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Thermal Conductivity of 1,1-Difluoroethane (HFC-152a)[1]

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Thermal conductivity measurements were performed on 1,1-difluoroethane (HFC-152a) using the polarized transient hot-wire technique in the temperature range of 214 to 294 K and at pressures up to 19 MPa. This technique was used previously for measurements on other halocarbons along the saturation line and in the compressed liquid phase. No dependence of the polarization voltage was found for the thermal conductivity values, demonstrating that the technique was used with success. Also, no influence of heat transfer by radiation or convection was detected, in all the range of densities studied. The samples were supplied with stated purities greater than 99.9%. The reproducibility of the experiments was found to be 0.03%, while the total uncertainty is estimated to be 0.5%. The experimental data were compared with data from other sources. Values for the thermal conductivity along the saturation line for several temperatures were achieved by extrapolating the high-pressure data to the saturation density for each isotherm. The data obtained were also correlated using a modification of the van der Waals model (smooth hard spheres) with an uncertainty of 1.1%, at a 95% confidence level.

KEY WORDS: 1,1-difluoroethane; HFC 152a; liquid; modified van der Waals model; thermal conductivity.

1. INTRODUCTION

After careful evaluation that involved several environmental, physicochemical and toxicity studies, 1,1-difluoroethane (HFC-152a) has been proposed

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as an alternative refrigerant, suitable to replace dichlorodifluoromethane (CFC 12). Its zero ODP (ozone depletion potential) and very low GWP (greenhouse warming potential) make it an attractive ozone-friendly refrigerant, although its flammability must be taken into account. It is used as a component of mixtures resulting in alternative nonflammable refrigerants for applications in domestic and commercial refrigeration.

A knowledge of the transport properties, particularly the thermal conductivity, is of invaluable need to the design of efficient refrigeration equipment. It also provides information on the intermolecular forces among the molecules of the fluids, although its dependence on them is highly complex, and almost impossible to obtain without simplifications in the theoretical models used [1]. In the case of the dense gas above the critical density, and for the liquid state, the hard-sphere model can be considered a realistic description of the molecular interactions, and it is by far the most successful and general molecular theory for the correlation and prediction of dense fluid transport coefficients [1]. For viscosity and diffusion modifications of the smooth hard-sphere theories introducing roughness factors were developed by Chandler [2–4] and by Theodosospoulos and Dahler [5], correcting the smooth hard-sphere results obtained by Enskog [6], and corrected by Dymond [7, 8] to account for the correlated motions of the spheres.

There is no theoretical justification to extrapolate the coupling between translational and rotational motions observed for density and viscosity to thermal conductivity. Although this is the way that some authors developed modifications to the rough hard-sphere theories, by introducing roughness factors for thermal conductivity to develop correlations for alkanes, aromatic hydrocarbons, *n*-alcohols, and refrigerants [9–12], and adjusting the value of the hard-core volume to reproduce as close as possible the available data for viscosity, thermal conductivity, and, in some cases, self-diffusion, we prefer to use a modification of the smooth hard-sphere theory, previously reported [13, 14], that corrects the value of the hard-core volume. The application of this model to several refrigerants was described by Gurova [15], but only the results for HFC-152a are described here.

The new data on the thermal conductivity of HFC-152a presented in this paper have been correlated as a function of both density (for scientific applications) and pressure (important for industrial use). The thermal conductivity was measured using the transient hot-wire (THW) technique with some modifications because of the permanent dipole moment of the fluid, which requires the use of an applied dc polarization to the studied fluid [16–18]. Comparisons with the available data in the literature are also presented, with discussions of the possible causes of the deviations between independent sets of data.

2. EXPERIMENTAL

The main advantage of the transient hot-wire method resides in the accurate determination of the temperature rise ΔT of a very thin wire (line heat source) surrounded by the fluid to be studied, as a function of time t, after the initiation of a constant heat pulse per unit length, q. The thermal conductivity λ is calculated from the slope of ΔT vs $\ln(t)$, according to the equation:

$$\Delta T = \frac{q}{4\pi\lambda} \ln\left(\frac{4at}{r_0^2 C}\right) \tag{1}$$

Here a is the thermal diffusivity of the fluid, C is the Euler constant, 1.781..., and r_0 is the wire radius.

