Unravelling Irreversible Adsorbate Thermodynamics through Adsorption Assisted Desorption

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Abstract. Strongly bound surface species like alkylamines adsorbed on the Brønsted acid site of aluminosilicate zeolites exhibit negligible rates of desorption, preventing them from achieving an equilibrated state on experimentally relevant timescales that limit the elucidation of their adsorption thermodynamics. Through adsorption assisted desorption, whereby distinct alkylamines facilitate desorption from Brønsted acid sites, we demonstrate that equilibrated states are achieved. Breakthrough adsorption measurements reveal that while sec-butylammonium on a Bronsted acid site is irreversibly adsorbed, it is readily desorbed when exposed to a distinct alkylamine like isopropylamine. As a result, two-adsorbate equilibrium was achieved when exposing Bronsted acid sites of aluminosilicate zeolites to a binary vapor phase alkylamine mixture. By varying relative vapor phase partial pressures and temperatures, we demonstrate the ability to experimentally measure the adsorption enthalpy and entropy of alkylammonium adsorbates on the mostly isolated Bronsted acid sites of H-ZSM-5 (Si/Al = 140). A multi-adsorbate Langmuir isotherm was found to quantitatively describe the co-adsorption of alkylamines varying in size and basicity over a wide range of conditions, through which the relative adsorption enthalpy and entropy of alkylamines was measured. Across a homologous family of sec-alkylamines (C3-C5) adsorbed on isolated Bronsted acid sites, a fixed contribution to the enthalpy (19 ± 4 kJ mol CH2⁻¹) and entropy (25 ± 4 J mol CH2⁻¹ K⁻¹) of adsorption per methylene unit of was found to exist, likely resulting from electrostatic interactions between the alkyl chain and surrounding pore environment.

1. Introduction. Adsorption of molecules on catalytic surfaces like zeolites and metal oxides is controlled by changes in enthalpy and entropy, with the role of entropy underscored at higher temperatures.¹ The energetics of adsorption has helped establish theories to predict rate constants of surface chemical reactions,² illustrating how adsorption affects rate and selectivity in catalytic cycles.¹, ³ Significant progress has been made in understanding adsorbate enthalpy, through calorimetry, by directly measuring the heat evolved upon adsorption.⁴⁻⁷ Conversely, adsorbate entropy is relatively not well understood despite it’s significant contribution to adsorption energetics; systematic studies that estimate adsorbed entropy are limited.²

Entropy details the capability of an adsorbate’s movement on surface, describing their mobility through fundamental motions (i.e. translation, rotation, and vibration).⁸ Prior work by Campbell and Sellers demonstrated that commonly applied approximations greatly underestimated the entropies adsorbates, providing a correlation that adsorbates retain approximately two thirds

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of their gas phase entropies. More recently, Dauenhauer & Abdelrahman extended the correlation to account for the confinement of a pore in microporous materials, finding that additional losses in rotational entropy led an adsorbate retaining less than two thirds its gas phase entropy. While the study of Campbell and Sellers focused on metal oxides, there was a basis to extend it to Zeolites a commonly used heterogeneous catalyst in the oil and gas industry for production of gasoline and other useful industrial feedstocks. Studies on the adsorption of hydrocarbons and gases in well-defined zeolite pores with varying porosity was aimed at predicting adsorption entropy in confined porous spaces. The adsorption entropies of these molecules was determined by the occupiable volume incorporating the effect of zeolite network on adsorbed molecule entropy prediction. Recent interest involves studying the role of confinement on adsorption energetics and its effect on acid-catalyzed reactions in zeolite catalyst emphasizing the importance of complete understanding of adsorption energetics. Lercher and co-workers studied ethanol adsorption in H-ZSM-5 and examined the spectroscopic and thermochemical effect of the confinement of organic molecules. Through IR spectroscopy, they noticed a difference in the interaction of ethanol with itself, and the zeolite acid site. At higher loadings of ethanol, dimers and a protonated molecule was formed, while a hydrogen bonded monomer of ethanol was the product at lower loadings, they theorized this was due to the impact of enthalpy and entropy of adsorption, and investigated the contribution of adsorption energetics critical to the quantitative understanding of adsorption and confinement of hydrocarbons in zeolite. Marin and co-workers studied the monomolecular cracking of alkanes in zeolites and concluded that both the adsorption enthalpy and adsorption entropy are critical in understanding cracking rates, while Eder and co-workers studied the adsorption of alkane in acidic molecular sieves through IR spectroscopy and gravimetry investigating the effect on zeolite pore size on the heat of adsorption of alkanes. Common to all measurements of adsorbate entropy, is that adsorbing molecules need to attain adsorption-desorption equilibrium. This is a limitation for chemisorbed moieties where desorption is significantly slower than adsorption, preventing adsorption-desorption equilibrium from being achieved at experimentally feasible timescales. The study of chemisorbed species interactions is relevant due to their similarity with the transition states of most relevant zeolite catalyzed reactions, like alkane cracking to produce ethylene/propylene, important feedstock in the polymer industry. An approach to achieving adsorption-desorption equilibrium for chemisorbed species would therefore provide relevant information about their adsorption energetics, which can be extended to the understanding transition states for zeolite catalyzed reactions, lending ideas to tailor make these catalysts for particular chemistries.

