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Liquid Sorption Equilibria of Selected Binary Hydrocarbon Systems in Type Y Zeolites

On NaY and HY, aromatic compounds are selectively adsorbed in preference to paraffins and naphthenes. Smaller aromatic compounds are adsorbed in preference to larger aromatic compounds. All the compounds studied can be sorbed into the pore structure of the zeolites and the selectivities are primarily a reflection of relative affinity for the zeolite and steric effects rather than a sieving effect.

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SCOPE

This study arose out of a primary interest in the factors that affect the rates of counterdiffusion of organic liquids in the pores of zeolites, especially the large pore zeolites of interest in catalysis. A knowledge of sorption equilibria is needed to determine the driving force for diffusion as well as being of interest in its own right in separation processes. A knowledge of relative adsorptivities can also be of major value in interpreting catalytic reaction phenomena where two or more species compete for the same type of sites. Single-component and counterdiffusion studies with the same binary systems are described elsewhere (Satterfield and Cheng, 1972 a, b).

CONCLUSIONS AND SIGNIFICANCE

Highly selective adsorption from a binary liquid system can occur on molecular sieve zeolites when both components have full access to the entire fine pore structure. The adsorption is caused by the relative affinity or interaction energy of the molecules for the zeolite structure. On NaY aromatic compounds are selectively adsorbed over paraffins and naphthenes. Within a group of aromatic compounds those having the smallest and most compact structure, for example, benzene and cumene, are selectively adsorbed over larger aromatics, for example, 1,3,5-triisopropyl benzene. On at least one system (trans-decalin –*n*-decane) the separation factor is little affected by temperature.

More limited studies on HY indicate that the separation factor between aromatic molecules, paraffins, and naphthenes is less than on NaY, which is consistent with the lower interaction energy between HY and aromatics.

Selective adsorption effects of the type studied here can lead to marked selectivity phenomena in the catalytic reaction of multicomponent systems.

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EXPERIMENT

NaY was provided by the Molecular Sieve Laboratory of Linde Division, Union Carbide Corporation, in a partially dehydrated powder form. It had a Si/Al atom ratio of 2.43. For some of the studies the NH_4Y form was obtained by ion exchange of NaY and converted to HY by heating under evacuation. Sodium analysis showed that 97.7% degree of sodium removal was obtained. The organic liquids were of the highest purity commercially available and in some cases were further purified by us. Further details are given by Cheng (1970) and Satterfield and Cheng (1972a, 1972b).

The experimental procedure involved contacting weighed amounts of freshly activated zeolite and a binary liquid solution of known composition until steady state was established. Typically about 30 grams of activated zeolite was subdivided into about twenty 2 × 2¾-in. screw-cap glass vials using an analytical balance with an accuracy of ±0.0005 g. To each vial a quantity of a binary liquid solution containing about 5 weight % of the preferentially adsorbed component was pipetted, and the ratio of solid to liquid was varied from vial to vial, in order to vary the final composition. A magnetic stirring bar was added to each vial, and the capped glass vials were further sealed with Teflon tape and were placed on top of a Fisher jumbo magnetic stirrer. The degree of agitation in each vial was thus the same, and all the experiments were carried out at 30°C.

Steady state was usually attained in less than two days, but compositions were redetermined at least four days after loading in every case. An F and M model 700 gas chromatograph equipped with a thermal conductivity detector was used to determine the composition in all systems. Two 6-ft., ¼-in. columns, one with 10 weight % Apiezon L and the other with 10 weight % Silicone Gum Rubber UCC-W-982, both of Anakron ABC mesh 70/80, were used for all of the analyses. A calibration curve of area % of one component versus weight % of that component was determined for each binary system.

THEORY

The thermodynamic analysis of separation by adsorption as applied to zeolites based on Gibbs' criteria for phase equilibrium is presented by Eltekov and Kiselev (1968) and by Cheng (1970). Sorption selectivity is usually presented in terms of a separation factor K or relative adsorptivity defined as follows

$$K = \frac{x_{a,1}/x_1}{x_{a,2}/x_2} \qquad (1)$$

where x_a and x represent the mole fractions in the adsorbed and liquid phases, respectively, at equilibrium. Component 1 refers to the preferentially adsorbed compound so K is always greater than unity. If the mixtures are ideal solutions

$$K = \exp\left[\left(\frac{\mu_1^* - \mu_{a,1}^*}{RT} \right) - \left(\frac{\mu_2^* - \mu_{a,2}^*}{RT} \right) \right] \qquad (2)$$

where μ_1^* and $\mu_{a,1}^*$ are the Gibbs' free energy per mole of pure component 1 in the liquid and zeolite-adsorbed phases, respectively, at the temperature and pressure under consideration

Equation (2) indicates that the separation factor for a given adsorbent (zeolite) and a binary system is a function of temperature and pressure only if the assumption of ideal solution in both phases is valid. The extent to which the separation factor varies with temperature can be readily obtained in terms of the heat of adsorption.

