al. (*2*). An unsaturated solution was dealt with an isothermal mixture of pure water and a saturated solution. The results are shown in Table III. The deviations between the experimental data and the predicted values were large, especially at high absorbent concentrations. Therefore, without using the predicted values on the basis of the principle of a corresponding state, it is necessary to measure heat capacity for this system.

Conclusions

The heat capacities of the three-component system using water as the working medium and lithium bromide-lithium iodide as the absorbent were measured at various temperatures and absorbent concentrations. An empirical formula for the heat capacity of this system was obtained by the least-squares method from the experimental data. The calculated values from this empirical formula were in good agreement with the experimental data. The heat capacity data of this system are very useful for the research and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers.

Glossary

A_n, B_n, C_n	constants in empirical formula 2
C_p	heat capacity at constant pressure, kJ kg^{-1} K^{-1}
n	integer exponent in empirical formula 2
T	absolute temperature, K
T_c	crystallization temperature, K
X	absorbent concentration, wt %

Greek Letter

ϵ	deviation, %

Subscripts

cal	calculated value from empirical formula 2
exp	experimental data
pre	predicted value on the basis of the principle of a corresponding state proposed by Kamoshida et al.

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The Water Content of a CO_2-Rich Gas Mixture Containing 5.31 mol % Methane along the Three-Phase and Supercritical Conditions

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The water content of a carbon dioxide (CO_2)-rich phase containing 5.31 mol % methane (CH_4) and balance CO_2 in equilibrium with a water-rich phase was measured above the initial hydrate formation conditions and at isobars of 6.21, 7.59, 10.34, and 13.79 MPa, or of 900, 1100, 1500, and 2000 psia, respectively, at temperatures ranging from 15.6 °C (60 °F) to 50.0 °C (122 °F). The measurements indicated that the presence of 5.31 mol % methane in CO_2 lowered the water content value by 20-30% from that of pure CO_2. The water content of the mixture is superimposed on the pure CO_2 data for comparison. The relevant water content data are presented in both tabular and graphical forms.

Introduction

Since most CO_2-rich gases are likely to contain nitrogen or light hydrocarbons even after purification, the effect of the diluents on the saturated water content should be known. Earlier corresponding states computations suggested that relatively small amounts of diluents (5 mol %) would lower the water content significantly. Experiments were, therefore, proposed to measure the water content of CO_2 "contaminated" with about 5 mol % methane.

The water content of the CO_2-rich fluid phases had been measured earlier by Wiebe and Gaddy (*1*) and more recently by Song and Kobayashi (*2*). The latter studies were conducted both in the nonhydrate and hydrate regions. The earlier studies indicated that the water content was extremely sensitive to fluid densities, particularly in the supercritical CO_2 region. Therefore, the experimental efforts were concentrated in this region of temperature and pressure.

Experimental Detail

The experimental apparatus is divided into two major parts. One is an equilibrium apparatus shown in Figure 1, and the other is an analytical section, line diagram shown in Figure 2, which detects the amount of water in the sample drawn from the equilibrium cell.

The equilibrium apparatus was initially used for the study of the methane-carbon dioxide system by Mraw et al. (*3*) and subsequently for numerous vapor-liquid equilibrium (VLE) studies. Shown are a visual cell and a magnetic pump to promote efficient mixing and rapid equilibration of the contents of the cell.

The cell with an internal volume of 100 cm^3 has four sampling ports plus a bottom port. The multiplicity of sampling ports facilitates the withdrawal of sample from each phase of interest without contamination. The sampling lines beyond the sampling ports are heated to a temperature high enough to prevent the

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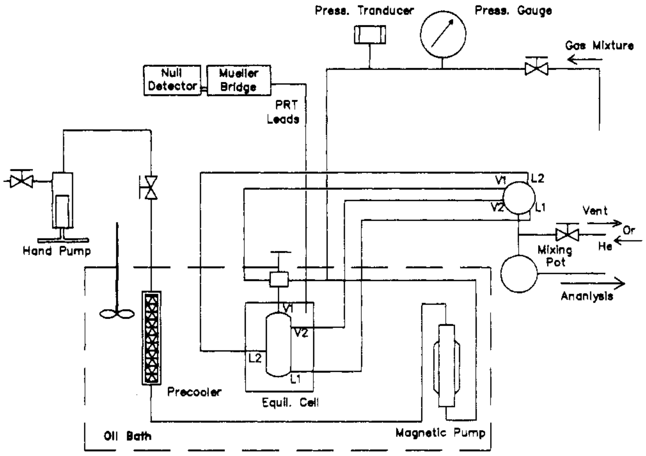

Figure 1. Line sketch of equilibrium apparatus.