The study of Lercher et al., showed experimental evidence of aiding desorption of chemisorbed species from a zeolite surface. In this study focused on methylamine production through the Bronsted acid sites of modernite zeolites, Lercher et al., realized that the formation of methylamine through amination of methanol was not the limitation to the reaction, rather desorption of the product from the active site. Under reaction conditions, they exposed the saturated methylamine surface to ammonia, using IR they could identify bands indicative of ammonium ion, displacing and eventually desorbing all of the methylamine from the surface of the catalyst. They termed this mechanism, adsorption-assisted-desorption. Other authors have discussed the concept of adsorption-assisted-desorption, as adsorbates of similar or different nature interact with catalyst surfaces. If one chemisorbed species can aid in the desorption of another from the acid site, at steady state, competitive adsorption would occur for interacting molecules on the acid site. With the idea of competitive adsorption applied to steady state reaction studies by Iglesia and co-workers stating that acid sites are incompletely saturated by either titrant (2-butanol or 2,6-di-tert-
butyl-pyridine) as they studied the genesis of BAS on a tungsten oxide catalyst, confirming the feasibility of the hypothesis. 56

Recognizing that adsorption-assisted desorption accelerates the effective rate of desorption, we sought to leverage this concept to study the equilibrated adsorption of molecule pairs. Here, we investigated the adsorption of alkylamines on the Brønsted acid sites of aluminosilicate zeolites as a model adsorption system, focusing on measuring energetic differences between chemisorbed alkylamines (Scheme 1). With adsorption equilibrium attained through adsorption-assisted desorption, the relationship between alkylamine chain length and adsorption energetics was examined. Reactive gas chromatography (RGC) 57 provided a measure of alkylamine coverages across a range of adsorption conditions, 58 which we rationalized through Langmuir isotherms to quantify adsorption energies. Controlling the Si/Al ratio of H-ZSM-5 to 140, differences in the energetics of mostly isolated adsorbed alkylammonium was measured, where a fixed energetic difference per methylene unit was observed.

Scheme 1. Competitive adsorption between isopropylamine and sec-butylamine over Brønsted acid sites, where relative coverages at equilibrium are dictated by relative free energies of adsorption. Coverages of the different alkylamines on the surface can be directly measured by quantifying their respective Hofmann elimination alkene product.

2. Experimental

2.1. Materials & Methods. Isopropylamine (99.5%, Sigma Aldrich), sec-butylamine (99%, Sigma Aldrich), sec-pentylamine (97%, Sigma Aldrich), n-heptane (99%, Sigma Aldrich), type 1 water (> 18.2 MΩ cm) using an in-house purifier, were used as adsorbates and/or for instrument calibration. He (99.999%, Airgas), Ar (99.999%, Airgas), N2 (99.999%, Airgas), Air (Ultra-zero, Airgas) were used as carrier gas and for zeolite pretreatment.

2.2. Zeolite pre-treatment. Ammonium-form ZSM-5 was obtained from Zeolyst International (CBV28014, Si/Al=140) and converted to its hydrogen form by ex situ calcination in a stream of air (100 sccm) at 823 K using a ramp rate of 2 K min⁻¹ for 10 hours. The calcination was performed in a downward flow quartz u-tube, where the flow of air was controlled by a mass flow controller (Brooks 5850). The zeolite temperature was monitored using a type K thermocouple encased in a quartz sheath, placed in contact with the zeolite bed. Details of the setup are provided in the supporting information (Sec. S1). To ensure a clean surface prior to adsorption, the zeolite bed was also calcined in-situ at 673 K with a ramp rate of 10 K min⁻¹ and 100 sccm of air.

2.3. Zeolite Pelletization. To control the particle size of zeolites, it was pelletized, broken, and sieved into different fractions. Typically, 100 mg of ex-situ calcined zeolite was loaded into the pellet setup with the zeolite sitting in between two mirror polished dice (13 mm diameter, Pike Technologies). The vertical hydraulic jack (YLJ-5-H, MTI Corporation), was used to pelletize the
zeolite with a pressure of ~20 Mpa, sufficient to form pellet without structural changes. The pelleted zeolite was carefully broken into small pieces using a Mortar & Pestle Agate, (89037-488, VWR), and sieved into the different pellet diameters using 3-inch sieves (EW-59985-13 and EW-59985-18, Cole Parmer) by shaking intermittently for 3-5 minutes.

