*Korean J. Chem. Eng.*, **17**(6), 649-651 (2000)

# Molecular Simulation for Adsorption of Chlorinated Hydrocarbon in Zeolites

**Kazuyuki Chihara†, Caroline F. Mellot*, Anthony K. Cheetham**, Shani Harms**, Hirotaka Mangyo, Masaki Omote and Ryuichi Kamiyama**

Department of Industrial Chemistry, Meiji University, 1-1-1 Higashimita, Tama-ku, Kawasaki, 214-8571, Japan
*Institut Lavoisier, Universite de Versailles, Saint-Quentin-en-Yvelines 45,
avenue des Etats-Unis, 78035, Versailles Cedex, France
**Material Research Laboratory, University of California, Santa Babara, CA93106-5130, U.S.A
(*Received 18 May 2000 • accepted 4 July 2000*)

**Abstract**−Equilibrium and isosteric heat of adsorption for the system of chloroform and USY-type zeolite were studied. The USY-type zeolite (PQ Co., $SiO_2/Al_2O_3$=70) was used both as a pure crystalline powder and as granulated particles with binder. Chloroform was reagent grade. The adsorption equilibria were measured using a gravimetric method and were expressed as isotherms. A chromatographic method (i.e. pulse response of chloroform through the USY column with helium carrier) was used to get the initial slope of the isotherms. In the simulation, the GCMC method was used to calculate amounts adsorbed for various conditions. FF parameters were confidently applied. And modified structure model was effective for simulation.

Key words: Molecular Simulation, Grand Canonical Monte Carlo Method, High Silica Zeolite, Chloroform, Adsorption Equilibrium

## INTRODUCTION

Molecular simulation has now become powerful tool for the study of adsorbed molecules in zeolites, and the Grand Canonical Monte Carlo (GCMC) method is especially useful for predicting adsorption equilibria. However, information on forcefield parameters and charges are often inadequate, even in systems where the structure is well known.

From the environmental point of view, the adsorption of chlorinated hydrocarbons by the use of zeolites may have some potential utility in ground water or soil remediation and other areas. Mellot et al. [1998b] recently reported new forcefield parameters and charges for chlorinated hydrocarbons in the faujasite zeolite: NaX, NaY and siliceous Y. These yield heats of adsorption that are in good agreement with calorimetric data [Mellot et al., 1998a].

In this study, their forcefield was used to simulate adsorption isotherms and isosteric heats of adsorption for chloroform in USY-type zeolite. The results are compared with gravimetric and chromatographic experiments.

## EXPERIMENT

### 1. Gravimetric Method

Fig. 1 shows experimental apparatus for gravimetric analysis. The zeolite sample (about 1 g) was placed in a quartz basket (K). Then the adsorbate in flask (B) was fed to adsorption tube (N). Whole the apparatus was in a constant temperature air bath. The temperature range was 303-323 K. The amount adsorbed was determined from the change in the length of quartz spring (G). The pressure of the vapor in the tube was measured by pressure sensor (O). In this way, adsorption isotherms were obtained (Fig. 2 and Fig. 7).

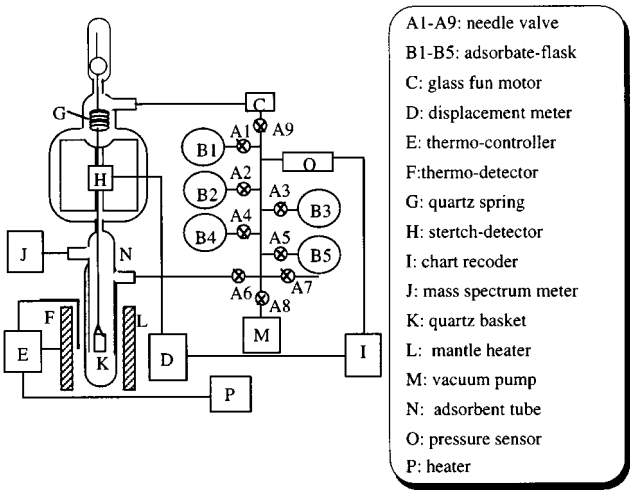


**Fig. 1. Experimental apparatus to measure adsorption equilibrium.**

### 2. Chromatographic Method [Chihara et al., 1978]

In order to study the isotherm at lower pressure range, we used a pulse response method with a gas chromatograph.

