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Liquid Viscosity of 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) along the Saturation Line

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Measurements of the viscosity of liquid 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) are reported over the temperature range 263.15 K to 343.15 K along the saturation line made with a calibrated capillary viscometer. An improved method was developed for calibrating the viscometer and measuring the viscosity. The uncertainty of the results is estimated to be no more than ±3%. The results were correlated as a function of temperature.

Introduction

The expected worldwide ban on many low-molar-mass chlorofluorocarbons has prompted a vigorous search for alternatives with zero ozone-depletion potential (ODP) and lower global-warming potential (GWP). HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) has zero ODP. It is a recently introduced, commercially available hydrofluorocarbon (HFC) useful in fire suppression, refrigeration, sterilization, and propellant applications. It can be used as an alternative to Halon, and blends containing HFC-227ea are potential alternatives to HCFC-22 and R502. Effective use of HFC-227ea requires that the thermodynamic and transport properties be accurately measured, but there is a very small amount of data available, especially for the transport properties. Wirbser et al. (1992) measured the specific heat capacity and Joule−Thomson coefficient of HFC-227ea. Robin (1994) listed the thermophysical properties of HFC-227ea including estimated transport properties based on experimental data of Salvi-Narkhede et al. (1992). Defibaugh and Moldover (1997) measured the P−V−T behavior and the saturated liquid density. Laesecke and Hafer (1998) measured the viscosity of HFC-227ea with a coiled capillary viscometer at low temperature and a straight capillary viscometer at high temperature. Huber et al. (1996) developed a database, REFPROP, to calculate the thermodynamic properties of refrigerants and refrigerant mixtures. It can provide the thermodynamic properties of HFC-227ea such as liquid density, vapor density, viscosity, etc.

In this paper, the viscosity of HFC-227ea was measured with a capillary viscometer at temperatures between 263.15 K and 343.15 K along the saturation line. The viscometer was precisely calibrated in order to reduce systematic uncertainty. The uncertainty of the results is estimated to be no more than ±3%. The results are used to correlate the viscosity as a function of temperature.

Instrumentation

The instrument used in this experiment and previous work (Han et al., 1995, and Sun et al., 1996) is shown in Figure 1.

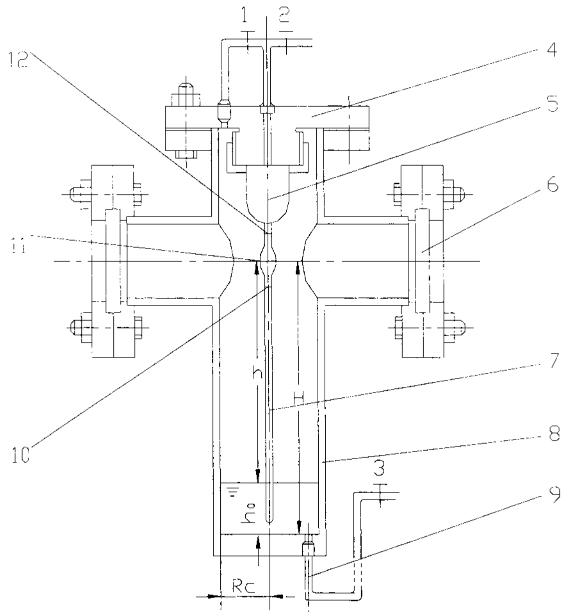

Figure 1. Instrument Schematic: (1) valve 1; (2) valve 2; (3) valve 3; (4) flange plate; (5) liquid storeroom; (6) observation window; (7) capillary; (8) pressure vessel; (9) liquid injection and discharging pipe; (10) mark 1; (11) liquid volume; (12) mark 2.

Three valves shown in Figure 1 are necessary for the experiment. Before the experiment, measured liquid is injected into the pressure vessel through valve 3. During experiment, valve 3 is always closed. Prior to each measurement, the liquid must be forced through the capillary to the upper volume above mark 2. When hoisting the height of the liquid surface in the capillary, valve1 is closed and valve 2 is open. The vapor in the capillary is connected with the atmosphere. When the saturation pressure in the pressure vessel is higher than 1 atm, the higher pressure in the pressure vessel can force the liquid into the capillary. When the saturation pressure in the pressure vessel is less than 1 atm, some instrument should be used to draw the liquid into the upper volume through the capillary. During each measurement, valve 2 is closed and valve 1 is opened, so the vapors in and out the capillary are connected. With the function of the weight, the liquid can flow down. After the experiment, valve 3 is used to let out the measured liquid.

