Liquid Sorption Equilibria of Selected Binary Paraffin Systems in NaY Zeolite

CHARLES N. SATTERFIELD and JAN K. SMEETS

Department of Chemical Engineering
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Apart from the molecular sieving effect, a zeolite will also preferentially adsorb one component from a binary mixture of hydrocarbons, in which both components have free access into the internal zeolite pore structure. Both physico-chemical adsorption and steric effects can play an important role in this selectivity. Previously we (Satterfield and Cheng, 1972a) have reported sorption equilibria studies of a wide variety of binary hydrocarbon systems on NaY. It was observed that aromatic compounds are selectively adsorbed in preference to paraffins and naphthenes and that within a group of aromatic compounds those having the smallest and most compact structure, for example, benzene and cumene, are selectively adsorbed in preference to large aromatic molecules, for example, 1,3,5 *tri*-isopropyl benzene.

In this investigation binary liquid-phase mixtures of *n*-octane with either *n*-decane, *n*-dodecane or *n*-tetradecane were studied to obtain a better understanding of systems where steric effects are expected to be dominant. These were chosen to make possible comparison with a study by Sundstrom and Krautz (1968) on 5A zeolite in which they used binary systems consisting of one of these three *n*-paraffins, but with *n*-hexane or *n*-decane as the second species.

EXPERIMENT

The NaY was the same as that previously studied and was activated to 500°C by the identical procedure (Satterfield and Cheng, 1972b) before use. Separation factors K were also measured by the same procedure, starting with initial concentrations of about 6 wt. % of the preferentially adsorbed component in the binary mixture. As before it was assumed in the analysis that NaY has an adsorption capacity of 0.25 ml/g. zeolite for all liquids studied. The method of data analysis was that previously used but with a different averaging procedure. An error analysis and more details are given by Smeets (1972). The separation factor $K = \dfrac{x_{a,1}/x_1}{x_{a,2}/x_2}$ where x_a and x represent the mole fractions in the adsorbed and liquid phases, respectively, at equilibrium. Component 1 is the preferentially adsorbed compound, so K always exceeds unity.

RESULTS AND DISCUSSION

For all three binary systems studied, the lower molecular weight paraffin was preferentially adsorbed relative to the higher molecular weight paraffin. The same behavior was reported by Sundstrom and Krautz who correlated their separation factors by an empirical relation:

$$K = \frac{C_H}{C_L}\gamma_H$$

where C_H and C_L are the carbon-numbers of the higher and lower molecular weight paraffin and γ_H is an empirical constant, based on the higher molecular weight paraffin.

Table 1 presents values of K obtained in this study for *n*-octane relative to the listed *n*-paraffin and also values of γ_H calculated from our results. Each value of K is the average of four runs. For comparison we include values of K relative to *n*-hexane on 5Å zeolite as reported by Sundstrom and Krautz and values of γ_H they reported from their overall results.

Two observations are noteworthy. Firstly, the lower molecular weight paraffin is adsorbed in preference to the higher molecular weight paraffin, which is opposite to that expected on conventional adsorbents according to Traube's rule. Secondly, in both studies a minimum in the value of K or γ_H occurred with the *n*-paraffin of intermediate carbon number, *n*-dodecane. If Traube's rule were followed, K as defined here (and also γ_H) would be less than unity. The absolute difference between the two sets of results can be attributed to the different pore sizes of the two molecular sieves. The type 5A has a minimum pore size of about 5 Å, the NaY zeolite has minimum pore sizes of about 9 Å, hence steric effects would be expected to be less pronounced for the latter. The critical diameter of all the *n*-paraffins is the same, namely 4.9 Å.

A brief study with cyclooctane showed that it was preferentially adsorbed on NaY from mixtures with *n*-octane ($K \simeq 3.2 \pm 1.0$). In an earlier study (Satterfield and Cheng, 1972a), *trans* and *cis* decalins were also found to be preferentially adsorbed on NaY from mixtures with *n*-decane ($K = 13$ and 6.3, respectively). These two observations suggest that a cycloparaffin in general may be the preferentially adsorbed component from a mixture with the *n*-paraffin of the same carbon number. Steric effects cannot explain this and the cyclic structure must cause some physico-chemical effect more strongly than that existing with the *n*-paraffins.