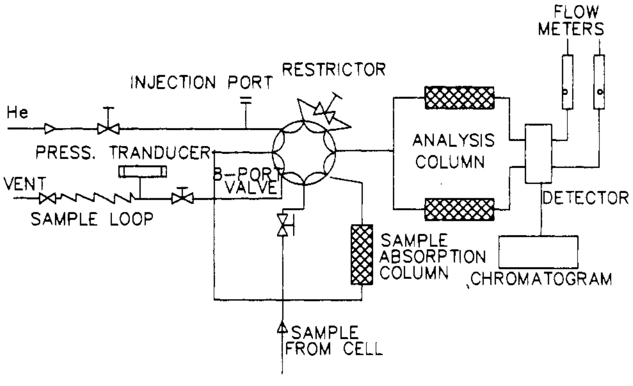

Figure 2. Analysis apparatus.

sample from condensing during the course of transfer to the analytical section.

The analytical section shown in Figure 2 employs a glycerol-packed absorption column and two split columns used for the analysis of water in the sample, Bloch and Lifland (*4*). This method has been applied successfully to measure the water content for such systems as methane-water by Sloan et al. (*5*) and Aoyagi et al. (*6*), methane-propane-water by Song and Kobayashi (*7*), and CO_2-water by Song and Kobayashi (*2*).

The sampling and analytical steps are the most tedious tasks due to the low water concentration, long sampling lines, delicate chromatographic columns, and the precise sequence of steps to be exercised.

A Ruska pump, not shown in Figure 1, was used to add the gas mixture to the system, and a hand pump was often used to inject water into the cell through the bottom port of the cell block and to pressurize or depress the cell content as needed.

Discussion of Results

The experimental water content values for the nonaqueous phases along the three-phase locus are tabulated isothermally in Table I. The tabulation includes the water content near the three-phase critical end point of the mixture and an estimate of the quadruple point.

Table II presents the isobaric water content of the nonaqueous (CO_2/methane-rich) fluid phase in the two-phase region. The water content data for pure CO_2 are superimposed on the data of this work in Figure 3, which indicates a substantial shift that is attributable to the small concentration of methane. Reductions as large as 20–30% of the pure CO_2–water content values were observed. The smoothed values are presented in Figure 4. Figure 5 shows a comparison of isothermal water content in the CO_2-rich phases plotted against molar volume at three different temperatures, 50, 43.3, and 32.2 °C, or 122, 110, and 90 °F, respectively, for CO_2–H_2O and CO_2–CH_4–H_2O systems. The molar volume has been calculated with an IBM PC by running the DDMIX program prepared by Ely (*8*). Every isotherm indicates that pure CO_2 is capable of containing more water than the diluted CO_2–CH_4 mixture at the same molar volume.

Table I. Water Content of a CO_2–CH_4 Mixture Containing 5.31 mol % CH_4 in CO_2 in Equilibrium with a H_2O(l)-Rich Phase along the Three-Phase Locus

temp, °F/°C	pressure, psia/MPa		10^3 × mole fracn of water	phase sampled
60/15.56	806.0	5.559	0.6266	vapor
60/15.66	835.5	5.762	1.0485	liquid
70/21.11	883.1	6.090	0.8420	vapor
70/21.11	920.0	6.345	1.3115	liquid
81.1/27.28	1016.0	7.007	1.1033	vapor
81.1/27.28	1090.0	7.517	1.3843	liquid
83.1/28.39[a]	1088.9	7.510		3-ϕ critical
53.0/11.67[b]	875.0	6.035		end point

[a] Experimental 3-ϕ critical end point condition. [b] Initial hydrate formation and quadruple point, estimated.

Table II. Isobaric Water Content of a CO_2–CH_4 Mixture Containing 5.31 mol % CH_4 in CO_2 in Equilibrium with a H_2O(l)-Rich Phase in the Two-Phase Region

pressure, psia/MPa	temp, °F/°C	10^3 × mole fracn of water
900/6.207	80.6/27.0	1.0171
900/6.207	89.6/32.0	1.2912
900/6.207	91.3/32.94	1.3622
1100/7.586	85.25/29.58	1.2289
1100/7.586	88.90/31.61	1.2404
1100/7.586	93.20/34.0	1.3316
900/6.207	109.4/43.0	2.2040
1100/7.586	109.4/43.0	2.0341
900/6.207	122/50.0	3.0034
1100/7.586	122/50.0	2.7513
1500/10.345	122/50.0	2.9571
1500/10.345	100.0/37.78	2.6423
1500/10.345	95.0/35.00	2.5689
1500/10.345	87.22/30.68	2.4399
1500/10.345	81.42/27.46	2.3382
1500/10.345	77.0/25.00	2.2900
2000/13.793	122/50.0	3.4522
2000/13.793	110/43.33	3.1410
2000/13.793	101.60/38.67	2.9464
2000/13.793	87.22/30.68	2.7996
2000/13.793	77.0/25.0	2.6423

