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THERMOPHYSICAL PROPERTIES OF HCFC ALTERNATIVES

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THERMODYNAMIC PROPERTIES OF HCFC ALTERNATIVES

**ARTI MCLR Project Number 660-50800
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ABSTRACT

Numerous fluids and fluid mixtures have been identified as promising alternatives to the HCFC refrigerants, but, for many of them, reliable thermodynamic data do not exist. In particular, reliable thermodynamic properties data and models are needed to predict the performance of the new refrigerants in heating and cooling equipment and to design and optimize equipment to be reliable and energy efficient. The objective of this project is to measure, with high accuracy, selected thermodynamic properties data for two pure refrigerants and nine refrigerant blends; these data will be used to fit equations of state and other property models which can be used in equipment design. The new data will fill in gaps in the existing data and resolve problems and differences that exist in and between existing data sets. Most of the studied fluids and blends are potential replacements for HCFC-22 and/or R502; in addition, one pure fluid and one blend are potential replacements for CFC-13 in low temperature refrigeration applications.

SCOPE

This project involves the measurement of primary thermodynamic data for eight binary mixtures and one ternary mixture (R125/143a; R32/143a; R125/143a; R143a/134a; R32/290; R125/290; R290/134a; R41/744; and R32/125/134a). These data will consist of simultaneous measurements of the coexisting liquid and vapor densities and coexisting liquid and vapor compositions as well as the bubble point pressures over a wide range of temperature and composition. These data will be used to determine the mixing parameters, including any temperature and/or composition dependence, for the Carnahan-Starling-DeSantis (CSD) equation of state and the extended corresponding states (ECS) model. Primary data will also be measured for the pure fluid HFC-41. These measurements will include the determination of vapor pressure; liquid density; liquid, two-phase, and ideal gas heat capacities; vapor sound speeds and virial coefficients; and a determination of the critical point parameters. These data will cover wide ranges of temperature and pressure and will be used (together with available literature data) to fit equations of state and other models of the thermodynamic properties. The original proposal called for similar measurements of primary data for HFC-245ca; such work on this fluid has been funded by another sponsor, and several alternatives to this task are outlined below. During the past quarter, preparations have been made to initiate measurements on the mixtures using the vapor-liquid equilibria apparatus. Plans for the measurement program are presented in this report.

WORK PLAN FOR ARTI PHASE III MEASUREMENTS

Primary mixture data for binary mixtures of relatively volatile components (R125/143a; R32/143a; R125/143a; R143a/134a; R32/290; R125/290; R290/134a)

This work will be carried out in the circulating VLE apparatus. The coexisting liquid and vapor densities and coexisting liquid and vapor compositions as well as the bubble point pressure are measured simultaneously. The apparatus operates along isotherms, which will be measured at 15 K intervals from 280 K to slightly below the critical temperature. For each isotherm, 6 to 8 data points covering a composition range of about 0.10 to 0.90 mole fraction will be measured. These measurements will provide an extensive mapping of the mixture surface, including information on any composition and/or temperature dependence of the mixing parameter. The mixing parameters for the CSD and ECS models will be determined from these data for inclusion in REFPROP.

Primary mixture data for a ternary mixture of relatively volatile components (R32/125/134a)

This work is essentially identical to the measurements for binary mixtures except in the way that the composition is varied. For each of about eight isotherms from about 280 K to the critical point, we will start with a binary mixture of the two least volatile components (R125 + R134a), gradually adding the third component (R32) to define a line of 6 to 8 compositions cutting across the ternary composition map. We will do two such lines, i.e., starting with 0.33/0.67 and 0.67/0.33 mole fraction blends of the two least volatile components.

Primary data for a very low-boiling fluid (HFC-41)

For this task, we are proposing a bit of a departure from what we have considered "primary data" in the past. This has resulted from both a reexamination of which data are required for equation of state fitting combined with wringing more data out of our existing apparatus. As we acquire more experience in fitting equations of state to the refrigerants, we have come to realize that some sort of "second order" data, such as heat capacities, are essential. We have also discounted the need for saturated vapor density data—this is a very difficult measurement, meaning that these data are often poor; they are often thrown out of the fit even when they are available. Furthermore, all of the data should cover as wide a range of pressure and, especially, temperature as possible—extrapolation to lower temperatures is fraught with difficulty. While these conclusions are drawn from experience with the MBWR equation of state, these additional data will also be invaluable for the simple equations, such as the CSD. We also would like to take data sufficient to fit an equation of intermediate complexity.

