THERMAL CONDUCTIVITY OF 1,1-DIFLUOROETHANE

(HFC 152a)[1]

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ABSTRACT

This paper reports on the thermal conductivity of 1,1-difluoroethane (HFC 152a). Measurements were performed using the polarised transient hot-wire technique in the temperature range 214 to 294 K and pressures up to 19 MPa, used previously for measurements in different halocarbons in the saturation line and compressed liquid phase. The samples were supplied with stated purities greater than 99.9%. No influence of heat transfer by radiation or convection was detected, in all the range of densities studied. The density of this refrigerant was obtained from the Tillner-Roth equation of state, while the heat capacity values were calculated from the REFPROP Database.

The reproducibility of the experiments was found to be 0.03% while the accuracy is estimated to be 0.5%.

The experimental data was compared with data obtained by different authors. Values for the thermal conductivity in 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 0.6%.

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

INTRODUCTION

It is now well known that the damage of the ozone layer is caused by the refrigerants containing chlorine. The replacement of such fluids is pointed out as an urgent need. So, in recent years, an effort is being made to find new environmentally acceptable refrigerants. It was considered the group of HFC's and its mixtures as promising fluids, since they contained no chlorine.

After a careful selection that involved several environmental, physicochemical and toxicity studies, 1,1-Difluoroethane (HFC 152a) was chosen as an alternative refrigerant, suitable to replace dichlorodifluoromethane (CFC 12). It's zero ODP (ozone depletion potential) and very low GWP (greenhouse warming potential) make it an interesting ozone-friendly refrigerant, keeping its flammability under control. It is used as a component of mixture to produce an alternative non-flammable refrigerant for applications in domestic and commercial refrigeration.

The knowledge of the transport properties data, particularly the thermal conductivity, is of invaluable need to the project 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 convoluted and impossible to obtain without several simplifications in the theoretical models employed [1]. In the case of the dense gas above the critical density and in 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 in the past by Chandler [2-4] 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 not any theorectical justification to extrapolate the coupling between translational and rotational motions observed for density and viscosity to thermal conductivity. Therefore, although this the way that some authors developed modifications to the rough hard sphere theories, introducing roughness factors for thermal conductivity to develop correlations for alkanes, aromatic hydrocarbons, alkan-1-ols and refrigerants [9-12], adjusting the value of the hard-core volume to reproduce as close as possible the available data for viscosity, thermal conductivity and, in certain 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 to several refrigerants is described by Gurova [15], but only its application to HFC 152a will be described here.

The new data on the thermal conductivity of HFC 152a presented in this paper have been correlated as a function of density for future scientific applications and as a function of pressure, which is important for industrial use. The thermal conductivity was measured using the polarised transient hot wire (THW) technique with some modifications induced by the polarisation of the studied fluid and previously described [16-18]. Comparisons with the available data in the literature are also presented, discussing the possible causes of the deviations between the several values.

EXPERIMENTAL

The main advantage of the transient hot-wire method resides in the accurate determination of the temperature rise *DT* 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 *l* is calculated from the slope of *DT* vs ln (*t*), according to equation:

$$DT = \frac{q}{4p\ l} ln\left(\frac{4a\,t}{r_0^2\,C}\right) \quad (1)$$

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

Since the studied fluid is a compound with high dipole moment in the liquid phase (m^* = 3.69 D) [19,20], the hot-wire technique in its original version could not be applied. An automatic Wheatstone bridge was used for the measurement of the thermal conductivity. The measurements were performed using the cell and the instrument previously employed [1-3]. 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 accuracy of 20 kPa. During the measurements no systematic curvature was found for the dependence of the experimental temperature rise of the hot-wire as a function of time, demonstrating the contribution of convection and radiation was negligible and that the polarisation introduced between the wire and the fluid cell was not influencing the accuracy of the measurements. The purity of the HCF 152a studied was ≥ 99.9%, with a content in acidic chlorine ≤ 1 ppm (Karl-Fisher test), an impurity of CFC 12 ≤ 100 ppm, and an estimated water content ≤ 10 ppm.