2.4. Inlet liner microcatalytic reactor. We have previously demonstrated the use of gas chromatography (GC) inlet liners as microcatalytic reactors and employ the same procedure here. Briefly, the zeolite bed was placed between two plugs of deactivated quartz wool (Restek, 24324) within a commercially available quartz GC inlet liner (Agilent 5190-3165). The quartz wool served as an inert physical support as well as a dispersant for injected liquid adsorbates to efficiently vaporize, prior to contacting the zeolite. The zeolite bed was always located between 20 and 40 mm from the bottom of the liner to ensure accurate temperature control and a negligible axial temperature distribution (< 1 K). Unless otherwise noted, zeolite particles were pelleted to control their diameter between 500–1000 μm. Typically, ~20 mg of pelleted zeolite was loaded into the inlet liner microcatalytic reactor; the mass of the entire microreactor packed with quartz wool was measured before and after adding the zeolite sample to ensure accurate loadings.

2.5. Fractional Coverage. Reactive gas chromatography was used to measure the fractional coverage of alkylamines (θi) occupying Brønsted acid sites (Fig. 1). We have previously reported details of this method elsewhere for single adsorbates, used to estimate the BAS density of aluminosilicate zeolites. Briefly, the zeolite containing quartz liner described in Sec. 2.4 was placed in the inlet of a gas chromatograph (7890B, Agilent), where it was first calcined at 673 K, then cooled down in He to the temperature at which the fractional coverages are measured (Fig. 1A,D,G). Using an automated liquid sampler, a mixture of alkylamines was injected at 1 µL min⁻¹ into the 1000 sccm He carrier stream, creating an alkylamine vapor mixture with defined partial pressures (Fig. 1 B,E,G). The molar composition of the pre-made liquid alkylamine mixture was independently confirmed on a separate gas chromatograph equipped with an HP-5 column (19091J-413, Agilent) and flame ionization detector (FID), coupled with a quantitative carbon detector (Polyarc, Activated Research Company). The zeolite was then exposed to the alkylamine vapor mixture until saturation (typically 15 µL total dose volume), after which the zeolite bed was purged for two hours in He (1000 sccm) to remove any physisorbed species. Prior to raising the temperature of the zeolite in the inlet liner, the temperature of the GC oven containing the chromatographic column (19091-Q04, Agilent) was lowered to 303 K. Directing the microcatalytic reactor effluent through the GC column at a low temperature, along with a suitable choice of column stationary phase, trapped desorbing molecules from the zeolite surface. The temperature of the microcatalytic reactor was then ramped at a rate of 10 K min⁻¹ to 673 K and held for 30 minutes, allowing for the adsorbed alkylamines to either desorb intact or undergo a Hofmann elimination to their respective products (alkene + NH₃). The temperature of the GC column, containing the trapped molecules, was raised from 303 to 543 K at a ramp rate of 10 K min⁻¹ and held there for 10 minutes. Alkene peaks corresponding to the respective alkylamines was detected. Based on our prior measurements, the Brønsted acid site density of H-ZSM-5 (Si/Al = 140) is taken to be 100 μmol H⁺ g⁻¹. REGARDLESS OF THE ALKYLAMINE COMBINATION CO-ADSORBED, THE TOTAL BRØNSTED ACID SITE DENSITY MEASURED WAS FOUND TO REMAIN UNCHANGED (∑i nAlkene,i = nBAS), and the coverage of vacant sites to be zero (θv = 0, supporting information, Sec. S3). The strong interaction of alkylamines with Bronsted acid sites results in a completely saturated surface, even at relatively limited alkylamine partial pressures. The total moles of alkene evolved (∑i nAlkene,i) was therefore taken to be equal to the number of Brønsted acid sites (nBAS) occupied by the
corresponding alkylamine, allowing the fractional coverage of a particular alkylamine was estimated,

$$\theta_i = \frac{n_{\text{Alkene},i}}{n_{\text{BAS}}} \times \frac{n_{\text{Alkene},i}}{\sum_i n_{\text{Alkene},i}}$$ (1)

For example, with isopropylamine and sec-butylamine (Scheme 1), the fractional coverage of isopropylamine is equal to the moles of propene evolved divided by the total moles of propene and butene(s) evolved.

Figure 1. Reactive Gas Chromatography (RGC) to measure co-adsorbed alkylamine coverage. 

A. Bronsted acid sites  B. Isopropylamine and sec-butylamine adsorption on Bronsted acid sites, fractional coverages are determined by relative adsorption energetics and partial pressures.  
C. Reactive desorption via Hofmann elimination, forming propene, butene(s) and ammonia.  
D. Pre-treatment: Zeolite calcined in-situ at 673 K, cooled to co-adsorption temperature under helium atmosphere.  
E. Co-adsorption: An automatic liquid sampler (ALS) injects a predetermined mixture of alkylamines into a helium flow, creating a relative alkylamine partial pressure ($P_{\text{Alkylamine,1}}/P_{\text{Alkylamine,2}}$) that co-adsorbs on the zeolite surface, then purged to remove physisorbed amines.  
F. Fractional coverage: Linear ramp of zeolite containing liner to 673 K
while desorbing alkenes are trapped in the column held at 303 K. The column temperature is then linearly ramped to elute the trapped alkenes corresponding to the originally adsorbed alkylamines, and independently quantified via a flame ionization detector (FID).

