Deformation of Nanoporous Materials in the Process of Binary Adsorption: Methane Displacement by Carbon Dioxide from Coal

Nicholas J. Corrente, Katarzyna Zarębska, and Alexander V. Neimark*

ABSTRACT: The phenomenon of adsorption-induced deformation of nanoporous materials has recently attracted a lot of attention in chemical, materials, and geoscience communities. Various theoretical and molecular simulation approaches have been suggested to predict the stress and strain induced by single component gas adsorption. Here, we develop a thermodynamic method based on the notion of the adsorption stress to predict the deformation effects upon multicomponent adsorption. As a practically important example, the process of the displacement of methane by carbon dioxide from microporous carbons is considered. This process is the foundation of secondary gas recovery from shales and coalbeds associated with carbon dioxide sequestration. Theoretical predictions are correlated with the original experimental data on CO2 and CH4 individual and binary adsorption on coal samples coupled with in situ strain measurements. With the model parametrized and verified against the experimental data at ambient temperature, the projections are made for the adsorption deformation at geological conditions of elevated pressure and temperature, which increase with the depth of the reservoir. The proposed approach may have multifaceted applications in modeling the behavior of hydrocarbon mixtures in nanoporous geomaterials, gas separations, and energy storage on flexible adsorbents.

1. INTRODUCTION

The problem of predicting adsorption and deformation properties of flexible nanoporous materials has recently attracted considerable attention across various scientific disciplines, from adsorption separations and gas storage in metal–organic frameworks (MOFs) and zeolites to nanoporous drug carriers and actuators to hydrocarbon recovery and carbon dioxide sequestration in shales and coal.1−7 The latter processes are critically important for the development of environmentally friendly energy technologies. Promising enhanced gas recovery techniques utilize the injection of CO2 to induce desorption of natural gas and simultaneous adsorption of CO2. This process offers higher yields of natural gas, reduced pollution by eliminating wastewater, and sequestration of CO2, a known greenhouse gas.5,6,8 Geosorbents such as coals and shales are composed of pores that can deform significantly upon gas adsorption and desorption.9−11 For example, organic fractions of shale have been shown to swell in excess of 20% upon the adsorption of hydrocarbons.12 Nanoporous matrix swelling causes shrinkage of the free gas pore volume and fracture aperture spacings and significant reduction of the reservoir permeability.13,14

Although the effects of adsorption-induced deformation and their practical importance are well documented for geosorbents and other nanoporous solids, most theoretical and experimental efforts are limited to single component adsorption. There are various approaches for modeling multicomponent adsorption on carbons, zeolites, and MOFs that do not take into account the adsorbent deformation.15−18 The density functional theory (DFT) and Monte Carlo (MC) molecular simulation models were suggested to study adsorption-induced deformation processes on the atomistic level.19,20 Adsorption-induced transformations in MOFs have received special attention.1−3,21−25 Several theoretical approaches have been suggested to extend the macroscopic poromechanics to nanoporous adsorbents and account for the adsorption effects.26−32 It is worth noting the works33−35 aimed at modeling secondary methane recovery and CO2 sequestration on coal. The progress in theoretical modeling is hindered by a lack of systematic experimental studies of adsorbent deformation during multicomponent adsorption. Most papers report the results of either adsorption or strain measurements, but rarely both.36−39 The comprehensive experimental data sets presented in this paper represent the unique exception. The goal of this work is to present a rigorous thermodynamic approach to predict the adsorption-induced deformation of...
flexible structures upon the adsorption of binary mixtures based on the information obtained from the single component measurements. In Section 2.1, we present the general thermodynamic foundations of the proposed approach and its implementation for the case of binary adsorption governed by the Langmuir model. Section 2.2 is devoted to the experimental methods employed for the volumetric adsorption and in situ strain measurements upon adsorption of CH₄, CO₂, and their binary mixtures on a low rank coal. A comparison of the theory and experimental data collected at room temperature is presented in Section 3.1. In Section 3.2, predictions are made for the coal matrix swelling induced by the displacement of CH₄ by CO₂ at the geological conditions at elevated pressure and temperature. Conclusions are briefly summarized in Section 4.

