Viscosity of the Saturated Liquid Phase of Six Halogenated Compounds and Three Mixtures

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Data are reported for the viscosity of six saturated liquids and three mixtures of these liquids over a temperature range from 250 to 330 K. The liquids studied are the halogenated compounds 1,1,1,2 tetrafluoroethane (R134a), bis(difluoromethyl) ether (RE134), 2-(difluoromethoxy)-1,1,1-trifluoroethane (RE245), pentafluoroethane (R125), 1-chloro-1,2,2,2-tetrafluoroethane (R124), and difluoromethane (R32). The mixtures studied are R125 + R134a, R32 + R134a, and R32 + R124, all at approximately 50% mole fraction. A capillary viscometer constructed of stainless steel and sapphire was used to obtain the data. The measurements are accurate to 3-5% of the kinematic viscosity. A free volume model of viscosity was used to correlate the data.

We report the viscosity of the saturated liquid phase of six halogenated ethanes, methanes, and ethers proposed as refrigerants. The chemical names, and the engineering names in parentheses, of the measured compounds are 1,1,1,2-tetrafluoroethane (R134a), bis(difluoromethyl) ether (RE134), 2-(difluoromethoxy)-1,1,1-trifluoroethane (RE245), pentafluoroethane (R125), 1-chloro-1,2,2,2-tetrafluoroethane (R124), and difluoromethane (R32).

Various mixtures have been proposed as working fluids to replace traditional refrigerant compounds or azeotropes (*1*), and this has motivated us to measure the viscosity of three mixtures of the above compounds: R125 + R134a, R32 + R134a, and R32 + R124, all at approximately 50% mole fraction. In particular, the mixture R32 + R134a has been proposed as a replacement for R22, for which no single, chlorine-free compound with acceptable physical properties has been discovered (*2, 3*). Additionally, the mixture data will be useful as a test of various theories for the viscosity of refrigerant mixtures (*4*).

The viscometer used to acquire the data has been described elsewhere (*5*). It is similar to an Ubbelhode capillary viscometer in design, and was constructed out of stainless steel with sapphire windows to withstand the high vapor pressures of the refrigerants. The measured data consist of data pairs of temperature, T, and the rate of fall, $\dot{h}$, of the liquid-vapor meniscus in the upper reservoir of the viscometer. The viscosity, η, is related to $\dot{h}$ through the working equation (*6*)

$$\frac{\eta}{\rho_l - \rho_v} = C_2\left[\frac{C_1}{\dot{h}} - m\frac{\rho_l}{\rho_l - \rho_v}\frac{A}{8\pi l}\dot{h}\right] \qquad (1)$$

where ρ_l and ρ_v are densities of the liquid and vapor phases, $A = 1.06\ \text{cm}^2$ is the cross section of the upper reservoir, and $l = 48$ cm is the length of the capillary. C_2 is an empirical correction factor for the curvature of the capillary (*7*):

$$C_2 = 1 - \left[1 - \left(\frac{11.6}{\kappa}\right)^{0.45}\right]^{1/0.45} \quad \text{for} \quad \kappa > 11.6$$

$$C_2 = 1 \quad \text{for} \quad \kappa \leq 11.6 \qquad (2)$$

$$\kappa = (Re)(d/D)^{1/2}$$

Table I. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for R134a

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
250.05	1365	6	0.3763
255.05	1350	7	0.3490
260.15	1335	9	0.3275
265.15	1320	11	0.3073
270.45	1303	13	0.2865
275.55	1286	16	0.2685
280.45	1269	18	0.2541
280.45	1269	18	0.2555
285.75	1251	22	0.2379
291.05	1233	26	0.2235
295.95	1214	30	0.2077
296.05	1214	30	0.2156
300.75	1196	35	0.1969
306.05	1175	41	0.1858

Table II. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for RE134

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
250.04	1502	1	0.5942
255.16	1489	2	0.5411
260.24	1476	2	0.5071
265.15	1464	3	0.4710
270.28	1450	4	0.4471
275.36	1437	5	0.4150
280.05	1424	6	0.3834
280.12	1424	6	0.3923
285.25	1409	7	0.3641
285.26	1409	7	0.3693
290.25	1395	8	0.3452
295.30	1381	10	0.3202
300.14	1368	11	0.3029
300.14	1368	11	0.3096
306.31	1349	14	0.2935
311.26	1334	16	0.2787
315.96	1320	19	0.2649
320.55	1305	22	0.2480

where Re is the Reynolds number, $d = 0.508$ mm is the diameter of the capillary bore, and $D = 15.1$ cm is the diameter of curvature for the capillary. The term proportional to m is a correction for inertial or kinetic energy effects. Simple theories give $m = 1$, but for glass viscometers, an empirical expression of $m = 0.037(Re^{1/2})$ has been used (*8*). We have chosen to use the empirical expression for the data in this paper. The maximum difference between these two models is equivalent to a 0.4% difference in η. The constant $C_1 = 2.50 \times 10^{-11}\ \text{m}^3/\text{s}^2$ was determined by calibrating the viscometer with liquids of known viscosity, including toluene, decane, methanol, and acetone at temperatures near 20 °C.