2.6. Breakthrough Adsorption Assisted Desorption. About 50 mg of zeolite was placed in a 1/2″ quartz downflow packed bed u-tube, with the zeolite bed resting on a plug of deactivated quartz wool. The packed bed was placed within a ceramic furnace (VF-360-1.5-6-S, Thermcraft) controlled using a PID temperature controller (CN 7823, Omega) and a 1/16″ thermocouple encased in a quartz sheath, placed on top of the bed. The entire heated assembly was housed within a larger forced convection oven (5890 Series II, Hewlett Packard) held at 373 K. Gas flows were controlled by a mass flow controller (5850S, Brooks Instrument). The zeolite was calcined in-situ under 60 sccm of air at 823 K for 4 hours with a ramp rate of 5 K min\(^{-1}\) and then cooled to 423 K, before purging in 100 sccm of He for 15 minutes. Liquid-phase alkylamines were fed to distinct vaporization sections through a 1/16″ PEEK capillary line (0.01″ I.D., TPK110, Vici Valco) using a syringe pump (Masterflex EW-74905-04, ColeParmer) and air-tight glass syringe (Hamilton Company). The PEEK line was then connected to a 1/16″ stainless-steel capillary line (0.01″ I.D., T50C10D, Vici Valco) through a PEEK union (ZU1FPK, Vici Valco), and the other end of the stainless-steel capillary line was placed inside the oven. The vaporized liquid was constantly swept by a 100 sccm stream of He, which bypassed or adsorbed onto the zeolite bed as determined by a four-port switching valve (4-PV). Sec-butylamine was introduced as the initial adsorbate at 0.3 kPa in He (100 sccm) at 423 K for 30 minutes, where protonated sec-butylammonium formed on the zeolite surface, followed by a 2-hour purge in He to remove any physisorbed sec-butylamine. The second adsorbate, iso-propylamine (IPA) was then introduced into a He stream, in a different vaporization section, bypassing the zeolite containing packed bed at a partial pressure of 0.3 kPa. The bypass stream was analyzed with an online residual gas analyzer (XT200M, ExTorr) with IPA at a mass to charge ratio (m/z) of 44. After ~30 minutes, the IPA containing He stream was sent through the packed bed using the four-port switching valve (4-PV), exposing the zeolite bed with protonated sec-butylammonium (SBA\(^{+}\)) to IPA. Desorption of the initially adsorbed SBA, assisted by the adsorption of the IPA, was observed by tracking m/z signals 44 and 55 associated with IPA and SBA, respectively.

3. Results & Discussion. Alkylamines interact strongly with the BAS of aluminosilicate zeolites, resulting in a complete transfer of the Brønsted acidic proton of the bridging hydroxyl (ZOH), forming an alkylammonium ion (RNH\(_{3}^{+}\))\(^{65-70}\)

\[
\text{RNH}_{2} + \text{ZOH} \rightleftharpoons \text{ZO}^{-} \cdot \text{RNH}_{3}^{+} \tag{2}
\]

Alkylamine adsorption on a Brønsted acidic proton is typically accompanied by a relatively large enthalpy change; isopropylamine adsorsbs on H-ZSM-5 with an adsorption enthalpy (\(\Delta H_{\text{ads}}\)) of \(\sim\) 200 kJ mol\(^{-1}\).\(^{59}\) As a result, alkylamines and other related molecules like pyridine are frequently used as BAS poisons, adsorbing strongly enough to displace most other adsorbates (e.g. alcohols,\(^{57}\), \(^{71}\) alkanes,\(^{72, 73}\) alkenes\(^{74}\)). Therefore, alkylamine adsorption is commonly treated as irreversible at moderate temperatures (T < 600 K). Here, we hypothesize that despite the highly favorable adsorption of alkylamines on BAS, two distinct alkylamines can sufficiently compete for
adsorption on the same BAS, resulting in constant alkyamine adsorption/desorption until an equilibrated state is reached. To our knowledge, the molecular desorption of an alkyamine intact from an aluminosilicate BAS, or displacement by another adsorbate has not been demonstrated. It is therefore necessary to confirm whether two distinct alkylamines (e.g. IPA and SBA) can displace one another from a BAS.

