Liquid Counterdiffusion of Selected Aromatic and Naphthenic Hydrocarbons in Type Y Zeolites

Rates of counterdiffusion are markedly affected not only by the critical molecular diameter of the diffusing molecules but also by other physicochemical properties of the liquids and the nature of the cation in the zeolite. The effective diffusivity in NaY or HY under counterdiffusion conditions is less by a factor of 10^{-1} to 10^{-3} than that for unidirectional diffusion into an initially empty pore structure.

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SCOPE

The factors affecting the rates of unidirectional diffusion and counterdiffusion of hydrocarbons in molecular sieve zeolites are of significant importance in conjunction with the use of zeolitic catalysts in reactors and of zeolitic sorbents in separation processes. Our previous studies of diffusion in zeolites include that of the desorption and counterdiffusion behavior of liquid benzene and cumene in H-mordenite (Satterfield et al., 1971), the single-component (unidirectional) diffusion of selected organic liquids in type Y zeolites (Satterfield and Cheng, 1972a), equilibria of selected binary organic liquid systems in type Y zeolites (Satterfield and Cheng, 1972b) and the effect on counterdiffusion of liquid hydrocarbons of the nature of the cation present in type Y zeolites (Satterfield and Katzer, 1971).

The present study focused on elucidating two aspects of the overall problem: 1. the relationship between the size and physicochemical properties of the diffusant molecule and its rate of diffusion in type Y zeolite in either the Na or H form and 2. the relationship between unidirectional, that is, single component, diffusion and counterdiffusion in binary systems.

CONCLUSIONS AND SIGNIFICANCE

Counterdiffusion of hydrocarbons in zeolites will not be observed if either adsorption equilibrium does not provide a significant driving force or the size and physicochemical properties of one of the diffusants is such that although it can penetrate an initially empty pore structure its mobility is very slight in the presence of another component in the pores. In the latter case a presorbed compound will not diffuse out even if equilibrium favors its desorption. The diffusion coefficient of any compound under counterdiffusion conditions is less than that under unidirectional diffusion because of molecule-molecule interactions between counterdiffusing species. The decrease in diffusivity for counterdiffusion as compared to unidirectional diffusion is markedly affected by the nature of the second substance and by the nature of the zeolitic cation.

EXPERIMENT

The NaY and HY and the carefully purified organic species were the same as those used and described previously (Satterfield and Cheng, 1972a, b). A description of the apparatus and experimental method has also been published (Satterfield and Katzer, 1971). The HY was prepared by ion exchange of the NaY with a large excess of 10 wt. % ammonium chloride solution at 70°C. By repeated contacting, 97.7% of the Na was exchanged to NH_4, as determined by analyses for sodium content by the Central Analytical Facility at M.I.T. The exchanged zeolite was converted to the HY form by spreading it in a thin layer in a container in an oven and heating it from 50° to 500°C under vacuum at a rate of 1°C/min., and then holding it at 500°C for an additional 3 hours. This material is designated here as HY(III). A few studies were also made with a material, designated as HY(I), in which 79% of the Na was exchanged to NH_4 and converted to HY by the same method. The procedures are similar to those used by Katzer (1969) and are described in more detail by Cheng (1970).

Counterdiffusion measurements were carried out in either of two ways. In both cases the zeolite was first saturated with the compound that was less strongly adsorbed. In the first procedure the compound of lesser adsorptivity was adsorbed onto the zeolite from the vapor phase and then the saturated zeolite was transferred to a stirred 500 ml Morton flask maintained isothermal in a water bath. (This method of saturation greatly reduces the amount of material adhering to the exterior of the zeolite particles.) At zero time a second organic liquid, the more strongly adsorbed, was added to the flask. Samples of the slurry were withdrawn from the stirred flask at pre-

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determined times after the addition of the second liquid, were rapidly filtered, and the liquid was analyzed for the concentration of the first compound by gas chromatography. These are termed desorption measurements since the compound being analyzed for was initially adsorbed in the zeolite. The excess material on the outside of the particles results in a nonzero initial concentration of desorbed species which is allowed for in the analysis. The net change in concentration of the desorbing species in the bulk liquid would typically be from about 0.1 wt. % to about 2.0 wt. %.

