An Apparatus for the Direct Measurement of Fugacity in Mixtures Containing Large and Small Molecules[1]

Shawn Collier[2], J. Douglas Way[2], and James F. Ely[2,3]

---

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado 80401 U.S.A.

[3] Author to whom correspondence should be addressed

ABSTRACT

The fugacity coefficients of carbon dioxide in carbon dioxide/isobutane mixtures were measured using a microporous hollow fiber silica membrane, coupled with a high accuracy pure component equation of state for carbon dioxide. The membrane is a size discriminator, allowing smaller carbon dioxide (kinetic diameter, σ = 0.33 nm) molecules to permeate, while blocking the flow of the larger isobutane (σ = 0.5 nm) molecules. Experiments were run at three temperatures: 323.15, 338.15, 348.15 K and two different carbon dioxide mole fractions. Using measured values of the temperature, permeate and mixture pressures, and carbon dioxide mole fraction, fugacity coefficient comparisons were made using an extended corresponding states model using the van der Waals one-fluid mixing rules.

KEYWORDS: carbon dioxide; isobutane; fugacity; inorganic membrane; silica hollow fiber membrane; gas separation

1. INTRODUCTION

In order to obtain fugacities through a thermodynamic formalism, a great deal of accurate and precise PVT data are needed as a function of temperature, pressure, and composition [1]. This method involves numerical differentiation and integration of the data and can be complex and very time-consuming. The application of membrane separation to determine physical equilibrium provides a great simplification to achieving the same goal. In the past however, these measurements have been limited to a very narrow class of mixtures with unique properties. The first membrane separation measurement of gas fugacities were reported by Krishnamurty [2] who used a silica glass semi-permeable membrane for the separation of helium in heavy gas mixtures. Additional studies have also been reported measuring gas mixture component fugacities by Bruno[3], Cooper[4], and Ghosal [5] in hydrogen mixtures using a palladium/silver alloy membrane. In the present work, an apparatus similar to that used in previous separations was built to utilize a microporous hollow fiber silica membrane for the separation of carbon dioxide/isobutane mixtures, on the basis of molecular size.

The silica fibers used were prepared by PPG Industries and were manufactured by melt extrusion, followed by acid leaching as described by Hammel and co-workers [6,7]. The silica fiber membranes have an outside diameter of 45 μm, an average wall thickness of 5 μm, and an approximate pore size of 0.7 to 1.0 nm. Membrane pore size was determined through physical adsorption of subcritical carbon dioxide and small angle x-ray diffraction. At elevated temperatures, the mechanism for transport across the membrane is primarily molecular sieving or size discrimination [8]. This means that the transport of a certain size

molecule is completely blocked whereas smaller molecules have free passage. This mechanism is not unlike the sieving mechanism observed in zeolites [9]. In our studies, the membrane is permeable to carbon dioxide, but much less permeable to larger penetrants. This permeation is driven by the equalization of the chemical potential or equivalently the fugacity, of one species, on both sides of the membrane.

The pressure and temperature of the carbon dioxide can be measured on the permeate side of the membrane, and the component fugacity can be found using pure component values in the virial equation of state

$$\ln \phi_i = \frac{B_i}{R}\left(\frac{P_p}{T}\right) + \frac{C_i - B_i^{\,2}}{2R^2}\left(\frac{P_p^2}{T^2}\right) \tag{1}$$

where the subscript *p* denotes the permeate side of the membrane.[3]. The second and third virial coefficients used were from data reported by Duschek, *et al*.[10]. Given the fugacity coefficient of pure carbon dioxide, the fugacity and fugacity coefficient of carbon dioxide in the mixture can be found from the equilibrium criterion:

$$\hat{f}_i = \phi_i P \tag{2}$$

and

$$\hat{\phi}_i = \frac{\phi_i P_m}{y_i P_f} \tag{3}$$

where P_f is the pressure of the carbon dioxide in the mixture feed, $\hat{f}_i$, and $\hat{\phi}_i$ are the fugacity and the fugacity coefficient of CO_2 in the mixture.

2. EXPERIMENTAL

The apparatus used in the present work is shown in Figure 1. The experimental chamber is a cylindrical 0.5 dm^3 volume reservoir made of 316 stainless steel. The reservoir is housed in a large convection oven to maintain a constant temperature. The large internal volume of the reservoir is necessary to ensure the consistency of the mixture composition as permeation occurs.

