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Experimental and Theoretical Studies of Dense Fluid Mixtures

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During the thirty-one months of this grant, we carried out extensive measurements of the speed of sound in three alternative refrigerants and in SF_6. We also modified and improved our equipment for measuring interfacial tension in pure fluids and mixtures and made a new set of measurements of interfacial tension over a wide range of temperature and pressure conditions for three mixtures of simple fluids. The results of these interfacial tension measurements were used to show that our new corresponding states theory of the variation of surface tension with temperature and composition is superior to the previous corresponding states theory. Computer simulations were performed on a system of molecules interacting via a Lennard-Jones potential that contained two liquid–vapor interfaces. Careful attention to the parameters of the simulation and to acheivement of equilibrium illuminated problems that had plagued earlier simulations.

Speed of sound measurements

We measured the speed of sound in R-134a on isotherms from 180 K to 380 K at intervals of 20 K over a range of pressures from the vapor pressure to 70 MPa or the freezing line, whichever came first. These measurements were performed concurrently with measurements of the density of another sample of the same material at Texas A & M University and constant volume heat capacity and vapor pressure measurements at NIST in Boulder, Colorado. The measurements were coordinated with those at Texas A & M so that speed of sound and density measurements were made at corresponding conditions. The results of these studies were reported at the March 1990 meeting of the American Institute of Chemical Engineers in Orlando, and were published in the *International Journal of Refrigeration* in their November 1992 issue. The data from these three sources for R-134a are much more extensive than any which had been obtained previously for this substance, and they have been used to determine the constants in modified Benedict-Webb-Rubin equations (both Jacobsen-Stewart and Schmidt-Wagner forms) at NIST in Boulder. These equations can then be used for accurate calculation of thermodynamic properties at any temperature and pressure in the range of the experiments, which will facilitate the design of new refrigeration equipment and will help with estimating the performance of existing equipment if the working fluid were changed from R-12 to R-134a. Comparisons between the new equations and our sound speed results are also reported in the November 1992 issue of the *International Journal of Refrigeration.*

We next studied the speed of sound in liquid sulfur hexafluoride. This substance was chosen for two reasons. It is a simple spherical molecule whose thermodynamic behavior ought to be representative of the behavior of the simplest fluids (those that obey the law of corresponding states) and experimentation on it is reasonably easy to do because room temperature falls within its liquid range. It is thus easier to study than the noble gases, whose critical points occur at temperatures below ambient. The other reason for studying it is that the IUPAC Thermodynamic Tables Center in

London was preparing a new book on SF_6, so new comprehensive sound speed data would be useful for their work. The speed of sound in SF_6 was measured between 230 and 333 K at pressures from saturation to 60 MPa. While we were performing the sound speed measurements on SF_6 we developed a new technique for locating the freezing transition at elevated pressure. We found that earlier measurements of the pressure/temperature trace of the freezing line had substantial error. Results of this work were reported at the 11th Thermophysical Properties Symposium in Boulder, Colorado in June 1991. The paper has been accepted for publication with the proceedings of the symposium in *Fluid Phase Equilibria.*

We turned next to another alternative refrigerant, R-123 (1,1-dichloro-2,2,2-trifluoroethane), an HCFC. At the time we began the study, it was believed that some HCFC's would be used as interim replacements for CFC's because they have less impact on the stratospheric ozone layer than CFC's. However, more recent political decisions have favored a quicker switch to HFC's, so it is doubtful that R-123 will ever be widely used commercially. The group at NIST, Boulder have proposed that equations of state for all of the substituted ethanes that are being considered as alternative refrigerants could be developed by using an equation of state for R-134a as a reference and by using polarity as a third correlation factor (in addition to temperature and density) much as the acentric factor is used for simple fluids. The equation of state for R-123 would be used for determining the effect of polarity. Thus, our results should still be of value. We made sound speed measurements at temperatures from 183 to 443 K at pressures from saturation to 47 MPa. A paper describing these results is in preparation.

The maximum pressure we could reach in the sound speed experiments was decreasing because there was a leak at the electrical feedthrough where the pulses enter and leave the pressure vessel. Before beginning a study of R-152a (1,1-difluoroethane), that feedthrough was disassembled and a new insulator of slightly different design was inserted. We decided to study R-152a and R-32 next because it appears that blends of these two refrigerants, which are both HFC's, with R-134a will be used to tune the thermodynamic properties of working fluids for HVAC machinery. Sound speed measurements in R-152a were made from 158 to 398 K at pressures from saturation to 84 MPa. A paper describing these results has been prepared, and will soon be submitted to the *Journal of Chemical Thermodynamics.*

Interfacial tension measurements

The apparatus for measuring tension between vapor and liquid in pure fluids and mixtures, which had been constructed in this laboratory by Kirk Nadler, has been extensively modified by Cynthia Holcomb. The biggest change was a modification to introduce a second method of measuring interfacial tension. The original apparatus used only the differential capillary rise technique, which requires that the operator be able to see and accurately measure the heights of interfaces in small capillaries contained inside the sapphire tube pressure vessel. Although this method is quite accurate, it is very difficult to perform the measurements. Thus, we have added the differential bubble pressure method to the apparatus. This method allows us to deduce interfacial tension from a pressure difference measurement which can be made with a transducer located outside the high pressure and low temperature environment of the liquid. The output of the differential pressure gauge is an electrical potential, which can be observed on a digital voltmeter and automatically recorded by a data acquisition system.