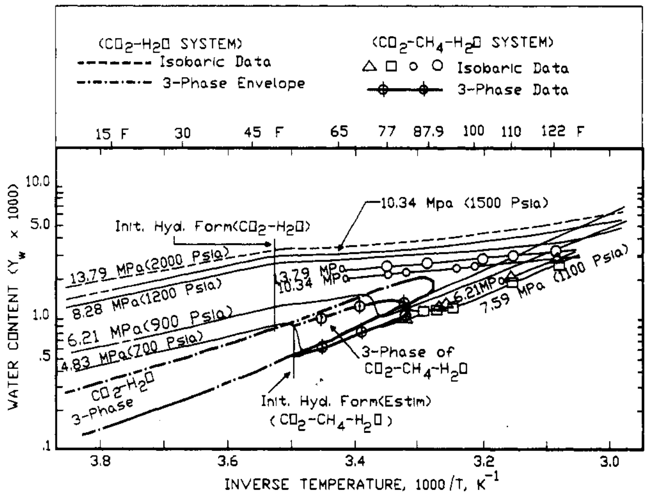

Figure 3. Water content of pure CO_2 and of a mixture containing 5.31 mol % CH_4 in CO_2 in equilibrium with water or hydrate.

As for the system of pure CO_2–H_2O reported by Song and Kobayashi (*2*), the enhancement of the vapor pressure of water resulted in a more intelligible plot, as shown in Figure 4. In fact, a cross plot of the enhancement factors in the two- and

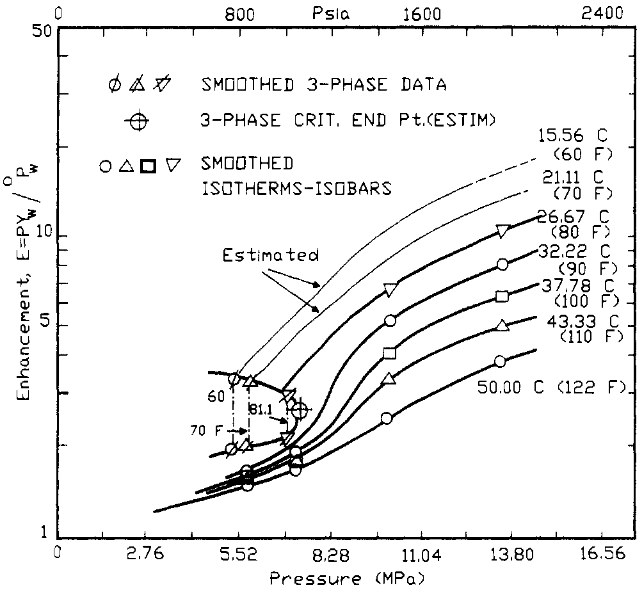

Figure 4. Enhancement of the water partial pressure due to the total pressure of a mixture of 5.31 mol % CH_4 in CO_2.

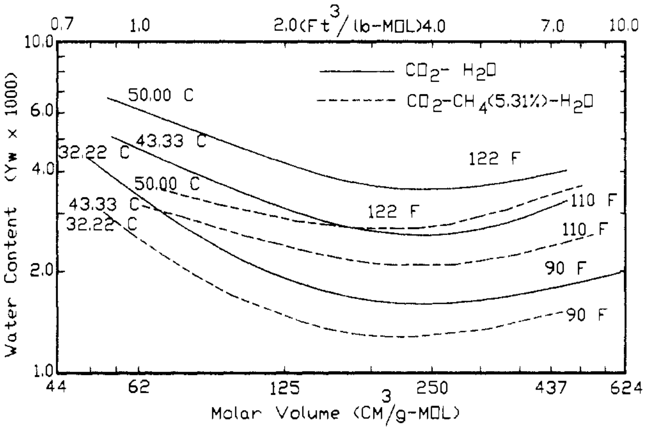

Figure 5. Isothermal water content of the CO_2-rich phase versus molar volume.

three-phase regions led to a "reasonable" extrapolation of the enhancement factors to lower temperatures. The enhancement factors at each condition studied in this report are presented in Table III.