As discussed in the introduction, the apparatus makes use of a hollow silica fiber membrane. The membrane assembly is inserted into one end of the reservoir and sealed in such a manner as to allow permeating gas out of the reservoir. The membrane assembly is constructed by running the fiber through an 1/8-inch stainless steel mounting tube. One end is then potted using a high temperature silicone rubber (Nusil Silicone Technology R-2160, Carpinteria, CA rated 300°C). The open end is flame sealed by melting in a high temperature hydrogen/oxygen flame[11]. Figure 2 shows a detailed schematic of the membrane assembly.

Temperature measurements were made using a Type J thermocouple. The thermocouple was placed inside of the feed gas reservoir and the probe has an estimated accuracy of ± 0.5 ° C. The pressures of the pure carbon dioxide and the mixture were measured using two Omega pressure transducers (model PX612, Stamford, CT). Both transducers were calibrated using a dead-weight pressure gauge. The pressure meters were found to be accurate within $\pm$ 55 kPa.

The gases used in these experiments were research grade isobutane of 99.95% purity and research grade carbon dioxide of 99.99% purity. The compositions of the gas mixtures

were determined gravimetrically. A two pan balance with an approximate error of ± 10 mg was used to weigh the mixture components. Mole fractions were also confirmed using a Hewlett-Packard model 5890 gas chromatograph with a calibrated thermal conductivity detector with a 1.8m HaySep-D packed column. To allow for sampling in the apparatus, a low volume "T" fitting was installed in the permeate stream. Gas chromatograph measurements, with TCD detection limits of ~ 0.01 mole %, showed no detectable levels of isobutane in the permeate.

The experimental procedure amounts to flushing and evacuating the system and then opening the gas reservoir to the feed side of the membrane. Equilibration times as determined by a steady pressure reading on the permeate side of the membrane are long—typically 2—4 days.

3. RESULTS AND DISCUSSION

Component fugacity coefficients for carbon dioxide were determined at three temperatures of 323.15, 338.15 and 348.15 K. Table I shows fugacity coefficient results for two different carbon dioxide mole fractions at varying pressures. The uncertainties shown in Table I result from an error propagation analysis which included estimates of the error in mole fraction, temperature, pressure, and the virial coefficients.

An extended corresponding states model, DDMIX [12], was used to predict fugacity coefficients for carbon dioxide in the mixture. In this model the fugacity of a component in solution is calculated from the expression

$$\ln\left(f_k / x_k p\right) = \ln\left(f_0 / p_0\right) + z_0^r H_{nk} + u_0^r F_{nk}$$

where the H_{nk} and F_{nk} are derivatives of the mixing rules (van der Waals one-fluid in this case) and z_o^r and u_0^r are the dimensionless residual compressibility factor and internal energy of the corresponding states reference fluid. The derivatives are given by

$$F_{nk} = \frac{n}{f_x}\left(\frac{\partial f_x}{\partial n_k}\right)_{T,V,n_{j\neq k}} \quad and \quad H_{nk} = \frac{n}{h_x}\left(\frac{\partial h_x}{\partial n_k}\right)_{T,V,n_{j\neq k}}$$

and the mixing rules for the scale factors *fx* and *hx* are given by

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \quad and \quad h_x = \sum_i \sum_j x_i x_j h_{ij}$$

Propane was the reference fluid and details of the application of this model can be found in the literature [13]

Figure 3 shows the fugacity coefficient of carbon dioxide in the mixture versus the two different carbon dioxide mole fractions for experimental data and DDMIX results. As compared to DDMIX, the experimental results were systematically lower than those predicted by the model. From a modeling point of view, carbon dioxide behaves as if it were in an ideal solution and no adjustment of the model parameters would cause the predicted results to be lowered. Results using the Peng-Robinson equation of state showed similar behavior. The calculated results do, however, agree with the experimental measurements to within the estimated uncertainty in the measurements, typically ± 5 %.

The experimental results also show more temperature dependence than that exhibited in the model calculations, although the general trend of the calculations and experimental results are the same. The fugacity coefficient of carbon dioxide decreases at lower mole fractions of isobutane in the system. Data were not taken at higher isobutane mole fractions

due to adsorption, leading to membrane fouling which causes permeation rates to decrease rapidly, creating prolonged equilibration times.

4. SUMMARY AND CONCLUSIONS

The physical equilibrium technique was used to measure component fugacity coefficients for three isotherms, for two different carbon dioxide rich mixtures. Experimental fugacity coefficients were found using the volume explicit form of the virial equation of state and were compared to values obtained from an extended corresponding states model. Experimental values were found to be systematically lower than predicted values. Although the dependence of the fugacity coefficient on temperature was shown to be of importance, due to a lack of sufficient data, no clear conclusions can be made regarding general trends in this area. Further experiments are being run to obtain a wider range of data. In order to improve the accuracy of the measurements, an improved pressure measuring system incorporating a high accuracy differential pressure gauge is being built. Future work will include incorporating a second membrane which is selective for the large, rather than small component, thus enabling the measurement of both fugacity coefficients and through thermodynamics, the residual Gibbs energy.

