Transport, Zwitterions, and the Role of Water for CO₂ Adsorption in Mesoporous Silica-Supported Amine Sorbents

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ABSTRACT: The uptake of CO₂ in highly loaded, silica-supported, polyethylenimine (PEI)-impregnated sorbents was investigated in a reaction-diffusion model of the CO₂ adsorption process. The model successfully replicated the pseudoequilibrium behavior experimentally observed in thermogravimetry (TGA) experiments. A parametric study and sensitivity analysis of the model revealed that the stability and mobility of diffusive intermediates—assumed in the model to be zwitterions—effectively control the observable capacity of the sorbent. A subsequent quantum chemical study called into question the stability of zwitterions in PEI but suggested that physically bonded moieties involving water, amines, and CO₂ may be better candidates for diffusive intermediates. The implications are a strong dependence of the observable CO₂ capacity of the sorbent on the presence of water in the gas stream, which was found to be consistent with TGA results.

INTRODUCTION

Given the enormous role of fossil fuels in global power generation and the slow pace of the scale-up of renewable resources, carbon capture and storage (CCS) is increasingly recognized as a key strategy in the fight against global climate change, but CCS faces its own challenges. One of the principal challenges is that the current state-of-the-art postcombustion separation technology—aqueous amine scrubbing—reduces the thermal efficiency of the generation process to which it is attached by approximately 30%, with a corresponding increase in the cost of electricity in the neighborhood of $0.07/kWh. New separation technologies—such as solid sorbents or ionic liquids—could decrease these numbers, but they remain unproven at industrial scales. The Department of Energy’s Carbon Capture Simulation Initiative (CCSI) is a project aimed at reducing the typical 20–30 year timeline for development and deployment of new technologies in the power generation sector through the use of science-based simulation. Solid sorbents have been the technology of primary focus in the first two years of the project; this article contains results on the physicochemical modeling and theoretical study of a particular class of sorbents—mesoporous silica-supported amine (SSA) sorbents—obtained during the course of the project’s first two years.

A review of the development history for SSA sorbents can be found in a broad review of carbon capture technology written by Choi et al. Generally amine groups are loaded onto a mesoporous silica substrate with either ordered porosity (such as SBA-15) or disordered porosity (silica xerogel). The amines may be covalently tethered to the substrate through the reaction of an aminosilane with silanol groups on the silica surface or through the direct impregnation of amines into the silica support.

It has long been clear that transport of CO₂ through the amine bulk is the key limiting factor for the reaction rate (and thereby the working capacity for uptake of CO₂) for SSA sorbents with a relatively high amine loading. Evidence comes in the form of the frequently reported maximum in capacity as a function of temperature, as well as the observed dependence of capacity on the internal surface area of the sorbent. However, previously reported kinetic models for SSA sorbents have utilized semiempirical kinetic approaches which are not suitable for describing these effects. The uptake of CO₂ in aqueous alkanolamines (which is the most intensively studied amine–CO₂ interaction) has most often been described as the formation of alkylammonium carbamates through a zwitterion mechanism. The zwitterion mechanism does not enjoy universal support, however, and an alternative termolecular mechanism—commonly represented as a reaction between gaseous CO₂ and an amine that is already in a hydrogen-bonded relationship with a free base—has been proposed. The distinction is a subtle one. The zwitterion mechanism is written

\[
\text{R}_2\text{NH} + \text{CO}_2(g) \rightleftharpoons \text{R}_2\text{NH}^+\text{CO}_2^- \quad (1)
\]

whereas the termolecular mechanism reads

\[
\text{R}_2\text{NH} + \text{R}_2\text{NH}^+\text{CO}_2^- \rightleftharpoons \text{R}_2\text{NCO}_2^- + \text{R}_2\text{NH}_2^+ \quad (2)
\]
\[
\text{CO}_2(\text{g}) + 2\text{R}_2\text{NH} \cdots \text{NHR}_2 \rightleftharpoons 2\text{R}_2\text{NCO}_2^- + 2\text{R}_2\text{NH}_2^+ \tag{3}
\]

The termolecular mechanism would suggest a reaction order of 2 relative to the amine in nonaqueous solutions, while fractional orders between 1 and 2 are experimentally observed.\(^{23}\) However, the lack of definitive evidence for the zwitterion in mono- and diethanolamine solutions has led to continued debate, including recent kinetic and computational studies arguing for\(^{27,28}\) and against\(^{29–32}\) the presence of zwitterions in aqueous alkanolamines.

However, for SSAs, there is a cogent argument in favor of a reactive intermediate due to the role such a species can play in explaining the ability of CO\(_2\) to diffuse through an immobilized amine bulk phase. It appears from the above-referenced studies on highly loaded SSAs\(^{33,34–36}\) that CO\(_2\) diffuses through the amine bulk in nominally anhydrous conditions. There are two plausible mechanisms for this diffusion: transfer of CO\(_2\) between amine sites and long-range translational motion of the amine sites themselves. The latter is clearly not possible in the grafted amine sorbents, and unlikely in directly impregnated sorbents, since an IR study by Wang et al. offers strong evidence that amines become anchored to the substrate through proton exchange with surface silanols, which leads to ionic association.\(^{33}\) In the absence of water, this leaves the zwitterion as the most logical candidate for a diffusive intermediate.

