International Journal of Thermophysics, Vol. 21, No. 1, 2000

Transport Property Measurements on the IUPAC Sample of 1,1,1,2-Tetrafluoroethane (R134a)

M. J. Assael,[1] A. Leipertz,[2] E. MacPherson,[3] Y. Nagasaka,[4] C. A. Nieto de Castro,[5] R. A. Perkins,[6] K. Ström,[7] E. Vogel,[8] and W. A. Wakeham[9, 10]

Received May 14, 1999

This paper reports the results of an international project coordinated by the Subcommittee on Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry. The project has been conducted to investigate the large discrepancies between the results reported by various authors for the transport properties of R134a and culminates the effort which was initially described in 1995. The project has involved the remeasurement of the transport properties of a single sample of R134a in nine laboratories throughout the world in order to test the hypothesis that at least part of the discrepancy could be attributed to the purity of the samples. This paper provides an intercomparison of the new experimental results obtained for the viscosity

---

[1] Department of Chemical Engineering, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece.

[2] Lehrstuhl für Technische Thermodynamik, Friedrich-Alexander Universität Erlangen-Nürnberg, Am Weichselgarten 8, D-91058 Erlangen, Germany.

[3] Institute for Environmental Research and Technology, National Research Council of Canada, Ottawa K1A 0R6, Canada.

[4] Department of System Design Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan.

[5] Departamento de Química e Bioquímica and Centro de Ciência e Moleculares de Materiais, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.

[6] Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303, U.S.A.

[7] Department of Chemical Engineering, Chalmers University of Technology, S-41296 Gothenburg, Sweden.

[8] Fachbereich Chemie, Universität Rostock, D-18051 Rostock, Germany.

[9] Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, United Kingdom.

[10] To whom correspondence should be addressed.

0195-928X/00/0100-0001$18.00/0

and thermal conductivity in the vapor, liquid, and supercritical gas phases. The viscosity measurements were made with a variety of techniques including the vibrating wire, oscillating disk, capillary flow, and falling body. Thermal conductivity was measured using transient bare and anodized hot wires, steady-state anodized hot wires, and light scattering. Agreement between a variety of experimental techniques using the standard round-robin sample is necessary to demonstrate that some of the discrepancies in earlier results were due to sample impurities. Identification of disagreement between data using one experimental technique relative to other techniques may suggest modifications that would lead to more accurate measurements on these highly polar refrigerant materials. It is anticipated that the new data which have been measured on this IUPAC round-robin sample will aid in the identification of the reliable data sets in the literature and ultimately allow the refinement of the IUPAC reference-data correlations for the transport properties of R134a.

KEY WORDS: R134a; dilute gas; refrigerant; saturation properties; 1,1,1,2-tetrafluoroethane; thermal conductivity; transport properties; viscosity.

1. INTRODUCTION

Identification of damage to the ozone layer caused by the use of cholorfluorocarbon (CFC) materials prompted an international effort to measure and correlate the thermophysical properties of alternative refrigerant fluids such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). It became apparent in the summer of 1991 that discrepancies between viscosity and thermal-conductivity data reported by a variety of laboratories for hydrofluorocarbon materials far exceeded the uncertainties claimed by the authors. The details of this situation and the events leading to the present IUPAC round-robin measurements have been described by Assael et al. [1]. Discrepancies of 15 to 30% were present in the viscosity data reported prior to 1992 for 1,1,1,2-tetrafluoroethane (R134a) [1, 2] and pentafluoroethane (R125) [1]. Similarly, discrepancies of up to 25% were present in the thermal-conductivity data reported for R134a prior to 1992 [1, 2]. Most of the materials that were measured prior to 1992 were synthesized in small batch quantities; and the purity, when it was reported, was usually attributed to the specifications of the supplier. Additionally, measurement of the transport properties of highly polar compounds such as HFCs, was a new experience for most of the laboratories involved. It may never be possible to quantify how much of the discrepancy in the literature prior to 1992 was due to sample impurity and how much was due to inexperience in dealing with highly polar materials. However, new measurements on a single well-characterized and very pure sample of R134a allow the situation to be studied further by eliminating complications due to uncertainties caused by differences in sample purities.

2. ROUND-ROBIN PROJECT

The only way in which the effect of the purity of the sample of R134a could be investigated in a satisfactory manner was to have various laboratories undertake measurements of the viscosity and/or thermal conductivity of R134a on the *same sample* with their own equipment. However, it was impractical to circulate the same sample among different laboratories since it is very time-consuming and there was significant danger of losing or contaminating the sample. The present authors decided that a single source of supply of R134a should be selected, with sufficient samples taken from that single source to allow provision of each laboratory with its own cylinder of sample. Furthermore, it was decided that water was a significant potential impurity in samples of R134a, which, even in trace amounts, could have significant consequences for the viscosity of R134a and could also have a serious effect upon the electrical measurements associated with the transient hot-wire technique. Thus, the water content of the R134a sample was determined, and special care was taken by each researcher to insure that the R134a sample was not contaminated by residual water in the sample-handling and measurement systems.

One company agreed to provide the single source of R134a, and filled nine cylinders from that same source, using procedures for pharmaceutical materials to ensure the cleanliness of the cylinders before use. The purity of the sample was verified by gas chromatography for organic compounds and the Karl–Fischer test for water. The purity of the batch was greater than 99.9%, and the principal impurity was R134 at a concentration of 850 ppm. Water was present at a concentration of 6 ppm. These nine cylinders of material were distributed in July 1993 to nine laboratories throughout the world that had volunteered in 1992 to participate in the project. The laboratories were asked to conduct measurements of the transport properties using their own preferred techniques on the sample, taking care (a) to maintain the purity of the sample and (b) to recover the sample after use for subsequent analysis to ensure that the purity had not been degraded. All the laboratories also agreed to analyze their data using the equation of state recommended by Annex 18 of the International Energy Agency for R134a [3, 4]. Since the work of all of these laboratories was entirely voluntary, it has not proved possible for all of them to carry out all of the originally desired measurements. The results that were obtained are summarized in Table I and are compared relative to the IUPAC recommendations for the transport properties of R134a [2]. The Krauss et al. [2] recommendations provide an unbiased basis for comparison of the new results since none of the new data were used during the formulation of the correlation. However, these recommendations must be extrapolated

Table I. Summary of the Measurements of Transport Properties Made on the Round-Robin Sample of R134a

