Alkane Adsorption on Zeolites

Molecular Competition Effects in Liquid-Phase Adsorption of Long-Chain *n*-Alkane Mixtures in ZSM-5 Zeolite Pores**

Joeri F. M. Denayer, Kurt De Meyer, Johan A. Martens, and Gino V. Baron*

Zeolite adsorbents play a vital role in molecular separation technology, industrial catalysis and pollution control. In spite of its relevance to these areas, few fundamental studies have thus far been devoted to the adsorption of mixtures. The complexity of the molecular filling patterns of zeolite micropores directed earlier investigations, rather, into the adsorption of a single compound. Herein, we report the investigation of the adsorption of binary mixtures of *n*-alkanes with chain lengths up to C_{22} from the liquid phase on ZSM-5 zeolite, and the discovery of unexpected selectivities depending on subtle differences in the number of carbon atoms. In some *n*-alkane mixtures, the uptake of the lighter molecule was favored, whereas in other mixtures the heavier molecule was preferred. With other alkane combinations, azeotropic behavior of the adsorbate phase was also encountered. Systematic exploration of binary mixtures in the carbon range C_5–C_{22} led to the identification of the underlying mechanisms.

Intriguing effects in the adsorption of single components in microporous environments, such as zeolites were found recently. For example, ferrierite behaves as a 1D pore system for long-chain *n*-alkane molecules ($>C_5$), whereas only shorter molecules can exploit its full 2D pore system.[1–4] With ferrierite and ZSM-22, the siting of dibranched alkane seems to depend subtly on their size. At low coverage the dibranched alkanes adsorb in parallel to the outer surface of the zeolite and as coverage increases, additional molecules adsorb in such a manner that propyl and butyl groups point into the pores.[5] Other studies focused on the relationship between pore size and energy of interaction of pure substances.[6,7] Efforts have been made in the study of adsorption of hydrocarbons on ZSM-5 and Silicalite-1. These zeolites have the MFI framework topology are among the most studied zeolites in the field of adsorption, diffusion and catalysis.[8] The pore system of these zeolites comprises linear channels, with a free pore diameter of 5.6×5.3 Å, that are

---

[*] Dr. Ir. J. F. M. Denayer, Ir. K. De Meyer, Prof. Dr. Ir. G. V. Baron
Department of Chemical Engineering, Vrije Universiteit Brussel
Pleinlaan 2, 1050 Brussel (Belgium)
Fax: (+32) 2-629-32-48
E-mail: Joeri.denayer@vub.ac.be

Prof. Dr. Ir. J. A. Martens
Center for Surface Chemistry and Catalysis
Katholieke Universiteit Leuven
Kasteelpark Arenberg 23, 3001 Leuven (Belgium)

[**] This research was financially supported by FWO Vlaanderen. J.F.M.D. is grateful to the F.W.O.-Vlaanderen, for a fellowship as postdoctoral researcher. J.A.M. acknowledges the Flemish government for financial support through a concerted research action (G.O.A.).

DOI: 10.1002/ange.200351012

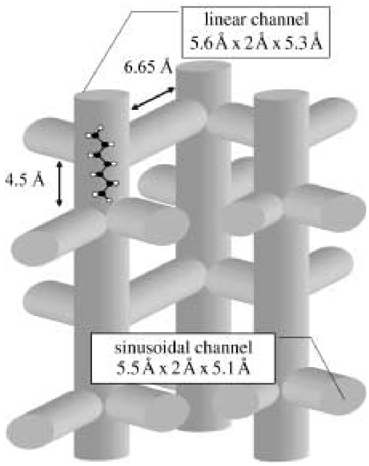

Figure 1. Schematic presentation of the structure of ZSM-5.

intersecting with sinusoidal channels, with free diameters of 5.5 × 5.1 Å (Figure 1). The length of a linear channel segment between two intersections is 4.5 Å. The sinusoidal channel segments measure 6.65 Å. Each unit cell contains four intersections, four sinusoidal segments and four linear segments.