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Table III. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for RE245

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
250.00	1505	1	0.8562
250.35	1504	1	0.8366
255.05	1492	1	0.7783
260.75	1479	1	0.7117
265.25	1468	1	0.6604
270.25	1456	2	0.6159
275.55	1443	2	0.5717
280.75	1430	2	0.5286
285.35	1419	3	0.4981
290.15	1407	4	0.4692
294.35	1396	4	0.4452
294.95	1394	4	0.4407
296.85	1389	5	0.4346
299.75	1382	5	0.4152
304.95	1368	7	0.3914
309.95	1355	8	0.3695
315.85	1339	10	0.3450
320.75	1326	12	0.3280
325.75	1312	14	0.3115
331.65	1294	16	0.2908

Table IV. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for R125

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
250.05	1421	19	0.2876
253.85	1406	22	0.2710
260.25	1380	28	0.2480
261.35	1376	29	0.2453
270.15	1337	39	0.2175
270.20	1337	39	0.2189
270.35	1336	39	0.2170
279.15	1294	52	0.1908
280.55	1287	54	0.1877
280.75	1286	54	0.1877
290.35	1236	73	0.1629
291.05	1232	75	0.1625
292.15	1226	77	0.1555
300.85	1173	101	0.1401
301.95	1166	104	0.1378

Table V. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for R124

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
251.65	1490	4	0.4530
256.65	1477	6	0.4234
261.70	1463	7	0.3979
266.95	1449	8	0.3691
274.75	1427	11	0.3382
278.15	1417	12	0.3228
280.05	1412	13	0.3157
288.15	1387	17	0.2849
288.25	1387	17	0.2889
295.25	1365	22	0.2665
297.95	1357	24	0.2568
303.25	1339	28	0.2429
308.15	1322	32	0.2305
313.05	1305	37	0.2189

Table VI. Saturated Liquid Viscosity and Density of the Vapor and Liquid Phases for R32

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
250.90	1128	10	0.2010
259.60	1103	14	0.1833
264.65	1087	16	0.1720
269.20	1071	19	0.1639
273.20	1058	21	0.1566
278.22	1041	25	0.1489
281.37	1029	27	0.1422
283.22	1022	29	0.1402
288.20	1003	33	0.1321
293.20	982	38	0.1247

Table VII. Saturated Liquid Viscosity, Density of the Liquid and Vapor Phases, and Mole Fraction of R125 in the Liquid Phase for a Mixture of Molar Composition *x*R125 + (1 – *x*) R134a

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)	x
251.83	1396	13	0.3151	0.493
258.43	1374	17	0.2876	0.492
263.75	1356	20	0.2700	0.491
268.57	1338	24	0.2519	0.490
275.43	1312	30	0.2317	0.488
280.75	1292	35	0.2166	0.487
281.81	1287	36	0.2145	0.486
286.39	1268	41	0.2031	0.485
289.05	1257	44	0.1958	0.484
290.47	1251	46	0.1925	0.484
293.98	1236	51	0.1813	0.483
298.32	1216	58	0.1752	0.482
304.40	1188	68	0.1599	0.480
309.89	1161	79	0.1512	0.478
311.04	1155	82	0.1480	0.478

Table VIII. Saturated Liquid Viscosity, Density of the Liquid and Vapor Phases, and Mole Fraction of R32 in the Liquid Phase for a Mixture of Molar Composition *x*R32 + (1 – *x*) R134a

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)	x
252.05	1274	9	0.2632	0.495
257.95	1256	11	0.2438	0.494
263.55	1238	14	0.2321	0.493
268.75	1221	16	0.2160	0.492
273.65	1205	19	0.2049	0.490
275.45	1199	20	0.2032	0.490
280.85	1180	24	0.1950	0.488
282.85	1173	25	0.1857	0.488
286.35	1160	28	0.1777	0.487
288.95	1151	30	0.1763	0.486
290.35	1146	32	0.1682	0.485
290.35	1146	32	0.1713	0.485
294.15	1131	35	0.1644	0.484
297.75	1117	39	0.1535	0.483
304.55	1090	47	0.1458	0.481

Because the Reynolds number depends on viscosity, the working equation must be solved iteratively to obtain η.

