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0	pure component
s	solid
vap	vaporization
∞	infinite

Registry No. CO_2, 124-38-9; $CH_3(CH_2)_{14}COOH$, 57-10-3; $CH_3(CH_2)_{14}CH_2OH$, 36653-82-4.

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Viscosity and Density of Some Lower Alkyl Chlorides and Bromides

W. M. Rutherford

Monsanto Research Corporation,[†] *Mound, Miamisburg, Ohio 45342*

A high-pressure capillary viscometer, used previously to measure the viscosity of methyl chloride [*J. Chem. Eng. Data* 1984, *29*, 163], was rebuilt to eliminate the first-order dependence of the measured viscosity on the value assumed for the density of the fluid being investigated. At the same time, the system was arranged so that part of the apparatus could be used to measure density by a volumetric displacement technique. Viscosity and density were measured for ethyl chloride, 1-chloropropane, 1-chlorobutane, methyl bromide, ethyl bromide, and 1-bromopropane. The temperature and pressure ranges of the experiments were 20–150 °C and 0.27–6.99 MPa, respectively. The accuracy of the viscosity measurements was estimated to be ±1% and of the density measurements, ±0.2%.

Introduction

A previous paper described the construction and calibration of a high-pressure capillary viscometer and its use to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C (*1*). The viscometer was a device of moderate precision, calibrated with respect to the known viscosity of helium at 25 °C.

Volumetric flow in the original device was established by piston displacement of the working fluid at a temperature of 25 °C. In order to derive the viscosity from the observed data, it was necessary to know the change in density of the fluid between pump temperature and the temperature of the viscosity measurement. For many compounds these data are not available in the temperature ranges of interest.

The viscometer was rebuilt, therefore, to eliminate the first-order dependence of the measured value on the density of the fluid. At the same time, the system was arranged so that part of the apparatus could be used to measure density.

This paper describes the revised viscometer and its use for measurement of the viscosity and density of ethyl chloride, 1-chloropropane, 1-chlorobutane, methyl bromide, ethyl bromide, and 1-bromopropane.

Apparatus

The apparatus (Figure 1) is a steady flow capillary device similar to the one described previously. Volumetric flow in the revised apparatus is established by displacement with mercury at the temperature of the viscosity measurement. The mercury in turn is displaced at 25 °C by the coupled movement of two identical piston syringe pumps driven by a synchronous motor through an adjustable gear train.

With this arrangement it is no longer necessary to know the density of the fluid as a function of temperature in order to calculate the volumetric flow rate through the capillary. The volumetric flow rate can now be established by using well-known density values for mercury.

The mercury displacement technique has the further advantage that heat transfer to mercury-filled lines is rapid. This reduces possible errors in volumetric flow rate resulting from incomplete temperature equilibration of the fluid as it passes from the pump thermostat to the capillary thermostat.

The apparatus can also be used for density measurements. To measure density, the inlet valve to the capillary is closed, and a known volume of fluid is displaced by mercury at constant pressure into an evacuated weighing bottle. The displaced volume is determined by counting turns of the precision lead screw on the mercury pump, and an appropriate correction is made for the temperature difference between the two thermostats.

As in the previous work viscosities were calculated from the modified Poiseuille equation. Thus, the viscosity η is given by

$$\eta = \eta_p - mX \quad (1)$$

where

$$\eta_p = \pi a^4 \Delta p / (8QL_{\mathrm{eff}}) \quad (2)$$

$$X = \rho Q / (8L_{\mathrm{eff}}) \quad (3)$$

[†] Mound is operated for the U.S. Department of Energy under Contract No. DE-AC04-76-DP00053.

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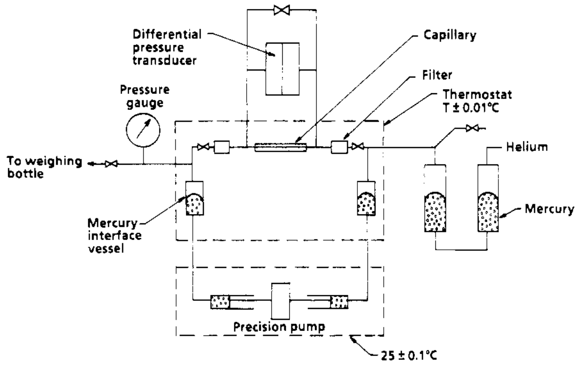

Figure 1. Experimental viscometer.