Adsorption isotherms of *n*- and isoalkanes on MFI type zeolites deviate from the usual Langmuir isotherm and contain a "kink" at a compound specific partial pressure. These kinks coincide with abrupt changes in adsorption enthalpy and entropy, ascribed to a transition from adsorption in one type of channel to both types and the intersections.[9–15] For example, isobutane is adsorbed in the channel intersections at low pressure, while at high pressure, the isobutane molecules invade the channel segments too.[16] For *n*-alkanes, sometimes contradicting adsorption models were proposed to explain experimental adsorption isotherms. Short alkanes were postulated to adsorb in the entire pore system, or in the intersections.[13,14,17] C_9 and C_{10} *n*-alkanes preferentially fill the sinusoidal channel and C_6-C_8 alkanes the straight channels.[17] According to another study, alkanes longer than C_4 occupied the sinusoidal channels.[13] A similar, confusing picture emerged from theoretical calculations, such as Configurational-bias Monte-Carlo and Molecular Dynamic approaches. In some studies short alkanes were found to adsorb in all regions.[18–20] Other studies showed selective adsorption in sinusoidal channels or in the intersections.[21,22] At low temperatures, longer alkanes are positioned in the straight channels but are distributed over the entire pore system at higher temperatures.[18] Configurational-bias Monte-Carlo simulations revealed a "commensurate freezing" phenomenon of hexane and heptane in the sinusoidal channels.[23] At low partial pressure, the alkanes move freely in the sinusoidal channels, and prevent other molecules from adsorbing in the linear channels. At higher pressures, molecules are frozen in the sinusoidal channels allowing the filling of linear channel segments as well.[23]

In mixtures, theoretically the selectivity for the shortest molecule increases with increasing loading.[24,25] This happens because the vacant sites in the pores can best be filled by the smallest molecules.[26] Until now, theoretical approaches have been applied to predict the behavior of mixtures of much shorter alkane than the ones studied in the present work.[27]

For some representative binary alkane mixtures, compositions in the adsorbed phase (X_i) are plotted versus the compositions of the external liquid phase (Y_i) in Figure 2. Preferential adsorption of the longest alkane chain was observed with C_8/C_{12}, C_9/C_{13}, and C_9/C_{11} (Figure 2; a–c). In the C_{14}/C_{15}, and C_{15}/C_{16} mixtures, the lightest alkane was selectively adsorbed (Figure 2; g, h). With C_6/C_{10}, and C_5/C_7 mixtures, the adsorbate phase behaved as an azeotrope (Figure 2; d, e). Azeotropic behavior was identified by a reversal of selectivity, at a specific composition where adsorbate and liquid have identical composition.[28] Thus the behavior of ZSM-5 zeolite is entirely different from mesoporous adsorbents, which do not discriminate among short and long alkanes when adsorbed from a liquid phase.[29]

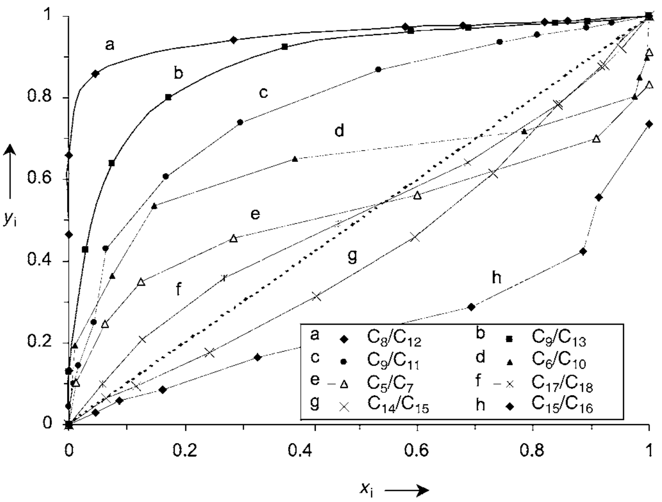

Figure 2. Selectivity diagrams for the adsorption of some binary alkane mixtures on ZSM-5. See also Table 1.