The accuracy for kinematic viscosities greater than 1.7 × 10^{-7} m^2 s^{-1} is 3% (all errors are two standard deviations uncertainty level). For lower viscosities, corrections for inertial effects and for the slight curvature of the capillary become important. Because the corrections for these effects are not well known, the accuracy decreases to 5% at a kinematic viscosity of 1.2 × 10^{-7} m^2 s^{-1}, the lowest value in the present work.

To find η from eq 1, the densities of the liquid and vapor phases must be measured or estimated. The Carnahan–Starling–DeSantis (CSD) equation of state implemented in the computer program REFPROP was used to do this for both the pure fluids and the mixtures (*9*). The estimated accuracy in $\rho_l - \rho_v$ is 0.05% for R32, RE134, RE245, R134a, and R125, 0.2% for R124, 2.0% for R134a + R125, 0.1% for R32 + R134a, and 3.0% for R32 + R124. The errors for the R134a + R125 and R32 + R124 mixtures are large because there are no density measurements available for these mixtures.

As a check on the validity of the working equation at low viscosities, where the curvature and inertia corrections become large, the viscosity of liquid CO_2 was measured. IUPAC values for the densities (*10*) were used in eq 1. The difference between the measured η values and a correlation of literature data (*11*) ranged from –1.5% to 0% over a temperature range from 250 to 263 K. This is consistent with the 5% error estimate for the present viscometer.

The purity of the samples as quoted by the manufacturers was as follows: 99.98% for R134a, 99.9% for RE245, 99.96% for R124, 99.8% and 99.7% (two suppliers) for R125, and

Table IX. Saturated Liquid Viscosity, Density of the Liquid and Vapor Phases, and Mole Fraction of R32 in the Liquid Phase for a Mixture of Molar Composition xR32 + $(1 - x)$ R124

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)	x
252.29	1298	10	0.3045	0.485
258.41	1279	13	0.2850	0.483
263.73	1262	15	0.2676	0.481
268.54	1246	18	0.2492	0.479
275.53	1223	22	0.2300	0.476
280.79	1204	26	0.2205	0.473
281.91	1200	27	0.2126	0.472
286.40	1184	30	0.2048	0.470
288.87	1175	33	0.1955	0.468
290.41	1169	34	0.1955	0.468
294.61	1153	38	0.1835	0.465
297.86	1140	42	0.1748	0.463
306.89	1103	53	0.1575	0.457
310.09	1090	58	0.1530	0.455

Table X. Values of the Fitting Parameters for the Best Fit of Equation 3 to the Data[a]

liquid	B/(10^7 s·m^{-2})	ρ_0/(kg·m^{-3})	deviation/%
R134a	2.2868	1624.3	0.9
RE134	2.3215	1688.5	1.3
RE245	2.0867	1643.3	0.5
R125	2.4850	1776.4	0.8
R124	2.5139	1715.4	0.6
R32	2.3244	1489.5	0.4
R125 + R134a	2.4030	1715.3	0.7
R32 + R134a	2.3326	1608.0	1.2
R32 + R124	2.2467	1599.5	0.9

[a] The column labeled deviation gives the average root-mean-square deviation of the data from the fit, as a percentage of the viscosity.

99.98% for R32. The RE134 sample was analyzed by gas chromatography and was found to have a purity of 96.9%, with the major impurity being R143 (1,1,2-trifluoroethane) (*12*). The samples of R124, R125, R32, and all three mixtures were degassed by twice freezing the sample in liquid nitrogen and pumping off any volatile gases remaining. The data for R134a and RE134 are from samples that were not degassed. Tests on R124 and RE134 showed no sensitivity to degassing, to within our experimental precision of 1.5%. However, R32 before degassing gave poor reproducibility and generally higher values of viscosity. All of the R32 data listed are for a degassed sample.

Mixtures were prepared by distilling the component refrigerants sequentially into a 2.5-mL stainless steel transfer vessel held at liquid nitrogen temperature. Weighing of the vessel after each distillation gave the mass of each component. The whole sample was distilled into the evacuated viscometer after chilling the lower chamber of the viscometer to −40 °C.

For the mixtures, the vapor phase is rich in the more volatile component, and the liquid phase is slightly depleted of this component by an amount approximately proportional to the vapor phase volume. The CSD equation was used at each temperature to find the vapor- and liquid-phase mole fractions that match the overall sample density and mole fraction. Inaccuracy of the sample weight, uncertainty in the composition of residual vapor left in the transfer vessel after distillation, and inaccuracy of the CSD equation result in a total uncertainty for the liquid-phase mole fraction of ±0.006 for R134a + R125 and R32 + R124, and ±0.003 for R32 + R134a.

