Adsorption Equilibria of n-Alkanes on Silicalite and ZSM-5

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Abstract The adsorption equilibria of n-heptane, n-octane and n-nonane on silicalite and ZSM-5 have been measured in the temperature range of 373.15—473.15 K under low pressure (0—5.332 kPa). All the experimental data can be represented by a generalized characteristic curve of the extended adsorption potential theory utilizing the parameter of the initial heat of adsorption, which is estimated reasonably by a new approach.
Keywords adsorption equilibria, heat of adsorption, n-alkanes, zeolite

1 INTRODUCTION

There has been continuous interest in adsorption of alkanes on zeolites because of its importance in chemistry and chemical engineering[1–3]. Smit and Siepmann[4,5] developed the configurational-bias Monte Carlo technique to simulate the adsorption of n-alkanes on zeolites in the zero coverage limit. Recently, this molecular simulation technique was employed to compute adsorption isotherms of short linear alkanes, methane, ethane, propane and butane in silicalite[6].

In this paper, the adsorption equilibria of n-heptane, n-octane and n-nonane on silicalite and ZSM-5 have been measured in the temperature range of 373.15—473.15 K under low pressure (0—5.332 kPa). The extended adsorption potential theory utilizing the initial heat of adsorption, originally developed by Ding et al.[7], is adopted to correlate the experimental adsorption data of three n-alkanes adsorption on two zeolites at various conditions. A new approach is proposed to estimate the initial heat of adsorption more accurately from the experimental data. The estimated initial heat of adsorption increases with the chain length of n-alkanes significantly, which is in agreement with the theoretical simulation results by Smit and Siepmann[4,5].

2 EXPERIMENTAL SECTION

2.1 Material

Silicalite and ZSM-5 were gifted from Worcester Polytechnic Institute (USA) in the form of crystalline powder, and they were pelletized via pressurization, crushed, and sieved to 1—2 mm size before use. The characteristic properties of both zeolites were listed in Table 1. The three n-alkanes, n-heptane, n-octane and n-nonane, were reagent-grade chemicals with purity higher than 99% and used without further purification.

Table 1 Characteristic properties of the zeolites

Adsorbent	SiO_2/Al_2O_3 mole ratio	Pore volume, $cm^3 \cdot g^{-1}$	Effective pore diameter, nm
silicalite	365	0.24	0.5—0.6
ZSM-5	49.9	0.18	0.5—0.6

2.2 Apparatus and procedure

The experimental apparatus was of gravimetric type, as shown in Fig. 1. It basically consisted of (1) an electrobalance system, (2) two micromanometers, (3) two vacuum pumps, (4) an electrical heater and temperature controller, and (5) pyrex glassware.
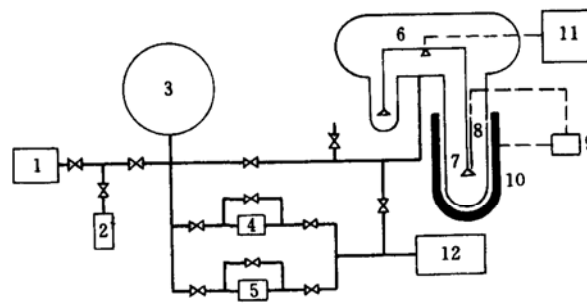

Figure 1 Schematic diagram of the adsorption apparatus
1—mechanical vacuum pump; 2—liquid adsorbate container;
3—vapor buffer vessel; 4—Barocel pressure sensor (Type 570);
5—Barocel pressure sensor (Type 590);
6—CAHN 2000 electrobalance; 7—adsorbent tray;
8—thermocouple;
9—temperature controller; 10—electrical heater; 11—recorder;
12—turbomolecular vacuum pump

CAHN 2000 electrobalance (CAHN Instruments, Inc., USA) with sensitivity of 10^{-4} mg was used to determine the adsorbent mass increment and to obtain the adsorption amount on per unit of adsorbent (N_a) at adsorption equilibrium. The equilibrium pressure (p) was measeured by Barocel pressure sensors Type 570 and Type 590 (Datametrics, Inc., USA), and their sensitivities were 0.1333 Pa and 1.333 Pa, respectively. Type 570 sensor was used when the sys-

tem pressure was lower than 1.333 kPa. Both reference ends of the sensors were maintained at a vacuum level of 1.333×10^{-3} Pa attained by the turbomolecular pump during adsorption runs. The temperature of the adsorption chamber was controlled within $\pm 0.05°C$. The maximum error in the measurement was estimated to be less than 1.5%.