ACKNOWLEDGMENTS

The author would like to thank Professors James F. Ely and J. Douglas Way for their support and advice. The financial support of the Department of Energy, Office of Basic Energy Sciences, Department of Chemical Sciences through grant No. DE-FG03-93 ER 14363 to JDW and grant No. DE-FG03-95 ER 14568 to JFE is gratefully acknowledged.

REFERENCES

1. G. N. Lewis and M. Randall, *Thermodynamics*, 2nd Edition, 1961, New York.
2. V. V. G. Krishnamurty, *Determination of the Fugacities of Helium in Gas Mixtures Using a Semi-Permeable Membrane*, Ph.D. Dissertation, Columbia University, New York, (1963).
3. T. J. Bruno, *J. Res. Natl. Bur. Stand.* (U.S.) **90**(2): 127 (1985).
4. H. W. Cooper, *The Dertermination of Fugacities of Hydrogen in Hydrogen and Propane Mixtures Using a Semi-Permeable Membrane*, Ph.D. Dissertation, Columbia University, New York, 1967.
5. A. B. Ghosal, *The Determination of Fugacities of Hydrogen in Hydrogen-Propane-Butane Mixtures*, Ph.D. Dissertation, Columbia University, New York, 1971.
6. J. J. Hammel, U.S. Patent 4,853,001 (August 1, 1989)
7. J. J. Hammel, W. J. Robertson, W. P. Marshall, H. W. Barch, B. Das, M. A. Smout and R. P. Beaver, U. S. Patent 4,842,620 (June 27, 1989)
8. J. D. Way and D. L. Roberts, *Sep. Sci. Tech*. **27**: 29 (1992)
9. R. M. Barrer, *Zeolites and Clay Materials as Sorbents and Molecular Sieves*, London, 1978.
10. W. Duschek, R. Kleinrahm and W. Wagner, J. Chem. Thermodynam. **22**: 841 (1990)
11. M. H. Hassan, J. D. Way, P. Thoen and A. C. Dillin, J. Memb. Sci. **104**: 27 (1995).
12. J. F. Ely, *DDMIX—Properties of CO2 Rich Mixtures*, Version 9.07 1988). Available form NIST Standard Reference Data, Gatihersburg, MD.
13. I. M. D. J. Marrucho-Ferreira, *Extended Corresponding States Theory: Application for Polar Compounds and Their Mixtures*, Ph.D. Dissertation, University of Lisbon, Lisbon, 1997.

Table I. Carbon Dioxide component Fugacity Coefficient for Carbon Dioxide + Isobutane Mixtures

Mole Fraction CO_2	Mixture Pressure (kPa)	Permeate Pressure (kPa)	Fugacity Coefficient ϕ_{CO_2} (Equation 1)	Fugacity Coefficient $\hat{\phi}_{CO_2}$ (Experimental)	Fugacity Coefficient $\hat{\phi}_{CO_2}$ (Predicted)
T = 323 K					
0.9432	2249.84	2080.91	0.923	0.905 ± 0.047	0.917
0.962	2350.00	2121.73	0.922	0.865 ± 0.044	0.913
T = 338 K					
0.9432	2374.64	2193.85	0.931	0.912 ± 0.043	0.925
0.962	2478.75	2287.07	0.927	0.889 ± 0.042	0.922
T = 348 K					
0.9432	2538.74	2305.50	0.934	0.899 ± 0.042	0.928
0.962	2573.21	2343.61	0.933	0.883 ± 0.041	0.927

FIGURE CAPTIONS

Fig. 1 Schematic of Membrane Apparatus

Fig. 2 Schematic of a Single Fiber Module

Fig. 3. Comparison of Calculated and Experimental Fugacity Coefficients of Carbon Dioxide in Carbon Dioxide Rich Mixtures. Experimental results: ◆ 323.15 K, ▲ 338.15 K, ■ 343.15 K. Calculated Results: 323.15 K, 338.15 K, 343.15 K.