At constant pressure, differentiating Equation (2) with respect to T gives

$$\frac{\partial \ln K}{\partial T} = \frac{1}{RT^2}\left[(H_{a,1} - H_1) - (H_{a,2} - H_2) \right] \qquad (3)$$

noting that

$$\left. \frac{\partial(\mu_i^*/T)}{\partial T} \right|_p = -\frac{H_i}{T^2} \qquad (4)$$

where H_i is the enthalpy per mole of pure i at the temperature T.

The term $(H_{a,i} - H_i)$ is the change in enthalpy $\Delta H_{i,\text{ads}}$ of the pure compound i from its liquid state to its zeolite-adsorbed state. It is the negative of the heat evolved when one mole of pure compound i is adsorbed by a zeolite at constant temperature and pressure.

Over small ranges it may be assumed that $\Delta H_{1,\text{ads}}$ and $\Delta H_{2,\text{ads}}$ are independent of temperature. Upon integration of Equation (3) the following relationship is obtained:

$$K = K_0 \exp\left[-\frac{\Delta H_{1,\text{ads}} - \Delta H_{2,\text{ads}}}{RT} \right] \qquad (5)$$

Equation (5) indicates that the separation factor K and its variation with temperature depend on the relative magnitudes of the heats of adsorption of the two compounds.

To calculate values of K from experimental data, the following expression may be used obtained by substituting $x_2 = 1 - x_1$ and $x_{a,2} = 1 - x_{a,1}$ in Equation (1) and rearranging:

$$\frac{x_1}{x_{a,1}} = \frac{1}{K} + \left(1 - \frac{1}{K}\right) x_1 \qquad (6)$$

In Equation (6) the equilibrium mole fraction in the liquid phase x_1 is readily measurable. The value of $x_{a,1}$ in equilibrium with x_1 is obtained by a material balance (Cheng, 1970) combined with the useful observation that the sorption capacity of X and Y zeolites for liquids of the type studied here is nearly constant at about 0.25 (Breck and Flanigen, 1968; Carman and Haul, 1954). Values of K were determined by equating the slope determined from a plot of $x_1/x_{a,1}$ versus x_1, to $(1 - 1/K)$, and the intercept to $1/K$. If $K >> 1$, this procedure is inadequate and an alternative method described by Cheng (1970) was used.

DATA REDUCTION

Two assumptions in determining the values of the separation factors from the data are the binary mixtures in both zeolite-adsorbed and free-solution phases are taken to be thermodynamically ideal, and the sorption capacity of the type Y zeolites studied is constant and equal to 0.25 ml of liquid per gram of dry zeolite regardless of the kind of substance being adsorbed.

The basis for the first assumption is that molecule-zeolite interactions have been proven to be much stronger than the interactions between individual molecules, so the properties of an occluded substance should depend strongly on the zeolite-molecule interactions and are probably less affected by the presence of a second component (Eltekov and Kiselev, 1968). In solution, the similarity in properties of all organic compounds studied here suggests that the assumption of ideal solution should be realistic, especially in the low concentration ranges studied.

Experimentally, this assumption was verified by checking the constancy of the values of the separation factor evaluated at several concentrations of x_1. Over a wide range of concentrations, values of K for other systems have been reported to be unchanged (Eltekov and Kiselev,

Table 1. Separation Factors for Liquid Mixtures on NaY and HY, 30°C

Binary liquid mixture	Separation factor, K[a] NaY	HY
1,3,5-trimethyl benzene (mesitylene)—1,3,5-triisopropyl benzene[b]	>2,000[b]	—
2,4,6-trimethyl aniline (mesidine)-mesitylene	18	30
cumene-cyclohexane	850	100
1,3,5-triisopropyl benzene—1,3,5-triisopropyl cyclohexane[b]	7[b]	—
naphthalene-*n*-decane	>2,000	—
naphthalene-1-decene	>2,000	—
trans-decalin-*n*-decane	13	11.5
cis-decalin-*n*-decane	6.3	—
mesitylene-cyclohexane	110	65
benzene-mesitylene[b]	42[b]	—
benzene-*n*-decane	>2,000	—
benzene-cumene	3.8	—

[a] The first component in each pair on the list is preferentially adsorbed.

[b] May not represent true equilibrium. See text.

1968; Kiselev and Shikalova, 1966). The assumption of ideal solutions in both phases thus appears to be reasonably valid.

