102 *J. Chem. Eng. Data* **2002,** *47,* 102−105

Dielectric Constants and Molar Polarizabilities for Vapor Mixtures of Methane + Propane and Methane + Propane + Hexane Obtained with a Radio Frequency Reentrant Cavity

Eric F. May[†] **and Reid C. Miller***

Department of Chemical Engineering, Washington State University, Pullman, Washington 99164

Anthony R. H. Goodwin

Schlumberger-Doll Research, Ridgefield, Connecticut 06877

A radio frequency reentrant resonator has been used to determine dielectric constants for one methane + propane mixture and two methane + propane + hexane mixtures along isotherms between 293 K and 313 K, at pressures to 10 MPa. These measurements were made simultaneously with density measurements on the same mixtures, allowing molar polarizabilities to be calculated. Changes in polarizability on mixing were estimated, with component values from literature sources, and were found to average less than 0.6% of mixture polarizability values.

Introduction

Dielectric constant measurements have been used to infer the densities of fluids at conditions where volumetric techniques are difficult to employ.[1−3] The molar density, ρ, and dielectric constant, ϵ, of a fluid are related to the total molar polarizability, P_t, through

$$P_t = \frac{1}{\rho}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) \tag{1}$$

Thus, densities of fluid mixtures can be obtained from dielectric constants, provided the mixture P_t is known. For ideal gases, the mixture P_t function is rigorously a mole fraction average of component values.[4] Since P_t is nearly independent of state for normal fluids, this same mixing rule may well work for both compressed gases and liquids. It has been tested for liquid mixtures containing simple species and light hydrocarbon components at cryogenic temperatures and near room temperature.[1−3] A change in polarizability on mixing can be defined by

$$\Delta P_t^{M}(P,T,y) = P_t(P,T,y) - \sum_i y_i P_{ti}(P,T) \tag{2}$$

where y_i is the mole fraction of the ith component and P_{ti} is its polarizability. For the liquid mixtures studied, the ΔP_t^{M} values were less than 0.2% of the mixture P_t functions, except for mixtures containing significant quantities of the weakly polar species propane and isobutane at low temperatures (near 100 K). No experimental verification of eq 2 appears to have been conducted for compressed vapor mixtures.

There are numerous methods by which the dielectric constant of gases can be measured, including methods based on the use of radio frequency reentrant cavities.[5,6] Recently, a dual-sinker densimeter was used to measure densities and dew points in several vapor mixtures of methane + propane and methane + propane + hexane.[7] During the course of these experiments, the dielectric constants of these mixtures were simultaneously measured with a modified version of the reentrant resonator developed by Anderson, Miller, and Goodwin.[8] The purpose of the current article is to report on the experimental system and the resulting dielectric constants, along with estimated P_t and ΔP_t^{M} values for these mixtures.

Experimental System

The dual-sinker densimeter was described previously by May et al.[7] Argon was used as a reference fluid for calibration. Experimental uncertainties in density for methane were estimated from an analysis of uncertainties in the individual measurements of ±(0.029% + 0.013 kg m^{-3}). Density measurements were performed for methane (99.99 mol % minimum purity) to confirm the estimated uncertainty, and the results were found to agree within these limits with densities from an equation of state from the literature.[9]

The stainless steel reentrant cavity of Anderson et al.[8] was modified to have two internal lobes of similar dimensions, and thus two primary resonant frequencies. The geometry is similar to that of a resonator described by Hamelin and co-workers.[10] A schematic diagram of the resonator is shown in Figure 1, with dimensions z_1, z_2, z_3, r_1, and r_2 listed in Table 1. The space defined by the dimensions z_4 = 44.0 mm and z_5 = 45.0 mm acts as a capacitor which is very weak compared with the primary capacitances C1 and C2. The cavity itself has an inner radius r_3 = 12.700 mm. The free volume of the cavity is about 43 cm^3, and the vacuum frequencies of the primary resonances are approximately 250 MHz and 660 MHz.

The complex transmission scattering parameter, S_{21}, was measured for the resonator as a function of frequency with a network analyzer. The complex resonant frequency, F =

---

* Corresponding author. Fax number: (509)335-4806. E-mail: millerrc@wsu.edu.

[†] Current address: Department of Physics, University of Western Australia, Nedlands, Western Australia 6907. E-mail: may@physics.uwa.edu.au.

