

Viscosities of HFC-32 and HFC-32/Lubricant Mixtures¹

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A modified capillary tube method has been used to measure viscosities for HFC-32 over a temperature range from -20 to 90°C and a pressure range from 0.1 to 5.3 MPa, and for the liquid mixtures of HFC-32 with a synthetic polyolester oil at temperatures from 20 to 75°C and oil mass fractions from 0.44 to 1 . Estimated uncertainties in the measured viscosities do not exceed ± 1.2 and $\pm 1.8\%$ for the pure fluocarbon and the mixtures, respectively. It is found that viscosity isotherms for HFC-32 at subcritical temperatures exhibit a minimum with increasing pressure, with the viscosity decreasing as much as 10% relative to its value at one atmosphere. Correlations are presented for dilute gas viscosities, excess viscosities, and saturated liquid and vapor viscosities. These correlations are shown to fit our data within experimental uncertainties. For HFC-32/lubricant mixtures, a free-volume viscosity model has been applied to correlate the experimental data.

KEY WORDS: capillary viscometer; free-volume model; lubricant oil; mixture; viscosity.

1. INTRODUCTION

Difluoromethane CH_2F_2 (HFC-32) is a chlorine-free compound that is one of the main components in refrigerant mixtures that are now proposed as replacements for the refrigerant HCFC-22. The application of these mixtures as working fluids in refrigeration and heat pump systems requires reliable transport property data for all the constituents. It is also especially important for the design of refrigeration compressors to have viscosities of

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mixtures with lubricant oil. Unfortunately, few experimental measurements of the viscosity of HFC-32 have been reported in the literature. Phillips and Murphy [1] have described an experimental study of saturated liquid viscosities over a temperature range from -73 to 14°C , Oliveira and Wakeham [2] have published the saturated liquid viscosity and the saturated vapor viscosity data of HFC-32 over a temperature range from -41 to 70°C and from -50 to 70°C , respectively, and Ripple and Matar [3] have reported the saturated liquid viscosity data of HFC-32 over a temperature range from -22 to 20°C . The goal of our work has been to measure HFC-32 viscosities for pure saturated liquid and vapor, as well as the dilute and dense gas, and to measure viscosities for mixtures of HFC-32 with a synthetic polyolester lubricant oil.

2. MEASUREMENTS

Viscosities were measured dangling the modified capillary tube method. A detailed description of the viscometer and the experimental procedure are given in an earlier paper [4]. The experimental technique involves creating a small pressure drop within a glass mercury pump that induces fluid flow through a capillary tube attached to the pump. The glass pump is placed inside a high-pressure vessel for measurements at elevated pressures. A special design feature of the pump provides for the return of mercury to its initial position after each experiment. Capillary tubes with inner diameters of 0.076 and 0.152 mm and a length of approximately 50 mm were used. Calibrations were performed to determine parameters such as the initial pressure drop, the final pressure drop, the volume of the fluid flow through the capillary during the experiment, etc. Viscosities were calculated taking into account corrections for capillary end effects, the thermal expansion of the capillary tube, and a kinetic energy factor. The sum of these corrections did not exceed 0.4% of the measured viscosity. The following additional assumptions were also made: (1) the fluid expands in the capillary tube; (2) fluid is compressed inside the pump during the experiment due to a decrease in the pressure drop associated with the decrease in the height of the mercury and (3) some energy dissipates to create the kinetic energy of fluid flow. As a consequence, an average value for the pressure drop, a density change due to the pressure change, and a change in the mass flow due to the pressure change have been employed.

The temperature was measured in our experiments to within ± 0.01 K dangling mercury thermometers, and pressure was measured to within ± 1 kPa with a digital pressure transducer.

The purity of HFC-32 samples was greater than 99.98%. All measurements of vapor-phase viscosities were carried out using a single

capillary tube but different pressure drops from 0.65 to 3.12 kPa, which correspond to *Reynolds* numbers from 10 to 1500. For liquid HFC-32 and for HFC-32/oil mixtures, the *Reynolds* numbers were between 250 and 500.

Samples of HFC-32/oil mixtures were prepared separately in a special mixing cell and then were charged into the viscometer. The final mixture composition was determined using our experimental vapor pressure–temperature data.