DISCUSSION

Measurements of the thermal conductivity of the 1,1-difluoroethane have been performed in the temperature range 214-294 K, from close to saturation up to 19 MPa. The experimental data for the thermal conductivity obtained were fitted to equations in the terms of density and pressure. The density was calculated from the fundamental

equation of state developed by Tillner-Roth [21], valid in the temperature range between the triple-point temperature (154.56K) to 435 K for pressures up to 30 MPa.

As it was observed, a slight temperature fluctuation during the measurements taken along each isotherm, the results of l are given for reference temperature, 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 l_{nom} [15,18], assuming that the variation of the thermal conductivity with temperature is linear (T_{ref} - $T_{nom} \leq 0.5$ K). Table I presents the experimental data obtained.

The experimental results were fitted as a function of density for future scientific applications and as a function of pressure for engineering use. A simple polynomial equation in the following form was adopted:

$$l = a_0 + a_1 r + a_2 r^2 \quad (2)$$

$$l = b_0 + b_1 p + b_2 p^2 \quad (3)$$

with p the pressure expressed in MPa, r the density in kg m^{-3} and l in mW m^{-1} K^{-1}. a_i are the coefficients of the regression analysis in Eq. (2) and b_i the coefficients of the regression analysis, 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 ±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 are presented in Table III.

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

340K and pressures up to 20 MPa, by Grebenkov et al. [26], using a concentric cylinder apparatus, from 290K to 405K and pressures up to 20 MPa, extrapolating the data to 160K. Gross et al. [27] presents data using also a transient hot-wire system, with glass cell, between 253 and 363K, with pressures up to 60 bar.

Figure 1 shows the deviations from eq.(3) of the thermal conductivity values obtained by other authors 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 ours within their mutual uncertainty. The data of Yata et al [24], without quoted uncertainty deviates from the present results between 0.9% and 3% (this value at 273.15 K). The data of Assael et al. [25] obtained with a claimed uncertainty of 0.5% deviate from these results between 1 and 3%. The data of Grebenkov et al. [26] has an estimated uncertainty of 3.5%, and it agrees with the present results within their mutual uncertainties, except for 224 K. The data of Gross et al. [27] used a bare hot wire and claimed an uncertainty of 1.6 %. Their data is 4 to 5.5% lower than the present results. Some of these comparisons show deviations beyond the claimed accuracy of the presented results. This is probably due to the impurities content of the different samples, produced by different manufacturers. This fact was considered relevant for HFC 134a [18, 27], and possibly justifies all the unexpected deviations, specially those with of Assael et al. [25], obtained with the anodised tantalum hot-wire instrument, as the agreement obtained for HFC134a with samples of the same origin (ICI,UK) was much better [18].

The experimental thermal conductivity data were interpreted, applying the van der Waals model. The use of this model in the interpretation of thermal conductivity of the studied fluid was tested, 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:

$$l^* = \frac{l}{l_0}\left(\frac{V}{V_0}\right)^{2/3} = F_l\left(\frac{V}{V_0}\right) \qquad (4)$$

where l_0 is the dilute gas thermal conductivity, V is the molar volume and V_0 the volume of close packing of the hard spheres [7,13]. The value of l^* can be calculated from the experimental data, assuming that the real fluid behave like am ensemble of hard spheres.

The direct application of this model to Ar and CH_4 showed previously [13,14] that it could not reproduce the experimental data within the accuracy claimed. For HFC 152a the result is the same, as systematic deviations between -3 and 3% are found. To correct this problem it was added to the original function a factor in the form of a linear function of V/V_0 as explained in previous works [13,14].

$$l^* = \frac{l}{l_0}\left(\frac{V}{V_0}\right)^{2/3} = F_l\left(\frac{V}{V_0}\right)\times\left(A+B\frac{V}{V_0}\right) \qquad (5)$$

A and B are empirically fitted parameters, whose values were found to be A = - 0.321 and B = 0.8295. This function was able to reproduce the experimental data for l of this refrigerant within the estimated experimental accuracy (0.5%).