2. METHODS

2.1. Thermodynamics of Adsorbent Deformation Induced by Multicomponent Adsorption. The deformation of a porous solid in the presence of adsorbing species is determined by the external pressure,  \( P_{ext} \), and the adsorption stress, \( \sigma_g \), exerted by the guest molecules interacting with the pore walls.\(^{19,29}\) In the simplest linear elastic approximation, the volumetric strain, \( \varepsilon \), of an isotropic solid is defined through the volumetric modulus of the solid, \( K \), as\(^{19}\)

\[
\varepsilon = V - V_0 = \left( \sigma_g - P_{ext} \right)/K
\]

(1)

where \( V \) is the sample volume at given conditions, and \( V_0 \) is the reference volume of the undeformed sample reduced per unit mass of the sample. In adsorption experiments, \( V_0 \) is the reference volume of the “dry” sample evacuated at negligibly small pressures.

At the conditions of thermodynamic equilibrium between the solid and gas mixture, the adsorption stress is rigorously defined as the negative derivative of the grand thermodynamic potential of the adsorbed phase \( \Omega_a(\{\mu_i\}, V, T) \) with respect to the sample volume \( V \)\(^{29}\)

\[
\sigma_g = -\frac{\partial \Omega_a}{\partial V}(\{\mu_i\}, T)
\]

(2)

at constant temperature \( T \) and chemical potentials of the mixture components \( \{\mu_i = \mu(\{y_i\}, p, T)\} \). The latter depend on the mixture composition (molar fractions \( \{y_i\} \)), pressure \( p \), and temperature \( T \); \( \mu_i = \mu(\{y_i\}, p, T) \). The grand thermodynamic potential of the adsorbed phase, \( \Omega_a(\{\mu_i\}, V, T) \), commonly referred to in the adsorption literature as the integral work of the adsorbed phase, \( \mu \), and adsorption energy, which depend on the sample volume \( V \) and temperature \( T \), can be calculated according to the Gibbs equation

\[
d\Omega_a(\{\mu_i\}, V, T) = -\sum N_i(\mu_i, V, T) d\mu
\]

(3)

The adsorption grand potential \( \Omega_a(\{\mu_i\}, V, T) \) can be calculated by integration of the Gibbs eq 3 along the trajectory of increasing pressure from a “vacuum” at \( p = 0 \) to the given value \( p \), keeping the mixture composition \( \{y_i\} \), sample volume, and temperature fixed

\[
\Omega_a(\{\mu_i\}, V, T) = -\int_0^p \sum N_i^{\text{theor}}(\{\mu_i\}, V, T) \frac{d\mu}{dp} dp
\]

(4)

Here, \( N_i^{\text{theor}}(\{\mu_i\}, V, T) = N_i^{\text{theor}}(\{y_i\}, p, V, T) \) is the adsorption isotherm of component \( i \) in the mixture of composition \( \{y_i\} \) at pressure \( p \). The superscript “theor” distinguishes this theoretical isotherm from the experimental isotherm \( N_i^{\exp}(\{\mu_i\}, V, T) \) that is measured on the sample of reference volume \( V_0 \), \( N_i^{\text{theor}} \) is the absolute adsorption isotherm that represents the total adsorbed amount of component \( i \), while the experimentally measured isotherm \( N_i^{\exp} \) is commonly reported as the excess isotherm.\(^{29}\)

Equations 1, 2, and 4 provide a general thermodynamic methodology for predicting the adsorption stress and strain induced by mixture adsorption based on the theoretical adsorption isotherms, which depend on the sample volume, \( V \), which varies due to the deformation. The theoretical adsorption isotherms can be determined by different means, similarly as it is done for single component systems: in particular, by using molecular level models of density functional theory\(^{29,40}\) and Monte Carlo simulations,\(^{20,41}\) or common phenomenological equations with parameters fitted against the experimental data, like Langmuir,\(^{2,21}\) Dubinin–Radushkevich,\(^{42}\) and Derjaguin–Broekhoff–de Boer,\(^{43}\) among others. Note that the sample volume, adsorption isotherms, thermodynamic potential, and other extensive characteristics can be expressed in the reduced units, as is customary in the adsorption literature, per unit mass of adsorbent. In the simulation methods, the sample volume is presented explicitly as the volume of the simulation cell, or the unit cell volume in the case of crystalline adsorbents. In the phenomenological models, the sample volume features implicitly through the physical parameters, such as adsorption capacity and adsorption energy, which depend on the sample deformation.

