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Determination of the Compressibility Factor $Z(p, T)$ of Three Methane–Ethane Mixtures Using the Dielectric Constant Method[1]

J. M. St-Arnaud,[2,3] R. Okambawa,[2] T. K. Bose,[2] and D. Ingrain[4]

The compressibility behavior of three mixtures of the CH_4–C_2H_6 system has been investigated experimentally by means of the dielectric constant method. Precise (±1 ppm) measurements of the dielectric constant (ε) as a function of the pressure (P) along one isotherm (T) are combined with the first three dielectric virial coefficients (A_ε, B_ε, and C_ε) in order to obtain accurate values of the molar density (ρ). The compressibility factor $Z = P/(\rho RT)$ was obtained from the measured values of ρ, P, and T. The coefficient A_ε is determined from the measurements of ε as a function of P, while the higher-order coefficients (B_ε and C_ε) are obtained by an expansion technique. We report the measured values of Z at 298.15 K up to 12 MPa for three mixtures of CH_4–C_2H_6 containing, respectively, 9.54, 35.3, and 75.4% (molar) of ethane. Their exact composition was determined by weighing during the mixing process. The first three dielectric virial coefficients and the mixed second dielectric virial coefficient for the CH_4–C_2H_6 system agree with the calculated or the literature values within the limits of uncertainties. For the mixture containing 90.46% CH_4 + C_2H_6, deviations in compressibility are of the order of 0.4% from GERG.

KEY WORDS: compressibility factor; density; dielectric constant; mixtures; CH_4; C_2H_6.

1. INTRODUCTION

The equation of state (EOS) chosen for predicting the compressibility factor for natural gas is a truncated version of a virial series in ascending

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[2] Institut de Recherche sur l'Hydrogène, Département de Physique, Université du Québec à Trois-Rivières, Trois-Rivières, Québec G9A 5H7, Canada.

[3] To whom correspondence should be addressed.

[4] Gaz de France, Centre d'Études et de Recherche sur les Sciences, Direction de la Recherche, 361 Avenue du Président Wilson, C.P. 33, 93211 La Plaine, Sainte Denis Cedex, France.

powers of the density. The AGA-8 [1] and GERG [2] EOS actually used, respectively, in North America and Europe are such equations. The structure of the virial equation is based on the statistical mechanics where the virial coefficients are directly related to the intermolecular forces. For example, the second virial coefficient is related to interaction of molecular pairs, and the third describes the interaction of molecular triplets. Moreover, the virial coefficients of a multicomponent mixture such as natural gas may be obtained from constituent virial coefficients by mixing rules which are formally rigorous within statistical mechanical theory. In order to obtain accurate EOS, it is necessary to measure precisely the mixed virial coefficients for binary and ternary mixtures. In this paper, we report the measurements for three binary mixtures of CH_4–C_2H_6 at 298.15 K up to 12 MPa using the dielectric constant method, which has already been proved [3] to be as precise as the PVT expansion techniques [4, 5] and the refractive index method [6, 7].

2. MATHEMATICAL DEVELOPMENT

The compressibility factor Z is given by

$$Z = P/(\rho RT) = 1 + A\rho + B\rho^2 + \cdots \tag{1}$$

where P is the pressure, $R = (8.314\,471 \pm 0.000\,014)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ is the molar gas constant [8], T is the absolute temperature, ρ is the molar density; and A and B are, respectively, the second and the third pressure virial coefficients. The objective of the dielectric method is to determine ρ from the Clausius–Mossotti relation:

$$P_t = (\varepsilon - 1)/[(\varepsilon + 2)\,\rho] = CM/\rho \tag{2}$$

where P_t is the total polarization and $CM = (\varepsilon - 1)/(\varepsilon + 2)$. The latter can be expanded in a virial series as

$$CM = A_\varepsilon \rho + B_\varepsilon \rho^2 + C_\varepsilon \rho^3 + \cdots \tag{3}$$

where A_ε, B_ε, and C_ε are, respectively, the first, second, and third dielectric virial coefficients.

