

**MOLECULAR MODELING OF ETHER ADSORPTION IN
ZSM-5 ZEOLITES**

**M.Sc. Thesis by
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Department : Chemical Engineering

Programme : Chemical Engineering

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**ZSM-5 ZEOLİTLERİNDEKİ ETER ADSORPSİYONUNUN
MOLEKÜLER DÜZEYDE MODELLENMESİ**

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FOREWORD

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ABBREVIATIONS

AA	: All atoms
AUA	: Anisotropic united atoms
CBMC	: Configurational bias Monte Carlo
COMPASS	: Condensed-phase optimized molecular potential for atomistic simulation studies
CVFF	: Consistent-valence force field
DAY	: Dealuminated Y
DEE	: Diethyl ether
DIPE	: Diisopropyl ether
DME	: Dimethyl ether
DMOE	: 1,2-dimethoxyethane
DPE	: Dipropyl ether
EME	: Ethyl methyl ether
EOS	: Equation of state
EPA	: Environmental Protection Agency
EU	: European Union
GAC	: Granular activated carbon
GCMC	: Grand Canonical Monte Carlo
GEMC	: Gibbs ensemble Monte Carlo
LJ	: Lennard-Jones
MC	: Monte Carlo
MTBE	: Methyl tertiary butyl ether
NOM	: Natural organic matter
NPT	: Isothermal-isobaric ensemble
NVT	: Canonical ensemble
PCFF	: Polymer consistent force field
TraPPE-UA	: Transferable potentials for phase equilibria-united atoms
UA	: United atoms
USA	: United States of America
VLE	: Vapor-liquid equilibrium
VOC	: Volatile organic compound

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LIST OF SYMBOLS

A	: Helmholtz free energy
c	: Molecular conformation
c_0, c_1, c_2, c_3	: Torsion (Fourier) coefficients
C_p	: Specific heat at constant pressure
C_v	: Specific heat at constant volume
E	: Potential energy
$E_{liq(inter)}$	: Molar intermolecular potential energy of liquid phase
F	: Error function
G	: Gibbs free energy
H	: Enthalpy
k_B	: Boltzmann constant
k_{bend}	: Bending constant
N	: Number of particles or molecules
n	: Number of values that is to be calculated
p	: Momentum
p	: Number of parameters optimized at once
P	: Pressure
p	: Probability
P_0	: Reference pressure
P_{acc}	: Acceptance probability
P_{sat}	: Saturated vapor pressure
q	: Partial charge
Q	: Sum of Boltzmann factors
Q_{st}	: Isosteric heat of adsorption
r	: Distance
R	: Ideal gas constant
r	: Position
S	: Entropy
s	: Statistical uncertainty
T	: Temperature
u	: Increase in potential energy with addition of a particle
U	: Potential energy
u_{bend}	: Bending energy
U_{ext}	: Intermolecular potential energy
U_{int}	: Intramolecular potential energy
u_{LJ}	: Lennard-Jones force center interaction energy with system
u_{tors}	: Torsion energy
V	: Volume
X	: A property
y	: Potential parameter
β	: Probability density (Boltzmann factor)
δ	: Distance of LJ force center from carbon nucleus
ΔH^o	: Isosteric heat of adsorption

ΔH_{vap}	: Molar vaporization enthalpy
ΔU	: Change in potential energy
ΔU_{ext}	: Intermolecular potential energy change
ΔV	: Volume change
ε	: LJ well depth
θ	: Bending angle
θ_0	: Equilibrium bending angle
μ	: Chemical potential
μ_{i0}	: Chemical potential of an ideal gas of molecule i
ρ	: Phase density
ρ	: Probability density
σ	: LJ size
ϕ	: Dihedral angle
ϕ_i	: Fugacity coefficient

MOLECULAR MODELING OF ETHER ADSORPTION IN ZSM-5 ZEOLITES

SUMMARY

Oxygenate content is needed in gasoline to burn it more completely in order to decrease harmful gases. Methyl tertiary butyl ether (MTBE) is a fuel additive that is used as oxygenate. Its blending characteristics and the economical reasons have played important roles on selecting MTBE as oxygenate in gasoline. One of the main properties of MTBE is its solubility in gasoline, water, alcohol and other ethers.

After its usage at high concentrations in gasoline, unexpected acute health symptoms were reported in the United States of America (USA) during the winter of 1992-1993. In addition to the health complaints, long term animal studies and the contamination reports to the water supplies from underground storage tanks in 1996 in the USA, made the authorities focus on MTBE. It was also discovered that MTBE caused a variety of cancer types in animals. Beyond these, the detection of MTBE in many water resources has interested the scientists for the removal studies. The adsorption of MTBE onto surfaces is one of the possible treatment processes. The adsorption processes have the advantage of producing no byproducts. High-silica zeolites, such as ZSM-5 and its all silica analogous silicalite, have successfully separated MTBE from water in the previous works.

Molecular simulation methods are widely used in chemical engineering to determine thermophysical properties. Particularly, Grand Canonical Monte Carlo simulations have been widely used to model adsorption of guest molecules in various nanoporous materials. Predicting MTBE adsorption in ZSM-5 zeolites accurately requires effective force field for ether molecules. Recently developed model, transferable potentials for phase equilibria-united atoms model, has inconsistent pseudo atom sizes in sequence. This disadvantage is thought to harm different molecular simulation applications of ethers. Thus, the new parameters were derived with anisotropic united atoms (AUA) model, which the force centers of the pseudo atoms are placed between the carbon and the hydrogen atoms. AUA model is considered as more advantageous than the classical united atoms model. Ether parameters were derived via vapor-liquid equilibrium calculations in Monte Carlo simulations. Force field parameters were optimized by the minimization of the quadratic error function by the gradient method. Therefore, it needed the partial derivatives of the functions with respect to the potential parameters. These derivatives were calculated by the statistical fluctuations method. After the derivation of ether parameters, the transferability of them was tested for the molecules that were not used in the optimization process.

Adsorption of MTBE molecules in ZSM-5 zeolites was investigated in comparison with the silicalite, in this work. Sodium atom(s) was/were utilized as the extraframework cation(s) in ZSM-5 zeolites. Adsorption simulations, which were carried out up to the normal boiling point of water with the AUA force field, predicted the isotherms successfully in silicalite, demonstrating the accuracy of the

force field for adsorption simulations at moderate temperatures. MTBE adsorption increased with decreasing Si/Al ratio. Despite changing of the loadings with temperature, a saturation capacity was determined at 4 MTBE molecules per unit cell for all temperatures and zeolites. MTBE molecules were seen to be placed at the intersections.

ZSM-5 ZEOLİTLERİNDEKİ ETER ADSORPSİYONUNUN MOLEKÜLER DÜZEYDE MODELLENMESİ

ÖZET

Oksijen içeriği, zararlı gazları azaltmak için, benzini daha fazla yakmak üzere benzin içerisinde ihtiyaç duyulur. Metil tersiyer bütül eter (MTBE) oksijenleyici olarak kullanılan bir yakıt katkısıdır. Harmanlanma özellikleri ve ekonomik sebepler, MTBE'nin benzin içerisinde oksijenleyici olarak seçilmesinde önemli roller oynamıştır. MTBE'nin temel özelliklerinden bir tanesi, benzin, su, alkol ve diğer eterler içerisindeki çözünürlüğüdür.

Benzin içerisinde yüksek derişimlerde kullanılmasından sonra, Amerika Birleşik Devletleri'nde (ABD) 1992-1993 kışı sırasında beklenmeyen akut sağlık bulguları rapor edilmiştir. Sağlık şikayetlerine ek olarak, uzun dönem hayvan çalışmaları ve 1996'da ABD'de su kaynaklarına yeraltı depolama tanklarından karışma raporları yetkililerin MTBE üzerine odaklanmasını sağlamıştır. Ayrıca MTBE'nin hayvanlarda çeşitli kanser türlerine sebep olduğu keşfedilmiştir. Bunların ötesinde, MTBE'nin birçok su kaynağında saptanması, bilim insanlarının giderme çalışmalarına ilgisini çekmiştir. MTBE'nin yüzeyler üzerinde adsorplanması, mümkün olan işleme süreçlerinden bir tanesidir. Adsorpsiyon süreçleri yan ürün üretmemeye getirisine sahiptir. ZSM-5 ve onun tamamen silikalı benzeri olan silikalit gibi yüksek silikalı zeolitler, önceki çalışmalarda MTBE'yi sudan başarılı bir şekilde ayırmıştır.

Moleküler benzetim yöntemleri, termofiziksel özelliklerin belirlenmesinde, kimya mühendisliğinde geniş bir biçimde kullanılmaktadır. Özellikle, Büyük Kanonik Monte Karlo benzetimleri, konuk moleküllerin çeşitli nanogözenekli malzemelerdeki adsorpsiyonunun modellenmesinde geniş bir şekilde kullanılmaktadır. ZSM-5 zeolitlerinde MTBE adsorpsiyonunu isabetli olarak tahmin etmek, eter molekülleri için etkin kuvvet alanı gerektirir. Henüz geliştirilmiş olan, faz dengeleri için transfer edilebilir poteansiyeller-birleşik atomlar modeli, sıralama olarak tutarsız pseudo atom büyüklüklerine sahiptir. Bu dezavantaj, eterlerin farklı moleküler benzetim uygulamalarına zarar verdiği düşünülmektedir. Dolayısıyla; yeni parametreler, pseudo atomların kuvvet merkezinin karbon ile hidrojen atomları arasında yer aldığı anizotropik birleşik atomlar (ABA) modeli ile türetilmiştir. ABA modeli klasik birleşik atomlar modeline göre daha avantajlı olduğu düşünülmektedir. Eter parametreleri buhar-sıvı dengeleri hesaplamaları aracılığıyla Monte Karlo benzetimlerinde türetilmiştir. Kuvvet alanı parametreleri, eğim yöntemi aracılığıyla ikinci dereceden hata fonksiyonunun minimize edilmesi ile optimize edilmiştir. Dolayısıyla, optimizasyon fonksiyonların potansiyel parametrelere göre kısmi türevlerine ihtiyaç duyar. Bu türevler istatistiksel dalgalanmalar yöntemiyle hesaplanmıştır. Eter parametrelerinin türetilmesinden sonra, transferedilebilirlikleri optimizasyon sürecinde kullanılmayan moleküllerde test edilmiştir.

MTBE moleküllerinin ZSM-5 zeolitlerindeki adsorpsiyonu bu çalışmada silikalitle karşılaştırmalı olarak araştırılmıştır. Sodyum atomu/atomları ZSM-5 zeolitlerindeki

ekstra iskelet yapısı katyonu/katyonları olarak kullanılmıştır. ABA kuvvet alanı ile suyun normal kaynama noktasına kadar gerçekleştirilen adsorpsiyon benzetimleri, kuvvet alanının orta sıcaklıklarda adsorpsiyon benzetimlerindeki isabetini gösterir bir biçimde, silikalitte izotermi başarıyla tahmin etmiştir. MTBE adsorpsiyonu azalan Si/Al oranı ile artmıştır. Yüklemelerin sıcaklıkla değişmesine rağmen, birim hücrede 4 MTBE molekülü doygunluk kapasitesi, bütün sıcaklık ve zeolitlerde belirlenmiştir. MTBE moleküllerinin kesişimlerde yer aldığı görülmüştür.

1. INTRODUCTION

Oxygenate content is needed in gasoline to burn it more completely in order to decrease harmful gases, carbon monoxide and ozone. The oxygen in gasoline also helps to reduce the gasoline components, such as sulfur and aromatics. Methyl tertiary butyl ether (MTBE) is a fuel additive that is used as oxygenate. Its blending characteristics and the economical reasons have played important roles on selecting MTBE as oxygenate in the motor fuel [1,2]. MTBE is synthetic, aliphatic ether which is synthesized via the reaction of methanol and isobutylene. Structural formula of MTBE can be seen in Figure 1.1. It is a volatile organic compound (VOC) with high flammability. MTBE, whose vapor may form explosive mixtures with air, is considered to be a moderate fire risk. Irritating, corrosive or toxic gases may be produced with the resulting fire. It is also unstable in acid solutions. MTBE is a colorless liquid at room temperature with a characteristic odor. One of the main properties is its solubility in gasoline, water, alcohol and other ethers. Its solubility in water is approximately 50 g/L at room temperature. No necessity for physical mixing in gasoline provides the advantage for long term usage as a commercial solvent in gasoline fuel [1,3].

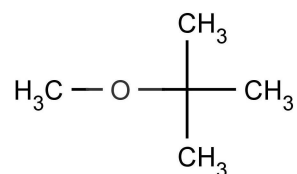


Figure 1.1 : Structural formula of methyl tertiary butyl ether

The production of MTBE started commercially in Italy in 1973 [4]. MTBE has been used since 1979 instead of lead. It has been present in gasoline at high concentrations (up to 15 % by volume) since 1992 so as to meet the standard oxygenate requirements. [1,2]. However, unexpected acute health symptoms were reported in the United States of America (USA) during the winter of 1992-1993 after the usage of high concentrated gasoline. In addition to the complaints, long term animal studies and the contamination reports to the water supplies from underground storage tanks

in 1996 in the USA, made the authorities focus on MTBE. The reports on contamination into the water resources in several regions of the country and the reduction of water supplies due to MTBE, caused to phase out the usage as fuel additive in 2002 in some states of the USA [5]. There have been several other states in the USA, which have taken action against MTBE usage, including the populous states [6]. MTBE content was limited to 7 % by volume in the commercial fuel in Japan [7], while the Danish government agreed with the petroleum industry to phase it out in 92- and 95-octane gasoline. The failure of agreement implementation would result with a tax increase in MTBE [8]. However, the European Union (EU) made no restrictions regarding the report of European Chemicals Bureau. They just proposed additional tests and reactive measurements, such as preventing the fuel releases from underground storage tanks [9].

Investigations about the effects of MTBE have gaining an increasing attention owing to the health concerns over humans and the other living things. Although there are not sufficient studies on humans, large number of investigations has been done over animals, especially on mice and rats. It has been found to cause a variety of cancer types, such as kidney, liver and testicles cancers in animals. Neurotoxic, allergic, and respiratory problems in humans from water and air were reported. Headache, anxiety, inability to concentrate, dizziness, ear, nose and throat irritation, skin rashes, sneezing and breathing problems, shortness of breath and bronchitis were the effects observed in humans. The reasonable concentration range in drinking water for taste and odor concerns was advised by Environmental Protection Agency (EPA) as 20-40 $\mu\text{g/L}$. However, the values change according to the sensitivity of people. The advised range was said to be undesirable for long range health concerns. The taste of MTBE in water was reported as nasty, bitter, nauseating and like rubbing alcohol [2,3].

MTBE can contaminate water supplies easily because of its high aqueous solubility. This feature also provides it not to be lumped together in the soil unlike the most of the other gasoline components. Swift transport through the soil, increase the environmental cost. Its resistance to chemical and biological degradation in water and its small size are the other source of the spreading. Underground storage tank damages are one of the reasons of water and soil pollution. Transfer or transportation spills, exhaust emissions and traffic accidents are the possible causes of air pollution by MTBE. Raining or precipitation of MTBE from air transfers it

onto the surface water supplies. It is important to emphasize that 5-10 % of VOC emissions of the gasoline burning vehicles is constituted by MTBE. Although there are not reliable data in food, food is not anticipated as an essential MTBE source of exposure [1,2,3].

The environmental and the health concerns make the scientists study on the removal of MTBE, which can be carried out by variety of treatment processes. Air stripping is a way of MTBE removal from water. MTBE is transferred from aqueous phase to the aero phase by the absorption columns [10]. Although air stripping is a cost-friendly method, and is the least effected with the water quality; the disposal of the waste gas is problematic for the environmental issues, and the low temperature operations become less effective [10]. Advanced oxidation processes, such as ultraviolet/H₂O₂ [10], and O₃/H₂O₂ [10,11] systems, deactivate MTBE through the oxidation agents. In addition, these processes produce hazardous byproducts. Removal of these byproducts enhances the costs [10,11]. The adsorption of MTBE onto surfaces is an alternative treatment process. No byproducts are produced and it is easy to use. Activated carbon is widely used in water purification. However, the activated carbon does not show a good performance at removing MTBE. Biological growth and competitive sorption of the other components are also the disadvantages of this material [10,12]. Microporous materials, especially high-silica zeolites have given prospective results for successfully separating MTBE from water. Some of those studies are introduced in the second chapter. It is noted that theoretical works in this area are very rare.