Since the studied fluid is a compound with a large dipole moment in the liquid phase ($\mu^* = 3.69$ D)[5] [19, 20], with very good solvent properties, the hot-wire technique in its original version could not be applied, as reported before [18]. A platinum wire is used as a thermometer and a heat source, the heat dissipation in the wire being generated by an electric current. When liquid refrigerants are present in the cell, the electric isolation between the bare platinum hot wires and the cell wall degrades and an electrochemical potential between them can be observed, possibly due to the solubility of very small quantities of ionic impurities. Although these small concentrations do not alter significantly the thermodynamic and transport properties of the fluid, the additional path in the liquid phase for electrical conduction between the hot wires and the cell wall introduces an error in the transient hot-wire thermal-conductivity measurement. Values of the polarizing voltage between 0.05 and 2 V were used.

The measurements were performed using the cell and the instrument previously described [13, 16, 18]. The temperature was measured with a platinum resistance thermometer to within 0.01 K. The pressure was produced with a single-end air-operated diaphragm-type compressor and measured with an Heise gauge, with an estimated uncertainty of 20 kPa. During the measurements no systematic trends were observed for the dependence of the experimental temperature rise of the hot wire as a function of time, demonstrating that the contribution of convection and radiation were negligible and that the polarization introduced between the wire and the fluid cell was not influencing the accuracy of the measurements. The purity of the HCF-152a studied was $\geqslant 99.9\,\%$, with a content of acidic

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[5] μ^* is the effective dipole moment in the liquid phase, related to the dipole moment in the gaseous phase (isolated molecules) μ through the Kirkwood correlation factor g, $\mu^* = g^{1/2}\mu$ [19, 20].

chlorine $\leqslant 1$ ppm (Karl–Fisher test), an impurity of CFC $12 \leqslant 100$ ppm, and an estimated water content $\leqslant 10$ ppm.

3. DISCUSSION

Measurements of the thermal conductivity of 1,1-difluoroethane have been performed in the temperature range from 214 to 294 K, from near to saturation up to 19 MPa. The experimental data for the thermal conductivity were fitted to equations in terms of density and pressure. The density was calculated from the fundamental equation of state developed by Tillner-Roth [21], which is valid in the temperature range between the triple-point temperature (154.56 K) and 435 K for pressures up to 30 MPa.

A slight temperature fluctuation was observed during the measurements taken along each isotherm; thus, the results of λ are given at the reference temperatures, which differ from each other by a small amount. Due to this fact, the experimental values were corrected to the nominal temperature, T_{nom}, and tabulated as λ_{nom} [15, 18], assuming that the variation of the thermal conductivity with temperature is linear ($T_{\text{ref}} - T_{\text{nom}} \leqslant 0.5$ K). In Table I are presented the experimental data.

The experimental results were fitted as a function of both density (for scientific applications) and pressure (for engineering use). Simple polynomial equations in the following form were adopted:

$$\lambda = a_0 + a_1 \rho + a_2 \rho^2 \tag{2}$$

$$\lambda = b_0 + b_1 p + b_2 p^2 \tag{3}$$

with p the pressure expressed in MPa, ρ the density in $\text{kg} \cdot \text{m}^{-3}$, and λ in $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. A_i are the coefficients of the regression analysis in Eq. (2), and b_i the coefficients of the regression analysis in Eq. (3). The numerical values of the coefficients are listed in Table II. The maximum deviation of the experimental thermal conductivity data from Eqs. (2) and (3) does not exceed $\pm 0.3\%$.

The compressed liquid data were extrapolated to the saturation line, using the density correlation presented by McLinden et al. [22]. The extrapolation introduces an error smaller than 0.1%. The values obtained for each nominal temperature and the corresponding calculated saturation density are presented in Table III.