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Operating Principles

The capillary viscometer is a classic method for measuring liquid viscosity. According to the Hagen−Posieuille principle, the fluid volume flow through the capillary is related to the pressure difference between the two ends of the capillary, the radius and length of the capillary, and the viscosity of the fluid by

$$\frac{Q}{t} = \frac{\pi R^4 \Delta P}{8\eta L} \tag{1}$$

Here, Q is the quantity of fluid flowing through the capillary for a given time t, R is the capillary radius, ΔP is the pressure difference between the two ends of the capillary, η is the fluid viscosity, and L is the capillary length. The effect of surface tension can be ignored because it is very small (Sun et al., 1996). Rewriting eq 1 in the following form can include the effect of local friction:

$$\eta = \frac{\pi(\rho_L - \rho_V)ghR^4}{8QL}t - \frac{\xi \rho_L Q}{8\pi L t} \tag{2}$$

Here ρ_L is the measured liquid density, ρ_V is the vapor density of the measured substance, g is the acceleration of gravity, h is the height difference between the fluid surface in the cell and the fluid surface in the capillary, and ξ is the local friction coefficient. Equation 2 can be rewritten as

$$\nu = kAt - B/t \tag{3}$$

where

$$k = \frac{\rho_L - \rho_V}{\rho_L} \tag{4}$$

$$A = \frac{\pi g h R^4}{8QL} \tag{5}$$

$$B = \frac{\xi \rho_L Q}{8\pi L} \tag{6}$$

A and B are irrelative with temperature, while k generally decreases when the temperature increases.

Since the viscosity of refrigerants is very small, a stock capillary viscometer cannot be used to measure the viscosity. Two stratagies can be used to obtain the desired conditions (Re < 2000) and yet keep the flowing time sufficiently long to reduce measurement uncertainty: either reduce the capillary radius or extend the capillary length or both. However, the length cannot be very long, otherwise the instrument would be too large, so the radius must be reduced. For a Reynolds number defined as

$$\mathrm{Re} = \frac{2RU}{\nu} \tag{7}$$

and Q defined as

$$Q = \pi R^2 U t \tag{8}$$

Here U is the velocity of the fluid in the capillary. Equation 3 can be rearranged as

$$4ghkR^3 - \mathrm{Re}^2 \nu^2 \xi R - 16 \mathrm{Re} \nu^2 L = 0 \tag{9}$$

The instrument used to measure the viscosity of HFC-227ea, Figure 1, had h = 98 mm, k = 0.9, L = 154 mm, and ξ = 0.5. The relation between R and ν is shown in Figure 2. For Re = 2000 and ν = 0.1 mm^2/s, which is expected to be the common viscosity of refrigerant, R must be less than 0.25 mm. In this work, the capillary radius R was calibrated with mercury to be 0.110 mm.

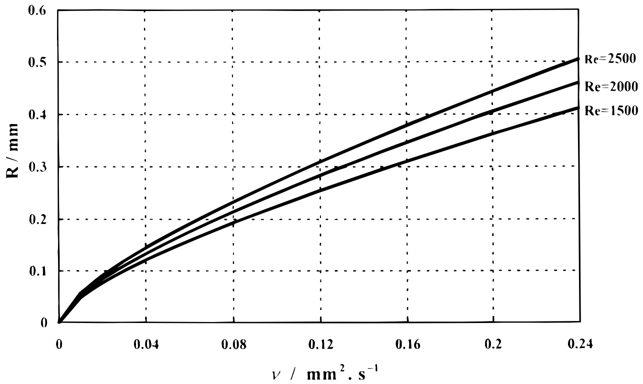

Figure 2. Selection of capillary radius using physical and geometive properties.

According to eq 5, A is proportional to h, which is related to the volume of the test liquid. However, A cannot be treated as a constant because of temperature and mass variations. Sun et al. (1996) proposed a method to modify A at different temperatures by using the following equation:

$$A = \frac{A_1}{h_1}(H - h_0) = \frac{A_2}{h_2}(H - h_0) \tag{10}$$

Here A_1 and A_2 are the calibration results using two different liquid volumes, V_1 (200 cm^3) and V_2 (250 cm^3), and h_2 can be obtained from V_1, V_2, and the cell radius R_c using

$$A_1/A_2 = h_1/h_2 \tag{11}$$

$$h_1 - h_2 = \frac{V_1 - V_2}{\pi {R_c}^2} \tag{12}$$

H is a constant of the instrument that can be determined from

$$H = h_1 + \frac{V_1}{\pi {R_c}^2} = h_2 + \frac{V_2}{\pi {R_c}^2} \tag{13}$$

h_0 is the liquid surface height in the cell that can be determined from

$$m = \rho_L V_L + \rho_V V_V \tag{14}$$

$$V = V_L + V_V \tag{15}$$

$$h_0 = \frac{V_L}{\pi {R_c}^2} \tag{16}$$

Here m is the experimental fluid mass, V is the cell volume, V_L and V_V are the volumes of saturated liquid and saturated vapor, and ρ_L and ρ_V are the saturated liquid and saturated vapor densities.