The results with the *n*-paraffin binary systems suggest that the packing characteristics of the higher molecular weight paraffin rather than physico-chemical properties play a dominant role in the adsorption selectivity on a zeolite. For both molecular sieves dodecane appears to have a relatively more favorable packing in the zeolite cavities than does decane or tetradecane.

The occurrence of an irregularity here in behavior as molecular weight is increased in the homologous series of *n*-paraffins has a parallel in the recent report of Gorring (1973) that the diffusivity of *n*-paraffins in zeolite T dropped to a minimum with an increase in molecular weight to the C_8 paraffin, then rose to a maximum with the C_{12} member of the series, dropping again with C_{14}. The results were interpreted in terms of a window effect in which maxima and minima were related to degrees of fit

TABLE 1. VALUES OF K AND γ_H

	$K_{C\text{-}8}$	$K_{C\text{-}6}$	$\gamma_{H,5A}$	$\gamma_{H,NaY}$
Decane	2.0 ± 0.2	5.2	3.64	1.70
Dodecane	1.7 ± 0.2	4.3	2.50	1.14
Tetradecane	2.9 ± 0.2	10.0	5.12	1.76

J. K. Smeets is at Palm Beach 16, Aruba, Netherlands Antilles.

of the diffusing molecule relative to crystal dimensions.

Sorption equilibria must likewise be related to the size and configuration of the sorbed molecules relative to the size of the cavities. Both type A and type Y zeolites have a three-dimensional pore structure consisting of supercavities connected by essentially circular and narrow apertures (5 Å and 9 Å, respectively), but the structural dimensions of the two zeolites are different and it is not apparent why dodecane should be able to take up a relatively more favored packing arrangement in both zeolites. We can visualize that the higher weight molecule finds its most favorable packing while the smaller molecule takes up the remaining space which it can do more readily because it is smaller. A dip in value of γ_H then represents a case in which the hydrocarbon molecule can fit well into a cavity or multiple of cavities as opposed to other hydrocarbon structures in which the molecule cannot achieve full packing in a cavity or must spread itself through more than one cavity, leaving substantial free space. Extending these studies to other paraffin systems could permit a more quantitative approach to prediction based on the known structure of zeolite pore systems and paraffin molecules.

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On Inventory Times in Approximate Dynamic Distillation Modeling

B. A. BUFFHAM

Department of Chemical Engineering
Lehigh University, Bethlehem, Pennsylvania 18015

In recent years Williams and his colleagues have devised methods for constructing approximate mathematical models of unsteady distillation column operation on the basis of a time constant called the inventory time (Moczek et al., 1965; Bhat, 1969; Bhat and Williams, 1969; Weigand et al., 1972). Their objective has been to develop models that use only steady state information and which are simple enough to be used, with periodic updating if necessary, for feedforward control. The methods are reasonably successful in the sense that adequate approximate models are obtained in suitable cases. The models are not required to be predictive in all cases, for it is possible to check the approximate model by comparison with a more precise model before it is used in the design of a control system. Weigand et al. (1972) have presented such comparisons for several distillation types.

Inventory times are defined in terms of steady state compositions and flow rates and have been shown by Williams and his co-workers to be related to the time constants of the response of a distillation column to disturbances in operation. For example, if the response to an upset in the feed is slow in one product stream and fast in the other, the inventory time is the sum of the time constants for the slower response (Moczek et al., 1965). Inventory times bear a strong resemblance to mean residence times as defined by Buffham and Kropholler (1973) for steady operation of complex flow networks. In this note it is shown that corresponding parameters can be defined for each species present in a distillation process without reference to the details of a mathematical model of the distillation process.

The simplest case of a mean residence or response time is Danckwerts' (1953) familiar result that the mean residence time for steady single-phase flow in a constant-volume mixing vessel is

$$\tau = \text{volume/flow rate}$$

For more complex configurations this becomes (Buffham and Kropholler, 1973)

$$\tau_i = \frac{\text{holdup of species } i}{\text{throughput of species } i}$$

B. A. Buffham is with Loughborough University of Technology, Loughborough, England.