3. RESULTS

Experiments for pure HFC-32 were carried out over the temperature range -20 to 90°C and pressures from 0.1 to 5.3 MPa. For the HFC-32/oil mixtures, measurements were made at 20, 50, and 75°C over a range of oil mass fractions from 0.44 to 1. The synthetic polyolester oil used in these experiments has the following physical properties: molecular mass = $550\text{ kg}\cdot\text{kmol}^{-1}$; density at 40°C = $968.7\text{ kg}\cdot\text{m}^{-3}$; kinematic viscosity at 40°C = $24.4 \times 10^{-6}\text{ m}^2\cdot\text{s}^{-1}$.

The estimated experimental uncertainty in the pressure drop was $\pm 0.2\%$ and that in the flowrate was $\pm 0.4\%$. The estimated uncertainties in the viscosities did not exceed $\pm 1.2\%$ for pure HFC-32 and 1.8% for HFC-32/oil mixtures (95% confidence level). Each experiment was repeated at least 10 times at each temperature. Deviations from the average value of the viscosity calculated on the basis of these individual measurements at each temperature did not exceed $\pm 0.2\%$. The average viscosities are given in Tables I and II for pure HFC-32 and for HFC-32/oil mixtures, respectively.

4. DISCUSSION

4.1. Viscosity of Pure HFC-32

The comparison of the saturated-liquid viscosity data obtained in this work with the results of Oliveira and Wakeham [2] shows deviations lower than 1.5%. The saturated-liquid viscosity data reported by Ripple and Matar [3] differ from our measurements by 2.4–4.8%. Data of Phillips and Murphy [1] differ from our results by more than 20%. It should be noted that viscosity data [1] for the refrigerants such as HCFC-11, HCFC-12, HCFC-22, and HFC-152a also differ by 10–20% from the results published recently, for example, from data of Kumagai and Takahashi [5]. For the saturated-vapor viscosity, deviations between our data and the results from [2] do not exceed 10%.

Table I. Measured Viscosities for Pure HFC-32

Temperature (°C)	Pressure (MPa)	Density ($\text{kg} \cdot \text{m}^{-3}$)	Viscosity ($\mu\text{Pa} \cdot \text{s}$)
-20	0.451	1118	193.7
0	0.102	2.851	11.27
0	0.493	12.58	10.76
0	0.862	1053	150.8
15	0.100	2.695	11.95
15	0.510	12.10	11.54
15	1.002	26.11	11.25
20	1.526	979.2	119.0
30	0.101	2.546	12.56
30	0.506	11.26	12.22
30	0.508	11.32	12.20
30	1.013	24.25	11.88
30	1.511	39.53	11.65
30	1.734	47.60	11.68
40	2.521	894.4	93.1
45	0.101	2.464	13.22
45	0.509	10.67	12.84
45	1.020	22.71	12.59
45	1.539	36.75	12.58
45	1.829	45.69	12.36
45	2.452	69.16	12.86
60	0.101	2.339	13.98
60	0.515	10.23	13.62
60	1.014	21.12	13.35
60	1.513	33.24	13.25
60	2.398	58.97	13.11
60	2.948	79.45	13.60
60	3.544	109.3	14.77
60	3.986	774.8	71.7
70	4.925	682.8	60.8
74	5.427	625.4	57.0
75	0.101	2.212	14.55
75	0.503	9.502	14.28
75	1.053	20.76	14.03
75	1.563	32.18	13.88
75	1.908	40.55	13.90
75	2.470	55.63	14.16
75	3.049	73.63	14.38
75	3.385	85.58	14.72
75	3.844	104.5	15.39
75	4.418	136.4	16.90
75	4.997	182.8	19.32
90	0.100	2.142	15.14
90	0.508	9.143	14.92
90	1.015	18.90	14.86
90	1.547	29.89	14.80
90	2.069	41.60	14.82
90	3.561	81.99	15.36
90	5.050	141.1	17.64
90	5.149	146.3	17.89
90	5.270	152.9	18.21

Table II. Experimental Viscosity Data for HFC-32/Oil Mixtures

Pressure (MPa)	Oil mass fraction	Viscosity (mPa · s)
$t = 20^{\circ}\text{C}$		
1.474	0	0.1190
1.464	0.440	1.400
1.458	0.500	1.612
1.419	0.592	2.05
1.290	0.720	4.03
1.071	0.801	6.73
0.826	0.869	11.97
0.561	0.922	19.94
0	1	57.8
$t = 50^{\circ}\text{C}$		
3.142	0	0.0820
3.110	0.448	0.840
3.097	0.490	0.949
3.083	0.505	0.984
2.948	0.598	1.238
2.632	0.707	1.923
2.129	0.795	2.99
1.703	0.852	4.18
0.936	0.930	7.92
0	1	15.80
$t = 75^{\circ}\text{C}$		
5.427	0	0.0560
5.351	0.465	0.549
5.258	0.520	0.633
4.961	0.597	0.702
4.267	0.701	1.154
3.142	0.810	1.961
2.426	0.863	3.06
1.187	0.940	4.86
0	1	7.55

