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Analysis of *n*-C4∼*n*-C10 mixtures in 5A molecular sieves using IAS theory with multi-site Langmuir isotherms

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Abstract The Constant-capacity Adsorption Solution (CAS) model for *n*-C4∼*n*-C10 mixture was built. Based on the adsorption experimental data, the Multi-site Langmuir (MSL) model was selected to describing the adsorption isotherms of *n*-C4∼*n*-C10 monocomponent. The CAS model was derived based on the IAS theory. The adsorption capacities predicted by the CAS model were compared with the experiment data of mixed gas adsorption. The results show the consistency. From the viewpoint of thermodynamics, the interactions between the normal paraffins of different carbon numbers were discovered. CAS model is applicative for the mixed gas in which the monocomponents have the similar adsorption capacities in the adsorbent.

Keywords Normal paraffins · Molecular sieves · Adsorption model

1 Introduction

Naphtha is more than 10% of the total crude oil refining amount. The normal paraffins in naphtha are quality feeds for producing ethylene through steam cracking process, while other components (iso-hydrocarbons, cyclanes and aromatics) are excellent feeds for producing aromatics through catalytic reforming process. Separating the normal paraffins from naphtha through adsorption process using 5A molecular sieves can realize the simultaneous optimization to improve the yields of both ethylene and aromatics (Liu et al. 2006). The normal paraffins in naphtha mainly include the components from *n*-butane to *n*-decane (*n*-C4∼*n*-C10). The adsorption equilibrium data of single normal paraffin have been reported in many literatures (Vavlitis et al. 1981; Jullian 1993; Doetsch et al. 1974; Silva and Rodrigues 1997a, 1997b; Ruthven and Loughlin 1971) but the mixed gas equilibrium data of two or three normal paraffins mainly concentrate on the components of *n*-C5∼*n*-C7 (Zhou et al. 1990, 1993; Li et al. 1995). The mixed gas equilibrium data of more normal paraffins is rare.

The importance of multicomponent adsorption model is to predict the adsorption capacity for mixed gas under the given temperatures and pressures using the adsorption isotherms of the monocomponents. Most studies on the multicomponent adsorption model were based on two or three components. Although these models can be extended to more components theoretically, they are hard to be solved for seven components (*n*-C4∼*n*-C10) because of the algorithmic complexity. At the same time, majorities of the mixed gas adsorption models (Myers and Prausnitz 1965) supposed that the different adsorption molecules occupy the same amount of adsorption sites in the adsorbent. Because the adsorption sites occupied by different normal paraffin molecules are obviously different, there is still not any proper mixed gas model for the normal paraffins—5A molecular sieves system so far.

The Constant-capacity Adsorption Solution (CAS) model was established combining MSL for single component and IAS predictions for mixtures. Based on the adsorption experimental data, the Multi-site Langmuir (MSL) model was selected to describing the adsorption isotherms of *n*-C4∼*n*-C10 monocomponent. And the parameters of the MSL model were abstracted from the literatures (Silva and Rodrigues 1999). According to the characteristics of the normal paraffin—5A molecular sieves system, supposing that

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the molecular number that certain adsorbent can adsorb for the specific normal paraffin is inversely proportional to its carbon number. The CAS model was derived based on the IAS theory. The adsorption capacities predicted by the CAS model were compared with the experiment data of mixed gas adsorption. The results show the consistency. The CAS model can describe the adsorption equilibrium of *n*-C4∼*n*-C10 mixed gas in 5A molecule sieves.

2 Modeling *n*-C4∼*n*-C10 monocomponent adsorption equilibrium data

Langmuir was the first to raise the Langmuir adsorption model (1) (Langmuir 1918) according to the dynamic equilibrium between the adsorbed phase and the gas phase supposing that adsorbed molecules would not break down.

$$K_{\mathrm{eq}} = \frac{1}{p}\frac{\theta}{1-\theta} \tag{1}$$

Considering the interaction between adsorption molecules, Fowler and Guggenheim introduced parameter u and raised the adsorption isotherm of (2) (Flower and Guggenheim 1939).

$$K_{\mathrm{eq}} \exp\left(\frac{2u\theta}{RT}\right) = \frac{1}{p}\frac{\theta}{1-\theta} \tag{2}$$