During experiments, some vapor must be vented and the mass in the cell changes. Since the viscosity at a fixed temperature must be constant, the volume of vented vapor

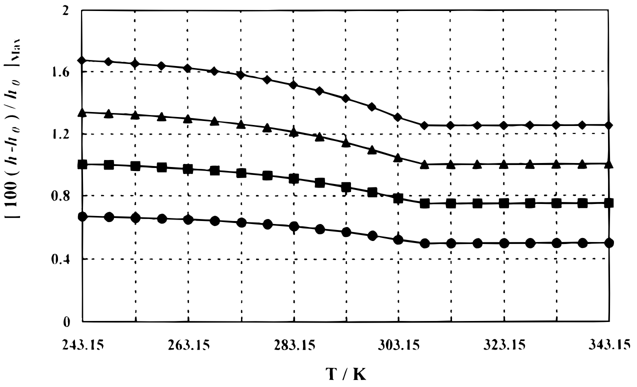

Figure 3. Greatest uncertainty estimated from different initial temperature with different venting vapor volumes δV: (●) 2 cm^3; (■) 3 cm^3; (▲) 4 cm^3; (◆) 5 cm^3.

can be estimated by solving eqs 17−20 assuming that the vented volumes δV are constant.

$$m_2 = m_1 - \sum_{i}^{n} \rho_i \delta V \tag{17}$$

$$\nu_1 = A_1 t_1 - B_1/t_1 \tag{18}$$

$$\nu_2 = A_2 t_2 - B_2/t_2 \tag{19}$$

$$\nu_1 = \nu_2 \tag{20}$$

Here m_1 and m_2 are the mass of the fluid for the two measurements at the same temperature, n is the venting time between these two measurements, ρ_i is the fluid density, ν_1 and ν_2 are two measured viscosities of the fluid for the first time and the second time, t_1 and t_2 are two measured time for the first time and the second time, A_1, B_2, A_2, and B_2 are the constants with m_1 and m_2, respectively.

The best experimental sequence is to begin with high temperatures and then reduce the temperature. However, the experimental time would be very long because the high-temperature-controlled bath has no cooling system. Its thick insulating layer makes the heat transfer rate very low, especially when the temperature is close to the room temperature. A suitable initial experimental temperature was determined by analyzing the effect of different initial temperatures, with the same venting vapor volumes, on the height difference between the fluid surface in the cell and in the capillary. The greatest uncertainty caused by different initial temperatures with different venting vapor volumes is shown in Figure 3. The uncertainty caused by the initial temperature varies little when the venting vapor volume is the same. So 288.15 K was chosen as the initial temperature. The experimental temperature was increased from 288.15 K to 343.15 K. Later, the temperature was decreased from 288.15 K to 263.15 K.

Calibration

To get the values of A and B, the liquids alcohol, hexane, and acetone were used to calibrate the instrument. The calibrating volumes were 200 cm^3 and 250 cm^3; the calibrating temperature was 323.15 K. Because these liquids have a high critical temperature, the value of k can be set as 1.0.

The constant B embodies the effect of local friction. As the viscosity increases, the flow time will also increase so that the second term in eq 3 will become much less than the first term. For the calibrating liquids having high viscosities, which makes ϵ (defined by eq 21) less than 0.1%, the effect of local friction can be ignored. As discussed before, A can be obtained from eq 3. With $\xi = 0.037\text{Re}^{0.5}$ and eqs 5 and 6, B can be calculated from eq 22.

$$\epsilon = \frac{B/t}{kAt} \tag{21}$$

$$B = 0.0011746Q^{3/2}/(LR^{1/2}A^{1/2}t) \tag{22}$$

Table 1. Calibration Results of the Instrument

V_1 (cm^3)	H (cm)	h (cm)	Q (cm^3)	A ($\times 10^{10}$ m^2 s^{-2})
200	15.385	9.716	2.114	2.1579
250	15.385	8.298	2.114	1.8431