In the following, a model of CO\(_2\) uptake in a highly loaded SSA sorbent is presented. It consists of a multiscale microstructural model, which enables the separation of gas-phase and amine bulk-phase transport of CO\(_2\). The latter is assumed to take place through a zwitterion-mediated mechanism. A detailed analysis of the model behavior, which includes a parametric and sensitivity study, reveals two important findings. One is that the model qualitatively captures the transport-limited behavior seen in experiments. The second is that the stability and mobility of the reactive intermediate play a dominant role, controlling not only the kinetics but also the experimentally observable CO\(_2\) capacity of the sorbent.

Subsequent to this analysis, a quantum chemical study of the energetics of zwitterion formation for ethylenamines in both dry and humidified environments was performed. It was found that zwitterions are only stable—at least for certain chemistries—in a polar environment similar to that of water. Additionally, a pair of gas-phase stable physically bonded conformations involving water, amine, and CO\(_2\) were discovered, either of which could serve as a reactive intermediate. This finding, combined with the importance of diffusive intermediates in determining sorbent capacity, suggests that in fact highly loaded SSAs will have very limited capacity for the uptake of CO\(_2\) in truly anhydrous conditions. As a result, measurements of CO\(_2\) capacity in nominally dry conditions may significantly underestimate the true capacity of these sorbents for the formation of carbamate.

### THERMODYNAMIC AND KINETIC THEORY

**Microstructural Model.** Nitrogen adsorption analyses for silica xerogels typically reveal significant pore volumes in the mesopore range, while SEM images and mercury porosimetry experiments reveal a macroporous structure.\(^{34–36}\) This implies a bimodal pore size distribution that manifests itself in a hierarchical pore structure. Gas moves freely through the macropores but is limited by Knudsen diffusion as it enters the mesoporous regions. Within the mesoporous regions, CO\(_2\) may diffuse in the gas phase or adsorb at the amine surface, diffusing through the bulk to reach amine sites not in contact with the gas.

It is therefore necessary to split the microstructure into three length scales. The largest length scale is that of the macroscale particle (generally on the order of millimeters), at which CO\(_2\) moves via gas-phase bulk diffusion, a process that we will assume is very fast compared to kinetic limitations at the lower length scales. The intermediate length scale is that of the mesoporous regions of the support, on the order of 100 nm to 10 \(\mu\)m.\(^{30}\) The smallest length scale will be that of the smaller regions within the mesoporous areas that are completely filled with PEI and silica—these regions can be viewed as areas of oxide and immobilized polymer found between the open mesopores. The length scale of these regions depends on the degree of mesoporosity remaining after polymer impregnation—it will approach that of the intermediate scale in the limit of zero remaining mesoporosity.

At each of the two smaller length scales, gas-phase CO\(_2\) (in the case of the intermediate scale) or adsorbed CO\(_2\) (for the smallest scale) diffuses in from multiple directions. SEM images suggest that the shape of the region at the intermediate scale is quasi-spherical,\(^{35,36}\) whereas it is probably reasonable to expect that the typical shape of the amine–silica composite at the smallest scales is not spherical. (Indeed, for ordered substrates such as MCM-41, a cylindrical model may be appropriate for this length scale. However, spheres can be utilized in principle without loss of generality.) The use of spheres can be thought of as a general method for modeling chemical penetration into a closed region of any arbitrary shape; empirical microstructural parameters can properly account for the difference between the spherical and actual cases if such parameters depend on the state of infiltration.

The spheres will not have fixed locations with respect to one another as in a conventional grain model because this presumes a certain structure for the spaces between grains. Rather, there is a certain “sphere density” at the large and intermediate length scales. These densities, the sphere radii, and the porosities and internal surface areas at each length scale are interrelated

\[
1 - \epsilon_1 = \rho_2 \frac{4}{3} \pi R_2^3 \tag{4}
\]

\[
a_1 = \rho_2 (1 - \epsilon_1) 4 \pi R_2^2 \tag{5}
\]

and

\[
1 - \epsilon_2 = \rho_3 \frac{4}{3} \pi R_3^3 \tag{6}
\]

\[
a_2 = \rho_3 4 \pi R_3^2 \tag{7}
\]

where \(\epsilon\) is the porosity; \(\rho\) is the number density of spheres; \(R\) is the sphere radius; and \(a\) is the internal surface area; and the subscripts 1, 2, and 3 denote the large, intermediate, and small length scales, respectively. Figure 1 illustrates the relationships between the different modeling scales.