Nitta et al. (1984) adopted statistic thermodynamic method and assumed that one molecule occupied n active sites when adsorbed then raised MSL model, whose equation is as (3).

$$K_{\mathrm{eq}} \exp\left(\frac{nu\theta}{kT}\right) = \frac{1}{p}\frac{\theta}{(1-\theta)^n} \tag{3}$$

where u is the interaction energy between adsorbed molecules (positive for attract and negative for repulsion), k is Boltzmann constant and K_{eq} is equilibrium constant and can be calculated by (4).

$$K_{\mathrm{eq}} = K_0 \exp\left(\frac{-\Delta H_{\mathrm{ads}}}{RT}\right) \tag{4}$$

A great deal of adsorption equilibrium data of the monocomponent of normal paraffins in 5A molecular sieves were collected by Silva and Rodrigues (Silva and Rodrigues 1999) and associated using Nitta's MSL model. The model parameters for the adsorption of *n*-paraffin monocomponent in 5A molecular sieves were listed in Table 1. The deviation between experimental and calculated result is 0.25 g/100 g molecular sieves.

It can be seen from the data in Table 1 (Silva and Rodrigues 1999) and Roma's (Roma and Ramirez-Pastor 2005) that, the number of active sites occupied by the normal paraffin molecule equals its carbon number. The adsorption of normal paraffins in 5A molecular sieves is different from other mixed gas adsorption systems. Therefore, it's necessary to consider the difference of the active site numbers occupied by different normal paraffin molecules, which is the starting point of the CAS model. From the parameters of the MSL model, it is noticed that the adsorption heat improves in accordance with the increase of the carbon number. Generally, the greater adsorption heat means the more stable status after the adsorbate molecules occupy the adsorption sites. So the normal paraffins with more carbon numbers have greater adsorptivity.

As there is no report related to *n*-nonane adsorption isotherm. The MLS parameters for *n*-nonane are got from the interpolation of different normal paraffins.

$$K_{90} = 1.32 \times 10^{-6}\ (\mathrm{kPa}^{-1}),$$

$$-\Delta \mathrm{H}_{\mathrm{ads}} = 21.2\ (\mathrm{kcal/mol})$$

Adsorption capacities of normal paraffin monocomponent at various temperatures and pressures can be calculated by MSL model (3) using the MSL model parameters. They are necessary for CAS model.

3 Multicomponent Constant-capacity Adsorption Solution (CAS) model

The Ideal Adsorption Solution (IAS) model (Myers and Prausnitz 1965) was derived by Myers and Prausnitz can

Table 1 MSL model parameters for *n*-paraffin monocomponent adsorption in 5A molecular sieves (Silva and Rodrigues 1999)

Paraffins	K_0 ($\times 10^{-7}$ kPa^{-1})	Adsorption heat $-\Delta H_{\mathrm{ads}}$ (kcal/mol)	Adsorption sites n	Interaction parameter $(u/k)/K$	$q_{\max}$ (g/100 g MS)	Error $\lvert\varepsilon\rvert = \lvert q_{\mathrm{exp}} - q_{\mathrm{cal}}\rvert$ (g/100 g MS)
n-Butane	882.6	10.2	4	1	13	0.18
n-Pentane	197.2	13.2	5	1	13	0.15
n-Hexane	553.1	14.2	6	1	13	0.08
n-Heptane	68.0	16.9	7	379	13	0.25
n-Octane	28.6	19.2	8	392	13	0.10
n-Decane	6.1	23.2	10	392	13	0.17

calculate the adsorption equilibrium of two or more components from the adsorption isotherms of monocomponents. But one assumption of the IAS model says that the adsorption possesses a temperature-invariant area which is the same for all adsorbates, that is, certain quantity of adsorbent can adsorb same number of molecules of different adsorbates. It would not be valid for a molecular sieve adsorbent, where the adsorbed molecule number depends on the size of the adsorbate molecule. According to Table 1, $q_{\max}$, the maximal adsorption capacity of each normal paraffin in 5A molecular sieves is the same, thus the CAS model assume that (1) the adsorbent is thermodynamic inert material. During the adsorption process under constant temperature, the thermodynamic characteristic change of adsorbent can be ignored; (2) meeting the assumption of Gibbs adsorption equation; (3) to different kinds of normal paraffins, certain quantity of adsorbent can adsorb same weight of different kinds of adsorbates, which means that, the molecule number that certain quantity of adsorbent can adsorb is inversely proportional to the carbon number of the normal paraffin, and can be summarized by (5).

$$\pi A = q_t RT = n_t MRT \tag{5}$$

where π is the spreading pressure, A is the effective area, q_t is the adsorption capacity of adsorbate, n_t is the number of adsorbate molecules, M is the molecular weight of the normal paraffin.