A slightly different approach for HFC-41 is also dictated because of the very low boiling point of this fluid and the existence of literature data. Data at high temperatures have been reported in the literature, but since the interest in HFC-41 is for very low temperature applications, further low temperature measurements are of prime importance. Our low temperature measurements combined with the literature data at higher temperatures will permit us to fit a MBWR equation of state. Specifically we propose:

Measurements of the liquid-phase isochoric heat capacity along about 10 isochores extending from near the triple point to about 340 K, with pressures to about 30 MPa; 6 to 12 points per isochore will be measured depending on the "steepness" of the isochore—about 6 points for a high density, low temperature isochore compared to 12 or more for an isochore near the critical density. These data will also yield isochoric PVT data with an uncertainty of about $\pm 0.2\%$. Also measured on this apparatus will be two-phase states yielding C_{sat} data. Besides being useful in their own right, these C_{sat} data will be used to "back out" vapor pressures below about 20 kPa (0.2 bar or 3 psia), where direct measurement is increasingly inaccurate.

Limited isochoric PVT measurements over a temperature and pressure range similar to the heat capacity measurements; 6 to 12 points will be measured for each of 6 to 8 isochores at an uncertainty of $\pm 0.05\%$. These data will serve as "checks" on the PVT data from the calorimeter; both sets of PVT data will be extrapolated to saturation to yield a saturated liquid density curve extending from near the triple point to about 20 K below the critical temperature. A vapor pressure curve from a temperature corresponding to a pressure of about 10 kPa to a temperature a few degrees below the critical temperature will also be measured in this apparatus.

Determination of critical temperature and density in visual cell. (The critical pressure would be determined by extrapolating the vapor pressure curve a few degrees to the critical temperature.) These measurements would include determination of the saturated liquid and saturated vapor densities near the critical point, thus augmenting the saturated liquid densities extracted from the isochoric PVT measurements. These measurements should be simplified by a critical temperature close to room temperature.

Vapor sound speed measurements in a spherical resonator over a temperature range of at least -40°C to 100°C with pressures up to about $1/2$ the vapor pressure. These data would yield ideal gas heat capacities and second virial coefficients. The very simple structure of this molecule means that ideal gas heat capacities calculated from spectroscopic measurements should be very accurate. Nevertheless, sound speed data are needed for the determination of second virial coefficients which will constitute the primary vapor phase information for equation of state fitting.

The dipole moment for this fluid has been reported in the literature and does not need to be redone.

These data will be combined with literature data to fit the coefficients to the MBWR equation of state.

An advantage of the planned measurements for this pure fluid is that all of the data are of "comprehensive data" quality. If, in the future, we would want to measure comprehensive data, the heat capacities and vapor sound speed work would be done, as would much of the liquid PVT. This would leave vapor PVT, critical region PVT, more closely spaced saturated liquid density points, perhaps a confirming vapor pressure curve, and not much else.

Primary mixture data for a binary mixture of very low-boiling components (R41/744)

This mixture requires a slightly different approach because the temperature range of interest is very low.

This work will be carried out in a cryogenic VLE apparatus that simultaneously measures the coexisting liquid and vapor compositions as well as the bubble point pressure. It operates along isotherms, yielding 6 to 8 data points covering a composition range of about 0.10 to 0.90 mole fraction per isotherm. About six isotherms covering a temperature range from near the triple point to about 300 K (slightly below the critical temperature) will be measured.

Liquid densities for an equimolar composition will be determined in the isochoric PVT apparatus, with 6 to 8 isochores being measured. These measurements provide somewhat less data than those for the other binary mixtures but still yield more data than available for most mixtures. The mixing parameters for the CSD and ECS models will be determined from these data for inclusion in REFPROP.

Proposed options for substitute for HFC-245ca in this project

As noted above, the work originally proposed for HFC-245ca is being funded by another sponsor. We would like to suggest additional high priority measurement needs which remain for other pure fluids and blends. Any one of these could be substituted for the original task on HFC-245ca within the present budget.