Under the assumption of the fast gas-phase diffusion of CO\(_2\) at the large scale and the assumption of spherical symmetry at the intermediate and small scales, the problem then becomes one of reaction and diffusion in two dimensions.

**Chemistry.** Assuming a homogeneous environment of amine sites that are active for the adsorption of CO\(_2\), the zwitterion mechanism for the anhydrous formation of carbamate is given by eqs 1 and 2. Assuming that eq 1 remains
in equilibrium and that the entire system follows ideal thermodynamics (neither of these assumptions have any particular justification, other than that they exclude from the analysis some factors not related to transport, which is the focus of this study), the surface site fraction of zwitterions is

\[ z_s = \frac{k_z p (1 - 2x_p)}{1 + k_z p} \]  

where \( p = p(CO_2); x = [R_2NCO_2^-]; k_z \) is the equilibrium constant; and the subscript \( s \) denotes the value at the gas–amine interface.

Further assuming ideal kinetics, the rate of the proton transfer step given by eq 2 is

\[ \frac{dz}{dt} = k_4 \left[ (1 - 2x - z)z - \frac{k_z x^2}{k} \right] \]  

where \( k \) is the equilibrium constant for the overall reaction 1, 2.

**Gas Diffusion.** The mass balance for diffusion at the intermediate length scale is

\[ \frac{\partial (e_z c)}{\partial t} = -V_N \frac{\partial \hat{N}_g}{\partial t} + q_2 \]  

where \( c \) is the concentration of CO\(_2\) in the gas; \( \hat{N}_g \) is the microstructure-averaged gas flux; and \( q_2 \) is the source term. The source term \( q_2 \) has both chemical and transport aspects, as CO\(_2\) is removed from the gas both through the progress of the chemical reactions 1 and 2 at the gas–amine interface and through the transport of CO\(_2\) away from the interface through diffusion into the amine bulk. A zwitterion balance for the layer of amine sites at the interface with the gas is

\[ n_z a_2 \frac{\partial z}{\partial t} = -q_2 - n_z a_2 \frac{\partial x}{\partial t} = q_{2,t} \]  

where \( n_z \) is the area density of amine sites at the interface, and \( q_{2,t} \) is the rate of transfer of zwitterions away from the surface layer and into the amine bulk. Differentiating eq 8 with respect to time leads to

\[ \frac{\partial z}{\partial t} = \frac{k_z (1 - 2x_p) \partial p}{(1 + k_z p)^2 \partial t} + \frac{p (1 - 2x_p) \partial k_z}{(1 + k_z p)^2 \partial t} - \frac{2k_z p \partial x}{1 + k_z p \partial t} \]  

Combining eqs 11 and 12 leads to an expression for \( q_2 \)

\[ q_2 = -n_z a_2 \left[ \frac{k_z (1 - 2x_p) \partial p}{(1 + k_z p)^2 \partial t} + \frac{p (1 - 2x_p) \partial k_z}{(1 + k_z p)^2 \partial t} \right] + \frac{1 - k_z p \partial x}{1 + k_z p \partial t} - q_{2,t} \]  

Since the pores at the intermediate length scale are less than 50 nm in diameter, Knudsen diffusion will dominate for gas transport

\[ \hat{N}_g = -\frac{e_z D_k V_x}{\tau_z} \]  

where \( \tau_z \) is the tortuosity. The Knudsen diffusivity is

\[ D_k = \frac{4}{3} K_n \left( \frac{8RT}{\pi M} \right)^{1/2} \]  

where \( M \) is the molar weight of CO\(_2\) and \( CO_2 \) and \( K_n \) is the Knudsen flow parameter (in units of length), which depends on the structure of the porosity.

**Diffusion in the Amine Bulk.** Further extending the assumption of ideality to the bulk transport model, the zwitterion mechanism for transport of CO\(_2\) in an immobilized amine bulk phase leads to the following expression for the mobility of zwitterions

\[ u_b = \zeta_b (1 - 2x - z) \exp \left( -\frac{\Delta G_b}{RT} \right) \]  

\[ = (1 - 2x - z) u_b^0 \]  

where \( \zeta_b \) is a factor depending on the average geometry surrounding the species and the frequency of collisions with other amine sites, and \( \Delta G_b \) is the free energy barrier for the hopping of a CO\(_2\) group from one amine site to the next. The form of the preexponential term (with no dependence on temperature) reflects the assumption that the sites in the amine, while spatially constrained, are nonetheless able to move translationally over short distances. The microstructure-modified diffusive flux of CO\(_2\) is then

\[ \hat{N}_b = -\frac{e_z n_z (1 - 2x - z) u_b^0 V_x \mu_z}{\tau_z} \]  

where \( e_z \) is the volume fraction of amine at the smallest length scale; \( \tau_z \) is the amine tortuosity; \( n_z \) is the number of amine sites (that are available for CO\(_2\) adsorption) per unit volume in the amine; and \( \mu_z \) is the chemical potential of zwitterions

\[ \mu_z = \mu_z^0 + RT \log \left( \frac{z}{1 - 2x - z} \right) \]  

the form of which accounts for site limitations. This leads to

\[ \hat{N}_b = -\frac{e_z RT n_z u_b^0 [(1 - 2x) V_x z + 2z V_x x]}{\tau_z} \]  