Table I. Calibration of Experimental Viscometer with Helium at 25 °C and 0.444 MPa

capillary	length, mm	$10^{16}a^4/L_{\text{eff}}$, m^3	compound
1	167.69	1.4737	ethyl chloride
2	169.55	1.4947	1-chloropropane
		1.5163	1-chlorobutane
		1.4870	ethyl bromide
3	149.90	6.5253	1-bromopropane
		6.5710	methyl bromide
		6.4532	methyl bromide

and where a is the radius of the capillary, L_{eff} is the effective length of the capillary, Δp is the pressure drop, and Q is the volumetric flow rate.

According to Kestin, Sokolov, and Wakeham (*2*), the inlet correction factor m is a function of Reynolds number and is given with adequate accuracy in the range $2 < \text{Re} < 200$ by

$$m = 1.17 + 11.04/\text{Re} \qquad (4)$$

Calibration

The apparatus was calibrated with compressed helium gas at 0.444 MPa and 25 °C. The reference value of 19.583 μPa·s was taken from the work of Kestin, Ro, and Wakeham (*3*). Reduction of the calibration data yielded the viscometer constant

$$C = a^4/L_{\text{eff}} \qquad (5)$$

Three capillaries were used in this work. Capillaries 1 and 2 were stainless steel with a nominal i.d. of 0.005 in. (0.127 mm). Capillary 3 was fused silica with a nominal i.d. of 0.2 mm. Capillary 1 was used for ethyl chloride, capillary 2 for 1-chloropropane, 1-chlorobutane, and ethyl bromide. Capillary 3 was used for methyl bromide and 1-bromopropane.

Results of the calibrations are given in Table I. The viscometer was thoroughly cleaned, reconditioned, and recalibrated for each compound. As evident in Table I, this process resulted in shifts of as much as ±1% in the viscometer constant. Within a given series of measurements, however, the capillary constant and the measured viscosity were reproducible to ±0.25% or less. The methyl bromide measurements were interrupted by equipment problems that required disassembly and cleaning of the apparatus. After the incident, which led to a shift of the capillary constant, repeat measurements at two temperatures yielded viscosity values that differed by no more than 0.3% from previous results. Shifts in the calibration constant could have resulted from several factors. The most likely causes are corrosion of the capillary or deposition of solids in the capillary during prolonged periods when the equipment was not in use, followed by possibly incomplete or ineffective cleaning procedures. The calibration constant was quite stable (typically ±0.2%) during each series of measurements lasting a few days, and the changes in calibration were usually encountered upon activating the apparatus after long period of disuse. Inasmuch as the constant was stable during the periods when measurements were taken, the accuracy of the results should not have been significantly affected by the changes.

Table II. Measured Density and Viscosity of Alkyl Chlorides

compound	t, °C	p, MPa	ρ, kg·m^{-3}	η, mPa·s
ethyl chloride	20	0.267	896.6	0.2517
		4.994	902.6	0.2598
	40	0.409	865.1	0.2104
		4.998	873.4	0.2181
	60	0.617	833.1	0.1775
		4.994	842.9	0.1849
	90	1.132	778.7	0.1380
		4.994	791.9	0.1444
	120	1.867	714.8	0.1063
		4.994	732.9	0.1124
	150	3.101	634.3	0.0789
		4.997	657.4	0.0845
1-chloropropane	20	0.274	893.7	0.3546
		4.994	898.9	0.3670
	40	0.274	867.3	0.2934
		4.994	874.6	0.3501
	60	0.274	841.6	0.2451
		4.994	848.9	0.2561
	90	0.467	798.6	0.1896
		4.994	808.7	0.1987
	120	0.946	752.8	0.1498
		4.994	765.5	0.1581
	150	1.536	699.6	0.1156
		4.994	715.5	0.1241
1-chlorobutane	20	0.274	888.7	0.4528
		4.994	892.3	0.4691
	40	0.274	865.7	0.3669
		4.994	871.8	0.3842
	60	0.274	842.7	0.3104
		4.994	849.1	0.3230
	90	0.274	806.4	0.2379
		4.994	814.9	0.2498
	120	0.398	767.4	0.1902
		4.994	778.7	0.2013
	150	0.674	726.1	0.1515
		4.994	738.8	0.1605

Viscosity and Density Measurements

Viscosity and density were measured for ethyl chloride, 1-chloropropane, and 1-chlorobutane at six temperatures in the range from 20 to 150 °C. Measurements were completed at two pressures, one slightly above the bubble point and one at a constant pressure of 4.99 MPa. The results are given in Table II.

