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The Thermal Conductivity of Liquid 1,1,1,2-Tetrafluoroethane (HFC 134a)

A. N. Gurova,[1] U. V. Mardolcar,[1] and C. A. Nieto de Castro[2, 3]

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The thermal conductivity of HFC 134a was measured in the liquid phase with the polarized transient hot-wire technique. The experiments were performed at temperatures from 213 to 293 K at pressures up to 20 MPa. The data were analyzed to obtain correlations in terms of density and pressure. This study is part of an international project coordinated by the Subcommittee on Transport Properties of Commission I.2 of IUPAC, conducted to investigate the large discrepancies between the results reported by various authors for the transport properties of HFC 134a, using samples of different origin. Two samples of HFC 134a from different sources have been used. The thermal conductivity of the first sample was measured along the saturation line as a function of temperature and the data were presented earlier. The thermal conductivity of the second one, the round-robin sample, was measured as a function of pressure and temperature. These data were extrapolated to the saturation line and compared with the data obtained, previously in order to demonstrate the importance of the sample origin and their real purity. The accuracy of the measurements is estimated to be 0.5%. Finally, the results are compared with the existing literature data.

KEY WORDS: HFC 134a; high pressure; 1,1,1,2-tetrafluoroethane; thermal conductivity.

1. INTRODUCTION

Transport properties data, including thermal conductivity, are needed for the design and efficiency of new refrigeration equipments and for the modification, of existing systems, usually called retrofitting. It is necessary

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[1] Departamento de Física, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal.

[2] Centro de Ciência e Tecnologia de Materiais e ICAT, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1700 Lisboa, Portugal.

[3] To whom correspondence should be addressed.

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to obtain accurate data on this property in order to formulate some general equations applicable to alternative refrigerants. Although the measurement of this property for nonpolar fluids has become standard, when we are dealing with the halocarbons, compounds with high dipole moments and high solvent power, the most rigorous methods of measurement, such as the transient hot-wire technique, have to be modified. In addition, it has been suggested that the purity of the samples is a possible source of the discrepancies found between the thermal conductivity data obtained by different authors [1]. In order to contribute to the clarification of this problem, we have measured the thermal conductivity of two HFC 134a samples from different origins, one at saturation and the other in the compressed liquid region.

This study was performed as part of an international project coordinated by the Subcommittee on Transport Properties of Commission I.2 of IUPAC, conducted to investigate the large discrepancies between the results reported by various authors for the transport properties of HFC 134a, using samples of different origin. Four laboratories were involved in the measurement of the thermal conductivity of HFC 134a, as a function of temperature and pressure, and in the saturation line, using anodized tantalum wires, bare Pt wires, and bare Pt wires with the polarization technique. The first results were published last year [2] and extended with further measurements obtained with the light scattering technique (photocorrelation spectroscopy) at saturation. This final report will be published elsewhere [3].

2. THEORY

In recent years, the transient hot-wire method used here has become established as the preferred technique for the measurement of the thermal conductivity of nonpolar fluids in the moderate temperature range. The working equation is obtained as a solution of the heat conduction equation [4] subjected to the convenient boundary conditions. The thermal conductivity is obtained from the slope of a linear regression of the temperature rise ΔT as a function of time. A platinum wire is used as a thermometer and a heat source, the heat dissipation in the wire being generated by an electric current. HFC 134a is a polar fluid with very good solvent properties, and as a result, some precautions must be taken. 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

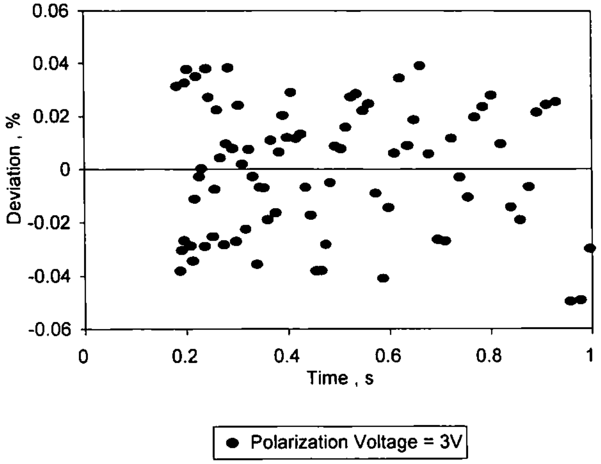

Fig. 1. Deviations of the experimental temperature rise in the transient hot wire from the calculated values for a typical run on HFC 134a at 292.74 K and 17.34 MPa.

