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Application of the Dielectric Constant Measurements to Study the Influence of the Small Quantities of Water Vapor on the Compressibility Factor of Methane

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Dielectric measurements have been applied successfully to obtain accurate values of the compressibility factor of methane in the presence of the small quantities of water vapor [20, 65, and 95 ppm(v)]. Up to about 95 ppm(v) of H_2O in CH_4, the compressibility factor decreases very slightly in the presence of H_2O. The compressibility factor of dry CH_4 determined by the dielectric method is compared with the best PVT results and the Goodwin equation of state. The compressibility factor of CH_4 having small quantities of water vapor is compared with the Goodwin, GERG, and AGA8 equations.

KEY WORDS: Clausius–Mossotti function; compressibility; dielectric constant; dielectric virial coefficients; expansion technique; methane; water.

1. INTRODUCTION

Natural gas contains quite frequently small quantities of water vapor. It is important to determine whether the presence of water influences in anyway the compressibility factor of CH_4. The purpose of this article is to show that the dielectric measurements can lead to precise determination of the compressibility factor of CH_4 in the presence of small quantities of water vapor [up to about 95 ppm(v)]. Since an electrical measuring technique is

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more amenable to technology transfer, the dielectric measurement appears to be very appropriate for industrial measurement of the compressibility factor.

2. MATHEMATICAL DEVELOPMENT

The compressibility factor Z is given by

$$Z = P/\rho RT \tag{1}$$

where P is the pressure, R is the universal gas constant, T is the temperature, and ρ is the molar density. We intend to determine ρ from the Clausius–Mossotti relation for the dielectric constant ε. This relation is given by

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

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.

From Eq. (3), the first approximation for the density is

$$\rho_1 = CM/A_\varepsilon \tag{4}$$

With this value of density, we get the first approximation for the compressibility factor

$$Z_1 = (P/RT)(A_\varepsilon/CM) \tag{5}$$

The second approximation for ρ is given by

$$\rho_2 = CM/A_\varepsilon - (B_\varepsilon/A_\varepsilon)(CM/A_\varepsilon)^2 \tag{6}$$

Replacing Eq. (6) in Eq. (1), we get the second approximation for the compressibility factor,

$$Z_2 = (P/RT)[A_\varepsilon/CM + B_\varepsilon/A_\varepsilon] \tag{7}$$

The third approximation for the density is given by

$$\rho_3 = \frac{CM}{A_\varepsilon} - \left[\frac{B_\varepsilon}{A_\varepsilon}\right]\left[\frac{CM}{A_\varepsilon}\right]^2 + \left[\frac{2B_\varepsilon^2 - A_\varepsilon C_\varepsilon}{A_\varepsilon^2}\right]\left[\frac{CM}{A_\varepsilon}\right]^3 \tag{8}$$

which leads to

$$Z_3 = \left[\frac{P}{RT}\right]\left[\frac{A_\varepsilon}{CM} + \frac{B_\varepsilon}{A_\varepsilon} + \left(\frac{A_\varepsilon C_\varepsilon - B_\varepsilon^2}{A_\varepsilon^3}\right)[CM]\right] \tag{9}$$

The compressibility factor Z can be obtained from accurate measurements of P, T, ε, A_ε, B_ε, and C_ε.

3. EXPERIMENTAL PROCEDURE

The experimental procedure consists of developing a dielectric method for the determination of the compressibility factor of CH_4 with traces of water present in the gas.

3.1. Dielectric Method

The first dielectric virial coefficient, A_ε, is obtained by measuring the dielectric constant ε as a function of pressure from 0 to 1.2 MPa. The equation of state given by

$$P/\rho RT = 1 + B_P\rho + C_P\rho^2 + \cdots \tag{10}$$

where B_P and C_P are, respectively the second and third pressure virial coefficients, is combined with Eq. (3) to give

$$[(\varepsilon - 1)RT]/[(\varepsilon + 2)P] = A_\varepsilon + (B_\varepsilon - A_\varepsilon B_P)(P/RT) + \cdots \tag{11}$$

A plot of the left-hand side of Eq. (11) versus (P/RT) generally gives a straight line in the low-pressure region with the intercept A_ε and the slope $(B_\varepsilon - A_\varepsilon B_P)$. Values of A_ε determined in this way can be reliable to a few parts in 10^4, being dependent on the accuracy of the measured quantities ε, P, and T. In Eq. (11), B_ε is only a small fraction of the second term. So a very small error in $(B_\varepsilon - A_\varepsilon B_P)$ can lead to a large error [1] in B_ε.