Viscosity and density measurements for methyl bromide, ethyl bromide, and 1-bromopropane were restricted to lower temperatures. Ethyl bromide and 1-bromopropane were found to attack the stainless steel components of the viscometer at 150 °C, and methyl bromide caused problems at 120 °C. The upper pressure for ethyl bromide and 1-bromopropane was 4.99 MPa and for methyl bromide, 6.99 MPa. Results for the bromides are reported in Table III.

Repeatability of the viscosity measurements was on the order of ±0.2%, and the estimated accuracy of the results is ±1%. Reynolds numbers for the experiments were in the range from 6 to 170, and the associated inlet corrections were 0.1–0.9% of the measured viscosity. Repeatability of the density measurements was on the order of ±0.1% and the corresponding estimated accuracy of the data is ±0.2%.

Viscosity and density values at the bubble point were evaluated by a short extrapolation of the experimental data. These results are reported in Table IV and Figures 2 and 3. Figure 2 is a plot of the viscosity of the alkyl chlorides, and Figure 3 is the corresponding plot for the alkyl bromides.

Table III. Measured Density and Viscosity of Alkyl Bromides

compound	t, °C	p, MPa	ρ, kg·m^{-3}	η, mPa·s
methyl bromide	20	0.793	1678.5	0.3171
		6.993	1696.0	0.3280
	40	0.793	1624.0	0.2678
		6.993	1642.9	0.2786
	60	0.965	1565.0	0.2302
		6.993	1584.7	0.2401
	90	1.477	1468.9	0.1866
		6.993	1495.2	0.1939
ethyl bromide	20	0.274	1462.7	0.3964
		4.994	1429.6	0.4075
	40	0.274	1421.3	0.3309
		4.994	1429.6	0.3415
	60	0.274	1378.8	0.2787
		4.994	1387.4	0.2874
	90	0.536	1309.0	0.2209
		4.994	1322.7	0.2288
	120	1.053	1233.5	0.1765
		4.994	1252.5	0.1843
1-bromopropane	20	0.270	1354.7	0.5225
		4.994	1362.1	0.5399
	40	0.270	1320.6	0.4281
		4.994	1330.4	0.4420
	60	0.270	1283.5	0.3574
		4.994	1295.7	0.3712
	90	0.270	1228.7	0.2813
		4.994	1242.8	0.2925
	120	0.616	1171.8	0.2272
		4.994	1187.1	0.2374

Table IV. Viscosity and Density of Alkyl Halides at Saturation

compound	t, °C	ρ, kg·m^{-3}	η, mPa·s
ethyl chloride	20	896.4	0.2515
	40	864.8	0.2101
	60	832.7	0.1772
	90	778.1	0.1377
	120	714.3	0.1061
	150	633.6	0.0787
1-chloropropane	20	893.4	0.3540
	40	867.0	0.2929
	60	841.4	0.2448
	90	798.4	0.1894
	120	752.1	0.1493
	150	698.6	0.1151
1-chlorobutane	20	888.5	0.4519
	40	865.4	0.3660
	60	842.4	0.3098
	90	806.2	0.2376
	120	767.2	0.1900
	150	725.8	0.1513
methyl bromide	20	1676.8	0.3160
	40	1622.7	0.2671
	60	1564.1	0.2297
	90	1467.2	0.1861
ethyl bromide	20	1462.3	0.3959
	40	1421.0	0.3305
	60	1378.7	0.2786
	90	1308.8	0.2208
	120	1232.7	0.1762
1-bromopropane	20	1354.3	0.5216
	40	1320.1	0.4274
	60	1283.0	0.3568
	90	1228.4	0.2811
	120	1171.2	0.2268