Because the differential bubble pressure technique has not previously been applied to making measurements with high precision, we have developed methods for deducing interfacial tension from the data and have demonstrated, by measuring interfacial tension simultaneously using both capillary rise and differential bubble pressure methods, that the results obtained by the two methods are equivalent. A paper describing calculation methods, that was completed before the beginning of this grant period, appeared in the *Journal of Colloid and Interface Science* in January 1990, and a second paper describing results of measurements on a variety of pure fluids at various temperatures and pressures appeared there in November 1992. In the latter paper, we carefully detail the conditions for making accurate differential bubble pressure surface tension measurements and explain how to make corrections for the effects of inertia and viscosity. Measurements of the interfacial tension of mixtures of argon and krypton, krypton and methane, and krypton and ethane were made using both methods. These measurements were both more extensive and more precise than the previous ones. They allow us make a more precise comparison between our "fugacity fraction" corresponding states theory of interfacial tension and the older "mole fraction" corresponding states theory. On theoretical grounds, one would expect that a corresponding states theory for phase equilibrium properties that is based on a field variable, such as the fugacity fraction, that is the same in both phases, would be more accurate than one based on a density variable, such as mole fraction, that is different in the equilibrium phases. The earlier results of Nadler gave some support to our theory, but his results had noise that was similar in magnitude to the difference between the theories, and his choice of experimental conditions called for substantial interpolation to calculate on lines of constant fugacity fraction. The new measurements on argon/krypton mixtures give more convincing support for the superiority of the fugacity fraction corresponding states principle. Krypton/methane mixtures are nearly ideal and the critical conditions of the two pure substances are very similar, so there is little difference between the predictions of the two theories. The krypton + ethane results should give a good test of the two theories, but we had some difficulty reducing our data for the system because we did not measure the coexisting liquid and vapor densities. Thus, there is potential for more testing of the theory when density data become available for that mixture. The experimental results for the mixtures were reported at the Eleventh Symposium on Thermophysical Properties and have been published in the proceedings in *Fluid Phase Equilibria*, in August 1992. A paper that focuses on the corresponding states theories has been prepared for submission to the *Journal of Chemical Physics.*

Equations of state for pure substances from density and speed of sound data

Although the group at NIST Boulder are using modified BWR equations to describe our results and predict thermophysical properties, those equations are not as good a representation of the equation of state of a dense fluid as one could hope for. Because an equation of state is required to describe simultaneously the vapor and liquid phases, compromises must be made between accuracy in describing liquid and vapor states. Because of the nature of a power series form of equation, it is usual that extrapolations of the equation outside the range for which its constants were determined leads rapidly to nonsensical results. Therefore, we have been working on an alternative representation of the properties of liquids using a rational approximant form. This form has the advantage that it can often be extrapolated beyond the range for which data have been used to determine its constants. It has the disadvantage, at least in its present form, that it cannot be used to describe both vapor and liquid states simultaneously. The rational approximant method has been applied to representing the square of the speed of sound in all of the fluids we have measured, and the results are included in the papers that describe the measurements. Additionally, the approach was described in a presentation at the Eleventh IUPAC Chemical Thermodynamics Meeting in August 1990.

Computer simulation of liquid-vapor interfaces

In parallel with the interfacial tension measurements, we also carried out computer simulations of the interface between liquid and vapor in model systems. A number of people have performed simulations of surface tension, but their results have been scattered, so our first task was to find out what effects potential cutoffs and finite system dimensions have on the observed interfacial tension in a simulation. Those effects have been figured out and a paper describing our results for a pure fluid interacting with a Lennard-Jones potential has been presented at the Eleventh Symposium on Thermophysical Properties and published in *Fluid Phase Equilibria.* A more detailed description of the work has been accepted for publication in *Molecular Physics.*

Papers submitted

1. Speed-of-sound measurements for liquid *n*-pentane and 2,2-dimethylpropane under pressure. J. Chem. Thermodynamics **1990**, 22, 937-948. A. Lainez, J. A. Zollweg, and W. B. Streett.

2. An Experimental and Theoretical Study of the Equation of State of CHF_3 in the Near Critical Region. J. Phys. Chem. **1991**, 95, 3351-3357. A. G. Aizpiri, A. Rey, J. Dávila, R. G. Rubio, J. A. Zollweg, and W. B. Streett.

3. Thermodynamic properties of simple molecular fluids: Tetrafluoromethane and Trifluoromethane. J. Chem. Eng. Data. **1991**, 171-184. R. G. Rubio, J. A. Zollweg, J. M. G. Palanco, J. C. G. Calado, J. Miller, and W. B. Streett.

4. Improved Differential Bubble Pressure Surface Tensiometer. J. Colloid & Interface Sci. **1992**, 154, 51-65. C. D. Holcomb and J. A. Zollweg.

5. Speed of sound in R-134a. Int. J. Refrigeration. **1992**, 15, 381-385. H. J. R. Guedes and J. A. Zollweg.

6. A Critical Study of Simulations of the Lennard-Jones Liquid-Vapor Interface. Fluid Phase Equilibria. **1992**, 75, 185-196. C. D. Holcomb, P. Clancy, S. M. Thompson and J. A. Zollweg.

7. Comparison of Interfacial Tension and Capillary Constant for Argon + Krypton, CH_4 + Krypton, and C_2H_6 + Krypton Using Two Independent Methods of Measurement. Fluid Phase Equilibria. **1992**, 75, 213-224. C. D. Holcomb and J. A. Zollweg.

8. A Critical Study of the Simulation of the Liquid-Vapour Interface of a Lennard-Jones Fluid. Molecular Physics. C. D. Holcomb, P. Clancy, and J. A. Zollweg (accepted)

9. Speed of Sound in Compressed Sulfur Hexafluoride. Fluid Phase Equilibria. V. Vacek and J. A. Zollweg (in press).

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