In order to determine precisely the second (B_ε) and the third (C_ε) dielectric virial coefficients, we used an expansion technique developed by Buckingham et al. [2]. This method essentially consists of first measuring the sum of capacitances of two similar cells, one of which is filled with gas at density ρ and the other evacuated. The gas is then allowed to fill both 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, the second and third dielectric virial coefficients are determined by the change in total capacitance. Details of this expansion technique are given by Kirouac and Bose [3] and Huot and Bose [4].

Let two quasi-identical cells (A and B) be, respectively, of volumes $V_A = V(1+\delta)$ and $V_B = V(1-\delta)$, where δ is small and $V = (V_A + V_B)/2$. The cells contain, respectively, capacitors of geometric capacitance $C_A = C_0(1+\Delta)$ and $C_B = C_0(1-\Delta)$, where Δ is small. Let A initially contain a gas of dielectric constant ε_1 and density ρ_1 while B is evacuated. The change of capacitance, D_A, on opening the valve is

$$\begin{aligned}\frac{D_A}{C_0(\varepsilon_1-1)} &= (\delta-\Delta) - \left[\frac{B_\varepsilon + A_\varepsilon^2}{6A_\varepsilon^2}\right](\varepsilon_1-1) \\ &\quad + \left[\frac{4B_\varepsilon^2 - 3A_\varepsilon C_\varepsilon + 2B_\varepsilon A_\varepsilon^2 + A_\varepsilon^4}{36A_\varepsilon^4}\right](\varepsilon_1-1)^2 \\ &\quad + \left[\frac{C_\varepsilon + 2A_\varepsilon B_\varepsilon + A_\varepsilon^3}{36A_\varepsilon^3}\right]\delta(\varepsilon_1-1)^2 + \cdots \qquad (12)\end{aligned}$$

where the density ρ_1 has been expressed in terms of the dielectric constant ε_1. Similarly, if B initially contains a gas of dielectric constant ε_2 and

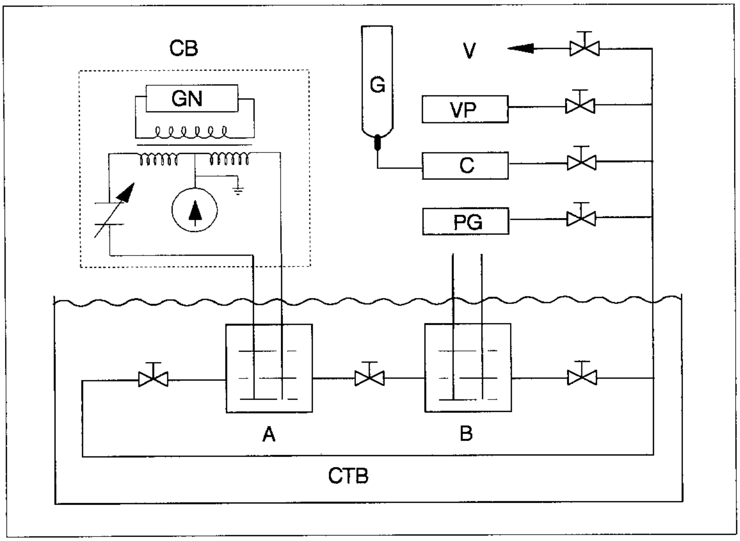

Fig. 1. Schematic diagram of the system using the dielectric technique. A and B, dielectric cells; C, compressor; CB, capacitance bridge; CTB, controlled temperature bath; G, gas cylinder; GN, generator; PG, pressure gauge; VP, vacuum pump.