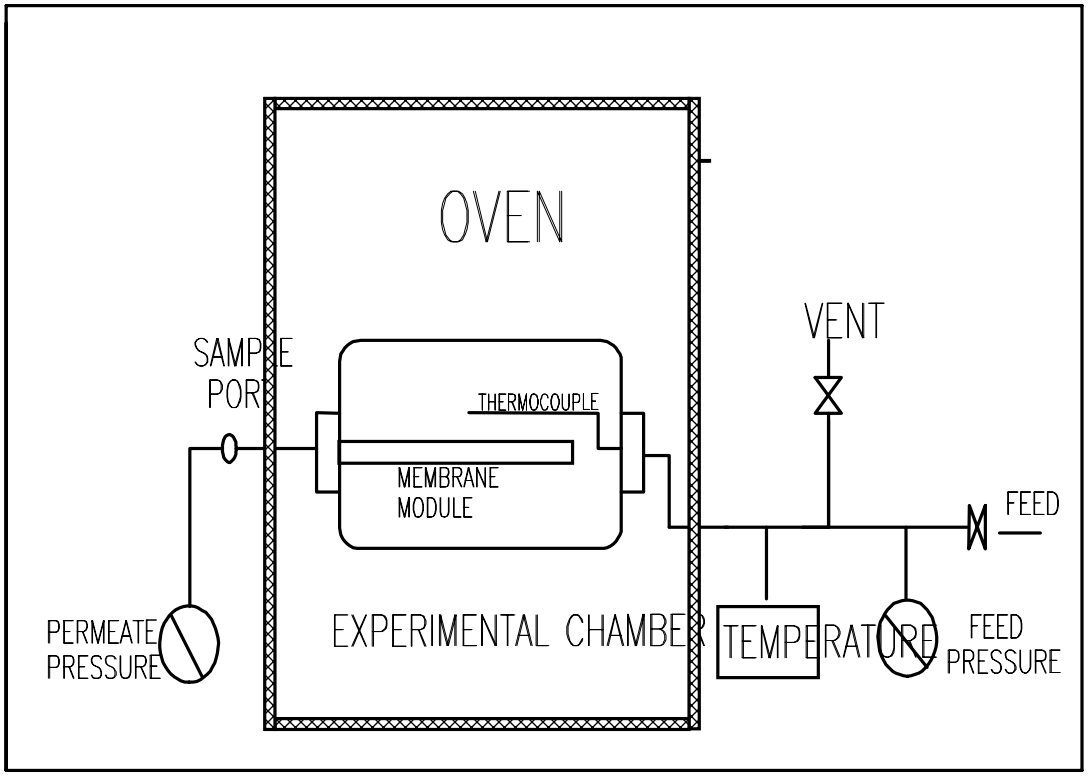

Figure 1. Schematic of Membrane Apparatus

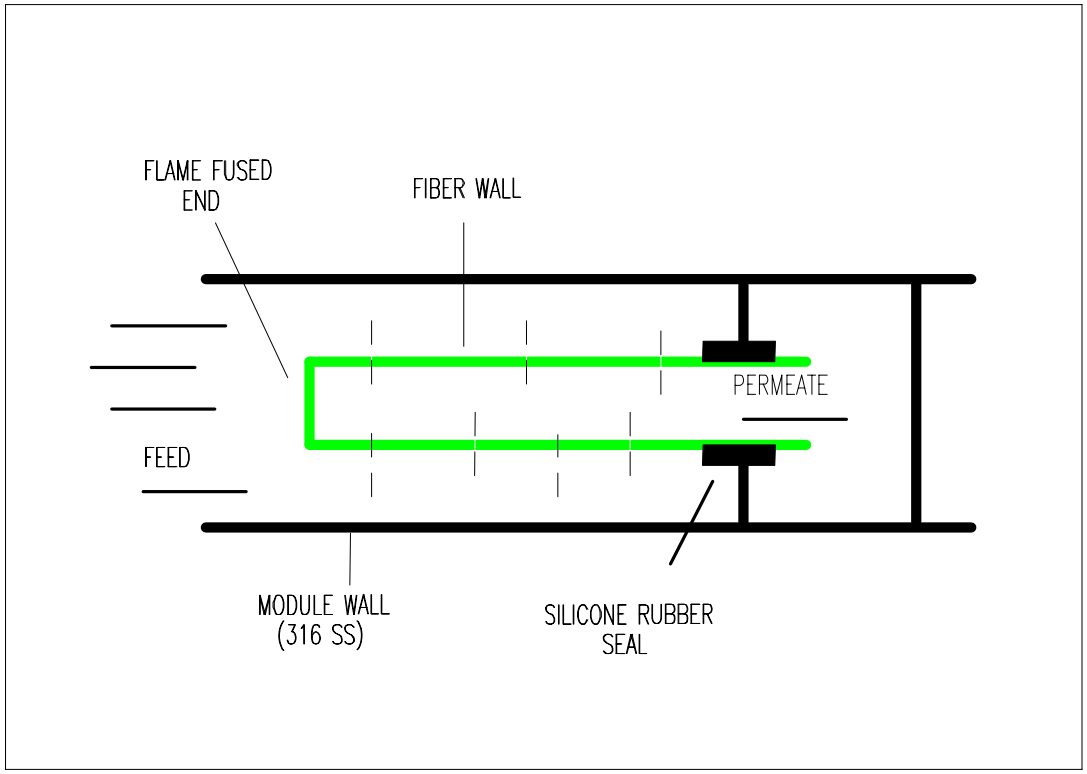

Figure 2. Schematic of Single Fiber Module