In the second procedure the zeolite was first saturated by directly mixing a large quantity of the weakly adsorbed organic liquid with activated zeolite in the flask. At zero time a small amount of the second, preferentially adsorbed, organic liquid was added to the flask. Periodically, samples of the slurry were removed, filtered, and analyzed for the concentration of the second compound in the same manner as before. Since the second component was initially in the bulk phase as a dilute solution (typically less than 2 wt. %) in the weakly adsorbed component, these are termed adsorption measurements. For all systems studied here, both components are capable of penetrating into the zeolite cavities, as shown by unidirectional diffusion studies into zeolites initially held in vacuum (Satterfield and Cheng, 1972), so the adsorption of one component is presumably accompanied by the desorption of an approximately equal volume of the second component. A binary system can be studied by either method. For example, runs IV-10 and IV-37, discussed below, refer to an adsorption measurement and a desorption measurement, respectively, in the system cyclohexane-mesitylene. In both cases the zeolite is initially saturated with cyclohexane, the more weakly adsorbed component. In run IV-10 the drop in concentration of mesitylene in the bulk liquid is followed, this bulk liquid comprising initially dilute mesitylene in cyclohexane. In run IV-37 the increase in concentration of cyclohexane in the bulk liquid is followed, this liquid initially comprising pure mesitylene.

If the zeolite is initially saturated with the more strongly adsorbed component, the potential driving force for desorption is low and it is difficult to make accurate measurements. As examples, a diffusion coefficient could not be determined when NaY saturated with mesitylene was placed in cyclohexane (distribution coefficient = 110 in favor of mesitylene) or when Na saturated with cumene was placed in cyclohexane (distribution coefficient = 850 in favor of cumene). With somewhat lower distribution coefficients, measurements by this method may be feasible.

Mass transfer resistance in the liquid phase was shown to be negligible compared to that in the zeolite (Katzer, 1969; Cheng, 1970). There was no evidence that any reaction occurred between adsorbate and zeolite, at least at temperatures of 100°C or lower, such as that observed by Satterfield et al. (1971) for cumene adsorbed in H-mordenite.

RESULTS AND DISCUSSION

Table 1 presents the results from the adsorption-type measurements and Table 2 those from the desorption-type measurements. The systems cumene-cyclohexane-NaY and mesitylene-cyclohexane-NaY were studied by both methods. D_E was evaluated from the initial portion of the adsorption curve.

For both of these systems, D_E from desorption measurements is higher than that from adsorption measurements (~ 300 vs. 150; 1-0.72 vs. 0.132 at 30°C, 0.25 vs. 0.033 at 15°C). More detailed studies, as of the effect of concentration on D_E, are needed to clarify the reasons for the differences between adsorption and desorption measurements. The potential driving force in the desorption measurements is always greater than that in the adsorption measurements. If a rate process indeed follows Fick's law, the driving force would not affect the diffusion coefficient but considerable deviations from Fick's law are frequently reported. Even in ordinary liquid systems Fick's law is not followed rigorously, that is, the diffusion coefficient may be a function of concentration. Slight differences in the value of D_E from zeolite sorption measurements can be obtained, especially from initial data, from insufficiently rigorous treatment of the boundary conditions, as discussed by Cheng (1970), but the differences here are believed to be due primarily to other factors. Sorption or desorption as such could also become a partially rate-limiting step in which case a different model must apply. Beyond this, the model assumes that equilibrium is established at the interface. Although this seems to hold for most cases of interphase mass transfer, it may not be true here where very high separation factors will cause a large change in concentration at the liquid-zeolite interface.

The above considerations are important in acquiring a better understanding of the mechanism of movement of

TABLE 1. ADSORPTION MEASUREMENTS

Run no.	Run temp., °C	Zeolite	Substance diffusing from zeolite	Substance diffusing into zeolite	Critical molecular diam., Å		Effective diffusion coefficient $D_E \times 10^{13}$, cm²/s
					In solid state	In liquid state (est.)	
IV-4	30	NaY	Cyclohexane	Cumene	6.8	6.5-6.7	150
IV-14	30	NaY	Cyclohexane	1,2,3-Trimethyl benzene	7.2	7.7	23
IV-15	30	NaY	Cyclohexane	1,2,4-Trimethyl benzene	7.2	7.0	44
IV-11	15	NaY	Cyclohexane	Mesitylene (1,3,5-trimethyl benzene)	8.4	8.4	0.033
IV-10	30	NaY	Cyclohexane	Mesitylene (1,3,5-trimethyl benzene)			0.13
IV-12	50	NaY	Cyclohexane	Mesitylene (1,3,5-trimethyl benzene)			0.35
IV-17	30	NaY	Cyclohexane	Mesidine (2,4,6-trimethyl aniline)	8.4	8.4	0.01
IV-13	50	NaY	Cyclohexane	Mesidine (2,4,6-trimethyl aniline)			0.052
IV-30	30	HY (I)	Cyclohexane	Mesitylene			~2
IV-32	30	HY (III)	Cyclohexane	Mesitylene			93
IV-33	30	HY (III)	Cyclohexane	Mesidine			0.039
IV-34	30	HY (III)	Mesitylene	Benzene	6.8	6.3	0.000

The substance diffusing into the zeolite is in each case preferentially adsorbed.

