# Detailed Investigation of the Binary Adsorption of Carbon Dioxide and Methane in Zeolite Na-ZSM-5 Studied Using in Situ ATR-FTIR Spectroscopy

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Ⓢ Supporting Information

ABSTRACT: The separation of carbon dioxide from methane is an important process when purifying biogas and natural gas. Zeolite membranes and adsorbents are among the technologies suggested for efficient separation of carbon dioxide from these gases. In the present work, the adsorption of carbon dioxide and methane from binary mixtures in a low alumina Na-ZSM-5 zeolite film at various gas compositions and temperatures was studied using in situ ATR-FTIR (attenuated total reflection Fourier transform infrared) spectroscopy. Adsorbed concentrations were successfully extracted from infrared spectra. The experimental values of the adsorbed phase mole fraction of carbon dioxide and methane were compared to values predicted using the ideal adsorbed solution theory (IAST). The values predicted with the IAST agreed very well with values determined experimentally. The CO_2/CH_4 adsorption selectivity was determined, and at 35 °C a selectivity of 15.4 was obtained for an equimolar gas mixture. At the highest (0.9) and lowest (0.03) investigated mole fractions of carbon dioxide in the gas phase, the selectivity was higher compared to the other investigated mole fractions. At 35 °C the highest observed selectivity values were 31.1 and 20.4 for the highest and the lowest adsorbed mole fraction, respectively. At compositions closest to those found in biogas and natural gas, there was a decrease in the selectivity at higher temperatures, indicating that separation of carbon dioxide from methane in biogas and natural gas may be more efficient at low temperatures.
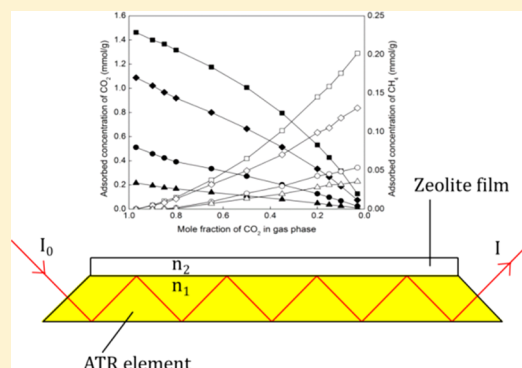
■ INTRODUCTION

In recent years there has been much focus toward the development of technologies for separation of carbon dioxide from methane. Amine absorption is the most commonly used technology today for the separation of carbon dioxide and methane, but the procedure is both expensive and complicated;[1] therefore more efficient separation processes are sought. Adsorption and membrane based technologies using zeolite adsorbents/membranes have been identified as attractive options.[2,3] For zeolite membranes, the membrane selectivity is usually dependent on both the adsorption selectivity and the diffusion selectivity; therefore, knowing the adsorption properties of the zeolite is of utmost importance also for membrane applications.

A large variety of zeolite and zeolite-like frameworks have been evaluated for carbon dioxide/methane separation both as membranes and as adsorbents.[4−13] The MFI framework, with the ZSM-5 and silicalite-1 zeolites, has been frequently studied both in adsorbent and, perhaps even more frequently, in membrane applications. Our group has previously reported successful separation of carbon dioxide from methane using MFI membranes.[14] The membrane was evaluated at different process conditions, and it was concluded that the MFI membranes were promising candidates for separation of carbon dioxide from, for example, biogas and natural gas. The

separation of carbon dioxide and methane from binary mixtures has also been investigated using membranes with different types of MFI films, viz., silicalite-1, Na-ZSM-5, and B-ZSM-5.[15] In that study it was found that the B-ZSM-5 zeolite showed the highest separation performance, and the authors attributed this to a stronger adsorption affinity for carbon dioxide toward the B-ZSM-5 compared to silicalite-1 and Na-ZSM-5. The behavior of binary mixtures of carbon dioxide and methane in MFI zeolite membranes has also been investigated using molecular dynamic simulations and Grand Canonical Monte Carlo simulations.[16−18] According to the simulations, the selectivity toward carbon dioxide increases with increasing pressure when adsorbed from an equimolar gas mixture. The ideal adsorbed solution theory (IAST) was used to predict the adsorbed loadings for binary mixtures, and it was reported that the IAST gave an accurate estimation of the loadings.