between the hot wires and the cell wall introduces an error in the transient hot-wire thermal-conductivity measurement. This error can be eliminated by the application of a fixed dc polarization voltage between the cell wall and the hot wires [5], the magnitude of the polarizing voltages depending on the fluid under study. This polarization voltage creates a compact double layer that does not introduce errors in the measurement of the temperature rise. This double layer contains solvated ions with a charge opposite to that of the metallic surface which they surround, shielding the ions in the bulk solution from the charges which are present on the metallic surfaces in the cell wall during the experiment. With this modification it is possible to use the transient hot-wire technique with bare wires to measure the thermal conductivity of moderately polar fluids with confidence, and with uncertainty levels comparable to its use in nonpolar or electrically nonconducting liquids. A typical plot of the scattering of the experimental ΔT points from the fitted line is shown in Fig. 1, for HFC 134a at 292.74 K with a polarization of 3.0 V. As can be seen, no curvature was observed and it can also be concluded that the present data are free of radiation and convection effects.

3. EXPERIMENTAL PROCEDURE

An automatic Wheatstone bridge was developed for the measurement of thermal conductivity. A general description of the cell is given in Ref. 6, and of the instrument in Ref. 7. 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 a Heise gauge, with an accuracy of 20 kPa. Sample 1 of HFC 134a was supplied by Solvay Fluor und Derivative, Gmbh, Germany and the results obtained were reported earlier [1]. Sample 2 was supplied by ICI Chemicals and Polymers, England. The stated purity-according to the suppliers is 99.9%, by weight, with less than 10 ppm of water. The samples were dried with molecular sieves (Dupont Co., USA).

4. DISCUSSION

Measurements of thermal conductivity were performed in the temperature range 213–293 K, from close to saturation up to 20 MPa for sample 2. The experimental data for the thermal conductivity of HFC 134a have been fitted to equations in terms of the density and pressure. The density was calculated from the equation of state described in Ref. 8. The results are presented in Table I. The experimental results were fitted as a

Table I. Experimental Values of the Thermal Conductivity of HFC 134a

T (K)	P (MPa)	ρ ($kg \cdot m^{-3}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
$T_{nom} = 213.15$ K, $(\partial \lambda / \partial T)_{\rho_{rel}} = 0.153\ mW \cdot m^{-1} \cdot K^{-2}$			
213.02	1.41	1477.24	121.552
213.04	2.00	1478.25	121.742
213.02	5.48	1484.44	123.201
213.01	7.41	1487.76	124.169
213.06	13.89	1498.21	127.014
213.10	17.61	1503.88	128.627
213.03	18.79	1505.85	129.216
213.11	21.20	1509.24	130.481
$T_{nom} = 24.15$ K, $(\partial \lambda / \partial T)_{\rho_{rel}} = 0.204\ mW \cdot m^{-1} \cdot K^{-2}$			
224.09	1.00	1445.65	115.259
224.09	3.41	1450.52	116.086
224.06	7.00	1457.56	117.722
224.06	11.82	1466.43	119.782
224.11	12.17	1466.92	119.937
224.33	14.93	1471.20	121.077
224.13	15.82	1473.24	121.241
224.14	17.27	1475.68	121.779
224.15	18.51	1477.73	122.243
224.31	20.20	1480.12	122.970