density ρ_2 while A is evacuated, the change of capacitance, D_B, on opening the valve is

$$\frac{D_B}{C_0(\varepsilon_2-1)} = -(\delta-\Delta) - \left[\frac{B_\varepsilon + A_\varepsilon^2}{6A_\varepsilon^2}\right](\varepsilon_2-1) + \left[\frac{(4B_\varepsilon^2 - 3A_\varepsilon C_\varepsilon + 2B_\varepsilon A_\varepsilon^2 + A_\varepsilon^4)}{36A_\varepsilon^4}\right](\varepsilon_2-1)^2 - \left[\frac{C_\varepsilon + 2A_\varepsilon B_\varepsilon + A_\varepsilon^3}{36A_\varepsilon^3}\right]\delta(\varepsilon_2-1)^2 + \cdots \tag{13}$$

Then, by combining Eqs. (12) and (13), we get

$$\frac{D_A}{C_0(\varepsilon_1-1)} + \frac{D_B}{C_0(\varepsilon_2-1)} = -\left[\frac{B_\varepsilon + A_\varepsilon^2}{6A_\varepsilon^2}\right][(\varepsilon_1-1)+(\varepsilon_2-1)] + \frac{1}{2}\left[\frac{4B_\varepsilon^2 - 3A_\varepsilon C_\varepsilon + 2B_\varepsilon A_\varepsilon^2 + A_\varepsilon^4}{36A_\varepsilon^4}\right][(\varepsilon_1-1)+(\varepsilon_2-1)]^2 + \cdots \tag{14}$$

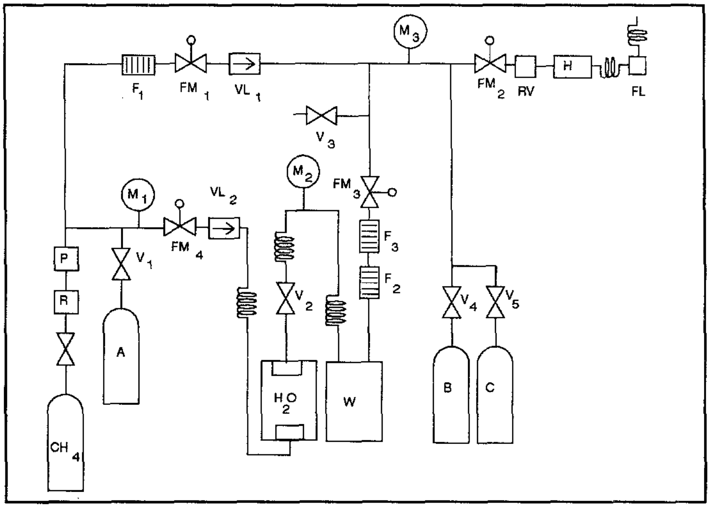

Fig. 2. Schematic diagram of the system for preparation and measurements of the amount of water vapor. A, buffer cylinder; B and C, sampling cylinder; F, filter; FL, flowmeter; FM, fine metering valve; H, hygrometer; M, pressure gauge; P, gas purifier; R, pressure regulator; RV, relief valve; V, valve; VL, no-return valve; W, water condensation.

For the quadratic term in Eq. (14), we assumed that $\varepsilon_1 \approx \varepsilon_2$. On plotting the left-hand side 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 dielectric measurements were carried out using a decade transformer bridge (General Radio, Type 1621) and a precision capacitance standard of 100 pF (GR 1408-B). The precision on capacitance measurement is estimated to be 3×10^{-7}. The cells used were of the three-terminal type. Each cell has a set of parallel plates 3.18 cm in diameter. The separation between the plates is adjusted to have a geometrical capacitance of about 10 pF. The plates were made of copper for better thermal conductivity. Details of construction are given by Huot and Bose [4]. The measuring system (dielectric cells and valves) was immersed into a constant temperature bath. Temperature was controlled by a circulating bath (Haake, Model A82) within ±0.01 K and was measured using a thermistor calibrated against a platinum resistance thermometer (Guildline 9540). The uncertainty in temperature measurements is 0.01 K.