Compressed liquid data have been presented by Kim et al. [23] using a transient hot-wire apparatus from 223 to 323 K with pressures up to 20 MPa, by Yata et al. [24] using the same technique in the temperature range of 250 to 350 K at pressures up to 30 MPa, by Assael et al. [25]

Table I. Experimental Values of the Thermal Conductivity of HFC-152a

P (MPa)	T_{ref} (K)	ρ_{calc} $(\mathrm{kg \cdot m^{-3}})$	λ_{exp} $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	λ_{nom} $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
	$T_{\mathrm{nom}} = 293.65$ K		$(\partial\lambda/\partial T)_{p\,\mathrm{ref}} = 0.160\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$	
2.79	294.29	916.56	102.597	102.495
8.03	293.91	933.15	106.181	106.139
10.03	292.64	941.25	107.882	108.044
13.00	293.83	946.23	109.823	109.794
15.89	293.40	953.96	112.154	112.194
17.96	294.09	957.28	113.680	113.610
	$T_{\mathrm{nom}} = 272.15$ K		$(\partial\lambda/\partial T)_{p\,\mathrm{ref}} = 0.112\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$	
3.00	272.27	967.63	114.286	114.273
4.03	272.35	969.90	114.947	114.925
5.82	272.35	974.02	116.082	116.060
8.10	272.20	979.36	117.663	117.657
10.37	272.30	983.94	118.851	118.834
11.20	272.06	986.11	119.188	119.198
12.10	271.57	988.88	119.814	119.879
16.51	272.23	996.06	122.549	122.540
	$T_{\mathrm{nom}} = 249.65$ K		$(\partial\lambda/\partial T)_{p\,\mathrm{ref}} = 0.213\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$	
0.79	249.52	1011.32	121.594	121.622
3.13	249.76	1015.24	122.774	122.751
5.55	249.68	1019.78	123.721	123.715
8.51	249.54	1025.18	124.968	124.991
9.75	249.68	1026.99	125.431	125.425
11.55	249.68	1029.95	126.413	126.407
14.17	250.07	1033.41	127.499	127.410
14.92	250.00	1034.71	127.789	127.714
17.34	250.00	1038.41	128.214	129.139
	$T_{\mathrm{nom}} = 223.65$ K		$(\partial\lambda/\partial T)_{p\,\mathrm{ref}} = 0.225\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$	
0.93	223.60	1063.52	133.132	133.143
3.65	223.64	1067.33	134.623	134.625
3.75	223.52	1067.70	134.664	134.693
4.79	223.58	1069.04	134.991	135.007
6.51	223.68	1071.22	135.969	135.962
7.68	223.47	1073.19	136.504	136.545
11.89	223.53	1078.60	138.629	138.656
17.34	223.44	1085.55	141.040	141.087
	$T_{\mathrm{nom}} = 211.65$ K		$(\partial\lambda/\partial T)_{p\,\mathrm{ref}} = 0.091\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$	
3.00	211.92	1088.58	140.933	140.908
10.75	211.92	1098.05	144.377	144.352
12.37	211.73	1100.27	144.911	144.904
14.37	211.84	1102.37	145.822	145.805
14.99	211.71	1103.30	146.028	146.023
16.58	211.70	1105.10	146.677	146.672
18.50	211.69	1107.23	147.528	147.524

Table II. Numerical Values of the Coefficients of Eqs. (2) and (3)[a]

T_{nom} (K)	a_0	a_1	$10^3 a_2$	b_0	b_1	$10^4 b_2$
293.65	2032.712	−4.3807	2.48	100.446	0.727	4.32
272.15	1015.804	−2.1107	1.22	112.394	0.640	−16.87
249.65	2486.960	−4.8782	2.51	121.392	0.398	23.49
223.65	−61.884	0.0097	0.16	132.676	0.523	−21.48
211.65	−50.818	0.0042	0.16	139.580	0.450	−11.99

[a] Density is expressed in $kg \cdot m^{-3}$, pressure in MPa, and thermal conductivity in $mW \cdot m^{-1} \cdot K^{-1}$.

using an anodizeded transient hot-wire system from 250 to 340 K at pressures up to 20 MPa, and by Grebenkov et al. [26] using a concentric cylinder apparatus in steady-state mode from 290 to 405 K at pressures up to 20 MPa. The latter authors extrapolated the data to 160 K and proposed a correlation valid between 160 and 400 K. Gross et al. [27] report data also using a transient hot-wire system, with glass cell, between 253 and 363 K with pressures up to 6 MPa.