The gas chromatograph (GC 9-A; Shimadzu Co., Ltd.) was used with helium carrier. Siliceous zeolite pellets (with binder) were crashed and screened to obtain particle size between $4.95\times10^{-4}$ to $8.33\times10^{-4}$ m (an average particle radius of $6.64\times10^{-4}$ m) and packed to the column (length, 30 cm, diameter, 3 mm). The experimental column pressure was kept 200 kPa, the experimental column tem-

†To whom correspondence should be addressed.
E-mail: chihara@isc.meiji.ac.jp
This paper was presented at The 5th International Symposium on Separation Technology-Korea and Japan held at Seoul between August 19 and 21, 1999.

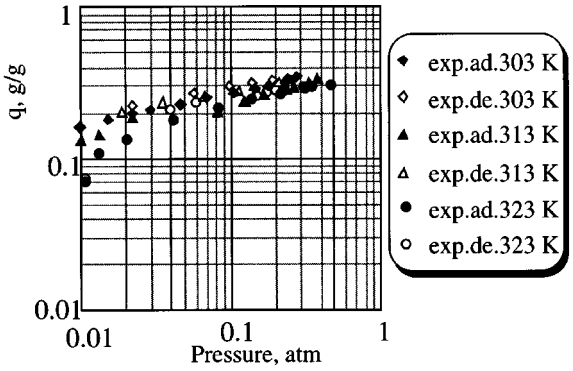


**Fig. 2. Adsorption isotherms for PQ-USY-chloroform system.**

perature was kept at 393, 423 and 453 K, respectively. Pulse responses of vaporized chroloform with helium were detected by TCD. Response data were stored and processed by a personal computer.

From retention time of pulse response, adsorption equilibrium constant at zero coverage was obtained and plotted in Fig. 3 as van't Hoff plot to get heat of adsorption (39.71 kJ/mol) and adsorption equilibrium constant extrapolated to 303 K. This extrapolated value was plotted in Fig. 7 as initial slope.

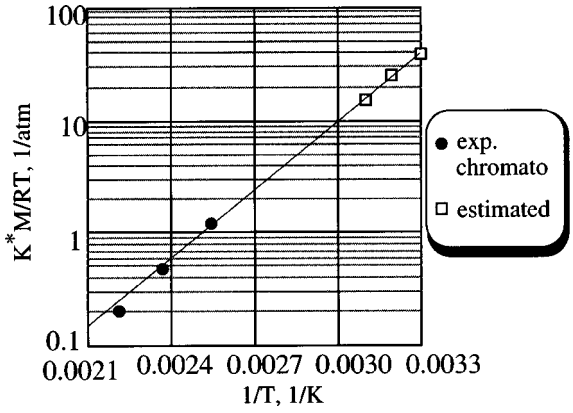


**Fig. 3. van't Hoff plot for PQ-USY-chloroform system.**

**Table 1. van der Waals parameter [Mellot et al., 1998b]**

| | ε/k, K | R_Min, Å |
|---|---|---|
| Si-Si | 0.000 | 0.000 |
| O-O | 0.000 | 0.000 |
| O-C | 87.058 | 3.253 |
| O-Cl | 162.000 | 3.430 |
| O-H | 90.535 | 2.698 |
| C-C | 25.860 | 3.753 |
| C-Cl | 55.650 | 3.787 |
| C-H | 26.730 | 3.358 |
| Cl-Cl | 119.800 | 3.822 |
| Cl-H | 57.530 | 3.392 |
| H-H | 27.630 | 2.963 |
| X-X | 0.000 | 0.000 |
| X-H | 0.010 | 6.000 |
| X-Cl | 0.010 | 6.000 |
| X-C | 0.010 | 6.000 |

## SIMULATION

Cerius2 (MSI Inc.) was used throughout the simulations. Forcefield parameters obtained by Mellot et al. [1998b] are listed in Table 1. The Grand Canonical Monte Calro method (under constant chemical potential (μ), volume (V), temperature (T)) was used to get the equilibrium amount adsorbed.