The separation of carbon dioxide from methane by zeolite adsorbents has been studied previously, primarily on other frameworks than MFI; however, a few experimental reports on the binary adsorption of carbon dioxide and methane in MFI exist.[19−21] For example, the binary adsorption in silicalite-1 was

studied experimentally using different concentration pulse methods.[19] It was reported that silicalite-1 adsorbed more carbon dioxide compared to methane according to the pure gas isotherm data and the pure gas adsorption capacity was decreasing with increasing temperature. The results were compared to predicted isotherms by a number of models such as extended Langmuir, extended dual-site Langmuir, extended Sips, ideal adsorbed solution theory, Flory–Huggins vacancy solution theory, and the statistical model. All six prediction models gave similar results and showed a big difference between the experimental and the predicted values. It was determined that none of the models could be used confidently. The separation factor was determined for various compositions of the gas phase at all temperatures showing that the experimentally determined separation factors were much higher compared to the values predicted from the models mentioned above. The binary adsorption of carbon dioxide and methane has also been studied in H-ZSM-5 adsorbents of various Si/Al ratios using concentration pulse chromatography, and the experimental values were compared to values predicted by models such as extended Langmuir, extended Nitta, ideal adsorbed solution theory, and the Flory–Huggins vacancy solution theory.[20,21] Again, none of the models predicted the values reasonably well, but the values predicted by the IAST were closest to the experimental values.

In a recent work we successfully measured single component adsorption isotherms at different temperatures and pressures for carbon dioxide, water, and methane in a low alumina Na-ZSM-5 zeolite film using in situ ATR-FTIR spectroscopy.[22] A one point (one gas composition, one temperature) adsorption experiment was also performed for an equimolar mixture of carbon dioxide and methane at 35 °C. The amount of adsorbed carbon dioxide and methane was extracted from the experimental data, and the values were compared to values predicted by the IAST. These preliminary results indicated that the IAST could correctly predict the amount of adsorbed carbon dioxide and methane in an equimolar mixture.

In the present work, we study the binary adsorption of carbon dioxide and methane in the same zeolite film as in our recent work in much greater detail, aiming at understanding the adsorption behavior of this binary mixture. The experimental data obtained were compared to values predicted by the IAST model to further investigate if the IAST is a reliable model capable of accurately predicting the values for various gas compositions and not only for an equilmolar mixture. This work builds on our previously reported adsorption data with a view to better understand the binary adsorption properties of MFI zeolite membranes in removal of carbon dioxide from biogas and natural gas.

■ EXPERIMENTAL SECTION

Film Preparation. The zeolite film used in the present work is the same as the zeolite film used in our previous work, and the preparation and characterization of the film has been reported in detail elsewhere.[22,23] Therefore, only a brief summary will be given here. The zeolite film (ZSM-5, Si/Al = 130, Na/Al = 1) was synthesized on an ATR element (trapezoidal ZnS crystal, 50 × 20 × 2 mm, 45° cut edges, Spectral systems). The ATR element was thoroughly cleaned before being rendered positively charged by immersing it in a solution containing a cationic polymer. Thereafter, the ATR element was immersed in a seed suspension containing 50 nm silicalite-1 seed crystals creating a monolayer of seed crystals on

the surface. Subsequently, the seeded ATR element was immersed in a synthesis solution for hydrothermal synthesis at 100 °C for 48 h under reflux. After cooling down, the zeolite film was rinsed with 0.1 M ammonia solution and distilled water. The zeolite film was dried overnight and thereafter calcined at 500 °C to remove the template molecules.

The calcined film was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm the zeolite phase and to determine the zeolite film thickness and morphology.

Adsorption Experiments. For the adsorption experiments, the zeolite coated ATR element was mounted in a heatable flow cell connected to a gas delivery system. The zeolite film was dried at 300 °C for 4 h under a flow of helium (AGA, 99.999%) prior to measurements, and a background spectrum of the dried film was recorded under a flow of helium. For each composition of the gas mixture (carbon dioxide, AGA, 99.995%, and methane, AGA, 99.9995%), spectra were recorded continuously until equilibrium was reached. All adsorption experiments were carried out at atmospheric pressure. Details of the equipment used have been given elsewhere.[22,24] Infrared spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector by averaging 256 scans at a resolution of 4 cm^{-1}.

