA

No liquid viscosity data could be found in the literature for CF_3H, CH_2ClF, or CH_2F_2.

The data for $CHCl_3$ agree reasonably well with those given in the International Critical Tables (*8*). A comparison is shown in Figure 2.

Our results on $CHCl_2F$ are intermediate between those of Benning and Markwood (*2*) and Kinser (*9*) (Figure 3).

Our results on $CHClF_2$ are in fair agreement with the recent data of Gordan (*7*), both of which are considerably lower than those of Benning and Markwood (*2*). Kinser's results deviate considerably from ours at higher temperatures (Figure 4).

Figure 5 compares available data with our data on methylene chloride. Agreement with Timmermans' (*12*) data is good, but below that reported by Dow (*5*).

NOMENCLATURE

C = viscometer constant, centistokes per sec
D = capillary diameter, cm
E = kinetic energy factor, centistokes × $(\text{sec})^2$
g = acceleration due to gravity, cm. per $(\text{sec})^2$
ΔH = differential liquid head, cm
L = capillary length, cm
r_1 = radius of meniscus, efflux bulb, cm
r_2 = radius of meniscus, capillary end, cm
t = efflux time, sec
V = efflux volume, cc
$(X_1 - X_2)$ = average liquid head, cm

Greek Letters

γ_1 = surface tension of diethyl ether, dynes per cm
γ_2 = surface tension of unknown liquid, dynes per cm
η = absolute viscosity, centipoises
ν = kinematic viscosity, centistokes
ρ = density, grams per cc

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