Table 2. Verification of the Instrument Calibration Results

V (cm^3)	liquid	ν_{ref} (mm s^{-1})	ν_{exp} (mm s^{-1})	100 × ($\nu_{\text{exp}} - \nu_{\text{ref}}$)/$\nu_{\text{ref}}$
200	alcohol	0.9187	0.9171	−0.17
	hexane	0.3629	0.3709	2.17
	acetone	0.3294	0.3247	−1.42
250	alcohol	0.9187	0.9178	−0.10
	hexane	0.3629	0.3697	1.84
	acetone	0.3294	0.3240	−1.63

Table 3. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for HFC-227ea

T (K)	ρ_l (kg cm^{-3})	ρ_v (kg cm^{-3})	η_{exp} (mPa s)	100 × ($\eta_{\text{exp}} - \eta_{\text{cal}}$)/$\eta_{\text{cal}}$
263.15	1522.56	10.95	0.4036	−0.09
268.15	1504.55	13.27	0.3738	−0.43
273.15	1486.18	15.95	0.3494	−0.01
278.15	1467.41	19.06	0.3284	0.88
283.15	1448.20	22.64	0.3052	0.57
288.15	1428.50	26.74	0.2829	−0.09
288.15	1428.50	26.74	0.2829	−0.10
293.15	1408.26	31.42	0.2643	−0.02
298.15	1387.44	36.75	0.2455	−0.52
303.15	1365.94	42.81	0.2289	−0.67
308.15	1343.70	49.69	0.2146	−0.24
313.15	1320.61	57.49	0.2010	0.09
318.15	1296.55	66.35	0.1876	0.14
323.15	1271.36	76.40	0.1752	0.27
328.15	1244.87	87.85	0.1631	0.20
333.15	1216.82	100.95	0.1523	0.46
338.15	1186.89	116.04	0.1411	0.08
343.15	1154.63	133.58	0.1304	−0.51

The calibrating results were listed in Table 1. The verification of the calibration results was listed in Table 2.

Results and Analysis

The viscosity of HFC-227ea was measured along the saturation line. The uncertainty of the temperature measurements was within ±10 mK, and thermal gradient of the bath used in the experiment was less than ±5 mK. The temperature range was 263.15 K to 343.15 K. Liquid densities were calculated using the equation provided by Defibaugh and Moldover (1997). The vapor densities were calculated using the Martin-Hou equation provided by Robin (1994). The mass purity of the HFC-227ea sample was 99.9%.

The experimental results listed in Table 3 were correlated as a function of temperature as follows:

$$\log(\eta/\text{mPa s}) = D + E/(T/\text{K}) + F(T/\text{K}) + G(T/\text{K})^2 \tag{23}$$

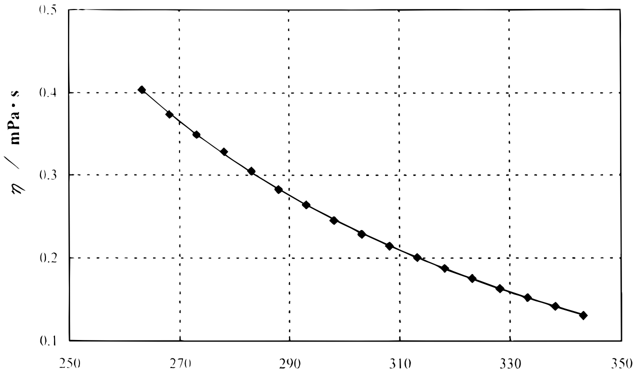

Figure 4. Viscosity of saturated liquid HFC-227ea.

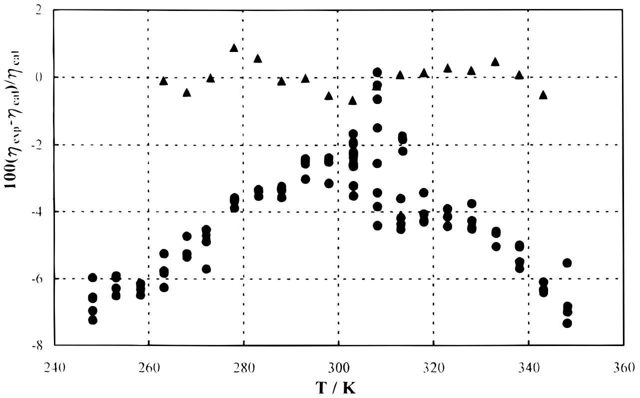

Figure 5. Relative deviations between the experimental data and correlation eq 23: (▲) this work; (▼) Laesecke and Hafer (1997).