The sorption capacity of zeolites may vary from one adsorbate to another, because of differences in the packing efficiency of different molecules in the zeolite cavities. The constant sorption capacity of 0.25 ml/g of Y zeolite assumed here for the group of compounds studied is justified by the results of studies on unidirectional diffusion (Satterfield and Cheng, 1972a) and verified by adsorption equilibria data for four systems in which the separation factor is so large that one species essentially exclusively occupies the pores of the zeolites: 1,3,5 trimethyl benzene—1,3,5 triisopropyl benzene; benzene—*n*-decane; naphthalene—*n*-decane, and cumene—cyclohexane. From these systems the sorption capacities for 1,3,5 trimethyl benzene, benzene, naphthalene and cumene were calculated to be 0.25, 0.263, 0.227, and 0.225 ml/g NaY respectively.

RESULTS AND DISCUSSION

Values of the calculated separation factor K for selected binary mixtures in type Y zeolites are presented in Table 1. Four binary mixtures were studied on HY. In certain cases the first component was almost exclusively adsorbed and the value of K is so large that it cannot be determined accurately. For those cases a value of K greater than 2,000 is indicated.

For all systems studied here, each component by itself is capable of penetrating into the zeolite cavities as shown by unidirectional diffusion studies in which an evacuated zeolite is contacted with a pure liquid (Satterfield and Cheng, 1972a). The steady state results are thus not affected by a sieving property in which one component is excluded by being too large to pass through pore restrictions in the zeolite. However, there are a few borderline systems in which, although either component of the binary system will readily penetrate initially empty zeolite, counterdiffusion occurs too slowly to be readily observed even if the zeolite is initially saturated with the less strongly adsorbed species and placed in the more strongly adsorbed liquid. Two of these borderline cases in which counterdiffusion could not be observed are mesitylene-1,3,5 triisopropyl benzene in NaY and mesitylene-benzene in NaY or HY (Satterfield and Cheng, 1972b). The pair 1,3,5 triisopropyl cyclohexane—1,3,5 triisopropyl benzene may also belong in this category, judging from the sizes of the molecules, but counterdiffusion studies were not performed on this system. When initially contacted with an evacuated zeolite, the more mobile of the two species in a binary mixture will penetrate the pore structure more rapidly. Even if it is the less strongly adsorbed of the pair, it may not be displaced by the more strongly adsorbed species if the latter has a critical diameter very close to that of the pores. The separation factors in Table 1 for these three systems may not represent true equilibrium but rather relative mobilities.

Factors Influencing Selective Adsorption

In the Russian literature, molecules which have common functional or structural features leading to a specific type of adsorption behavior in zeolites are classified into groups. Their so-called "B-group molecules" include compounds having π-electron bonding structures, such as the alkenes, aromatics, and naphthalenes. Molecules possessing permanent dipole groups, for example, alcohols and amines, are classified as D-group. Considerable experimental evidence from infrared and electron-spin-resonance studies shows that these two groups of molecules are capable of interacting specifically with zeolites. Molecules in their A-group include the permanent gases and the alkanes. These latter substances do not interact with zeolites any more strongly than with other sorbents, such as activated carbon and silica gel (Kiselev and Lopatkin, 1968). According to this classification, Kiselev and Lopatkin (1968) found that the heats of adsorption for B-group molecules on NaX are about 2 to 3 kcal/g-mol higher, and for the D-group molecules about 10 kcal/g-mol higher than for the corresponding A-group molecules of similar size and structure.

In general, the results here indicate that in a solution the component which interacts more strongly with the zeolite is selectively adsorbed. Benzene is preferentially adsorbed over *n*-decane, cumene over cyclohexane, and mesitylene over cyclohexane. Eltekov and Kiselev (1968) also reported similar selectivity by NaX with other liquid solutions; *n*-octene-1 from *n*-octane ($K \approx 150$), *p*-xylene from *n*-octane ($K \approx 700$) and from *n*-octene-1 ($K \approx 30$), and benzene from *n*-hexane ($K \approx 700$). The relatively small separation factor for the system 1,3,5 triisopropyl benzene—1,3,5 triisopropyl cyclohexane may be caused by shielding of the ring from the pore by the isopropyl groups so that π-bond interaction becomes less important and alkyl-group interaction more significant.

