THERMOPHYSICAL PROPERTIES OF ALTERNATIVE REFRIGERANTS

A.N. Gurova[1], M.T. Barão[1], A.T. Sousa[1],
C.A. Nieto de Castro[1], U.V. Mardolcar[2], P.S. Fialho[3]

[1] Departamento de Química and ICAT, Faculdade de Ciências
da Universidade de Lisboa, Campo Grande, Ed. C1, Piso 5,
1700 Lisboa, Portugal
[2] Departamento de Física, Instituto Superior Técnico
Av. Rovisco Pais, 1096 Lisboa Codex, Portugal
[3] Departamento de Ciências Agrárias, Universidade dos Açores,
9702 Angra do Heroísmo Codex, Portugal

ABSTRACT

The need for new environmentally acceptable refrigerants, with low or zero ozone depletion potential and low global warming potential, led the industrial and the scientific community to launch a significant research effort on the thermophysical properties of these compounds. It is the purpose of this paper to give an overall view of the current research in this field, started in 1990 by our group, in collaboration with the LIMHP-CNRS, Villetaneuse, France, and the NIST, Boulder, USA. The effort has been concentrated in developing equipments to measure density dielectric constant and thermal conductivity in the liquid phase, covering the temperature and pressure ranges necessary for the normal duty of these fluids. The dielectric constant and the thermal conductivity of three provisional replacements, HCFC 123, HCFC 141b, HCFC 142b and two class A fluids, HFC 134a and HFC 152a, have been measured in the temperature range 200 to 300 K and pressures up to 20 MPa, using a direct capacitance method, by measuring the capacitance of a cylinder filled with the sample and in vacuum, using an impedance analyzer, and the polarized hot wire technique. The density of HCFC 142b, HCFC 22 + HCFC 142b and HCFC 141b was measured with a vibrating fork densimeter, calibrated with toluene, 2,2,4-trimethylpentane and vacuum. The instruments are capable of obtaining the dielectric constant with an absolute uncertainty of 0.1 %, the thermal conductivity with 0.5 % and the density with 0.1 %. An Hard Sphere De Santis equation of state has been used to develop an universal estimation scheme for the density of pure refrigerants and of their mixtures, based only upon the properties of pure fluids, capable of calculating the density of the liquid phase with an uncertainty better than 1.5 % for $T/T_c < 0.9$. The density dependence of the dielectric constant has been studied using the concept of Eulerian strain and the Onsager-Kirkwood theories. The dipole moments of the several refrigerants in the liquid phase were obtained.

INTRODUCTION

Accurate data of thermophysical properties is very important for the development, design, planning and operation of processes in several industries. For example, modern processes in the chemical industry, environmental protection and plant safety are becoming increasingly important. Thermophysical data constitute one of the most important cornerstones in the development of processes for several industries.

The search for the replacement of harmful halocarbons used in the refrigeration, air conditioning and foam blowing industries lead the international community to the establishment of a concerted effort to determine the thermophysical properties of the alternative compounds, chosen to have a small or zero ozone depletion potential and small global warming potential.

The use of these compounds in heat exchangers, expansion valves, condensers and other units involved in the heat transfer needs the knowledge of the transport properties as thermal conductivity and the thermal diffusivity $a = \lambda/\rho C_p$, of the thermodynamic properties as the density and the equation of state, and of dielectric properties as the dielectric constant. The measurement of these properties for non polar fluids has now became standard, even in regions close to the critical point. However, when we are dealing with the halocarbons, polar fluids with reasonably high dipole moments ($0.3\ D < \mu < 3.2\ D$), the most rigorous methods of measurement, as the transient hot-wire technique for thermal conductivity an the direct capacitance method for the dielectric constant, have to be modified to take account of this fact and of the high solubility capacity of these compounds. In addition, the transfer of heat by radiation playing an important role in the process, has to be considered with a different approach. In addition there is a need for universal estimation schemes, theoretically based, specially for density of mixtures of these fluids in the liquid state.

Recent analysis of the existing data demonstrates that there are discrepancies between the different authors that exceed the estimated mutual uncertainties, a fact that does not happen for the major part of normal fluids.