The final mass-balance equation at the smallest length scale then becomes

\[ n_z a_2 \frac{\partial z}{\partial t} = -\frac{e_z RT n_z u_b^0}{\tau_z} [(1 - 2x) V_x z + 2z V_x x] - n_z \frac{\partial x}{\partial t} \]  

**Assembly of the Model.** Now that the equations for each length scale have been derived, it remains to assemble them into an integrated model. This begins with the observation that each length scale corresponds to a separate three-dimensional domain. The functions \( x \) and \( z \) are field variables over all three sets of coordinates, while \( p \) is a field variable over the largest two length scales. In general, this means that \( x \) and \( z \) are functions over nine spatial dimensions plus time and that \( p \) is a function over six spatial variables plus time. However, the
approximations that gas diffusion is fast at the largest length scale, combined with spherical symmetry at the lower two length scales, will reduce the number of spatial dimensions to two for \( x \) and \( z \) and one for \( p \). The indices for these coordinate systems are labeled \( r_2 \) and \( r_p \) such that
\[
\begin{align*}
  x &= x(r_2, r_p, t) \\
  z &= z(r_2, r_p, t) \\
  p &= p(r_2, t)
\end{align*}
\]

Distinct mass balances are written in dimensionless form, with the balance at the intermediate length scale restricted to the axis at \( r_3 = 0 \). It is coupled to the mass balance at the smallest length scale through its source term. Combining eq 10 and eqs 13--15 (along with the observation that \( k_{2,3} = RTu^b(n,N_e)^1/3 \), with \( N_e \) Avogadro’s number) and eq 20 leads to
\[
\begin{align*}
  \left[ \frac{\varepsilon_1 + RTn_1}{r_2} \frac{1/3}{(1 + \varepsilon_3 p)^2} \right] \frac{d\rho}{dt} &= \frac{4\varepsilon_1}{3r_2} \left( \frac{8RT}{\pi M} \right)^{1/2} \\
  \n_3 \left[ \frac{1 - \varepsilon_3 p}{1 + \varepsilon_3 p} \right] \frac{\partial \zeta}{\partial t} &= \frac{p(1 - 2x_1) \delta x_1}{1 + (1 + \varepsilon_3 p)^2} \frac{\partial \zeta}{\partial t} - RT\delta \eta
\end{align*}
\]

where
\[
\begin{align*}
  q_{2,3} = RTn_1u_1^b(n,N_e)^{1/3} [z_3(1 - 2x_1 - z_3) - z_2(1 - 2x_2 - z_2)]
\end{align*}
\]
and
\[
\begin{align*}
  V_3^2 &= \frac{1}{r_2^2} \left( \frac{\partial \zeta}{\partial r_2} \right)^2
\end{align*}
\]

The mass balance in the solid phase is written
\[
\begin{align*}
  \varepsilon_1 \frac{\partial \zeta}{\partial t} &= \frac{\varepsilon_1}{r_3} \left( \frac{8RT}{\pi M} \right)^{1/2} \left[ (1 - 2x) \frac{\partial \zeta}{\partial x} + 2z \frac{\partial \zeta}{\partial z} \right] - \frac{\partial \frac{\partial \zeta}{\partial t}}{\partial t}
\end{align*}
\]

where
\[
\begin{align*}
  \frac{\partial \frac{\partial \zeta}{\partial t}}{\partial t} &= \frac{1}{r_3^2} \left( \frac{\partial \zeta}{\partial r_3} \right)
\end{align*}
\]

\[
\begin{align*}
  V_3 = \frac{\partial \delta \theta}{\partial r_3}
\end{align*}
\]

When combined with eq 9, eqs 22–24 form a closed set of partial differential equations for the reaction–diffusion system. The boundary conditions are zero flux at \( r_3 = 0 \) and \( r_3 = 0 \), a Dirichlet boundary condition for the pressure (given by the composition of the bulk gas) at \( r_2 = R_2 \). The flux 23 links the domains 2 and 3 at \( r_3 = R_3 \). The remaining influence of the microstructure on transport comes from the empirical parameters \( K_{ff}, \tau_2 \) and \( \tau_3 \), referring to Knudsen diffusion, gas-phase tortuosity, and polymer-phase tortuosity, respectively. The Knudsen flow parameter, \( K_{ff} \), is a constant which depends only on the mesoporous structure. The parameters \( \tau \), on the other hand, characterize not only the relevant microstructure as it affects the respective transport process but also the difference in transport modes between that of a sphere and the actual microstructure-averaged geometry. They are strictly functionals of the spatial coordinates of the appropriate field variables
\[
\begin{align*}
  &\tau_2 = \tau_2[p] \\
  &\tau_3 = \tau_3[z]
\end{align*}
\]

The form of these functionals is not general. If the microstructure-averaged shape is spherical, however, then \( \tau \) is a constant; this will be the assumption used at both length scales. The microstructural parameters \( (K_{ff}/\tau_2, \tau_3) \) therefore belong to the studied set.

