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Configurational Entropy Effects during Sorption of Hexane Isomers in Silicalite

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Santilli (*J. Catal.* 99, 335–341, 1986) has presented experimental data for sorption of hexane isomers, *n*-hexane (n-C_6), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB), in various zeolites. The experimental data on the loadings of the isomers at various temperatures using silicalite are particularly intriguing; 3MP and 22DMB are both seen to exhibit maxima in the sorption loadings with increasing temperature. We rationalise the experimental results by performing configurational-bias Monte Carlo simulations of sorption isotherms at various temperatures and pressures. While the linear n-C_6 can locate at either the straight or zigzag channels, configurational effects make the branched isomers locate only at the intersections. At a total mixture loading of four molecules per unit cell, all the intersections are fully occupied. Both branched isomers 3MP and 22DMB demand an extra "push" to locate within the channel interiors. Configurational entropy effects cause these branched isomers to be progressively "replaced" by n-C_6 in order to achieve higher mixture loadings. The net result is that the branched isomers exhibit maxima at a total mixture loading of four molecules per unit cell. We discuss how configurational entropy effects can be exploited to separate hexane isomers with high selectivities. © 2001 Academic Press

Key Words: **configurational-bias Monte Carlo simulations; hexane isomers; ternary mixture.**

1. INTRODUCTION

In the petroleum industry catalytic isomerisation is used to convert the linear alkanes to their branched isomers (1). Isomerisation processes generate a mixture of isomers that usually require separation and recycle of the nonisomerised components. For example, the effluent of a paraffin isomerisation reactor may contain normal alkanes, mono-methyl alkanes, and di-methyl alkanes. Traditionally, only the normal alkanes would be separated from the mixture by adsorption and recycled to the isomerisation reactor, and any mono methyl alkanes would be collected with the di-methyl alkanes as product (2). However, it is the di-methyl alkanes that are the most desired and have the highest octane number components. Consider for example the isomers of hexane: *n*-hexane (n-C_6) has a RON (research octane number) = 30 whereas the corresponding RON values for its isomers are 2-methylpentane (2MP) = 74.5; 3-methylpentane (3MP) = 75.5; 2,2-dimethylbutane (22DMB) = 94; 2,3-dimethylbutane (23DMB) = 105. Therefore, the more efficient approach would be to adsorptively separate only the di-methyl alkanes as product and recycle the normal and the mono-methyl alkanes to the isomerisation reactor (3).

Consider the specific case of separating a mixture of n-C_6, 3MP, and 22DMB. The Henry coefficients of these isomers in, say, silicalite-1 are close to one another (4) and the separation factors are below 3, which is too low for commercial exploitation. In this context, the experimental data reported in the paper by Santilli (5) are quite interesting. In a paper published in this journal, Santilli described a new experimental probe for measuring the concentration of molecules inside porous materials such as zeolites. To demonstrate the usefulness of his new probe he reported data on the sorption loadings of an equimolar mixture of n-C_6, 3MP, and 22DMB at a variety of temperatures in various zeolites. The data on the loadings reported for silicalite-1 are particularly intriguing and have been replotted in Figs. 1a and 1b. The behaviour of n-C_6 is "normal," inasmuch as increasing temperature, at constant total pressure, results in a decrease in the sorption loading. The behaviours of 3MP and 22DMB, in sharp contrast, are quite "abnormal;" these branched isomers initially show an *increase* in the loading with increasing temperature until a maximum is reached and beyond this point the loadings decrease with increasing temperature. In Fig. 1c the n-C_6/3MP and n-C_6/22DMB selectivities, defined as the ratio of the loadings, are plotted against the temperature. We note that the selectivities approach unity at high temperatures and increase significantly as the temperature is reduced to below 400 K.

Curiously, Santilli (5) does not even comment on these data, and focuses his discussions on demonstrating the efficacy of his measurement probe! We aim to show in this paper that the Santilli data are of practical significance in the context of the development of improved sorption based separations of alkanes isomers. We begin by attempting to