Figure 1 shows the deviations of the thermal conductivity values obtained by other authors from Eq. (3) (present work) as a function of pressure. Also included are the data found in the literature. The data of Kim et al. [23] agree with the present study within their mutual uncertainty. The data of Yata et al. [24], with no quoted uncertainty, deviate from the present results by 0.9 to 3% (this value at 273.15 K). The data of Assael et al. [25], with a claimed uncertainty of 0.5%, deviate from the present results between 1 and 3%. The data of Grebenkov et al. [26] have a minimum estimated uncertainty of 3.5%, and they agree with the present results within the mutual uncertainty, except for 224 K. The data of Gross et al. [27] were obtained using a bare hot wire with a claimed uncertainty

Table III. Values of Thermal Conductivity of HFC-152a Extrapolated to Saturation

T_{nom} (K)	ρ_{sat}[21] ($kg \cdot m^{-3}$)	λ_{Sat} ($mW \cdot m^{-1} \cdot K^{-1}$)
211.65	1087.9	140.61
223.65	1064.2	133.42
249.65	1011.1	121.70
272.15	961.6	112.91
293.65	910.2	101.55

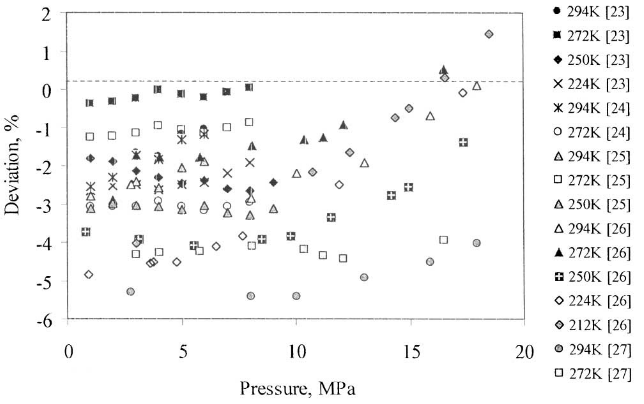

Fig. 1. Deviations, $(\lambda_{\text{exp}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}$, as a function of pressure. λ_{corr} is the value obtained from Eq. (3).

of 1.6%. Their data are 4 to 5.5% lower than the present results. Some of these comparisons show deviations beyond the claimed accuracy of the presented results. This may be due to the impurities of the different samples produced by different manufacturers. This comment is made based on the results of an international round-robin set of thermal conductivity measurements on HFC-134a [18, 27]. Compared to that observed in the present study, the agreement was much better for HFC-134a when the samples for measurements in different laboratories were taken from the same origin (ICI, UK).

The experimental thermal conductivity data were analyzed applying the van der Waals model. The use of this model in the analysis of the thermal conductivity of the studied fluid is based on the Enskog theory. The method developed by Dymond [7, 8] to predict the thermal conductivity applies the van der Waals model, assuming that the molecules behave like hard spheres with a temperature-dependent diameter, according to the following function:

$$\lambda^* = \frac{\lambda}{\lambda_0} \left(\frac{V}{V_0} \right)^{2/3} = F_\lambda \left(\frac{V}{V_0} \right) \tag{4}$$

where λ_0 is the dilute-gas thermal conductivity, V is the molar volume, and V_0 is the volume of close packing of the hard spheres [7, 13]. The value of λ^* can be calculated from the experimental data, assuming that the real fluid behaves like an ensemble of hard spheres.