The pressures were measured with a quartz pressure transducer (Paroscientific, Model 740). This transducer was calibrated against a pressure standard manufactured by 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 precision is estimated to be of the order of 1×10^{-4} for pressures above 1.5 MPa. The methane was obtained from Matheson

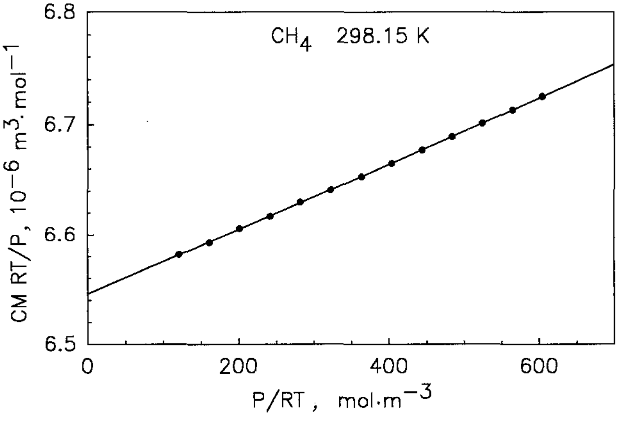

Fig. 3. Clausius–Mossotti function of CH_4 at 298.15 K as a function of *P*/*RT*. Points are experimental and the curve is the least-squares fit.

Company and had a minimum purity of 99.99%. The humidity, measured with a calibrated hygrometer (MCM, Model Dewmatic 600 D), was less than 5 ppm(v).

For all the results reported here, we included a correction for the effect of pressure on geometric capacitance C_G of the cells. The relation between $C_G(P)$, the geometric capacitance at pressure P, and the vacuum geometric capacitance $C_G(0)$ is

$$C_G(P) = C_G(0)[1 - KP] \tag{15}$$

Table I. Comparison at 298.15 K Between Our Experimental Values (Z_3) for Dry CH_4 and Values Calculated from Goodwin (Z_{GO}), GERG (Z_{GE}), and AGA8 (Z_{AG}) Equations

Pressure P (MPa)	Compressibility factor			
	$Z_3 \pm \Delta Z_3$	Z_{GO}	Z_{GE}	Z_{AG}
15.002	0.8187 ± 0.0009	0.8174	—	0.8186
14.532	0.8201 ± 0.0009	0.8189	—	0.8200
13.987	0.8222 ± 0.0008	0.8211	—	0.8221
13.018	0.8271 ± 0.0008	0.8263	—	0.8270
12.056	0.8335 ± 0.0007	0.8329	—	0.8333
11.014	0.8420 ± 0.0007	0.8416	0.8417	0.8419
10.043	0.8514 ± 0.0006	0.8512	0.8512	0.8513
9.0339	0.8625 ± 0.0006	0.8625	0.8624	0.8624
8.0296	0.8748 ± 0.0005	0.8747	0.8747	0.8747
7.0007	0.8885 ± 0.0005	0.8883	0.8884	0.8884
6.0086	0.9026 ± 0.0005	0.9022	0.9024	0.9025
5.0079	0.9176 ± 0.0004	0.9170	0.9174	0.9176
3.9980	0.9335 ± 0.0004	0.9327	0.9332	0.9333
3.0004	0.9496 ± 0.0004	0.9490	0.9493	0.9495
2.0011	0.9663 ± 0.0004	0.9658	0.9659	0.9660
1.4987	0.9747 ± 0.0004	0.9744	0.9743	0.9744
1.4001	0.9764 ± 0.0004	0.9760	0.9760	0.9761
1.3000	0.9781 ± 0.0004	0.9777	0.9777	0.9778
1.2001	0.9798 ± 0.0004	0.9794	0.9794	0.9795
1.1001	0.9815 ± 0.0004	0.9811	0.9811	0.9812
1.0002	0.9832 ± 0.0004	0.9828	0.9828	0.9829
0.9001	0.9849 ± 0.0004	0.9845	0.9845	0.9846
0.8001	0.9866 ± 0.0004	0.9862	0.9862	0.9863
0.7001	0.9884 ± 0.0004	0.9879	0.9879	0.9880
0.6001	0.9901 ± 0.0005	0.9896	0.9897	0.9897
0.5001	0.9918 ± 0.0005	0.9913	0.9914	0.9914
0.4001	0.9937 ± 0.0005	0.9930	0.9931	0.9931
0.3001	0.9953 ± 0.0006	0.9947	0.9948	0.9948