The ATR Technique. The ATR technique[25] is based on internal reflection where the infrared beam is totally reflected in a waveguide (ATR element), see Figure 1. An electromagnetic
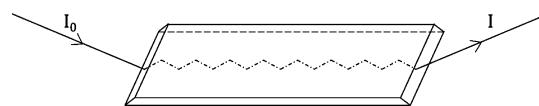
Figure 1. Schematic figure illustrating the ATR technique where the infrared beam is totally reflected inside a trapezoidal ATR element.

field originating from the infrared beam may interact with the sample in the vicinity of the waveguide, where some of the energy may be absorbed by the sample. The amplitude of the electromagnetic field will attenuate exponentially with distance from the element surface, making the ATR technique very useful for studying surfaces and thin films. The penetration depth of the electromagnetic field, d_p, is a rough measure of the distance outside the waveguide that is probed (typically a couple of hundreds of nm to a few μm) and can be determined by[26]

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}{}^2)^{1/2}} \quad (1)$$

where λ_1 is the wavelength of the infrared radiation inside the ATR crystal, θ is the angle of incidence, and n_{21} is the ratio of the refractive indices of the zeolite film and the ATR element. The refractive index of ZnS is 2.25, whereas for the zeolite film the refractive index varies with loading.[27] To account for the change in refractive index with loading, a linear model[28] was assumed; however, as the refractive indices[29] of carbon dioxide and methane are quite similar to that of the zeolite film, the net effect was small under the conditions studied in the present work.

Theory. To calculate the adsorbed concentrations from infrared spectra, the Lambert–Beers law used for transmission experiments is not directly applicable to the ATR technique due

to the exponential decay of the electric field. However, Tompkins[30] and Mirabella[25] have derived expressions for determining adsorbed concentrations from ATR experiments. The procedure and details for calculating the adsorbed concentrations in the zeolite films have been described in detail in our previous work[22] and are provided in the Supporting Information.

The IAST[31] was used to predict the adsorbed concentrations of carbon dioxide and methane in binary mixtures, and the values were compared to the experimental data. Details of the calculations used for the IAST have been described in our previous work[22] and are also included in the Supporting Information.

The CO_2/CH_4 adsorption selectivity[32] was determined as

$$\alpha_{CO_2/CH_4} = \frac{X_{CO_2}/X_{CH_4}}{Y_{CO_2}/Y_{CH_4}} \quad (2)$$

where X is the mole fraction in the adsorbed phase and Y is the mole fraction of the gas phase at equilibrium.

RESULTS AND DISCUSSION

Film Characterization. The zeolite film was characterized in detail in our previous work.[22] In brief, XRD data confirmed that the films consisted of randomly oriented zeolite ZSM-5 crystals. The SEM analysis showed that the films consisted of well-intergrown crystals forming a dense and homogeneous film without any sediment and with a film thickness of about 550 nm. Both the SEM images and the XRD patterns were very similar to those in previous reports on zeolite coated ATR elements.[23,28] The Si/Al ratio was determined to 130 by ICP-MS, and this particular Si/Al ratio was chosen as it is representative of the composition of the low-alumina ZSM-5 membranes prepared in our group.[33]