Let us consider the proposed general approach applied to the binary adsorption systems with the isotherms described by the conventional Langmuir model of binary adsorption

\[
N_{i/2} = \frac{N_i^{0} K_i y_i P}{1 + K_i y_i P + K y P}
\]

(5)

where \( N_i^0 \) and \( K_i \) are the maximum adsorption capacity and the Henry constant, respectively, of individual component \( i = 1, 2 \). The Langmuir model is the most simple and commonly used model for the description of adsorption of hydrocarbons and other light chemicals on microporous adsorbents, including the adsorption of CH₄ and CO₂ on coal.\(^{45,46}\) The practical advantage of the Langmuir model is that it depends on the physical parameters, \( N_i^0 \) and \( K_i \), which vary with the alteration of the sample volume affected by deformation. At the same time, it is oversimplified and has apparent limitations; it implies the ideal gas phase and ignores the pore size distribution and surface energy heterogeneity.

It is noteworthy that the Henry constants \( K_i \) depend on the energy of adsorption and decrease with temperature following the van’t Hoff equation

\[
K_i(T) \sim \exp \left( -\frac{\Delta H_i}{RT} \right)
\]

(6)

where \( \Delta H_i \) is the equilibrium enthalpy of adsorption of species \( i \).\(^{47}\) Equation 6 allows for the prediction of the temperature dependence of the adsorption and strain isotherms, as shown below.

For the Langmuir model (eq 5), the integral in eq 4 is calculated explicitly. In the case of a binary ideal gas mixture implied by the Langmuir model (eq 5), the chemical potential of the individual components is equal to \( \mu_i = RT \ln(y_i p) \), and eq 4 is given in a simple form
Figure 1. (left) Adsorption (upper) and strain (lower) isotherms for pure carbon dioxide (green), pure methane (blue), and binary mixtures (red, purple) on coal sample B322. Green points represent experimental pure CO2 data, blue points—pure CH4 data, red and purple crosses—experimental mixture data, and lines and red and purple squares—pure species and mixture predictions, respectively, from eqs 5 and 9. (right) Prediction of the variation of adsorption and strain as functions of the estimated CO2 fractions, yCO2, in the process of displacement of CH4 by CO2 at various gas pressures. Experimental data points correspond to pure CO2 (diamonds) and CH4 (circles) at yCO2 = 0, 1, and mixtures (crosses) at the CO2 fractions estimated from material balances; the left set corresponds to the final yCO2 = 0.142, and the right corresponds to yCO2 = 0.575. Predictions for the mixtures (solid lines) and pure CO2 and CH4 (dashed and dotted lines, respectively) are calculated at pressures of 0.203 MPa (red), 0.63 MPa (purple), 1.158 MPa (brown), 1.931 MPa (pink), and 2.825 MPa (gray). The strain is counted from the reference “dry” state of the adsorbent at P = 0.

\[
\sigma_i = -RT \frac{1}{p} \int_0^p [N_i(y_1, y_2, p, V, T) + N_i(y_1, y_2, p, V, T)] dp
\]

For the Langmuir model (eq 5), the grand thermodynamic potential (eq 7) reduces to the following simple relationship

\[
\sigma_i = -RT \frac{1}{p} \ln (1 + K_{y_1} + K_{y_2}) \frac{dN_{i}^0}{dV} \frac{dV}{dK_{y_1} + K_{y_2}} + \frac{RTK_{y_1} \ln (1 + K_{y_1} + K_{y_2})}{K_{y_1} + K_{y_2}} \frac{dN_{i}^0}{dV} \frac{dV}{dK_{y_1} + K_{y_2}}
\]

Here, \(\frac{dN_{i}^0}{dV}\) represents the change in the maximum adsorption capacity with the variation of the sample volume, and \(\frac{dV}{dK_{y_1} + K_{y_2}}\) is related to the respective change in the energy of adsorption according to eq 6. The adsorption stress for pure component adsorption can be found from eq 8 by setting the respective mole fraction \(y_1 = 1\).

\[
\sigma_{i,1} = RT \left[ \frac{N_{i1}^0}{1 + K_{i1/m}} \frac{dK_{i1/m}}{dV} + \ln (1 + K_{i1/m}) \frac{dN_{i1/m}^0}{dV} \right]
\]

It is noteworthy that eq 10 for single component adsorption was derived and employed earlier for modeling breathing transitions in MIL-53 MOFs.