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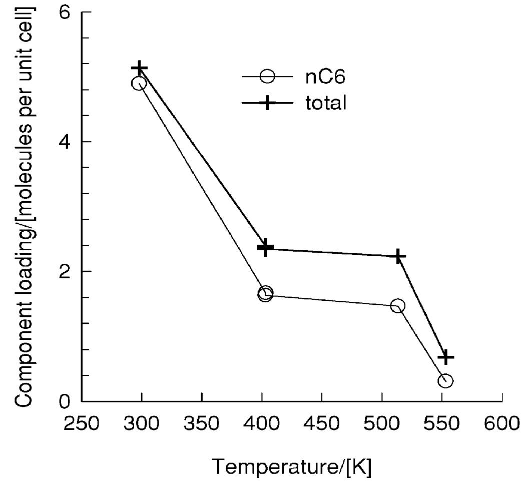
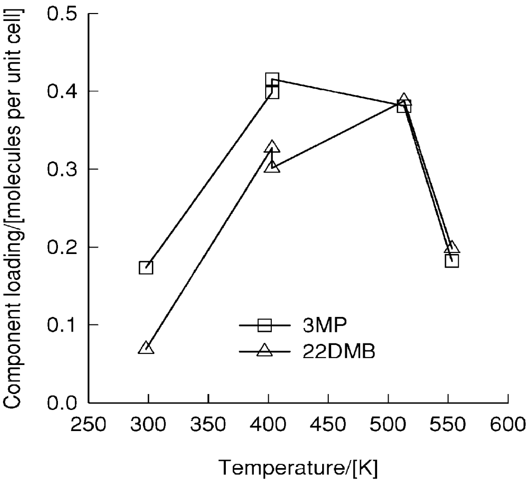
(a) nC6& total mixture loadings



(b) 3MP & 22DMB loadings



(c) nC6/3MP & nC6/22DMB selectivities

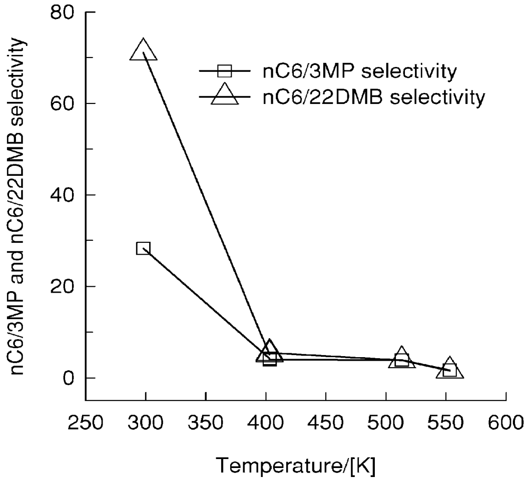


FIG. 1. (a and b) Component loadings for an equimolar mixture of n-C_6, 3MP, and 22DMB as a function of temperature. (c) Sorption selectivity as a function of temperature. Experimental data at constant pressure from Santilli (5).

rationalise the experimental results of Santilli by performing configurational-bias Monte Carlo (CBMC) simulations of the sorption isotherms for pure components, three binary mixtures, and the ternary mixture in silicalite. We had used the CBMC simulation technique in earlier publications to study single and binary sorption isotherms of alkanes (6–8); the computational details are to be found in Ref. (7). We have extended the CBMC technique to calculate ternary sorption isotherms, for which the number of Monte Carlo cycles was increased to 1×10^8.

2. CONFIGURATIONAL-BIAS MONTE CARLO (CBMC) SIMULATION TECHNIQUE

The linear and branched alkanes are described with a united-atom model, in which CH_3, CH_2, and CH groups are considered as single interaction centres. When these pseudoatoms belong to different molecules or to the same molecule but separated by more than three bonds, the interaction is given by a Lennard-Jones potential. The bonded interactions include bond-bending and torsion potentials. We consider the zeolite lattice to be rigid and we assume that interactions of an alkane with the zeolite are dominated by the dispersive forces between alkane pseudoatoms and the oxygen atoms of the zeolite. These interactions are described by a Lennard-Jones potential, with parameters given in Ref. (7).

Adsorption isotherms are computed using a Monte Carlo simulation in the grand canonical ensemble. In this ensemble the temperature and chemical potentials are imposed. The average number of adsorbed molecules per unit cell of the zeolite follows from the simulations. Characteristic of these types of simulations is that during the calculations attempts are made to change the total number of particles by making attempts to insert a molecule into or remove a molecule from the zeolite. To make these types of moves possible for the long-chain alkanes, we use the configurational-bias Monte Carlo (CBMC) technique. Instead of inserting a molecule at a random position, in a CBMC simulation a molecule is grown atom by atom in such a way that the "empty spots" in the zeolite are found. This growing scheme gives a bias that is removed exactly by adjusting the acceptance rules (7). CBMC simulations were performed in cycles and in each cycle, an attempt to perform one of the following moves was made:

(1) Displacement of a randomly selected chain. The maximum displacement was adjusted to an overall acceptance of 50%.

(2) Rotation of a chain around its centre of mass. The chain is chosen at random and the maximum rotation angle is selected to accept 50% of the moves.

(3) Partly regrowing of a chain; a chain is selected at random and part of the molecule is regrown using the CBMC

scheme. It is decided at random which part of the chain is regrown and with which segment the regrowing is started.

(4) Exchange with a reservoir. It is decided at random whether to add or to remove a molecule from the zeolite following the acceptance rules derived by Vlugt *et al.* (7).