Similar to the derivation of IAS model, the equilibrium equation for the mixed-gas adsorption is

$$Py_i = P_i^0(\pi)\gamma_i x_i \quad \text{(constant } T\text{)} \tag{6}$$

In (6), γ_i is the activity coefficient; $P_i^0(\pi)$ is the equilibrium gaseous pressure of pure component i under adsorption phase temperature and spreading pressureπ.

To an ideal solution, activity coefficient is 1, and get

$$Py_i = P_i^0(\pi)x_i \quad \text{(constant } T\text{)} \tag{7}$$

Gibbs adsorption isothermal equation is

$$-Ad\pi + \sum n_i d\mu_i = 0 \quad (T \text{ is constant}) \tag{8}$$

To a pure component, integrating (8) gives

$$\pi(P_i^0) = \frac{RT}{A}\int_{t=0}^{P_i^0} n_i^0(t)\, d\ln t \quad \text{(constant } T\text{)} \tag{9}$$

According to the adsorption isotherm of pure component, the equation between n_i^0 and P_i^0 can be expressed as

$$n_i^0 = \frac{q_i^0}{M} = F_i(P_i^0) \tag{10}$$

Substituting (10) into (9) and we can get the relationship between π_i^0 and P_i^0:

$$\pi_i^0 = \psi_i(P_i^0) \tag{11}$$

For the pseudo-mixing process under constant spreading pressure π,

$$\pi_1^0 = \pi_2^0 = \pi_i^0 \tag{12}$$

$P_i^0(\pi)$ of pure components under the same spreading pressure can be calculated from (11)–(12), which will be used for the calculation of (7).

To the adsorbed phase and the gas phase, normalizing equations are

$$\begin{aligned} x_1 + x_2 + \cdots + x_n &= 1 \\ y_1 + y_2 + \cdots + y_n &= 1 \end{aligned} \tag{13}$$

Equations (7), (11), (12) and (13) compose the multicomponent Constant-capacity Adsorption Solution model.

To solve the CAS model, the key problem is to get the $P_i^0(\pi)$ under certain spreading pressure. As the spreading pressure cannot be directly measured, it must be described using (5). For the Ideal Adsorption Solution model

$$n_t = \frac{\pi A}{RT} \tag{14}$$

For the CAS model, according to the assumption (3),

$$q_t = \frac{\pi A}{RT} \tag{15}$$

For the adsorption of normal paraffins in 5A molecular sieves, the same spreading pressure is equivalent to the same adsorbate weight q_t adsorbed.

According to (3), under certain adsorption capacity (certain spreading pressure as well), the gas phase equilibrium pressure of pure component can be expressed as

$$P_i^0 = \frac{1}{K_{\text{eq}}}\frac{\theta}{(1-\theta)^n}\exp\left(-\frac{nu\theta}{kT}\right) \tag{16}$$

where $\theta = \frac{q_t}{q_{\max}}$.

P_i^0 can be expressed as the explicit function of q_t when MSL equation is adopted to describe the adsorption isotherm of pure component.

For the adsorption of n-C4$\sim$$n$-C10 multi-components in 5A molecular sieves, it's not capable to list all the diagrams for all the compositions. Using the SPC naphtha as a sample, the adsorption equilibrium data for the mixed gas was solved. The gas phase compositions of normal paraf-

Table 2 Unitary composition of n-C_4^0 ~n-C_{10}^0 in SPC naphtha

	n-C_4^0	n-C_5^0	n-C_6^0	n-C_7^0	n-C_8^0	n-C_9^0	n-C_{10}^0	$\sum$
Content (mol%)	0.72	3.86	11.73	25.12	36.93	19.60	2.04	100.00

fins in SPC naphtha are $y_1, y_2, \ldots, y_n$, which are constants. Because of the excellent shape selective characteristics of 5A molecular sieves, iso-paraffins, cyclanes and aromatics can be treated as inert components. Therefore, n-C4~n-C10 were normalized and listed in Table 2.