Adsorption Experiments. An infrared spectrum of carbon dioxide and methane adsorbed simultaneously in Na-ZSM-5 at 35 °C and a total pressure of 1 atm is shown in Figure 2. The partial pressures of carbon dioxide and methane in the gas phase were 3 and 98.3 kPa, respectively. The characteristic band of adsorbed carbon dioxide appears at 2338 cm^{-1} and is assigned to the asymmetric stretching vibration of physisorbed
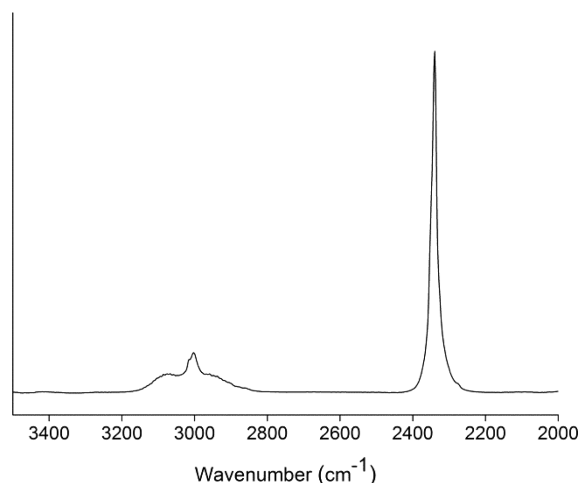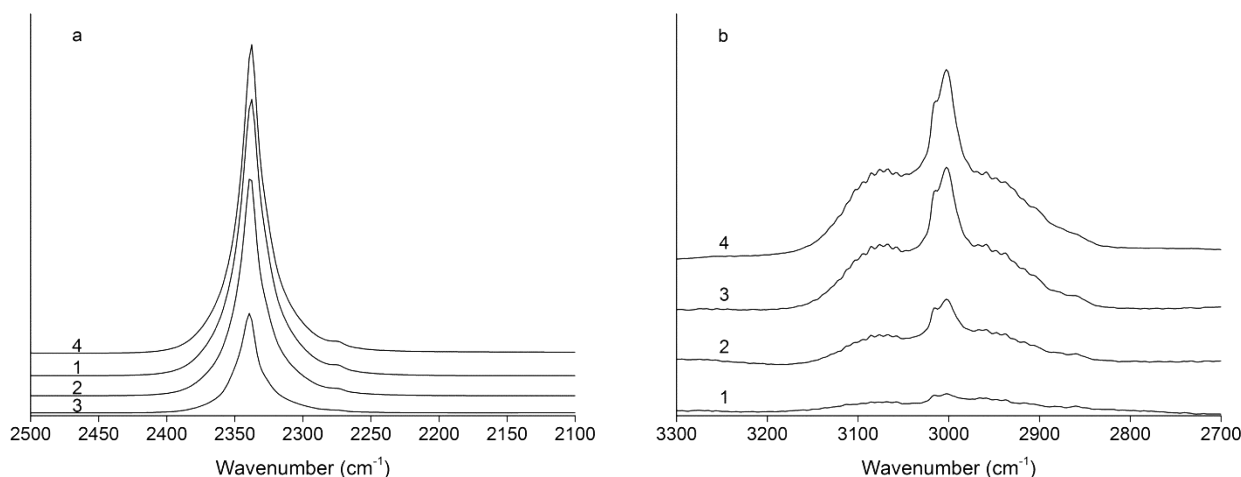

Figure 2. Infrared spectrum of carbon dioxide and methane adsorbed in Na-ZSM-5 film at 35 °C and a total pressure of 1 atm for a binary mixture of carbon dioxide and methane with a mole fraction of carbon dioxide in the gas phase of 0.03.

carbon dioxide.[34] The characteristic band of methane appears in the 3000−3030 cm^{-1} region with two peaks at 3015 cm^{-1} and 3003 cm^{-1} and is assigned to the C−H stretching vibrations.[35,36] The absorption bands assigned to carbon dioxide and methane are well separated in the spectrum and may therefore be used to monitor the change in adsorbed loading with changing partial pressure of the gases. Infrared spectra recorded at higher temperatures (50, 85, and 120 °C) were very similar in appearance but with less intensity of the bands, as expected due to the reduced adsorption at higher temperatures. In our previous work we performed experiments with an uncoated ATR element to assess the contribution from the gas phase on the measurements.[22] It was concluded that, at the conditions used in that work, as well as in the present work, the signal originating from the gas phase was negligible compared to the strong signal emanating from the adsorbed phase.

Figures 3a and 3b show the infrared spectra of adsorbed carbon dioxide and methane at various binary gas phase compositions as well as reference spectra recorded from single component adsorption for each gas. First of all, it is evident that the intensity of the absorption bands increases when the partial pressure of the gas increases, indicating an increased adsorption at higher partial pressures in the gas phase, as may be expected. Moreover, when comparing the bands in the spectra recorded with one adsorbed component to those recorded for adsorption from the binary mixture, the band positions and shapes are the same, indicating that there is no strong interaction between carbon dioxide and methane when adsorbed from the binary mixture.

The adsorbed concentrations were extracted from the IR spectra using the calculations presented in the Supporting Information and were plotted as a function of the mole fraction of carbon dioxide in the gas phase, see Figure 4. The amount adsorbed increases with increasing mole fraction in the gas phase and with decreasing temperature, as expected. Moreover, carbon dioxide is preferentially adsorbed compared to methane with adsorbed concentrations of carbon dioxide being almost 1 order of magnitude larger than that for methane at the same mole fraction in the gas phase. The preferential adsorption of carbon dioxide over methane is consistent with the larger Langmuir adsorption coefficients and heat of adsorption observed for carbon dioxide than for methane[16,19,21,22] (see Table 1 in the Supporting Information).

