

The Viscosity of Liquid R134a

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The paper reports new measurements of the viscosity of liquid R134a over the temperature range 235 to 343 K and pressures up to 50 MPa. The measurements have been carried out in a vibrating-wire viscometer calibrated with respect to the viscosity of several liquid hydrocarbons. It is estimated that the uncertainty in the viscosity data reported is $\pm 0.6\%$. The data therefore have a lower uncertainty than that of earlier measurements of the viscosity of this environmentally acceptable refrigerant. The viscosity data have been represented as a function of density by means of a formulation based upon the rigid, hard-sphere theory of dense fluids with a maximum deviation of $\pm 0.3\%$. This representation allows the present body of experimental data to be extended to regions of thermodynamic state not covered by the measurements.

KEY WORDS: high pressure; refrigerants; R134a; viscosity.

1. INTRODUCTION

R134a is now commercially available as an environmentally acceptable replacement refrigerant for domestic refrigeration. Nevertheless, there remains a considerable uncertainty with respect to its viscosity in the liquid phase as a result of several discordant and independent measurements [1]. More recent measurements [2] than those contained in the review of Stephan and Krauss [1] do provide support for some of the original results but have a claimed accuracy of only $\pm 3.0\%$. Thus, it is clear that further measurements of greater precision are necessary before unequivocal statements about the viscosity of this fluid can be made. The present work is concerned with the measurement of the viscosity of R134a in the liquid phase from the saturation pressure to 50 MPa over the range of

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temperature from 235 to 343 K. The measurements have been made with a vibrating-wire viscometer described in detail elsewhere [3], which has a precision of $\pm 0.3\%$ and an accuracy of $\pm 0.6\%$.

2. EXPERIMENTAL

The vibrating-wire viscometer employed for the present measurements was exactly that described earlier [3]. It comprises a 100- μm -diameter straight tungsten wire, suspended from the top plate of a pressure vessel, and carrying a tensioning weight on its lower end. The wire is set into transverse vibration electromagnetically and the subsequent motion of the wire within the test fluid observed by electromagnetic induction. The decay of the transverse vibrations, which conform to a damped sinusoidal oscillation, is related to the viscosity and the density of the test fluid by the working equation

$$\Delta = \frac{(\rho/\rho_s) k' + 2\Delta_0}{2[1 + (\rho/\rho_s) k]} \quad (1)$$

Here, Δ is the logarithmic decrement of the oscillation in the fluid, Δ_0 the logarithmic decrement *in vacuo*, ρ the fluid density, and ρ_s the density of the wire material. In addition, k and k' are quantities that depend [4] upon the viscosity of the fluid through the equations

$$k = -1 + 2 \operatorname{Im}(A) \quad (2)$$

$$k' = 2 \operatorname{Re}(A) + 2\Delta \operatorname{Im}(A) \quad (3)$$

where

$$A = (i - \Delta_0) \left\{ 1 + \frac{2K_0(s)}{sK_1(s)} \right\} \quad (4)$$

and

$$s = [(i - \Delta) \Omega]^2 \quad (5)$$

$$\Omega = \rho \omega R^2 / \eta \quad (6)$$

in which R is the radius of the vibrating wire and ω the frequency of oscillation. The symbols $K_{0,1}$ are modified Bessel functions.

It follows from these equations that measurements of the decrement and frequency of the oscillation of the wire *in vacuo* and in the fluid serve to determine the viscosity of the fluid given a knowledge of its density, provided that the radius of the wire and its density are available. It has not

been possible to determine the latter quantities directly with sufficient accuracy so that they have been determined by calibration of the instrument with fluids of known viscosity as described in detail elsewhere [5]. As in our earlier work we have employed viscosity data under saturation conditions at 303.15 K for toluene, *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane reported by Gonçalves et al. [6] and Knapstad et al. [7], to perform the calibration. The results are identical to those described earlier [5].

The samples of R134a were provided by ICI Chemicals and Polymers Ltd. with a purity of better than 99.9%. During the measurements various samples were withdrawn for analysis to confirm that there had been no contamination. In the evaluation of the viscosity of R134a we have consistently made use of the equation of state of Saltoh et al. [8], for which the estimated uncertainty in the density is $\pm 0.1\%$. Thus, accounting for the accuracy of the calibration data and the precision of individual measurements, it is estimated that the overall accuracy of the reported viscosity data is $\pm 0.6\%$. The precision of the measurements is $\pm 0.3\%$, which is significantly better since the majority of the inaccuracy arises from the calibration viscosity data.