Primary contact	Viscosity measurements	Thermal conductivity measurements
M. J. Assael	Vibrating wire (liquid and vapor)	Transient hot wire (liquid and vapor; Ta wire)
Aristotle University	Polimatidou, Papadopoulos (saturation, compressed)	Karagiannidis (saturation, compressed)
assael@transp.eng.auth.gr		
A. Leipertz		Light scattering (liquid and vapor)
Friedrich-Alexander Universität Erlangen		Kraft (saturation)
sek@ltt.uni-erlangen.de		
E. MacPherson	Falling ball (liquid)	
National Research Council Canada	MacPherson (saturation)	
Y. Nagasaka		Transient hot wire (liquid; Pt wire)
Keio University		Yamada (saturation, compressed)
nagasaka@sd.keio.ac.jp		
C. A. Nieto de Castro		Transient hot wire (liquid; Pt wire)
Universidade de Lisboa		Gurova (saturation, compressed)
carlos.castro@fc.ul.pt		
R. A. Perkins		Transient hot wire (liquid and vapor; Pt wire)
NIST Physical and Chemical Properties Division		Transient hot wire (liquid and vapor; Ta wire)
		Steady-state hot wire (vapor; Ta wire)
richard.perkins@boulder.nist.gov		Perkins, Howley, Gurova, Ramires, Cusco (saturation, compressed, supercritical)
K. Ström	Höppler falling body (liquid)	
Chalmers University of Technology	Ström (compressed)	
E. Vogel	Oscillating disk (vapor)	
Universität Rostock	Wilhelm (dilute limit)	
eckhard.vogel@chemie.uni-rostock.de		
W. A. Wakeham	Vibrating wire (liquid)	
Imperial College	Oliveira and Fenghour (saturation)	
w.wakeham@ic.ac.uk	Wilhelm (compressed)	

below their lower-temperature limits of 290 K (viscosity) and 240 K (thermal conductivity) to 200 K. This extrapolation has little consequence for the comparisons between the data sets described below. Weaknesses in the present IUPAC recommendations can be identified through this comparison, where the results of multiple experimental techniques agree with each other yet deviate systematically from the baseline correlation [2].

3. VISCOSITY COMPARISONS FOR THE ROUND-ROBIN SAMPLE

It is important to characterize the uncertainties estimated for the baseline viscosity correlation of Krauss et al. [2]. Understanding these correlation uncertainties is necessary to assess the reduction in experimental uncertainty due to the use of a single well-characterized sample in the present IUPAC round-robin study. The viscosity correlation is composed of three terms according to

$$\eta(\rho, T) = \eta_0(T) + \Delta_{\mathrm{R}}\eta(\rho) + \Delta_{\mathrm{C}}\eta(T, \rho) \tag{1}$$

where η is the viscosity in $\mu\ \mathrm{Pa} \cdot \mathrm{s}$, η_0 is the dilute gas viscosity, $\Delta_{\mathrm{R}}\eta$ is the residual viscosity, $\Delta_{\mathrm{C}}\eta$ is the viscosity critical enhancement, T is the temperature in K, and ρ is the fluid density in $\mathrm{kg} \cdot \mathrm{m}^{-3}$. Krauss et al. [2] estimate a relatively high uncertainty of $\pm 4\%$ in the dilute-gas viscosity function at temperatures from 290 to 430 K. The uncertainty in the residual gas viscosity function was estimated [2] to be $\pm 2\%$ in the vapor phase and $\pm 3\%$ in the liquid phase. None of the viscosity data considered in this paper are close enough to the critical point for a significant viscosity critical enhancement, so uncertainties in the critical enhancement are not considered here. Thus, the uncertainty of the overall correlation for viscosity likely ranges from ± 4 to $\pm 6\%$.

3.1. Dilute Gas

The vapor-phase viscosity of the round-robin sample was measured by Wilhelm and Vogel [5, 6], using an oscillating-disk viscometer at the University of Rostock in Germany, and by Assael and Polimatidou [7], using a vibrating-wire viscometer at Aristotle University in Greece. The data of Wilhelm and Vogel [5] were measured along isochores at temperatures from 290 to 440 K, extrapolated to zero density [6], and are estimated to have an uncertainty of $\pm 0.2\%$. The data of Assael and Polimatidou [7] were measured with a 7.36-μm-diameter wire along isotherms at temperatures from 280 to 330 K at higher pressures and densities than for the oscillating-disk data, up to the saturated vapor, and

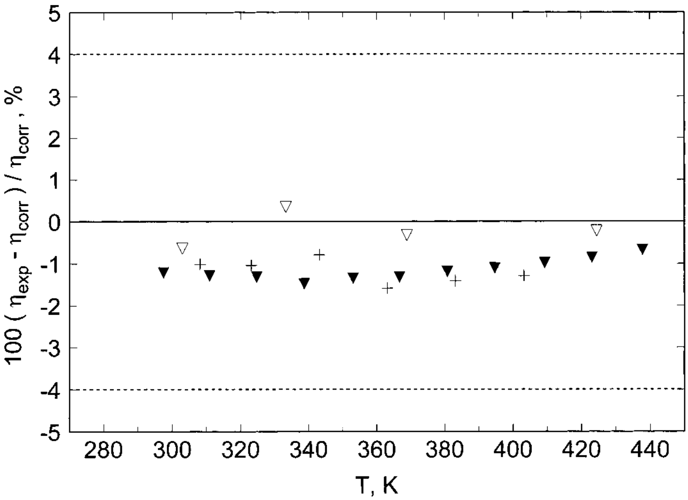

Fig. 1. Deviations of the measurements of the viscosity of R134a in the dilute-gas state from the correlation of Krauss et al. [2]. Round-robin sample: ▼, Wilhelm and Vogel [6]. Literature: +, Dowdell and Matthews [8]; ▽, Nabizadeh and Mayinger [9].

are estimated to have an uncertainty of ±1%. No zero-density values were obtained, and therefore, these data are used only in the gas-phase comparisons. Figure 1 shows the comparison with the Krauss et al. [2] correlation of the oscillating-disk data [6], and this correlation is generally about 1% high. This deviation is much less than the ±4% uncertainty estimated for the baseline correlation [2]. Some of the literature data [8, 9] upon which the Krauss et al. [2] correlation were based are also shown in Fig. 1 to provide some perspective. The present measurements [5, 6] on the round-robin sample are in much better agreement than the earlier measurements, where the deviations approached 6%.