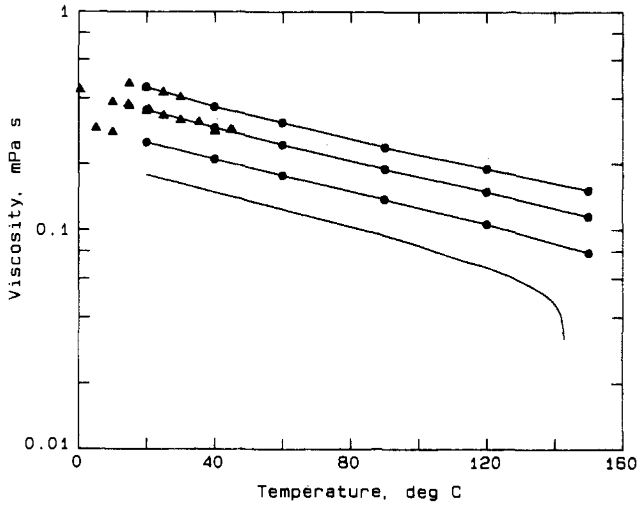

Figure 2. Viscosity of the alkyl chlorides at saturation. The curves represent, in ascending order, the data for methyl chloride, ethyl chloride, 1-chloropropane, and 1-chlorobutane. The filled circles are data from this investigation; the filled triangles are from the literature (*4*–*10*). The methyl chloride curve is taken from ref *1*.

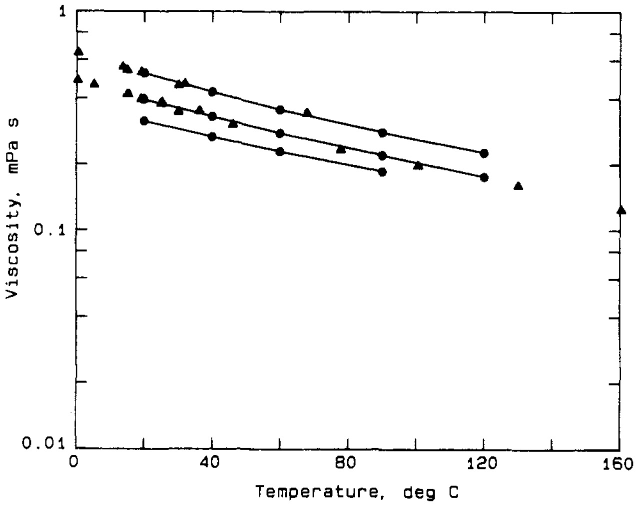

Figure 3. Viscosity of the alkyl bromides at saturation. The curves represent, in ascending order, the data for methyl bromide, ethyl bromide, and 1-bromopropane. The filled circles are data from this investigation; the filled triangles are from the literature (*4*–*10*).

Table V. Parameters for the Modified Rackett Equation

compound	Z_{RA}	T_c, K	p_c, atm	av % dev
ethyl chloride	0.266 67	460.4	52.0	0.09
1-chloropropane	0.268 27	503.2	45.2	0.07
1-chlorobutane	0.260 35	542.2	36.4	0.22
methyl bromide	0.304 42	464.0	83.4	0.33
			75.0	0.09
ethyl bromide	0.291 29	503.8	61.5	0.34
1-bromopropane	0.291 98	544.4	53.2	0.44

Also plotted in Figures 2 and 3 are viscosity values from the literature (*4*–*11*). For the most part these are restricted to temperatures below 40 °C. With a few exceptions, the agreement seems to be quite good.

Interpolated values of the density at saturation were compared with 17 values reported in the literature for the six compounds (*4*–*11*). The literature values were in the temperature range from 20 to 30 °C. The average deviation of the density was found to be +0.082% with a maximum deviation of 0.21%. Thus the results of this investigation appear to have a slight positive bias relative to those reported by other workers.