### 1. Models

3 models were considered here. Pure siliceous faujasaite (Y-type) (Fig. 4) was in the data base of Cerius2. Dummy atoms were put in sodalite cages to avoid impossible occupation of adsorbates. PQ-USY was dealuminated in preparation. So it definitely contains silanol nest. PQ-USY has the silica-alumina ratio of $SiO_2/Al_2O_3$=70. So there remains aluminum. Then we put 7 silanol nest as in Fig. 5

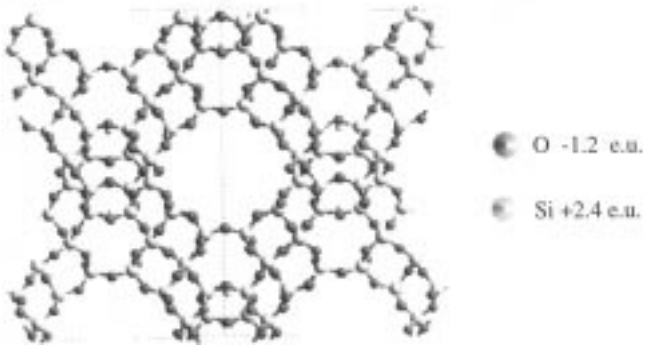


**Fig. 4. Pure siliceous Y type model.**

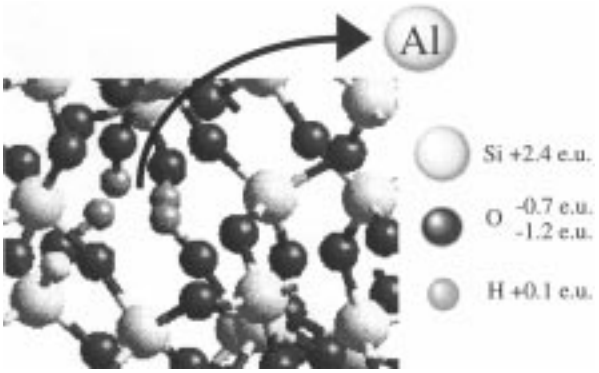


**Fig. 5. Silanol nest model.**

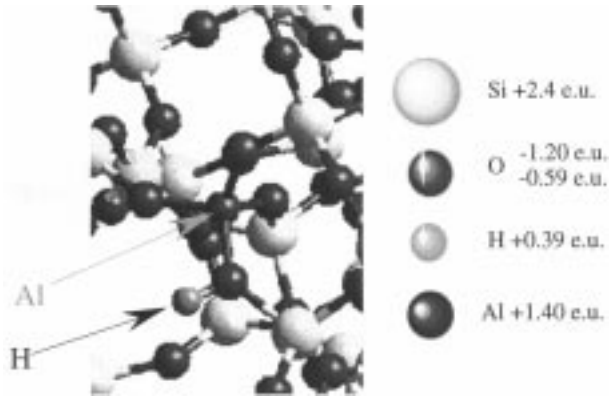


**Fig. 6. Acid site model.**

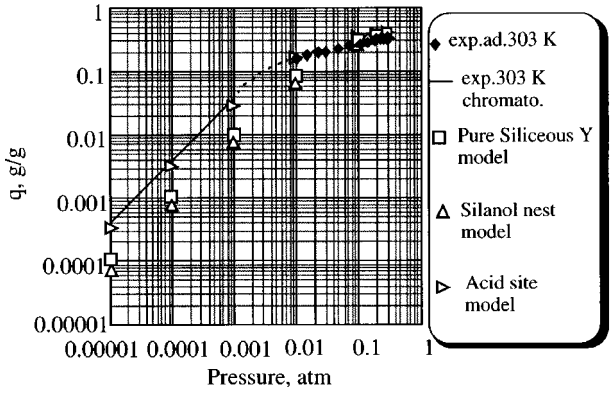


**Fig. 7. Comparison between experiments and simulations for adsorption isotherms of PQ-USY-chloroform system.**

and 4 acid site as in Fig. 6. Charges for Si and O were set to be +2.4 e.u and −1.2 e.u, respectively, as usual. H and O in silanol nest were assumed to have the charges as +0.1 e.u and −0.7 e.u, respectively. Al, O and H in replaced Al were assumed to have the charges as +1.4 e.u, −0.59 e.u and 0.39 e.u. Si charges were adjusted after these setting to neutral by averaging.

## RESULTS AND DISCUSSION

In Fig. 7, experimental adsorption isotherm for chloroform in PQ-USY at 303 K is shown. Initial slopes for 303 K is also shown. This whole range of adsorption isotherm at 303 K could be compared with simulation.

At higher pressure (0.1 atm), all the simulation are coincident and almost correspond to gravimetric data.

At lower pressure, simulations for the acid site model was good agreement with chromatographic data.

Experimental heat of adsorption obtain by chromatography at zero coverage is compared with simulated heat of adsorption for 3 models in Table 2. Here simulation for the acid site model was closer to the experimental value than the pure siliceous model and the silanol nest model.

Molecular Simulation was found to be reasonable in this case, from two standpoints, amount adsorbed and heat of adsorption, which were the key factor in adsorption equilibrium. Further, precise observation of adsorption state around the acid site and oxygen site in the frame would give more information about adsorption mechanism.

