An apparatus for the direct measurement of fugacity in mixtures containing large and small molecules

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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, $\sigma = 0.33$ nm) molecules to permeate, while blocking the flow of the larger isobutane ($\sigma = 0.5$ nm) molecules. Experiments were run at two temperatures and four 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 and with the Peng–Robinson equation of state. © 1998 Elsevier Science B.V. All rights reserved.

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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 dense silica glass membrane for the separation of helium in heavy gas mixtures. Due to the extremely low permeability

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of dense silica glass, this approach was limited to mixtures containing helium. Additional studies have also been reported measuring gas mixture component fugacities by Bruno [3], Cooper [4], and Ghosal [5] in hydrogen mixtures using a dense palladium/silver alloy membrane. Palladium and its alloys are semipermeable for hydrogen only. The transport mechanism consists of several rate processes in series, dissociative adsorption of hydrogen followed by dissolution and diffusion of hydrogen atoms through the metal matrix [6]. Consequently, use of a Pd alloy membrane in the measurement of gas mixture fugacity is limited to mixtures containing hydrogen.

In the present work, an apparatus similar to that used in previous research on separation applications 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 microporous silica fibers used were prepared by PPG Industries and were manufactured by melt extrusion, followed by acid leaching as described by Hammel [7] and Hammel et al. [8]. 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 [9]. 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 [10]. 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 current work differs from previous studies using semi-permeable membranes to measure the fugacity of a component in mixtures because of the transport mechanism responsible for the selectivity. In the microporous silica fibers and in other microporous membranes such as molecular sieve carbon [11] and zeolites [12–14], separations are achieved by size discrimination. Since the molecular sieving mechanism of the silica hollow fiber membranes allows the separation primarily based on molecular size, the approach has many possible applications in the measurement of fugacity of mixtures of small and large molecules and is not limited to mixtures containing helium or hydrogen.

2. Experimental

The apparatus used in the present work is shown in Fig. 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 Section 1, 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-in. 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 [16]. Fig. 2 shows a detailed schematic of the membrane assembly.
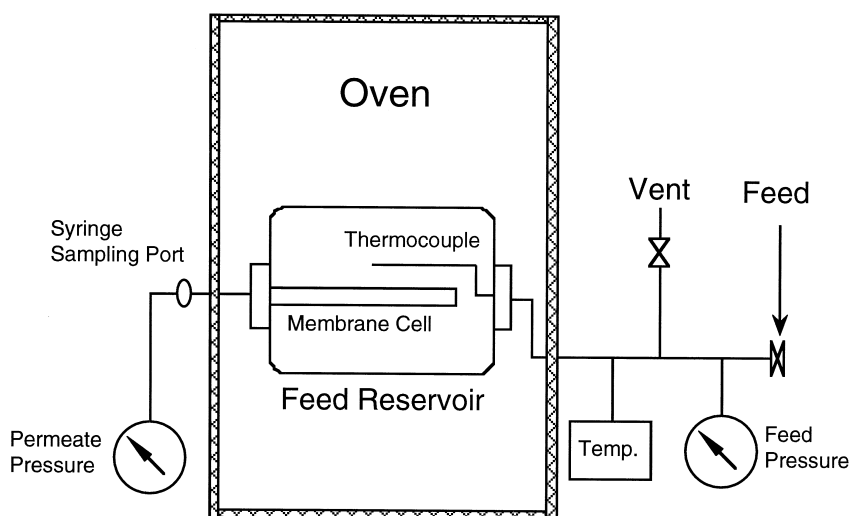
Fig. 1. Apparatus schematic.

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 $\pm 0.5°C$. 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 transducers were found to be accurate within ± 30 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 and a 1.8 m HayeSep-D packed column. To allow for syringe sampling in the apparatus, a low volume tee fitting with a septum was
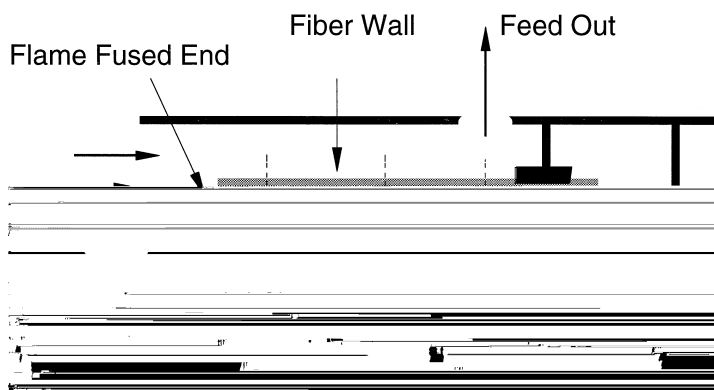

Fig. 2. Schematic of a single microporous fiber module.

installed in the permeate stream. Gas chromatograph measurements, with TCD detection limits of ~ 0.01 mol%, 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 2–7 days. Equilibration times were reduced in later experiments by pressurizing the permeate side of the system with pure CO_2 to approximately 90% of the CO_2 partial pressure in the feed mixture.