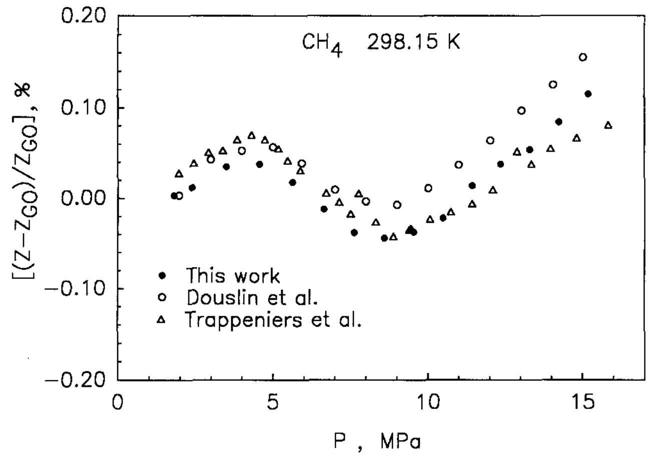

Fig. 4. Deviations (%) of the experimental values of Z_3 from Z_{GO} values calculated using the Goodwin equation of state as a reference.

Table II. Comparison at 298.15 K Between Our Experimental Values (Z_3) for CH_4 Having 20 ppm(v) of H_2O and Values Calculated from Goodwin (Z_{GO}), GERG (Z_{GE}), and AGA8 (Z_{AG}) Equations

Pressure P (MPa)	Compressibility factor			
	$Z_3 \pm \Delta Z_3$	Z_{GO}	Z_{GE}	Z_{AG}
15.081	0.8185 ± 0.0009	0.8172	—	0.8184
14.027	0.8220 ± 0.0008	0.8209	—	0.8219
13.037	0.8269 ± 0.0008	0.8261	—	0.8268
12.019	0.8337 ± 0.0007	0.8331	—	0.8336
10.990	0.8422 ± 0.0007	0.8418	0.8419	0.8421
10.028	0.8518 ± 0.0006	0.8514	0.8513	0.8515
9.0149	0.8627 ± 0.0006	0.8627	0.8626	0.8626
7.9900	0.8752 ± 0.0005	0.8752	0.8752	0.8752
7.0112	0.8883 ± 0.0005	0.8881	0.8882	0.8883
6.0236	0.9024 ± 0.0005	0.9019	0.9022	0.9023
5.0033	0.9177 ± 0.0004	0.9170	0.9175	0.9176
4.0044	0.9332 ± 0.0004	0.9326	0.9331	0.9332
3.0035	0.9496 ± 0.0004	0.9489	0.9492	0.9494
1.9737	0.9666 ± 0.0004	0.9663	0.9663	0.9664
1.5038	0.9745 ± 0.0004	0.9743	0.9742	0.9743
1.4006	0.9762 ± 0.0004	0.9760	0.9760	0.9761
1.3000	0.9780 ± 0.0004	0.9777	0.9777	0.9778
1.1965	0.9797 ± 0.0004	0.9795	0.9795	0.9795
1.0424	0.9823 ± 0.0004	0.9821	0.9821	0.9822
0.8914	0.9849 ± 0.0004	0.9846	0.9847	0.9847
0.8000	0.9865 ± 0.0004	0.9862	0.9862	0.9863
0.6943	0.9882 ± 0.0004	0.9880	0.9880	0.9881
0.5253	0.9910 ± 0.0005	0.9908	0.9909	0.9910
0.3296	0.9943 ± 0.0006	0.9942	0.9943	0.9943

where K is the compressibility. For copper, K is equal to 2.4×10^{-6} MPa^{-1}. Corrections to A_ε, B_ε, and C_ε are, respectively, given by $KRT/3$, $(KRT/3)(A_\varepsilon + B_\mathrm{P})$, and $(KRT/3)(A_\varepsilon B_\mathrm{P} + B_\varepsilon - 2A_\varepsilon^2 + C_\mathrm{P})$.