Table I. Viscosity of R134a Along the Saturation Line

Temperature (K)	Expt. pressure P (MPa)	Density $\rho(T, P)$ ($\text{kg} \cdot \text{m}^{-3}$)	Expt. viscosity $\eta(T, P)$ ($\text{mPa} \cdot \text{s}$)	Saturation pressure P_s (MPa)	Viscosity at saturation $\eta(T, P_s)$ ($\text{mPa} \cdot \text{s}$)
237.74	0.092	1400.4	0.4298	0.065	0.4296
244.14	0.136	1382.6	0.3955	0.089	0.3951
248.23	0.138	1370.5	0.3767	0.108	0.3765
251.06	0.253	1362.5	0.3632	0.122	0.3626
253.86	0.193	1353.9	0.3512	0.138	0.3510
261.39	0.209	1330.9	0.3183	0.188	0.3183
268.10	0.305	1310.0	0.2925	0.244	0.2925
270.96	0.624	1302.0	0.2812	0.271	0.2798
271.26	0.703	1301.3	0.2801	0.274	0.2785
279.07	0.759	1275.6	0.2532	0.362	0.2517
289.30	0.729	1239.6	0.2229	0.507	0.2221
293.35	0.664	1224.6	0.2116	0.576	0.2110
303.14	0.923	1187.8	0.1877	0.770	0.1871
313.15	1.159	1147.2	0.1654	1.016	0.1648
323.15	1.389	1102.3	0.1451	1.317	0.1448
333.15	1.875	1054.9	0.1277	1.680	0.1267
343.15	2.303	999.6	0.1116	2.114	0.1104

3. RESULTS

The viscosity data for R134a are contained in Table I for measurements near the saturation line and in Table II for those isotherms for which measurements were performed as a function of pressure. The tables list the temperature, pressure, density, and viscosity for the fluid. In view of the fact that it may be possible to recalibrate the viscometer in the future if more accurate viscosity data for the reference fluids become available, the raw experimental data for calibration and the measurements on R134a have been retained. However, they are omitted from the tabulations in the interests of brevity.

3.1. Saturation Line

Not all of the measurements near the saturation vapor pressure were performed exactly at saturation. Thus, in order to provide values exactly at the saturation conditions given by Saltoh et al. [8], the data have been corrected to the saturation density for each temperature by the application of a small (1.0%) correction. The correction has been deduced from the representation of the viscosity as a function of density discussed later. The magnitude of this correction is sufficiently small that the additional uncertainty introduced by its application is no more than 0.1%. The data at the saturation density given by Saltoh et al. [8] are included in Table I.

The temperature dependence of the viscosity of R134a along the saturation line has been represented by the equation

$$\eta = \exp \left\{ \sum_{i=0}^4 a_i T^{-i} \right\} \quad (7)$$

where

$$\begin{aligned} a_0 &= -39.05765, & a_1 &= 3.616708 \times 10^4 \text{ K} \\ a_2 &= -1.372566 \times 10^7 \text{ K}^2, & a_3 &= 2.409684 \times 10^9 \text{ K}^3 \\ a_4 &= -1.61014 \times 10^{11} \text{ K}^4 \end{aligned} \quad (8)$$

and η is measured in mPa · s. Figure 1 contains a plot of the deviations of the present experimental data from this correlation; they do not exceed $\pm 0.4\%$, while the standard deviation is $\pm 0.2\%$. The same figure contains a comparison with the results of earlier work. The data of Ripple [2], for the lower temperature range, depart from the present representation by no more than $\pm 4\%$, which is broadly consistent with the estimated error in his measurements of $\pm 3\%$. The results of Kumagai and Takahashi [9]