The carbon dioxide fugacity in the mixture is determined by the equivalence of the pure permeate fugacity and that of CO_2 in the mixture. The permeate fugacity is calculated using the measured pressure and temperature and the virial equation of state

$$\ln \varphi_i = \ln(f_i/P_p) = \frac{B_i P_p}{RT} + \frac{C_i - B_i^2}{2}\left(\frac{P_p}{RT}\right)^2 \tag{1}$$

where the subscripts i and p denote carbon dioxide and the permeate side of the membrane, respectively. The second and third virial coefficients used were from data reported by Duschek et al. [15]. 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:

$$\hat{f} = f_i = \varphi_i P_p \tag{2}$$

and

$$\hat{\varphi}_i = \frac{\varphi_i P_p}{y_i P_f} \tag{3}$$

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

3. Results and discussion

Component fugacity coefficients for carbon dioxide mixed with isobutane were determined at temperatures of 323 and 348 K. Table 1 shows fugacity coefficient results for four different mole

Table 1
Carbon dioxide component fugacity coefficient in carbon dioxide + isobutane mixtures

T (K)	Y_{CO_2}	P_{feed} (psia)	P_{perm} (psia)	ϕ_{CO_2}	$\hat{\phi}_{CO_2}^{EXP}$	$\hat{\phi}_{CO_2}^{PR}$	$\hat{\phi}_{CO_2}^{ECST}$
323	0.9690	264.3	242.0	0.9360	0.8843[a]	0.9242	0.9320
	0.9581	263.3	250.9	0.9336	0.9285	0.9246	0.9324
	0.9073	150.2	136.2	0.9637	0.9638	0.9572	0.9624
	0.8595	163.0	140.5	0.9626	0.9652	0.9547	0.9597
348	0.9690	288.5	271.0	0.9424	0.9136	0.9350	0.9424
	0.9581	288.2	261.8	0.9443	0.8953[a]	0.9352	0.9426
	0.9073	162.7	147.7	0.9684	0.9690	0.9636	0.9683
	0.8595	177.1	152.0	0.9674	0.9661	0.9614	0.9666

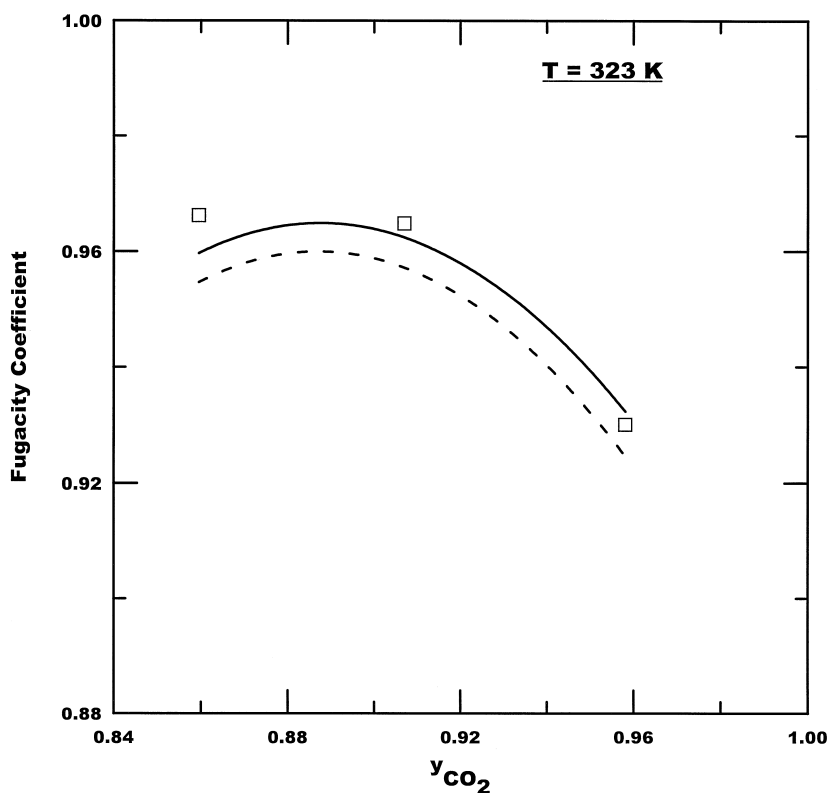[a]Experiment was terminated prior to reaching equilibrium.

Fig. 3. Comparison of experimental and predicted fugacity coefficients of carbon dioxide in mixtures of carbon dioxide and isobutane at 323 K. Experimental; ——— ECST predictions; --- Peng–Robinson predictions.

fractions at varying pressures. The uncertainties in the data shown in Table 1 are estimated to be $\pm 4\%$ based on an error propagation analysis that included estimates of the error in mole fraction, temperature, pressure, and the virial coefficients.