For further analysis, it is useful to introduce the dimensionless parameters, which represent the adsorption capacity and Henry constant susceptibility factors, \(\lambda_{N_{i1/m}} = \frac{dN_{i1/m}^0}{dV} \frac{V_0}{N_{i1/m}^0(V_0)}\) and \(\lambda_{K_{i1/m}} = \frac{dK_{i1/m}}{dV} \frac{V_0}{K_{i1/m}(V_0)}\). The susceptibility factors, \(\lambda_{N_{i1/m}}\) and \(\lambda_{K_{i1/m}}\), show the percentage of the adsorption capacity and Henry constant changes induced by the volumetric strain of 1%.

Equations 5 and 9 allow for the prediction of the adsorption isotherm and stress in the process of binary adsorption at different mixture compositions, pressures, and temperatures based on the experimental data of pure component adsorption measured at one temperature. To this end, the adsorption capacities and Henry constant, \(N_{i1/m}^0\) and \(K_{i1/m}\), and their susceptibility factors, \(\lambda_{N_{i1/m}}\) and \(\lambda_{K_{i1/m}}\), are determined from the experimental pure component adsorption and strain isotherms, respectively. The adsorption isotherms are fitted by the single component Langmuir equation (eq 5 with \(y_1 = 1, 0\)) to determine \(N_{i1/m}^0\) and \(K_{i1/m}\). The pure component strain isotherms are fitted by eq 1 with the adsorption stress \(\sigma_{i,1}\) given by eq 10; the external pressure in
the gas adsorption experiment is equal to the gas pressure, $P_{ext} = P$.

2.2. In Situ Measurements of Coal Deformation during CO$_2$ and CH$_4$ Adsorption. In order to illustrate the proposed approach, we consider the adsorption of pure CH$_4$ and CO$_2$ and their mixtures on a low rank coal at the room temperature of 298 K. Sorption and deformation measurements were taken using the specially designed apparatus described in ref 48. The system comprises a low-pressure (glass) dosing unit used for degassing and calibration and a high-pressure ampule (made of metal), which enables the gas sorption tests in the elevated pressures by the volumetric method. The pressure is monitored over the range 0–4.0 MPa with an accuracy of ±1 kPa. The system was assumed to be at a near-equilibrium state when the pressure variations in the ampule fell within ±2 kPa. The in situ deformation measurements during adsorption of pure CH$_4$ and CO$_2$ and their mixture are performed by tensiometers affixed to the surface of the coal sample placed in the high-pressure ampule. Variation of the sample strain is determined from the strain gauge resistances measured by the compensating method, using the Wheatstone bridge.

Repeated measurements are performed with increasing pressures in the dosing unit. The composition of the gas mixture in the ampule is measured with a gas chromatograph after the final pressure measurement is obtained. The detailed conditions of the experiments are described in earlier papers.45,48

Below, we use the experimental data collected on two samples from the Brzeszcze coal mine in the Upper Silesia Coal Basin, denoted B32.2 and B32.1. For sample B32.2, the mixture experiments were performed for two feed compositions of 27% and 75% carbon dioxide. The mixture adsorption and strain experimental data for 27% and 75% CO$_2$ feed composition correspond to the CO$_2$ fraction in equilibrated gas phase of 14.2% and 57.5%, respectively, at the highest pressure. We use the recalibrated raw data on adsorption and strain isotherms reported separately in refs 48 and 49. During recalibration, the CO$_2$ fractions for lower pressure were estimated using the material balances (for details, see the Supporting Information, Section S1).

For sample B32.1, the adsorption isotherms and pure CH$_4$ and mixture strain isotherms were reported earlier in refs 45 and 46 while the pure CO$_2$ strain isotherm on this sample is presented here for the first time. The mixture experiments were performed with the feed mixture of 41.5% CO$_2$ that corresponded to the 23.4% CO$_2$ fraction in equilibrated gas phase at the highest pressure.

3. RESULTS AND DISCUSSION

3.1. Correlation of Theory and Experiments. Figure 1 illustrates the application of the proposed methodology. The left panel shows the correlation of the theoretical predictions with the experimental adsorption and in situ strain data for pure carbon dioxide and methane and their binary mixtures on sample B32.2 at the room temperature of 298 K. The set of model parameters, $N^0_i$, $K_i$, $\lambda_{N_i}$, and $\lambda_{K_i}$ fitted to reproduce the pure component measurements is listed in Table 1.