It is the purpose of this paper to give a general, but necessarily brief, view of the work developed by our group in Lisbon, both experimental and semi-theoretical.

EXPERIMENTAL APPARATUS AND MEASUREMENTS

The properties measured experimentally where density, thermal conductivity and dielectric constant. The density was measured with a densimeter (Anton Paar DMA 60) equipped with a high temperature-high pressure cell (DMA 512). Details of the instrument and of the measuring principle were fully described the in reference [1]. This type of densimeters operates in relative mode and the density of a sample at a given temperature and pressure, can be obtained from the measured period of vibration of the mechanical oscillator filled with the sample and in vacuum. The accuracy of the data is 0.08 %.

The thermal conductivity was measured using a modification of the transient hot wire technique, as bare platinum wires used in non polar liquids [2] can not be used. Unexpected electrical effects (secondary path for the flow of current in the cell, polarization of the liquids at the surface of the wire, combined resistance/capacitance effects), as well as chemical effects leading to polymerization appear when this technique is used for the measurement of λ polar fluids, such as fluorocarbons, and so the final result is affected by a huge uncertainty. The reproducibility is greatly increased when a dc polarization voltage is applied between the hot wires and the cell wall [3]. The permanent dc polarization voltage establishes compact double layers near the surfaces in the resulting electric field. They contain solvated ions with a charge with opposite signal of that of the metallic surface which they surround , in order to keep a neutral electrical field inside the solution. In effect, they shield 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. Results obtained for several HCFC's and HFC's in Lisbon and Boulder [4,5] have shown that the uncertainty is 0.5 % to 1 %.

The measurements of the dielectric constant were made using a direct capacitance method, by measuring the ratio of the capacitances of a cell filled with the sample and under vacuum. The experimental set up and its performance have been described in detail by Gurova et al. [4], while a description of the cell was made by Mardolcar et al.[6]. The sample handling was also described in reference [4]. The principal addition to the measuring system was the high pressure line, composed by a HIP liquid pressure generator and a Newport Scientific gas compressor, and a pressure transducer, from Setra Systems with a precision of 0.1 bar. Measurements were made at an average of twelve isotherms separated by 10 K, in steps of 10 bar, from slightly above the saturation pressure to 20 MPa. The values of the experimental data where obtained at a frequency of 10 kHz, with an estimated precision of 0.01% and an accuracy better than 0.1%.

Table I shows the fluids studied, the properties measured, and the temperature and pressure ranges covered. For most of the fluids only the liquid phase was covered, but for HCFC 142b and HFC 134a it was possible to make measurements from the dilute gas, vapour, liquid and supercritical regions. New results were obtained in the last four months that are not yet published. However they deserve mentioning, specially because the thermal conductivity of HCFC 123, HCFC 141b and HFC 134a has been measured in the same temperature intervals than those reported in reference [4], but for pressures up to 20 MPa. These results will be published in a near future [16].

A sample of the results obtained is presented in figures 1 to 3. Figure 1 displays the density of the mixture HCFC 22 + HCFC 142b 40/60 wt%, as a function of the temperature and pressure. The lines represent the first application of the hard-sphere-De Santis equation of state (HSDS) [4]. This equation has the form:

$$\frac{PV}{RT}=\sum_{i=1}^{10} C_i\left(\frac{b}{V}\right)^{i-1} - \frac{a}{RT(V+b)} \qquad (1)$$

In this equation the repulsive part is represented by the virial coefficient expansion, with the 10 virial coefficients obtained from molecular dynamics simulation. The values of the constants *a* and *b* were assumed to have quadratic dependence on the molar fraction.