10.1021/je010224c CCC: $22.00

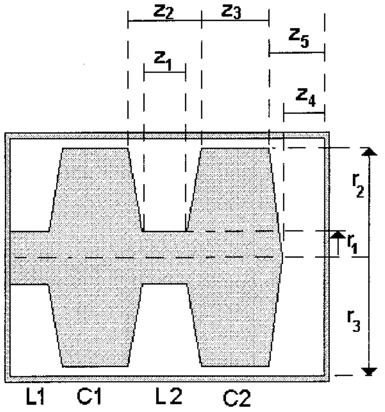

Figure 1. Location of main inductors (L1, L2) and capacitors (C1, C2) and definition of dimensions z_i and r_i for the reentrant cavity resonator.

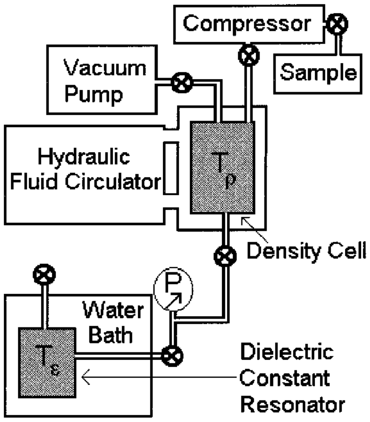

Figure 2. Schematic of the apparatus for simultaneous density and dielectric constant measurements.

Table 1. Reentrant Resonator Dimensions for Each Inductor/Capacitor Section As Defined in Figure 1

section	r_1/mm	r_2/mm	z_1/mm	z_2/mm	z_3/mm
L1, C1	4.003	12.194	19.977	20.977	20.020
L2, C2	4.008	12.192	19.995	21.995	19.964

$f + ig$, was determined for each mode by fitting the S_{21} data near each resonant frequency to a theoretical resonance function.[5,8,10] The statistical uncertainties in the values of f and g determined from the fit were always less than 0.002 MHz.

The resonator was suspended in a cylindrical copper vessel containing atmospheric air, and immersed in a stirred water bath which was controlled to better than ±0.02 K.[8] The temperatures of both the bath and the resonator were monitored by use of calibrated platinum resistance thermometers (ITS-90), with an estimated uncertainty of ±0.02 K. Pressures were measured with an oscillating quartz gauge, which was calibrated against an oil-operated piston gauge. Pressures reported here have an estimated uncertainty of ±(0.015% + 0.001 MPa). Gas mixtures were prepared gravimetrically as described previously.[7] The reported mixture mole fractions have an estimated uncertainty of ±0.0001.

A diagram of the apparatus is shown in Figure 2. The fluid line connecting the densimeter to the resonator, which contained the pressure gauge, is exposed to room temperature (about 21 °C). All mixtures studied had cricondentherms (maximum temperatures for their dew point curves) below 18 °C, making significant adsorption on the tubing walls unlikely.

Table 2. Mixture Mole Fraction Compositions and Average Molar Masses

	mixture 1	mixture 2	mixture 3
methane	0.8419	0.9150	0.9397
propane	0.1581	0.0790	0.0525
hexane		0.0060	0.0078
molar mass	20.478	18.680	18.063

In the experiments reported here, the dielectric constant and density of each mixture were measured simultaneously. One methane + propane mixture and two methane + propane + hexane mixtures were studied, with mole fraction compositions and molar masses listed in Table 2. The densities have been reported previously.[7] The estimated uncertainties for the mixture densities are ±(0.036% + 0.013 kg m^{-3}) for the binary mixture and ±(0.058% + 0.013 kg m^{-3}) for the ternary mixtures. These uncertainties are larger than those for pure methane because of uncertainties in mixture compositions.[7]

Experiments were conducted along isotherms in pressure increments of about 1 MPa. A compressor was used to transfer sample to the experimental system from the sample cylinder. After a change in pressure, six measurement sets were recorded over the period of 1.5 h, which was found to be sufficient for equilibrium to be achieved. Data from the final three sets were averaged to give the temperature, pressure, density, and dielectric constant of the fluid before the system pressure was changed. Between isotherms, the system was allowed at least 10 h for equilibration before measurements were continued.