The direct application of this model to Ar and CH_4 [13, 14] showed that it could not reproduce the experimental data within the claimed

Table IV. Values of the Modified Hard-Core Volume, V_0, as a Function of Temperature

T_{nom} (K)	$10^5 V_0$ ($m^3 \cdot mol^{-1}$)	σ (%)
211.65	4.0929	0.16
223.65	4.0629	0.07
249.65	4.0141	0.18
272.15	4.0135	0.26
293.65	3.9168	0.71

accuracy. For HFC-152a the result is the same, as systematic deviations between −3 and 3% are found. To correct this problem, the original function was modified by a linear function of V/V_0 as explained previously [13, 14].

$$\lambda^* = \frac{\lambda}{\lambda_0}\left(\frac{V}{V_0}\right)^{2/3} = F_\lambda\left(\frac{V}{V_0}\right) \times \left(A + B\frac{V}{V_0}\right) \tag{5}$$

A and B are empirically fitted parameters, whose values were found to be $A = -0.321$ and $B = 0.8295$. Table IV shows the values of the modified hard-core volumes obtained for the five nominal temperatures. The deviations between the predicted values using the modified hard-sphere theory, λ_{mhs}, and the experimental results, λ_{exp}, are presented in Fig. 2, while the values of V_0 with their standard deviations are listed in Table IV. The average standard deviation is 0.3%, consistent with the experimental

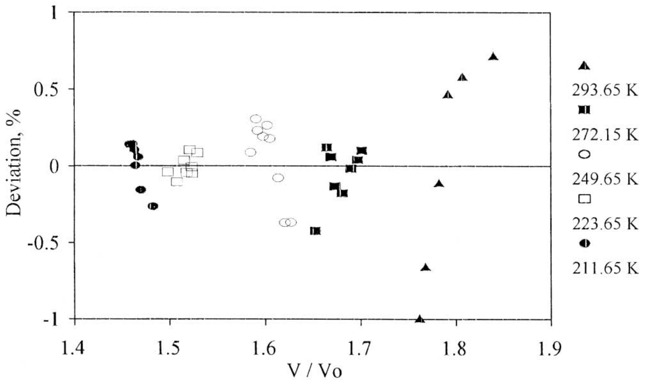

Fig. 2. Deviations, $(\lambda_{mhs} - \lambda_{exp})/\lambda_{exp}$, as a function of V/V_0. λ_{mhs} is the value given by the modified hard-sphere theory, Eq. (5).

uncertainty. Equation (5) can be used to reproduce the experimental data for λ of HFC-152a with a total uncertainty of 1.1% at a 95% confidence level. The values of V_0 decrease with temperature as predicted by theory and can be interpolated using Eq. (6),

$$V_0 = 4.4895 - 0.001877T \tag{6}$$

with V_0 in $m^3 \cdot mol^{-1}$, and T in K, and with a standard deviation of 0.025 $m^3 \cdot mol^{-1}$.

Assael and Dymond [11, 12] developed a prediction method based on the use of the same values of the hard-core volumes for viscosity and thermal conductivity, with an estimated uncertainty of 5%. Applying this method to HFC-152a, we can predict the experimental data with a maximum deviation of 4.5%, which is consistent with the accuracy of the predictive method.

4. CONCLUSIONS

The thermal conductivity of HFC-152a has been measured along isotherms in the range of temperatures between 212 and 294 K, and at pressures from atmospheric up to 19 MPa. The measured values are correlated with Eqs. (2) and (3) with a maximum deviation of ±0.3%. The reproducibility of the data is better than ±0.03%, and the estimated uncertainty is ±0.5%. The thermal conductivity of this refrigerant was measured using the polarized transient hot-wire method The compressed liquid data were extrapolated to the saturation density at five nominal temperatures to generate data for the saturation line.

Comparisons with available data in the literature show deviations larger than the claimed uncertainty of the reported data. This may be caused by the different origins of the compounds, all of which could have dissolved impurities that affect the accuracy of the reported measurements. The data were also correlated using a modification of the van der Waals model (smooth hard spheres), with a total uncertainty of 1.1% at a 95% confidence level.