3.2. Preparation and Measurement of the Quantity of Water Vapor

Various quantities of water vapor in CH_4 were added by taking account of the partial pressure of water vapor. A schematic diagram of the experimental setup is shown in Fig. 2. The amount of water vapor was measured with a hygrometer. After an equilibrium time of the order of 12 hr, measurements of the quantity of water vapor were carried out at

Table III. Comparison at 298.15 K Between Our Experimental Values (Z_3) for CH_4 Having 65 ppm(v) of H_2O and Values Calculated from Goodwin (Z_{GO}), GERG (Z_{GE}), and AGA8 (Z_{AG}) Equations

Pressure P (MPa)	Compressibility factor			
	$Z_3 \pm \Delta Z_3$	Z_{GO}	Z_{GE}	Z_{AG}
15.089	0.8182 ± 0.0009	0.8171	—	0.8184
14.016	0.8218 ± 0.0008	0.8209	—	0.8219
12.879	0.8277 ± 0.0008	0.8271	—	0.8278
12.012	0.8336 ± 0.0007	0.8332	—	0.8336
11.014	0.8418 ± 0.0007	0.8416	0.8416	0.8419
10.031	0.8513 ± 0.0006	0.8513	0.8513	0.8514
9.0409	0.8622 ± 0.0006	0.8624	0.8623	0.8623
8.0397	0.8744 ± 0.0005	0.8746	0.8745	0.8746
7.0238	0.8879 ± 0.0005	0.8879	0.8880	0.8881
6.0010	0.9025 ± 0.0005	0.9023	0.9025	0.9026
5.0134	0.9173 ± 0.0004	0.9169	0.9173	0.9175
4.0076	0.9330 ± 0.0004	0.9326	0.9330	0.9332
3.0138	0.9490 ± 0.0004	0.9488	0.9491	0.9492
1.9946	0.9658 ± 0.0004	0.9659	0.9660	0.9661
1.5069	0.9740 ± 0.0004	0.9742	0.9742	0.9743
1.4001	0.9758 ± 0.0004	0.9760	0.9760	0.9761
1.2999	0.9774 ± 0.0004	0.9777	0.9777	0.9778
1.2001	0.9792 ± 0.0004	0.9794	0.9794	0.9795
1.0999	0.9809 ± 0.0004	0.9811	0.9811	0.9812
1.0000	0.9825 ± 0.0004	0.9828	0.9828	0.9829
0.9000	0.9841 ± 0.0004	0.9845	0.9845	0.9846
0.8000	0.9858 ± 0.0004	0.9862	0.9862	0.9863
0.7000	0.9874 ± 0.0004	0.9879	0.9879	0.9880
0.6001	0.9891 ± 0.0005	0.9896	0.9897	0.9897
0.5001	0.9908 ± 0.0005	0.9913	0.9914	0.9914
0.4001	0.9925 ± 0.0005	0.9930	0.9931	0.9931

atmospheric pressure while maintaining a 500 ml · min^{-1} flow in the hygrometer. The measurements were done before and after the determination of Z and gave the following mean values: 20 ± 3, 65 ± 6, and 95 ± 10 ppm(v).

4. EXPERIMENTAL RESULTS AND DISCUSSION

Using Eq. (11), we obtain A_ε for dry CH_4 to be $(6.551 \pm 0.002) \times 10^{-6}\ m^3 \cdot mol^{-1}$ (see Fig. 3). The above value is corrected for pressure as shown in Eq. (15). The determination of the second (B_ε) and third (C_ε) dielectric virial coefficients were obtained with the expansion method by Bose et al. [5]. At 298.15 K, the extrapolated values are $B_\varepsilon = 7.77 \times 10^{-12}\ m^6 \cdot mol^{-2}$ and $C_\varepsilon = -284 \times 10^{-18}\ m^9 \cdot mol^{-3}$.

Since the quantity of water vapor added to CH_4 is very small, we

Table IV. Comparison at 298.15 K Between Our Experimental Values (Z_3) for CH_4 Having 95 ppm(v) of H_2O and Values Calculated from Goodwin (Z_{GO}), GERG (Z_{GE}), and AGA8 (Z_{AG}) Equations