3.2. Gas Phase

The vibrating-wire viscosity data of Assael and Polimatidou [7] were measured at pressures from near 0.1 MPa up to the saturation pressure, so they are generally obtained at higher pressures than the oscillating-disk data of Wilhelm and Vogel [5, 6]. It is not possible to examine deviations between the two round-robin data sets at saturation. Instead, deviations relative to the Krauss et al. [2] correlation are shown in Fig. 2 as a function of fluid density. With the exception of two points at a density near $5\ \text{kg} \cdot \text{m}^{-3}$ in the data set of Assael and Polimatidou [7], the two sets of

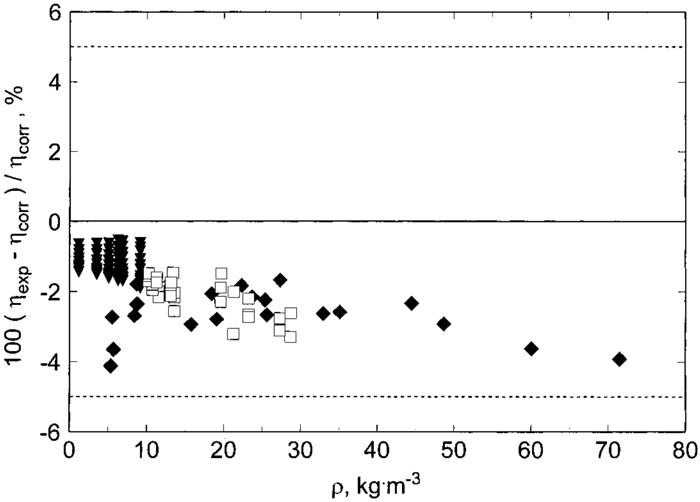

Fig. 2. Deviations of the measurements of the viscosity of vapor R134a as a function of fluid density from the correlation of Krauss et al. [2]. Round-robin sample: ▼, Wilhelm and Vogel [5]; ◆, Assael and Polimatidou [7]. Literature: □, Pasekov and Ustyuzhanin [10].

measurements on the IUPAC round-robin sample appear to be in agreement within their mutual uncertainty. Also shown are the data recently obtained by Pasekov and Ustyuzhanin [10] in a capillary-flow instrument at temperatures between 275 and 371 K with an uncertainty of ±1%. These data agree very well with the round-robin data, in the overlapping density range. The viscosities, calculated with the baseline correlation [2], are systematically higher than the experimental data as the vapor density increases. It is likely that the viscosity recommendations for R134a could be improved in this vapor region with the new results [6, 7, 10].

3.3. Saturated Liquid

Using the round-robin sample, the liquid-phase viscosity at saturation was measured by Oliveira and Wakeham [11] at Imperial College in London, Assael and Polimatidou [7] at Aristotle University of Thessaloniki in Greece, and MacPherson [11] at NRC Canada. The measurements at Imperial College and Aristotle University have been performed with vibrating-wire viscometers with 100-μm-diameter tungsten wires. These vibrating-wire instruments differ from each other in both the cell geometry and measurement electronics. Both of these groups estimate that the viscosity measurements have an uncertainty of ±0.5%, largely as a result of the need for calibration against standard reference values. The vibrating-wire viscometer cell used in the liquid measurements in Greece has a much different geometry (14 times larger wire diameter) than the cell used for the vapor measurements described previously. The measurements by MacPherson [11] were obtained with a falling ball viscometer which was calibrated with *n*-hexane. No estimate of the uncertainty in the viscosity was provided by MacPherson.

Figure 3 compares the results of these three sets of measurements with the correlation of Krauss et al. [2]. Over the temperature range from 240 to 340 K, the maximum spread between the vibrating-wire results is approximately ±1%, although they all lie substantially above the correlation of Krauss et al. [2]. The falling-ball results of MacPherson are in excellent agreement at lower temperatures but are systematically lower at higher temperatures, suggesting some difficulties in operating this instrument at high temperatures. If scatter in the data set of MacPherson, which appears to be ±2%, were equal to the uncertainty of the data, then deviations of 3% between all three data sets would be considered consistent. The falling-ball results are nearly 6% lower than the vibrating-wire results at 330 K, and this deviation cannot presently be explained. The spread of results among the vibrating-wire measurements on the round-robin sample is considered to be consistent with the claimed mutual uncertainty of these

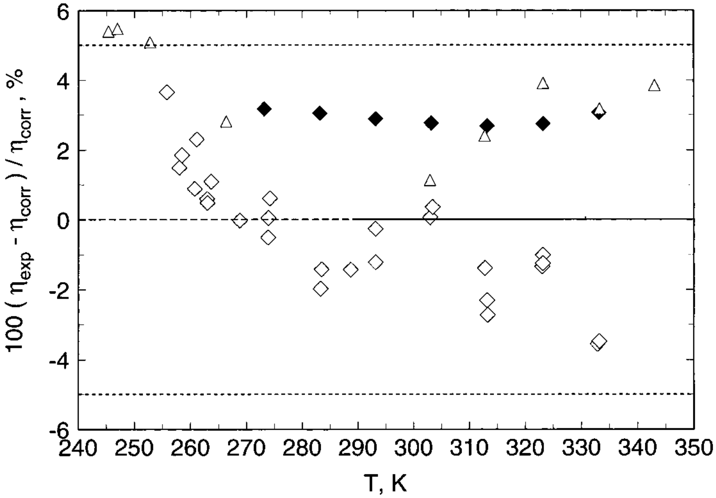

Fig. 3. Deviations of the measurements of the viscosity of liquid R134a along the saturation line from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael and Polimatidou [7]; △, Oliveira and Wakeham [11]; ◇, MacPherson [11].

two instruments. It is noteworthy that the results from these two laboratories are also consistent with their earlier results on different samples. This indicates that the purities of the samples used in these previous vibrating-wire studies were comparable to that of the present round-robin sample and did not affect the measured viscosity.

3.4. Compressed Liquid

The viscosity of the round-robin sample of R134a at elevated pressures was measured along isotherms at 300 and 320 K by Wilhelm in London and at 273, 293, 313, and 333 K by Assael and Polimatidou [7] in Greece, both with the vibrating-wire instruments described in the previous section. Again, the estimated uncertainty is ±0.5%. Ström [12], in Sweden, also made measurements with a Höppler falling-body viscometer with an estimated uncertainty of ±2%. The results of Ström [12] are at temperatures of 260, 268, 278, 288, 298, 308, and 318 K. Figure 4 compares the results of the three sets of measurements as a function of density with the correlation of Krauss et al. [2]. The deviations between the two vibrating-wire viscometers and the falling-body viscometer are generally within ±3%, and the dependence of the deviations on density is similar.