We paid particular attention in our experiments to viscosities in the single-phase, dense gas region at subcritical pressures along isotherms of 0, 15, 30, 45, 60, 75, and 90°C in order to determine the dependence of the viscosity on pressure; or equivalently the excess viscosity, $\mu - \mu_0$ (where μ_0 is the dilute gas viscosity), on density. A result of theoretical studies by Rainwater and Friend [6], and later by Bich and Vogel [7], based on the assumption that a pure gas at low density can be modeled as a mixture of monomers and dimers shows a temperature dependence in the excess viscosity. This result is in good agreement with the experiments for a number of gases, especially for highly associated fluids.

The results of our measurements of viscosities in the gas region are shown in Fig. 1. The densities were calculated dangling a Martin-Hou equation of state [8]. As indicated in Fig. 1, the measured viscosities along subcritical isotherms ($t_c = 78.4^\circ\text{C}$ for HFC-32) exhibit a local minimum when plotted against either the pressure or density. The slope of these isotherms is also more negative at the lower temperatures. Thus, at low pressures, the viscosity will initially decrease with increasing pressure before increasing monotonically with pressure at higher pressures.

The equation for the excess viscosity in this region should be presented as a function of both density and temperature. However, the temperature dependence is rather weak and may not be taken into consideration for practical use. Therefore, the following simplified equation for the excess

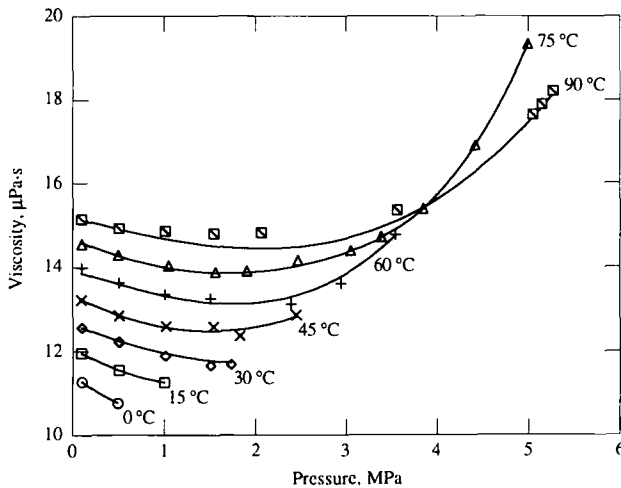


Fig. 1. HFC-32 viscosities as a function of pressure [solid curves are values calculated by Eq. (1)].

viscosity as a function of density has been obtained by regressing our experimental data:

$$\begin{aligned} \mu - \mu_0 = & 4.013 \times 10^{-2} \rho + 6.102 \times 10^{-4} \rho^2 - 1.724 \times 10^{-6} \rho^3 \\ & + 2.158 \times 10^{-9} \rho^4 - 9.074 \times 10^{-13} \rho^5 \end{aligned} \quad (1)$$

where $\mu_0 = 11.28 + 4.31 \times 10^{-2} t$; ρ is the density in $\text{kg} \cdot \text{m}^{-3}$; μ is in $\mu\text{Pa} \cdot \text{s}$; and t is in $^{\circ}\text{C}$.

Deviations between experimental excess viscosities and those calculated by Eq. (1) do not exceed 2.5%. Eq. (1) is valid within a temperature range from 0 to 100°C and a density range from 0 to $200 \text{ kg} \cdot \text{m}^{-3}$.

Saturated liquid and vapor viscosities can be calculated from the following equations:

$$\mu_{\text{sliq}} = 151.0 - 1.847t + 1.281 \times 10^{-2} t^2 - 6.830 \times 10^{-5} t^3 \quad (2)$$

$$\mu_{\text{svap}} = 10.82 + 3.757 \times 10^{-2} t - 1.097 \times 10^{-3} t^2 + 3.255 \times 10^{-5} t^3 \quad (3)$$

where μ is in $\mu\text{Pa} \cdot \text{s}$, and t is in $^{\circ}\text{C}$.