Table I - Halocarbons measured, Properties measured and corresponding temperature and pressure ranges

FLUID	Density	Reference	Thermal conductivity	Reference	Dielectric constant	Reference
HCFC 123	-	-	227 - 194 K saturation line	[4,10]	200 - 300 K saturation line	[4]
HCFC 141b	260 - 320 up to 16 MPa	[7,8]	200 - 305 K saturation line	[4,10]	200 - 300 K saturation line	[4]
HCFC 142b	300 - 370 K up to 19 MPa	[9]	206 - 273 K saturation line 290 - 590 up to 20 MPa	[4,10] [11]	200 - 300 K up to 20 MPa	[4,15]
HFC 134a	-	-	200 - 300 K up to 20 MPa 200 - 390 K up to 70 MPa	[10,12] [13]	200 - 300 K up to 20 MPa	[4,15]
HFC 152a	-	-	200 - 300 K up to 20 MPa	[14]	200 - 300 K up to 20 MPa	[14]
HCFC 22 + HCFC 142b	300 - 370 K up to 19 MPa	[9]	-	-	-	-

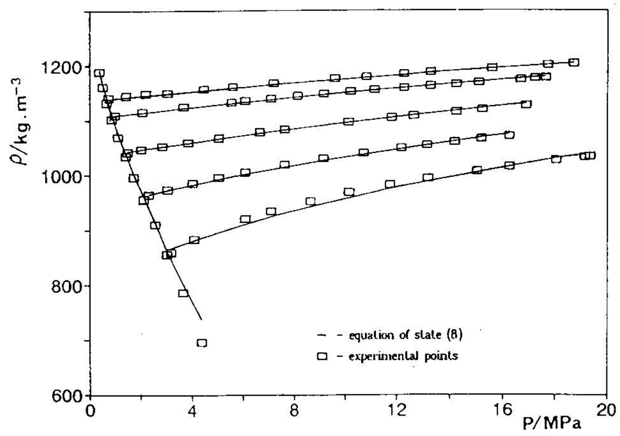

Fig. 1. The density of the mixture HCFC 22 + HCFC 142b 40/60 wt %, as a function of temperature and pressure.

Figure 2 shows the thermal conductivity of HFC 134a in the saturation line, between 200 and 300 K, compared with the values obtained by other authors. It has been suggested that purity of the samples is a possible source for the discrepancies found between the thermal conductivity data obtained by different authors. Therefore we have measured samples of different origin (Solvay Fluor und Derivative and Imperial Chemical Industries). Both sets of results [10,13] are displayed in this figure.

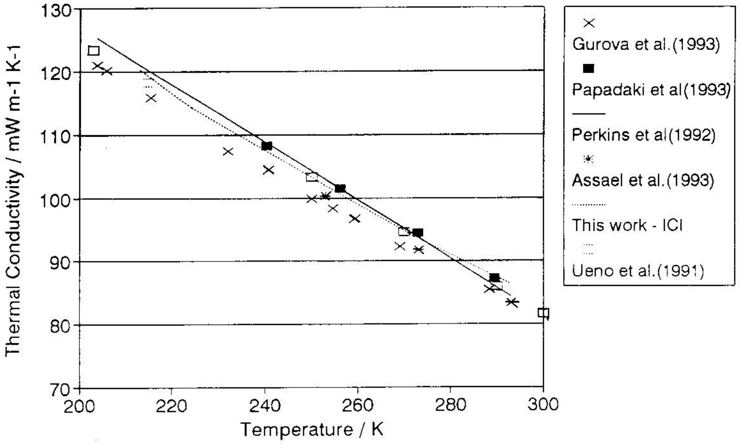

Fig. 2. The thermal conductivity of HFC 134a in the saturation line as a function of temperature, from different sources [10,13, 17-19].

It can be seen that the discrepancies between the several sets of data is about 2.5 %, well beyond their mutual uncertainty. A round robin test, with the same sample distributed to several laboratories around the world is undergoing, trying to explain the reason for these discrepancies. The first results were presented recently at the 12th STP in Boulder [20].

Figure 3 shows the variation of the dielectric constant of HFC 134a with density. Aplication of the Kirkwood-Onsager theory permitted the calculation of the dipole moments of several fluids in the liquid phase [14,15]. These values are presented in Table II, along with the values for the gas phase [21] and the Kirkwood correlation factors, g.