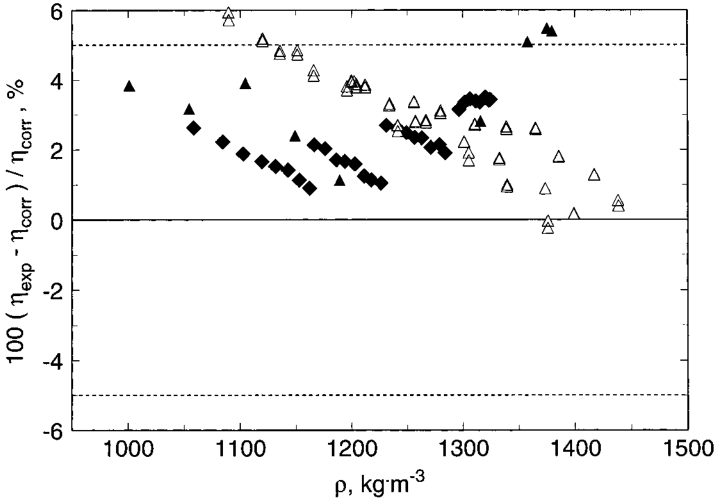

Fig. 4. Deviations of the measurements of the viscosity of liquid R134a at elevated pressure from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael and Polimatidou [7]; △, Wilhelm and Vogel [5]; ▲, Ström [12].

All of the data agree within their mutual uncertainty and are consistent with the saturated-liquid values using the vibrating-wire instruments. The falling-ball results of MacPherson, obtained at saturation [11] appear (Fig. 3) to be too low at elevated temperatures. Figures 3 and 4 show that the viscosity data on saturated and compressed liquid using the round-robin sample are generally higher than the correlation of Krauss et al. [2]. All the data fall within the ±4–6% uncertainty limit which was estimated for the correlation. The correlation [2] appears to extrapolate well below its lower-temperature limit of 290 K.

4. THERMAL-CONDUCTIVITY COMPARISONS FOR THE ROUND-ROBIN SAMPLE

As with the viscosity, it is important to characterize the estimated uncertainty of the baseline thermal conductivity correlation. The thermal conductivity correlation is composed of three terms according to

$$\lambda(\rho, T) = \lambda_0(T) + \Delta_{\mathrm{R}}\lambda(\rho) + \Delta_{\mathrm{C}}\lambda(T, \rho) \tag{2}$$

where λ is the thermal conductivity in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, λ_0 is the dilute-gas thermal conductivity, $\Delta_{\mathrm{R}}\lambda$ is the residual thermal conductivity, $\Delta_{\mathrm{C}}\lambda$ is the thermal conductivity critical enhancement, T is the temperature in K, and ρ is the fluid density in $\mathrm{kg \cdot m^{-3}}$. Krauss et al. [2] estimate the uncertainty of the dilute-gas thermal conductivity function to be ±1.5% at temperatures from 270 to 340 K, increasing to ±3% at temperatures below 270 K, and ±5% at temperatures above 340 K. The uncertainty in the residual thermal conductivity function was estimated [2] to be ±5% for subcritical liquid and vapor, increasing to ±10% in the critical region. Thus, the uncertainty of the overall correlation for thermal conductivity likely ranges from ±5 to ±10%.

4.1. Dilute Gas

The thermal conductivity of the round-robin sample of R134a was measured in the dilute-gas state, near 1 bar pressure, with both the transient hot-wire technique and the steady-state hot-wire technique. The dilute gas presents special difficulties for transient instruments due to the very high thermal diffusivity of the gas in the limit of zero density [13]. The optimum transient hot-wire system should have a small wire diameter and a large outer boundary. The wire should be electrically isolated from the fluid. The transient instruments in this study included a bare 12.7-μm-diameter platinum hot-wire system with an 8-mm-diameter outer boundary at NIST in Boulder [14] and a 15.11-μm-diameter anodized tantalum hot-wire system with a 12-mm-diameter outer boundary at Aristotle University [15]. Because of large inner and outer boundary corrections in transient hot-wire measurements, the uncertainty at low densities is generally larger than that at higher densities. The uncertainty of the platinum hot-wire system at NIST is estimated to be ±3%, while the uncertainty of the Aristotle University system is ±1%. A steady-state hot-wire cell with a 25-μm-diameter anodized tantalum hot wire was used at NIST in Boulder [14] and is estimated to have an uncertainty of ±3%. This tantalum hot-wire cell can also be operated in a transient mode, but the corrections were considered too large to approach the dilute-gas limit.

The results from these three sets of measurements on the round-robin sample are shown in Fig. 5, along with some recent results using other techniques and samples. All of the measurements on the round-robin sample agree within their mutual estimated uncertainties and are systematically lower than the Krauss et al. [2] correlation at temperatures below 300 K but higher at temperatures above 360 K. The high-temperature steady-state results are consistent with those of Hammerschmidt [16], who used a steady-state parallel-plate apparatus, and with those of Tsvetkov et al. [17], who used a steady-state concentric-cylinder apparatus. There is good

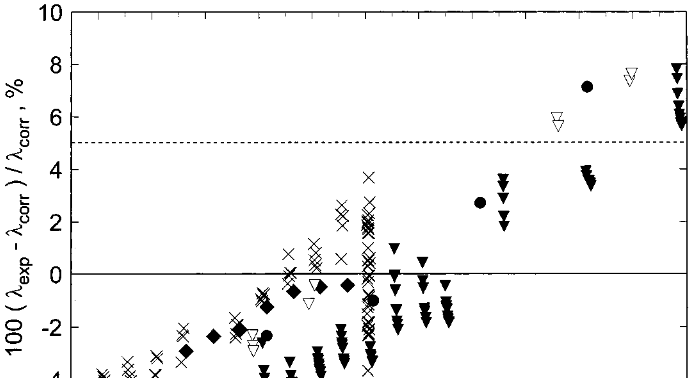

Fig. 5. Deviations of the measurements of the thermal conductivity of R134a in the dilute-gas state from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael et al. [15]; ×, Perkins [14] (Tr–Pt); ▼, Perkins [14] (SS–Ta). Literature: ●, Hammerschmidt [16]; ▽, Tsvetkov et al. [17].

agreement between all of these data sets at temperatures from 260 to 460 K. The systematic deviations indicate that improvement in the Krauss et al. [2] correlation is possible with the new data, although the data generally agree with the correlation within its estimated uncertainty, except for high temperatures.