\section*{Chemical Equilibrium and Kinetic Parameters}

The equilibrium parameters are the enthalpies \( \Delta H_2, \Delta H_3 \) and entropies \( \Delta S_2, \Delta S_3 \) associated with reactions 1 and 2. The kinetic parameters are the activation enthalpy \( \Delta H^a \) and preexponential factor \( \zeta \) (a parameter which includes the activation entropy) of the forward reaction rate constant \( k \).

\section*{Transport and Site Density}

There are two transport parameters associated with the mobility of CO2 in bulk PEI: the preexponential factor and activation energy, \( \zeta^a \) and \( \Delta H^a \), respectively, for the mobility \( u_2^a \). The volumetric density \( n_v \) of adsorption sites in PEI is included in the study due to the uncertainty about the density of immobilized PEI as well as the extent of association between amine sites and the substrate. Finally, the number of sites per unit area of the gas–PEI interface is \( n_i = f(n_i)^{2/3}/N_0^{1/3} \), where \( f \) is an estimated parameter and \( N_0 \) is Avogadro’s number.

\section*{Dispensation of Model Parameters}

The principal sensitivity analysis was performed using variance decomposition. The vector of model parameters is denoted for the model described above as \( \Theta = \{\partial_1, ..., \partial_{12}\} \). Of particular interest is the total variance index \( T_{\partial j} = 1, ..., 12; \) this measure is reviewed in detail in refs 40--43. The total variance index \( T_{\partial j} \) for a model parameter \( j \) at a particular state point \( \xi = \{p, T, t\} \) is calculated as
\[
\text{dx.doi.org/10.1021/jp4076417 J. Phys. Chem. C 2013, 117, 26617--26627}
\begin{align}
\mathcal{T}_j(\xi) &= \frac{E[\text{Var}(w(\xi, \Theta)|\Theta_{-j})]}{\text{Var}(w(\xi, \Theta))} = 1 - \frac{\text{Var}(E[w(\xi, \Theta)|\Theta_{-j}])}{\text{Var}(w(\xi, \Theta))} \\
&= 1 - \sum_{k=1}^{p} \sum_{r=1}^{p} f_{j,k}(\theta_j, \theta_k) + \cdots + f_{1-p}(\Theta) \tag{26}
\end{align}

where \(E(Y)\) and \(\text{Var}(Y)\) are expected value and variance, respectively, of a random variable \(Y\) given \(Z\), and \(\Theta_{-j} = \{\theta_1, \theta_2, \ldots, \theta_{j-1}, \theta_{j+1}, \ldots, \theta_p\}\). The functional \(\mathcal{T}_j\) can be interpreted as the proportion of the total variance of the model output (at \(\xi\)) that is due to parameter \(\theta_j\), including the effects of its interactions with other parameters. Evaluating the integrals involved with the calculation of the \(\mathcal{T}_j\) requires numerical methods of quadrature, the most convenient being Monte Carlo integration.

**Model Emulator.** The Monte Carlo process needed to calculate the \(\mathcal{T}_j\) typically requires many thousands of evaluations of the sorbent model. As this is not computationally feasible, a model emulator can be used to provide estimates for \(s_j\) and \(\mathcal{T}_j\).\(^{43-47}\) That is, first collect a modest number of model runs from the computer model, fit a response surface (i.e., the emulator), then use the emulator to perform the computationally intensive calculations.

The emulator used to produce the SA results below is the Adaptive Component Selection and Shrinkage Operator (ACOSSO).\(^{48}\) It belongs the Smoothing Spline (SS) ANOVA class of nonparametric regression methods. The SS-ANOVA approach is to estimate the functional components of the functional ANOVA decomposition

\[
f(\Theta) = b_0 + \sum_{j=1}^{p} f_j(\theta_j) + \sum_{j=1}^{p} \sum_{k=j+1}^{p} f_{j,k}(\theta_j, \theta_k) + \cdots + f_{1-p}(\Theta) \tag{27}
\]

where \(f_j\) are the main effect functions; \(f_{j,k}\) are the two-way interaction functions; and \(p\) is the dimension of \(\Theta\). In general, the expansion in eq 27 extends up through \(p\)-way interactions. However, it is rarely the case in practice that interactions beyond orders of two or three are very important. Therefore, the model is usually truncated after the two-way interactions, and three-way can be added if any lack of fit is present. The two-way interaction model was used to produce the results below. The functional components \((f_j, f_{j,k})\) are estimated by adding a roughness penalty to a least-squares optimization over a rich class of smooth functions, just as in the simple univariate smoothing spline problem (see ref 49 for example). The ACOSSO approach uses an \(L_1\) type penalty (like that used in the LASSO\(^{50}\)) to simultaneously achieve smooth estimates of the functional components and sparse solutions (i.e., variable selection). See ref 48 for the full details of the ACOSSO emulation method.