Molecular simulation methods are widely used in chemical engineering to determine thermophysical properties. They represent the bulk systems in very small systems with a few nanometers size. These methods fill the gap between experimentally-obtained properties and molecular structure [13]. The adsorption of hydrocarbons in zeolites interest scientists especially for separation processes in petrochemical applications. Grand Canonical Monte Carlo (GCMC) simulations can model the adsorption of hydrocarbons in zeolites [14,15]. Monte Carlo (MC) methods have become very effective not only in qualitative analysis, but also in quantitative analysis with the development of successful force fields for predicting equilibrium properties of molecules.

The objective of this study is modeling MTBE adsorption in ZSM-5 zeolites utilizing MC methods. The adsorption isotherms were plotted for the organophilic zeolites. A special ZSM-5 zeolite that has no aluminum is called silicalite. Investigation of the effect of Si/Al ratio on adsorption phenomenon constitutes the important part of this study.

In order to predict MTBE adsorption accurately, effective force field is needed for ether molecules. As vapor-liquid equilibrium (VLE) has an important part in chemical engineering applications, derivation of ether parameters via VLE calculations in MC simulations can be a nice way of obtaining MTBE force field for adsorption simulations. Therefore, a new set of parameters were created for short ethers and the transferability of them was tested for the molecules that were not used in the optimization process.

2. BACKGROUND

Considering the environmental and the health concerns, several scientists have studied the adsorption of methyl tertiary butyl ether (MTBE) on a variety of adsorbents. Microporous materials have been widely utilized in those researches, since they have utmost advantages for separation processes: The main characteristic of microporous adsorbents is the selectivity for certain types of molecules. This provides an extraordinary separation degree that cannot be acquired by the conventional materials. Therefore, the required membrane area is diminished when membranes are employed for separation. Adsorption processes, especially microporous materials, do not need extreme conditions, thus energy consumptions are lowered. Such materials are also readily-available and have very low investment costs in addition to the low energy costs. Some of those studies are summarized in this section.

Adsorption of MTBE solution, containing also chloroform and trichloroethylene, was studied on different adsorbents, including mordenite, ZSM-5, faujasite and activated carbon, by Anderson [16]. Anderson pointed out that mordenite was the most successful one at removal of MTBE from water with 96 %, while faujasite was the worst. ZSM-5 came after mordenite with 63 % removal. This was explained by the fact that mordenite had low electrostatic charge and larger pores, which easily accommodate MTBE molecules [16].

Methanol-MTBE mixture separation was investigated in MFI zeolites by Noack *et al.* [17]. They showed that MTBE had a molecular diameter of 0.63 nm, which was larger than that of the MFI pore (0.55 nm). Thus, they claimed that MTBE molecules should not have passed through the MFI pores effectively. It was also determined that more MTBE molecules entered the pores of ZSM-5, comparing to the silicalite pores. Caro *et al.* [18] explained these findings by the MTBE transport through the defects of the crystal layers of the zeolite.

Li and coworkers [19] studied the MTBE adsorption in siliceous beta zeolite. Siliceous beta has a three dimensional, 12-membered ring with 0.71×0.73 nm sized

pores. This hydrophobic zeolite removed 95 % of MTBE from water at 298 K though 30 minutes of equilibration period. Increasing Si/Al ratio of the beta zeolites was observed to enhance the separation of MTBE from water [19].

A detailed study with zeolites was published in 2004 by Erdem-Şenatalar *et al.* [20]. Zeolites whose $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ranged from 80 to 1000 (silicalite has a value, minimum 1000) were used as adsorbents in comparison with activated carbon. Considered zeolite types were silicalite, mordenite, zeolite beta and dealuminated Y (DAY). Silicalite was found to be the best at low concentrations, which are the most encountered cases in contaminated water resources. Its saturation capacity was determined as 15.5 % while activated carbon had about 90 % saturation capacity. Mordenite came after silicalite. All the isotherms at low concentrations were linear. DAY type zeolite showed the best performance at high concentrations although it was the worst of all at low concentrations. This was due to the residence of water molecules in the DAY pores at low concentrations. The results about the silicalite were contrary to the previous works asserting that the passage of MTBE molecules was impossible through silicalite. Their explanation for this finding was that although the z-dimension of the molecule is larger than the pores, a slight deformation of the molecules or vibrations in the crystal lattice might be the reason of MTBE molecules' residence in the pores, in addition to the possibility of crystal defects. It was concluded that high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and small pores were the main factors of efficient adsorption at low concentrations and; high hydrophobicity and large pores were required to get high capacities at higher concentrations [20].

In another recent study, adsorption capacities of mordenite and two types of carbonaceous resins were tested by Hung and Lin [21]. They suggested that natural organic matter (NOM) could reduce the performance of adsorbents. Groundwater and surface water was used in comparison with deionized water. Hung and Lin postulated that the natural waters contained NOM; without showing any water analysis [21]. However, NOMs in water have different molecular sizes and types, such as simple organic acids and short-chained hydrocarbons. NOMs that come from humans usually are made up of from one third to one half of the dissolved carbon in water. They have various functional groups such as carboxylic and phenolic groups, and different aromatic rings [22]. MTBE was added into those water patterns prior to the experiments. The competition effect of NOM molecules was not found

significant in mordenite for all water sources and in one type of resin for groundwater. It was thought that NOM molecules could not enter the pores of those adsorbents. Mordenite had a slower adsorption kinetics compared to the other adsorbents due to its smaller pore sizes [21].

Rossner and Knappe [23] studied on silicalite, coconut-shell-based granular activated carbon (GAC) and spherical carbonaceous resin adsorbents for MTBE removal from ultrapure water. River water was also used to see NOM effect on silicalite and GAC. Silicalite and the resin demonstrated better sorption performance than GAC. Sorption capacity was found to have reverse effect on sorption kinetics, related to the pore size, as determined by Hung and Lin [21].

Considering slow mass transport through the zeolites due to their small pores, Lu *et al.* [24] planned to investigate MTBE adsorption on nano zeolite composites. They immobilized silicalite seeds on two sorts of silica-rich supporters, diatomite and fly ash cenosphere. Because of more silicalite content (about twice), fly ash cenosphere mixture had maximum adsorption capacity approximately twice of diatomite. Although synthesis of fly ash cenosphere mixture was more energy-saving, diatomite composite was more economical due to its cheaper organic template. The authors expressed that both of the supporters were economical and environmentally friendly, and could be used for large scale applications. However, fly ash cenosphere might have contained trace of heavy metals [24].

Gironi *et al.* [25] researched the adsorption of MTBE + air, 1-methylbutane + air and MTBE + 1-methylbutane + air mixtures, since atmospheric MTBE is one of the reasons of water contaminations, especially for surface waters. It is mainly produced by motor exhaust gases and vapor emissions at gasoline stations. Adsorbing MTBE and hydrocarbon vapors via activated carbon could be a solution. Activated carbon had 55 % and 45 % maximum adsorption capacity by weight for MTBE and 1-methylbutane, respectively. When the ternary mixtures were examined, 1-methylbutane existence decreased the adsorption of MTBE [25].

There are only a limited number of theoretical studies in the literature on MTBE adsorption. One of them was a simulation study done by Yazaydın and Thompson [26]. Adsorbents, silicalite, mordenite, and zeolite beta, were investigated in addition to the effect of Na⁺ cation loadings. They used the transferable potentials for phase

equilibria-united atoms (TraPPE-UA) [27] force field to model molecular interactions. Silicalite and zeolite beta adsorbed more than mordenite at very low pressures. Zeolite beta was the best at high pressures, while mordenite and silicalite had close saturation values. The capacity of zeolite beta was measured as three times larger than that of silicalite and mordenite. The larger pores of the zeolite beta were the reason of this phenomenon, determined by the snapshots. The effect of Na^+ cation was not found important. However, it enhanced the loadings- except for mordenite- at very low pressures owing to the oxygen atom of MTBE molecule. Selecting aluminum atoms close to each other in mordenite made the Na^+ cations plug the pores, preventing MTBE molecules. The researchers also expressed the importance of aluminum atoms' position in zeolite beta. Though the loadings were close to each other at high pressures, the zeolite which had the aluminum atoms far from each other adsorbed more at low pressures in zeolite beta. This was the same as the case in mordenite [26].

Ahunbay *et al.* [28] carried out a combined simulation and experimental study. Pure MTBE adsorption was implemented in silicalite at different temperatures. They showed that polymer consistent force field (PCFF) [29] predicted the isotherm better than the other force fields- applied in the work- at 298 K. Experimental and simulated results confirmed Yazaydin and Thompson's work [26] that silicalite had a maximum 4 molecules per unit cell loading. The adsorption simulations were also repeated at higher temperatures (425-600 K). It agreed well with the experiments, especially at low temperatures and high pressures. However, it failed at high temperatures and low pressures (at lower loadings). Possible effects of silicalite symmetry transition were also investigated, but no important change was observed [28].

3. MONTE CARLO SIMULATIONS

Molecular simulation is a set of computational methods that calculates interactions of molecules whose structure is explicitly defined. It is interested in the molecular systems which range from less than 1 nanometer to 1 micrometer; therefore it is a part of nanotechnology. Molecular simulation methods have been widely used in chemical engineering in order to determine thermophysical properties of little known systems. They help scientists to comprehend the relation between molecular structure and property differences. They have been now seen as the gap filler between experimental data and engineering models, especially for unknown chemicals, tough conditions of temperature, pressure, toxic substances and so on, by the chemical industry. Although the scale of the molecular simulation systems are so small compared to the real systems, molecular simulation often represents chemical reactions, equilibrium and transport properties successfully. Disordered systems such as gases and liquids are well predicted in addition to regular structures such as microporous adsorbents and catalysts [13,30].

Monte Carlo (MC) is a molecular simulation method used so as to calculate equilibrium properties. The name, Monte Carlo, comes from the famous casino town of Monaco, reminding the generation of random numbers. MC methods take only the configuration space into account. The configuration space is linked to the statistical method, which contain the probability distribution. Particles of microscopic systems make irregular movements owing to the collisions with the other particles. However, these movements are present in macroscopic systems although they cannot be seen by naked eyes. Equilibrium properties of microscopic systems fluctuate owing to these movements although those fluctuations in the properties can't be measured easily for macroscopic systems. Thus, macroscopic equilibrium systems and their representative microscopic systems are related by statistical thermodynamics [13,30].

3.1. Statistical Ensembles and Partition Function

The collection of multiple snapshots of any microscopic system to derive average properties is called a statistical ensemble. In more clear words, a statistical ensemble is a collection of distinct states of the system which are different with regard to the positions and velocities of the component particles. The phase space is called the space of all possible system states. A suitable probability distribution must be used to represent a real system with a statistical ensemble. Statistical ensembles are summarized in Table 3.1 with their specific properties [30].

Table 3.1 : Statistical ensembles, adapted from Reference [30]

Statistical ensemble	Imposed variables	Associated thermodynamic potential	Probability density	Applications
Canonical ensemble	N, V, T	$A = E - TS$ (Helmholtz free energy)	$\exp(-\beta E)$	Phase properties ($P, H, C_v, \mu, \dots$)
Grand canonical ensemble	μ_i, V, T	PV (i.e. $E - TS - \sum \mu_i N_i$)	$\exp \left(-\beta E + \beta \sum_i \mu_i N_i \right)$	Adsorption isotherms, selectivities
Isothermal-isobaric ensemble	N, P, T	$G = H - TS$ (Gibbs free energy)	$\exp(-\beta E - \beta PV)$	Phase properties ($H, C_p, \rho, \mu, \dots$)
Gibbs ensemble at imposed global volume (m phases)	$N = N_I + \dots N_m,$ $V = V_I + \dots V_m,$ T	$A = E - TS$ (Helmholtz free energy of the whole system)	$\exp(-\beta E)$	Phase equilibrium of pure components and mixtures
Gibbs ensemble at imposed pressure (m phases)	$N = N_I + \dots N_m,$ P, T	$G = H - TS$ (Gibbs free energy of the whole system)	$\exp(-\beta E - \beta PV)$	Phase equilibrium of mixtures

The statistical average of a property X (volume, energy,...) is calculated through an arithmetic average of the configurations as seen Equation 3.1, after enough number of configurations are produced [13].

$$\langle X \rangle = \frac{1}{n} \sum_{i=1}^n X_i \quad (3.1)$$

Probability density (or Boltzmann factor) for all ensembles are shown in Table 3.1. The expression β in the Boltzmann factors is defined as $\beta = 1/(k_B T)$, where k_B is the Boltzmann constant ($k_B = 1.381 \times 10^{-23}$ J/K) and where T is the temperature. According to the Boltzmann factor, low energy is more favorable than high energy and temperature increases the distribution of energy. Thus, the probability of a given state is defined as division of the probability density by the partition function. The partition function, Q , is the sum of the Boltzmann factors for all possible different states in the phase space (Equation 3.2). The expression, $N! = 2 \times 3 \times 4 \times \dots \times N$, comes from the possible combinations of N particles with the same state. It is a function of position, r , and momentum, p , of each state, i [30].

$$Q = \frac{1}{N!} \sum_{r_i} \sum_{p_i} \text{probabilitydensity}(r_i, p_i) \quad (3.2)$$

The canonical (NVT) ensemble is used for a system with imposed volume (or known density) and temperature for monophasic fluids to determine the properties such as energy, pressure and chemical potential. The isothermal-isobaric (NPT) ensemble is used to calculate phase properties such as monophasic fluid density at known pressure and temperature. Gibbs ensemble is employed for the systems that have more than one phase so as to compute their phase equilibrium properties by either imposing the total volume or the total pressure. Although number of particles may change in any simulation boxes due to the transfer move, the total number of particles does not vary. When adsorption of substances in a solid adsorbent system is needed to compute, the grand canonical ensemble must be performed. The temperature, the volume and the chemical potential of the system must be imposed. In this ensemble, the number of the adsorbate particles can vary different to the other ensembles [13,30].

3.2. The Metropolis Algorithm

MC simulations are executed by random moves. However, it is a kind of gambling where a trick is used. In order to get a meaningful probability distribution, an

appropriate criterion must be used. This biased criterion, which is called the Metropolis algorithm, compares the change of the system from i state to j state. After a random standard move is applied, the new configuration is accepted or rejected to get the most likely states. The principle of the Metropolis algorithm is defined with the Equation 3.3:

$$P_{acc}(old \rightarrow new) = \min\left(1, \frac{\rho_{new}}{\rho_{old}}\right) \quad (3.3)$$

where P_{acc} is the acceptance probability and ρ is the probability density. In classical definition of MC, the number of accessible configurations is important to get the most probable states. However, it is impossible to determine it in an infinite three dimensional space. Therefore, the Metropolis algorithm uses the ratio of the new configuration probability density to the old configuration probability density (Equation 3.4 for an NVT ensemble). It helps to find the systems with minimum energy. The minimum limit of the probability must be defined for the case that the energy of the new configuration is larger than old one. If the probability is lower than the defined value, the new configuration is rejected and the old one is added to the ensemble [30-32].

$$P_{acc}(old \rightarrow new) = \min(1, \exp(-\beta(U_{new} - U_{old}))) \quad (3.4)$$

3.3. Monte Carlo Moves and Configurational Bias

3.3.1. Translation

Translation is the most widely used basic move in MC simulations. The particle moves without any change in internal conformation. This move can be applied to more than one particle at the same time, but it is generally applied to one particle simultaneously. A random molecule is selected, and a random translation vector is selected. The vector comprises three dimensional displacement values. These values must be lower than the dimensions of the simulation box, in reasonable finite interval. If the parameters are very large, the new configuration probably has high energy and as a result it will be rejected. If they are very small, the potential energy change is likely small. Thus, the most moves will be accepted; but it will not sample

the configuration space properly. After the selections are made, the Metropolis algorithm takes up the duty [30,32].

3.3.2. Rotations

There are two sorts of rotation moves in MC methods. One of them is internal rotation. The rotation angle is usually very limited due to the high energy shift with conformational rotation. The angle and the molecule are selected randomly as in the translation move. Internal rotation move can be applied on flexible or semi-flexible bending or torsion. This move is very important to relax the internal structure while the bending and torsion parameters do not represent the structure decently. It can also be very useful in adsorption simulations to curl the molecules in the pores of adsorbents. The Metropolis algorithm is utilized in this move [31,32].