4.2. Saturated Vapor

The thermal conductivity of the round-robin sample of R134a was measured near the saturated-vapor line with three transient hot-wire instruments and was also obtained from dynamic light-scattering measurements of thermal diffusivity. The transient hot-wire measurements were obtained with the same three cells described for the dilute-gas measurements, except that in this case, the 25-μm-diameter anodized-tantalum hot-wire cell at NIST was operated in a transient mode. The estimated uncertainties are $\pm 2\%$ for both NIST cells and $\pm 1\%$ for the Aristotle University cell [15]. The light-scattering measurements of thermal diffusivity, a, from Universität Erlangen-Nürnberg [18, 19] were converted to thermal conductivity with the Krauss et al. [2] correlation and the relation $\lambda = a\rho C_{\mathrm{p}}$. Light scattering has the advantage of not requiring a thermal gradient for measurements so there is no driving force for natural convection, making it particularly suitable for measurements near the gas–liquid critical point. However, the intensity of scattered light depends both on the proximity to the critical point and on the density of the scattering molecules. Consequently, there is a limited region near the critical point, especially for the low-density vapor, where reliable measurements are possible with an estimated uncertainty of $\pm 1\%$ for the thermal diffusivity [17]. The uncertainty of the thermal conductivity obtained from such thermal diffusivity measurements must be increased due to the uncertainty of the equation of state in the Krauss et al. [2] correlation.

Measurements within 0.324 K of the critical point were not considered in the present comparisons, because the observed critical point temperature [17] differed from that reported by Krauss et al. [2]. Such differences in the measured critical-point temperature could be due either to impurities or to small temperature gradients in the optical cell.

The deviations of the thermal conductivity of the saturated vapor from the Krauss et al. [2] correlations are shown in Fig. 6 as a function of temperature. The four data points obtained using light-scattering technique near 360 K are systematically 4% lower than the other data. Since an equation of state was used to derive the thermal conductivity from the measured thermal diffusivity data, the uncertainty of the equation of state [2] must be considered. Krauss et al. [2] do not provide estimates of uncertainty for

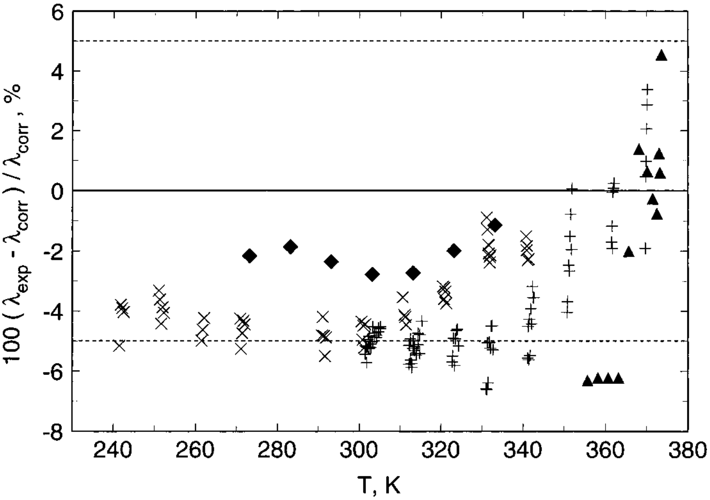

Fig. 6. Deviations of the measurements of the thermal conductivity of vapor R134a along the saturation line from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael et al. [15]; ×, Perkins [14] (Tr–Pt); +, Perkins [14] (Tr–Ta); ▲, Kraft and Leipertz [18, 19].

their crossover equation of state, but the uncertainty is likely dominated by the uncertainty of the heat capacity since only one liquid-phase point was available in the critical region. The increased uncertainty due to the equation of state is of the order of 3 to 5%. Considering the effect of the equation of state uncertainty on the conversion of the light-scattering results, the deviations are all within the estimated mutual uncertainty of each measurement technique. Even though the critical temperature observed during the light-scattering measurements differed from literature recommendations, the derived thermal conductivity is in good agreement with the other transient hot-wire measurements. Agreement between light-scattering and the transient hot-wire measurements near the critical point indicates that free convection was not significant during the transient hot-wire measurements.

4.3. Saturated Liquid

The thermal conductivity of the round-robin sample of R134a was measured near the saturated liquid line with five transient hot-wire instruments, and data were also obtained from dynamic light scattering measurements of thermal diffusivity. Transient hot-wire measurements of polar liquids are susceptible to errors due to polarization of and electrical conduction through the fluid surrounding the wires. Electrical conduction through polar fluids such as R134a is greatly enhanced by the presence of small quantities of water in the sample and increases with the fluid temperature. The water content of the present samples was verified to be low by Carl-Fischer titration.

Two measurement cells in the present study were designed specifically for use with electrically conducting fluids, with their tantalum hot wires electrically insulated from the fluid by anodized tantalum pentoxide layers. The cell used by Gurova et al. [20] was operated with a dc polarization voltage to minimize the effect of transient polarization of the fluid, while the remaining cells used bare hot wires.

The transient hot-wire measurements were made with (a) an apparatus at NIST in Boulder with bare 12.7-μm-diameter platinum wires and no polarization, (b) an apparatus at Universidade de Lisboa [20] with bare 7-μm-diameter platinum wires and a dc polarization voltage, (c) an apparatus at Keio University with bare 10-μm-diameter platinum wires and no polarization, (d) an apparatus at Aristotle University [15] with anodized 25-μm-diameter tantalum wires, and (e) an apparatus at NIST with anodized 25-μm-diameter tantalum wires [14]. The uncertainty of all these transient hot-wire instruments is less than ± 0.5–1% for non-electrically conducting liquid measurements which are not near the critical point. The thermal conductivity was also obtained from light-scattering measurements at Universität Erlangen Nürnberg [18, 19], as described for the saturated vapor, with an estimated uncertainty of $\pm 1\%$ in thermal diffusivity. Deviations of these results from the correlation of Krauss et al. [2] are shown in Fig. 7.