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REFERENCES

1. J. Millat, J. H. Dymond, and C. A. Nieto de Castro (eds.), *The Transport Properties of Fluids—Their Correlation, Prediction, and Estimation* (Cambridge University Press, London, 1996).
2. D. Chandler, *J. Chem. Phys.* **60**:3500 (1974).
3. D. Chandler, *J. Chem. Phys.* **60**:3508 (1974).
4. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
5. M. Theodosopulu and J. S. Dahler, *J. Chem. Phys.* **60**:4048 (1974).
6. D. Enskog, *Kungl. Sv. Vetenskapsakad. Handl.* **63**, No. 4 (1922).
7. J. H. Dymond, *Physica* **75**:100 (1975).
8. J. H. Dymond, *Physica B* **144**:267 (1987).
9. M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, *Int. J. Thermophys.* **13**:269 (1992).
10. M. J. Assael, J. H. Dymond, and P. M. Patterson, *Int. J. Ihermophys.* **13**:895 (1992).
11. M. J. Assael, J. H. Dymond, and S. K. Polimatidou, *Int. J. Thermophys.* **15**:189 (1994).
12. M. J. Assael, E. Karagiannidis, and S. K. Polimatidou, *High Temp. High Press.* **25**:259 (1993).
13. J. C. G. Calado, U. V. Mardolcar, C. A. Nieto de Castro, H. M. Roder, and W. A. Wakeham, *Physica A* **143**:314 (1987).
14. U. V. Mardolcar and C. A. Nieto de Castro, *Ber. Bunsenges. Phys. Chem.* **91**:152 (1987).
15. A. N. Gurova, *Thermal Conductivity of Environmentally Acceptable Refrigerants*, Ph.D. thesis (University of Lisbon, Lisbon, 1996).
16. A. N. Gurova, M. T. Barão, C. A. Nieto de Castro, and U. V. Mardolcar, *High Temp. High Press.* **26**:25 (1994).
17. A. N. Gurova, U. V. Mardolcar, and C. A. Nieto de Castro, *Thermal Conductivity 22* (Technomic, Lancaster, PA, 1994), p. 167.
18. A. N. Gurova, U. V. Mardolcar, and C. A. Nieto de Castro, *Int. J. Thermophys.* **18**:1077 (1997).
19. M. T. Barão, C. A. Nieto de Castro, and U. V. Mardolcar, *Int. J. Thermophys.* **18**:419 (1997).
20. M. T. Barão, U. V. Mardolcar, and C. A. Nieto de Castro, *Fluid Phase Equil.* **150–151**:753 (1998).
21. R. Tillner-Roth, *Int. J. Thermophys.* **16**:91 (1995).
22. M. O. McLinden, M. L. Huber, and S. L. Outcalt, ASME Winter Annual Meeting, New Orleans, LA (1993), Paper 93-WA/HT-29.
23. S. H. Kim, D. S. Kim, M. S. Kim, and S. T. Ro, *Int. J. Thermophys.* **14**:937 (1993).
24. J. Yata, M. Hori, T. Kurahashi, and T. Minamiyama, *Fluid Phase Equil.* **80**:287 (1992).
25. M. J. Assael, L. Karagiannidis, S. K. Polimatidou, and W. A. Wakeham, *Proc. Int. Conf. CFC's, The Day After* (Padova, Italy, 1994), p. 411.
26. A. J. Grebenkov, Y. G. Kotelevsky, V. V. Saplitza, O. V. Beljaeva, T. A. Zajatz, B. D. Timofeev, *Proc. Int. Conf. CFC's The Day After, Joint Meet. IIR B1, B2, E1, and E2* (Padova, Italy, 1994), p.419.
27. U. Gross, Y. W. Song, and E. Hahne, *Int. J. Thermophys.* **13**:957 (1992).
28. M. J. Assael, Y. Nagasaka, C. A. Nieto de Castro, R. A. Perkins, K. Ström, E. Vogel, and W. A. Wakeham, *Int. J. Thermophys.* **16**:63 (1995).
29. M. J. Assael, A. Liepertz, E. MacPherson, Y. Nagasaka, C. A. Nieto de Castro, R. A. Perkins, K. Ström, E. Vogel, and W. A. Wakeham, submitted for publication.
30. M. J. Assael, J. H. Dymond, and S. K. Polimatidou, *Int. J. Thermophys.* **16**:761 (1995).