The second type of the rotation is rigid body rotation. The internal conformation of the molecule does not change while the molecule rotates with the randomly selected limited angle. It doesn't matter whether the molecule is flexible or rigid; because the bending and torsion angles are preserved. The Metropolis acceptance rule is valid here, too [30,31].

3.3.3. Volume change

Although the volume of a molecular system changes in NPT ensembles, the volume of each phase boxes can change in Gibbs ensembles. However, the total volume in Gibbs ensembles is kept while fluctuating in NPT ensembles. Random volume change value, ΔV , is selected in a limited region. This value can either be negative or positive. The conformational properties unchanged in this move. This is supplied by proportional coordinate change of the force centers, resulting with a kind of translation move of the particles. The Metropolis algorithm is used in volume change moves. Equation 3.5 shows the acceptance criterion for NPT ensembles. It is similar for Gibbs ensembles as seen in Equation 3.6. A and B refer the simulation boxes of two phases [30,32,33].

$$P_{acc}(old \rightarrow new) = \min \left(1, \left(\frac{V + \Delta V}{V} \right)^N \exp(-\beta(U_{new} - U_{old} + P\Delta V)) \right) \quad (3.5)$$

$$P_{acc} = \min \left(1, \left(\frac{V^A + \Delta V}{V^A} \right)^{N^A} \left(\frac{V^B - \Delta V}{V^B} \right)^{N^B} \exp(-\beta(\Delta U^A + \Delta U^B)) \right) \quad (3.6)$$

3.3.4. Configurational bias Monte Carlo moves

Configurational bias Monte Carlo (CBMC) method overcomes the problem where the Metropolis algorithm is insufficient. When a new particle is added to the system, the energy of the system will change so much that the probability of the new move is declined. Building a molecule partially or totally is impossible with the Metropolis algorithm. Thus, the probability of the move is calculated by rate of the probability density of the selected position to the sum of the increase in the probability densities of all possible (or tried) positions (Equation 3.7):

$$p(r_i) = \frac{\exp(-\beta u(r_i))}{\sum_{k=1}^{k_{\max}} \exp(-\beta u(r_k))} \quad (3.7)$$

$u(r_k)$ represents the increase in potential energy with the addition of the new particle in position r_k . $k_{\max}$ is the number of tested possible locations. Either CBMC method or the Metropolis method includes the Boltzmann factor. This provides the realism of the configuration presence at the considered temperature. CBMC is a good way to build flexible linear or branched molecules. However, it is problematic for cyclic molecules owing to low acceptance ratio of closing the ring. CBMC is also used with insertion and deletion, transfer, partial regrowth, reptation and displacement moves [30,32].

3.3.4.1. Transfer

Characteristic of the Gibbs ensemble is transfer move. Purpose of this move is to equal the chemical potentials of the phases. It is implemented through deleting a randomly selected molecule from one phase and inserting it into a randomly selected location in the other phase. The transfer move of molecule i from simulation box A to box B has an acceptance probability displayed in Equation 3.8. N_i^A and N_i^B are the number of molecules in the specified phase before the transfer move. ΔU^A and ΔU^B are the change in potential energy for the phase A and B, respectively [30,32].

$$P_{acc}(transfer) = \min\left(1, \frac{N_i^A V^B}{V^A (N_i^B + 1)} \exp(-\beta(\Delta U^A + \Delta U^B))\right) \quad (3.8)$$

3.3.4.2. Insertion-deletion

The number of type i molecules fluctuates in Grand Canonical Monte Carlo (GCMC) ensemble. Adsorption characteristics of a phase are determined mainly by this way. So, the insertion and deletion moves supply the fluctuation of the molecule number in the adsorbent phase. Both of the moves must be tried with the same weight in order to acquire a proper probability distribution [30].

In insertion move, a randomly selected type i molecule is inserted in a random position. However, after the first bead of the molecule is inserted, the other beads of the molecule are built by CBMC technique. The acceptance criterion of this move is shown in Equation 3.9:

$$P_{acc}(insertion) = \min\left(1, \frac{VP_0}{(N_i + 1)k_B T} \exp(-\beta(\Delta U_{ext} - \overline{\mu_i}))\right) \quad (3.9)$$

where the chemical potential is introduced as $\overline{\mu_i} = \mu_i - \mu_{i0}$ (μ_{i0} is the chemical potential of an ideal gas of molecule i at temperature T under reference pressure P_0) and where ΔU_{ext} is the external potential energy change with the move ($\Delta U_{ext} = U_{ext}^{new} - U_{ext}^{old}$). Pressure and chemical potential increase the acceptability of the insertion, while temperature and density (with the number of molecules and high energy change) reduce it [30].

In deletion move, a randomly selected type i molecule is destroyed from the simulation box. If very high loading are accepted with insertion move, this is used to equilibrate the system. The acceptance criterion of deletion can be seen in Equation 3.10. The parameters of the criterion affect the acceptance rate with the opposite effect of the insertion parameters as expected [30].

$$P_{acc}(deletion) = \min\left(1, \frac{N_i k_B T}{VP_0} \exp(-\beta(\Delta U_{ext} + \overline{\mu_i}))\right) \quad (3.10)$$

3.3.4.3. Partial regrowth

Partial (internal) regrowth move is employed to flexible molecules. This move is implemented by cancelling a part of the molecule up to the end of it, and regrowing the destroyed part randomly via CBMC technique as described in Equation 3.7. [30].

3.4. Reservoir Bias

When CBMC is useless for building or rebuilding molecules, a reservoir containing molecular conformations solves the problem. Reservoir consists of molecules that are built according to Boltzmann distribution of internal energies. Reservoir bias can be utilized for branched molecules so as to improve the efficiency of CBMC through selecting the trial positions in accordance with the bending angles of the molecules in the reservoir. Reservoir bias is applied with the following steps: In the first step, very simple particle (usually the bigger particle in the molecule) is tested in random k positions. The most probable location is selected with a probability criterion (Equation 3.11), which is similar to that of CBMC:

$$p(r_i) = \frac{\exp(-\beta u_{LJ}(r_i))}{\sum_{k=1}^{k_{\max}} \exp(-\beta u_{LJ}(r_k))} \quad (3.11)$$

where u_{LJ} is the Lennard-Jones (LJ) force center interaction energy with the system. Then, different molecular conformations, c_k , are taken from the reservoir randomly and inserted into the system with the center of mass that is selected in the first step. The selection probability is described as in Equation 3.12:

$$p(c_i) = \frac{\exp(-\beta U_{ext}(c_i))}{\sum_{k=1}^{k_{\max}} \exp(-\beta U_{ext}(c_k))} \quad (3.12)$$

The selected final position is accepted or declined according to the criterion of the move [30]. Once regrowing a molecule, the location of each particle is selected according to bending angles in the reservoir with partial regrowth move acceptance criterion.

3.5. Molecular Force Field

Kinetic energy is not calculated in MC simulation, because the kinetic energy is a function of time. However, MC method relates with equilibrium state that do not change with time. Therefore, the total energy, E , is considered as the potential energy, U . The total potential energy is the sum of intramolecular energy (internal energy, U_{int}) and intermolecular energy (external energy, U_{ext}) [30]. Intramolecular energy consists of bending and torsion potential in this study. Stretching energy is neglected, keeping the bond lengths constant. In addition, distant neighbor potential is calculated in intermolecular energy as in all the other MC works. Intermolecular potentials in this study contain electrostatic and dispersion-repulsion energy.

Three particles which have two bonds form bending energy with the angle θ between two successive bonds. The equation for calculating the bending energy is a kind of harmonic potential (Equation 3.13). θ_0 is the equilibrium bending angle, k_{bend} is the bending constant and k_B is the Boltzmann constant in this equation [30].

$$\frac{u_{bend}}{k_B} = \frac{1}{2} k_{bend} (\theta - \theta_0)^2 \quad (3.13)$$

Torsion energy is constituted by four beads which have three bonds. The minimum torsion energy is generally obtained at a dihedral angle ϕ of 180° for trans configurations. The expression for the torsion energy is shown in Equation 3.14. c parameters are the Fourier (torsion) coefficients [30].

$$\frac{u_{tors}}{k_B} = \frac{c_0}{k_B} + \frac{c_1}{k_B} [1 + \cos(\phi)] + \frac{c_2}{k_B} [1 - \cos(2\phi)] + \frac{c_3}{k_B} [1 + \cos(3\phi)] \quad (3.14)$$

The molecules that have permanent electrostatic charges are represented with electrostatic potential in its intermolecular energy. The partial charges are located at the selected sites in the molecule. The total electrostatic charge in the molecule must be zero, except for the ions. The main feature of the electrostatic interactions is that it is long-ranged potential and more effective than repulsive-dispersive interactions for distant particles. Equation 3.15 shows the Coulomb's law to calculate the electrostatic energy for a pair of groups. q is the partial charge on the specified

group, $\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ and r is the distance between the two groups [30].

$$u(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (3.15)$$

Dispersion-repulsion energy is essential part of the intermolecular energy. This is generally modeled with power law. The cohesion of liquids or adsorptions of solids are defined with dispersive (attractive) forces. When dispersive forces are more effective, different expressions can be applied. Repulsive term saves the molecules from overlapping one another. The mostly used dispersion-repulsion model is LJ 6-12 equation. Repulsion-dispersion interactions between two atom groups, i and j , are represented in Equation 3.16. Lorentz-Berthelot combining rules (Equation 3.17-18) are employed so as to acquire the common LJ parameters. r , ϵ , and σ are the separation, LJ well depth, and LJ size, respectively, for the specified pair of groups [30-32].

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3.16)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (3.17)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (3.18)$$

4. OPTIMIZATION OF NEW ETHER FORCE FIELD

Vapor-liquid equilibrium (VLE) is the state that liquid and vapor phases coexist. It is the most commonly encountered coexisting phases in industrial applications. VLE calculations in chemistry and chemical engineering are implemented by empirically-based thermodynamic equation of state (EOS) and/or liquid-state activity coefficient models as conventional methods [34,35]. Molecular simulation techniques are powerful tools for predicting equilibrium properties of molecules. Monte Carlo (MC) methods are used for this purpose [13]. Therefore, the development of accurate and efficient potential models for representing molecular interactions is essential to acquire accurate thermodynamic predictions by molecular simulation techniques to match the industrial needs [36, 37].

All atoms (AA) model, which describes each atom by a separate (Lennard-Jones) LJ force center, is realistic, but very expensive way of simulating most of the hydrocarbons [38-40]. Consequently, several authors [41-43] have made use of united atoms (UA) model. In this model, the carbon atom and its hydrogen atoms are shown with a single LJ force center, which is positioned at the center of the carbon atom [36,37].

An alternative method to represent a molecule for potential calculations is anisotropic united atoms (AUA) model, which was proposed by Toxvaerd [44,45]. Force center of the pseudo atom is located between the carbon and the hydrogen atoms (with distance, δ , from the carbon nucleus). This model has been developed for several hydrocarbons, yielding good results over a large range of carbon numbers and temperatures. This allows to predict equilibrium and transport properties more accurately for variety of molecules and temperatures due to the contribution of the hydrogen atoms [36,37,46-49].

Investigation of the thermophysical properties of ethers has been gaining considerable attention. Aliphatic ethers and polyethers are used as gasoline additives and as cosolvents in supercritical fluids. They are also present in chromatographic stationary phases, and generally present in nonionic surfactants [27]. Ethers have

boiling points that are close to the hydrocarbons with the same molecular weight. However, their boiling point is lower than the alcohols with the same molecular weight [50]. Experimental data exists only for low molecular weight ethers or for larger ethers only at low temperatures because of their thermal decomposition. It is important to apply the same potential to lots of different molecules that comprise the same groups (transferability of the potential) in the point of industrial view for molecular simulation. Therefore, molecular simulation using empirical force field can determine the physical properties of larger ethers at high temperatures [27,36].

Stubbs *et al.* [27] developed transferable force field with UA representation for ethers. However, LJ parameters of the model are inconsistent with the size of the pseudo atoms. This disadvantage is thought to harm different molecular simulation applications of ethers, such as determination of adsorption properties. In addition, AUA model is considered as more advantageous than UA model. Therefore, the aim of the present article is to develop AUA force field parameters for ethers, and to test their transferability for longer chained ethers.

4.1. Simulation Method

4.1.1. Potential energy and structural models

Intermolecular dispersion-repulsion interactions between two atom groups were represented effectively by the LJ 6-12 model, using the Lorentz-Berthelot combining rules. In addition to the LJ interactions, intermolecular potential was described by the Coulombic interactions. The partial charges were obtained from Reference [51]. They were only used for the oxygen atoms and the groups neighboring the oxygen atoms. However, the charges were located on the nucleus of oxygen and carbon atoms as Javier utilized. The LJ parameters of the hydrocarbon groups, which are the neighbors of the groups with carbon atoms, were supplied from Reference [36], while the LJ parameters of the oxygen atom were acquired from Reference [51].

The bond lengths between the atom groups were assumed constant, and the intramolecular interactions were calculated by the contributions of bending, torsion, and distant neighbor interaction energies. The distant neighbor energy between groups separated by more than three bonds was considered in the LJ intermolecular interactions, which was described with the AUA potential parameters. The constant

bond lengths were from Reference [27] and [36]. The torsion parameters were used from Reference [27], as the bending parameters. All the force field parameters used in this study are given in Table 4.1-4.

Table 4.1 : Bond lengths for ether molecules

Bond type	Bond length (Å)
CH _x -CH _y	1.535
C-CH _x	1.54
CH _x -O	1.41

Table 4.2 : Force field parameters for bending interactions

Bending type	θ_0 (degree)	k_{bend} (K)
CH _x -CH _y -O	112	50300
CH _x -O-CH _y	112	60400
CH _x -CH ₂ -CH _y	114	62500
CH _x -CH-CH _y	112	62500
CH _x -C-CH _y	109.47	62500

Table 4.3 : Force field parameters for torsion interactions

Torsion type	ϕ (degree)	c_0/k_B (K)	c_1/k_B (K)	c_2/k_B (K)	c_3/k_B (K)
CH _x -CH _y -O-CH _z	180	0	725.35	-163.75	558.20
CH _x -CH ₂ -CH ₂ -O	180	0	176.62	-53.34	769.93
O-CH ₂ -CH ₂ -O	180	503.24	0	-251.62	1006.47

Table 4.4 : Force field parameters for nonbonded interactions

Type of force center	σ (Å)	ϵ/k_B (K)	δ (Å)	q (e)
CH ₃	3.6072	126.2264	0.21584	0.185726785
CH ₂	3.5412	80.5143	0.3891	0.185726785
CH	3.4125	41.36	0.681	0.185726785
C	3.345	4.9529	0	0.185726785
O	2.991	59.69	0	-0.37145357
CH ₃ (neighboring the group with carbon atom)	3.6072	120.15	0.21584	0
CH ₂ (neighboring the group with carbon atom)	3.4612	86.29	0.38405	0

4.1.2. Statistical ensembles and Monte Carlo algorithms

The MC simulations were executed in the Gibbs and the isothermal-isobaric (NPT) ensembles with periodic boundary conditions using the minimum image conventions [30, 31]. A spherical cutoff radius that was equal to half of the simulation box length, with standard long range corrections, was applied for the pair-wise potential interaction calculations. For Ewald summation method, parameters k_{max} and n_q were set as 7 and 2, respectively. Ether molecules were considered as flexible and

configurational bias Monte Carlo (CBMC) technique was used in the simulations. It should be noted that regrowth of branched ether molecules was considerably difficult due to strong intramolecular interactions. Therefore, sufficient trial numbers were employed in formation of reservoir and in CBMC moves for all ether molecules. In addition, the angles for the trials of reservoir formation were assigned carefully in branched molecules.

4.1.3. Gibbs ensemble simulations

The phase equilibria calculations above the boiling point of ethers were carried out via the Gibbs ensemble Monte Carlo (GEMC) method. The basic idea of the method is utilizing two different simulation boxes in order to imitate two phases. These boxes have no interaction with each other. This provides the neglecting of the interface effects. The equalization of the chemical potentials of the vapor and the liquid phases is needed for equilibrium condition. The idea of simulating two boxes at the same time retrieves trial of several simulations for equalizing the chemical potentials [33].