The CAS model can be solved as the following procedure:

1. Choose a series of adsorption capacity values q_t by fixed interval from 0–13 (0–$q_{\max}$).
2. Calculate θ for each adsorption capacity q_t, and compute $P_1^0, P_2^0, \ldots, P_n^0$ (n is component number) using (16) according to the adsorption temperature T and parameters of MSL model.
3. Give a certain gas phase pressure P and calculate the fractional pressure for each component according to the composition of the mixed gas.
4. Solve $x_1, x_2, \ldots, x_n$ from (7).
5. According to $x_1 + x_2 + \cdots + x_n > 1$ or $x_1 + x_2 + \cdots + x_n < 1$ and change the gas phase pressure P, till $x_1, x_2, \ldots, x_n$ satisfies the normalized (12).
6. Draw the $q_t \sim P$ curve, which is the total adsorption isotherm for mixed gas (Fig. 1).
7. Calculate the adsorption isotherm for each normal paraffin using (7) according to P, y_i and P_i^0.

It can be seen from Fig. 1 that the isotherm of mixed gas is similar with that of normal paraffin monocomponent. The adsorption capacity improves rapidly with the increase of the adsorption pressure in the scope of relatively low pressure. Taking the adsorption at 300 °C as an example, the adsorption capacity of normal paraffin under atmospheric pressure is approximately 7.0 g/100 g MS, while it is 8.3 g/100 g MS under 0.5 MPa and is 8.7 g/100 g MS under 1.0 MPa. The growth rate of the adsorption capacity on the adsorption pressure decreases with the increase of the adsorption pressure.

Under the same pressure, the equilibrium adsorption capacity of mixed gas at low temperature is higher than that of high temperature. Taking the adsorption at 100 kPa as an example, the adsorption capacity is 9.7 g/100 g MS at 200 °C, while it is 4.9 g/100 g MS at 350 °C.

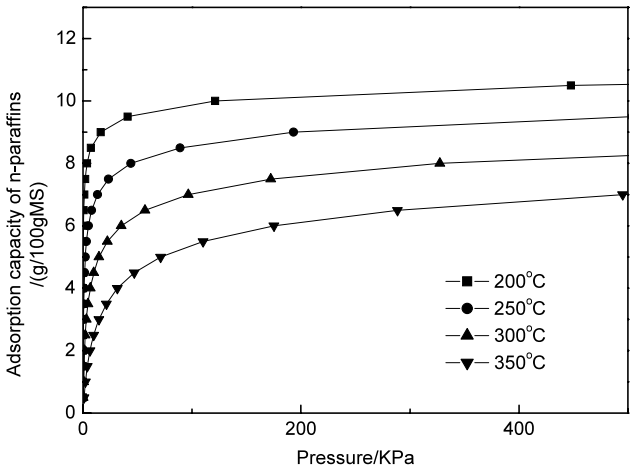

Fig. 1 Total adsorption capacities of n-C4~n-C10 mixture in 5A molecular sieves [Compositions from Table 2]

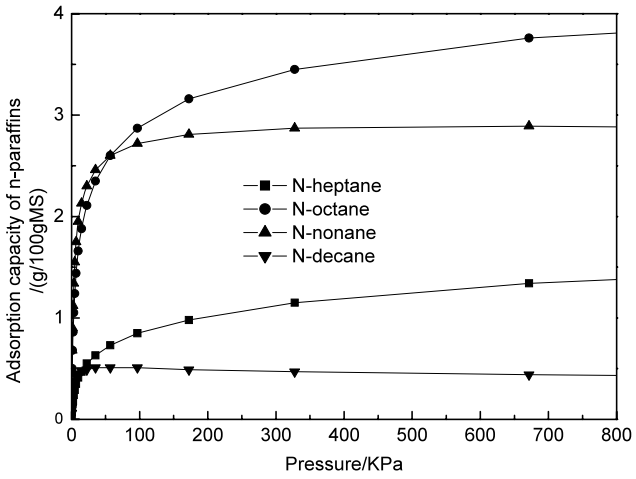

Fig. 2 Equilibrium adsorption capacities of n-C7~n-C10 monocomponents at different pressures [Compositions from Table 2]

4 Prediction using CAS model

4.1 The equilibrium adsorption capacity for each normal paraffin in mixed gas adsorption

According to the CAS model, the equilibrium adsorption capacities of normal paraffin monocomponents at atmospheric pressure and 300 °C are listed in Table 3.