For the conversion of the calculated adsorption stress into the strain, the volumetric modulus, $K$, is taken as 2 GPa, which is typical for coals.50 The theoretical adsorption and strain isotherms for pure components calculated with fitted parameters agree reasonably with the experimental data. As expected, CO$_2$ adsorption is stronger than CH$_4$ adsorption that is characterized by larger adsorption capacity and larger adsorption stress and strain. This trend was found in other similar systems.5,6

At sufficiently low pressures, the strain is negative meaning that the sample contracts upon adsorption. Although the contraction effect is small, this behavior is typical for all microporous adsorbents, including carbons, zeolites, and MOFs.19,42,43

Contraction at low gas pressures is accounted for by the negative Henry constant susceptibility factor, $\lambda_{K_{CO_2}}$ (see Table 1), that is related according to eq 6 to the change of the adsorption energy with the pore size, $\lambda_{K_{CO_2}} \approx - \frac{\Delta H / \partial V}{RT}$: the smaller the pore, the larger the adsorption energy, $\Delta H$. This effect leads to the negative adsorption stress exerted on the pore walls that tends to pull them inward. With a further increase of pressure and adsorbate density, the repulsion between adsorbed molecules causes the positive stress that tends to push against the pore walls and leads to swelling. For adsorption in this sample, the contraction effect was not revealed in the experiments, as it likely occurs at lower pressures than those measured. However, it is visible for CH$_4$ adsorption on sample B32.1 (see Figure S2 in the Supporting Information).

Predicted mixture adsorption and strain isotherms gradually increase as the CO$_2$ fraction, $y_{CO_2}$ increases. The experimental data (limited to the range of $y_{CO_2} = 0.091–0.156$ and $y_{CO_2} = 0.575–0.628$ for each feed mixture) agree with the theoretical predictions within acceptable deviations. These deviations are likely due to the experimental uncertainty in the gas composition measurements.

The model developed allows for theoretical predictions of the variation of the adsorption and strain in the process of displacement of CH$_4$ by CO$_2$. The respective adsorption and strain isotherms as functions of the CO$_2$ fraction, $y_{CO_2}$, at the selected fixed gas pressures at 298 K, are shown in the right panel of Figure 1. As expected, due to a higher affinity of CO$_2$ to carbon, the total gas adsorption gradually increases between the values of pure component CH$_4$ and CO$_2$ adsorption at a given pressure. Respectively, the strain measured from the initial volume of the sample saturated with pure CH$_4$ increases monotonically, which reflects swelling of the coal upon the CH$_4$ displacement by CO$_2$. The available experimental data for two mixture compositions, $y_{CO_2} = 0.142$ and $y_{CO_2} = 0.757$, are correlated with the theoretical predictions.

Similar calculations compared with experimental data for sample B32.1 are presented in the Supporting Information, Section S3.

3.2. Prediction of Coal Deformation during CH$_4$ Displacement by CO$_2$ at Geological Conditions. It is of practical interest to estimate the effects of coal swelling at the geologically relevant conditions,51,52 where both temperature and pressure increase with the depth of the gas reservoir. The interpolation to the higher temperature is done with the van’t Hoff equation, eq 6. For the given sample, the enthalpy of CO$_2$ adsorption, $\Delta H_{CO_2} = -36.911 \text{ kJ/mol}$, was determined from the

| $K_i$, MPa$^{-1}$ | $N^0_i$, cm$^3$ NTP/g | $\lambda_{N_i}$ | $\lambda_{K_i}$ |
|-----------------|-----------------------|----------------|--------------|
| CO$_2$          | 0.951                 | 38.2           | -0.386       | 0.943        |
| CH$_4$          | 0.380                 | 30.1           | -0.429       | 0.772        |
isothersms measured at 298 and 323 K. For CH₄ adsorption, we used the enthalpy $\Delta H_{\text{CH}_4} = -33.4$ kJ/mol reported in ref 53 for a similar coal sample. Equation 6 is also used to recalculate the Henry constant susceptibility factor as a function of temperature, $\lambda_{Ki/ff} \sim 1/T$.