Translation, rigid body rotation, internal rotation, transfer, volume change, and configurational bias partial regrowth moves were applied. Total volume of the simulation boxes were always kept constant, though the volume of the phase boxes changed. A two-step statistical bias was used to complete the simulations. In a first step, $1-4 \times 10^6$ iterations were performed for relaxation of the system. In a second step, $13-25 \times 10^6$ moves were tried to obtain the statistical averages. Transfer moves were not implemented in the first steps, while the probabilities of transfer moves were set as 39.5 % and 49.5 % for dimethyl ether and for the other ether molecules, respectively. The probabilities of the other moves were distributed equally, except volume change moves that were set as 5 %. The simulations were performed with a total number of 220 molecules per system.

The average liquid density was calculated from the ratio of the average mass of the liquid simulation box to its volume. Vapor pressure of the system was computed from the average pressure in the vapor simulation box. Another important equilibrium property, the molar vaporization enthalpy was determined via the difference between the average molar enthalpies of the liquid and the vapor simulation boxes.

The statistical uncertainties of the equilibrium properties were calculated through the block averaging technique [30-32]. The uncertainties were estimated with 99 % confidence. The critical temperature was estimated, after the computation of the phase densities, by fitting the critical scaling law (Equation 4.1). The critical density was determined from the law of rectilinear diameters (Equation 4.2), using the critical temperature calculated with the scaling law. λ and γ represent the constants, determined by minimizing the total of square errors.

$$\rho_l - \rho_v = \lambda (T_c - T)^{0.325} \quad (4.1)$$

$$\frac{1}{2} (\rho_l + \rho_v) = \rho_c + \gamma (T - T_c) \quad (4.2)$$

4.1.4. Equilibrium properties below the normal boiling point

Low-temperature simulations were performed via the NPT ensemble to determine the saturated liquid properties. It is due to the fact that, the acceptance ratio of transfer moves in the Gibbs ensemble is very low for reduced temperatures lower than 0.6, which correspond to the temperatures below the boiling point [46,47]. The simulations were carried out with a two-step statistical bias. $1-2 \times 10^6$ iterations were used in a first step for relaxation of the system, and $10-20 \times 10^6$ iterations were used in a second step for calculating the statistical averages, using monophasic simulation boxes for each system. The probabilities of volume change moves were set as 5 %, while translation, rigid body rotation, internal rotation and configurational bias partial regrowth moves were set as equal to one another. The simulations were performed with 200 molecules per system.

The molar vaporization enthalpy at low temperatures was obtained from Equation 4.3:

$$\Delta H_{vap} = - \langle E_{liq(int er)} \rangle + RT \quad (4.3)$$

where $\langle E_{liq(int er)} \rangle$ is the average molar intermolecular potential energy in the simulation. The equation comprises two assumptions: (i) the molar volume of the liquid phase is very low compared to the vapor phase and (ii) the vapor is an ideal gas. These assumptions are true below the normal boiling point due to the low density of the saturated vapor [37,46,47].

The saturated vapor pressure was determined by the thermodynamic integration of the Clapeyron equation with a second order numerical integration algorithm. Therefore, the temperatures of the NPT ensemble were selected to secure constant intervals in $1/T$ scale. The Clapeyron equation was integrated with the following form (Equation 4.4):

$$\left(\frac{d \ln P_{sat}}{d(1/T)} \right) = - \frac{\Delta H_{vap}}{R} \quad (4.4)$$

Integrating Equation 4.4 gave Equation 4.5:

$$\ln P_{sat}^{(n+2k)} = \ln P_{sat}^{(n)} - \frac{2}{R} \Delta \left(\frac{1}{T} \right) \sum_{i=1}^k \Delta H_{vap}^{n+2i-1} \quad (4.5)$$

where $\Delta(1/T) = 1/T_i - 1/T_{i+1}$ and n is the temperature where a Gibbs ensemble simulation was implemented [46,47,52].

4.1.5. Optimization method of force field parameters

Force field parameters of ethers were optimized by the minimization of the quadratic error function by the gradient method. Thus, it needed the partial derivatives of the functions with respect to the potential parameters. These derivatives were calculated by the statistical fluctuations method [53].

The error criterion (Equation 4.6) is the maximum likelihood criterion [36,37,46,48,53] which contains the uncertainties:

$$F = \frac{1}{n} \sum_{i=1}^n \frac{(X_i^{calc} - X_i^{exp})^2}{s_i^2} \quad (4.6)$$

where s_i is the estimated statistical uncertainty on the calculated variable, X_i^{calc} , and where X_i^{exp} is the experimental value. n is defined as the number of points that were used for optimization. F is a function of the optimized force field parameters. The minimum condition for the error criterion is that every partial derivatives of F with respect to potential parameters y_j must be zero (Equation 4.7):

$$\frac{\partial F}{\partial y_j} = \frac{1}{n} \sum_{i=1}^n \frac{2(X_i^{calc} - X_i^{exp}) \frac{\partial X_i^{calc}}{\partial y_j}}{s_i^2} = 0 \quad \text{for } j = 1, \dots, p \quad (4.7)$$

where p is the number of the parameters optimized at once. Using the first-order Taylor expansion of X_i^{calc} around the starting point, y^0 , of the optimization gives Equation 4.8:

$$X_i^{calc}(y^0 + \Delta y) = X_i^{calc}(y^0) + \sum_{k=1}^p \frac{\partial X_i^{calc}(y^0)}{\partial y_k} \Delta y_k \quad \text{for } i = 1, \dots, n. \quad (4.8)$$

where $\Delta y_k = y_k - y_k^0$. Thus the minimum condition becomes as Equation 4.9:

$$\sum_{i=1}^n \frac{\left(X_i^{calc}(y^0) - X_i^{exp} + \sum_{k=1}^p \frac{\partial X_i^{calc}}{\partial y_k} \Delta y_k \right) \frac{\partial X_i^{calc}}{\partial y_j}}{s_i^2} = 0 \quad (4.9)$$

The partial derivatives, $\frac{\partial X_i^{calc}}{\partial y_k}$, were determined by the fluctuations method [53].

The experimental values used in this work were obtained from Reference [54], which was the pseudo-experimental correlations database. The molar vaporization enthalpy with liquid density values in NPT ensemble and liquid density with the natural logarithm of the saturated vapor pressure values in Gibbs ensemble were used in the optimization. The optimization process started with CH group parameters in diisopropyl ether (DIPE) molecule. Then, diethyl ether (DEE), dimethyl ether (DME) and methyl tertiary butyl ether (MTBE) potential parameters were optimized, respectively. Finally, the optimized parameters were tested on ethyl methyl ether (EME), dipropyl ether (DPE), and 1,2-dimethoxyethane (DMOE).

4.2. Results and Discussions

The new optimized intermolecular AUA potential parameters for ethers were utilized to predict the thermodynamic properties, comparing to the experimental data. The results were summarized in Table 4.5-11.

Table 4.5 : Equilibrium properties of DME obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
340.00	GEMC	586.3	578.6	1.3	15.3	15.4	-0.8	1622.8	1692.4	-4.1
320.00	GEMC	622.6	618.0	0.8	16.9	17.0	-0.7	1041.2	1063.1	-2.1
295.00	GEMC	664.5	661.1	0.5	18.6	18.7	-0.7	544.4	540.7	0.7
271.44	GEMC	697.4	697.7	0.0	19.8	20.1	-1.4	259.3	251.7	3.0
260.82	GEMC	713.7	713.1	0.1	20.4	20.7	-1.2	180.5	169.4	6.6
251.00	GEMC	724.2	727.0	-0.4	20.8	21.2	-1.7	115.6	113.5	1.8
241.89	NPT	737.3	739.5	-0.3	21.5	21.7	-0.8	85.1	75.7	12.3
233.42	NPT	747.7	750.9	-0.4	21.8	22.0	-1.1	53.3	50.4	5.8
225.53	NPT	758.0	761.3	-0.4	22.1	22.4	-1.3	38.8	33.4	16.3
218.15	NPT	768.0	770.8	-0.4	22.4	22.7	-1.3	24.0	22.0	9.1
211.24	NPT	777.6	779.6	-0.3	22.7	23.0	-1.3	17.3	14.5	19.4
204.75	NPT	781.8	787.8	-0.8	22.8	23.3	-1.9	10.6	9.5	11.4
198.65	NPT	791.9	795.3	-0.4	23.2	23.5	-1.6	7.6	6.2	22.2
192.90	NPT	797.6	802.3	-0.6	23.4	23.8	-1.8	4.6	4.0	13.3
187.47	NPT	805.2	808.9	-0.5	23.6	24.0	-1.6	3.3	2.6	24.2
182.35	NPT	811.2	815.1	-0.5	23.8	24.2	-1.6	2.0	1.7	14.9
177.49	NPT	816.6	820.8	-0.5	24.0	24.4	-1.6	1.4	1.1	25.5
172.89	NPT	822.7	826.2	-0.4	24.2	24.6	-1.5	0.8	0.7	16.0
average of absolute deviations				0.5			1.3			11.6

Table 4.6 : Equilibrium properties of DEE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
397.00	GEMC	572.1	569.8	0.4	19.8	19.5	1.8	1041.1	1085.8	-4.1
373.00	GEMC	610.3	609.2	0.2	22.1	21.8	1.5	635.2	649.0	-2.1
357.00	GEMC	633.4	632.7	0.1	23.5	23.2	1.4	431.0	442.2	-2.5
340.57	GEMC	655.6	655.3	0.0	24.8	24.5	1.3	274.0	286.2	-4.2
324.02	GEMC	677.7	676.7	0.2	25.9	25.7	1.0	177.2	175.4	1.0
309.00	GEMC	694.8	695.2	-0.1	26.9	26.7	0.8	97.2	106.7	-8.8
295.31	NPT	711.1	711.3	0.0	27.7	27.6	0.5	67.1	64.2	4.4
282.79	NPT	725.8	725.6	0.0	28.3	28.3	0.1	35.8	38.4	-6.7
271.28	NPT	738.7	738.4	0.0	28.9	29.0	-0.2	24.1	22.7	6.3
260.67	NPT	749.0	749.8	-0.1	29.4	29.6	-0.5	12.6	13.3	-5.2
250.86	NPT	760.9	760.2	0.1	30.0	30.1	-0.5	8.3	7.7	8.3
241.77	NPT	770.9	769.7	0.2	30.5	30.6	-0.5	4.3	4.4	-3.4
233.30	NPT	780.0	778.3	0.2	30.9	31.1	-0.4	2.8	2.5	10.4
225.42	NPT	788.5	786.3	0.3	31.4	31.5	-0.3	1.4	1.4	-1.1
218.04	NPT	795.1	793.6	0.2	31.7	31.8	-0.4	0.9	0.8	13.2
211.14	NPT	803.0	800.4	0.3	32.1	32.2	-0.2	0.4	0.4	2.3
204.66	NPT	809.9	806.7	0.4	32.5	32.5	0.0	0.3	0.2	17.3
198.56	NPT	814.9	812.6	0.3	32.7	32.8	-0.2	0.1	0.1	6.5
average of absolute deviations				0.2			0.6			6.0

Table 4.7 : Equilibrium properties of DIPE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
425.00	GEMC	552.8	561.8	-1.6	21.6	21.6	0.2	914.7	836.7	9.3
400.00	GEMC	588.9	599.7	-1.8	24.6	24.2	1.5	575.0	492.8	16.7
385.96	GEMC	598.5	619.0	-3.3	25.4	25.5	-0.4	439.3	353.7	24.2
352.00	GEMC	608.6	661.5	-8.0	26.0	28.3	-8.3	257.4	140.2	83.7
323.53	NPT	702.0	693.8	1.2	31.3	30.4	2.8	92.0	54.5	68.8
299.32	NPT	722.1	719.5	0.4	32.2	32.0	0.7	39.3	20.9	88.3
278.48	NPT	746.0	740.6	0.7	33.5	33.3	0.6	13.3	7.9	68.3
260.36	NPT	762.4	758.3	0.5	34.6	34.4	0.6	5.2	2.9	78.3
244.44	NPT	781.7	773.3	1.1	35.8	35.3	1.7	1.7	1.1	52.8
230.37	NPT	794.2	786.3	1.0	36.7	36.0	1.8	0.6	0.4	53.4
average of absolute deviations				2.0			1.9			54.4

Table 4.8 : Equilibrium properties of MTBE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
423.00	GEMC	587.3	574.9	2.2	19.0	20.5	-7.1	1314.0	1041.0	26.2
398.00	GEMC	621.0	613.8	1.2	21.9	22.8	-3.9	778.4	635.6	22.5
383.00	GEMC	639.1	634.8	0.7	23.3	24.1	-3.2	558.6	456.9	22.2
366.26	GEMC	663.6	656.8	1.0	24.6	25.4	-3.1	406.0	304.8	33.2
347.19	GEMC	683.3	680.3	0.4	25.5	26.7	-4.4	232.6	181.8	28.0
330.00	GEMC	700.7	700.4	0.0	26.2	27.8	-5.9	160.8	107.3	49.8
314.44	NPT	712.0	717.8	-0.8	27.6	28.8	-3.9	90.5	62.8	44.1
300.27	NPT	721.7	733.0	-1.5	28.0	29.6	-5.5	59.3	36.4	63.0
287.33	NPT	734.1	746.6	-1.7	28.5	30.3	-5.9	33.0	20.9	57.7
275.46	NPT	752.4	758.7	-0.8	29.4	31.0	-5.0	21.2	11.9	78.0
264.53	NPT	774.1	769.6	0.6	30.5	31.5	-3.2	11.4	6.7	69.6
254.43	NPT	787.5	779.5	1.0	31.2	32.0	-2.7	7.0	3.8	86.7
245.08	NPT	799.6	788.5	1.4	31.8	32.5	-2.1	3.7	2.1	76.2
236.39	NPT	810.2	796.7	1.7	32.4	32.9	-1.6	2.2	1.2	91.9
228.29	NPT	825.8	804.3	2.7	33.2	33.3	-0.2	1.1	0.6	79.6
220.74	NPT	837.7	811.3	3.3	33.8	33.7	0.5	0.7	0.4	92.5
213.66	NPT	833.3	817.8	1.9	33.6	34.0	-1.2	0.3	0.2	77.9
207.03	NPT	847.2	823.8	2.8	34.3	34.3	0.0	0.2	0.1	94.8
average of absolute deviations				1.4			3.3			60.8

Table 4.9 : Equilibrium properties of EME obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
372.00	GEMC	578.7	582.0	-0.6	17.3	17.3	0.1	1364.2	1396.7	-2.3
350.00	GEMC	613.8	619.6	-0.9	19.4	19.3	0.5	834.5	858.3	-2.8
330.00	GEMC	642.4	649.8	-1.1	20.9	20.8	0.5	497.1	517.4	-3.9
311.65	GEMC	669.4	675.2	-0.9	22.1	22.1	0.1	314.9	304.2	3.5
297.73	GEMC	690.2	693.3	-0.5	23.0	23.0	0.1	209.5	193.1	8.5
285.00	GEMC	704.2	709.1	-0.7	23.6	23.8	-0.6	131.9	121.6	8.4

Table 4.9 : (continued) Equilibrium properties of EME obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
262.55	NPT	732.0	735.6	-0.5	24.9	25.0	-0.3	54.7	47.1	16.1
252.60	NPT	742.3	746.9	-0.6	25.3	25.5	-0.8	36.3	29.0	25.2
243.38	NPT	754.3	757.1	-0.4	25.8	26.0	-0.9	21.9	17.7	23.8
234.81	NPT	762.2	766.3	-0.5	26.1	26.4	-1.3	14.3	10.7	33.4
226.82	NPT	770.8	774.8	-0.5	26.4	26.8	-1.5	8.6	6.5	32.2
219.36	NPT	778.4	782.6	-0.5	26.8	27.2	-1.6	5.5	3.9	42.8
212.37	NPT	788.5	789.8	-0.2	27.2	27.5	-1.2	3.3	2.3	41.7
205.81	NPT	795.0	796.5	-0.2	27.4	27.8	-1.4	2.1	1.4	52.7
199.65	NPT	801.3	802.7	-0.2	27.7	28.1	-1.4	1.2	0.8	52.2
193.84	NPT	808.2	808.5	0.0	28.0	28.3	-1.2	0.8	0.5	64.3
188.37	NPT	814.2	813.8	0.0	28.2	28.6	-1.1	0.4	0.3	64.1
average of absolute deviations				0.5			0.8			27.5