The difference in temperature between the resonator and densimeter was minimized; in all but a few cases it was less than 0.04 K. The maximum relative temperature difference for all the reported measurements was 0.04%. Temperatures quoted here are those measured in the densimeter and reported previously.[7]

Data Analysis

A lumped-parameter model developed for a similar resonator by Hamelin et al.[10] was adopted to determine dielectric constants from complex resonance frequencies. No external coupling corrections were required.[8,10] Incorporating quality factors ($Q = f/2g \approx 200$), to first order in Q^{-1}, the working equation for the dielectric constant is

$$\epsilon = \left(\frac{F_0}{F}\right)^2 \frac{1 + (-1 + i)(1/Q)}{1 + (-1 + i)(1/Q_0)} \qquad (3)$$

In eq 3, F_0 ($f_0 + ig_0$) and Q_0 ($f_0/2g_0$) correspond to the vacuum complex resonant frequency and quality factor. These two parameters depend on both resonator temperature and pressure,[5,8,10]

$$f_0 = f_{00}(1 - \alpha t)(1 + \beta P) \quad \text{and} \quad g_0 = g_{00} \qquad (4)$$

where f_{00} and g_{00} correspond to the vacuum values of f and g at the reference temperature (296.13 K), α is the coefficient of thermal expansion of the resonator material, β is related to the elastic properties of the resonator, P is the absolute pressure, and t is T/K − 296.13. Values for g_{00} were estimated from vacuum measurements at ambient temperature, and α was taken from the literature.

The parameters f_{00} and β in eq 4 were determined by forcing agreement between experimental methane dielectric constants and those calculated from the dielectric virial expansion, with coefficients and densities from the literature. Resonant frequencies were measured with research grade methane along the 313.04 K isotherm at six pres-

Table 3. Constants of Eq 4 and Uncertainties (σ) Determined from Measurements of Vacuum and Methane Resonant Frequencies

mode	f_{00}/MHz	$\sigma_{f_{00}}$/MHz	$10^5\beta$/MPa^{-1}	$10^5\sigma_\beta$/MPa^{-1}	g_{00}/MHz
low	249.522	0.003	14.29	0.23	1.071
high	660.236	0.003	16.43	0.09	1.462

sures between 2 MPa and 9 MPa. Reference values of the dielectric constant were calculated from

$$P_t = \frac{1}{\rho}\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = A_\epsilon + B_\epsilon\rho + C_\epsilon\rho^2 \qquad (5)$$

with dielectric virial coefficients from Moldover and Buckley[11] at 50 °C ($A_\epsilon = 6.5468$ cm^3 mol^{-1}, $B_\epsilon = 7.33$ cm^6 mol^{-2}, and $C_\epsilon = -124$ cm^9 mol^{-3}) and densities from the equation of state of Setzmann and Wagner.[9] The small temperature dependencies of the dielectric virial coefficients were neglected. Table 3 contains the parameters f_{00}, β, and g_{00} determined for each mode. The value of α was taken as the volumetric coefficient of thermal expansion for type 316 stainless steel (15.9×10^{-6} K^{-1}).[12]

The scatter in the measurements corresponding to the low-frequency mode was significantly larger than that for those corresponding to the high-frequency mode, but no systematic deviations were found between the two modes. Only dielectric constants and polarizabilities determined from the high-frequency mode are reported here. The fractional uncertainty in the dielectric constants of mixtures reported here is estimated to be 1×10^{-4}.

Mixture Results

All three mixtures were studied along isotherms at least 6 K above the dew point, where adsorption effects were negligible. Measured temperatures, pressures, densities (reported previously[7]), dielectric constants, molar polarizabilities, and estimated uncertainties in molar polarizabilities are listed for each mixture in Table 4.

To calculate the value of ΔP_t^M at a state point (eq 2), experimental mixture polarizabilities were combined with component polarizabilities from the literature. Methane P_t values were taken from the correlation of Moldover and Buckley,[11] with densities from the equation of state of Setzmann and Wagner.[9] Propane P_t values were taken from the correlation of Younglove and Ely,[13] with their MBWR equation of state for densities. Under the conditions of this study, the component polarizability ranges are (6.547 to 6.561) cm^3 mol^{-1} for methane and (16.046 to 16.096) cm^3 mol^{-1} for propane. The polarizability for hexane was assumed to be a constant (29.99 ± 0.30 cm^3 mol^{-1}), as estimated from density and refractive index data for liquid alkanes at 25 °C.[14] On the basis of quoted uncertainties for the component values, the uncertainties in the calculated ΔP_t^M are estimated to be nearly identical (within 0.01 cm^3 mol^{-1}) to the uncertainties in P_t listed in Table 4.