3 RESULTS AND DISCUSSION

The experimental isotherms of n-heptane, n-octane and n-nonane adsorption on silicalite and ZSM-5 in the temperature range of 373.15—473.15 K under low pressure (0—5.332 kPa) are illustrated in Fig. 2. The adsorption amount decreases with increasing temperature. Another major observation is that the initial adsorption amount increment of a longer alkane (n-nonane) is much greater than that of a shorter alkane (n-heptane).

According to Dubinin-Polanyi potential theory, for a given adsorbent-adsorbate system there is a unique temperature-independent relation between the adsorption potential (E) and the volume of fluid adsorbed (W), where $E = RT \ln(p^0/p)$, $W = N_a/d_a$, and p^0 and d_a are the saturation vapor pressure of the adsorbate and the density of the adsorbate in the adsorbed phase at the adsorption absolute temperature (T), respectively[8]. Fig. 3 shows that all the experimental data of three n-alkanes on two zeolites are expectedly located on their respective characteristic curves.

More generally, adsorption equilibrium data for different adsorbent-adsorbate systems at various pressure and temperature can be expressed by the following universal relation[7,9,10]

$$\ln \left(\frac{W}{W_0} \right) = f \left(\frac{E}{\beta} \right) \qquad (1)$$

where W_0 is the saturated volume of the adsorbed phase and can be well approximated by pore volume of the adsorbent[9,10], f is the universal adsorption function, and β is the affinity coefficient. Ding et al.[7] inferred that the initial heat of adsorption would be the most pertinent quantity to be compared with β, since any effect of interaction between neighboring adsorbed molecules can be neglected in the zero coverage limit. The affinity coefficient β is given by[7]

$$\frac{\beta}{\beta_{\text{ref}}} = \frac{q}{q_{\text{ref}}} K \qquad (2)$$

where q is the initial heat of adsorption, β_{ref} and q_{ref} are the affinity coefficient and the initial heat of adsorption of a reference system, respectively, and K is a correction factor. The initial heat of adsorption can be estimated by Clausius-Clapeyron equation[7]