Table 4.10 : Equilibrium properties of DPE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
451.00	GEMC	560.8	570.0	-1.6	24.0	24.2	-0.6	816.9	811.2	0.7
424.00	GEMC	602.2	607.9	-0.9	27.1	26.9	0.8	471.8	473.6	-0.4
417.00	GEMC	609.3	616.9	-1.2	27.6	27.5	0.4	401.9	407.1	-1.3
409.88	GEMC	618.9	625.8	-1.1	28.4	28.1	0.9	340.2	347.0	-1.9
386.14	GEMC	651.7	653.7	-0.3	30.6	30.1	1.8	199.6	194.0	2.8
365.00	GEMC	672.4	676.9	-0.7	32.1	31.6	1.6	97.0	107.3	-9.6
346.05	NPT	695.0	696.5	-0.2	33.7	32.9	2.4	62.6	58.6	6.9
328.98	NPT	714.3	713.3	0.1	34.8	34.0	2.4	28.8	31.6	-8.8
313.51	NPT	729.8	728.1	0.2	35.7	34.9	2.2	17.8	16.8	6.2
299.43	NPT	743.3	741.1	0.3	36.5	35.7	2.3	7.9	8.8	-10.0
286.56	NPT	755.4	752.7	0.3	37.3	36.4	2.4	4.8	4.6	4.1
274.75	NPT	770.0	763.2	0.9	38.2	37.1	3.1	2.1	2.4	-12.4
263.87	NPT	779.0	772.6	0.8	38.8	37.6	3.1	1.2	1.2	0.2
253.82	NPT	788.9	781.1	1.0	39.5	38.1	3.5	0.5	0.6	-15.8
244.52	NPT	798.8	789.0	1.2	40.2	38.6	4.0	0.3	0.3	-4.2
235.86	NPT	804.0	796.1	1.0	40.5	39.0	3.6	0.1	0.1	-20.2
227.80	NPT	813.2	802.7	1.3	41.2	39.4	4.4	0.07	0.07	-8.6
220.28	NPT	819.2	808.8	1.3	41.6	39.8	4.4	0.03	0.04	-24.7
average of absolute deviations				0.8			2.5			7.7

Table 4.11 : Equilibrium properties of DMOE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
456.00	GEMC	637.0	658.7	-3.3	24.5	24.0	1.9	894.2	1105.4	-19.1
429.00	GEMC	687.3	701.2	-2.0	27.7	26.9	2.9	601.6	650.8	-7.6
416.00	GEMC	704.3	719.8	-2.2	28.9	28.1	2.9	459.8	490.4	-6.2
402.33	GEMC	723.7	738.5	-2.0	30.0	29.3	2.7	341.6	355.9	-4.0
379.43	GEMC	750.9	767.8	-2.2	32.0	31.1	2.8	167.2	195.5	-14.5

Table 4.11 : (continued) Equilibrium properties of DMOE obtained by simulation (with AUA potential), compared to the DIPPR [54] correlation of experimental measurements

T (K)	simul. type	ρ_l (kg/m ³)			ΔH_{vap} (kJ/mol)			P_{sat} (kPa)		
		AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
340.66	NPT	802.2	813.4	-1.4	35.0	33.8	3.3	49.5	56.7	-12.8
324.09	NPT	819.0	831.7	-1.5	35.9	34.9	2.8	28.2	29.9	-5.7
309.07	NPT	836.7	847.8	-1.3	36.9	35.8	3.0	13.6	15.6	-13.3
295.38	NPT	848.2	862.1	-1.6	37.6	36.7	2.5	7.5	8.1	-7.5
282.84	NPT	860.6	874.9	-1.6	38.3	37.4	2.4	3.5	4.1	-15.3
271.33	NPT	873.2	886.4	-1.5	39.1	38.0	2.8	1.9	2.1	-10.0
260.72	NPT	888.9	896.8	-0.9	40.1	38.6	3.8	0.9	1.0	-18.4
250.91	NPT	896.5	906.3	-1.1	40.5	39.1	3.5	0.4	0.5	-14.9
241.81	NPT	906.9	915.0	-0.9	41.1	39.6	3.8	0.2	0.3	-22.8
233.34	NPT	914.4	923.0	-0.9	41.6	40.0	3.9	0.1	0.1	-20.0
225.45	NPT	922.5	930.4	-0.9	42.1	40.4	4.2	0.04	0.06	-27.6
218.08	NPT	930.0	937.2	-0.8	42.6	40.8	4.5	0.02	0.03	-25.5
average of absolute deviations				1.5				3.2		

Figure 4.1 shows the simulated equilibrium liquid density data, with the experimental data. The predicted liquid density results are in good agreement with the DIPPR [54] data. The maximum average absolute deviations value, 2.0 %, is seen on DIPE because of the deviations around the boiling point. Highest deviations are generally seen as approaching the critical points. It was also observed that the highest uncertainties were determined near the critical temperatures for all equilibrium properties.

Another important equilibrium property that is important to optimize and validate force field parameters is molar vaporization enthalpy. Molar vaporization enthalpies of ethers are given in Figure 4.2. Computed results are generally in good agreement with the experimental data. MTBE reveals the highest deviations before DMOE. DIPE and MTBE display shifts from the experimental data around their boiling points.

Saturated vapor pressures were computed with Gibbs ensemble. However, they were calculated below the normal boiling point as explained in the previous section, exploiting the molar heat of vaporization data obtained from the NPT ensembles. Saturated vapor pressure is the hardest property to predict excellently. Therefore, deviations below 30 % are accounted in the good category. MTBE represents the saturated vapor pressure with the maximum average absolute deviation with 60.8 %. Although the predictions are in good agreement above the boiling point, they become worse due to the deviations of molar vaporization heat predictions around the boiling

point. DIPE shows a similar behavior with 54.4 % average absolute deviation. Figure 4.3 shows the saturated vapor pressure values, calculated through the simulations comparing to the DIPPR [54] data.

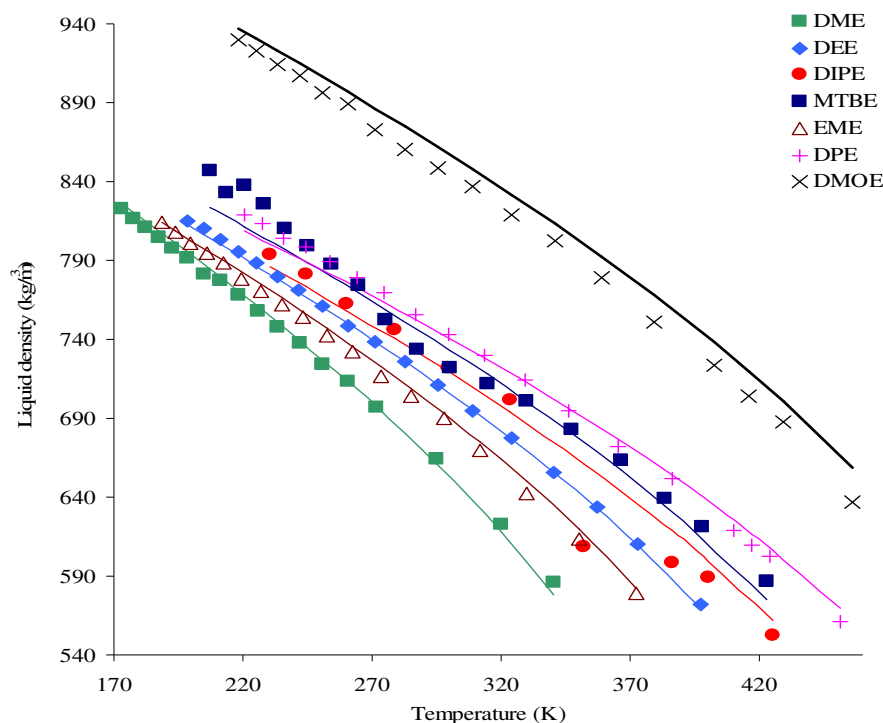


Figure 4.1 : Saturated liquid density of ethers obtained via the simulations with the AUA potential, comparing with the correlations of experimental data [54] (solid lines)

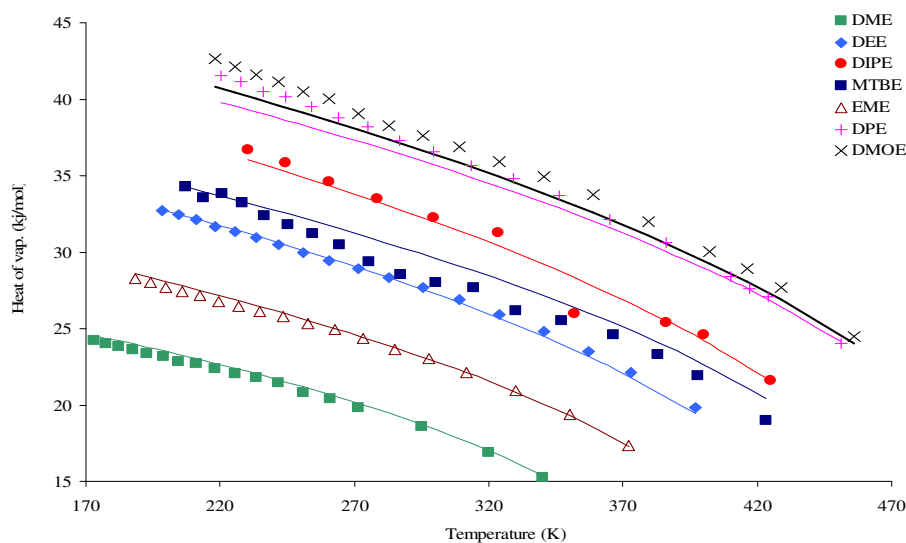


Figure 4.2 : Molar vaporization heat of ethers obtained via the simulations with the AUA potential, comparing with the correlations of experimental data [54] (solid lines)

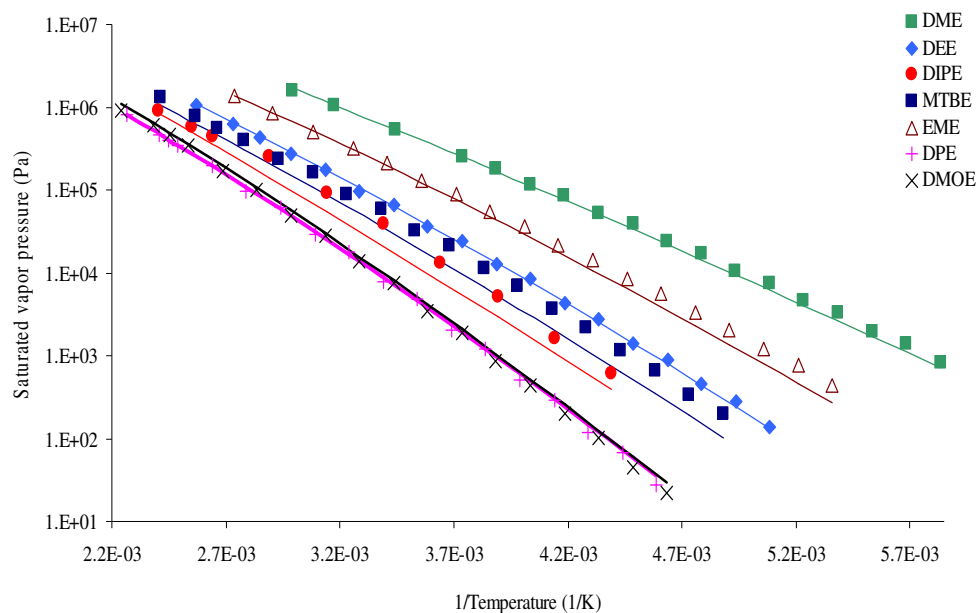


Figure 4.3 : Saturated vapor pressures of ethers obtained via the simulations with the AUA potential, comparing with the correlations of experimental data [54] (solid lines)

Critical points predicted are shown in Table 4.12. Although the critical temperatures were predicted very well (except for DIPE), the critical densities predicted were not as accurate as the temperatures. DIPE is the most unsuccessful estimation, with 11.5 % deviation, for critical temperature, while DMOE is the most unsuccessful one, with -14.9 % deviation, for critical density. The estimations of critical properties can be improved by using a more advanced iteration algorithm, because the liquid density predictions above the boiling points agree well with the experimental data. Boiling points of ethers were estimated with the aid of Antoine equation, and the results are revealed in Table 4.12. It can be seen that the AUA force field predicted the boiling points in excellent agreement with the experimental values. The highest average deviation was calculated for DIPE with -0.4 %, because the saturated vapor pressure predictions are the highest near the boiling point of DIPE.

Figure 4.4-6 reflect the intermolecular potential parameters matching with the ones in the earlier works [27,36]. Stubbs *et al.* [27] used TraPPE-UA force field for ether molecules. σ and ε/k_B parameters must increase with the number of hydrogen atoms in the pseudo-atoms. However, their σ parameters increase with the number of hydrogen atoms, though ε/k_B parameters show logical sequence. Martin and Siepmann [41,42] also used TraPPE-UA force field for normal and branched alkanes

and came up with the same problem. Bourrasseau *et al.* [36] studied on branched alkanes and long chain n-alkanes with AUA force field. Their σ and ϵ/k_B parameters display meaningful sequence as the optimized AUA parameters used in this work. In addition, δ parameters of this work are arranged in the same order as the delta parameters of alkanes. These essential improvements will likely provide more benefits for different applications of ethers.

Table 4.12 : Estimated critical properties and boiling points of ethers, comparing to the experimental data

	T_c (K)			ρ_c (kg/m ³)			T_b (K)		
	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.	AUA	exptl. [54]	% dev.
DME	409.2	400.1	2.3	268.3	269.9	-0.6	248.3	248.3	0.0
DEE	475.5	466.7	1.9	258.0	263.8	-2.2	307.0	307.6	-0.2
DIPE	557.4	500.1	11.5	270.2	262.2	3.1	340.2	341.5	0.4
MTBE	502.5	497.1	1.1	282.5	267.9	5.5	328.2	328.4	-0.1
EME	445.1	437.8	1.7	265.3	272.4	-2.6	280.2	280.5	-0.1
DPE	535.6	530.6	0.9	250.8	267.5	-6.2	363.0	363.2	-0.1
DMOE	544.6	536.2	1.6	283.3	333.0	-14.9	357.8	357.8	0.0
	average of absolute deviations		3.0	average of absolute deviations		5.0	average of absolute deviations		0.1