For all mixtures and all isotherms, $100\Delta P_t^M/P_t$ values (including estimated error bars) are plotted as a function of density in Figure 3. The average values for mixtures 1−3 (compositions defined in Table 2) are +0.4%, +0.6%, and +0.1%, respectively, with average estimated uncertainties for all three mixtures of ±0.2%. Thus, ΔP_t^M values for mixtures 1 and 2 indicate small, positive deviations from a mole fraction average mixing rule, while those for mixture 3 are not statistically different from zero. However, as discussed by May et al.,[7] the close proximity of mixture 3 to its dew point at room temperature may have led to small amounts of adsorption on the sample cylinder walls. Thus, the sample transferred to the measurement system may have contained slightly less of the higher alkanes than indicated by the composition listed in Table 2, which could account for the smaller ΔP_t^M values for this mixture.

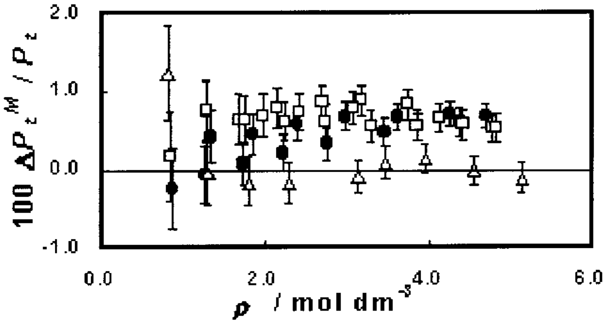

Figure 3. ΔP_t^M as a percentage of the mixture P_t value versus density for the three mixtures with compositions defined in Table 2: ●, mixture 1; □, mixture 2; △, mixture 3.

Table 4. Densities ρ, Dielectric Constants ϵ, Molar Polarizabilities P_t, and Uncertainties in Molar Polarizabilities $\sigma(P_t)$, Measured at Temperature T and Pressure P for Three Mixtures with Compositions Defined in Table 2

T/K	P/MPa	ρ/mol dm^{-3}	ϵ	P_t/cm^3 mol^{-1}	$\sigma(P_t)$/cm^3 mol^{-1}
		Mixture 1			
297.08	2.993	1.333	1.0327	8.08	0.03
297.06	3.993	1.844	1.0454	8.08	0.02
297.08	4.994	2.392	1.0592	8.08	0.02
297.10	6.017	2.991	1.0744	8.09	0.01
297.09	6.993	3.606	1.0901	8.08	0.01
297.08	7.982	4.263	1.1071	8.08	0.01
313.13	2.128	0.863	1.0209	8.03	0.04
313.13	3.029	1.258	1.0307	8.04	0.03
313.13	4.073	1.742	1.0427	8.05	0.02
313.13	5.048	2.218	1.0546	8.06	0.02
313.13	6.082	2.752	1.0681	8.06	0.01
313.13	7.370	3.453	1.0860	8.07	0.01
313.12	8.093	3.864	1.0966	8.07	0.01
313.12	9.491	4.686	1.1181	8.08	0.01
		Mixture 2			
293.93	2.915	1.284	1.0291	7.49	0.03
293.93	4.317	1.978	1.0450	7.48	0.02
293.93	5.150	2.415	1.0552	7.48	0.01
293.93	6.344	3.077	1.0706	7.48	0.01
293.93	8.086	4.120	1.0951	7.46	0.01
303.11	3.007	1.277	1.0289	7.49	0.03
303.11	4.011	1.745	1.0396	7.48	0.02
303.12	5.009	2.234	1.0509	7.47	0.02
303.11	6.009	2.747	1.0628	7.47	0.01
303.11	7.010	3.284	1.0753	7.46	0.01
303.11	8.020	3.846	1.0885	7.45	0.01
303.11	9.007	4.412	1.1020	7.45	0.01
303.10	9.720	4.828	1.1119	7.44	0.01
313.16	2.080	0.835	1.0188	7.45	0.04
313.15	4.028	1.674	1.0380	7.48	0.02
313.15	5.073	2.153	1.0491	7.48	0.02
313.15	6.195	2.689	1.0616	7.49	0.01
313.15	7.173	3.176	1.0730	7.48	0.01
313.15	8.266	3.740	1.0863	7.48	0.01
313.15	9.439	4.369	1.1010	7.45	0.01
313.15	10.179	4.772	1.1105	7.44	0.01
		Mixture 3			
297.56	1.944	0.811	1.0179	7.32	0.04
297.65	3.011	1.300	1.0284	7.22	0.03
297.58	4.047	1.792	1.0392	7.21	0.02
297.57	5.030	2.279	1.0501	7.20	0.02
297.58	6.660	3.139	1.0694	7.20	0.01
297.57	7.259	3.470	1.0770	7.21	0.01
297.58	8.128	3.962	1.0882	7.21	0.01
297.58	9.138	4.555	1.1017	7.20	0.01
297.58	10.082	5.125	1.1147	7.19	0.01

The small, positive ΔP_t^M values may be real but (possibly) could be reduced by use of component P_t values for propane and hexane extrapolated from gas-phase data, instead of using liquid-phase values. It is also possible that the mixture experimental errors were underestimated, which would result in larger error bars, and calculated ΔP_t^M values would not be statistically different from zero.