The dielectric virial coefficients of a mixture are related to the dielectric virial coefficients of the components [9, 10] as

$$B_\varepsilon = \Sigma\Sigma x_i x_j (B_\varepsilon)_{ij} \tag{4}$$

$$C_\varepsilon = \Sigma\Sigma\Sigma x_i x_j x_k (C_\varepsilon)_{ijk} \tag{5}$$

From Eq. (1), the density can be calculated by including the first three dielectric virial coefficients as

$$\rho = \frac{CM}{A_\varepsilon} - \frac{B_\varepsilon}{A_\varepsilon}\left[\frac{CM}{A_\varepsilon}\right]^2 + \frac{2B_\varepsilon^2 - A_\varepsilon C_\varepsilon}{A_\varepsilon^2}\left[\frac{CM}{A_\varepsilon}\right]^3 + \cdots \tag{6}$$

which leads to the compressibility factor

$$Z = \frac{P}{RT}\left[\frac{A_\varepsilon}{CM} + \frac{B_\varepsilon}{A_\varepsilon} + \left(\frac{A_\varepsilon C_\varepsilon - B_\varepsilon^2}{A_\varepsilon^3}\right) CM\right] + \cdots \tag{7}$$

3. MEASUREMENTS

The coefficient, A_ε, is determined by measuring the dielectric constant ε as a function of pressure. The coefficient A_ε is obtained from the intercept of the relation

$$CM\left(\frac{RT}{P}\right) = A_\varepsilon + \left(\frac{B_\varepsilon - A_\varepsilon B}{A_\varepsilon}\right) CM + \frac{A_\varepsilon C_\varepsilon - B_\varepsilon^2(B^2 - C)}{A_\varepsilon^3}(CM)^2 + \cdots \tag{8}$$

In order to determine precisely B_ε and C_ε, we used an expansion technique developed by Buckingham et al. [11]. This method essentially consists of first measuring the sum of capacitances of two similar cells, one

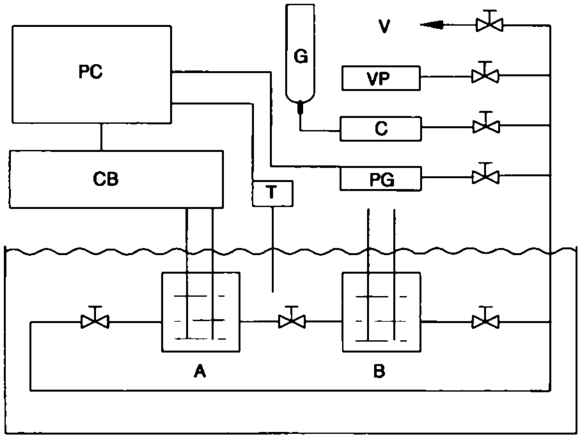

Fig. 1. Schematic diagram of the experimental setup for the dielectric constant technique. A and B, measurement cells; C, gas compressor; CB, capacitance bridge; CTB, controlled-temperature bath; G, gas; PC, personal computer; PG, pressure gauge; T, thermometer; V, vent; VP, vacuum pump.

of which is filled with gas at density ρ_A and the other evacuated (see Fig. 1). The gas is then allowed to fill both the cells, the density is almost halved, and the sum of capacitances is measured again. In this process, the linear term in density remains the same before and after the expansion, but the quadratic and higher orders change. Therefore, B_ε and C_ε are determined by the change in total capacitance. Details of this expansion technique are given by Huot and Bose [12]. The working relation for the determination of B_ε and C_ε is

$$\begin{aligned} \frac{D_A}{C_0(\varepsilon_1 - 1)} + \frac{D_B}{C_0(\varepsilon_2 - 1)} &= -\left[\frac{B_\varepsilon + A_\varepsilon^2}{6A_\varepsilon^2}\right] [(\varepsilon_1 - 1) + (\varepsilon_2 - 1)] \\ &\quad + \frac{1}{2}\left[\frac{4B_\varepsilon^2 - 3A_\varepsilon C_\varepsilon + 2B_\varepsilon A_\varepsilon^2 + A_\varepsilon^4}{36A_\varepsilon^4}\right] [(\varepsilon_1 - 1) + (\varepsilon_2 - 1)]^2 + \cdots \end{aligned} \tag{9}$$