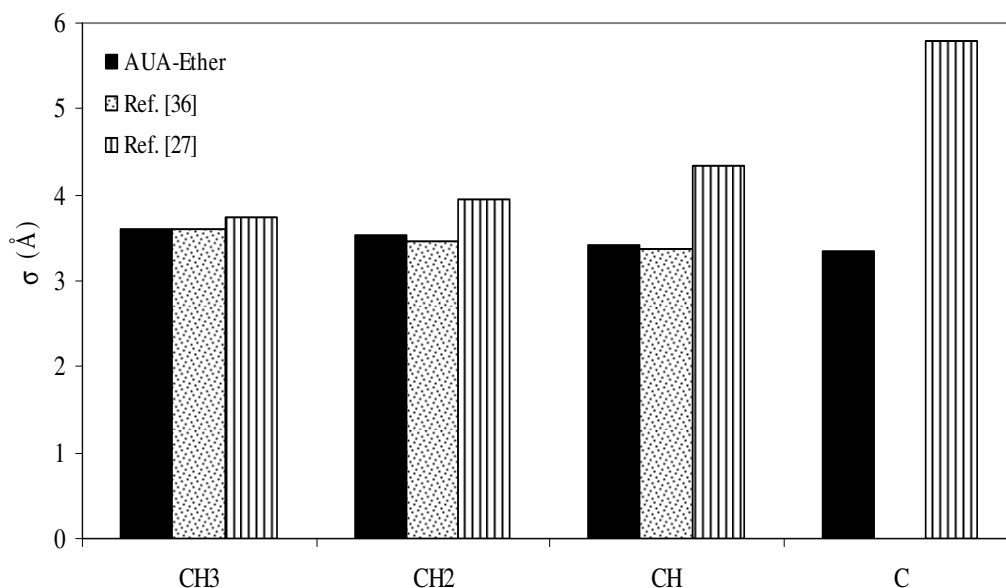


Figure 4.4 : LJ diameters used in this work and in the previous works

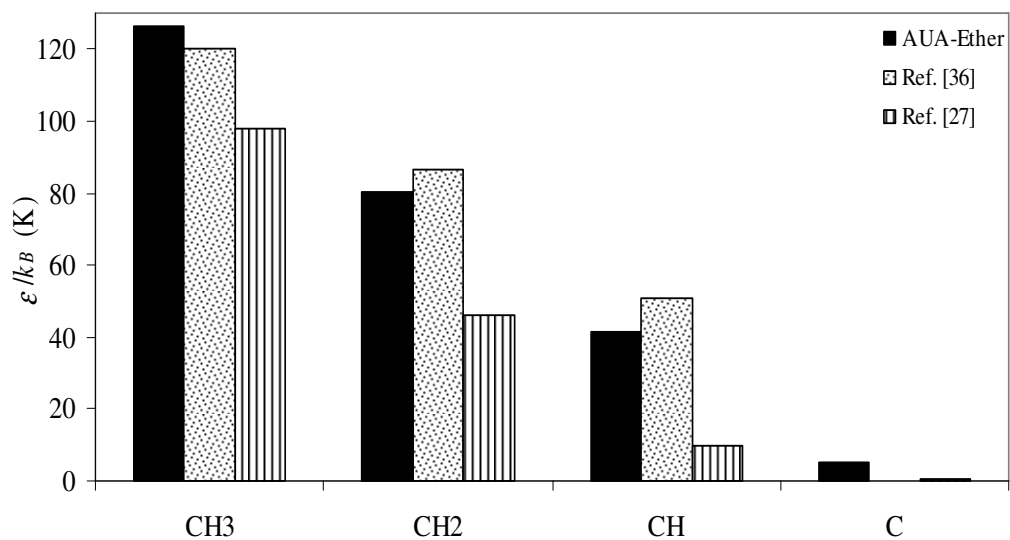


Figure 4.5 : LJ energetic parameters used in this work and in the previous works

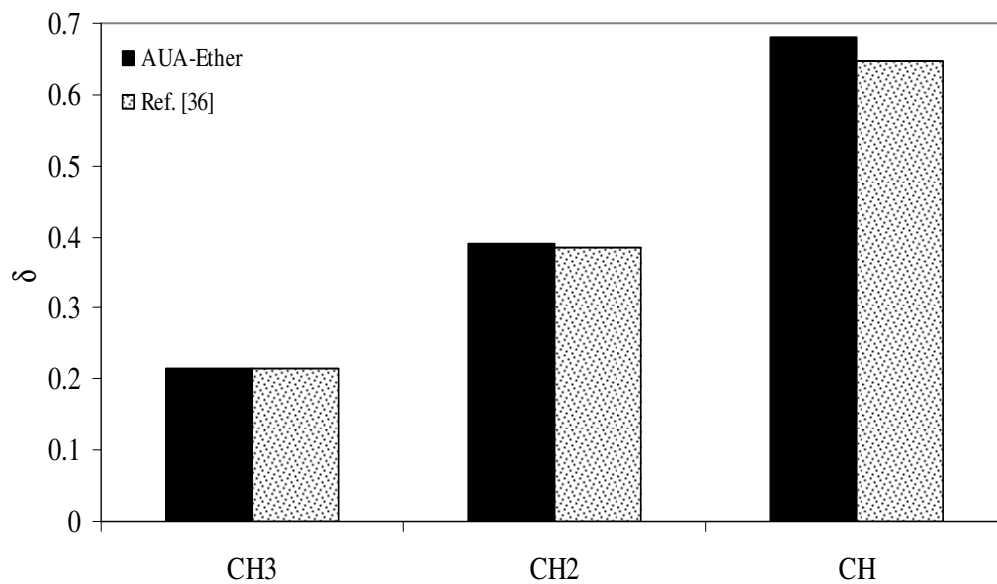


Figure 4.6 : δ parameters used in this work and in the previous works

5. ADSORPTION SIMULATIONS

Zeolites are special materials that can have one-, two-, three-dimensional microporous framework structures [55]. They have been being widely used with an increasing interest in industry owing to their well-defined pores, high internal surface, high ion-exchange capacity, and high thermal stability [56,57]. Zeolitic separation processes are important part of chemical engineering works. Zeolites can adsorb molecules as molecular sieves.

The experiments, conducted to study the adsorption of molecules, are usually insufficient to explore the microscopic properties of the phenomena. They have generally given macroscopic data, such as adsorption heats and adsorption isotherms [55,56]. Therefore, the molecular simulation techniques, such as MC methods, are complementary for the adsorption experiments.

In the Monte Carlo (MC) simulations for adsorption studies, chemical potential, volume and temperature of the system (μ , V , T) are kept constant. This statistical ensemble is called Grand Canonical Monte Carlo (GCMC). Chemical potential of a system is equal to the external system in equilibrium conditions. This is the reason to fix the chemical potential of the system [58].

The adsorption of methyl tertiary butyl ether (MTBE) in ZSM-5 zeolites will be discussed, comparing within the silicalite zeolite in this chapter. In addition, the previous theoretical works [26,28] will be compared to the results. The potential model for MTBE, introduced in the previous chapter, was used for the adsorption simulations. The model is the specialty of this study. Detailed information about the zeolite models and the simulations will be given in the forthcoming sections.

5.1. Zeolite Structures

Zeolites are microporous, crystalline solids that have well-defined structures. They are composed of TO_4 tetrahedra (T: Silicon or aluminum) which are linked one another by the bridging oxygen atoms. Zeolites possess characteristic voids and

channels as a result of their well-defined structures. Considering aluminum atom(s) in the silica framework, the framework of the zeolite is charged negatively. Therefore, the zeolite needs extraframework cation(s), which can be inorganic and organic, to make the overall framework neutral [58,59].

MFI zeolites are formed by two different, 10-ring channels. Those are straight channels (with pore diameters between 5.3-5.6 Å) and sinusoidal channels (with pore diameters between 5.1-5.5 Å). Straight channels lie along the y-direction, while the sinusoidal channels are along the x-direction [60]. There are four straight, four sinusoidal channels, and four intersections per unit cell. Their volume fractions are about 33, 45, and 22 %, respectively [30]. The intersections allow the adsorbed molecules to move along the three directions, although MFI zeolites have two-dimensional structures [58]. Adsorption of MTBE molecules in ZSM-5 zeolites was investigated in comparison with another MFI-type zeolite, the silicalite, in this work. ZSM-5 zeolites are in the category of high-silica zeolites, having Si/Al ratios as more than 10. The main difference between their structures is the existence of aluminum atom(s) [58]. Aluminum atom(s) was/were located instead of the silicon atom(s) at the intersection(s), because the intersections are the largest cavities in MFI zeolites. When there is more than one aluminum atom, the distance between them was set as much as possible [26]. As a result of aluminum atom(s)' presence, ZSM-5 zeolites require extraframework cation(s). Sodium atom(s) was/were selected to meet this requirement, as the diameter of sodium atom is small enough to let MTBE molecules pass through the channels.

The simulated zeolites have orthorhombic crystal system (*Pnma* space group) with $a=20.022$ Å, $b=19.899$ Å, and $c=13.383$ Å. ZSM-5 zeolites, considered in the simulations, have 191, 95, and 47 Si/Al ratios. The zeolites of the study are composed of eight (2×2×2) unit cells, and they are shown in Figures 5.1-5.4 from different sides. Yellow, red, purple and pink colors represent silicon, oxygen, sodium, and aluminum, respectively.

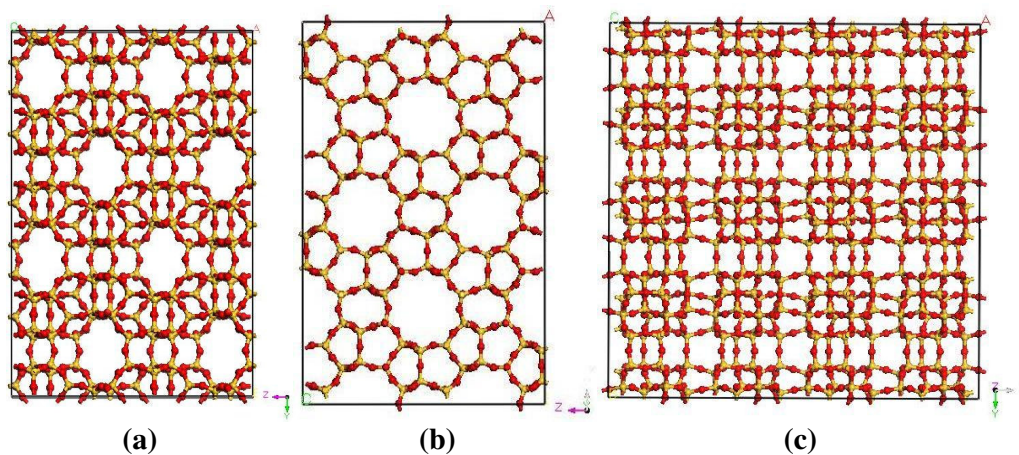


Figure 5.1 : A silicalite supercell composed of eight ($2 \times 2 \times 2$) unit cells along (a) the x-direction (b) the y-direction (c) the z direction

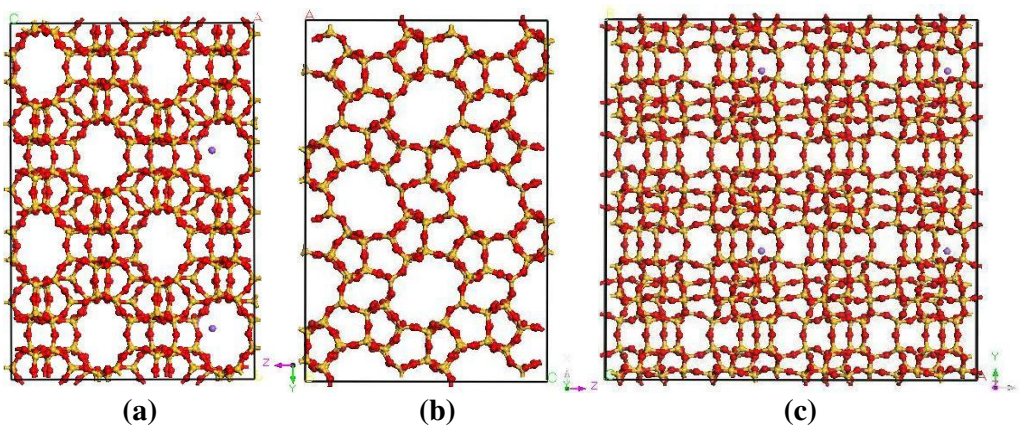


Figure 5.2 : A ZSM-5 (Si/Al=191) supercell composed of eight ($2 \times 2 \times 2$) unit cells along (a) the x-direction (b) the y-direction (c) the z direction

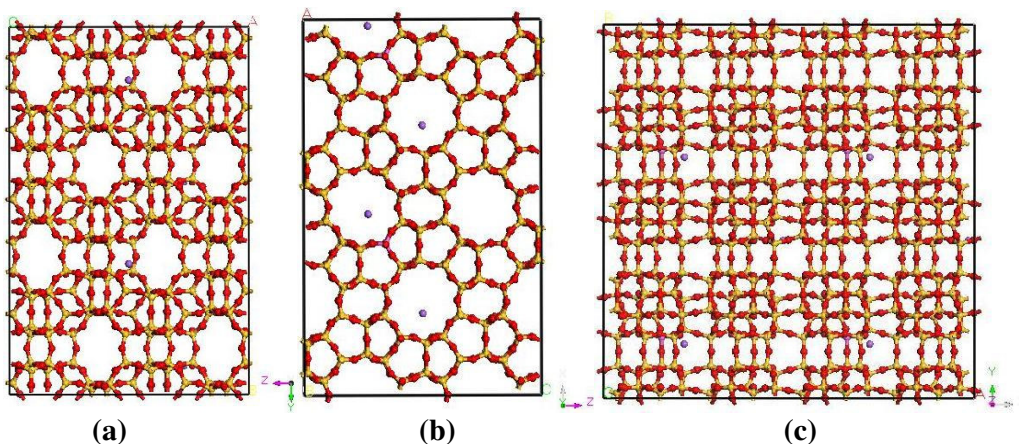


Figure 5.3 : A ZSM-5 (Si/Al=95) supercell composed of eight ($2 \times 2 \times 2$) unit cells along (a) the x-direction (b) the y-direction (c) the z direction

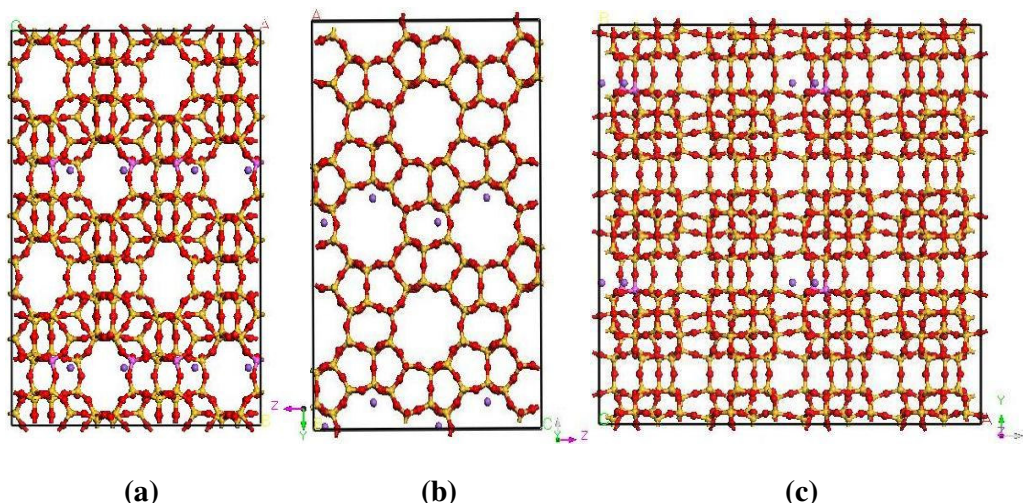


Figure 5.4 : A ZSM-5 (Si/Al=47) supercell composed of eight ($2 \times 2 \times 2$) unit cells along (a) the x-direction (b) the y-direction (c) the z direction

5.2. Simulation Method

MFI framework is quite flexible, and the symmetry changes with the composition, temperature and the existence of adsorbed molecules. However, those fluctuations in the structure are not so effective for thermodynamic equilibrium calculations due to involving very low energy barriers [58]. Thus, the zeolite frameworks were considered as rigid. Aluminum atom location(s) was/were selected as mentioned in the previous section for ZSM-5 zeolites. Then, the sodium cation(s) was/were positioned through a GCMC of 2×10^5 steps. The most probable position was fixed as part of the rigid framework.

The host-guest interactions were calculated by uniformly-distributed grids. Those grids were created before the simulations. The distance between each point is $0.2 \text{ \AA}$ in three-dimensions. Eight ($2 \times 2 \times 2$) unit cells of zeolite with periodic boundary conditions were employed. Long-range electrostatic interactions were corrected via Ewald method, and cutoff distance was set as the half of the minimum box size. Parameters $k_{\max}$ and n_{α} were set to 10 and 2, respectively.

5.2.1. Potential energy

Force field to model MTBE was taken from the newly optimized ether parameters. These parameters were used for the intermolecular interactions involving MTBE molecules and the intramolecular interactions of MTBE. The interactions between adsorbent and adsorbate are called host-guest interactions in MC simulations. There

are two types of potential to compute host-guest interactions. These potentials are Lennard-Jones (LJ) 6-12 (dispersion-repulsion) potential and electrostatic potential.

The partial charges of the zeolite atoms were determined from the work of Beerdsen *et al.* [57], which had been used for MFI zeolites. Although the rule of the partial charges had been originally developed for X and Y zeolites [61], it was successfully adapted to MFI zeolites by Beerdsen *et al.* [57]. The partial charges for zeolite atoms are demonstrated in Table 5.1.

Repulsive and dispersive forces of zeolites are calculated with a different approach than of fluids. This is called Kiselev approximation. Despite adding the electrostatic parameters for all atoms in zeolites, only the oxygen atoms of the main framework are used in LJ calculations, neglecting T atoms (Si and Al) [14,15,56]. LJ parameters of the oxygen atom in the framework were set as $\sigma = 3 \text{ \AA}$ and $\epsilon/k_B = 93.53 \text{ K}$ [14,15], while the parameters of sodium cation were assigned as $\sigma = 2.584 \text{ \AA}$ and $\epsilon/k_B = 50.34 \text{ K}$ [62]. Lorentz-Berthelot rule was used so as to combine the parameters for the interactions between both host-guest and guest-guest beads.