**QUANTUM CHEMICAL METHODS**

Density functional theory (DFT) and wave function-based methods were performed using Gaussian 09.\(^{51}\) For DFT, B3LYP\(^{52}\) and PBE0\(^{53,54}\) functionals were used. The wave function methods were second-order Møller–Plesset perturbation theory (MP2) along with a couple cluster approach with single and double substitutions (CCSD).\(^{55}\) The basis set used for all calculations was 6-31++G**. For calculations of species in solution, the polarized continuum model (PCM) was employed.

Electronic structure calculations as applied to the formation of carbamic acid in alkanol- and ethyleneamines were reviewed in a recent study on the uptake of CO\(_2\) in supported amine sorbents.\(^{56}\) This included an assessment of the accuracy of quantum chemical methods, based on recent benchmarking studies.\(^{57,58}\) In conjunction with an accurate basis set (like 6-311++G**) it was concluded that MP2 is expected to be the most accurate method, although the hybrid DFT approach of PBE0 was also within “chemical accuracy” of 1 kcal/mol (4.2 kJ/mol). In comparison to the calculated enthalpies for the adsorption of CO\(_2\) for a number of different ethylamines, a small spread in binding energy was observed. This relatively small spread denotes a weak dependence on both the alkyl chain length (methyl vs ethyl) and primary vs secondary amine. With this weak dependence, it was concluded that the results were transferable to the PEI polymer chain. Such observations enable a focus on smaller molecules in place of more arduous computations using macromolecules. The molecules considered in the present study were monomethylamine (MMA), dimethylenamine (DMA), and diethylenetriamine (DETA).

**EXPERIMENTAL SECTION**

**Sorbent Synthesis.** An SSA sorbent created at NETL was investigated via thermogravimetric analysis (TGA), providing a set of results against which the model output can be evaluated. This sorbent, labeled NETL-196C, consists of linear PEI (molecular weight 423 g/mol) impregnated on a commercially available silica xerogel substrate (Fuji Silysia) with an as-received pore volume of 1.77 cm\(^3\)/g and mean pore diameter of 24.0 nm. Full details of the sorbent synthesis are available in a prior publication.\(^{39}\)

**Thermogravimetric Analysis.** CO\(_2\) adsorption data for the sorbent were experimentally obtained using a Thermo Scientific ThermMax 300 thermogravimetric analyzer. In a typical experiment, a 50 mg sample was loaded within a microbalance quartz sample bowl. Prior to adsorption measurements, the samples were heated to 105 °C in nitrogen (flow rate: 100 mL/min) at a heating rate of 5 °C/min and held isothermally for 90 min to remove preadsorbed CO\(_2\) and moisture. The temperature was then increased to the initial adsorption temperature (108 °C) before switching to a dry mixture of 4%, 10%, and 18.5% CO\(_2\), balance nitrogen, maintaining a flow rate of 100 mL/min. Subsequent CO\(_2\) adsorption steps were conducted at 100, 92, 65, 57, 49, and 41 °C, followed by desorption steps at 65 and 108 °C. The hold time was approximately 90 min for each step. For TGA runs containing moisture, the purge gas stream was run through a sparger imparting the requisite moisture content.

**RESULTS AND DISCUSSION**

**TGA.** The TGA results for dry CO\(_2\) atmospheres appear in Figure 2. While it is clear that equilibrium is not reached at 65, 57, and 49 °C, the weight profile reaches a plateau at 41 °C. This is followed, however, by an increase of the temperature to 65 °C, upon which the sorbent weight, after an initial sharp drop, begins to rise again. This behavior shows that the plateau at 41 °C is not indicative of equilibrium. What is indicated instead is that after an initial adsorption at that temperature a kinetic barrier is reached, effectively cutting off further adsorption. The clearest explanation for this effect is that
CO₂ is able to adsorb at the gas—amine interface at 41 °C but unable to move appreciably into the amine bulk. By contrast, the TGA curves collected with 9% H₂O in the gas—seen in Figure 3—show no such pseudoequilibria. Contrast of the weight gain at 10% CO₂ between humid and dry conditions shows a considerable increase upon the introduction of water. This increase is not fully explained by the uptake of water by the sorbent, as the TGA trace for 9% H₂O, balance N₂ (red curve in Figure 3) shows. The anomalous data at low temperatures seen in the CO₂−H₂O mixture are likely due to low-temperature condensation of carbonic acid.