where C_0 is the mean geometric capacitance of each cell $[C_0 = (C_A + C_B)/2]$, and D_A is the change of capacitance when the gas (ε_1, ρ_1) in cell A is expanded into the evacuated cell B. Similarly, if the expansion takes place from cell B (ε_2, ρ_2) to cell A, the change in capacitance is D_B. The combination of the two expansions eliminates the mismatch of capacitors and volumes between the two cells. On plotting the left-hand side of Eq. (9) against $[(\varepsilon_1 - 1) + (\varepsilon_2 - 1)]$, one can determine B_ε from the slope and C_ε from the curvature. The schematic diagram of the experimental setup is presented in Fig. 1. The capacitor was made of parallel plates and the measurements were carried out at 1 kHz using a decade transformation bridge [Andeen Hagerling Model 2500A]. The dielectric constant, ε, is given by the relation $\varepsilon = C(P)/C(0)$, where $C(P)$ is the capacitance value under pressure and $C(0)$ is the capacitance value under vacuum. The precision on capacitance measurement is estimated to be 3×10^{-7} pF. The capacitor used was of the three-terminal type. The plates were made of copper for better thermal conductivity. Details of the construction are given by Huot and Bose [12]. The measuring system (dielectric cells and valves) was immersed into a constant-temperature bath controlled within ±0.01 K. Temperature was measured by means of a calibrated thermistor. The pressures were measured with a quartz pressure transducer calibrated against a pressure standard (Desgranges and Huot Model 5213] having a precision of the order of 0.005%. A polynomial for the pressure values in terms of the readings on the transducer was fitted for the purpose of calibration. Considering the fitting and small errors due to the temperature, the final uncertainty is estimated to be of the order of 0.01% for pressures above 1.5 MPa.

4. RESULTS AND DISCUSSION

The mixtures were used as supplied by Air Liquide (Canada). The exact composition of the three binary systems containing 9.54, 35.3, and 75.4% (molar) of ethane was determined by weighing during the mixing process and verified by gas chromatography. Figure 2 shows comparative curves of Eq. (8) for the determination of A_ε for the mixtures and for pure CH_4 and C_2H_6. Figure 3 shows curves of Eq. (9) for the determination of B_ε and C_ε. Table I gives the values of A_ε, B_ε, and C_ε for the three mixtures and pure gases. Uncertainties correspond to three standard deviations. The values of B_ε and C_ε are determined according to Eq. (9). Values of A_ε, B_ε, and C_ε are associated with the measurement of ε as a function of P for the mixtures in order to obtain ρ and Z according to Eqs. (6) and (7), respectively. The deviations ΔZ are reported in Fig. 4 as a function of P for 90.46% $CH_4 + C_2H_6$. The GERG EOS is not valid for the other mixtures. In Fig. 4, Z_m are the measured values [Eq. (7)] and Z_{ca} are the calculated values of the compressibility factor according to GERG [2]. The deviation (ΔZ) between Z_m and Z_{ca} are such that $\Delta Z = [(Z_{ca} - Z_m)/Z_{ca}]$ 100%. Deviations (ΔZ) are less than 0.4% for pressures up to 12 MPa. On expanding Eq. (4), one gets

$$B_\varepsilon = (B_\varepsilon)_{11}(1-x)^2 + (B_\varepsilon)_{12}\,x(1-x) + (B_\varepsilon)_{22}\,x^2 \qquad (10)$$

where B_ε is the second dielectric virial coefficient for the mixture, x is the mole fraction of C_2H_6, $(B_\varepsilon)_{11}$ and $(B_\varepsilon)_{22}$ are, respectively, related to

Table I. Dielectric Virial Coefficients for Methane, Ethane, and Methane–Ethane Mixtures at 298.15 K (Uncertainties Are $\pm 3\sigma$ of the Measurements)

Gas (molar fraction)	A_ε $(cm^3 \cdot mol^{-1})$	B_ε $(cm^3 \cdot mol^{-1})^2$	C_ε $(cm^3 \cdot mol^{-1})^3$
CH_4	6.551 ± 0.002	7.23 ± 0.31	−246 ± 18
90.47% $CH_4 + C_2H_6$	7.001 ± 0.002	7.65 ± 0.40	−220 ± 30
64.70% $CH_4 + C_2H_6$	8.164 ± 0.002	10.4 ± 0.5	−233 ± 30
24.69% $CH_4 + C_2H_6$	10.091 ± 0.002	21.9 ± 0.6	−700 ± 90
C_2H_6	11.186 ± 0.003	32.2 ± 1.8	1180 ± 873