Pressure P (MPa)	Compressibility factor			
	$Z_3 \pm \Delta Z_3$	Z_{GO}	Z_{GE}	Z_{AG}
15.050	0.8183 ± 0.0009	0.8173	—	0.8185
14.017	0.8218 ± 0.0008	0.8210	—	0.8219
13.012	0.8269 ± 0.0008	0.8263	—	0.8270
12.024	0.8335 ± 0.0007	0.8331	—	0.8336
11.011	0.8418 ± 0.0007	0.8416	0.8417	0.8419
10.030	0.8513 ± 0.0006	0.8513	0.8513	0.8514
9.0172	0.8624 ± 0.0006	0.8626	0.8626	0.8626
8.0189	0.8746 ± 0.0005	0.8748	0.8748	0.8748
5.9630	0.9029 ± 0.0005	0.9028	0.9031	0.9032
5.0117	0.9172 ± 0.0004	0.9169	0.9173	0.9175
4.0122	0.9328 ± 0.0004	0.9325	0.9329	0.9331
3.0003	0.9492 ± 0.0004	0.9490	0.9493	0.9494
2.0009	0.9655 ± 0.0004	0.9658	0.9659	0.9660
1.5005	0.9739 ± 0.0004	0.9743	0.9743	0.9744
1.3976	0.9756 ± 0.0004	0.9761	0.9760	0.9761
1.2999	0.9772 ± 0.0004	0.9777	0.9777	0.9778
1.1990	0.9789 ± 0.0004	0.9794	0.9794	0.9795
1.0015	0.9822 ± 0.0004	0.9828	0.9828	0.9829
0.9016	0.9839 ± 0.0004	0.9844	0.9845	0.9846
0.7989	0.9856 ± 0.0004	0.9862	0.9862	0.9863
0.6997	0.9871 ± 0.0004	0.9879	0.9879	0.9880
0.5973	0.9887 ± 0.0005	0.9896	0.9897	0.9898
0.5001	0.9902 ± 0.0005	0.9913	0.9914	0.9914

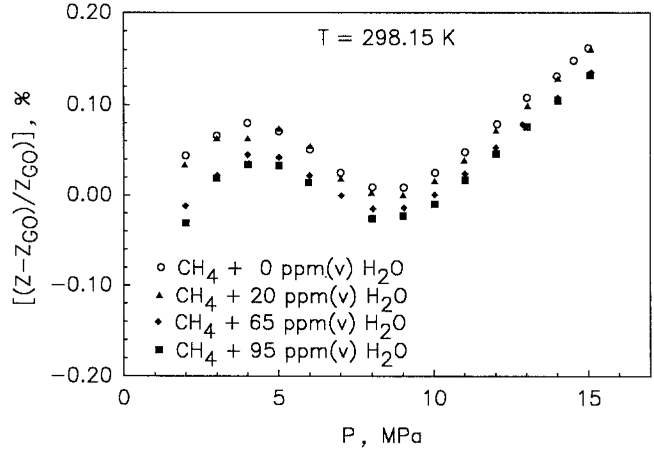

Fig. 5. Deviations (%) of the experimental values Z_3 from values calculated using the Goodwin equation of state as reference.

determine Z for CH_4–H_2O by using the same values of A_ε, B_ε, and C_ε as for dry CH_4.

In Table I, we compare our experimental values of Z_3 for CH_4 with values calculated according to the GERG [6], AGA8 [7], and Goodwin [8] equations of state. One can see from Fig. 4 that our values of Z_3 are in good agreement with the experimental values of Douslin et al. [9] and Trappeniers et al. [10] with respect to the Goodwin equation of state. In Tables II, III and IV, we present our experimental values of Z_3 for

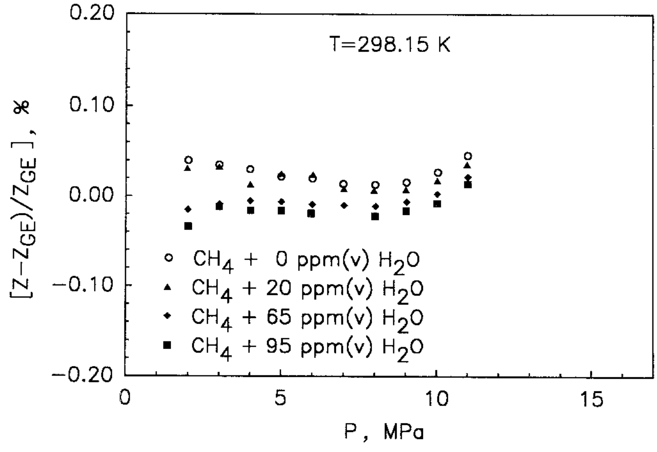

Fig. 6. Deviation (%) of the experimental values Z_3 from values calculated using the GERG equation of state as a reference.