Table II. Viscosity of R134a as a Function of Pressure

Temperature T (K)	Pressure P (MPa)	Density ρ ($\text{kg} \cdot \text{m}^{-3}$)	Viscosity η ($\text{mPa} \cdot \text{s}$)
293.35	0.664	1224.6	0.2116
	2.222	1232.3	0.2172
	4.976	1245.8	0.2271
	6.808	1253.6	0.2337
	9.997	1267.1	0.2445
	17.05	1292.0	0.2677
	20.06	1301.6	0.2772
	27.94	1323.8	0.3017
	29.76	1328.5	0.3075
	40.17	1353.0	0.3387
	41.06	1354.9	0.3409
	51.01	1375.1	0.3705
	303.14	0.923	1187.8
0.929		1187.9	0.1873
4.806		1211.2	0.2019
6.207		1218.6	0.2069
10.20		1237.5	0.2204
16.85		1264.0	0.2416
20.30		1276.0	0.2519
30.45		1306.5	0.2814
39.90		1330.5	0.3083
50.47		1353.8	0.3377
313.15	1.160	1147.2	0.1654
	6.844	1186.5	0.1860
	10.30	1205.2	0.1981
	25.92	1267.6	0.2441
	39.79	1307.4	0.2815
323.15	50.97	1333.9	0.3106
	1.389	1102.3	0.1451
	3.159	1119.8	0.1529
333.15	7.324	1152.3	0.1684
	1.875	1054.9	0.1276
	3.893	1080.2	0.1367
343.15	5.552	1097.1	0.1435
	2.303	999.6	0.1116
	3.911	1027.9	0.1183
	5.842	1053.7	0.1270
	9.829	1093.1	0.1417
	18.84	1152.9	0.1712
	26.64	1190.1	0.1895
	30.07	1204.0	0.2003
	40.36	1240.0	0.2245
	50.24	1269.0	0.2470

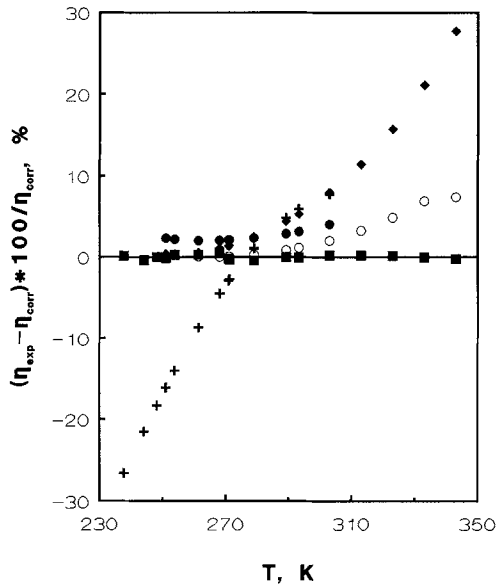


Fig. 1. Deviations of experimental viscosity data for R134a along the saturation line from the representation of them by Eq. (7) and (8). (■) Present work; (●) Ripple [2]; (○) Kumagai et al. [9]; (+) Diller et al. [10]; (◆) Shankland et al. [11].

show quite good agreement in the intermediate temperature range, although the departure increases to $\pm 6\%$ at the highest temperatures. The data of Diller et al. [10] and Shankland et al. [11], on the other hand, show a quite different temperature dependence, leading to very large discrepancies at high and low temperatures. Figure 1 illustrates the wide

Table III. Coefficients of the Correlating Eq. (9) for the Viscosity of R134a

Temperature T (K)	Pressure P' (MPa)	b_0	b_1	b_2
293.35	25.8	0.2061	0.0184	0.0704
303.14	25.7	0.1803	0.0241	0.0631
313.15	26.1	0.1560	0.0308	0.0572
323.15	4.4	0.1344	0.0133	0.0100
333.15	3.7	0.1139	0.0126	0.0095
343.15	27.1	0.0844	0.0773	0.0308

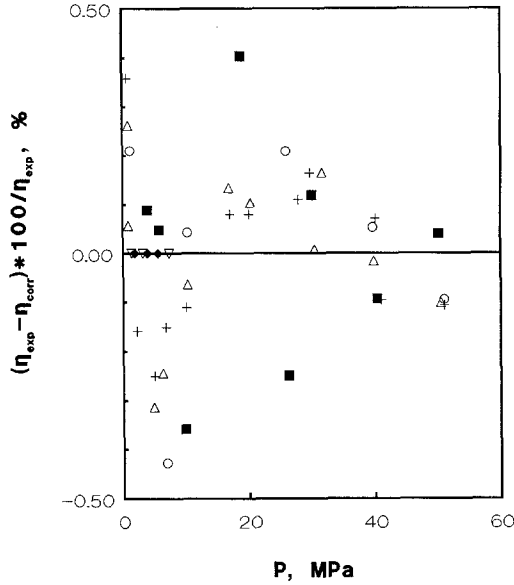


Fig. 2. Deviations of the viscosity data for R134a from the representation of it as a function of pressure by Eq. (9): (+) 293.35 K; (Δ) 303.15 K; (\circ) 313.15 K; (∇) 323.15 K; (\blacklozenge) 333.15 K; (\blacksquare) 343.15 K.

divergence of results for the viscosity of R134a that exist in the literature. While the present data support the results of Ripple [2] and of Kumagai and Takahashi [9], there are still discrepancies at elevated temperatures greater than can be explained by the claimed uncertainties.