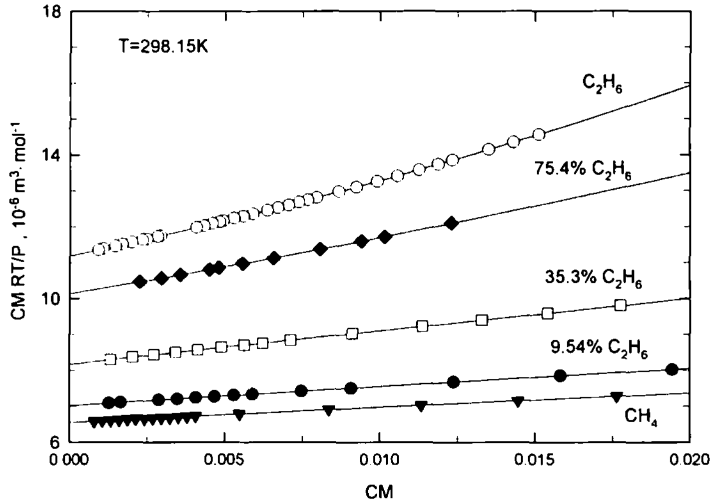

Fig. 2. Curves of $CM\ RT/P$ as a function of $CM = [(\varepsilon - 1)/(\varepsilon + 2)]$ for gaseous CH_4 (▼), 90.46% $CH_4 + C_2H_6$ (●), 64.7% $CH_4 + C_2H_6$ (□), 24.6% $CH_4 + C_2H_6$ (◆), and C_2H_6 (○) at 298.15 K.

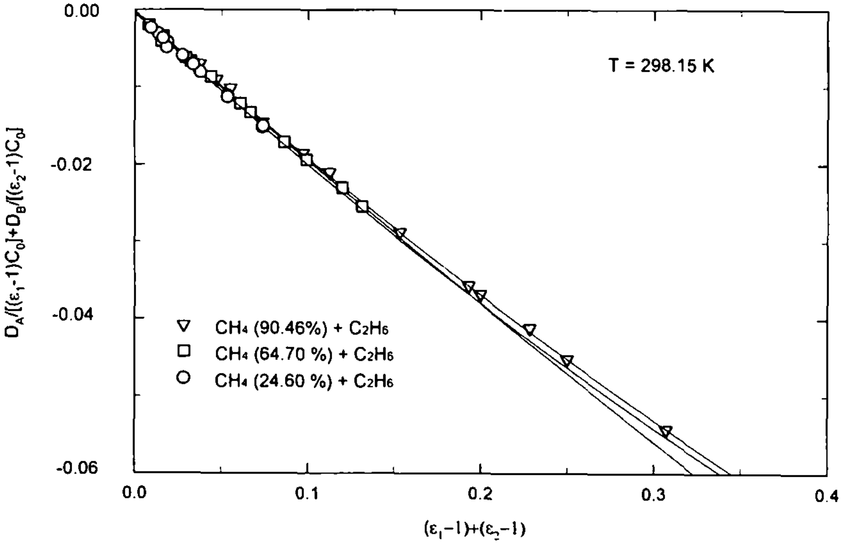

Fig. 3. Plot of $[D_A/C_0(\varepsilon_1 - 1)] + [D_B/C_0(\varepsilon_2 - 1)]$ as a function of $[(\varepsilon_1 - 1) + (\varepsilon_2 - 1)]$ for the determination of the second (B_ε) and third (C_ε) dielectric virial coefficients of 90.46% $CH_4 + C_2H_6$ (▽), 64.7% $CH_4 + C_2H_6$ (□), and 24.6% $CH_4 + C_2H_6$ (○) at 298.15 K.