(5) Change of identity (only in the case of mixtures). One of the components is selected at random and an attempt is made to change its identity.

The numbers of Monte Carlo cycles performed for one-component, two-component, and three-component isotherms were, respectively, 2×10^7, 5×10^7, and 1×10^8. The relative probabilities of moves were 15% displacements, 15% rotations, 15% partial regrowths, and 50% exchanges with the reservoir, and the remaining 5% of the moves were attempts to change the identity of a molecule.

3. SIMULATION RESULTS AND DISCUSSION

Before mixture effects are considered let us examine the pure component sorption isotherms calculated using CBMC techniques at 362 K, a temperature within the range studied by Santilli (5); the pure component isotherms are shown in Fig. 2. We see that n-C$_6$ shows a slight inflection at a molecular loading $\Theta = 4$ due to commensurate freezing (9). The branched isomer 3MP shows a pronounced inflection at $\Theta = 4$ because these molecules prefer to locate at the intersections between the straight and zig-zag channels of silicalite; to push them into the channel interiors requires an extra "push," leading to inflection behaviour. The isomer 22DMB is so bulky that it can be located only at the intersections; there is no inflection for this component.

The sorption isotherms for 50–50 mixtures of the three binary pairs are shown in Fig. 3. The n-C$_6$–3MP and 3MP–22DMB binaries have been determined at 362 K and the

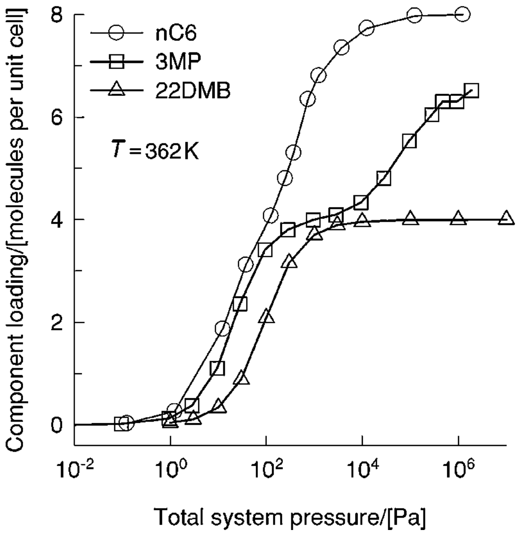
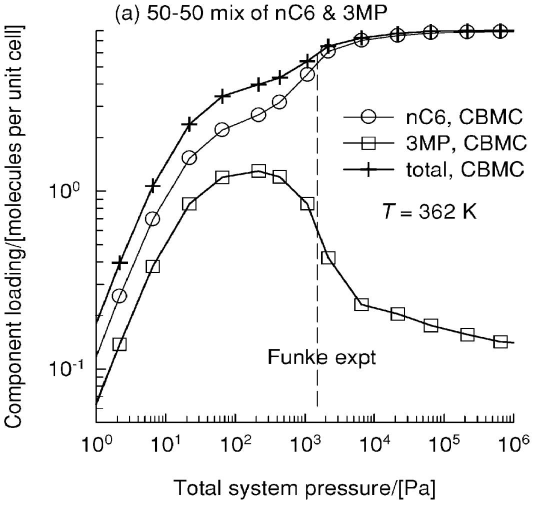
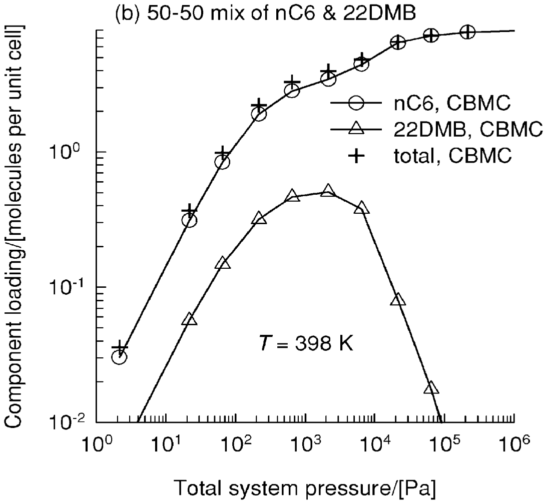


FIG. 2. Pure component isotherms for n-C$_6$, 3MP, and 22DMB at 362 K obtained from CBMC calculations.