Table I. *(Continued)*

T (K)	P (MPa)	ρ ($\mathrm{kg \cdot m^{-3}}$)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
$T_{\mathrm{nom}} = 249.15$ K, $(\partial\lambda/\partial T)_{\rho_{\mathrm{ref}}} = 0.153\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$			
249.21	8.00	1390.86	108.045
249.19	11.48	1399.14	109.268
249.20	13.99	1404.78	110.173
249.20	14.51	1405.93	110.339
249.33	14.79	1406.20	110.406
249.22	14.99	1406.92	110.552
249.27	15.48	1407.86	110.657
249.20	15.82	1408.78	110.796
249.34	16.51	1409.89	110.970
249.25	18.92	1415.19	111.859
$T_{\mathrm{nom}} = 272.15$ K, $(\partial\lambda/\partial T)_{\rho_{\mathrm{ref}}} = 0.216\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$			
272.34	0.38	1297.82	93.838
272.32	3.82	1310.60	96.178
272.24	5.82	1317.71	97.163
272.19	6.75	1320.93	97.535
272.18	7.07	1322.00	97.722
272.24	12.37	1338.02	100.667
272.08	12.72	1339.47	100.906
272.19	14.58	1344.40	101.642
272.22	16.44	1349.38	102.793
272.16	17.44	1352.19	103.261
272.20	18.54	1354.94	103.655
272.18	19.34	1357.04	104.076
272.10	21.34	1362.25	105.235
$T_{\mathrm{nom}} = 292.65$ K, $(\partial\lambda/\partial T)_{\rho_{\mathrm{ref}}} = 0.156\ \mathrm{mW \cdot m^{-1} \cdot K^{-2}}$			
292.88	0.86	1227.93	86.725
292.88	1.48	1231.25	87.297
292.78	2.79	1238.33	88.054
292.81	3.62	1242.29	88.602
292.82	5.48	1250.93	90.107
292.86	6.51	1255.36	90.602
292.83	8.20	1262.61	91.951
292.79	9.00	1265.99	92.342
292.68	12.13	1278.34	94.235
292.73	13.48	1283.07	95.242
292.64	13.99	1285.13	95.499
292.74	17.34	1296.14	97.557

Table II. Numerical Values of the Coefficients in Eqs. (1) and (2)[a]

	Eq. (1)			Eq. (2)		
T(K)	a_0	a_1	$10^4 a_2$	b_0	b_1	$10^3 b_2$
292.8	479.3677	−0.77244	3.69	86.13086	0.72492	−3.87
272.2	446.2594	−0.69598	3.27	93.73419	0.59408	−2.86
249.2	644.3654	−0.91882	3.83	105.1339	0.37070	−0.85
224.0	184.0168	−0.31358	1.84	114.7058	0.45280	−2.28
213.1	3221.641	−4.4235	15.74	120.9472	0.41123	1.66

[a] Density is expressed as kg·m^{-3}, pressure as MPa, and thermal conductivity as mW·m^{-1}·K^{-1}.

function of density for future scientific applications and as a function of pressure for engineering use. A polynomial equation in the following form was adopted

$$\lambda = a_0 + a_1 \rho + a_2 \rho^2 \qquad (1)$$

$$\lambda = b_0 + b_1 p + b_2 p^2 \qquad (2)$$

with p in MPa, ρ in kg·m^{-3} and λ in mW·m^{-1}·K^{-1}. The numerical values of the coefficients are listed in Table II. The maximum deviation of the experimental thermal conductivity data from Eqs. (1) and (2) does not exceed 0.25%, as can be seen in Fig. 2 for the case of Eq. (2). These equations

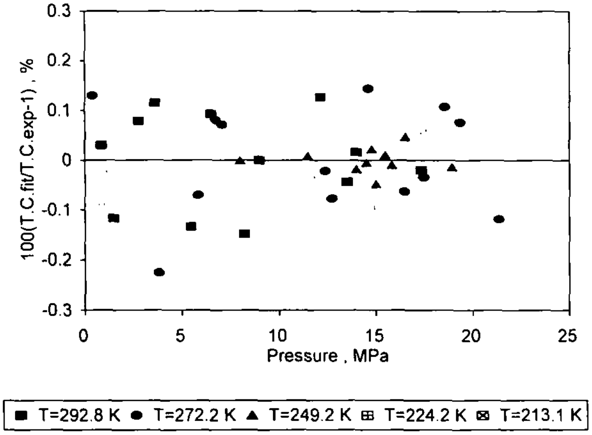

Fig. 2. Deviations of the reported experimental data from Eq. (2): (■) 292.8 K; (●) 272.2 K; (▲) 249.2 K; (⊞) 224.2 K; (⊠) 213.1 K.

can be used as interpolating equations at each given temperature. The values obtained can be corrected to values at a nominal temperature, T_{nom}, as the temperature for each pressure level fluctuates slightly around a mean temperature. Assuming that the variation of the thermal conductivity with temperature along the isochore ρ_{ref} is linear as $T_{\mathrm{ref}} - T_{\mathrm{nom}}$ never exceeds 0.2 K, we can write

$$\lambda(T_{\mathrm{nom}}, \rho_{\mathrm{ref}}) = \lambda(T_{\mathrm{ref}}, \rho_{\mathrm{ref}}) + \left(\frac{\partial \lambda}{\partial T}\right)_{\rho_{\mathrm{ref}}} (T_{\mathrm{nom}} - T_{\mathrm{ref}}) \tag{3}$$

The values of the derivatives were evaluated from the experimental data and are also shown in Table I.