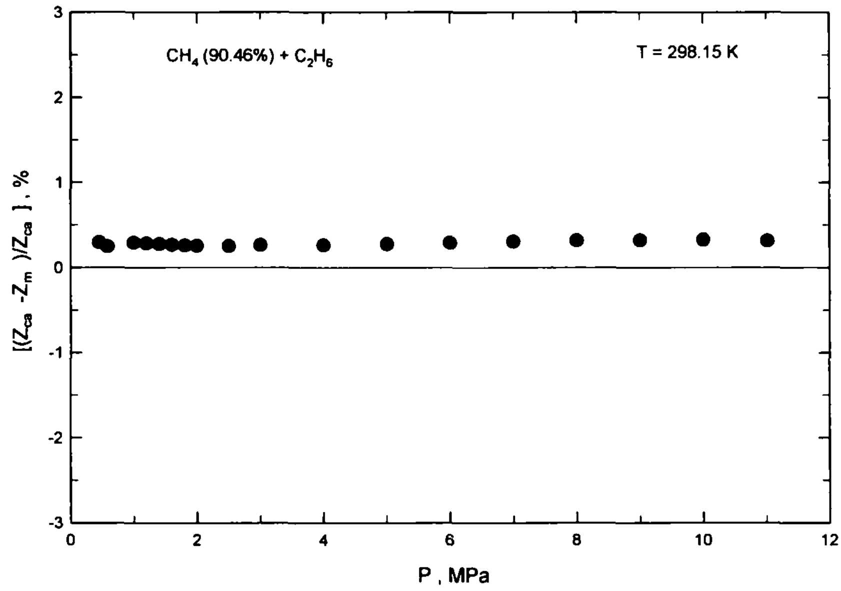

Fig. 4. Pressure dependence of the deviations $[(Z_{ca}-Z_{m})/Z]$ (%) between the measured values, Z_m, of the compressibility factor and those calculated, Z_{CA}, according to GERG for 90.46% $CH_4+C_2H_6$ at 298.15 K.

CH_4 and C_2H_4, and $(B_\varepsilon)_{12}$ is the mixed second dielectric virial coefficient. A plot of $[B_\varepsilon-(B_\varepsilon)_{11}(1-x)^2]\,x^{-1}$ against x is shown in Fig. 5. The intercept gives $(B_\varepsilon)_{12}=16.14$ $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})^2$, which agrees within 3% with the Lorentz combination rule given by

$$(B_\varepsilon)_{12}=[(B_\varepsilon)_{11}^{1/3}+(B_\varepsilon)_{22}^{1/3}]^3/8 \tag{11}$$

The agreement (see Table II) is worse for the geometric mixing rule $(B_\varepsilon)_{12}=[(B_\varepsilon)_{11}\cdot(B_\varepsilon)_{22}]^{1/2}$ and the linear mixing rule $(B_\varepsilon)_{12}=[(B_\varepsilon)_{11}+(B_\varepsilon)_{22}]/2$.

Table II. Mixed Second Dielectric Virial Coefficient for the CH_4–C_2H_6 System at 298.15 K

	$(B_\varepsilon)_{12}$ $(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})^2$ calculated		
Expt	Geometric rule	Linear rule	Lorentz combination
16.14	15.16	19.51	16.61

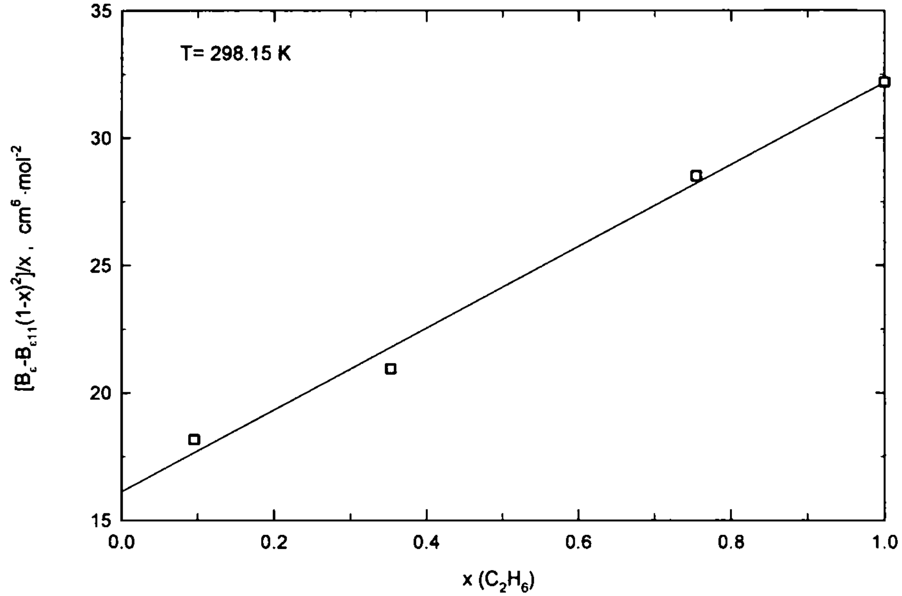

Fig. 5. Plot of $[B_\varepsilon - (B_\varepsilon)_{11}(1-x^2)]x^{-1}$ as a function of mole fraction (x) of C_2H_6 in CH_4-C_2H_6 mixtures at 298.15 K.

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