**Parametric Study.** The parameter ranges used in the study are found in Table 1. Model evaluations at several parameter settings, \( w(\xi_i; \Theta) \), \( i = 1, \ldots, n_i \), were collected. In this case, two samples of 128 and 64 runs, respectively, for a total of 192 model evaluations were obtained at the points \( \Theta_{1}, \ldots, \Theta_{192} \). Of these 192 runs 61 of them failed, to leave a total of 131 valid runs. The sample was obtained via a Latin Hypercube Sampling technique, but with a constraint on the entropy of reactions for 1 and 2, namely, that \( \Delta S_{1} < \Delta S_{2} \), reflecting the fact that the transition from the gas to the adsorbed state should dominate the total entropy change in the formation of carbamate from gaseous CO₂.

For each successful run, a set of simulated TGA curves was created, with a program of temperature changes at four set oxygen partial pressures adhering precisely to the program described above. Those curves were qualitatively evaluated to determine whether or not they captured the behavior indicative of diffusion-limited pseudoequilibria seen in the experimental system. This was in fact achieved for several cases; one of the clearest is shown in Figure 4. Inspection of the simulation data shows that, in fact, concentration gradients remain frozen in place upon a decrease in temperature, indicating diffusive control of not only the kinetic but also the apparent equilibrium behavior of the system.

The emulator was then fit to these data (at a particular state point \( \xi \)) and then used to produce estimates of the \( s(\xi) \) and \( T_{s}(\xi) \) via Monte Carlo integration. A separate emulator was fit to the data \( w(\xi_i; \Theta) \), \( i = 1, \ldots, n_i \), for the four distinct pressures, each at 100 separate time points. The resulting estimated total variance indices are plotted across time for each of the four pressure settings in Figure 5. The results show that three of the four most sensitive parameters are those that control the stability and mobility of zwitterions, with the most sensitive parameter the entropy of zwitterion formation (\( \Delta S_{1} \)).

![Figure 2](image1.png) ![Figure 3](image2.png)

**Figure 2.** (a) TGA results for NETL-196C and (b) a close-up view of the same data highlighting the pseudoequilibrium at 41 °C. (The legend in part (a) pertains to both figures.) Time \( t = 0 \) in the plots corresponds to the point at which CO₂ was introduced into the chamber.

**Figure 3.** TGA results for NETL-196C in gas containing 9% H₂O and either 0% or 10% CO₂, balance N₂.

**Table 1. Parameter Ranges Used in the Study**

<table>
<thead>
<tr>
<th>parameter</th>
<th>low</th>
<th>high</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log_{10}(K_{1}/\tau_{2}) )</td>
<td>−10.5</td>
<td>−8.0</td>
</tr>
<tr>
<td>( \Delta_{1} )</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>( n_{i} ) (mol/m³)</td>
<td>5000</td>
<td>25000</td>
</tr>
<tr>
<td>( f )</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>( \Delta_{H_{1}} ) (kJ/mol)</td>
<td>−57.9</td>
<td>−4.8</td>
</tr>
<tr>
<td>( \Delta_{S_{1}} ) (J/mol K)</td>
<td>−200</td>
<td>−41.6</td>
</tr>
<tr>
<td>( \Delta_{H_{2}} ) (kJ/mol)</td>
<td>−91.7</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta_{S_{2}} ) (J/mol K)</td>
<td>−200</td>
<td>−10</td>
</tr>
<tr>
<td>( \Delta_{H_{2}}^{\prime} ) (kJ/mol)</td>
<td>9.6</td>
<td>96.4</td>
</tr>
<tr>
<td>( \log_{10}(\xi) )</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>( \Delta_{H_{2}}^{\prime} ) (kJ/mol)</td>
<td>19.2</td>
<td>125</td>
</tr>
<tr>
<td>( \log_{10}(\xi_{b}) )</td>
<td>−11</td>
<td>−2</td>
</tr>
</tbody>
</table>

![Table 1](image3.png)
scatter plots—plots of the average weight gain of all parametrizations studied versus the value of a single parameter—shown in Figure 6 confirm that the parameters controlling the number and mobility of diffusive intermediates are the most influential on average.

With any problem involving a complicated model it is important to assess the robustness of the results. A simple, but effective, approach to accomplish this in SA studies is to apply alternative emulators. Thus, we also applied the traditional squared exponential covariance Gaussian process model and the Bayesian Smoothing Spline ANOVA model to produce the SA quantities. All approaches gave very similar results, so only those for ACOSSO are shown. All of these emulation approaches are reviewed in ref 47.