(a) 50-50 mix of nC6 & 3MP



(b) 50-50 mix of nC6 & 22DMB



(c) 50-50 mix of 3MP& 22DMB

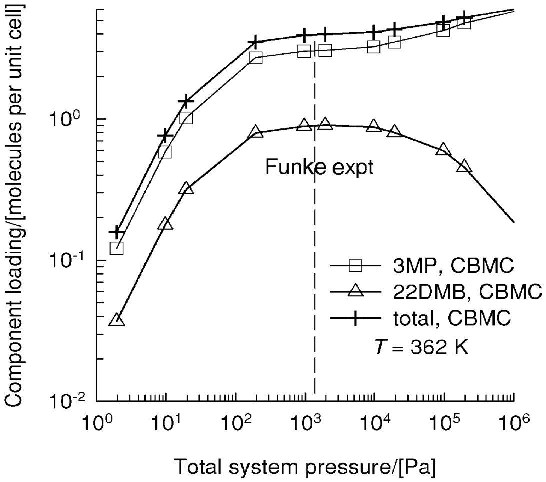


FIG. 3. (a) CBMC simulations of loadings for 50–50 mixtures of (a) n-C$_6$–3MP at 362 K, (b) n-C$_6$–22DMB at 398 K, and (c) 3MP–22DMB at 362 K for various pressures.

n-C_6–22DMB binary at 398 K, in order to allow comparison with the membrane permeation data of Funke *et al.* (10) and Gump *et al.* (11).

For the binary mixture of n-C_6 and 3MP at 362 K (see Fig. 3a), it is interesting to note the maximum in the loading of 3MP when the total mixture loading is precisely four molecules per unit cell, when the intersections are all occupied; this occurs at a total pressure of about 100 Pa. When the pressure is raised above 100 Pa the loading of 3MP reduces virtually to zero. The n-C_6 has a higher packing efficiency within the silicalite matrix than the 3MP molecules. It is more efficient to obtain higher loading by "replacing" the 3MP with n-C_6; this *configurational entropy* effect is the reason behind the curious maxima in the 3MP loading in the mixture.

Funke *et al.* (10) measured the permeation selectivities for 50–50 mixtures of n-C_6 and 3MP at 362 K, keeping the upstream hydrocarbons pressure at 15 kPa; see Table 3 of their paper. The permeation selectivity, defined as the ratio of permeation fluxes of the linear and branched alkanes, is proportional to the ratio of the loadings of the two components, i.e., the sorption selectivity, at the upstream face of the membrane. Funke *et al.* (10) observed that the permeation selectivity was 24, which was much higher than the permeation selectivity obtained on the basis of pure component permeation data, i.e., 1.3. This high permeation selectivity can be explained by examination of Fig. 3a, where the upstream pressure (15 kPa) condition of the Funke experiment is indicated by the dashed vertical line. The upstream pressure corresponds to a situation well beyond the pressure at which the 3MP loading exhibits a maximum. At this upstream pressure of 15 kPa the sorption selectivity is significantly higher than that at upstream pressures below 100 Pa. Funke *et al.* (10) also report permeation selectivities for 50–50 mixtures at four different temperatures, keeping the upstream hydrocarbons pressure at 15 kPa; see Fig. 4. We performed CBMC simulations at various temperatures keeping the total hydrocarbons pressure at 15 kPa and have compared the ratio of the sorption loadings of n-C_6 and 3MP with the permeation selectivity; see Fig. 4. We note that the permeation and sorption selectivities show the same trend with temperature and are in good agreement with each another. The increase in the n-C_6/3MP selectivity with decreasing temperature is to be attributed to the fact that the total mixture loading increases to values in excess of four molecules per unit cell when all the intersections are occupied; this occurs at a temperature of 400 K. Furthermore, we note that the temperature dependence of the n-C_6/3MP selectivity follows the same trend as that seen in Fig. 1c for the Santilli data.

Consider now the 50–50 binary mixture of n-C_6 and 22DMB at 398 K; see Fig. 3b. The di-branched isomer 22DMB shows a pronounced maximum when the total mixture loading is 4; this occurs at a total hydrocarbons pressure of 2000 Pa. Gump *et al.* (11) have reported the permeation fluxes of 50–50 mixtures of n-C_6 and 22DMB across a silicalite membrane at 398 K for various upstream hydrocarbon pressures; see Figs. 5 and 6 of their paper. Since the flux of any component is proportional to the loading at the upstream face, we would expect the flux of 22DMB to go through a maximum as the upstream compartment pressure is increased, in steps, from say 100 Pa to 100 kPa. This is precisely what Gump *et al.* (11) have observed in their experiments. The experimental fluxes of 22DMB are compared in Fig. 5 with the 22DMB loadings obtained from