An extended corresponding states model, DDMIX [17] and Peng–Robinson equation of state [18], were used to predict fugacity coefficients for carbon dioxide in the mixture. In the extended corresponding states model the fugacity coefficient of a component k in solution is calculated from the expression

$$\ln \hat{\varphi}_k = \ln \varphi_0 + z_0^r H_{nk} + u_0^r F_{nk} \tag{4}$$

where the H_{nk} and F_{nk} are derivatives of the mixing rules (van der Waals one-fluid in this case) and z_0^r and u_0^r are the dimensionless residual compressibility factor and internal energy of the corresponding states reference fluid. The subscript 0 denotes a reference fluid property. The derivatives are given by

$$F_{nk} = \frac{n}{f_x} \left(\frac{\partial f_x}{\partial n_k} \right)_{T,V,n_{j \neq k}} \quad \text{and} \quad H_{nk} = \frac{n}{h_x} \left(\frac{\partial h_x}{\partial n_k} \right)_{T,V,n_{j \neq k}} \tag{5}$$

and the mixing rules for the scale factors f_x and h_x are given by

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \text{ and } h_x = \sum_i \sum_j x_i x_j h_{ij} \tag{6}$$

where $f_{ij} = \sqrt{f_i f_j}(1 - k_{ij})$ and $h_{ij} = (h_i^{1/3} + h_j^{1/3})^3/8$. The equivalent reference fluid (propane) state point is determined by the relations $p_0 = p_x h_x / f_x$ and $T_0 = T_x / f_x$ where the subscript x denotes the mixture. Details of the application of this model can be found in the literature [19].

Fig. 3 shows the experimental fugacity coefficient of carbon dioxide at 323 K and four carbon dioxide mole fractions. Also shown as lines in this figure are the model predictions. Similar results are shown in Fig. 4 at 348 K. In general, the agreement between the calculated and experimental results is very good. Two data points given in Table 1 (marked with a footnote) did not, in our opinion, reach equilibrium and are not shown in Figs. 3 and 4. The DDMIX predictions with $k_{ij} = 0.14$ and $l_{ij} = -0.028$ are typically closer to the experimental results than the predictions obtained with the Peng–Robinson equation of state with $k_{ij} = 0.11$. The interaction parameters were not adjusted to the experimental results so it is reasonable to assume that the agreement of both models with the data could be somewhat improved. In both cases, the calculated results agree with the experimental measurements to within the estimated uncertainty in the measurements, typically $\pm 2\%$.
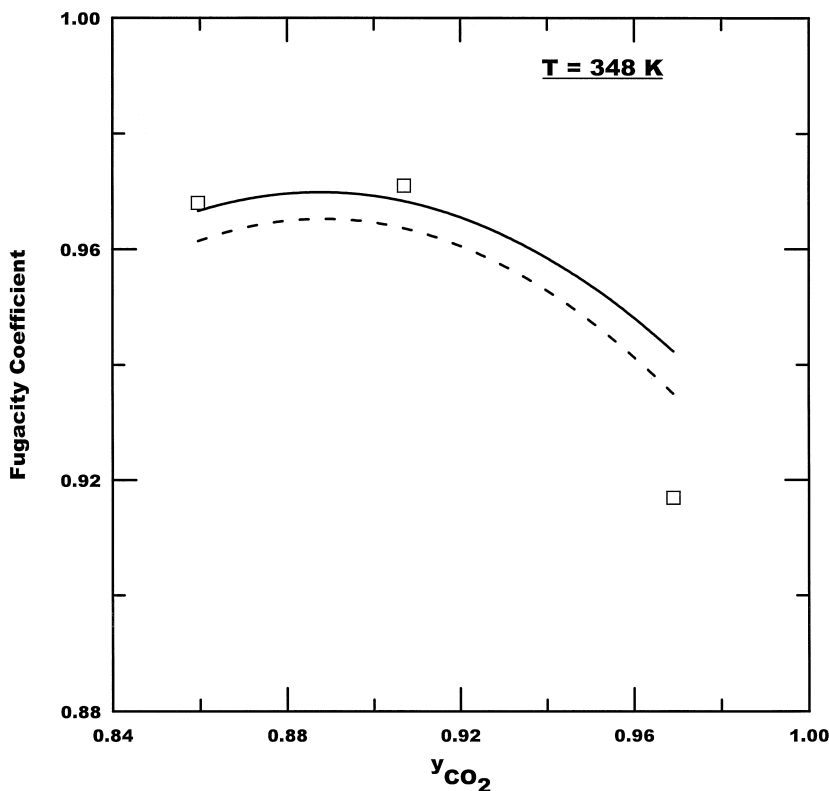

Fig. 4. Comparison of experimental and predicted fugacity coefficients of carbon dioxide in mixtures of carbon dioxide and isobutane at 348 K. Experimental; ——— ECST predictions; --- Peng–Robinson predictions.

4. Summary and conclusions

The physical equilibrium technique was used to measure component fugacity coefficients for three isotherms, for four different carbon dioxide rich mixtures. Experimental fugacity coefficients were found using the virial equation of state and were compared to values obtained from an extended corresponding states model and the Peng–Robinson EOS. Experimental values were found to be systematically lower than predicted values. The models track the pressure and composition dependence of the fugacity coefficients quite well but we have not yet collected sufficient data to make any conclusions on temperature dependence trends. Further experiments are being performed to explore wider ranges of temperature and composition. 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.

Acknowledgements

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