Comparison between Measured Adsorbed Concentrations and Those Predicted by the Ideal Adsorbed Solution Theory (IAST). The IAST was used to predict the amount adsorbed from binary mixtures using the Langmuir parameters (q_{sat} and b) determined in our previous work, see Table 1 in the Supporting Information. Figure 5 shows the adsorbed phase mole fractions of carbon dioxide and methane predicted by the IAST (solid lines) compared to the experimental data (markers) obtained in this work. As can be seen, the values predicted by the IAST agree very well with the experimental values. This is in accordance with findings previously reported by Krishna and van Baten,[16] but in contrast to the findings reported by Tezel and co-workers.[19−21] It can be seen that the curves for the three lowest temperatures are quite similar but the trend is that the adsorbed mole fraction of carbon dioxide is decreasing with increasing temperature. This trend is even clearer when including also the highest temperature, which shows a significantly lower adsorbed mole fraction of carbon dioxide compared to the lower temperatures.
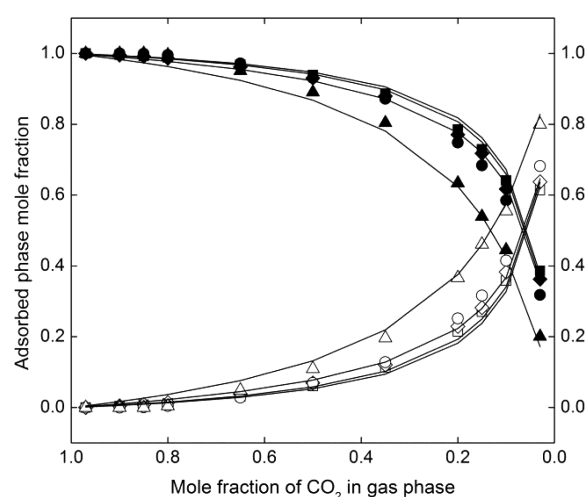
Figure 3. Infrared spectra of carbon dioxide (a) and methane (b) adsorbed in Na-ZSM-5 film at 35 °C for binary mixtures containing various mole fractions of carbon dioxide in the gas phase: 0.85 (1), 0.50 (2), 0.15 (3), and single gas[22] (4). The total pressure was 101.3 kPa.
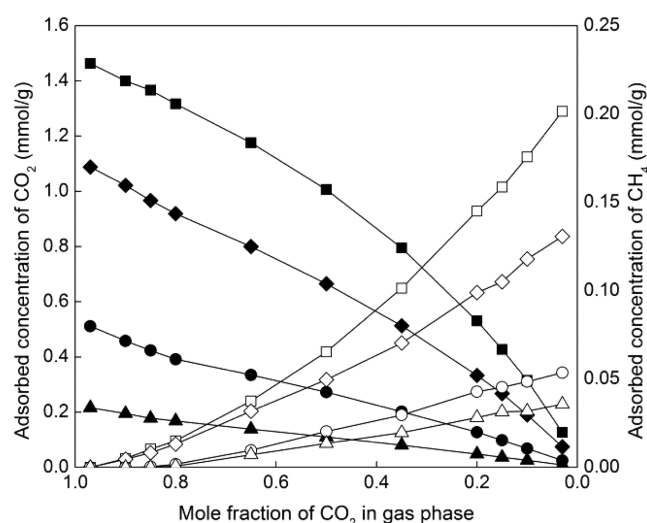
Figure 4. Adsorbed concentrations of carbon dioxide and methane as a function of the mole fraction of carbon dioxide in the gas phase at 35 °C (□), 50 °C (◇), 85 °C (○), and 120 °C (△). The filled symbols represent carbon dioxide, and the open symbols represent methane. Lines are only guides for the eyes.

Figure 5. Experimentally determined adsorbed phase mole fraction as a function of the gas phase composition at 35 °C (□), 50 °C (◇), 85 °C (○), and 120 °C (△) compared to values predicted by the IAST. The filled symbols represent carbon dioxide, the open symbols represent methane, and the lines represent values predicted using the IAST. The total pressure was 101.3 kPa.