Our data are compared with those of other researchers in Fig. 3, as deviations of the data presented by different authors to the present data, calculated from their own regression lines. The data of Ref. 9, a set of tables with an uncertainty of 1.5%, is in agreement within the mutual uncertainty of the data for the isotherms at low temperatures (max. deviation, 2%), departures increasing at room temperature (max. deviation, 3.5%). The data of Assael and Karagiannidis [10] were obtained with the coated transient hot-wire technique, in the temperature range 250–340 K at pressures up to 30 MPa, with an estimated uncertainty of 0.5%. The deviations between the two sets of data are somewhat larger than the mutual uncertainty of the data, especially the isotherm at 292.8 K. The measurements of Ueno et al. [11] were performed with a transient hot-wire instrument

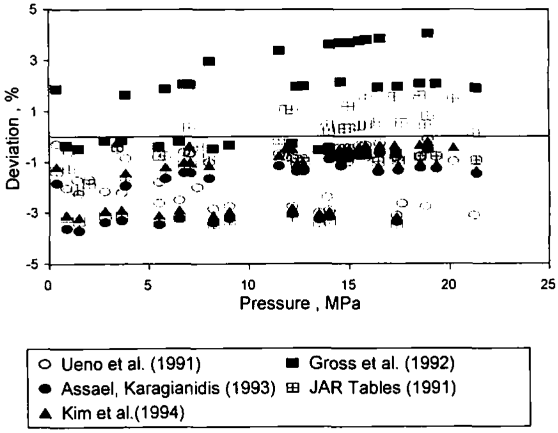

Fig. 3. Comparison of the present data with the data presented by several authors for the compressed liquid: ⊞ [9]; ● [10]; ○ [11]; ■ [12]; ▲ [13]. The baseline is Eq. (2).

using a single wire in the temperature range from 193 to 353 K and in the pressure range from 1 to 30 MPa, with an uncertainty of 1%. These measurements show a maximum deviation of −3.1% from the present values, although most of their data are within −1%, which is commensurate with the mutual uncertainty of both sets of data. The data of Gross et al. [12] agree with ours at 292.8 K within their mutual uncertainty, but the deviations are about 2% at 272.2 K and of the order of 3.5% at 249.2 K. These authors used also a bare platinum wire without polarization, but with the cell walls made of glass. The data of Kim et al. [13] were obtained with a transient hot instrumentation, between 223 and 323 K and pressures up to 20 MPa, with an uncertainty of 2%. The agreement with our data is quite reasonable, the deviations being smaller than the mutual uncertainty, except at room temperature.

A correlation was recently proposed by Krauss et al. [14] for temperatures between 240 and 410 K and densities up to 1500 $kg \cdot m^{-3}$, with an uncertainty of 1.5%. The present results do not deviate from this correlation by more than 1%, except for $T = 213$ K, where the domain of the correlation was exceeded, and the deviations increase to 2.5%.

The compressed liquid data were extrapolated to the saturation line, using the density values from Ref. 15, and compared at the same temperature with the data measured in our laboratory along the saturation line, using the sample supplied by Solvay Fluor und Derivative, Germany, presented elsewhere [7]. The extrapolation introduces an error smaller than 0.1%. It can be observed in Table III that the data obtained with the ICI sample is on average 2.8% greater, with a maximum deviation around this average of 0.35%, commensurate with the accuracy of the two sets of data. Values for the isotherm $T = 249$ K were not extrapolated, due to lack of enough pressure levels near saturation. Compared with the thermal conductivity data of other authors [1, 10–12, 16, 17] (see Fig. 4), better

Table III. Near-Saturation Line Values of the Thermal Conductivity of HFC 134a ($mW \cdot m^{-1} \cdot K^{-1}$) for Sample 1 [1] and Sample 2

T (K)	ρ_{sat} ($kg \cdot m^{-3}$)	Sample 1[a]	Sample 2,[b] round-robin	Difference (%)
292.79	1225.20	83.740	86.378	3.15
272.20	1296.54	91.351	93.739	2.61
224.15	1441.18	111.55	114.26	2.43
213.05	1471.64	116.69	120.32	3.10

[a] Solvay Fluor und Derivative.
[b] Imperial Chemical Industries.