The temperature of the viscometer was controlled to ±50 by immersion in a thermostated bath. Measurement of the temperature was accurate to 0.2 K for all runs, except for RE134, R32, and the mixtures R134a + R125 and R32 + R124, which have temperatures accurate to 0.05 K.

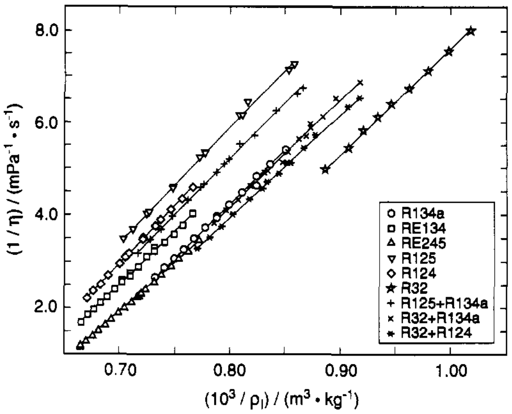

Figure 1. Reciprocal of the viscosity as a function of the reciprocal of the liquid density for nine liquid halogenated compounds and mixtures at the saturated vapor pressure. The straight lines show the parameterization of eq 3, with parameter values as listed in Table X.

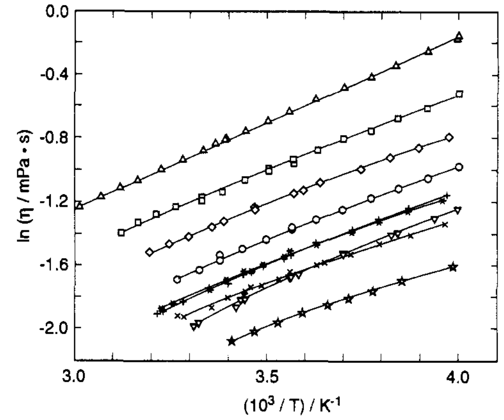

Figure 2. Viscosity versus temperature for nine liquid halogenated compounds and mixtures at the saturated vapor pressure. The lines show the parameterization of eq 3.

Tables I–IX list all of the results. The simple functional form

$$\frac{1}{\eta} = B\left(\frac{1}{\rho_l} - \frac{1}{\rho_0}\right) \tag{3}$$

has been fitted to the data values for η and T, where B and ρ_0 are fitted constants. The density of the liquid phase is a function of temperature along the saturation boundary, and this gives the temperature dependence of η. Diller et al. (*13, 14*) have demonstrated that, for pressures below a few megapascals, eq 3 describes compressed liquids as well as saturated liquids. Table X lists the parameters of the best-fit curves shown in the figures as well as the rms deviation of the data from the curves. The reciprocal of the viscosity is plotted versus the reciprocal of the density in Figure 1. The temperature dependence of the viscosity is shown in the Arrhenius plot in Figure 2. The curvature of the data indicates that a simple Arrhenius function,

$$\eta = a_1 \exp(a_2/T) \tag{4}$$

with a_1 and a_2 constants, does not fit the data well. Deviations of the data and selected data from the literature from the best-fit curves are shown in Figures 3 and 4. For R32, the data of Phillips and Murphy (*17*) have been recalculated using the densities of vapor and liquid phases from the CSD equation of state and assuming that Phillips and Murphy did not correct for the density of the vapor phase in their calculation of η.