Table IV shows the values of the modified hard core volumes obtained, for the five nominal temperatures studied. The deviations between the predicted values using the modified hard-sphere theory, l_{mhs}, and the experimental results, l_{exp}, are presented in Fig. 2, while the values of the V_0 with their standard deviations are listed in Table IV. The average standard deviation is 0.3%, commensurate with the experimental uncertainty. These values decrease with temperature as predicted by the theory, and can be calculated for interpolation through eq.(6):

$$V_0 = 4.4895 - 0.001877T \quad (6)$$

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

Assael and Dymond [13,14] 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 commensurate with the accuracy of the predictive scheme.

CONCLUSIONS

The thermal conductivity of one class A alternative refrigerant, namely HFC152a, has been measured along isotherms in the range of temperatures between 212 to 294K and pressures from the atmospheric up to 19MPa. The measured values are correlated with the equations (2) and (3) with a maximum deviation of ±0.3%. The reproducibility of the data is better than ±0.03% and the estimated accuracy ±0.5%. The thermal conductivity of this refrigerant was measured using the polarised transient hot-wire method. The compressed liquid data was extrapolated to the saturation density at five nominal temperatures, to generate data for the saturation line.

The comparison with the available data on the literature shows deviations beyond the claimed accuracy of the reported data. This is probably caused by the different origin of the compounds used all of which can have impurities dissolved that affect the quality of the reported measurements.

The data obtained were also correlated using a modification of the van der Waals model (smooth hard spheres), with an uncertainty of 0.6%.

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Table I. Experimental values of the thermal conductivity of HFC 152a.

P (MPa)	T_{ref} (K)	r (kg m^{-3})	l_{exp} (mW m^{-1} K^{-1})	l_{nom} (mW m^{-1} K^{-1})
	T_{nom} = 293.65 K		$(\P\ l / \P T)_{r\mathrm{ref}}$ = 0.160 mWm^{-1}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_{nom} = 272.15 K		$(\P\ l / \P T)_{r\mathrm{ref}}$ = 0.112 mWm^{-1}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_{nom} = 249.65 K		$(\P\ l / \P T)_{r\mathrm{ref}}$ = 0.213 mWm^{-1}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	129.214	129.139

Table I. (cont'd)

P (MPa)	T_{ref} (K)	r (kg m^{-3})	l_{exp} (mW m^{-1} K^{-1})	l_{nom} (mW m^{-1} K^{-1})
	T_{nom} = 223.65 K		$(\P\ l / \P T)_{r\mathrm{ref}}$ = 0.225 mWm^{-1}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_{nom} = 211.65 K		$(\P\ l / \P T)_{r\mathrm{ref}}$ = 0.091 mWm^{-1}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 in eqs.(2) and (3).

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

Density is expressed in kg m^{-3}, Pressure in MPa, and Thermal Conductivity in mW m^{-1}K^{-1}

Table III. Values of thermal conductivity of HFC 152a extrapolated to the saturation line

T_{nom} (K)	r_{sat} (kg m^{-3})	l_{Sat} (mW m^{-1} 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

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 mol^{-1})	σ (%)
211.65	4.0929	0.16
223.65	4.0629	0.07
249.65	4.0135	0.26
272.15	4.0141	0.18
293.65	3.9168	0.71