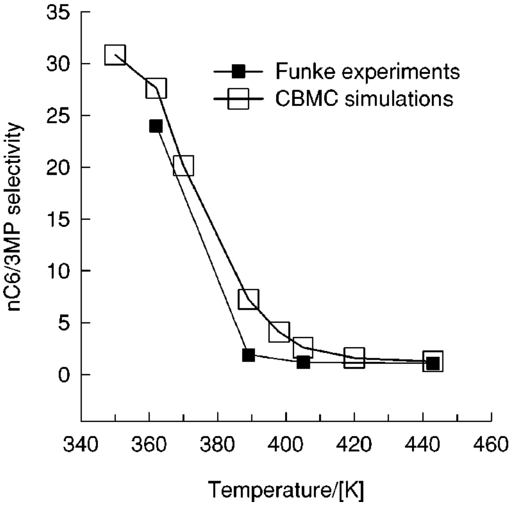


FIG. 4. n-C_6/3MP selectivity for 50–50 mixture permeation across silicalite membrane. The experimental data of Funke *et al.* (10) are compared with CBMC simulations at various temperatures. The total hydrocarbons pressure is maintained at 15 kPa.

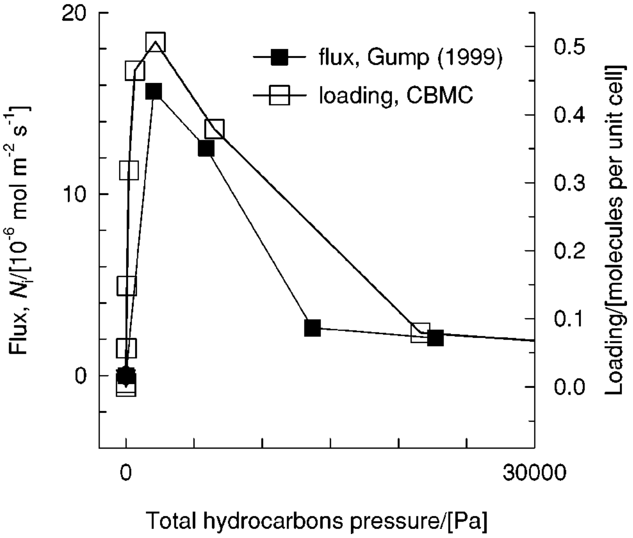


FIG. 5. Flux of 22DMB during permeation of a 50–50 mixture of n-C_6 and 22DMB across silicalite membrane at 398 K, measured by Gump *et al.* (11), compared with 22DMB loading obtained from CBMC simulations.

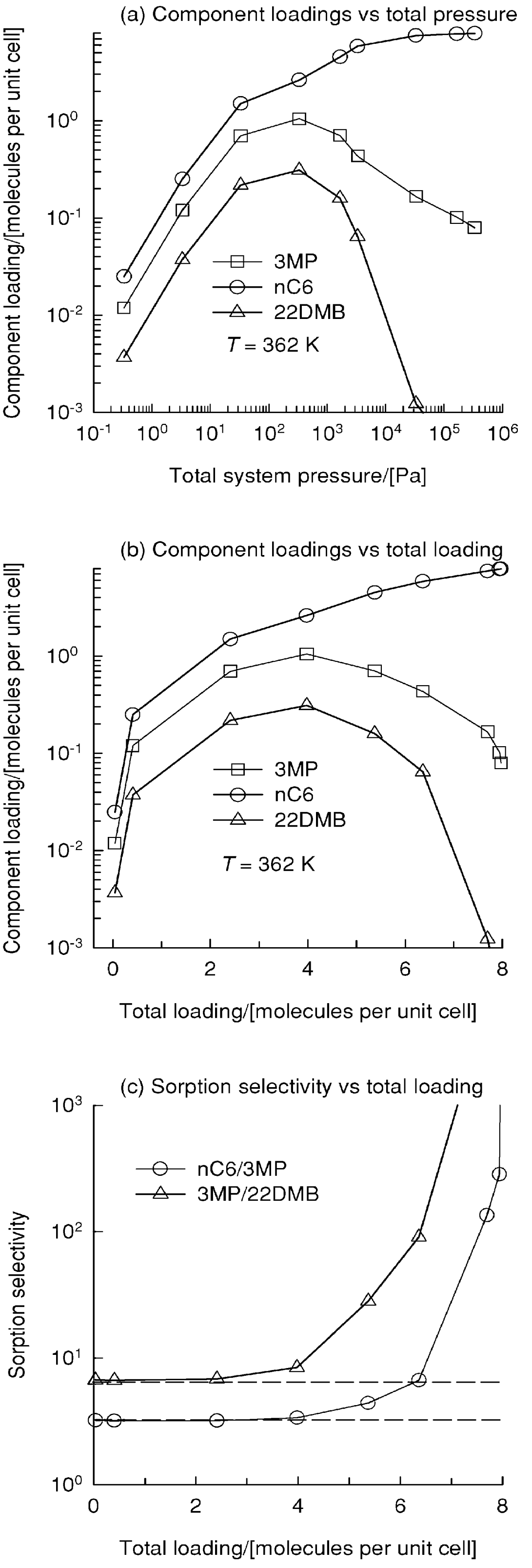


FIG. 6. (a) CBMC simulations of loadings for equimolar mixture of n-C_6–3MP–22DMB at 362 K. (b) Component loadings vs total mixture loading. (c) Sorption selectivities as a function of total loading.