The behavior of investigated *n*-alkane mixtures, in terms of the formation of azeotropes, or selective adsorption of the longest or shortest molecule, is summarized in Table 1.[30] Selective adsorption of the short alkane compound was observed with C_{14}/C_{15} and C_{15}/C_{16}, azeotropic behavior with C_5/C_7, C_6/C_7, C_6/C_8, C_7/C_8, C_6/C_{10}, C_{13}/C_{14}, C_{17}/C_{18}, and C_{20}/C_{22}. Selective adsorption of the heaviest molecule occurred with C_5/C_6, C_6/C_{14}, C_8/C_9, C_8/C_{12}, C_9/C_{11}, C_9/C_{12}, and C_9/C_{13}. In Table 1, the adsorption selectivity is further quantified by two parameters, namely 1) the external mole fraction (X_{ext}) of short chains needed to obtain an equimolar concentration in the pores, and 2) the mole fraction of long chains in the pores (X_{int}) at an equimolar composition in the external liquid phase. The adsorption selectivity was most pronounced with C_8/C_{12}. For example, the C_8 mole fraction in the external liquid phase must exceed 0.99 to reach a 50:50 mixture inside the pores (Table 1, entry 8). The very pronounced selectivity for C_{15} versus C_{16}, that is alkanes with a difference in chain length of one C atom, is striking (Table 1, entry 14: $X_{ext} = 0.10$).

Table 1: Summary of the behavior encountered in the adsorption of alkane mixtures on ZSM-5

Entry	Mixture	Adsorption behavior[a]	X_{ext}[b]	X_{int}[b]	Pore filling [%][c]
1	C_5/C_7	A	0.59	0.53	75–85
2	C_5/C_6	L	0.66	0.65	72–87
3	C_6/C_7	A	0.42	0.66	89–87
4	C_6/C_8	A	0.55	0.52	85–64
5	C_6/C_{10}	A	0.87	0.67	81–85
6	C_6/C_{14}	L	0.86	0.73	85–100
7	C_8/C_9	L	0.82	0.80	64–74
8	C_8/C_{12}	L	>0.99	0.97	66–92
9	C_9/C_{11}	L	0.89	0.85	74–89
10	C_9/C_{12}	L	0.91	0.91	74–92
11	C_9/C_{13}	L	0.96	0.95	74–100
12	C_{13}/C_{14}	A	0.44	0.65	~100
13	C_{14}/C_{15}	S	0.37	0.38	~100
14	C_{15}/C_{16}	S	0.10	0.23	~100
15	C_{17}/C18	A	0.52	0.52	~100
16	C_{20}/C_{22}	A	0.45	0.46	~100

[a] A = azeotrope formation; L = longest chain adsorbed preferentially at all mixture compositions; S = shortest chain adsorbed preferentially at all mixture compositions. [b] X_{ext} = external mole fraction of shortest chain at equimolar concentration in the pores; X_{int} = mole fraction of longest chain in the pores at equimolar composition in the external liquid phase. [c] Pore filling, first figure: pure short alkane; second figure: pure long alkane.[30]

The remarkable adsorption selectivity of ZSM-5 should reflect a special organization of the *n*-alkane molecules in this specific pore system. The straight and sinusoidal pore segments are narrow and impose stretching of the alkyl chains along the pore axis, and minimize intermolecular interactions. The strong interaction with the pore walls implies a high adsorption enthalpy but also a significant loss of freedom, and strongly negative adsorption entropy. At high loading, the dense packing of the molecules contributes a second, negative contribution to the adsorption entropy. This compaction limits the reorganization capabilities and mobility of individual molecules in the adsorbate phase.