$$q = RT_1 T_2 \left(\frac{\ln p_1 - \ln p_2}{T_1 - T_2} \right) \qquad (3)$$

where p_1 and p_2 represent the adsorbate pressure corresponding to the same adsorption amount at different temperature T_1 and T_2 in the low pressure region, respectively.
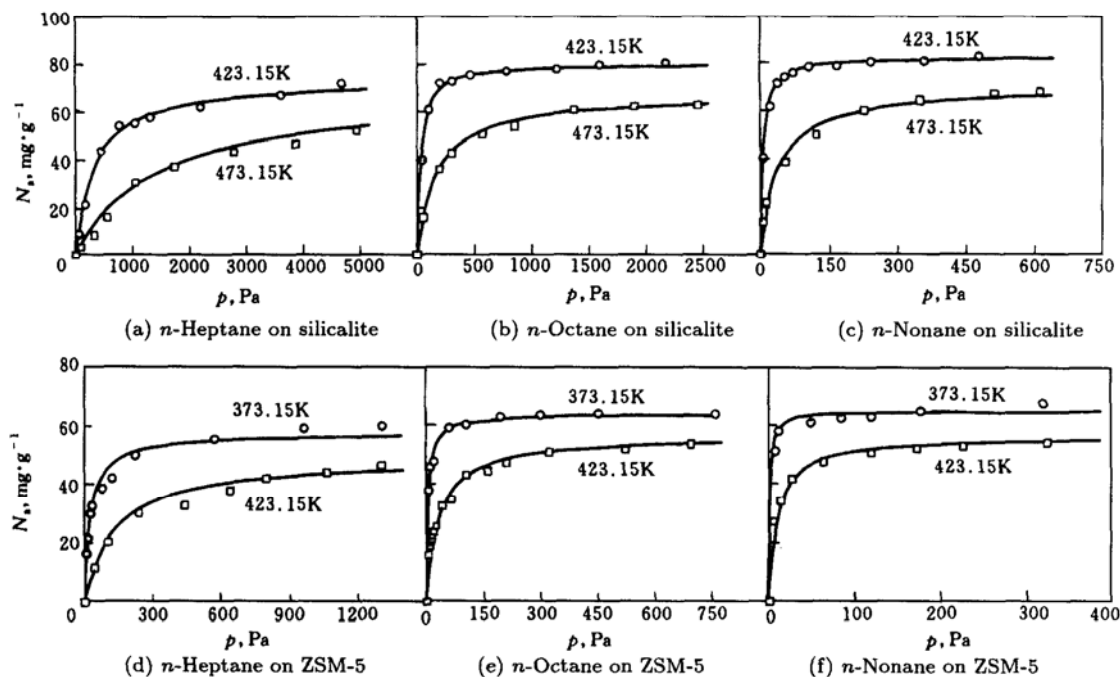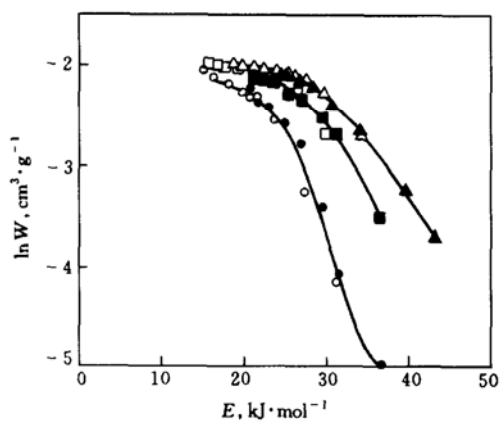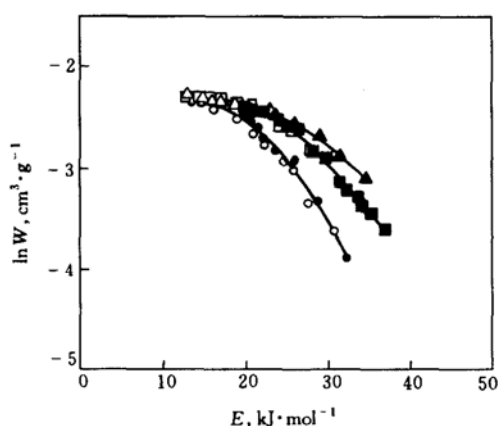

Figure 2   Adsorption isotherms of n-alkanes on zeolites
—— Langmuir isotherms; ○ □ experimental data

(a) Silicalite

O n-heptane at 423.15 K; □ n-octane at 423.15 K;
△ n-nonane at 423.15 K; ● n-heptane at 473.15 K;
■ n-octane at 473.15 K; ▲ n-nonane at 473.15 K

(b) ZSM-5

O n-heptane at 373.15 K; □ n-octane at 373.15 K;
△ n-nonane at 373.15 K; ● n-heptane at 423.15 K;
■ n-octane at 423.15 K; ▲ n-nonane at 423.15 K

Figure 3   ln$W$-E curves for adsorption of n-alkanes on zeolites

Conventionally the p values are read directly form the experimental isotherms[7], but it is subject to significant error. A new method to estimate q is suggested in this paper. In view of that the experimental adsorption data form an asymptotic isotherm and extend only up to about 56% of the saturation capacity

in this study, the Langmuir equation is reasonable to represent the data from low concentration region to near zero coverage limit

$$\theta = \frac{N_a}{N_{a,0}} = \frac{bp}{1 + bp} \qquad (4)$$

where θ is the fractional coverage, $N_{a,0}$ and b are Langmuir equation parameters. Both parameters may be easily obtained from the slope and intercept of the plot of N_a/p and N_a. Since in the low pressure limit,. $\theta \to 0$, $N_a \to 0$, $p \to 0$, $(1 + bp) \to 1$ and $p \to N_a/(bN_{a,0})$, a practical equation to estimate the initial heat of adsorption is derived from Eq. (3) by substituting $N_a/(bN_{a,0})$ for p

$$q = R\frac{T_1 T_2}{T_1 - T_2} \ln \frac{(bN_{a,0})T_2}{(bN_{a,0})T_1} \qquad (5)$$

The Langmuir equation parameters for three n-alkanes on two zeolites at different temperature are summarized in Table 2.