It can be seen from Table 3 that when n-C4~n-C10 mixed gas reaches adsorption equilibrium, the adsorption capacity of short-chain normal paraffin is very small, long-chain normal paraffin has distinct competitive advantage of adsorption. In a fixed absorber, short-chain normal paraffins adsorbed in the molecular sieves can be desorbed by the long-chain normal paraffins in the following feed. The displaced short-chain normal paraffins moves forward with the

Table 3 Equilibrium adsorption capacities of *n*-paraffins at 300 °C and atmospheric pressure

	n-C_4^0	n-C_5^0	n-C_6^0	n-C_7^0	n-C_8^0	n-C_9^0	n-C_{10}^0	$\sum$
Adsorption amount (g/100 g MS)	0.00074	0.0057	0.048	0.85	2.87	2.72	0.51	7.00

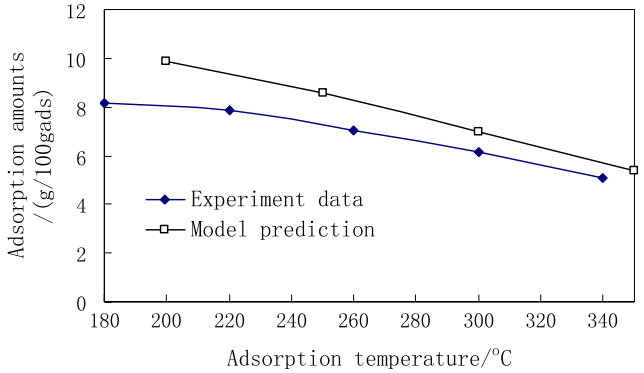

Fig. 3 Comparison of model prediction equilibrium and experimental dynamic adsorption quantity [Compositions from Table 2]

main body flow of the feed, and then will be adsorbed by the molecular sieves ahead, then will be displaced again.

For the SPC naphtha, the adsorption equilibrium capacity of *n*-C7∼*n*-C10 normal paraffin at 300 °C and different pressures is show in Fig. 2 (the adsorption capacities of *n*-C4∼*n*-C6 are small, so they are not included).

It can be seen from Fig. 2 that the change trend of equilibrium adsorption capacities are different for different normal paraffins. The increasing trend of *n*-heptane is the most significant, and *n*-octane is the second. The *n*-nonane's equilibrium adsorption capacity nearly doesn't changes when the pressure is higher than 100 kPa, while the trend slightly decreases for *n*-decane. This phenomenon is due to the different increasing trends of adsorption capacities with the pressure for normal paraffin monocomponents. The competitive adsorption capabilities of *n*-heptane and *n*-octane increase evidently with the pressure. Although the adsorption capabilities of *n*-nonane and *n*-decane are strong, the increasing trends along with the pressure are relatively smooth. According to the characteristics of 5A molecular sieves, the adsorption capacity is restricted by the volume of the 5A pore. When the pressure increases to certain degree, total adsorption capacity nearly doesn't increase with the pressure. Therefore, the higher the pressure is, the greater the proportion of short chain normal paraffin in the adsorption phase will be. Then the increasing trend of the adsorption capacity for low carbon number normal paraffin with the pressure is more sharply than that of high carbon number normal paraffin.