3.1. Alkylamine Adsorption Assisted Desorption. While the exact mechanism by which the exchange of alkylamines could proceeds is unclear, we propose a potential mechanism based on the concept of adsorption assisted desorption. In the case where SBA is initially adsorbed, it first adsorbs and abstracts a proton from the Brønsted acid site to form a sec-butylammonium ion (SBA\(^+\)). When a second adsorbate like iso-propylamine is subsequently introduced, it abstracts a proton from SBA\(^+\) and forms iso-propylammonium (IPA\(^+\)). The overall process can be described through three elementary steps:

\[
\begin{align*}
SBA + ZOH & \rightleftharpoons ZO\cdot SBA^+ \quad (3) \\
IPA + ZOH & \rightleftharpoons ZO\cdot IPA^+ \quad (4) \\
IPA + ZO\cdot SBA^+ & \rightleftharpoons SBA + ZO\cdot IPA^+ \quad (5)
\end{align*}
\]

where ZOH and ZO\(^-\) represent the protonated and deprotonated state of the BAS, respectively. Eq. 3 and 4 represent the thermodynamic information associated with the distinct alkylamines adsorption. We propose that transfer of the proton from one alkylamine to another (Eq. 5) occurs in a concerted fashion, passing through an activated transition state (Scheme 2). Ultimately, iso-propylamine facilitates the displacement of sec-butylamine from the Brønsted acid site through adsorption assisted desorption.
Scheme 2. Alkylamine Adsorption Assisted Desorption over a Brønsted Acid Site

A. Adsorption of sec-butylamine onto an aluminosilicate Brønsted acid site, followed by a proton abstraction and its subsequent desorption by iso-propylamine.

B. Adsorption enthalpy of iso-propylamine and the relative adsorption enthalpy of sec-butylamine as it displaces iso-propylamine from the surface through an activated complex of both amines.

C. Adsorption entropy of iso-propylamine and the relative adsorption entropy of sec-butylamine as it displaces iso-propylamine from the surface, while forming an activated complex of both amines.

To investigate the possibility of alkylamine adsorption assisted desorption, a breakthrough type analysis of competitive alkylamine adsorption was leveraged. H-ZSM-5 with complete coverage of sec-butylamine (adsorbed as sec-butylammonium), was exposed through an instantaneous switch to an iso-propylamine containing helium stream in a continuous flow packed bed (Fig. 2). H-ZSM-5 was first saturated with a vapor phase stream of sec-butylamine at 423 K, resulting in a surface completely covered by sec-butylammonium moieties at all anionic bridging oxygen locations in the zeolite framework (Eq. 3). Once exposed to iso-propylamine, sec-butylamine was observed to desorb from the surface, replaced by iso-propylamine over the Brønsted acid sites (adsorbed as iso-propylammonium, Fig. 2). Increasing the temperature of the sec-butylammonium covered H-ZSM-5 to 498 K prior to iso-propylamine exposure led to similar observations of adsorption assisted desorption (supporting information, Sec. S4).
Figure 2. Isopropylamine assisted desorption of sec-butylamine on H-ZSM-5. Breakthrough of iso-propylamine adsorption assisted desorption over a sec-butyrammonium saturated H-ZSM-5 at 423 K. Effluent iso-propylamine and sec-butylamine were tracked through mass to charge ratios (m/z) of 44 and 55, respectively.

To verify that an initially adsorbed alkylamine was in fact displaced by a second adsorbing alkylamine, forming a distinct alkylammonium adsorbate, alkylammonium surface coverages in the course adsorption assisted desorption were quantitatively measured. Similar to the breakthrough analysis, H-ZSM-5 was first saturated with an alkylamine (initial adsorbate) and purged to remove any physisorbed species, followed by exposure to another distinct alkylamine (second adsorbate). Initial and second alkylamine adsorbates with distinct Hofmann elimination alkene products were selected, such that their respective coverages could be readily determined. Consistent with the observed displacement based on gas phase partial pressures (Fig. 2), the surface of H-ZSM-5 initially saturated with sec-butyrammonium, exhibited complete coverage of isopropylammonium once exposed to isopropylamine. The reverse was also found to be true, sec-butyramine as a second adsorbate quantitatively displaced isopropylammonium from the surface of H-ZSM-5. Regardless of alkylamine combination and sequence, distinct alkylamines were able to displace one another from a BAS (Table 1), suggesting that when multiple alkylamines are concurrently present, they continuously displace each other until an equilibrium coverage is attained. As a control, we examined second adsorbates more-weakly bound than alkylamines; both n-heptane and water were incapable of displacing sec-butyramine adsorbed on a Bronsted acid site (Table 1). The inability to displace sec-butyramine is not surprising given the large difference in proton affinity between n-heptane (680 kJ mol\(^{-1}\)) or water (691 kJ mol\(^{-1}\)) and sec-butyramine (927 kJ mol\(^{-1}\)). Similarly, Gorte et. al reported that n-hexane could not displace pyridine adsorbed on a BAS within H-ZSM-5, while the reverse was shown to be possible.\(^{75}\)
Table 1. Fractional coverages of alkylamines on H-ZSM-5 as exposed to initial and second adsorbates