It is clear that changes in polarizability on mixing are small for the mixtures studied. The question of how small might be refined by improved performance of the resonator used to make the dielectric constant measurements. The resonator was not characterized with fluids of well-known dielectric properties, such as helium and argon. It is plausible that doing so might reduce the uncertainty in the measured dielectric constants. Nevertheless, the resonator was calibrated to the recent methane dielectric data of Moldover and Buckley[11] obtained using a toroidal cross capacitor, a technique with entirely different systematic errors.

Acknowledgment

The authors are grateful to Dr. Zhengjun Shan of the Center for Applied Thermodynamic Studies at the University of Idaho for assistance with the research. The authors would like to thank Dr. Terry Edwards and Dr. Cyril Edwards of the University of Western Australia (research advisors for E.F.M.) for helpful collaboration.

Literature Cited

(1) Pan, W. P.; Mady, M. H.; Miller, R. C. Dielectric Constants and Clausius-Mossotti Functions for Simple Liquid Mixtures: Systems Containing Nitrogen, Argon and Light Hydrocarbons. *AIChE J.* **1975**, *21* (2), 283−289.
(2) Thompson, R. T.; Miller, R. C. Densities and Dielectric Constants of LPG Components and Mixtures at Cryogenic Storage Conditions. *Adv. Cryog. Eng.* **1980**, *25*, 698−708.
(3) Luo, C. C.; Miller, R. C. Densities and Dielectric Constants for some LPG Components and Mixtures at Cryogenic and Standard Temperatures. *Cryogenics* **1981**, *21*, 85−93.
(4) Hirschfelder, J. O.; Curtis, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids;* Wiley: New York, 1954.
(5) Goodwin, A. R. H.; Mehl, J. B.; Moldover, M. R. Reentrant Radio-Frequency Resonator for Automated Phase-Equilibria and Dielectric Measurements in Fluids. *Rev. Sci. Instrum.* **1996**, *67* (12), 4294−4303.
(6) May, E. F.; Edwards, T. J.; Mann, A. G.; Edwards, C.; Miller, R. C. Development of an Automated Phase Behaviour Determination System for Lean Hydrocarbon Fluid Mixtures with Re-Entrant RF/Microwave Resonant Cavities. *Fluid Phase Equilib.* **2001**, *185* (1−2), 339−347.
(7) May, E. F.; Miller, R. C.; Shan, J. Densities and Dew-Points of Vapour Mixtures of Methane + Propane and Methane + Propane + Hexane Using a Dual-Sinker Densimeter. *J. Chem. Eng. Data* **2001**, *46* (5), 1160−1166.
(8) Anderson, G. S.; Miller, R. C.; Goodwin, A. R. H. Static Dielectric Constants for Liquid Water from 300 K to 350 K at Pressures to 13 MPa Using a New Radio-Frequency Resonator. *J. Chem. Eng. Data* **2000**, *45* (4), 549−554.
(9) Setzmann, U.; Wagner, W. A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting Line to 625 K at Pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061−1151.
(10) Hamelin, J.; Mehl, J. B.; Moldover, M. R. Resonators for Accurate Dielectric Measurements in Conducting Liquids. *Rev. Sci. Instrum.* **1998**, *69* (1), 255−260.
(11) Moldover, M. R.; Buckley, T. J. Reference Values of the Dielectric Constant of Natural Gas Components Determined with a Cross Capacitor. *Int. J. Thermophys.* **2001**, *22* (3), 859−885.
(12) Bauccio, M., Ed. *ASM Metals Reference Book;* ASM International: Ohio, 1993; p 155.
(13) Younglove, B. A.; Ely, J. F. Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane and Normal Butane. *J. Phys. Chem. Ref. Data* **1987**, *16* (4), 577−582.
(14) *Technical Data Book—Petroleum Refining*, 3rd ed.; American Petroleum Institute: Washington, DC, 1976.

Received for review August 2, 2001. Accepted November 6, 2001. Equipment was provided through Grant BES-9601721 from the U.S. National Science Foundation. E.F.M. would also like to thank the University of Western Australia, Washington State University, and the Minerals and Energy Research Institute of Western Australia for scholarships that allowed him to undertake this research.

JE010224C