4.2 Total equilibrium adsorption capacity of *n*-C4∼*n*-C10 in naphtha

The CAS model can predict the total equilibrium adsorption capacity of *n*-C4∼*n*-C10 in SPC naphtha in 5A molecular sieves at different temperatures. Figure 3 contrasts the CAS model predicting total equilibrium adsorption capacity with the experimental dynamic adsorption quantity under atmospheric pressure. Due to the effect of diffusion and axial backmixing, the experimental dynamic adsorption quantity is lower than predicting equilibrium adsorption capacity by 10%∼15%. The difference is smaller when the adsorption temperature is higher. At higher temperature, the molecular motion is fast, so the internal and external diffusion control becomes weak. Then the model predicting equilibrium adsorption capacity will be more appropriate to the experimental dynamic adsorption quantity.

According to the assumption (3) of the CAS model, CAS model is also applicative for the mixed gas in which the monocomponents have the similar adsorption capacities in the adsorbent.

5 Conclusion

The Constant-capacity Adsorption Solution model (CAS) model, which is proper to normal paraffin—5A molecular sieves system was built. The adsorption capacities predicted by the CAS model were compared with the experiment data of mixed gas adsorption. The results show the consistency. The model discloses the interaction between the normal paraffins with different carbon numbers. CAS model is also applicative for the mixed gas in which the monocomponents have the similar adsorption capacities in the adsorbent.

References

Liu, J., Shen, B., Sun, H.: Adsorption behavior of *n*-paraffins in a fixed adsorber containing 5A molecular sieves. Adsorpt. Sci. Technol. **24**, 311–320 (2006)

Vavlitis, A.P., Ruthven, D.M., Loughlin, K.F.: Sorption of *n*-pentane, *n*-octane and *n*-decane in 5A zeolite crystals. J. Colloid Interface Sci. **84**, 526–531 (1981)

Jullian, S.: The methodology of gas adsorption process design. Validation of adsorption models for hydrocarbon separation and fuel gas fractionation. European Commission, Final Report of the Joule Programme, Project JOUE2-0052-C, 1993

Doetsch, I.H., Ruthven, D.M., Loughlin, K.F.: Sorption and diffusion of *n*-heptane in 5A zeolite. Can. J. Chem. **52**, 2717–2724 (1974)

Silva, J.A., Rodrigues, A.E.: Sorption and diffusion of *n*-pentane in pellets of 5A zeolite. Ind. Eng. Chem. Res. **36**, 493–500 (1997a)

Silva, J.A., Rodrigues, A.E.: Equilibrium and kinetics of *n*-hexane sorption in pellets of 5A zeolite. AIChE J. **43**, 2524–2534 (1997b)

Ruthven, D.M., Loughlin, K.F.: Sorption of light paraffins in type A zeolites. Can. J. Chem. **49**, 696–708 (1971)

Zhou, X., Chen, S., Sun, H., Huang, G., Chang, K., Li, C.: Equilibrium of *n*-C5/C6/C7 mixture in 5A molecular sieves. J. East China Univ. Sci. Technol. **19**(6), 690–696 (1993)

Zhou, X., Chen, S., Huang, G., Li, C.: Adsorption of *n*-C5/C6 in 5A molecular sieves. Acta Petrolei Sinica (Petroleum Processing Section) **6**(2), 100–106 (1990)

Li, B., Chen, S., Zhou, X., Tang, C.: Adsorption separation of light normal and iso-paraffin. Acta Petrolei Sinica (Petroleum Processing Section) **11**(1), 40–46 (1995)

Myers, A.L., Prausnitz, J.M.: Thermodynamics of mixed-gas adsorption. AIChE J. **11**, 121–127 (1965)

Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. **40**, 163 (1918)

Flower, R.H., Guggenheim, E.A.: Statistical Thermodynamics. Cambridge University Press, Cambridge (1939)

Nitta, T., Shigetomi, T., Kuro-Oka, M., Katayama, T.: An adsorption isotherm of multi-site occupancy model for homogeneous surface. J. Chem. Eng. Jpn. **17**, 39 (1984)

Silva, J.A.C., Rodrigues, A.E.: Multisite Langmuir model applied to the interpretation of sorption of *n*-paraffins in 5A zeolite. Ind. Eng. Chem. Res. **38**(6), 2434–2438 (1999)

Roma, F.J.L., Ramirez-Pastor, A.J.: Statistical thermodynamics models for polyatomic adsorbates: application to adsorption of *n*-paraffins in 5A zeolite. Langmuir **21**(6), 2454–2459 (2005)