Table II. Dipole moments and Kirkwood correlation factor for HFC 134a, HCFC 142b and HFC 152a in the liquid state [14,15]

Fluid	μ^*	μ **[21]**	**g**
HFC 134a	3.54	2.06	2.96
HFC 142b	3.17	2.14	2.20
HFC 152a	3.69	2.26	2.67

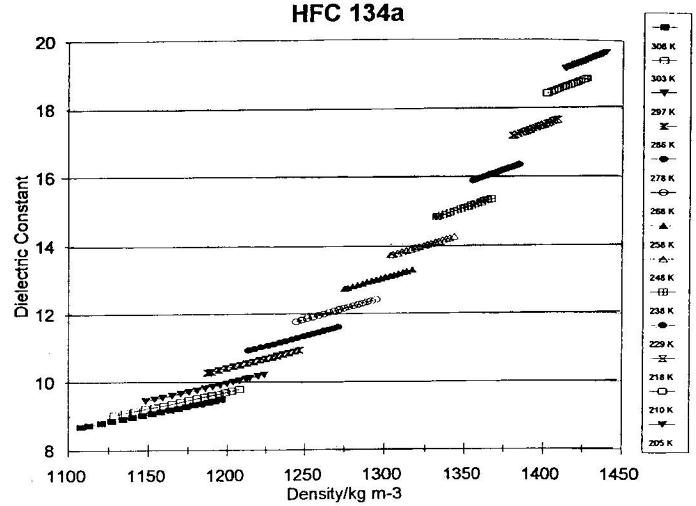

Fig. 3. The dielectric constant of HFC 134a as a function of temperature and pressure [15].

The increasing need for information on liquid density for the new refrigerants, has led the authors to try to implement a new scheme to correlate and estimate them from the fewer experimental available information. As a starting point we have used the Hard Sphere DeSantis equation (1) to correlate the available experimental data of the density of liquid refrigerants (R114, R123, R142b, R152a, R22), in order to be able to obtain the parameters *a*(*T*) and *b*(*T*) needed to develop the model of the reduced equation of state. Details of the application can be foun for pure liquids and liquid mixtures associating it with mixing and combination rules in references [22,23]. The application to mixtures only uses pure component data.

A comparison between the new model (HSDS) and the Hankinson-Brobst-Thomson (HBT) was used to demonstrate the better behaviour of the HSDS equation that is able to estimate in ±1.5% for $T^* = T/T_c$ less or equal 0.9, the liquid density of the refrigerants, in comparison to the -5 to 30% of the HBT model.

The new model has been used to predict the data available for other fluids R32, R125, R134a, R134, R141b, R142b+R22, R22+R152a, R152a+R142b and R114+R22, and for the ternary mixture of R22+R152a+R142b the error found being within ±1.5% for T^* less or equal to 0.9. To the author's best knowledge there is no other density estimation method applicable to the halocarbons with such a high accuracy. Figure 4 shows the results ontained for binary mixtures.

CONCLUSIONS

Experimental determinations of density, thermal conductivity and dielectric constant of alternative refrigerants and a powerfull estimation scheme for the density of liquid refrigerants and of their mixtures have been summarized. Dipole moments of the HCFC 142b, HFC 134a and HFC 152a have been obtained. This paper reports the work performed by the group in Lisbon and in collaboartion with Dr. Tufeu and Le Neindre at the LIMHP-CNRS, Villetaneuse, France, and Dr. Perkins at the NIST, Boulder, Colorado, USA. Further data and theoretical interpretations will be published in a near future, including HFC 32.