Quantum Chemistry. Given the results of the parametric study, which indicate the importance of the stability of diffusive intermediates to the effective capacity of amine sorbents, zwitterion stability in ethylamines was considered in the context of a quantum chemical study. Figure 7 depicts a zwitterion formed with dimethylamine (DMA). The energies of formation for this species along with that of two other ethylamine zwitterion species—monomethylamine (MMA) and diethyltri-
amine (DETA)—in the gas phase and in solution were calculated according to the methods detailed previously. The results appear in Table 2. All results appearing in the table were calculated using the PCM solvation model (where appropriate) and the 6-311++G** basis set. The zwitterion was found to be unstable for all chemistries investigated and all levels of theory in the gas phase and in a polar environment ($\varepsilon_r = 2.9$) similar to that of anhydrous PEI. (Positive formation energies are estimated using a stable zwitterion configuration obtained in a much more highly polar medium.) For a dielectric medium similar to that of water ($\varepsilon_r = 78$), results are mixed: PBE0 yields a stable zwitterion for both monoamine chemistries. MP2 yields a slightly downhill reaction for DMA but an unstable zwitterion for MMA. The CCSD calculation for DMA also yields a stable zwitterion, with a slightly positive formation energy. B3LYP predicts no stable zwitterions in H$_2$O, although this is perhaps the least reliable of all the methods used. The results for DETA are more uniformly uphill. A reasonable conclusion is that ethylamine zwitterions may be

Figure 6. Scatterplots of the integral over time of the CO$_2$ loading curve for partial pressure of 10% versus the model parameters along with the corresponding estimated main effect curves from ACOSSO (red line) for (a) enthalpy and (b) entropy of zwitterion formation and (c) enthalpy and (d) entropy of carbamate formation from the gas.

Figure 7. Zwitterion formed with dimethylamine.

<table>
<thead>
<tr>
<th>$\varepsilon_r$</th>
<th>MMA</th>
<th>DMA</th>
<th>MMA</th>
<th>DMA</th>
<th>MMA</th>
<th>DMA</th>
<th>DETA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>50.1</td>
<td>45.1</td>
<td>25.1</td>
<td>37.6</td>
<td>9.2</td>
<td>2.9</td>
<td>10.5</td>
</tr>
<tr>
<td>PBE0</td>
<td>40.1</td>
<td>33.9</td>
<td>12.5</td>
<td>8.4</td>
<td>-0.4</td>
<td>-0.4</td>
<td>5.0</td>
</tr>
<tr>
<td>MP2</td>
<td>60.2</td>
<td>42.6</td>
<td>-8.4</td>
<td>-10.9</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>68.1</td>
<td>49.8</td>
<td>15.9</td>
<td>4.9</td>
<td>14.6</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Formation Energies (kJ/mol) for Zwitterion Species According to Various Methods of Calculation and Ethylamine Chemistries in Dielectric Media Representing the Gas Phase, DPA (as a Proxy for PEI), and Water.
barely stable in an aqueous environment, depending on the specific chemistry, but are not stable in a polar environment similar to that of anhydrous PEI.

Explicit water molecules were also considered as a part of the study. From these calculations, two different types of bound associates involving amine, water, and CO$_2$ emerged. These are shown in Figure 8(a) (linear topology) and (b) (ring topology). Energies of formation in the gas phase were found to be −28.0 and −47.2 kJ/mol for linear and ring topologies, respectively, using B3LYP.

## DISCUSSION

The salient conclusions of the study arise from the comparison of the sensitivity results with the quantum chemical results. The former emphasize the importance of diffusive intermediates: it is the concentration of those intermediates that controls the measured capacity of the sorbent because a diffusion mechanism is required to open up amine sites in the polymer bulk for the formation of carbamate. The quantum study raises interesting questions about the identity of those intermediates: the stability of zwitterions even in aqueous solution is questionable; it seems therefore unlikely that the zwitterion could serve as a diffusive intermediate in anhydrous PEI. However, quantum calculations have also shown that there are other candidates for the intermediate in humid CO$_2$. To be sure, the existence of the associates shown in Figure 8 is still hypothetical, but it is at least not foreclosed by the quantum calculations as is the case with the zwitterion. Additionally, if the concentration of diffusive intermediates controls capacity, then the TGA results of Figure 3 become strong evidence in favor of a role for water in the formation of diffusive intermediates. Direct experimental evidence of the proposed intermediates could be available through IR spectroscopy, if the vibrational modes of water are affected appreciably by the physical bonds formed with CO$_2$ and the amine.

There remains the question of adsorption in dry conditions, which under the hypothesis presented would not involve access to amine sites in the polymer bulk. It is possible that the observed dry CO$_2$ capacity reflects primarily surface or near-surface adsorption, as reflected in the dependence of the capacity on the internal surface area of the sorbent. In addition, trace amounts of water in the nominally dry experiment may lead to the formation of a small concentration of diffusive intermediates, leading to limited transport of CO$_2$ in the polymer bulk.

## CONCLUSIONS

A combination of modeling, statistical analysis, quantum chemical calculations, and experimental results have led to a new hypothesis for CO$_2$ capacity in highly loaded, PEI-impregnated SSA sorbents. This new hypothesis holds that capacity is primarily controlled by the availability of diffusive intermediates for the transport of CO$_2$ in bulk PEI. These intermediates are, in turn, dependent on the availability of water molecules. Specific chemistries for the intermediates have been proposed.

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**Notes**

The authors declare no competing financial interest.

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