3.2. Pressure Dependence

The pressure dependence of the viscosity of R134a along each isotherm has been represented, for the purposes of interpolation, by the equation

$$\eta = \sum_{i=0}^2 b_i (P/P')^i \quad (9)$$

with the coefficients listed in Table III. Figure 2 contains the deviations of the data for the various isotherms from this representation. The deviation does not exceed $\pm 0.4\%$, the standard deviation being 0.2%. There are no published data for comparison.

4. DENSITY DEPENDENCE OF THE VISCOSITY

Semiempirical representations of the viscosity of liquid hydrocarbons and their mixtures based upon the rigid-sphere model of a fluid have proved to be remarkably successful [12]. Such methods not only allow the interpolation of data, but also the extension of data to regions of thermodynamic state beyond that covered by direct measurement. The present experimental data provide an opportunity to examine whether a similar procedure is applicable to refrigerants.

The most important result of the rigid-sphere theory of transport in dense fluids is the conclusion that the dimensionless quantity, η^* , defined by equation [12]

$$\eta^* = 6.035 \times 10^8 [1/MRT]^{1/2} \eta V^{2/3}/R_\eta \quad (10)$$

is a function only of the ratio of the molar volume, V , to a characteristic molar volume V_0 . Here, R is the universal gas constant, M the molar mass of the species, and R_η a scaling factor that accounts for the roughness of the rigid-sphere system. It is expected that R_η is dependent on the molecular species, but independent of temperature and density, while V_0

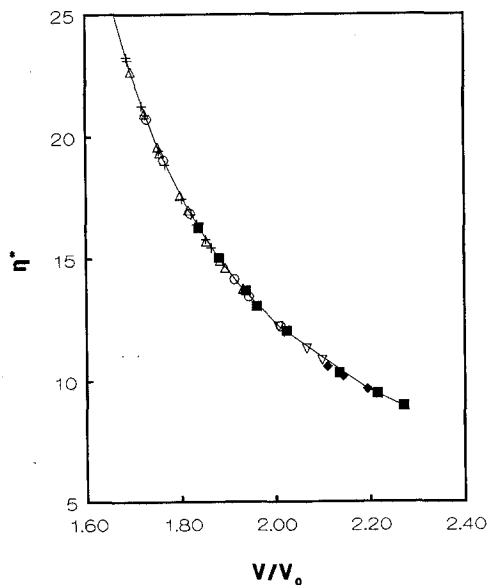


Fig. 3. The reduced viscosity for R134a as a function of the reduced molar volume: (+) 293.35 K; (Δ) 303.15 K; (\circ) 313.15 K; (∇) 323.15 K; (\blacklozenge) 333.15 K; (\blacksquare) 343.15 K.

Table IV. Coefficients of the Correlating Eq. (11) for the Viscosity of R134a

Index i	c_i
0	0.65031
1	2.41753
2	-0.70771
3	0.153854

may be weakly temperature dependent, reflecting the fact that the true forces between the molecules in the fluid have a repulsive component which is not infinitely steep. Accordingly, it is first appropriate to examine whether, for R134a, the experimental data support the fact that η^* is a function only of (V/V_0) . For this purpose we have evaluated η^* from our experimental data and adopted an arbitrary reference value for V_0 at a temperature of 293.35 K. Then, by selecting appropriate values for V_0 at other temperatures, we have constructed the single curve of η^* against