Mixtures of alkanes heavier than C_{12} completely fill up the pores (Table 1, entries 12–16, last column). The complete filling of the 2D pore system of ZSM-5 by long alkanes requires a very high flexibility and degree of organization. Pronounced adsorption selectivity for the short chain is observed with C_{14}/C_{15} and C_{15}/C_{16}. The chain length of C_{14} corresponds to the length of two sinusoidal channel segments and an intersection, but also fits into two linear-channel segments and two intersections. The length of a C_{15} molecule exceeds the dimensions of two sinusoidal-channel segments and an intersection but still fits into two linear-channel segments and two intersections. A stretched C_{16} molecule does not fit into either of these combinations, and thus always blocks an additional intersection compared to C_{15} or C_{14}. We ascribe the favorable adsorption of C_{14} and C_{15} to this matching with characteristic dimensions of the pore system. With other long-chain alkanes matching less with the characteristic pore lengths, such as C_{13}/C_{14}, C_{17}/C_{18}, and C_{20}/C_{22}, selectivities are less pronounced (Figure 2, f and Table 1, entries 12, 15 and 16).

A similar reasoning in terms of the matching of alkyl-chain lengths and pore-segment lengths explains the behavior of mixtures containing C_5 or C_6. These molecules fit neatly into a sinusoidal channel segment, whereas longer alkanes block intersections. Admixing C_5 or C_6 with a longer alkane fitting less well with a characteristic pore length gives rise to azeotrope behavior (C_5/C_7, C_6/C_7, C_6/C_8, C_6/C_{10}). These mixtures fill the pores only partially (Table 1, entries 1–5). At low concentration of the long chain, it is preferentially adsorbed because of its higher adsorption enthalpy. From a critical concentration of these long chains on, C_5 or C_6 adsorption is preferred because of their better fitting with the sinusoidal channels. This reversal of selectivity, depending on concentration, explains the azeotropic behavior.

In two further experiments, alkanes with excellent matching with specific structural elements of the pore architecture were mixed, namely (C_5/C_6 and C_6/C_{14}). As expected, adsorption of the long chain was preferred.

A last series of experiments was performed with alkanes with chain lengths in between the optima of C_5–C_6 and C_{14}–C_{15} (C_8/C_9, C_8/C_{12}, C_9/C_{11}, C_9/C_{12}, C_9/C_{13}, Table 1, entries 7–11). As expected for situations with partial pore filling (Table 1), the selective adsorption of the longest chain was observed.

The practical applicability of the observed adsorption effects was verified by performing preparative separation chromatography experiments with selected mixtures. Figure 3 shows the breakthrough profiles of a C_8/C_{12} mixture obtained with a 12 cm HPLC column filled with ZSM-5. Pure octane elutes first, and dodecane is selectively accumulated in the ZSM-5 adsorbent.

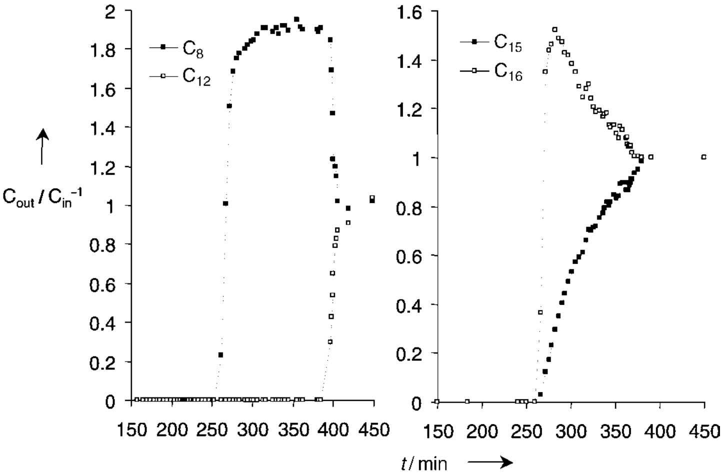

Figure 3. Breakthrough profiles of equimolar mixtures of octane and dodecane (left) and pentadecane and hexadecane (right) on a 12 cm column packed with ZSM-5.