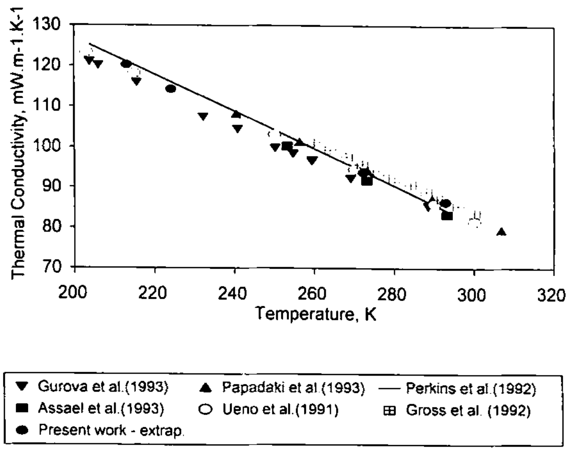

Fig. 4. Comparison of the saturation data values for samples 1 and 2 and other investigators': ▼, sample 1, [1]; ■ [10]; ○ [11]; ▲ [16]; —— [17]; ⊞ [12]; ●, this work, sample 2.

agreement is found with some of these authors [11, 12, 16, 17]. However, the results seem to run more or less parallel to each other, which might justify the existence of systematic errors in the measurements performed by different instruments. This fact also demonstrates that different kinds of samples used by different authors, in addition to the use of two different samples with the same manufacturer-stated purity in the same instrument, show different values of thermal conductivity.

As stated in Section 1 a round-robin exercise with samples of HFC 134a prepared by ICI, UK, was distributed to five laboratories, in order to measure the thermal conductivity of this refrigerant, in the temperature and pressure zone used in the refrigeration industry. In the first report of the study, presented by Assael et al. [2] in 1995, Fig. 7 demonstrates the agreement between our data for the saturation line with those of Assael and Karagiannidis [10] and Perkins et al. [18], although deviations of up to 6% were found from measurements by Yamada et al. [19]. The same situation was found for the compressed liquid, see Fig. 8 of Ref. 2. It was decided to investigate more carefully the reason for these discrepancies, by repeating the measurements at Keio University and obtaining measurements with the light scattering technique, of Kraft and Liepertz [20], with an expected uncertainty of 1% in the thermal diffusivity. The data obtained by those authors show a excellent agreement with the data obtained in this work, confirming that the comparison published in Ref. 2 was correct. The results from Keio University showed a low resistivity, 1 MΩ, while the earlier results [11], obtained with a sample with an electrical resistivity in excess of 20 MΩ, agree very well with our data and the data presented by all the other authors. The increasing departure with increasing temperature suggests that a diffusional process is controlling the leakage of current from the hot wire through the sample to the cell walls.

The latter result seems to demonstrate that the sample previously used by us and reported in Ref. 1 was probably contaminated and had a lower electrical resistivity, justifying the average departure from sample 2 of 2.8%.

5. CONCLUSION

The thermal conductivity of one class A alternative refrigerant, namely, HFC 134a, has been measured along isotherms in the range of temperatures between 213 and 293 K and pressure up to 20 MPa, with an estimate uncertainty of 0.5%, as part of an international effort coordinated by the Subcommittee on Transport Properties of Commission I.2 of IUPAC, conducted to investigate the large discrepancies between the results reported by various authors for the transport properties of HFC 134a, using samples of different origin. The measured values of each substance are correlated with Eqs. (1) and (2) with a maximum deviation of 0.25%. The comparison with the available data in the literature and previous results obtained in our laboratory with a different sample shows deviations beyond the claimed accuracy of the reported data. This is, in our opinion, due to the different origin of the compounds used, which may have different kinds of impurities dissolved from the origin or from handling in each instrument, causing different electrical resistivities of the samples and, therefore, creating secondary paths for electron conduction that distort the signals and make dubious assignments to the power applied to the hot wires. In this context a round-robin measurement, with samples prepared in the same way by the same manufacturer [2], is very important in pinpointing the reasons for these disagreements. This study shows that the agreement among the data of Assael and Karigiannidis in Greece, Perkins in the United States, and this work is of the order of 2%, still slightly greater than the mutual uncertainty. Further results presented by Krall and Liepertz [20] for thermal diffusivity and converted to thermal conductivity data using the equation of state of Ref. 8 and by Perkins et al. [18] show a good agreement with our data [3]. In our opinion, these differences, much smaller when the resistivity of the samples used is similar, must be caused by different handling of the samples in different instruments. We do not exclude the possible existence of some small systematic errors in the transient hot-wire technique applied to polar fluids not yet discerned.

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