<table>
<thead>
<tr>
<th>T[K]</th>
<th>Initial Adsorbate</th>
<th>Second Adsorbate</th>
<th>θ_{Initial}</th>
<th>θ_{Second}</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>SBA</td>
<td>IPA</td>
<td>0.94</td>
<td>0.06</td>
</tr>
<tr>
<td>473</td>
<td>IPA</td>
<td>SBA</td>
<td>0.99</td>
<td>0.01</td>
</tr>
<tr>
<td>498</td>
<td>SPA</td>
<td>IPA</td>
<td>0.84</td>
<td>0.16</td>
</tr>
<tr>
<td>423</td>
<td>IPA</td>
<td>SPA</td>
<td>0.99</td>
<td>0.01</td>
</tr>
<tr>
<td>473</td>
<td>SPA</td>
<td>SBA</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>423</td>
<td>SBA</td>
<td>SPA</td>
<td>0.97</td>
<td>0.03</td>
</tr>
<tr>
<td>423</td>
<td>SBA</td>
<td>n-heptane</td>
<td>1.00</td>
<td>n.m.</td>
</tr>
<tr>
<td>423</td>
<td>SBA</td>
<td>H₂O</td>
<td>1.00</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

IPA; isopropylamine, SBA; sec-butylamine, SPA; sec-pentylamine.

3.2. Alkylamine Competitive Adsorption. Having established alkylamine adsorption assisted desorption, through sequential exposure, the competitive adsorption of gas phase alkylamine mixtures on Brønsted acid sites in H-ZSM-5 was examined. Measuring the fractional coverages of two distinct adsorbing alkylamines provides a measure of their relative adsorption energetics. It is therefore necessary to ensure that measured fractional coverages are not influenced by non-thermodynamic contributions. Given the relative dimensions of MFI pores and alkylamine molecular diameters, the potential influence of mass transfer was examined. Changes in total pressure, while fixing relative alkylamine partial pressure, lead to no measurable change in the distribution of alkylamine fractional coverage (Fig. 3A); alkylamine coverages on the surface are only dictated by vapor phase mole fractions. Similarly, the average H-ZSM-5 pellet diameter was inconsequential to the measured fractional coverage (Fig. 3B). Conversely, the flow rate of the vapor phase from which alkylamines adsorbed on H-ZSM-5 was found to influence measured fractional coverages; increasing the flow rate from 10 - 1000 sccm led to an increase in the fractional coverage of isopropylammonium (Fig. 3C). Beyond a vapor phase flow rate of ~100 sccm, no measurable change in fractional coverage was observed. An increased flow rate likely increases the rate of alkylamine diffusion to Brønsted acid sites from the bulk vapor phase, relative to the rate of adsorption assisted desorption. The flow rate of all subsequent fractional coverage measurements was therefore fixed at 1000 sccm.

The kinetics of adsorption assisted desorption and/or diffusion into the pore may necessitate a larger molar exposure to ensure complete coverage. Here, we define the extent of exposure as the moles of amine exposed to the zeolite, normalized by the zeolite Al molar content,

\[
\text{Extent of Exposure} = \frac{n_{\text{amine}} \cdot \text{exposure}}{n_{\text{Al}}} \quad \text{[moles of alkylamine exposed]} \quad \text{moles of bulk Al in zeolite}
\]

Where \( n_{\text{amine}} \), \( \text{exposure} \), and \( n_{\text{Al}} \), are the amine molar flowrate, exposure time, and the moles of Al available in the zeolite bed over which adsorption assisted desorption takes place. As the exposure time increases, the moles of amine that the zeolite is exposed to increases, allowing for fractional coverages to equilibrate as dictated by relative adsorption energetics. Indeed, as the extent of sec-butylamine exposure increased, even beyond stoichiometric requirements, the fractional coverage of sec-butylammonium increased while that of iso-propylammonium decreased (Fig. 3D). The relative trend observed with increasing extent of sec-butylamine exposure is consistent with a slower rate of diffusion, relative to the smaller iso-propylamine. We note that a similar conclusion can be reached from the breakthrough measurements in Section 3.1, where the effluent partial pressure of adsorbing iso-propylamine achieves steady state well before that of the displaced sec-
butylamine (Fig. 2). As a result, extents of exposure in excess of an order of magnitude were utilized to ensure fractional coverage measurements not influenced by mass transfer.

Figure 3. Fractional coverage of IPA (△), and SBA (○) on H-ZSM-5 at 423 K and P_{IPA}/P_{SBA} = 3 as a function of A. He carrier gas flow rate B. Alkylamine extent of exposure (Eq. 7) C. Average zeolite pellet diameter D. Total pressure, P_{IPA}/P_{SBA} = 50.