Only when the pores are saturated with dodecane do we observe its sharp breakthrough. A similar experiment was performed with a C_{15}/C_{16} mixture (Figure 3). The eluent is clearly enriched in C_{16}, and C_{15} is retained on the column, thus reflecting the adsorption equilibrium (Table 1, entry 14).

In conclusion, the adsorption of binary alkane mixtures can be rationalized in terms of the agreement between lengths of alkyl chains and channel segments. With alkanes not capable of filling the entire pore system, preferential adsorption of the longest chain is encountered with mixtures of alkanes in which both fit with the channel system, or with mixtures of alkanes of which neither fit. Azeotrope formation or preferential adsorption of the shortest chain is encountered in all other cases. The present findings can be exploited in molecular separation and catalytic-conversion processes. Many zeolites show 2D and 3D intersecting tubular pore systems. Probably, similar systems exist in related zeolite materials.

Experimental Section

Batch adsorption experiments were performed with an H-ZSM-5 zeolite (CBV 8014, Zeolyst, Si/Al = 40). Zeolite samples (~1 g) were put in 10 mL glass vials. After regeneration overnight at 673 K, the vials were immediately sealed with a cap containing a septum to avoid water uptake. Mixtures of two linear alkanes in a nonadsorbing solvent (*iso*-octane, 99.5 % purity, Acros) were prepared so to obtain 14 liquid mixtures of different composition. The total concentration of the adsorbing components was between 0.12 and 0.15 $g\,g^{-1}$. Immediately after the samples were sealed and weighed, about 10 mL of the mixture was injected through the septum into vials containing zeolite, and another 10 mL was added to a vial without zeolite, which was to be used as blank sample. Samples were kept at 277 K, so that no compounds could evaporate, and were stirred continuously. Liquid samples were taken after 24 h and 48 h, to check if equilibrium between the adsorbed and bulk phase had occurred, and analyzed in a GC with a flame ionization detector (FID). For every binary mixture, a calibration line was obtained by analysis of the blank samples. This approach guaranteed a very high precision in the calculation of the amounts adsorbed, obtained by calculation of the mass balance:

$$q_{\text{sorbate}} = \left(\frac{(\text{wt}\,\%_{\text{blanco}} - \text{wt}\,\%_{\text{zeolite}})\,(m^0_{\text{sorbate}} + m^0_{\text{solvent}})}{100\,\rho_{\text{sorbate}}\, m_{\text{zeolite}}} \right)$$

Breakthrough experiments were performed by HPLC. A column (120 mm length, 4.9 mm internal diameter) was packed with zeolite and regenerated overnight under N_2 flow at 400 °C. Dried *iso*-octane was used as a nonadsorbing carrier. Firstly, the HPLC setup and column were flushed with *iso*-octane. Subsequently, a mixture of *iso*-octane and equimolar trace amounts of adsorbates were pumped (0.1 $mL\,min^{-1}$) over the column. Liquid samples were taken every four minutes and analyzed by GC.

Received: January 24, 2003 [Z51012]

Keywords: · adsorption · alkanes · zeolites

---

[1] W. J. M. Van Well, X. Cottin, J. W. de Haan, R. A. Van Santen, B. Smit, *Angew. Chem.* **1998**, *110*, 1142–1144; *Angew. Chem. Int. Ed.* **1998**, *37*, 1081–1083.

[2] W. J. M. Van Well, X. Cottin, J. W. de Haan, B. Smit, G. Nivarthy, J. A. Lercher, J. H. C. Van Hooff, R. A. Van Santen, *J. Phys. Chem. B* **1998**, *102*, 3945–3951.

[3] W. J. M. Van Well, X. Cottin, B. Smit, J. H. C. Van Hooff, R. A. Van Santen, *J. Phys. Chem. B* **1998**, *102*, 3952–3958.

[4] F. Eder, J. A. Lercher, *J. Phys. Chem. B* **1997**, *101*, 1273–1278.

[5] J. A. Z. Pieterse, S. Veefkind-Reyes, K. Seshan, J. A. Lercher, *J. Phys. Chem. B* **2000**, *104*, 5715–5723.