Take the adsorption system of n-heptane on silicalite as the reference system and let the corresponding $\beta_{ref} = 1$ and $K = 1$, then the other five correction factors are obtained by matching the experimental data to the reference plot of $\ln(W/W_0)$ and (E/β). The characteristic parameters for all the six systems are listed in Table 3. The calculated initial heat of adsorption on silicalite and ZSM-5 increases with the chain length of the n-alkanes significantly, consistent with the experimental observation that the adsorption amount of a longer alkane is much greater than that of a shorter alkane in the low pressure region. This result is in agreement with the configuration-bias Monte Carlo simulation results by Smit and Siepmann[4,5]. Table 3 also shows that the calculated initial heat of adsorption of the same n-alkanes is greater on silicalite than on ZSM-5. This observation is attributed to preferential adsorption of n-alkanes on zeolite with a higher Si/Al ratio.

Table 2   Langmuir equation parameters for adsorption systems

Adsorbent	Adsorbate	T_1		T_2	
		b, kPa^{-1}	$N_{a,0}$, mg·g^{-1}	b, kPa^{-1}	$N_{a,0}$, mg·g^{-1}
		$T_1 = 423.15$ K		$T_2 = 473.15$ K	
silicalite	n-heptane	3.14	73.0	0.728	68.6
	n-octane	11.3	79.8	6.31	66.7
	n-nonane	182	82.4	26.3	70.2
		$T_1 = 373.15$ K		$T_2 = 423.15$ K	
ZSM-5	n-heptane	36.9	57.5	7.65	48.9
	n-octane	207	63.7	29.7	56.5
	n-nonane	825	64.7	96.8	56.3

**Table 3 Characteristic parameters for adsorption systems**

Adsorbent	Adsorbate	Q, kJ·mol^{-1}	q/q_{ref}	K	β
silicalite	n-heptane*	50.7	1.00	1	1.00
	n-octane	61.8	1.22	1	1.22
	n-nonane	69.7	1.38	1	1.38
ZSM-5	n-heptane	45.6	0.90	1.17	1.05
	n-octane	54.1	1.07	1.17	1.25
	n-nonane	59.9	1.18	1.17	1.38

* reference system

Fig. 4 shows that all the experimental data of n-alkanes adsorption on zeolite cluster closely on a generalized characteristic curve, which can be described by the improved Dubinin-Astakhov adsorption equation[9]

$$
\ln\left(\frac{W}{W_0}\right) = (-9.36 \times 10^{-2})\left(\frac{E}{\beta}\right)
$$
$$
+ (5.88 \times 10^{-3})\left(\frac{E}{\beta}\right)^2
$$
$$
+ (-1.69 \times 10^{-4})\left(\frac{E}{\beta}\right)^3 \quad (6)
$$

where the coefficients are obtained by the nonlinear regression method.
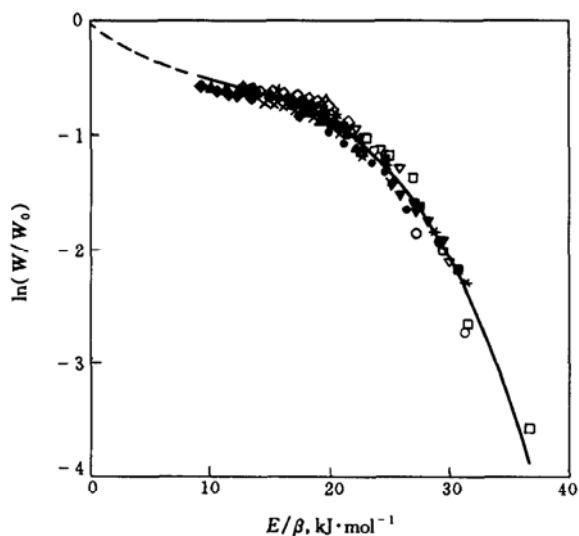
Figure 4　Generalized correlation curve for adsorption of n-alkanes on zeolites