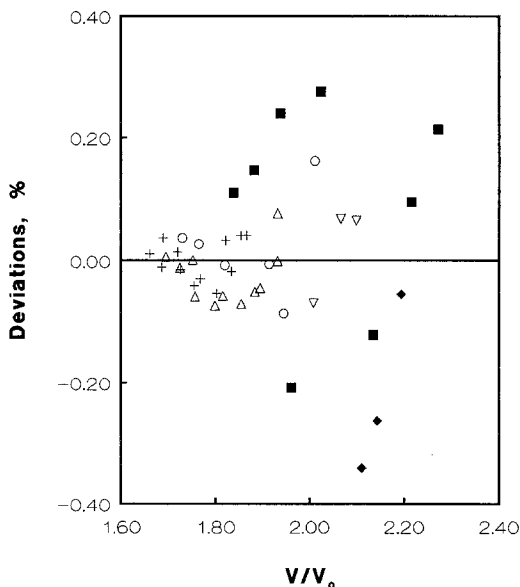


Fig. 4. Deviations, $[100(\eta_{\text{exp}} - \eta_{\text{calc}})]$, of the present viscosity data from the representation of them as a function of volume by means of Eq. (11): (+) 293.35 K; (Δ) 303.15 K; (\circ) 313.15 K; (∇) 323.15 K; (\blacklozenge) 333.15 K; (\blacksquare) 343.15 K.

Table V. The Characteristic Molar Volume V_0 for R134a

Temperature T (K)	Characteristic volume $10^6 V_0$ ($\text{m}^3 \cdot \text{mol}^{-1}$)
293.35	44.46
303.14	44.26
313.15	44.00
323.15	43.89
333.15	43.74

(V/V_0), which is shown in Fig. 3. This single function has been represented by the equation

$$\ln \eta^* = \sum_{i=0}^3 c_i [V_0/(V - V_0)]^i \quad (11)$$

The coefficients c_i are listed in Table IV. Figure 4 contains plots of the deviations of the experimental data from this common representation and

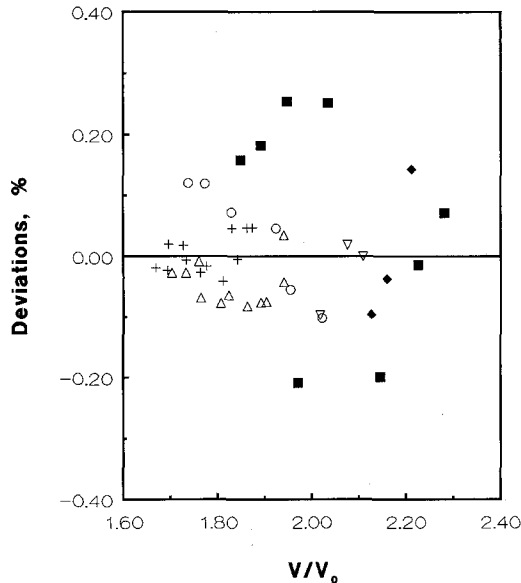


Fig. 5. Deviations, $[100(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{calc}}]$, of the present viscosity data for R134a from the representation of them by means of the correlation of Assael et al. [12] for n -alkanes: (+) 293.35 K; (Δ) 303.15 K; (\circ) 313.15 K; (∇) 323.15 K; (\blacklozenge) 333.15 K; (\blacksquare) 343.15 K.

it can be seen that they do not exceed 0.3%, which provides substantial evidence for the result that η^* depends only upon (V/V_0) .

A second point of interest is to what extent the data for R134a conform to the representation of η^* for the normal alkanes given by Assael et al. [12]. We have therefore sought to secure the optimum representation of the present experimental data for R134a by means of the function η^* given by Assael et al. [12]. In this process we have allowed both $V_0(T)$ and R_η to be determined in the fitting. The resulting deviations are shown in Fig. 5 and the values of V_0 listed in Table V; the optimum value of R_η was $R_\eta = 1.022175$. It can be seen from Fig. 5 that the representation of the experimental data for R134a by an equation based on results for nonpolar systems is essentially the same as when the fluid is treated in isolation. This is a remarkable result that is well within the combined uncertainty of the viscosity and the density.

5. CONCLUSIONS

The viscosity of R134a has been measured along the saturation line and over a range of pressures in the temperature range 235 to 343 K. The results along the saturation line confirm the most recent measurements by other workers but have a lower uncertainty. The results at higher pressures have been used to demonstrate that methods of representing the viscosity of this liquid refrigerant based upon the rigid-sphere model are as successful as they have proved for liquid hydrocarbons. This makes it possible to extend the range of data beyond that covered by direct measurement.

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