The density data of Table IV were successfully correlated by using the modified Rackett equation of Spencer and Adler (*12*)

$$1/\rho = (RT_c/p_c)Z_{RA}[1 + (1 - T_R)^{2/7}] \qquad (6)$$

where ρ is the density, g/cm^3, R the gas constant, (cm^3·atm)/(g·mol), T_c the critical temperature, K, p_c the critical pressure, atm, Z_{RA} an empirical constant, and T_r the reduced temperature. The quantity Z_{RA} was selected for each compound to give the best fit to the experimental data. The critical parameters, Z_{RA}, and the resulting average deviations of the calculated densities are given in Table V. Critical parameters were taken from Reid, Sherwood, and Prausnitz (*13*). Those not given in ref *13* were calculated by using Lydersen's method. Note that a reduction of p_c for methyl bromide from 83.4 to 75 atm results in a marked improvement in the fit. The 83.4 atm value is calculated from Lydersen's method. There appears to be no experimental vapor pressure data upon which to base a better estimate of the critical pressure. Published values of the vapor pressure of methyl bromide above the normal boiling temperature appear to have been obtained by extrapolation of the low-temperature data of Egan and Kemp (*14*).

The density of 1-chlorobutane at 25 °C was found to be slightly high (+0.21%) relative to the results of other workers (*11*). This can be accounted for by the presence of 0.6–0.7% of dichlorobutanes in the sample.

Materials

Ethyl chloride and methyl bromide purchased from the Matheson Co. were stated to have purities of 99.7 and 99.5%, respectively. 1-Chloropropane, 1-chlorobutane, and 1-bromopropane were purchased from MCB Manufacturing Chemists. Ethyl bromide from Fisher Scientific Co. was purified by liquid-phase thermal diffusion. A gas chromatographic analysis of 1-choropropane showed that it contained 0.4% 2-chloropropane and no other detectable impurities. A similar analysis of 1-bromopropane indicated that the sample was 99.6% 1-bromopropane. There were no detectable impurities in the purified ethyl bromide sample (sensitivity: 0.01 area %).

Registry No. 1-Chloropropane, 540-54-5; 1-chlorobutane, 109-69-3; methyl bromide, 74-83-9; ethyl bromide, 74-96-4; 1-bromopropane, 106-94-5.

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Isobaric Vapor–Liquid Equilibrium of 2,2,2-Trifluoroethanol with Water and 1-Propanol Binary Systems

Roger Jadot* and Mustapha Fralha

Department of Chemistry, Faculte Polytechnique de Mons, 7000 Mons, Belgium

Liquid–vapor equilibrium data of two binary systems containing 2,2,2-trifluoroethanol with water and 1-propanol are reported. The results are correlated by Van Laar, Wilson, and NRTL equations. The excess Gibbs energies of the two binary systems are compared to those of ethanol with the same components.

Introduction

Organic fluorocarbons and their water mixtures have been identified and proposed for use in Rankine engines for various terrestrial and space applications (*1*).

Among those, pure trifluoroethanol, commercially called fluorinol, and its water mixtures, have been selected and subjected to extensive dynamic testing for thermal stability (*2*). Unfortunately, thermodynamical properties and liquid–vapor equilibrium data for trifluoroethanol and its water mixtures are scarce.

The development of prediction methods such ASOG or UNIFAC requires data on some representative binary systems. In this paper isobaric liquid–vapor equilibrium data of two binary systems, trifluoroethanol and water and 1-propanol, are reported. The data are correlated by the Van Laar, Wilson, and NRTL equations.

Table I. Physical Properties of Compounds[a]

	water	fluorinol	1-propanol
T_{nb}, °C	100	73.94[c]	97.30[c]
A	7.9668	6.84069[d]	7.9973[b]
B	1668.21	952.466[d]	1569.70[b]
C	228.00	166.587[d]	209.50[b]
N_D	1.3333	<1.3000[c]	1.3850[c]
v_{25}	18.00	72.25[c]	74.75[c]

[a] A, B, and C are the Antoine constants of $\log P = A - B/(C + t)$, P in Torr, t in °C. v_{25} is the molar volume in cm^3/mol at 25 °C. [b] Reference *4*. [c] This work. [d] Reference *3*.

Experimental Section

***Purity of Materials*.** All chemicals are commercially available. The trifluoroethanol was employed without further purification after gas chromatographic analysis failed to show any significant impurities. The other components were distilled twice. The propanol was dried on molecular sieve 3 Å. The main physical properties of the three components are shown in Table I.

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