Equations (2) and (3) are valid within a temperature range from -20 to 75°C .

Viscosities for the superheated vapor over a temperature range of 0 – 100°C and a pressure range of 0.1 – 5 MPa , as well as for the saturated liquid and vapor, are given in Table III.

Table III. HFC-32 Viscosities ($\mu\text{Pa} \cdot \text{s}$) Calculated with Eqs. (1)–(3)

Temperature ($^{\circ}\text{C}$)	Pressure (MPa)							Saturated vapor	Saturated liquid
	0.1	0.5	1	2	3	4	5		
-20	10.42	—	—	—	—	—	—	10.07	193.6
-10	10.85	10.46	—	—	—	—	—	10.39	170.8
0	11.28	10.90	—	—	—	—	—	10.71	151.0
10	11.71	11.34	11.07	—	—	—	—	11.04	133.7
20	12.14	11.78	11.52	—	—	—	—	11.44	118.6
30	12.57	12.22	11.97	—	—	—	—	11.96	105.3
40	13.00	12.67	12.42	12.37	—	—	—	12.74	93.3
50	13.43	13.11	12.86	12.77	13.65	—	—	13.95	82.1
60	13.87	13.56	13.32	13.18	13.80	—	—	16.01	71.5
70	14.30	14.00	13.77	13.60	14.05	15.54	—	19.34	61.1
80	14.73	14.44	14.21	14.03	14.36	15.47	18.07	—	—
90	15.16	14.88	14.65	14.46	14.71	15.57	17.36	—	—
100	15.59	15.32	15.09	14.89	15.08	15.77	17.13	—	—

4.2. Viscosity of HFC-32/Oil Mixtures

The measured viscosities of HFC-32/oil mixtures were correlated by applying a free-volume model [9] in which the viscosity is related to the molar volume of the fluid by

$$\mu^{-1} = B(V - V_0)/V_0 \quad (4)$$

where V is the molar volume, V_0 is a hypothetical molar volume corresponding to the disappearance of molecular transport, and the coefficient B represents the capacity of the molecule to absorb externally imposed momentum.

This model has been applied to various pure liquids and liquid mixtures by several researchers. One of the most successful applications to liquid mixtures was described by Liu and Wang [10], who used the model with temperature-independent parameters. The average deviation for 60 binary mixtures, containing both nonpolar and polar components, was found to be less than 4%. We applied the following, similar mixing rules [10] to the HFC-32/oil binary mixtures,

$$V_{0,m} = \Sigma V_{0,i} x_i \quad (5)$$

$$\log B_m = \Sigma (\log B_i) \theta_i \quad (6)$$

where the subscripts m and i denote quantities for the mixture and the pure components, respectively, x_i is the mole fraction of component i and $\theta_i = x_i V_i / V_m$.

A comparison of calculated viscosities with our experimental data shows that the RMS deviation is approximately 7% and the maximum deviation is approximately 20%. This agreement is quite reasonable considering that the viscosities for pure HFC-32 and the oil differ by a factor of approximately 1000. Based on these results, we conclude that the free-volume model can provide satisfactory initial estimates of viscosities for HFC refrigerant/oil mixtures.

REFERENCES

1. T. W. Phillips and K. P. Murphy, *J. Chem. Eng. Data* **15**:304 (1970).
2. C. M. B. P. Oliveira and W. A. Wakeham, *Int. J. Thermophys.* **12**:105 (1991).
3. D. Ripple and O. Matar, *J. Chem. Eng. Data* **38**:560 (1993).
4. V. Z. Geller, M. E. Paulaitis, D. B. Bivens, and A. Yokozeki, in *Proc. Int. Conf. Energy Effic. Refrig. Global Warm. Impact* (Belgium, May, 1993), p. 227.
5. A. Kumagai and T. S. Takahashi, *Int. J. Thermophys.* **12**:105 (1991).

6. J. C. Rainwater and D. G. Friend, *Phys. Rev.* **A36**:4062 (1987).
7. E. Bich and E. Vogel, *Int. J. Thermophys.* **12**:27 (1991).
8. R. Singh, E. Lund, and I. Shankland, in *Proc. Int. CFC Halon Alt. Conf.* (Baltimore, December, 1991), p. 451.
9. J. H. Hildebrand, *Viscosity and Diffusivity* (Wiley, New York, 1977), pp. 15–29.
10. H. Liu and W. Wang., *Ind. Eng. Chem. Res.* **30**:1617 (1991).