3.3. Relative Energetics of Alkylamine Adsorption. Using the established parameters in the previous section, the competitive adsorption of isopropylamine and sec-butylamine on H-ZSM-5 was carried out between 373-498 K, varying the relative partial pressure of adsorbates (P_{IPA}/P_{SBA}) from 0.5 – 50 (Fig. 4). Under the adsorption conditions considered, the Brønsted acid sites of H-ZSM-5 were completely covered by both adsorbates (θ^* = 0, supporting information, Sec. S3).
Here, we rationalize alkylamine fractional coverages through a dual-adsorbate Langmuir isotherm (supporting information, Sec. S5),

$$\theta_i = \frac{1}{1 + \frac{P_i}{P_i^0} \exp \left( \frac{\Delta G_{ads,i}^0 - \Delta G_{ads,j}^0}{RT} \right) }$$

(8)

$$\Delta G_{ads,i} - \Delta G_{ads,j} = \Delta \Delta H_{ads,ij} - T \Delta \Delta S_{ads,ij}$$

(9)

where an alkylamine’s fractional coverage ($\theta_i$) is dictated by its vapor phase partial pressure ($P_i$) and adsorption free energy ($\Delta G_{ads,i}$). By comparing predicted ($\theta_{i,\text{Predicted}}$) and measured ($\theta_{i,\text{Measured}}$) fractional coverages, the relative adsorption enthalpy ($\Delta \Delta H_{ads,ij}$) and entropy ($\Delta \Delta S_{ads,ij}$) were fit through a least square regression (Fig. 4A). All confidence intervals for fitted values were reported at a 95% confidence level. Despite the similar nature of alkylamine adsorption, the additional methylene unit results in a significant adsorption energetic difference; sec-butylamine loses more entropy than isopropylamine upon adsorption ($\Delta \Delta S_{ads} = 24 \pm 7$ J mol$^{-1}$ K$^{-1}$) but is more enthalpically stabilized ($\Delta \Delta H_{ads} = 19 \pm 3$ kJ mol$^{-1}$). As a result, a relative partial pressure in excess of one order of magnitude ($P_{IPA}/P_{SBA} > 10$) is needed for IPA to command a larger fractional coverage than SBA on the Bronsted acid sites of H-ZSM-5 (498 K, Fig. 4B). Extending the length of the carbon chain over a similar range of experimental conditions (373-498 K, $P_{SBA}/P_{SPA} = 0.5$-46, Fig. 4C,D), sec-pentylamine loses more entropy than sec-butylamine upon adsorption ($\Delta \Delta S_{ads} = 25 \pm 7$ J mol$^{-1}$ K$^{-1}$) but is more enthalpically stabilized ($\Delta \Delta H_{ads} = 18 \pm 3$ kJ mol$^{-1}$). A more favorable enthalpy of adsorption and the accompanying loss in entropy with increasing chain length, creating a compensation effect between the two thermodynamic quantities, is consistent with prior reports of other hydrocarbon adsorbates in zeolites.81, 82
Figure 4. Alkylamine co-adsorption over H-ZSM-5

A. Parity plot comparing measured and predicted coverages of IPA at 373 K (■), 423 K (●), 473 K (▲) and 498 K (◇), based on a two-adsorbate competitive Langmuir adsorption isotherm for IPA and SBA.

B. Fractional coverages of IPA (■) and SBA (●) as a function of their relative partial pressure at 498 K, dashed line indicates the total coverage.

C. Parity plot comparing measured and predicted coverages of SBA at 373 K (■), 423 K (●), 473 K (▲) and 498 K (◇), based on a two-adsorbate competitive Langmuir adsorption isotherm for SBA and SPA.

D. Fractional coverages of SBA (●) and SPA (▲) as a function of their relative partial pressure at 498 K, dashed line indicates the total coverage.

ΔΔH_{ads} = 19 ± 3 kJ mol^{-1}

ΔΔS_{ads} = 24 ± 7 J mol^{-1} K^{-1}
3.4. Predicted and Measured Adsorption Energetics. With the assumed thermodynamic nature of alkylamine adsorption assisted desorption, the measured relative adsorption energetics are expected to behave as state functions,

\[
\Delta \Delta H_{\text{ads},ij} = \Delta \Delta H_{\text{ads},ik} + \Delta \Delta H_{\text{ads},kj} \quad (10)
\]
\[
\Delta \Delta S_{\text{ads},ij} = \Delta \Delta S_{\text{ads},ik} + \Delta \Delta S_{\text{ads},kj} \quad (11)
\]

where i, j, and k are three distinct adsorbing alkylamines. Here, we compared the relative adsorption energetics of IPA, SBA, and sec-pentylamine (SPA, Fig. 5A). Taking the measured IPA-SBA (1) and SBA-SPA (2) relative adsorption enthalpy, the predicted IPA-SPA (3) relative adsorption enthalpy of 37 kJ mol\(^{-1}\) is in excellent agreement with an experimentally measured value of 36 kJ mol\(^{-1}\) (Fig. 5B). Similarly, the predicted and measured IPA-SPA relative entropy of adsorption were found to be in excellent agreement (49 and 56 J mol\(^{-1}\) K\(^{-1}\), respectively). As expected for thermodynamic quantities, any combination of alkylamine adsorbates provide a consistent relative enthalpy and entropy of adsorption.