In a homologous series one might expect higher molecular weight compounds to be more strongly adsorbed, but here steric considerations appear to be particularly important. Seemingly, the component with the smaller and more compact molecular geometry is better able to satisfy the steric requirements for aligning with and entering cavities. For the four aromatics studied, the adsorption selectivity of Y zeolites follows the order:

$$\text{benzene} \geqq \text{cumene} > \text{mesitylene}$$
$$> \text{1,3,5 triisopropyl benzene}$$

Benzene, the smallest in molecular geometry, is preferentially adsorbed. Sundstrom and Krantz (1968), in a study of adsorption equilibria of binary liquid normal paraffins on Linde 5A zeolite, similarly reported that lower molecular weight compounds are preferentially adsorbed. The selectivity followed the order:

$$n\text{-C}_6 > n\text{-C}_{10} > n\text{-C}_{12} > n\text{-C}_{14}$$

Beshty (1970) showed that the separation factor for the system *trans*-decalin—*n*-decane on NaY does not vary significantly over the temperature range from 30 to 120°C. By correlating his data according to Equation (3), the difference between the heats of adsorption of pure liquid *trans*-decalin and *n*-decane on NaY was found to be only 1.0 kcal/g-mol. A negligible temperature effect on the separation factor for normal paraffins over the range 30 to 90° has been reported on 5A molecular sieve (Sundstrom and Krantz, 1968).

Effect of Cation on the Separation Factor

The number, size, and valency of zeolitic cations which are believed to be the centers for interaction between zeolite and adsorbate are expected to play an important role on adsorption equilibria. To examine the effect of cations the adsorption equilibria of four binary systems with either NaY or HY were studied. The results shown in Table 1 indicate that HY has slightly less selectivity than NaY towards the cumene-cyclohexane and the mesitylene-cyclohexane systems. For the system 2,4,6 trimethyl aniline (mesidine)-mesitylene, the selectivity of HY is much higher.

The results can be explained qualitatively on the basis of the differences in magnitude between the zeolite-molecule interactions on these two cationic forms of Y zeolite. The heat of adsorption, which is a measure of the strength of such interaction, is found in general to be higher in NaY than in HY for B-group aromatic molecules. Consequently, NaY would be expected to show a higher selectivity than HY toward adsorption of aromatics from a mixture with type A molecules. Mesidine has the characteristics of both B- and D-group molecules, and the strength of the molecule-zeolite interactions does not change significantly between NaY and HY. The net result in the system mesidine-mesitylene is an increase in selectivity on going from NaY to HY, associated with a decrease in the interaction energy of the mesitylene.

Selective Adsorption and Reaction Selectivity

Selectivity effects upon catalytic reaction of mixtures can in many cases be interpreted in terms of the relative adsorptivity of the species present. The studies here help to explain some selectivity phenomena reported on molecular sieve catalysts. Beecher et al. (1968) studied the hydrocracking of pure *n*-decane, decalin, and a 46/54 mole % mixture over Pd-H-mordenite. They found that with the 46/54 mixture of *n*-decane and decalin, relatively little *n*-decane was converted, although *n*-decane alone was more readily hydrocracked than decalin. The observation here that decalin is preferentially adsorbed over *n*-decane suggests that during reaction few catalyst sites were available for decane to become adsorbed and react. A similar situation was also noted by Voorhies and Hatcher (1969) for the hydrocracking of mixtures of cyclohexane and *n*-hexane on Pd-H-mordenite and Pd-faujasite (SK-100).

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NOTATION

$H_{a,1}$ = enthalpy per mole of pure compound 1 in the zeolite-adsorbed state at temperature T, kcal/mol
$H_{a,2}$ = enthalpy per mole of pure compound 2 in the zeolite-adsorbed state at temperature T, kcal/mol
H_1 = enthalpy per mole of pure compound 1 in the liquid state at temperature T, kcal/mol
H_2 = enthalpy per mole of pure compound 2 in the liquid state at temperature T, kcal/mol
H_i = enthalpy per mole of pure compound i, kcal/mol
$\Delta H_{1,\mathrm{ads}}$ = the change in enthalpy of pure compound 1 from liquid state to zeolite-adsorbed state, kcal/mol
$\Delta H_{2,\mathrm{ads}}$ = the change in enthalpy of pure compound 2 from liquid state to zeolite-adsorbed state, kcal/mol
K = separation factor, see Equation (1)
K_0 = a constant
R = gas constant, 1.987 cal/g-mol, °K
T = temperature, °K
$x_{a,1}$ = mole fraction of component 1 in the zeolite phase
x_1 = mole fraction of component 1 in liquid solution phase (in equilibrium with $x_{a,1}$)
$x_{a,2}$ = $(1 - x_{a,1})$
x_2 = $(1 - x_1)$

Greek Letters

$\mu_{a,1}^*$, $\mu_{a,2}^*$ = chemical potentials of pure compounds 1 and 2, respectively, in the zeolite-adsorbed phase at temperature and pressure under study
μ_1^*, μ_2^* = chemical potentials of pure liquid compounds 1 and 2, respectively, at temperature and pressure under study

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