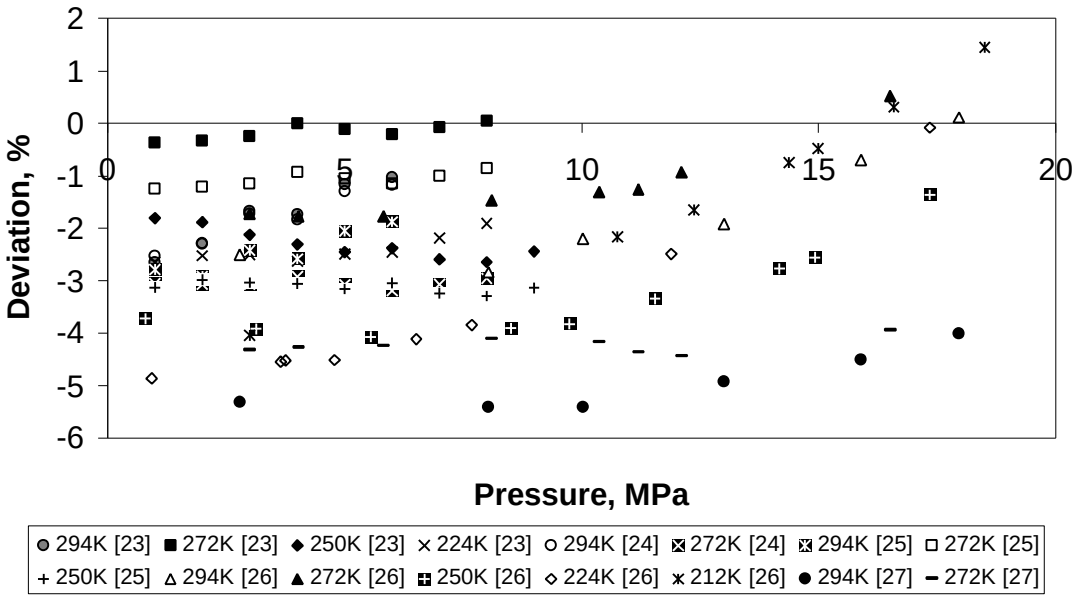

Fig.1 Deviations, $(l_{exp} - l_{corr})/ \ l_{corr}$, as a function of pressure.

l_{corr} is the value obtained from Eq. (3).

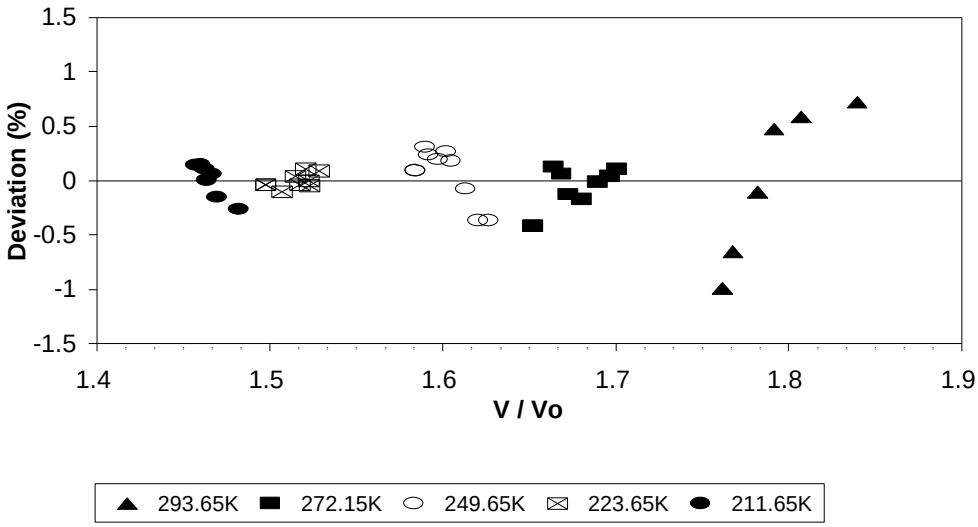

Fig.2 Deviations $(l_{mhs} - \ l_{exp}) / \ l_{exp}$ as a function of V/V_0