Since biogas and natural gas mainly consist of methane, the region with lower mole fraction of carbon dioxide is of special interest. For example, at a mole fraction of 0.2 of carbon dioxide in the gas phase, the corresponding mole fraction of carbon dioxide in the adsorbed phase is approximately 0.8 at 35 °C, indicating that, at a CO_2/CH_4 ratio in the gas phase typical for natural gas, the zeolite is selective toward carbon dioxide. At 120 °C and the same composition in the gas phase (a mole fraction of carbon dioxide of 0.2), the composition of the adsorbed phase is about 65% of carbon dioxide and 35% of methane, showing that the zeolite is less selective toward carbon dioxide at higher temperatures as may also be expected from the higher adsorption enthalpies for carbon dioxide than for methane.

As shown in the present work, the IAST provides a good estimation of the total amount of adsorbed gas in the zeolite film and can thus be satisfactorily used for predicting binary adsorption of carbon dioxide and methane in this low aluminum MFI zeolite.

Selectivity. The CO_2/CH_4 adsorption selectivity as a function of the mole fraction of carbon dioxide in the gas phase is presented in Figure 6a. At 35 °C the CO_2/CH_4 adsorption selectivity increases at the highest (0.9) and lowest (0.03) mole fractions of carbon dioxide in the gas phase with the highest selectivity values of 31.1 and 20.4, respectively. The same trend, with higher selectivities at the highest and lowest gas phase concentrations, is also observed at 50 °C. At 85 and 120 °C, however, the selectivity could not be determined for all mole fractions as the adsorption of methane was sometimes too low to be determined from the spectra, in particular at the higher temperatures and low methane content in the gas phase. Nevertheless, it can still be seen that the CO_2/CH_4 adsorption selectivity increases at the highest (0.65) and the lowest (0.03) mole fractions of carbon dioxide in the gas phase also at 85 and 120 °C. The CO_2/CH_4 adsorption selectivity predicted using the IAST as a function of the mole fraction of carbon dioxide in the gas phase is also presented in Figure 6a. As can be seen, the experimental data and the values predicted using the IAST lie in
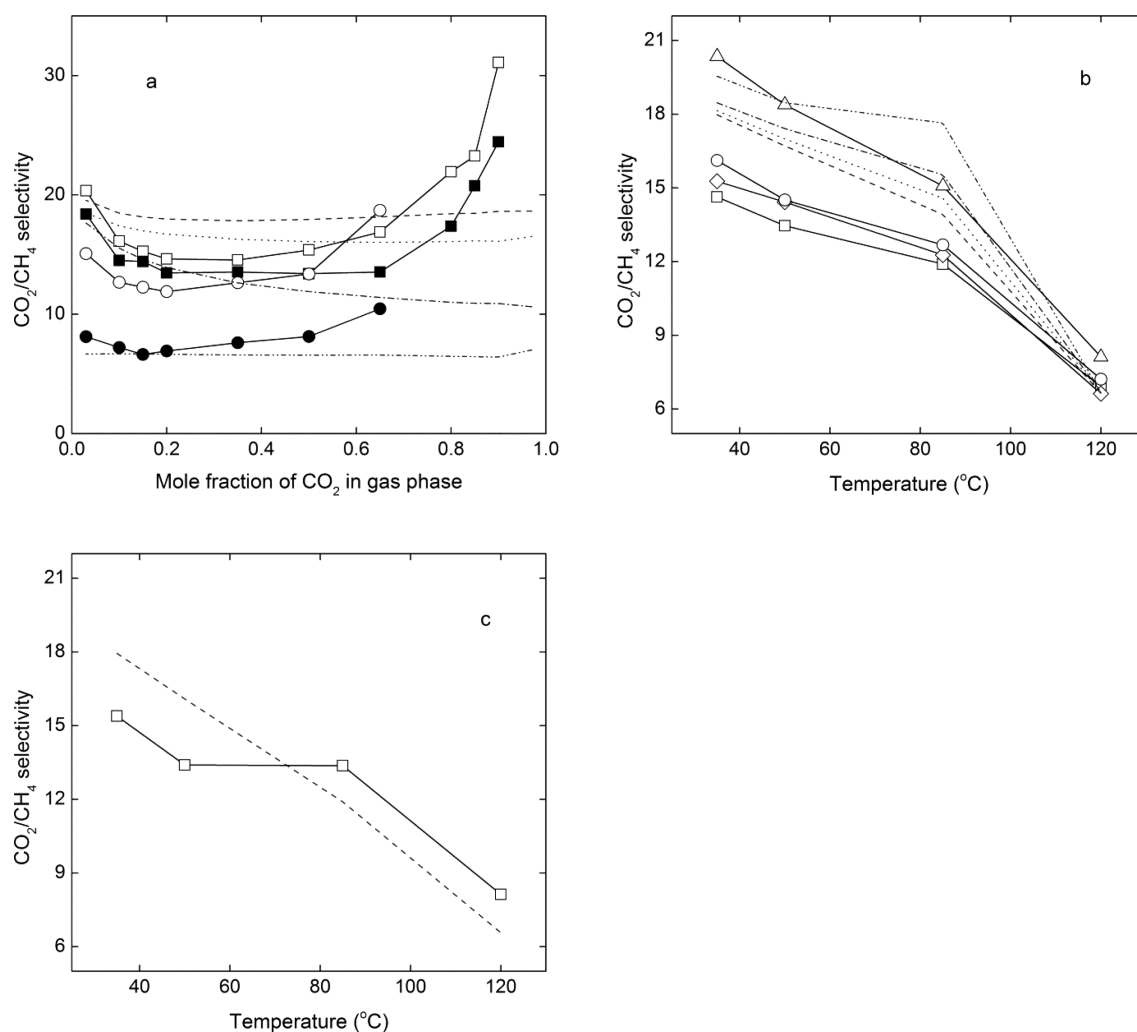
Figure 6. (a) Experimenlly determined CO_2/CH_4 selectivities at 35 °C (□), 50 °C (■), 85 °C (○), and 120 °C (●) compared to selectivity values predicted by the IAST at 35 °C (- - -), 50 °C (···), 85 °C (—●—), and 120 °C (—●●—). (b) Experimentally determined CO_2/CH_4 selectivity as a function of temperature for various mole fractions of carbon dioxide in the gas phase indicated in the figure, 0.20 (□), 0.15 (◇), 0.10 (○), and 0.03 (△), along with selectivity values predicted by the IAST, 0.20 (- - -), 0.15 (···), 0.10 (—●—), and 0.03 (—●●—). (c) Experimentally determined CO_2/CH_4 selectivity (□) as a function of temperature in an equimolar mixture of carbon dioxide and methane compared to selectivity values predicted by the IAST (- - -). The total pressure was always 101.3 kPa, and the solid lines are only guides for the eyes.