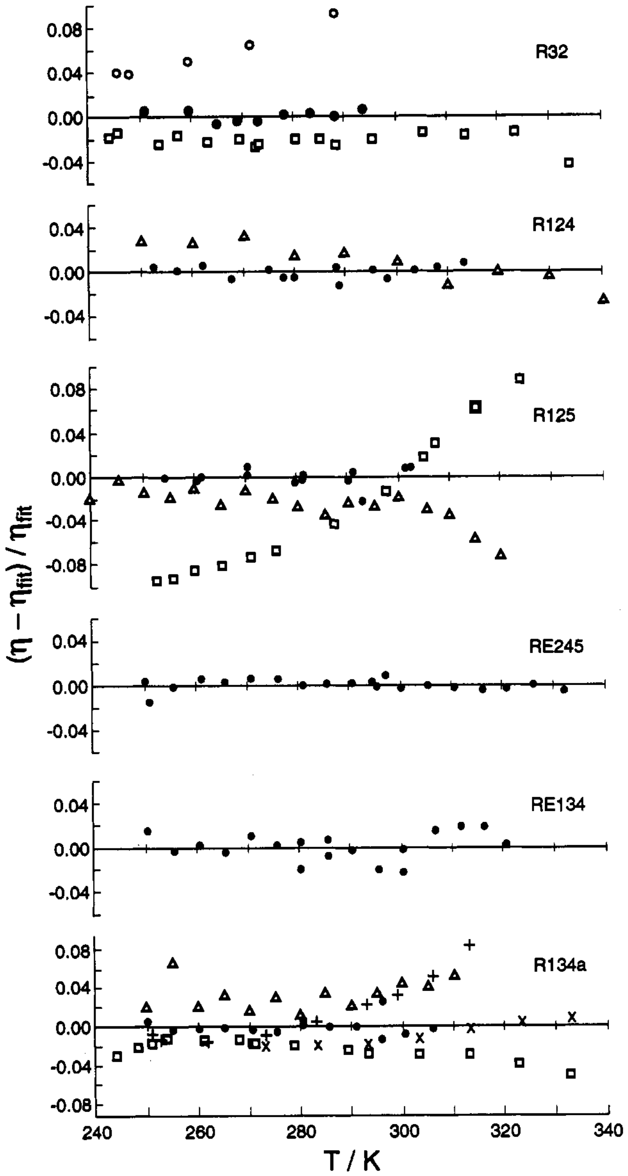

Figure 3. Deviations from the fit in Table X for the liquid viscosity of six saturated liquids. The filled circles are data for the present work, the data of Diller et al. (*13, 14*) are shown as triangles, the data of Kumagai and Takahashi (*15*) as crosses, the data of Shankland et al. (*16*) as plusses, the data of Phillips and Murphy (*17*) as circles, and the data of Oliveira and Wakeham (*18, 19*) as squares.

Viscosity values from the present work agree well with previously published values for R134a and R124, but there are discrepancies of up to 10% in comparing the present data with the data of Phillips and Murphy (*17*) for R32 and the data of Oliveira and Wakeham (*19*) for R125. The work of Phillips and Murphy has two significant problems: no correction was used for the curvature of the capillary in their viscometer, and for R32 in particular their density values disagree with presently accepted values. The cause of the disagreement for R125 is unknown.

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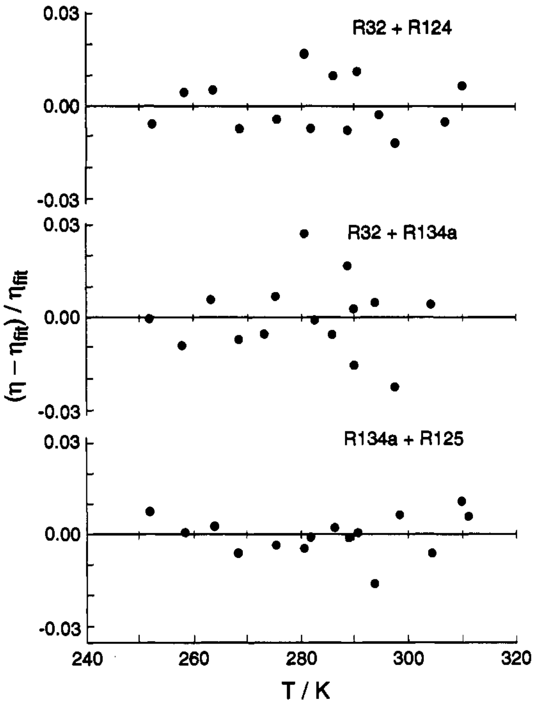

Figure 4. Deviations from the fit in Table X for the liquid viscosity of three mixtures at the saturated vapor pressure. The mole fraction of each of the three mixtures varies slightly with temperature, as listed in Tables VII–IX.

Glossary

A	cross sectional area of the viscometer reservoir
a_1, a_2	constants in the Arrhenius function of eq 4
B	constant in the parameterization for η, eq 3
C_1	calibration constant in eq 1
C_2	correction in eq 1 for capillary curvature
d	diameter of the capillary bore
D	diameter of curvature of the capillary
$\dot{h}$	rate of fall of the meniscus in the viscometer
l	length of the capillary
m	correction factor for the inertial term in eq 1
Re	Reynolds number $[(4A\dot{h}\rho_l)/(\pi\eta d)]$
T	temperature
x	mole fraction of the most volatile component of a mixture
η	viscosity
ρ_l,ρ_v	densities of the liquid and vapor phases
η_0	constant in the parameterization for η, eq 3

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