1. Primary thermodynamic data for pure HFC-227ea.
2. Primary thermodynamic data for pure HFC-134.
3. Selected thermodynamic measurements on HFC-23 to be combined with literature data to bring that fluid to "comprehensive data" status.
4. Selected thermodynamic measurements on a hydrocarbon, such as pentane or propylene, to be combined with literature data to bring that fluid to "comprehensive data" status.
5. Comprehensive mixture data for a binary system, such as R125/143a, for which VLE measurements are already scheduled.

The measurements of "primary thermodynamic data" for a pure fluid would be similar to those outlined above for HFC-41. The "selected thermodynamic measurements" for a pure fluid would fill in gaps and resolve inconsistencies in the existing literature data and would permit the fitting of a high-accuracy MBWR equation of state. They would be analogous to the thermodynamic portion of the task for HFC-152a in the Phase I task recently completed at NIST. "Comprehensive mixture data" would involve pressure-volume-temperature (PVT) measurements along about ten isochores in the liquid phase and five isochores at moderately high densities in the vapor phase over the temperature range from -50°C to near the critical temperature. Isochoric heat capacity data over a similar range of temperatures and densities would also be measured. Such a task would be similar to work we are carrying out for the U.S. Department of Energy for the mixtures R32/134a and R32/125 (see section "Related Work" below).

RELATED WORK

For several years, NIST has been conducting research on safe alternatives to the CFC and HCFC refrigerants for the Refrigeration Systems Program of the U.S. Department of Energy. The objective of this work is to provide the air conditioning and refrigeration industries with the fundamental data needed to accelerate the introduction of highly efficient, environmentally benign alternative refrigerants in response to the Montreal Protocol and the Clean Air Act, which regulate the CFC and HCFC refrigerants now in use. It is, thus, directly related to the ARTI work.

The research program currently underway includes two major research areas:

1. Thermodynamic performance of alternative refrigerants.
2. Thermophysical properties research.

The primary objective of the properties work is to develop new and highly advanced thermophysical properties models for incorporation into the REFPROP computer package, distributed by NIST. These models are required by industry to evaluate alternative working fluids as potential CFC and HCFC substitutes in air conditioning and refrigeration applications and for equipment design. A task in support of this modeling work involves experimental mixture measurements which are complementary to the ARTI work; this task is outlined below. The research on "Thermodynamic performance of alternative refrigerants" is being carried out in the Building and Fire Research Laboratory of NIST.

COMPREHENSIVE THERMODYNAMIC PROPERTIES OF HFC MIXTURES

Obtain thermodynamic properties for two compositions of the refrigerant mixture R32/134a and one composition of the mixture R32/125. For each composition, obtain pressure-volume-temperature (PVT) measurements along ten isochores in the liquid phase and five isochores at moderately high densities in the vapor phase over the temperature range from -50°C to near the critical temperature. Obtain isochoric heat capacity data over a similar range of temperatures and densities. For the R32/134a and R32/125 systems obtain vapor-liquid-equilibrium (VLE) data along five isotherms from 20°C to near the critical temperature with 6 to 8 compositions per isotherm covering the composition range of 0.10 to 0.90 mole fraction.

Year 1:

Measure PVT and heat capacity data for one composition of R32/134a.

Measure VLE data for the R32/134a system.

Year 2:

Measure PVT and heat capacity data for one composition of R32/125 and one additional composition of R32/134a

Measure VLE data for the R32/125 system.

Progress—We are nearing the end of the Year 1 work. Comprehensive PVT and C_p measurements have been completed for the equimolar mixture of R32 + R134a. VLE measurements for the R32/134a system are in progress.

COMPLIANCE WITH AGREEMENT

NIST has complied with all terms of the grant agreement modulo small shifts in the estimated level of effort from one property and/or fluid to another.

PRINCIPAL INVESTIGATOR EFFORT

Dr. W.M. Haynes is the NIST Principal Investigator for the MCLR program. During the second quarter of calendar year 1994, Dr. Haynes devoted approximately one week to planning this project, monitoring and reviewing the research, and preparing the report. The project involves multiple researchers and capabilities in Gaithersburg, MD and Boulder, CO.

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