the same range but the values do not fit very well. Both the experimental data and the predicted values show an increase in the CO_2/CH_4 adsorption selectivity at lower mole fraction of carbon dioxide in the gas phase. At low content of carbon dioxide in the gas phase, the carbon dioxide will primarily be adsorbed on the high affinity sites (site 2 in Table 1 in the Supporting Information). There are only a few of these sites as evidenced by the relatively low saturation loading of 0.04 mmol/g compared to a total saturation capacity of 2.82 mmol/g. These high affinity sites likely correspond to polar sites associated with the sodium cations or silanol groups. As carbon dioxide is quadropolar and also has a higher polarizability than methane,[2,3] the adsorption selectivity should be higher for these sites than for sites not involving sodium cations or polar silanol groups. Indeed, other groups[2,15] have previously reported increasing adsorption selectivities of carbon dioxide over methane with increasing aluminum content and thus increasing polarity. The predicted values are a bit higher compared to the experimental data at 35, 50, and 85 °C, indicating that the IAST predicts a higher amount of adsorbed carbon dioxide at those temperatures than what is actually adsorbed in the zeolite film.

According to the experimental data, the CO_2/CH_4 adsorption selectivity increases again also at higher mole fraction of carbon dioxide in the gas phase. This is probably the result of the low amount of adsorbed methane in the zeolite film which seemingly yields higher selectivities. The predicted CO_2/CH_4 adsorption selectivity values only show a slight increase at higher mole fraction of carbon dioxide in the gas phase (if any increase at all), indicating that the IAST cannot fully predict the CO_2/CH_4 adsorption selectivity when the amount of adsorbed methane in the zeolite film becomes too low.