Two samples of the round-robin R134a were studied at Keio University. The first sample received at Keio University exhibited an unusually low electrical resistance of 1 MΩ when the liquid was filled in the hot-wire cell, so a subsample from the NIST cylinder, with a higher electrical resistivity, was sent to Keio University for study. The data obtained in Keio University with the first sample were systematically lower than those for the other data sets, by up to 4% at temperatures from 240 to 290 K, as shown in Figs. 7 and 8 of Ref. [1]. The Keio results for the NIST subsample are shown to agree very well with the other measurements in Fig. 7. Earlier results from Keio University on another sample of R134a [22], with an electrical resistance in the cell of more than 20 MΩ, are also in good agreement with the present results on the round-robin sample. Thus, contamination of the first Keio sample cylinder, as indicated by its low electrical resistivity, is shown to introduce significant deviations in the measured thermal conductivity of this sample. This figure also illustrates that over the same temperature region, good agreement is obtained with

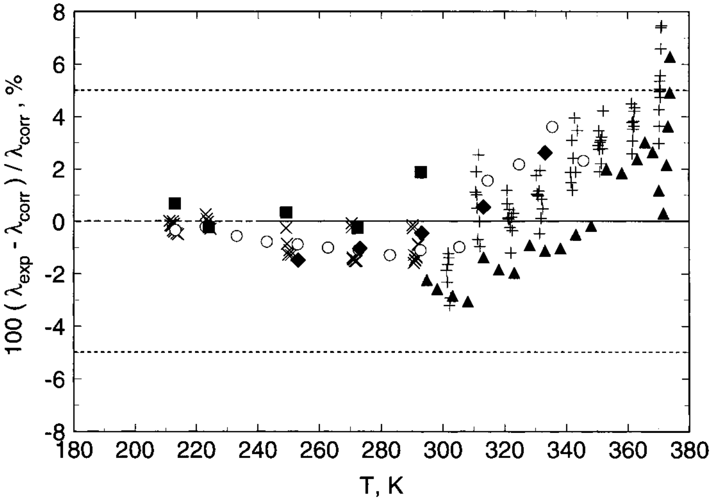

Fig. 7. Deviations of the measurements of the thermal conductivity of liquid R134a along the saturation line from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael et al. [15]; ×, Perkins [14] (Tr–Pt); +, Perkins [14] (Tr–Ta); ■, Gurova et al. [20]; ○, Nagasaka [21]; ▲, Kraft and Leipertz [18, 19].

electrically insulated, anodized hot wires (Aristotle University [12], NIST), polarized hot wires (Universidade de Lisboa [20]), and bare hot wires (NIST [14], Keio University [21]) for pure samples with a high electrical resistivity. Furthermore, there is good agreement at temperatures from 300 K to the critical point, within mutual uncertainty, between transient hot-wire measurements and the light-scattering results from Universität Erlangen Nürnberg [18, 19]. The baseline correlation of Krauss et al. [2] seems to extrapolate well at temperatures below its lower recommended limit of 240 K but is systematically low at temperatures above 340 K. It is useful to note that the same trend of systematic deviations is apparent in Fig. 6 for the saturated vapor as the critical density is approached, indicating that improvements in the correlation are possible with the new data.

4.4. Compressed Liquid

The thermal conductivity of the round-robin sample of R134a was measured at elevated pressures with the same five transient hot-wire instruments described in the previous section. The deviations of these compressed liquid data from the correlation of Krauss et al. [2] are shown

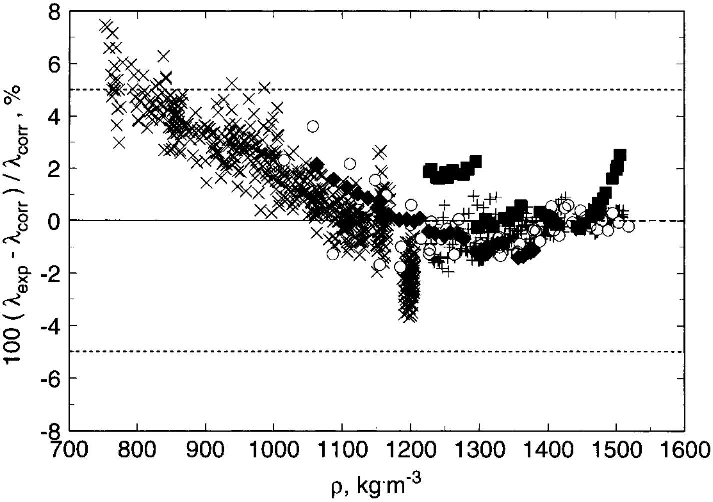

Fig. 8. Deviations of the measurements of the thermal conductivity of liquid R134a at elevated pressures from the correlation of Krauss et al. [2]. Round-robin sample: ◆, Assael et al. [15]; ×, Perkins [14] (Tr–Pt); +, Perkins [14] (Tr–Ta); ■, Gurova et al. [20]; ○, Nagasaka [21].

in Fig. 8 as a function of fluid density. At low densities approaching the critical point, the data are all systematically higher than the correlation. All of the transient hot-wire data sets are in good agreement with each other. Good agreement, $\pm 2\,\%$ at 2σ, is obtained between transient hot-wire instruments that use bare hot wires (NIST [14], Keio University [21, 22]), polarized hot wires (Universidade de Lisboa [20]), and electrically insulated, anodized, hot wires (Aristotle University [15] and NIST [14]) when measurements are made on samples with a high electrical resistivity.

4.5. Supercritical Fluid

Measurements of the thermal conductivity of R134a at supercritical temperatures from 390 to 450 K and at pressures to 70 MPa were obtained with a transient hot-wire cell with anodized tantalum hot wires at NIST in Boulder. Deviations between steady-state measurements obtained with the same cell at NIST and the correlation of Krauss et al. [2] have already been shown along with other literature data for the dilute gas in Fig. 5. The NIST measurements are the only ones that were carried out on the round-robin sample of R134a at temperatures above the critical temperature [2] (374.274 K). Hence, any comparisons must rely on literature data obtained on other samples. Because of issues such as natural convection, which are especially pronounced near the critical point, it is useful to make comparisons with data from other methods that do not require a temperature gradient such as dynamic light-scattering measurements of thermal diffusivity. The light-scattering data of Kruppa and Straub [23] were selected for this comparison to verify the absence of free convection and because they were key in the formulation of the correlation of Krauss et al. [2], which was used for the present baseline. Deviations of two transient hot-wire isotherms at 390 and 420 K are shown in Fig. 9 relative to the correlation of Krauss et al. [2] as a function of density. Three isotherms from Kruppa and Straub [23] are also shown in Fig. 9. Kruppa and Straub [23] obtained densities experimentally from refractive index measurements which are more accurate than those calculated from the correlation of Krauss et al. [2], given the uncertainty of their reported pressures. The experimental densities are used in computing the Kruppa and Straub [23] deviations shown in Fig. 9. The deviations of transient hot-wire measurements on the round-robin sample exhibit a characteristic maximum near the critical density of 515 $\text{kg} \cdot \text{m}^{-3}$, which is consistent and about 5% higher than the correlation [2] shown in Figs. 6 to 8 for the liquid and vapor as the critical point is approached. The transient hot-wire deviations in the limit of low-density dilute gas are about 4% high at 390 K and 7%