![Figure 5. Relative adsorption energetics of IPA, SBA, and SPA A. Relative energy levels of adsorbed isopropylammonium, sec-butylammonium, and sec-pentylammonium B. Comparison of measured and predicted IPA-SPA relative adsorption enthalpy and entropy.](https://doi.org/10.26434/chemrxiv-2023-5kzdk)

### Table: Predicted and Measured Adsorption Energetics

<table>
<thead>
<tr>
<th></th>
<th>(\Delta \Delta H_{\text{ads}}) [kJ mol(^{-1})]</th>
<th>(\Delta \Delta S_{\text{ads}}) [J mol(^{-1}) K(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IPA-SBA(^n)</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>SBA-SPA(^n)</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>IPA-SPA(^n)</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>IPA-SPA(^n)</td>
<td>36</td>
</tr>
</tbody>
</table>

3.5. Alkylamines and Alkanes. Comparing the relative adsorption energetics of the two distinct alkylamine pairs (IPA /SBA and SBA/SPA), a fixed contribution to the overall enthalpy and entropy of alkylamine adsorption per methylene unit is apparent. With each increasing methylene unit in the alkylamine carbon chain, an additional enthalpic stabilization of \(\sim 19\) kJ mol CH\(_2\)\(^{-1}\) was experienced (Fig. 6A). Previous investigations on alkane adsorption in H-ZSM-5 reported an enthalpic stabilization of \(\sim 10\) kJ mol CH\(_2\)\(^{-1}\)\(^8,24,82-85\) attributed to lateral interactions between the alkanes and the lattice oxygen of zeolites. The change in alkane adsorption enthalpy was also accompanied by an entropic loss of \(\sim 10\) J mol CH\(_2\)\(^{-1}\) K\(^{-1}\), resulting from the additional confinement experienced by alkane adsorbates with increasing chain length.\(^82,86\) For the primary alkylamines in this work, each additional methylene unit lead to an additional 25 J mol CH\(_2\)\(^{-1}\) K\(^{-1}\) entropic penalty (Fig. 6A). Similar energetic trends therefore exist across the two homologous...
adsorbate families, albeit, with larger enthalpic and entropic contributions per methylene unit for alkylamines (Fig. 6B). One possible explanation for the larger enthalpic stabilization per methylene unit in alkylamines is their larger proton affinity relative to alkanes (~ 900 vs ~ 600 kJ mol⁻¹), which can play a role even for the adsorption of weakly basic alkanes on aluminosilicate surfaces. While alkanes adsorb on Brønsted acid sites through weaker interactions like hydrogen bonding, alkylamines abstract the proton to form alkylammonium ions on the zeolite surface (Eq. 2, Fig. 6C). Nevertheless, the similar trends in methylene contribution to adsorbate energetics suggest that Van der Waal interactions between adsorbates and the host zeolite environment are also likely responsible for changes in alkylamine adsorption energetics with chain length.

![Figure 6. Adsorption Energetics per Methylene Unit of Alkanes and Alkylamines.](https://doi.org/10.26434/chemrxiv-2023-5kzdk)

**Figure 6.** Adsorption Energetics per Methylene Unit of Alkanes and Alkylamines. A. Parity plot comparing experimentally measured coverages of sec-alkylamines (IPA, SBA, and SPA) and the predicted coverages based on two adsorbate competitive Langmuir adsorption isotherm for IPA-SBA (●), and SBA-SPA (○), fitted to a single relative adsorption enthalpy and entropy per mol CH₂. B. Adsorption enthalpy and entropy increment per mol CH₂ for alkylamines and alkanes over H-ZSM-5. C. Proton abstraction of alkylamines to form alkylammonium ions, and alkane interaction with the proton of an aluminosilicate zeolite.

4. **Conclusion.** While typically considered irreversible, alkylamine adsorption on aluminosilicate Bronsted acid sites was demonstrated to be reversible through adsorption assisted desorption. Under conditions free of any significant transport limitations, the competitive adsorption of distinct alkylamine pairs allowed adsorption-desorption equilibria to be approached over H-ZSM-5 (Si/Al = 140), facilitating the measurement of the relative adsorption thermodynamics of the alkylamine pair on mostly isolated Bronsted acid sites. Fractional coverages of alkylamines competitively adsorbing onto H-ZSM-5 demonstrate that under reversible conditions, alkylamine adsorption is quantitatively described by a Langmuir isotherm. Across the adsorption of isopropyl, sec-butyl, and sec-pentylamine, each additional methylene (-CH₂) unit provides a fixed enthalpic stabilization and entropic penalty. We propose that the enthalpy and entropy associated with methylene units results from electrostatic interactions between adsorbate alkyl chains and their surrounding pore environment, qualitatively similar to
alkane adsorption in zeolites. While enthalpic information has previously been reported for adsorbed alkylamines, the ability demonstrated here to measure adsorbate entropy will provide new information to aid the design of heterogeneous catalysts.

**Supporting Information.** Details of the experimental setup, fractional coverage measurements, and isotherm derivations are available in the supporting information.

**References**