Table 5.1 : The partial charges of the zeolite particles

Particle	q (e)	Zeolite type
Si	2	ZSM-5
Al	1.7	ZSM-5
O (adjacent to Si)	-1	ZSM-5
O (adjacent to Al)	-1.175	ZSM-5
Na	1	ZSM-5
Si	2	silicalite
O	-1	silicalite

5.2.2. Grand canonical Monte Carlo ensemble simulations

When simulating adsorption isotherms of pure components or multicomponent systems, temperature and partial pressures of the species must be imposed. The ensemble for simulating adsorption with these imposed variables is GCMC ensemble. The partial pressures are imposed via the chemical potentials of the species. The numbers of the species fluctuate, giving the amounts of adsorbed molecules or atoms as thermodynamic properties [30,32].

Adsorption of MTBE molecules were observed by GCMC ensemble with 5×10^6 iterations. The moves, which were done by MTBE in GCMC ensemble, are insertion/deletion with 40 % frequency, translation with 20 % frequency, rigid body-

and internal-rotations with 15 % frequencies, and partial regrowth with 10 % frequency. The chemical potential of the system was calculated through fugacity of the vapor phase by the ideal gas relation (Equation 5.1). ϕ_i is the fugacity coefficient of MTBE that was obtained using Peng-Robinson equation of state. P_0 is the reference pressure that equals one molecule ideal gas per cubic Angstrom.

$$\frac{\mu_i}{k_B} = T \ln \frac{\phi_i P}{P_0} \quad (5.1)$$

The isosteric heat of adsorption is the difference between the molar enthalpy of adsorbate in vapor phase and the partial molar enthalpy in the adsorbate phase as shown in Equation 5.2:

$$-\Delta H^o = H_g - H_s \quad (5.2)$$

where g term represents the vapor phase, as s term is for the adsorbed phase. The enthalpy is the sum of internal energy and the product PV . If the gas is assumed to be ideal, PV term equals the product RT . Then, the molecular volume of adsorbed phase is neglected due to having very low values; thus the isosteric heat can be expressed with the total molar potential energies (Equation 5.3). The total molar potentials are calculated through the partial derivatives of average total energy with respect to the average number of adsorbate molecules in GCMC simulations (Equation 5.4). Using the fluctuations method gives the expression shown in Equation 5.5. Q_{st} is the heat of adsorption from now on. Another GCMC simulation in vapor phase is needed to calculate the vapor term of the equation; however the number of molecules would be very small, although the dimensions of the simulation box would be very large. Therefore, the vapor phase is again postulated to be ideal; and the total molar energy of the vapor phase is equal to the molar intramolecular energy. Finally, if the internal degrees of freedom are considered not to shift by the adsorption, the molar intramolecular energies of the phases are equal (Equation 5.6) [14,30].

$$-\Delta H^o = RT - \overline{E_{tot}^s} + \overline{E_{tot}^g} \quad (5.3)$$

$$-\Delta H^o = RT - \frac{\partial \langle E_{tot}^s \rangle}{\partial \langle N \rangle} + \frac{\partial \langle E_{tot}^g \rangle}{\partial \langle N \rangle} \quad (5.4)$$

$$Q_{st} = RT - \frac{\langle E_{tot}^s N \rangle - \langle E_{tot}^s \rangle \langle N \rangle}{\langle N_s^2 \rangle - \langle N_s \rangle^2} + \frac{\langle E_{tot}^g N \rangle - \langle E_{tot}^g \rangle \langle N \rangle}{\langle N_g^2 \rangle - \langle N_g \rangle^2} \quad (5.5)$$

$$Q_{st} = RT - \frac{\langle E_{ext}^s N \rangle - \langle E_{ext}^s \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (5.6)$$

5.3. Results and Discussions

Validation of the new ether force field for adsorption simulations can be done by comparing them with the available experimental results. The only available experimental results are for silicalite [28]. There are no experimental data for ZSM-5 zeolites. Figure 5.5 shows the optimized anisotropic united atoms (AUA) force field results comparing to the experimental results and the other simulation results at 298 K. The other force fields that are compared to the AUA force fields are transferable potentials for phase-equilibria-united atoms (TraPPE-UA) force field [27], polymer consistent force field (PCFF) [29], condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [40], and consistent-valence force field (CVFF) [63], and. It can be seen that the AUA force field predicted the adsorption more accurately than the other force fields. The simulations, which were carried out above the normal boiling point of water with the AUA force field, did not predict the isotherms accurately (Figure 5.6). The pressure values of the simulation results in Figure 5.6 are the fugacity values. The fugacity coefficients vary between 0.999 and 1 in the simulated range. Inaccuracy of the AUA force field at high temperatures means that it does not predict the isotherms successfully at those temperatures. However, these high temperatures are outside the operating temperature range for MTBE removal from water, which is not expected to exceed the normal boiling temperature of water. Therefore, the inaccuracy of the estimations at high temperatures does not create a concern.

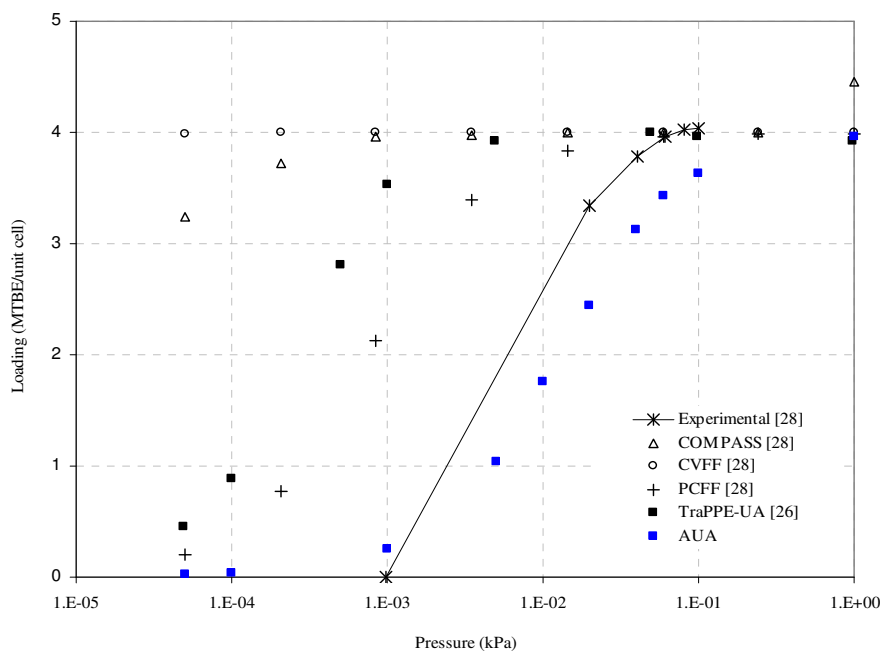


Figure 5.5 : Comparison of the experimental and different force fields of simulation adsorption isotherm of MTBE in silicalite at 298 K

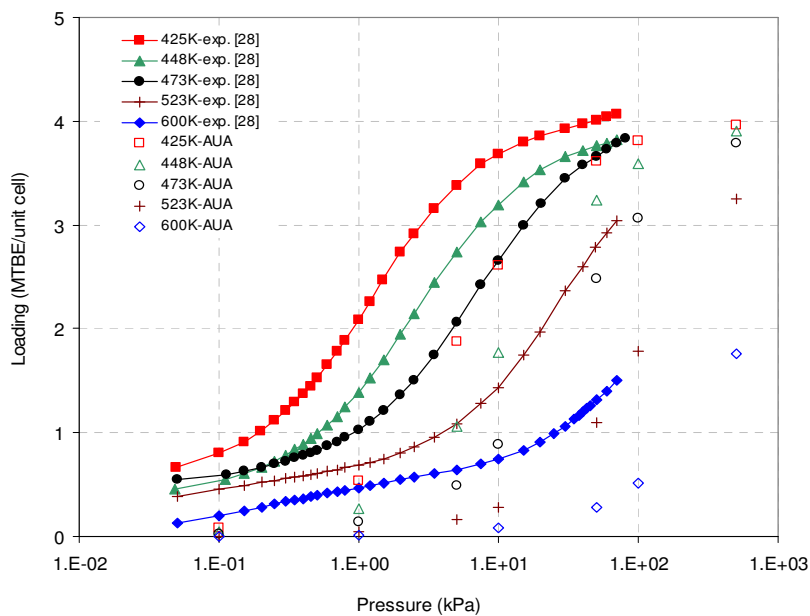


Figure 5.6 : Adsorption isotherms of MTBE in silicalite at different temperatures

Figures 5.7-5.9 display the adsorption isotherms of MFI zeolites with different Si/Al ratios, at different temperatures. The isotherms exhibit a decreasing trend for MTBE adsorption with increasing Si/Al ratio. However, comparison of the isotherms for the zeolite with Si/Al ratio of 191 and for the zeolite with Si/Al ratio of 95 shows that the positions of aluminum atoms in zeolites are also effective on the adsorption capacity.

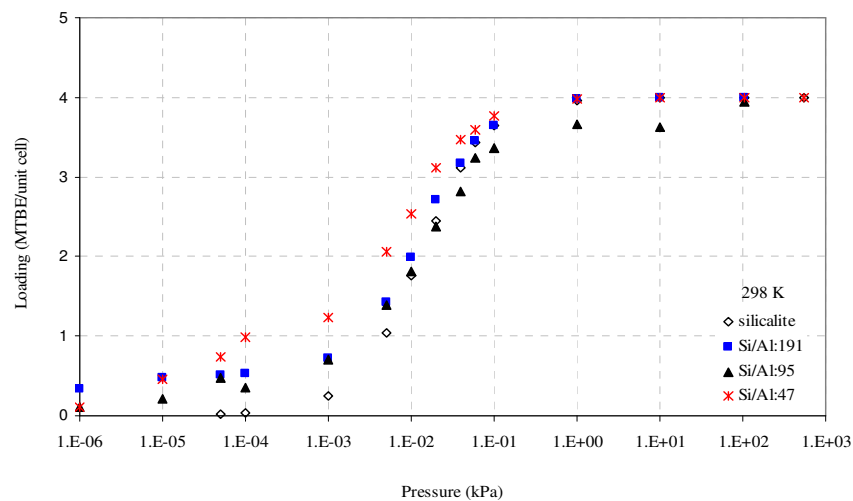


Figure 5.7 : Adsorption isotherms of MTBE in silicalite and ZSM-5 zeolites at 298 K

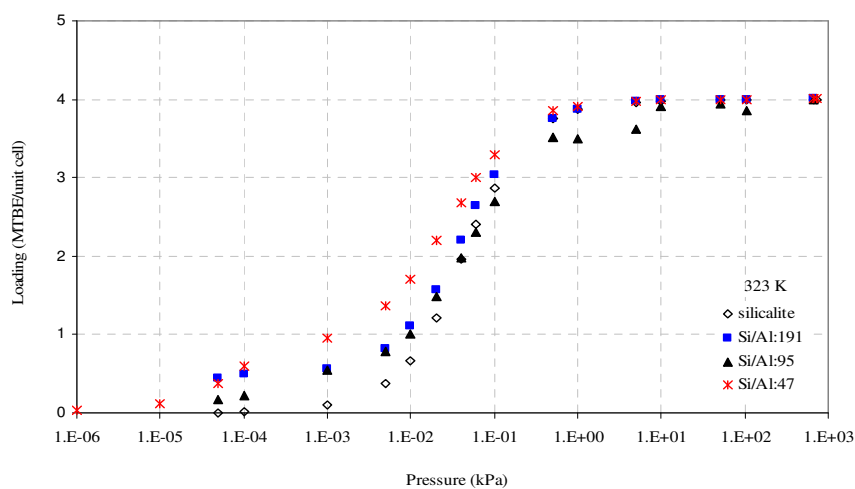


Figure 5.8 : Adsorption isotherms of MTBE in silicalite and ZSM-5 zeolites at 323 K

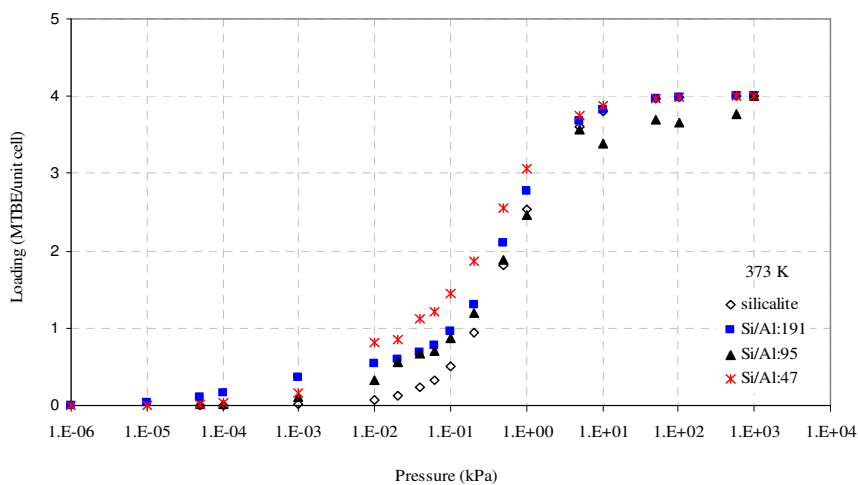


Figure 5.9 : Adsorption isotherms of MTBE in silicalite and ZSM-5 zeolites at 373 K

At lower pressures; ZSM-5 zeolite show better adsorption capacities than silicalite, except at 373 K. At 373 K, the performance of ZSM-5 zeolites increases at intermediate pressures. The reason why Si/Al ratio is not so effective at lower loadings at 373 K is the adsorption reduction with increasing temperature. Although the loadings change with temperature, saturation is observed at around 4 MTBE molecules per unit cell for all temperatures and zeolites. These results show that the extraframework cations do not have an effect on the saturation capacity. However, the extraframework cations significantly increase the loadings at lower pressures. The little saturation stations for ZSM-5 zeolites at low pressures are notable. Those pressures may be the saturation of cation sites. MTBE is a polar molecule due to the presence of an oxygen atom, which makes its separation from water difficult because of hydrogen bonding with MTBE and water. The effect of extraframework cation must be also investigated with MTBE-water mixture. It is expected to be a competition between the oxygen of the molecules.

MTBE molecules enter the pores, even as the presence of sodium cations. MTBE molecules reside at the intersections of straight and sinusoidal channels, approving the work of Yazaydin *et al.* [26]; because they are the largest cavities, which can also accomodate the extraframework cations. While MTBE molecules reside near the sodium cations at lower loadings (Figure 5.10), the other regions are filled at higher loadings (Figure 5.11). This is valid for all temperatures and zeolites considered here in detail.

Figure 5.12 compares the adsorption isotherms at 298 K with the results of Reference [26]. Significant difference can be seen between the results, though the same trend and the saturation limit are observed. The AUA force field is more reliable than TraPPE-UA force field due to the accuracy of the AUA force field as discussed above.

Isosteric heats of adsorption decrease with increasing temperatures in silicalite (Figure 5.13) and in ZSM-5 (Figure 5.14-5.16). However, the results are flat and similar at middle loadings and quite different at higher loadings and lower loadings. According to Figure 5.14-5.16, no certain consequence can be brought out about the effect of Si/Al ratio on the heat of adsorption. ZSM-5 zeolites have more variable values than silicalite; it is probably due to the entropic effects of sodium cations. At lower loadings, the isosteric heats per mole vary more, because of limited adsorption

and because of adsorption near the cations. The heat values vary at higher values, as well, because there are not enough spaces in zeolites, and every move of the molecules shifts the adsorption heats significantly. It must be added that the uncertainties of isosteric heats at higher and lower loadings are very large.