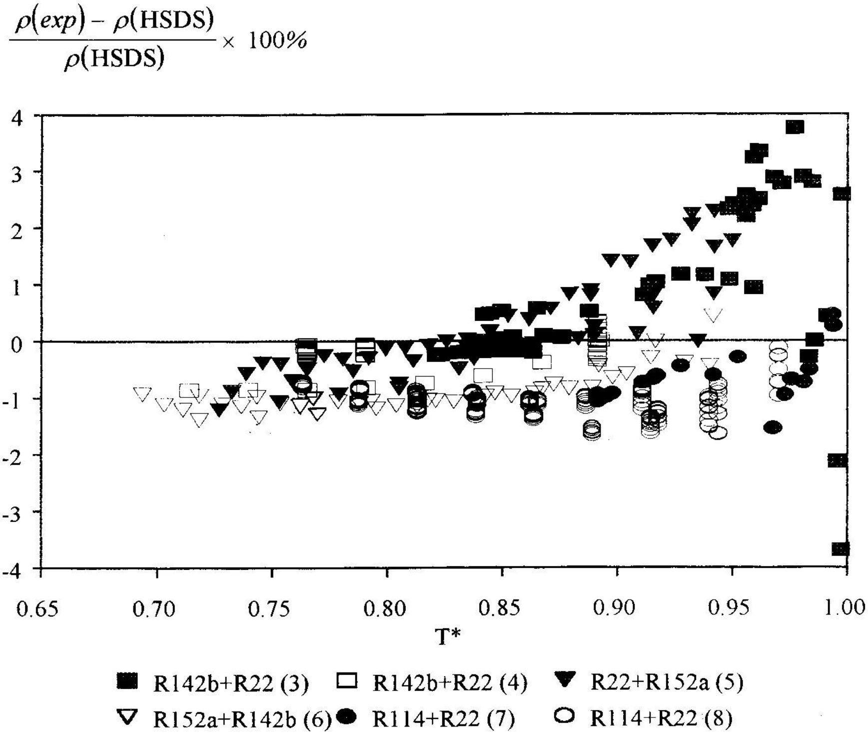

Fig. 4. Deviations between the experimental density, obtained for diferent binary mixtures of refrigerants, and the one predicted by the reduced HSDS model with the arithmetic and geometriccombination rules for the heteromolecular interaction and the quadratic mixing rules for the properties. The numders in brackets in the mixture identification refer to experimental works [23].

NUMENCLATURE

P - Pressure
T - Thermodynamic temperature
V - Molar Volume
a, *b* - HSDS equation of state constants
R - Gas constant
C_i - Hard sphere virial coefficients
*T** - reduced temperature

ε - dielectric constant
λ - Thermal conductivity
ρ - density
μ - dipole moment in gas phase
μ^* - dipole moment in liquid phase
g - Kirkwood factor

REFERENCES

[1] Sousa, A. T., Nieto de Castro, C. A., Tufeu, R., Le Neindre, B.(1992). Density of 1-chloro-1,1-difluoroethane (R142b). *High Temperatures-High Pressures,* 24, 185-194.

[2] Mardolcar, U. V., Fareleira, J. M. N. A., Nieto de Castro, C. A., Wakeham, W. A. (1985). Measurement of the thermal conductivity of argon: a test of the accuracy of a transient hot wire instrument. *High Temperatures-High Pressures,* 17, 469-476.

[3] Nieto de Castro, C. A., Dix, M., Fareleira, J. M. N. A., Li, S. F. Y., Wakeham, W. A. (1989). Thermal conductivity of chlorobenzene at pressures up tp 430 MPa. Physica A, 156, 534-546.

[4] Gurova, A. N.;, Barão, T. G., Mardolcar, U. V., Nieto de Castro, C. A. (1994). The thermal conductivity and dielectric constant of HCFC 141b, HCFC 123, HCFC 142b and HFC 134a. *High Temperatures-High Pressures,* xxx, in press

[5] Perkins, R. A., Laesecke, A., Nieto de Castro, C. A. (1992). Polarized transient hot-wire thermal conductivity measurements. *Fluid Phase Equilibria,* 80, 275-286.

[6] Mardolcar, U. V., Nieto de Castro, C. A.,. Santos, F. J. V, *Fluid Phase Equilibria,* 79, 255 (1992)

[7] Sousa, A. T., Fialho, P. S., Nieto de Castro, C. A. (1994).). The density of 1,1-dichloro-1-difluoroethane (R141b). *International Journal of Thermophysics,* 15, 375-376.