Calculations of the adsorption and strain were performed for the coal sample B32.2 that would be placed at different depths below the surface level at 0 m ($T = 298 K$, $P = 0.1$ MPa), 500 m ($T = 313 K$, $P = 5.1$ MPa), 1000 m ($T = 328 K$, $P = 10.1$ MPa), 1500 m ($T = 343 K$, $P = 15.1$ MPa), and 2000 m ($T = 358 K$, $P = 20.1$ MPa). Here, the temperature and pressure gradients are assumed as 0.03 K/m and 0.01 MPa/m. With the depth of the reservoir, pure component adsorption and sample deformation dependencies are nonmonotonic, as shown in Figure 2, left panel. The respective values of temperature and pressure are given in the figure. The nonmonotonic behavior is caused by a competition between the pressure and temperature effects, which act in opposite directions; see more details in the Supporting Information, Section S2. Pure component adsorption and strain sharply increase with the depth up to 500 m due to the pressure increase by an order of magnitude. However, a further increase of pressure in the diapason of depths 1000–2000 m is compensated by the rise of temperature, and the adsorption reaches a near plateau at about 14 and 25.5 cm³ NTP/g for CH₄ and CO₂, respectively. Thersewith, the adsorption induced strain decreases for the pure components at the depths below 500 m. The nonmonotonic behavior of the strain with the depth of the reservoir is attributed to the negative Henry constant susceptibility factor, $\lambda_{Ki/ff}$, as shown in the Supporting Information, Section S2 and Figure S1. Note that here the strain is counted from the reference state of the “dry” adsorbent at $T = 298 K$ and $P = 0$. The strain induced due to the complete CH₄ displacement by CO₂ is estimated as the difference in the strain for pure components (green data in Figure 2, left), which increases with the reservoir depth achieving a plateau below 500 m. The resulting swelling is estimated to be about 1.25%.

The right panel of Figure 2 depicts the calculated adsorption and strain isotherms as functions of the bulk CO₂ mole fraction during the process of CH₄ displacement by CO₂ assuming the constant temperature and pressure corresponding to the given depths below the surface level. The adsorption strain is counted from the strain of the sample saturated by pure CH₄ to demonstrate the effect of CH₄ displacement by CO₂. The theoretical predictions suggest that coal swelling due to CH₄ displacement by CO₂ is progressively pronounced with the depth of the reservoir, reaching approximately 1.55% volumetric strain at the depth of 1000 m and decreasing slightly with the depth at 1500 m and below. This nonmonotonic effect is due to the initial elevated underearth pressure and, respectively, the enhanced adsorption of both CH₄ and CO₂, with the latter having a stronger affinity to coal. At increasing depths above 1000 m, the effect of the increase in temperature overcomes the pressure enhancement, and the strain and adsorption decrease with increasing depth.

Similar calculations for sample B32.1 showing the same trends are presented in the Supporting Information, Section S3 and Figure S3.

4. CONCLUSIONS

The proposed adsorption stress theory allows for predicting the deformation of nanoporous materials induced by the adsorption of gas mixtures based on the experimental data for pure gas mixture components. Using the Langmuir adsorption model, we demonstrate the correlation of the theoretical predictions with the experimental adsorption and strain data for pure CO₂, CH₄, and their binary mixtures on the coal samples at ambient temperature. The model parametrized based on the experimental data on pure component adsorption at ambient temperature is further employed for evaluating the swelling of coal in the process of...
displacement of CH₄ by CO₂ at the geological conditions. In the absence of relevant experimental data, these theoretical predictions may have important implications for the CO₂ assisted secondary gas recovery and CO₂ sequestration in geological reservoirs.

It should be noted that while the Langmuir model is widely used for the description of binary adsorption on various microporous materials, it has apparent limitations. The proposed general approach requires the knowledge of the theoretical adsorption isotherms, which can be determined by various methods including more complex phenomenological adsorption models, or direct MC and DFT simulations of gas adsorption on model solid structures. With proper modifications, the proposed approach can be extended and applied for other practical applications, including various gas mixture separation processes on flexible nanoporous adsorbents, like zeolites and MOFs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c07363.

Estimation of the CO₂ fraction in the equilibrium gas phase during adsorption measurements; explanation of model predictions at geological conditions; and comparison of the theoretical predictions and experimental data for sample B32.1 (PDF)

AUTHOR INFORMATION

Corresponding Author
Alexander V. Neimark — Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States; orcid.org/0000-0002-3443-0389; Email: aneimark@rutgers.edu

Authors
Nicholas J. Corrente — Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States; orcid.org/0000-0001-5765-1806

Katarzyna Zarębska — AGH University of Science and Technology, 30-059 Kraków, Poland

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.1c07363

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work is supported by the National Science Foundation (CBET Grant 18334339).

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