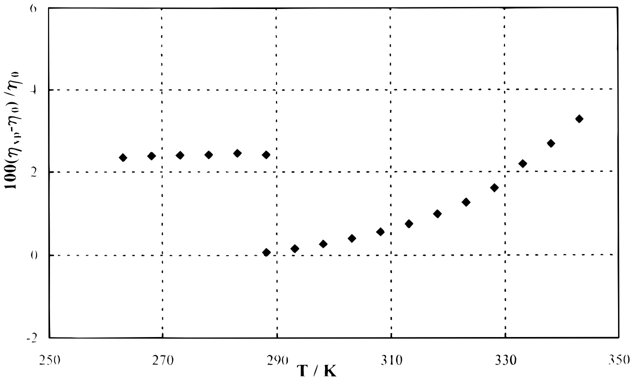

Figure 6. Estimated uncertainty caused by vapor venting.

where

$$D = -6.67316 \quad E = 7.84234 \times 10^{2}$$

$$F = -1.31035 \times 10^{-2} \quad G = 2.90379 \times 10^{-5}$$

Figure 4 shows the viscosity of HFC-227ea as a function of temperature. The standard deviation and the maximum relative deviation of the experimentally measured results from the prediction of eq 23 are 0.4% and 0.88%. Figure 5 show the deviations between the experimental data of different authors and correlation eq 23. The experimental viscosities of Laesecke and Hafer (1998) are less than the values reported here, and the maximum relative deviations shown in Figure 5 are less than ±8%. The estimated data of Robin (1994) are much less than the values reported here with a maximum relative deviation from eq 23 of about 40%.

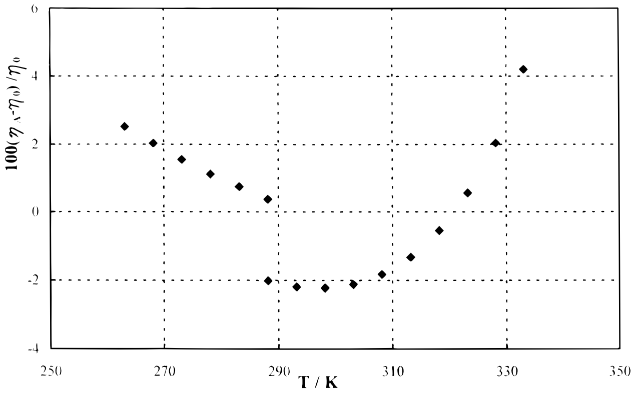

Figure 7. Estimated uncertainty when the coefficient *A* is regarded as a constant that is equal to the value when the liquid volume is 250 cm^3.

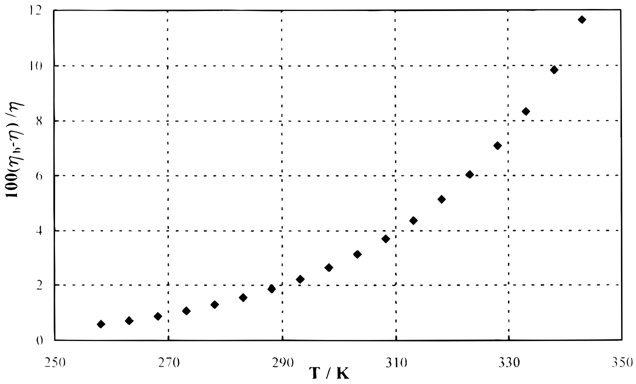

Figure 8. Uncertainty caused by the vapor buoyancy.

In this work, the venting volumes were about 5 cm^3 using the initial temperature (288.15 K). Measurements were made twice at every temperature point to avoid occasional error. Venting twice made the greatest uncertainty much greater than that show in Figure 3. The uncertainties caused by vapor venting at different temperatures in this work are shown in Figure 6. The estimated uncertainties arising from assuming that *A* is the constant value for the calibrating liquid volume of 250 cm^3 are shown in Figure 7. Because the experimental temperature is first increased and then decreased, there are sudden changes at the temperature of 288.15 K in the two figures. The two figures show that both corrections are necessary. Figure 8 shows the uncertainties caused by the vapor buoyancy.

Conclusion

An improved method was developed for measuring the viscosity of saturated liquids with a capillary viscometer. The viscosity of liquid HFC-227ea was measured over a wide temperature range with an uncertainty of less than ±3%.

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