Since methane is the main component in biogas and natural gas, with a content of 70–90%, the CO_2/CH_4 adsorption selectivity in this region is especially interesting, and we will therefore investigate this region more closely. Figure 6b shows the selectivity as a function of temperature for the four gas compositions with the highest methane content. All gas compositions show the same trend with the highest selectivity at the lowest temperature, reflecting the greater heat of adsorption (in absolute terms) of carbon dioxide compared to methane (see Table 1 in the Supporting Information), as discussed before. The CO_2/CH_4 adsorption selectivity

predicted using the IAST as a function of temperature is also included in Figure 6b. In general, the predicted values are slightly higher compared to the experimental data, which, again, indicate that the IAST predicts a higher amount of adsorbed carbon dioxide than what is actually adsorbed in the zeolite film. The higher selectivities at low temperatures indicate that the separation of carbon dioxide from methane in biogas and natural gas may be more efficient at lower temperatures.

Selectivities from equimolar gas mixtures are commonly reported in the literature, and therefore we highlight this data as well. Figure 6c shows the CO_2/CH_4 adsorption selectivity when adsorbed from an equimolar gas mixture at different temperatures. Again, the highest selectivity of 15.4 was obtained at the lowest investigated temperature, and, in accordance with the results for the gas mixtures with low carbon dioxide content, the CO_2/CH_4 adsorption selectivity decreases with increasing temperature. The CO_2/CH_4 adsorption selectivity predicted using the IAST is also presented in Figure 6c, showing the same trend as the experimental data: decreasing with increasing temperature. The adsorption of carbon dioxide and methane in silicalite-1 has previously been studied by Li and Tezel.[19] When adsorbed from an equimolar mixture at 40 °C, the separation factor was reported to be 7. This value is a bit lower than the selectivity reported in the present work, which could be due at least partly to the temperature difference. The lower selectivity value could also be affected by the difference in Si/Al ratio as carbon dioxide in general adsorbs more strongly in the polar zeolites than in the hydrophobic pure silica analogue.[2] Moreover, different amounts of intracrystalline defects in the zeolite used in the work reported by Li and Tezel and in our work may also have affected the result. Intracrystalline defects create polar silanol groups which present different adsorption sites than the pore walls of zeolites without any defects. Krishna et al.[16] studied the separation of carbon dioxide from methane in a variety of zeolites using grand canonical Monte Carlo and molecular dynamics simulation techniques. It was reported that the CO_2/CH_4 sorption selectivity in MFI zeolite increased with increasing total loading: from 2 to 20 when the total loading increased from 0 to 6 mol/kg. A selectivity of 2.2 for silicalite-1 and 13 for Na-ZSM-5 with Si/Al = 23 at 27 °C and a pressure of 0.1 MPa has been reported by Krishna and van Baten.[2]

Compared to the literature, the relatively high selectivity values obtained in this study indicate that the separation of carbon dioxide from methane in biogas and natural gas may be efficient using membranes prepared from MFI zeolite. The presence of other components frequently encountered in biogas and natural gas such as water, hydrogen sulfide, and heavier hydrocarbons and how they affect the separation are also of great interest. The effect of some of these components on the adsorption of carbon dioxide and methane in MFI will be studied in forthcoming work.

CONCLUSIONS

The binary adsorption of carbon dioxide and methane in a low alumina Na-ZSM-5 zeolite film at various gas compositions and temperatures was studied using in situ ATR-FTIR spectroscopy. Adsorbed concentrations were retrieved from infrared spectra, and the values obtained were compared to values predicted using the ideal adsorbed solution theory. The predicted values were in good agreement with the experimental values showing that the IAST can be used for predicting adsorbed phase concentrations for various compositions of

binary mixtures of carbon dioxide and methane in low alumina Na-ZSM-5. The CO_2/CH_4 adsorption selectivity determined showed an increase at the highest and lowest mole fractions of carbon dioxide in the gas phase at all studied temperatures. At 35 °C the highest selectivity values were 31.1 for the highest mole fraction (0.9) and 20.4 for the lowest mole fraction of carbon dioxide (0.03). The highest selectivity value observed for an equimolar mixture was 15.4 at 35 °C. The observed selectivity generally decreased with increasing temperature, indicating a more efficient separation of carbon dioxide from methane at lower temperatures. The relatively high selectivity values obtained in this study indicate that the separation of carbon dioxide and methane in biogas and natural gas may be efficient at low temperatures using a membrane prepared from the studied zeolite.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Theory behind the calculation of the adsorbed concentrations from infrared spectra and the ideal adsorbed solution theory (IAST). Parameters of the dual site Langmuir model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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