Experimental Precision and Accuracy

The bath temperature was controlled to better than 0.05 °C with a Thermotrol manufactured by Hallikainen Instruments Co., and the temperature was measured by a L & N platinum resistance thermometer (PRT; SN 1331413), whose calibration is traceable to an NBS-certified PRT. A Muller Bridge, L & N Model 8067, and DC Null Detector 9834 were connected to the PRT.

The system pressure was measured by a pressure transducer manufactured by Setra System, Inc., Model 204, with a pressure range of 0–3000 psia and certified to be better than 0.1% of its full scale.

The accuracy of the tabulated water content based on the calibration is estimated to be generally within 5–6% for all experimental results.

Table III. Enhancement of Water Partial Pressue Due to the Total Pressure of a CO_2–CH_4 Mixture Containing 5.31 mol % CH_4 in CO_2 in Equilibrium with a H_2O(l)-Rich Phase

t, °C/°F	P, MPa/psia	$10^3 \times$ mole fracn of water	$P_w°$,[a] $10^3 \times$ MPa/psi	$E = Py_w/P_w°$
15.6/60	5.72/830.0	0.6168	1.786/0.259	1.977
15.6/60	5.72/830.0	1.0495	1.786/0.259	3.363
21.1/70	6.21/900.0	0.8151	2.524/0.366	2.004
21.1/70	6.21/900.0	1.3267	2.524/0.366	3.262
27.3/81.1	7.24/1050.0	1.0690	3.648/0.529	2.122
27.3/81.1	7.24/1050.0	1.5011	3.648/0.529	2.980
27.0/80.6	6.21/900.0	1.0162	3.586/0.520	1.759
32.0/89.6	6.21/900.0	1.2893	4.779/0.693	1.674
32.9/91.3	6.21/900.0	1.3606	5.041/0.731	1.675
29.6/85.3	7.59/1100.0	1.2265	4.179/0.606	2.227
31.6/88.9	7.59/1100.0	1.2399	4.676/0.678	2.012
34.0/93.2	7.59/1100.0	1.3305	5.345/0.775	1.888
43.0/109.4	6.21/900.0	2.1966	8.621/1.250	1.582
43.0/109.4	7.59/1100.0	2.0285	8.621/1.250	1.785
50.0/122.0	6.21/900.0	2.9944	1.234/1.789	1.506
50.0/122.0	7.59/1100.0	2.7438	1.234/1.789	1.687
50.0/122.0	10.34/1500.0	2.9483	1.234/1.789	2.475
50.0/122.0	13.79/2000.0	3.4403	1.234/1.789	3.846
43.3/110.0	13.79/2000.0	3.1311	8.648/1.254	4.994
43.3/110.0	10.34/1500	2.8395	8.648/1.254	3.397
37.8/100.0	13.79/2000	3.0086	6.552/0.9500	6.334
37.8/100.0	10.34/1500	2.6353	6.552/0.9500	4.161
32.2/90.0	13.79/2000	2.8201	4.843/0.7022	8.032
32.2/90.0	10.34/1500	2.4507	4.843/0.7022	5.235
26.7/80.0	13.79/2000	2.6633	3.541/0.5134	10.375
26.7/80.0	10.34/1500	2.3208	3.541/0.5134	6.781
21.1/70.0	13.79/2000	2.4959	2.524/0.3660	13.639
21.1/70.0	10.34/1500	2.1511	2.524/0.3660	8.816
15.6/60.0	13.79/2000	2.3549	1.786/0.259	18.184
15.6/60.0	10.34/1500	2.0039	1.786/0.259	11.606

[a] Reference 9, pp 1927–9. $\log P = A - [B/(t + C)]$ (P, mmHg; t °C), where $A = 8.277\,31$, $B = 1838.675$, and, $C = 241.413$ for $0 < t < 30$ and $A = 8.078\,99$, $B = 1733.926$, and $C = 233.665$ for $31 < t < 60$.

A certified primary grade gas mixture of 5.31 mol % methane in carbon dioxide was purchased from Airco Gas Co. Triply distilled water was used throughout the studies. Ultrapure grade helium was used as a carrier gas and was purchased from the U.S. Bureau of Mines. Its minimum purity was stated to be 99.9999 mol %. Both the helium and the gas mixture from the supply containers were drawn through a filter-gas purifier, Model 452 of Matheson Gas Products.

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