CBMC simulations. It is heartening to note that the experimentally observed maximum flux of 22DMB is obtained at the same pressure at which the 22DMB exhibits a maximum in its loading, i.e., 2000 Pa.

Let us now consider sorption of a 50–50 mixture of 3MP and 22DMB at 362 K (see Fig. 3c); both 3MP and 22DMB prefer to locate themselves at the intersections, which are roomy enough to accommodate the side chains. However, at a total loading $\Theta = 4$, the intersections are all fully occupied; this occurs at a total pressure of 1 kPa. Increasing the pressure from 1 to 10 kPa has practically no influence of the loadings of 3MP, 22DMB, and of the total mixture. At pressures in excess of 20 kPa, it is possible to “push” 3MP into the channel interiors. Hence, the 3MP loading and that of the total mixture increase. However, the 22DMB molecules are too bulky to be located in locations other than at the intersections. Interestingly, we note that at pressures in excess of 2 kPa, the 22DMB loadings *decrease* with increasing pressure. Apparently it is energetically more efficient for the silicalite matrix to fill itself with 3MP and “throw” out the stubborn 22DMB molecules. Configurational entropy effects are the reason behind the “table mountain” maximum in the loading of 22DMB. At sufficiently high pressures, not of technological relevance, the 22DMB loading in the mixture would reduce to practically zero.

Funke *et al.* (10) have also reported the permeation selectivities for a 50–50 mixture of 3MP and 22DMB across a silicalite membrane at 362 K, keeping the upstream hydrocarbons pressure at 15 kPa; see Table 5 of their paper. At a pressure of 15 kPa, the sorption selectivities are expected to be low and Funke *et al.* (10) report permeation selectivities of unity, i.e., practically no separation of the two isomers. Had their experiments been carried out with an upstream hydrocarbons pressure in excess of 100 kPa, they would have obtained much higher selectivities. Since at such high pressures, the hydrocarbon mixture would be in the liquid phase, one technological solution would be to operate in the pervaporation mode (upstream compartment in the liquid phase; downstream compartment in the vapour phase). Matsufuji *et al.* (12) have shown that high selectivities for the separation of hexane isomers can be obtained by operating in the pervaporation mode, underlining our arguments.

Having underlined the influence of configurational entropy effects during sorption of the binary pairs of hexane isomers, we consider the importance of these effects in a ternary mixture. CBMC simulations for an equimolar ternary mixture of n-C_6, 3MP, and 22DMB at 362 K are shown in Fig. 6a for a range of total pressures. The loadings of the three components follow “normal” behaviour for pressures below 50 Pa and the sorption loadings follow the hierarchy dictated by the Henry coefficients. At a pressure of 500 Pa, the total mixture loading is four molecules per unit cell; at this loading all the intersection sites are fully occupied. At pressures exceeding 500 Pa, the silicalite matrix prefers to accept *n*-C_6 into its matrix rather than either of the branched isomers. The loadings of both 3MP and 22DMB decrease as the pressure is increased beyond 500 Pa. There are three types of entropic “battles” in play at pressures exceeding 500 Pa. The battle between linear isomer and its branched isomers is won by the linear isomer. The battle between the mono-methyl and dimethyl isomers is won by the mono-methyl isomer.

A more useful way to examine the ternary sorption data is to plot the component loadings against the total mixture