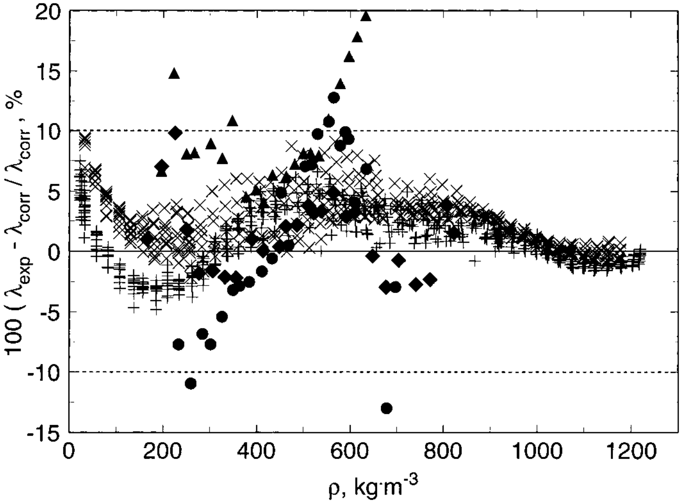

Fig. 9. Deviations of the measurements of the thermal conductivity of supercritical R134a from the correlation of Krauss et al. [2]. NIST transient hot wire on round-robin sample [14]: +, 390 K; ×, 420 K. Light scattering based on tabulated densities [19]: ●, 377 K; ◆, 390 K; ▲, 411 K.

high at 420 K, which are consistent with all of the steady-state deviations for the dilute gas that are shown in Fig. 5. The estimated uncertainty of the transient hot-wire measurements is about ±3% in the critical region because of increased problems due to free convection, but systematic deviations are not observed relative to the light-scattering data of Kruppa and Straub [23] where no temperature gradient is present. The light-scattering data show some relatively large deviations at densities removed from the critical density, which are likely due in part to uncertainties in the estimated isobaric heat capacity, C_p, obtained from the correlation of Krauss et al. [2], which was used to convert the measured thermal-diffusivity data to thermal-conductivity data. Figure 9 confirms that improvements in both the dilute-gas function and the residual function used in Eq. (2) of the correlation of Krauss et al. [2] are possible with the data on the round-robin sample of R134a. The uncertainty of ±10% which was estimated for the correlation of Krauss et al. [2] in the critical region appears to be consistent with all of the data.

5. CONCLUSIONS

Early studies of the transport properties of polar alternative refrigerants have been troubled by large discrepancies of more than 15 to 20% between established researchers that used a variety of experimental techniques. The magnitude and quantity of these discrepancies have been such that the credibility of transport properties measurement has been brought into question. The present study has been able to explore the effect of sample purity on the uncertainty and consistency of transport-property measurements of polar alternative refrigerants. The general conclusion of this study is that sample purity must be carefully assessed during all phases of transport-property measurements. It is not enough to obtain a high-purity sample from a reputable supplier and then to make measurements assuming that this high purity is maintained throughout the experiments, in particular, for materials such as polar refrigerants which are also very good solvents. Even the materials of the supply cylinder are potential sources of contamination that should not be overlooked. This source of contamination was evidenced by the high electrical conductivity that was observed in one cylinder of the round-robin R134a. Different sample cylinders were required during this study to satisfy the import/export regulations of the countries where the round-robin participants were located, complicating the delivery of a uniform sample to multiple researchers. The materials of construction of the measurement apparatus must also be assessed to insure that the pure sample is not contaminated. Elastomeric materials in seals and residual water, even at an adsorbed concentration level, can introduce dramatic errors during measurements of transport properties. Finally, it should not be overlooked that many materials of construction can have catalytic effects on the decomposition and polymerization of polar refrigerants. Reaction rates normally increase exponentially with temperature, so reactions must be carefully considered during high-temperature measurements. Optimally, the purity of the discharge sample from the measurement system should be assessed each time, although this is rarely possible and was not possible in the present study.

Despite weaknesses due to the resources available, the present study demonstrates that a group of informed and careful researchers, given a single high-purity sample which is carefully prepared by the supplier, can dramatically improve the reliability of their measurements such that they generally all agree within their estimated uncertainty for multiple measurement techniques. It is also shown that different experimental techniques are susceptible to errors from specific types of contamination. This was apparent in the transient hot-wire measurements made with bare hot wires at Keio University on their first sample. Such bare wire measurements of thermal conductivity are susceptible to errors when the electrical conductivity of the sample is high. This was also confirmed by Gurova et al. [20], by comparing data along the saturation line obtained with a round-robin sample and a sample of different origin that was obtained several years earlier. Measurements at Keio University with a new sample of low electrical conductivity showed good agreement, confirming that it is possible to use bare wires for samples with a low electrical conductivity. Excellent agreement was found with other techniques, including light scattering. Many viscometer transducers have a similar sensitivity to the polarity and electrical conductivity of the sample. The sensitivity of many transport property transducers to fine particulate contamination of measurement surfaces should not be overlooked. Several participants in the present study reported fine particulates if the sample was drawn from the sample cylinder in the liquid phase and, therefore, filled their measurement cells from the vapor phase. But such a procedure does not avoid all problems, as contaminants of low molecular weight may be concentrated in the vapor phase of the sample cylinder. Thus, it must be concluded that although high-purity samples are required, it is ultimately the care used during measurements, and the experience which each researcher has measuring similar materials, which lead to reliable results. In the case of measurements of transport properties of alternative refrigerants, early measurements were plagued both by unreliable sample composition and by inexperience in dealing with the effects of specific impurities on transducers which were perfectly reliable for nonpolar fluids.