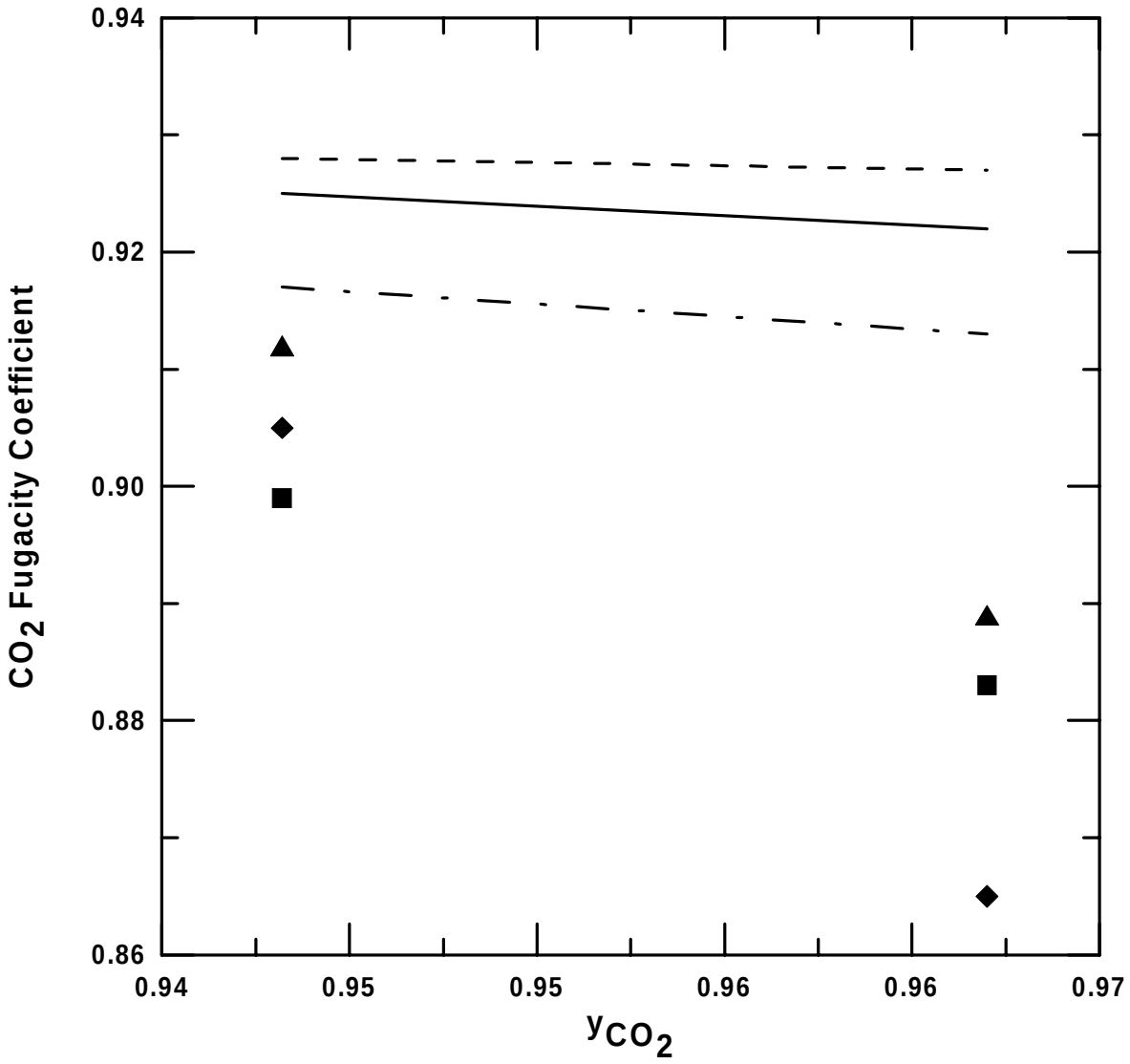
0.94
0.92
0.90
0.88
0.86
CO2 Fugacity Coefficient
0.94
0.95
0.95
0.96
0.96
0.97
yCO2

Figure 3