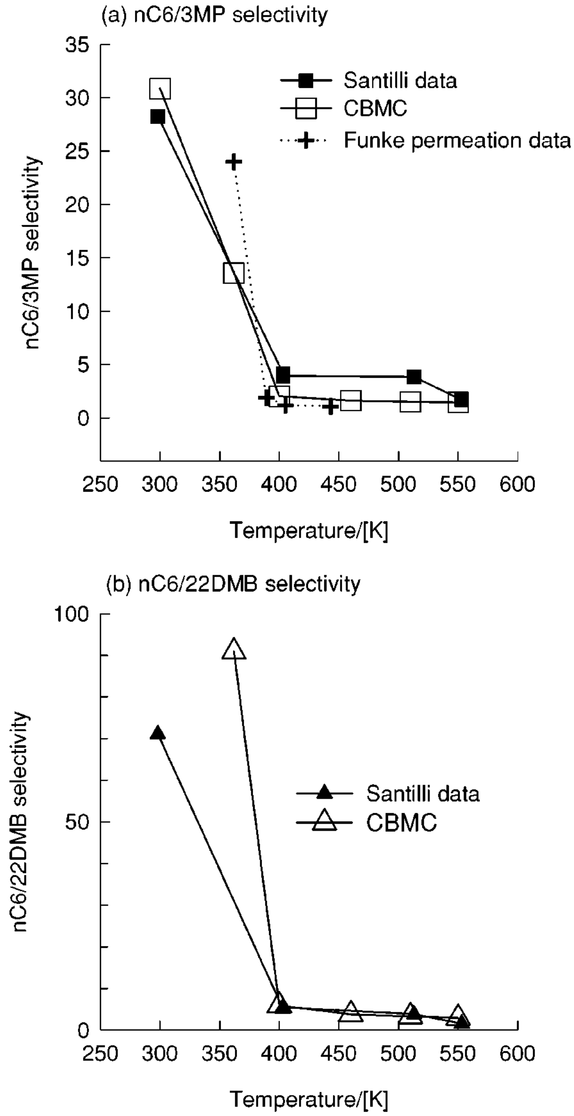


FIG. 7. Comparison of sorption selectivity for (a) *n*-C_6/3MP and (b) *n*-C_6/22DMB in equimolar ternary mixtures. The experimental data of Santilli (5) are compared with calculations from CBMC simulations. The CBMC simulations have been carried out at a total pressure of 3 kPa. Also shown in (a) are the permeation *n*-C_6/3MP selectivities obtained by Funke *et al.* (10).

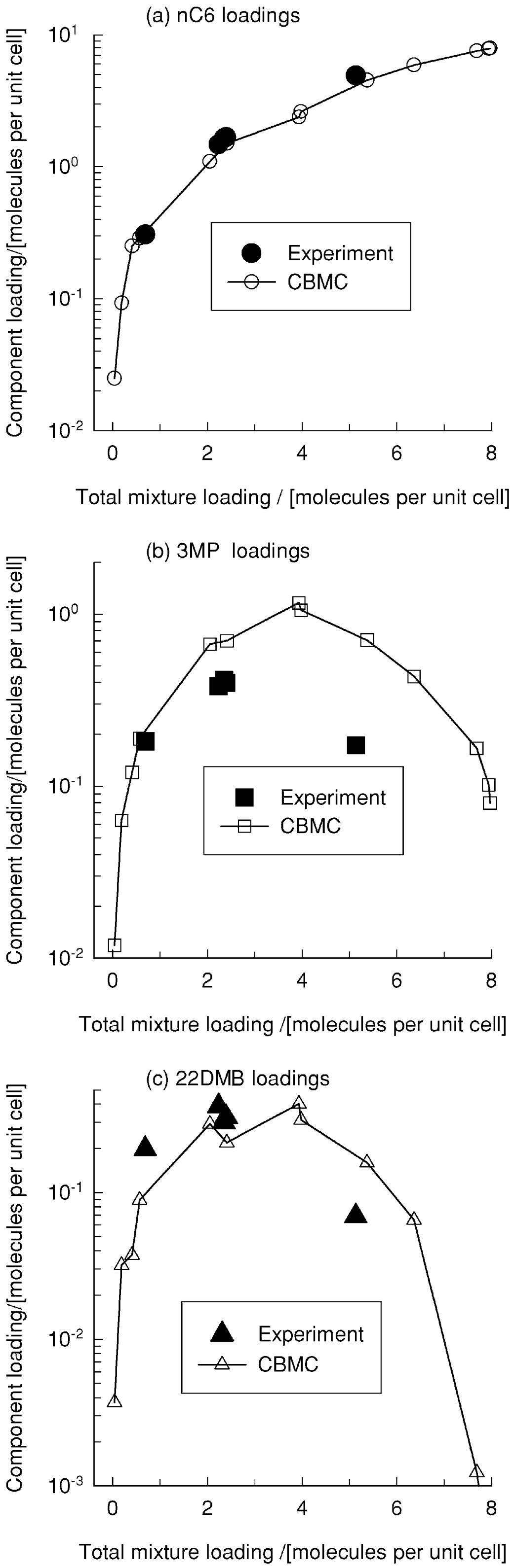


FIG. 8. Component loadings for an equimolar mixture of *n*-C_6–3MP–22DMB as a function of total mixture loading. Experimental data of Santilli (5) are compared with CBMC simulations. The CBMC simulations were carried out at (i) $T = 300$, 362, 400, 460, 510, 550 K and pressure = 3 kPa and (ii) $T = 362$ K and a variety of pressures.

loading; see Fig. 6b. We clearly note the maxima in the 3MP and 22DMB loadings when the total mixture loading equals 4. The n-C_6/3MP and 3MP/22DMB sorption selectivities increase significantly when the total mixture loading exceeds 4; see Fig. 6c.