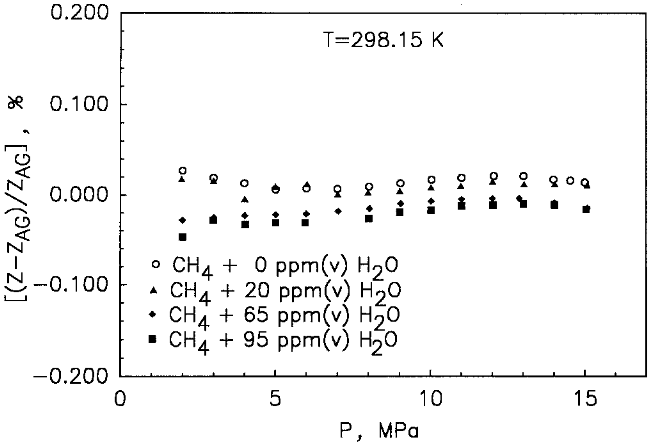

Fig. 7. Deviations (%) of the experimental values of Z_3 from values calculated using the AGA8 equation of state as a reference.

mixtures of CH_4–H_2O having, respectively, water contents of the order of 20, 65, and 95 ppm(v). As the quantity of water is very small for all mixtures, we compared our values of Z_3 with values calculated according to the Goodwin, GERG, and AGA8 equations of state for dry CH_4. In Figs. 5, 6, and 7, we illustrate the deviation $[(Z_3 - Z_{EQ})/Z_{EQ}]\%$ as a function of pressure for dry CH_4 and mixtures of CH_4–H_2O, respectively.

Precisions in the determination of Z_3 are of the order of 0.07% for pressures less than 10 MPa and of the order of 0.10% between 10 and 15 MPa. As presented in Tables II to IV, and illustrated in Figs. 6 and 7, our experimental values of Z_3 agree well with the GERG and the AGA-8 equations of state. The differences in Z between dry CH_4 and the three mixtures CH_4–H_2O are less than the uncertainties on Z.

Determination of the compressibility factor of dry CH_4 and mixtures CH_4–H_2O shows that the compressibility factor decreased very slightly due to the presence of water vapor in small quantities [up to 95 ppm(v)]. This decrease is of the order of the uncertainties.

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REFERENCES

1. T. K. Bose, in *Phenomena Induced by Intermolecular Interactions*, G. Birnbaum, ed. (Plenum, New York, 1986).
2. A. D. Buckingham, R. H. Cole, and H. Sutter, *J. Chem. Phys.* **52**:5960 (1970).
3. S. Kirouac and T. K. Bose, *J. Chem. Phys.* **64**:1580 (1976).
4. J. Huot and T. K. Bose, *J. Chem. Phys.* **94**:3849 (1991).
5. T. K. Bose, J. S. Sochanski, and R. H. Cole, *J. Chem. Phys.* **57**:3592 (1972).
6. M. Jaeschke, S. Audibert, P. van Caneghem, A. E. Humphreys, R. Janssen-van Rosmalen, Q. Pellar, J. P. J. Michels, J. A. Schouten, and C. A. Ten Seldam, *High Accuracy Compressibility Factor Calculation for Natural Gases and Similar Mixtures by Use of a Truncated Virial Equation* (GERG TM2, VDI, Verlag, Düsseldorf, 1988).
7. K. E. Starling, *Compressibility and Supercompressibility for Natural Gas and Other Hydrocarbon Gases*, AGA Transmission Measurement Committee Report, No. 8 (1985).
8. R. D. Goodwin, The Thermophysical Properties of Methane from 90 K to 500 K at Pressures to 700 bar, Technical Note 653 (Natl. Bur. Stand., Boulder, Colo., 1974).
9. D. R. Douslin, R. H. Harrison, R. T. Moore, and J. P. McCullough, *J. Chem. Eng. Data* **9**:358 (1964).
10. N. J. Trappeniers, R. Wassenaar, and J. C. Abels, *Physica* **98A**, 289 (1979).