**Table 2. Heat of adsorption kJ/mol**

| | |
|---|---|
| Exp. chromato. | 39.71 |
| Pure siliceous Y model | 34.21 |
| Silanol nest model | 33.82 |
| Acid site model | 40.17 |

## CONCLUSION

Equilibrium and isosteric heat of adsorption for the system of chloroform-USY-type zeolite were studied.

The adsorption equilibria were measured using a gravimetric method and were expressed as isotherms. A chromatographic method was used to get the initial slope of the isotherms. In the simulation, GCMC method was used to calculate amounts adsorbed for various conditions. To get better coincidence between experimental data and simulation, we tried simulation of silanol nest model and acid site model, which was the modification from pure siliceous Y zeolite. Then, it was found to be necessary to account for aluminum rather than silanol nest.

As a conclusion, FF parameters were confidently applied. And modified structure model are effective for simulation.

## ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under grant NO. DE-FG03-96ER14672. K. Chihara acknowledges Meiji University for the university fund for a research in foreign country.

## NOMENCLATURE

$K^*$ : adsorption equilibrium constant [cc/g]
M : molecular weight [g/mol]
q : amount adsorbed [g/g]
R : gas constant [J/K mol]
R_Min : Bond Length Equilibrium [Å]
T : temperature [K]
ε : potential energy minimum [eV]
k : Boltzmann constant [J/K]

## REFERENCES

Chihara, K., Suzuki, M. and Kawazoe, K., "Adsorption Rate on Molecular Sieving Carbon by Chromatography," *AIChE J.*, **24**, 237 (1978).

Mellot, C. F., Cheetham, A. K., Harms, S., Savitz, S., Gorte, R. J. and Myers, A. L., "Calorimetric and Computational Studies of Chlorocarbon Adsorption in Zeolites," *J. Am. Chem. Soc.*, **120**, 5788 (1998a).

Mellot, C. F., Davidson, A. M., Eckert, J. and Cheetham, A. K., "Adsorption of Chloroform in NaY Zeolite: A Computational and Vibrational Spectroscopy Study," *J. Phys. Chem. B*, **102**, 2530 (1998b).