[6] S. Savitz, F. Siperstein, R. J. Gorte, A. L. Myers, *J. Phys. Chem. B* **1998**, *102*, 6865–6872.

[7] K. F. Czaplewski, T. L. Reitz, Y. J. Kim, R. Q. Snurr, *Microporous Mesoporous Mater.* **2002**, 56, 55–64.

[8] G. T. Kokotailo, S. L. Lawton, D. H. Olson, W. M. Meier in *Atlas of zeolite structure types* (Eds.: W. M. Meier, D. H. Olson, C. Baerlocher), Elsevier, New York, **1996**, pp. 146–147.

[9] Y. Yang, L. V. C. Rees, *Microporous Mater.* **1997**, *12*, 117–122.

[10] B. Millot, A. Methivier, H. Jobic, *J. Phys. Chem. B* **1998**, *102*, 3210–3215.

[11] O. Talu, C.-J. Guo, D. T. Hayhurst, *J. Phys. Chem.* **1989**, *93*, 7294–7298.

[12] M. S. Sun, O. Talu, D. B. Shah, *J. Phys. Chem.* **1996**, *100*, 17276–17280.

[13] R. E. Richards, L. V. C. Rees, *Langmuir* **1987**, *3*, 335–340.

[14] W. Zhu, J. M. van der Graaf, L. J. P. van den Broeke, F. Kapteijn, J. A. Moulijn, *Ind. Eng. Chem. Res.* **1998**, *37*, 1934–1942.

[15] W. J. M. van Well, J. P. Wolthuizen, B. Smit, J. H. C. Van Hooff, R. A. Van Santen, *Angew. Chem.* **1995**, *107*, 2765–2767; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2543–2544.

[16] W. Zhu, F. Kapteijn, J. A. Moulijn, *Phys. Chem. Chem. Phys.* **2000**, *2*, 1989–1995.

[17] P. A. Jacobs, H. K. Beyer, J. Valyon, *Zeolites* **1981**, *1*, 161–168.

[18] E. J. Maginn, A. T. Bell, D. N. Theodorou, *J. Phys. Chem.* **1995**, *99*, 2057–2079.

[19] B. Smit, J. I. Siepmann, *J. Phys. Chem.* **1994**, *98*, 8442–8452.

[20] R. L. June, A. T. Bell, D. N. Theodorou, *J. Phys. Chem.* **1992**, *96*, 1051–1060.

[21] J. B. Nicholas, F. R. Trouw, J. E. Mertz, L. E. Iton, A. J. Hopfinger, *J. Phys. Chem.* **1993**, *97*, 4149–4163.

[22] J. O. Titiloye, S. C. Parker, F. S. Stone, C. R. A. Catlow, *J. Phys. Chem.* **1991**, *95*, 4038–4044.

[23] B. Smit, T. L. M. Maesen, *Nature* **1995**, *374*, 42–44.

[24] J. Talbot, *AIChE J.* **1997**, *43*, 2471–2478.

[25] D. M. Ruthven, K. F. Loughlin, K. A. Holborow, *Chem. Eng. Sci.* **1973**, *28*, 701.

[26] R. Krishna, S. Calero, B. Smit, *Chem. Eng. J.* **2002**, *88*, 81–94.

[27] R. Krishna, B. Smit, S. Calero, *Chem. Soc. Rev.* **2002**, *31*, 185–194.

[28] D. M. Ruthven, *Principles of adsorption and adsorption processes*, Wiley-Interscience, New York, **1984**, p. 111.

[29] J. F. M. Denayer, A. Bouyermaouen, G. V. Baron, *Ind. Eng. Chem. Res.* **1998**, *37*, 3691–3698.

[30] The pore filling is defined as the number of adsorbed alkane carbon atoms in the experimental conditions divided by the maximum number of alkane carbon atoms that can be adsorbed in the pore system of ZSM-5 multiplied by 100.