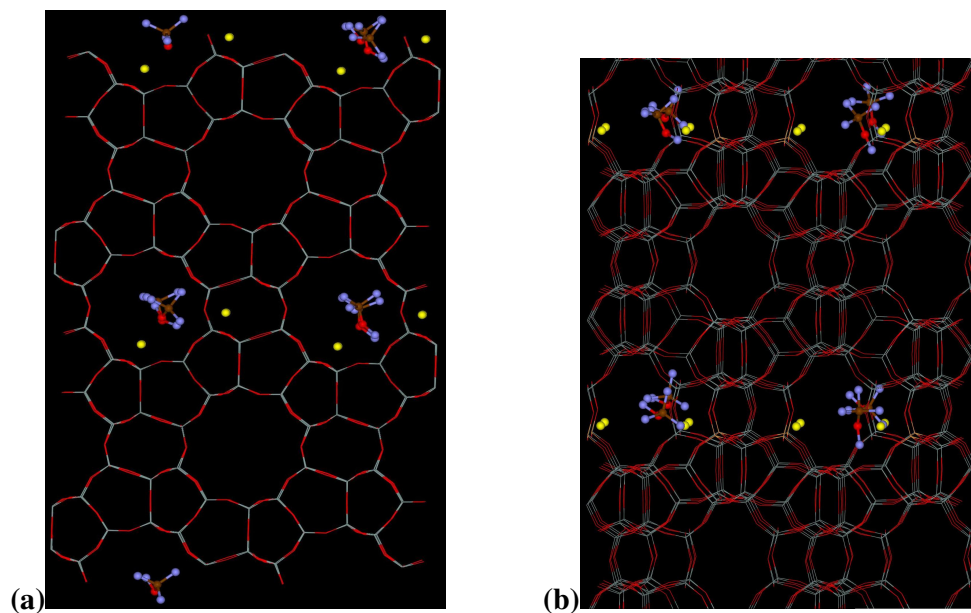


Figure 5.10 : Snapshot from the adsorption at 298 K and 0.0001kPa along (a) the straight channels, (b) the sinusoidal channels. Orange: Aluminum; Yellow: Sodium; Grey: Silicon; Red: Oxygen; Brown: Carbon; Blue: Methyl group

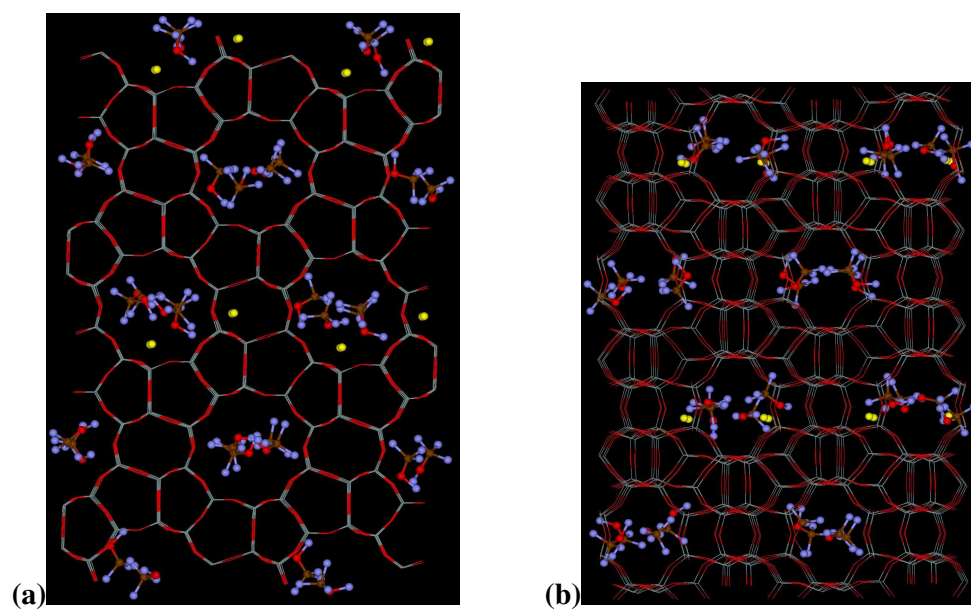


Figure 5.11 : Snapshot from the adsorption at 298 K and 1kPa along (a) the straight channels, (b) the sinusoidal channels. The colors are as described above

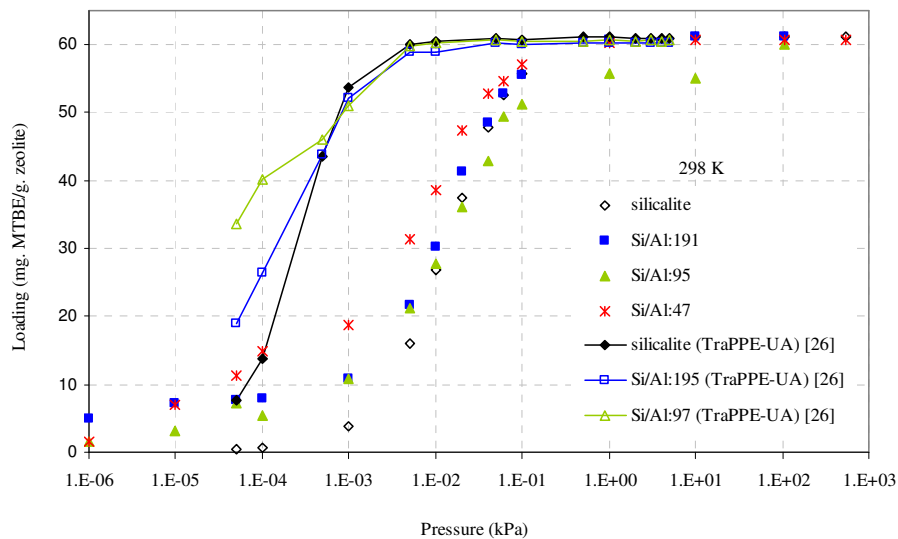


Figure 5.12 : Comparison of AUA and TraPPE-UA force fields of simulation adsorption isotherms of MTBE in zeolites at 298 K

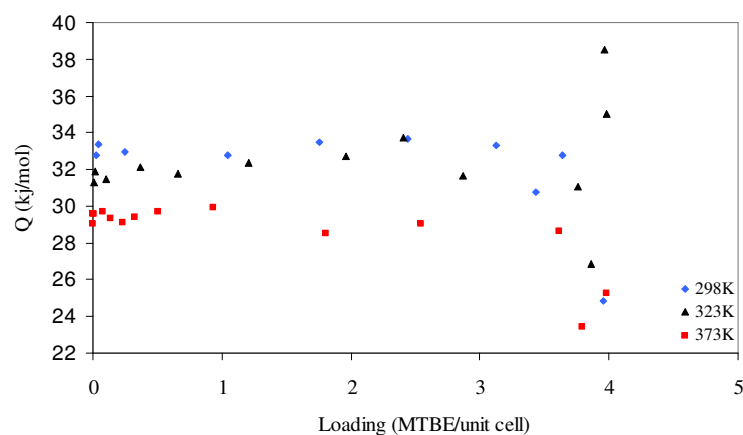


Figure 5.13 : Heats of adsorption at different loadings in silicalite at different temperatures

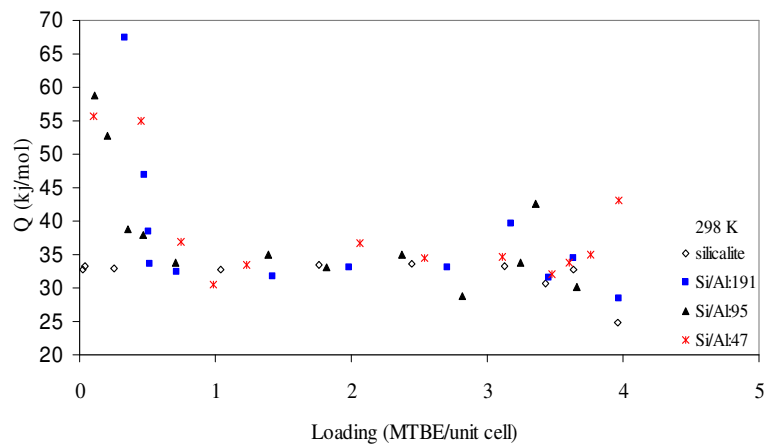


Figure 5.14 : Heats of adsorption at different loadings in zeolites at 298 K

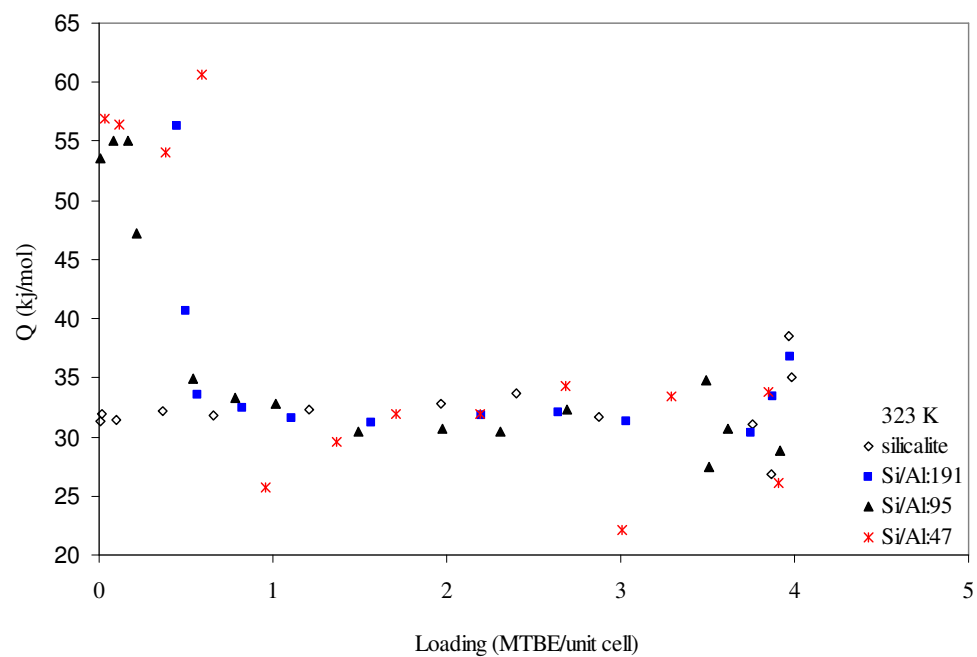


Figure 5.15 : Heats of adsorption at different loadings in zeolites at 323 K

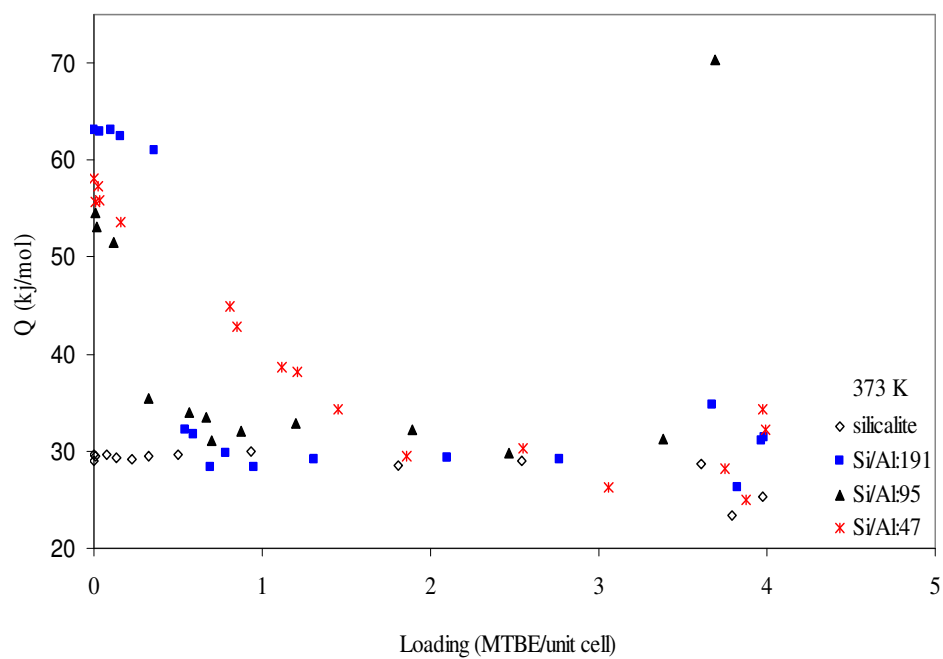


Figure 5.16 : Heats of adsorption at different loadings in zeolites at 373 K

6. CONCLUSIONS

Methyl tertiary butyl ether (MTBE) is an important synthetic additive for gasoline to reduce harmful exhaust gas emissions. It makes the gasoline burn more completely. After its usage at high concentrations in gasoline, serious health symptoms have been observed on some people. Researches on animals and humans have enhanced the concerns about MTBE usage. In addition, its high transport in nature- especially in water- and its low biodegradation have worried the scientists about the future accumulation in nature. Thus, besides the efforts for banning MTBE usage; the separation of MTBE from water has been being widely investigated by different techniques. Adsorption by organophilic substances like zeolites and activated carbon is more common techniques. However, the theoretical works on MTBE removal is very rare. Therefore, this work was carried out to study MTBE adsorption in ZSM-5 zeolite in comparison to silicalite via molecular simulations.

Monte Carlo (MC) methods are used to estimate phase equilibria. However, predicting equilibrium properties, such as phase density, vapor pressure, and heat of vaporization, successfully needs efficient force fields. Anisotropic united atoms (AUA) force field was developed for this purpose because of the fact that it was considered to be a more realistic approach of representing atom groups. Developing transferable force field for short ethers was carried out through comparing predicted vapor-liquid equilibrium (VLE) properties with the experimental ones. Employing fluctuations method instead of finite difference method is more efficient way to optimize force field parameters. The new parameters were derived with diisopropyl ether (DIPE), diethyl ether (DEE), dimethyl ether (DME) and methyl tertiary butyl ether (MTBE) molecules. Then, the optimized parameters were tested on ethyl methyl ether (EME), dipropyl ether (DPE), and 1,2-dimethoxyethane (DMOE). The highest average absolute deviation for liquid density prediction is 2.0 % for DIPE, while the average absolute deviation of molar vaporization heat prediction is the highest with 3.3 % for MTBE. The maximum average absolute difference is 60.8 % for saturated vapor pressure values, determined for MTBE. Largest deviation for

critical temperature prediction is observed with DIPE (11.5 %). Another critical property, which is critical density, has the maximum deviation, -14.9 %, with DMOE. Among the boiling point estimations, DIPE has the maximum error with -0.4 %, due to the deviations of saturated vapor pressure predictions near the boiling point.

The new potential parameters have good consistency and real physical meaning. These essential improvements will likely provide more benefits for different thermodynamic applications of ethers, especially in adsorption applications. In addition, application of the new parameters on the branched ethers must be performed with sufficient number of trials for configurational bias Monte Carlo (CBMC) moves because of the strong intramolecular interactions in the branched molecules. Reservoir creation must be also handled carefully.

The new force field is more successful at predicting adsorption of MTBE in MFI zeolites, if the silicalite isotherm at 298 K is regarded as a reference. However, it fails at elevated temperatures. The adsorption simulations with the new potential parameters confirmed that MFI zeolites can adsorb MTBE molecules. MTBE molecules were adsorbed at the intersections of straight and zigzag channels with a 4 MTBE/unit cell saturation capacity.

Si/Al ratio was found to decrease the adsorption, however did not change the saturation capacity. Although the ratio affects organophilicity positively, MTBE adsorption is affected negatively. The reason that lies behind this fact is probably the effect of the oxygen atom on MTBE. Oxygen makes MTBE polar like a water molecule. MTBE is adsorbed near the extraframework cations especially at lower loadings, and this shows that oxygen atoms are attracted more dominantly by the extraframework cations.

Temperature reduces the adsorption performance as expected in all physical adsorption phenomena due to having more intermolecular interactions at lower temperatures. However, this is an advantage of the adsorption processes for MTBE removal to find use in industrial applications, because those processes can be operated at lower temperatures, reducing the energy consumption. Isosteric heats of adsorption also decrease with increasing temperature.

The adsorption isotherms at 298 K for ZSM-5 zeolites were compared with the previous theoretical work. Although there are differences in quantitative results, the new AUA force field gives more reliable results considering its success in prediction of the silicalite isotherm.

MTBE being adsorbed primarily near the extraframework cations, it can be speculated that ZSM-5 zeolites can be fields for water-MTBE competition. Therefore, water-MTBE mixture adsorption must be also investigated in ZSM-5 zeolites. The resulting future works will possibly elucidate the phenomenon entirely.

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