In order to rationalise the Santilli data shown in Fig. 1, we performed a series of simulations at constant total pressure of 3 kPa and temperatures of 300, 362, 400, 460, 510 and 550 K. Figure 7a compares the n-C_6/3MP selectivity obtained from the CBMC simulations with those reported by Santilli. Also plotted in Fig. 7a are the permeation selectivities reported by Funke *et al.* (10). The three sets of selectivities are in agreement with one other. We therefore may conclude that the increase in selectivity with decreasing temperature is due to the fact that the mixture loading increases to values significantly higher than 4 when the temperature is decreased below 400 K. The Santilli data (5) provide a direct confirmation of the concept of configurational entropy affecting mixture sorption and lend credence to our CBMC simulations.

In Fig. 7b the n-C_6/22DMB sorption selectivity obtained from CBMC simulations is compared with the data of Santilli (5); again good agreement is obtained. The strong increase in the selectivity when the temperature is reduced below 400 K is again to be attributed to strong configurational entropy effects which favour the linear molecule.

For direct comparison of the Santilli data with CBMC simulations, we plot the component loadings of the three hexane isomers as a function of the total mixture loadings in Figs. 8a, 8b and 8c. Also shown in Fig. 8 are CBMC simulation results obtained at (i) $T = 300, 362, 400, 460, 510, 550$ K and pressure $= 3$ kPa and (ii) $T = 362$ K and a variety of pressures. Figure 8a shows good agreement between the experimentally determined n-C_6 loadings and those calculated from CBMC. In Figs. 8b and 8c we note that the CBMC simulations predict maxima in the 3MP and 22DMB loadings when the total mixture loading is four molecules per unit cell. Unfortunately, the Santilli data are available only for total loadings of two and six molecules per unit cell. Nevertheless, the experiments confirm that there is a maximum in the loading of the branched alkane, 3MP and 22DMB, at a mixture loading between two and six molecules per unit cell.

The results shown in Fig. 8 have practical implications. Provided the mixture loading within silicalite is higher than four molecules per unit cell, the sorption hierarchy is as follows: n-$C_6 \gg$ 3MP $\gg$ 22DMB, with the di-branched alkane being virtually excluded from the zeolite. It appears from the patent of Dandekar *et al.* (3) that the entropy-based separation concept is recognised by industry and that a combined sorption–reaction process is being developed relying on this separation principle.

4. CONCLUDING REMARKS

We have rationalised the “curious” experimental data of Santilli (5) by performing CBMC simulations. Configurational entropy effects come into play when the total mixture loading is higher than four molecules per unit cell and if these conditions are maintained we obtain the sorption hierarchy n-$C_6 \gg$ 3MP $\gg$ 22DMB, with the di-branched alkane being virtually excluded from the zeolite. Further support of the Santilli data is provided by the permeation data of Funke *et al.* (10) and Gump *et al.* (11) for 50–50 mixtures of n-C_6–3MP and n-C_6–22DMB across a silicalite membrane. The entropy-based sorption principle has commercial potential, which has been recognised by industry (3); our paper provides the scientific background for the separation concept.

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REFERENCES

1. Chen, N. Y., Degnan, T. F., and Smith, C. M., “Molecular transport and reaction in zeolites. Design and application of shape selective catalysts.” VCH, New York, 1994.
2. Haizmann, R. S., Hibbs, F. M., and Raghuram, S., US 5043525 to UOP, Inc., 1993.
3. Dandekar, H. W., Funk, G. A., and Zinnen, H. A., US 6069289 to UOP, Inc., 2000.
4. Denayer, J. F., Baron, G. V., Martens, J. A., and Jacobs, P. A., *J. Phys. Chem. B* **102**, 3077 (1998).
5. Santilli, D. S., *J. Catal.* **99**, 335 (1986).
6. Krishna, R., Smit, B., and Vlugt, T. J. H., *J. Phys. Chem. A* **102**, 7727 (1998).
7. Vlugt, T. J. H., Krishna, R., and Smit, B., *J. Phys. Chem. B* **103**, 1102 (1999).
8. Schenk, M., Vidal, S. L., Vlugt, T. J. H., Smit, B., and Krishna, R., *Langmuir* **17**, 1558 (2001).
9. Smit, B., and Maesen, T. L. M., *Nature* **374**, 42 (1995).
10. Funke, H. H., Argo, A. M., Falconer, J. L., and Noble, R. M., *Ind. Eng. Chem. Res.* **36**, 137 (1997).
11. Gump, C. J., Noble, R. D., and Falconer, J. L., *Ind. Eng. Chem. Res.* **38**, 2775 (1999).
12. Matsufuji, T., Watanabe, K., Nishiyama, N., Egashira, Y., Matsukata, M., and Ueyama, K., *Ind. Eng. Chem.* **39**, 2434 (2000).