[8] Sousa, A. T., Nieto de Castro, C. A., Tufeu, R., Le Neindre, B.(1994).). The density of 1,1-dichloro-1-difluoroethane (R141b) as a function of temperature and pressue. *Proceedings of the 12th Symposium on Thermophysical Properties, Bouder, Colorado, USA, June, to be published in International Journal of Thermophysics.*

[9] Sousa, A. T., Nieto de Castro, C. A., Tufeu, R., Le Neindre, B.(1992). Density of HCFC 142b and of its mixture with HCFC 22. *Fluid Phase Equilibria,* 80, 213-225.

[10] Gurova, A. N., Mardolcar, U. V., Nieto de Castro, C. A. (1994). The thermal conductivity of environmentally acceptable liquid refrigerants. *Thermal Conductivity 22,* T. Tong ed., Plenum Press.

[11] Sousa, A. T., Fialho, P. S., Nieto de Castro, C. A., Tufeu, R., Le Neindre, B.(1992). The thermal conductivity of 1-chloro-1,1-difluoroethane (HCFC 142b). *International Journal of Thermophysics,* 13, 383-399.

[12] Gurova, A. N., Mardolcar, U. V., Nieto de Castro, C. A. (1994). The thermal conductivity of liquid HFC 134a. *Proceedings of the 12th Symposium on Thermophysical Properties, Bouder, Colorado, USA, June, to be published in International Journal of Thermophysics.*

[13] Laesecke, A., Perkins, R. A., Nieto de Castro. (1992). Thermal conductivity of R134a. *Fluid Phase Equilibria,* 80, 263-274.

[14] Gurova, A. N., Barão, M. T., Mardolcar, U. V., Nieto de Castro, C. A. (1994). The density dependence of the dielectric constant and thermal conductivity of HFC 152a. Paper presented at the *12th Symposium on Thermophysical Properties, Bouder, Colorado, USA, June.* To be published

[15] Barão, T. G., Mardolcar, U. V., Nieto de Castro, C. A. (1994). The dielectric constant of liquid HFC 134a and HCFC 142b. *Proceedings of the 12th Symposium*

on Thermophysical Properties, Bouder, Colorado, USA, June, to be published in International Journal of Thermophysics.

[16] Gurova, A. N., Mardolcar, U. V., Nieto de Castro, C. A. (1994). To be published.

[17] Assael, M. J., Karagiannidis, E. (1993). Measurements of the thermal conductivity of R22, R123, and R134a in the temperature range 250-340 K, at pressures up to 30 MPa. *International Journal of Thermophysics,* 14, 183-197.

[18] Nagasaka, Y., Ueno, Y., Koboyashi, Y., Nagashima, A. (1991). Thermal conductivity of CFC alternatives. Measurement of HCFC 123 and HFC 134a in the liquid phase by the transient hot wire method. *Transactions of the Japanese Society of Mechanical Engineers,* **57**, 3169-3175.

[19] Papadaki, M., Schmitt, M., Seitz, A., Stephan, K., Taxis, B., Wakeham W. A. (1993). Thermal Conductivity of R134a and R141b Within the Temperature Range 240-307 K at the Saturation Vapour Pressure. *International Journal of Thermophysics,* 14, 173-181.

[20] Assael, M. J., Nagasaka, Y., Nieto de Castro, C. A., Perkins, R. A., Strom, K., Vogel, E., Wakeham, W. A. (1994). Round-Robin on the transport properties of R134a. Paper presented at the *12th Symposium on Thermophysical Properties, Bouder, Colorado, USA, June.* To be published.

[21] Morrison, G. (1993). REFPROP, NIST Database 23, Version 4.0.

[22] Fialho, P. S., Nieto de Castro, C. A. (1994) The Density of Liquid Hydrochlorofluorocarbons (HCFC's) and Hydrofluorocarbons (HFC's) - Part I - Pure Fluids. Submitted to *Fluid Phase Equilibria.*

[23] Fialho, P. S., Nieto de Castro, C. A. (1994) The Density of Liquid Hydrochlorofluorocarbons (HCFC's) and Hydrofluorocarbons (HFC's) - Part II - Liquid Mixtures. Submitted to *Fluid Phase Equilibria.*