The present measurements were all compared with the baseline correlation of Krauss et al. [2] for the transport properties of R134a. The uncertainty levels which were estimated by Krauss et al. [2] for this correlation are confirmed by measurements of the viscosity, thermal conductivity, and thermal diffusivity for the round-robin sample. The correlation is found to extrapolate to temperatures well below the minimum recommended temperatures both for viscosity (290 K) and for thermal conductivity (240 K). However, the present results indicate that improvements are possible in both the viscosity and the thermal-conductivity correlations for R134a with the data obtained on the round-robin sample. The range of measurements and the variety of measurement techniques which were used on the round-robin sample is remarkable given that each researcher, in conjunction with their respective research institutions, provided the resources required to make this study possible. The viscosity of the round-robin sample was measured with an oscillating-disk viscometer, three vibrating-wire viscometers, a falling-ball viscometer, a capillary flow viscometer, and a falling-body viscometer. The largest discrepancy for vapor viscosity was 2.5% with oscillating-disk and vibrating-wire viscometers in the low-density vapor. The largest discrepancy for liquid viscosity was 6% obtained with a falling-ball viscometer at high temperatures, with the maximum deviations between the falling-body and the vibrating-wire viscometers less than 3%.

The thermal conductivity of the round-robin sample was measured with a steady-state hot-wire system, and five transient hot-wire systems, and was derived from light scattering measurements of thermal diffusivity. There were three types of transient hot-wire cells used in the study: bare wires, polarized wires, and electrically insulated wires. Steady-state measurements of dilute-gas thermal conductivity [14] appear to be 4% lower than the transient measurements made on the same sample at NIST, but still agree to within their mutual uncertainty. Measurements with the cell optimized for dilute-gas studies at Aristotle University [12] fall between the NIST transient and the steady-state measurements [14], as do several steady-state studies of other samples. Agreement between three transient hot-wire systems and light-scattering measurements for the saturated-vapor thermal conductivity is generally within a band of ±2%. Agreement between the five transient hot-wire instruments and light-scattering measurements of saturated liquid thermal conductivity is also generally within a band of ±2%. Agreement between the compressed liquid thermal-conductivity measurements of the five transient hot-wire instruments is also generally within a band of ±2%. Transient hot-wire measurements using a bare hot wire in a sample with a high electrical conductivity are up to 4% lower than the mean of the data near 300 K. This is significantly less than the discrepancies of more than 15% which prompted this study. Supercritical transient hot-wire measurements on the round-robin sample exhibit no systematic offsets from earlier light-scattering measurements but have a much reduced scatter of ±4% relative to the deviations of 10 to 20%, which are observed in the light scattering data [19].

ACKNOWLEDGMENTS

The authors are grateful to the very large group of people who have made it possible to realize this international collaborative project. First, they acknowledge the willing and enthusiastic support of ICI Chemicals and Polymers in the United Kingdom. Not only did the company supply the cylinders of R134a free of charge to the various laboratories in the face of a plethora of different regulations, but they also made extensive efforts to maintain the purity of the samples and to analyze them. In particular, Mark Barley and Bob Wheelhouse of the company deserve special mention for their personal contributions. It has not been possible for practical reasons to include all of the students and staff of the institutions concerned as authors of this paper, although they have all been acknowledged in Table I and in the text. Their contributions to the work are very much appreciated. Finally, the authors thank Mo Williams, Executive Secretary of IUPAC, and Pat O'Hare, former Chairman of IUPACs Commission on Thermodynamics, for their support, which ensured that the project could be recognized as an important international project by IUPAC.

REFERENCES

1. M. J. Assael, Y. Nagasaka, C. A. Nieto de Castro, R. A. Perkins, K. Strom, E. Vogel, and W. A. Wakeham, *Int. J. Thermophys.* **16**:63 (1995).
2. R. Krauss, J. Luettmer-Strathmann, J. V. Sengers, and K. Stephan, *Int. J. Thermophys.* **14**:951 (1993).
3. R. Tillner-Roth and H. D. Baehr, *J. Phys. Chem. Ref. Data* **23**:657 (1994).
4. S. G. Penoncello, R. T. Jacobsen, K. M. de Reuck, A. E. Elhassan, R. C. Williams, and E. W. Lemmon, *Int. J. Thermophys.* **16**:781 (1995).
5. J. Wilhelm and E. Vogel, *Proc. 4th Asian Thermophys. Prop. Conf.* (Tokyo, 1995), Vol. 3, p. 627.
6. J. Wilhelm and E. Vogel, *Fluid Phase Equil.* **125**:257 (1996).
7. M. J. Assael and S. K. Polimatidou, *Int. J. Thermophys.* **18**:353 (1997).
8. D. C. Dowdell and G. P. Matthews, *J. Chem. Soc. Faraday Trans.* **89**:3545 (1993).
9. H. Nabizadeh and F. Mayinger, *High Temp.-High Press.* **24**:221 (1992).
10. M. F. Pasekov and E. E. Ustyuzhanin, *Teplofiz. Vys. Temp.* **32**:630 (1994).
11. E. MacPherson, personal communication (National Research Council, Ottawa, Ontario, Canada).
12. K. Ström, personal communication (Chalmers University of Technology, Göteborg, Sweden).
13. C. M. B. P. Oliveira and W. A. Wakeham, *Int. J. Thermophys.* **20**:365 (1999).

14. R. A. Perkins, J. Howley, M. L. V. Ramires, A. N. Gurova, and L. Cusco, National Institute of Standards and Technology, NISTIR (in press).
15. M. J. Assael, N. A. Malamataris, and L. Karagiannidis, *Int. J. Thermophys.* **18**:341 (1997).
16. U. Hammerschmidt, *Int. J. Thermophys.* **16**:1203 (1995).
17. O. B. Tsvetkov, Y. A. Laptev, and A. G. Asambaev, *Int. J. Refrig.* **18**:373 (1995).
18. K. Kraft and A. Leipertz, *Proc. 4th Asian Thermophys. Prop. Conf.* (Tokyo, 1995), Vol. 2, p. 251.
19. K. Kraft and A. Leipertz, *Fluid Phase Equil.* **125**:245 (1996).
20. A. N. Gurova, U. V. Mardolcar, and C. A. Nieto de Castro, *Int. J. Thermophys.* **18**:1077(1997).
21. Y. Nagasaka, personal communication (Keio University, Yokohama, Japan).
22. Y. Ueno, Y. Kobayashi, Y. Nagasaka, and A. Nagashima, *Trans. JSME*, **B57**-541:309 (1991).
23. B. Kruppa and J. Straub, *Fluid Phase Equil.* **80**:305 (1992).