○ n-heptane on silicalite, 423.15 K; □ n-heptane on silicalite, 473.15 K; △ n-octane on silicalite, 423.15 K; ▽ n-octane on silicalite, 473.15 K; ◇ n-nonane on silicalite, 423.15 K; * n-nonane on silicalite, 473.15 K; ● n-heptane on ZSM-5, 373.15 K; ■ n-heptane on ZSM-5, 423.15 K; ▲ n-octane on ZSM-5, 373.15 K; ▼ n-octane on ZSM-5, 423.15 K; ◆ n-nonane on ZSM-5, 373.15 K; × n-nonane on ZSM-5, 423.15 K;

It is interesting to notice that the correction factor is dependent on the characteristic properties of the zeolite rather than the chain length of the n-alkane as illustrated in Table 3, which implies that the experimental data of these three n-alkanes on the same adsorbent can be located on one generalized characteristic curve utilizing solely the parameter of the initial heat of adsorption. Nevertheless, the correction factor is necessary for a general correlation of the experimental data on different adsorbents. Generally, adsorption on different microporous zeolites will suffer the effect of framework structure. Experimental data for more systems and further theoretical research applying Monte Carlo technique may need to quantify the effect of zeolite framework structure on the adsorption and the correction factor.

NOMENCLATURE

b	Langmuir equation parameter, kPa^{-1}
d_a	density of adsorbate in the adsorbed phase, mg·cm^{-3}
E	adsorption potential, kJ·mol^{-1}
K	correction factor
N_a	adsorption amount on per unit of adsorbent, mg·g^{-1}
$N_{a,0}$	Langmuir equation parameter, mg·g^{-1}
p	equilibrium pressure of adsorbate, Pa
p^0	saturation vapor pressure of adsorbate, Pa
q	initial heat of adsorption, kJ·mol^{-1}
R	gas constant
T	temperature, K
W	volume adsorbed, cm^3·g^{-1}
W_0	pore volume of the adsorbent, cm^3·g^{-1}
β	affinity coefficient
θ	fractional coverage

Subscript

ref　reference system

REFERENCES

1 Stach, H., Lohse, U., Thamm, H., Schirmer, W., "Adsorption equilibrium of hydrocarbons on highly dealuminated zeolites", Zeolites, 6, 74—90 (1986).

2 Thamm, H., "Adsorption site heterogeneity in silicalite: A calorimetric study", Zeolites, 7, 341—346 (1987).

3 Hufton, J. R., Danner, R. P., "Chromatographic study of alkanes in silicalite: Equilibrium properties", AIChE J., 39, 954—961 (1993).

4 Smit, B., Siepmann, J. I., "Simulating the adsorption of alkanes in zeolites," Science, 264, 1118—1120 (1994).

5 Smit, B., Siepmann, J. I., "Computer simulations of the energetics and siting of n-alkanes in zeolites," J. Phys. Chem., 98, 8442—8452 (1994).

6 Du, Z., Manos, G., Vlugt, T. J. H., Smit, B., "Molecular simulation of adsorption of short linear alkanes and their mixtures in silicalite", AIChE J., 44, 1756—1764 (1998).

7 Ding, T. F., Ozawa, S., Yamazaki, T., Watanuki, I., Ogino, Y., "A generalized treatment of adsorption of methane onto various zeolites", Langmuir, 4, 392—396 (1988).

8 Dubinin, M. M., "The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces", Chem. Rev., 60, 235—241 (1960).

9 Ozawa, S., Kusumi, S., Ogino, Y., "Physical adsorption of gases at high pressure (IV) An improvement of the Dubinin-Astakhov adsorption equation", J. Colloid Interface Sci., 56, 83—91 (1976).

10 Wakasugi, Y., Ozawa, S., Ogino, Y., "Physical adsorption of gases at high pressure (V) An extension of a generalized adsorption equation to systems with polar adsorbents", J. Colloid Interface Sci., 79, 399—409 (1981).