TABLE 2. DESORPTION MEASUREMENTS

Run no.	Run temp., °C	Zeolite	Substance diffusing into zeolite	Substance diffusing from zeolite	Effective diffusion coefficient $D_E \times 10^{13}$, cm^2/s
IV-7	30	NaY	Cumene	Cyclohexane	~300
IV-21	30	NaY	Benzene	Mesitylene	0.000
IV-23	30	NaY	Benzene	Cumene	0.331
IV-37	30	NaY	Mesitylene	Cyclohexane	1.00
IV-39	30	NaY	Mesitylene	Cyclohexane	0.72
IV-38	15	NaY	Mesitylene	Cyclohexane	0.25
IV-42	30	HY (III)	1,3,5-Triisopropyl benzene	Cyclohexane	5.00
IV-43	30	HY (III)	1,3,5-Triisopropyl cyclohexane	Cyclohexane	1.13
IV-47	30	NaY	1,3,5-Triisopropyl benzene	Cyclohexane	0.0036
IV-48	30	NaY	1,3,5-Triisopropyl cyclohexane	Cyclohexane	0.014

The substance diffusing into the zeolite is in each case preferentially adsorbed.

sorbates in molecular sieves and in evaluating reported values for diffusivities. The goal of the present study, however, was rather to make a broad comparison of diffusivities under unidirectional and counterdiffusion conditions, which could be followed later by more refined studies.

Effect of Critical Molecular Diameter

One of the important factors affecting the rate of counterdiffusion is, as in the case of unidirectional diffusion, the critical molecular diameter, the diameter of the smallest cylinder that can contain the molecule. Estimation of this dimension is somewhat more uncertain than might seem to be the case initially. One approach is to start with crystal structure determinations of molecules in the solid state, applying estimated values of van der Waal's radii for the outermost atoms. Although this provides a reasonably precise method of proceeding, in the liquid state most molecules are readily deformable so the effective critical diameter of molecules migrating in the zeolite pore system may be somewhat different. A priori estimation of effective critical diameters in liquids requires judgments on conformation and the degree of steric hindrance involved in distorting a molecule into the most compact form in two dimensions. Predictions may be particularly difficult for the more asymmetric and complex molecules. Tables 1 and 3 list values as estimated for the solid state by Cheng (1970) and for the liquid phase as estimated by Pitcher (1972). The ranges given for the latter represent minimum and maximum values for several plausible conformations. Although the values are in some cases slightly different than those calculated for the solid state, this has no significant effect on the general conclusions reached here.

Figure 1 shows the fractional uptake of four aromatic C_9H_{12} isomers having different molecular diameters (see Table 1) into cyclohexane-saturated NaY at 30°C, on a M_t/M_∞ vs. $\sqrt{t}$ plot. Mesitylene has the largest critical molecular diameter and diffuses much more slowly than the other three isomers which are smaller in critical molecular diameter.

Effect of Molecule-Zeolite Interactions

Also plotted in Figure 1 is the uptake of 2,4,6-trimethyl aniline (mesidine), which has a similar molecular shape and size to mesitylene but is instead an aromatic amine. The diffusion rate of mesidine is much slower than that of mesitylene, indicating that steric considerations are by no means the only determining factor on diffusivities in zeolites. Other factors that affect the mobility of diffusate, resulting from strong interactions between molecules and zeolite, must also be considered.

As discussed in more detail elsewhere (Satterfield and Cheng, 1972a, b), it is useful to classify molecules into groups as is done in the Russian literature (see, for example, Kiselev and Lopatkin, 1968; Eltekov and Kiselev 1968). *A* group molecules are substances such as permanent gases and alkanes which do not interact any more strongly with molecular sieves than with other sorbents such as activated carbon and silica gel, *B* group molecules have π-electron bonding, for example, aromatics such as mesitylene, and *D* group molecules have permanent dipole groups, for example, alcohols and amines such as mesidine. The *D* group molecules interact most strongly and *A* group molecules the least strongly with zeolites, as shown, for example, by heats of adsorption.

In unidirectional studies, the diffusion coefficient for mesitylene at 30°C in NaY was about 10 times that of mesidine, about the same ratio as that observed here for counterdiffusion in the presence of cyclohexane. In the unidirectional studies, the activation energy, based on data over the small temperature range of 0° and 30°C was about 9 kcal/g-mol for mesitylene and 17 for mesidine. All of these observations are consistent with the postulate that mesidine interacts more strongly with the zeolite than does mesitylene.

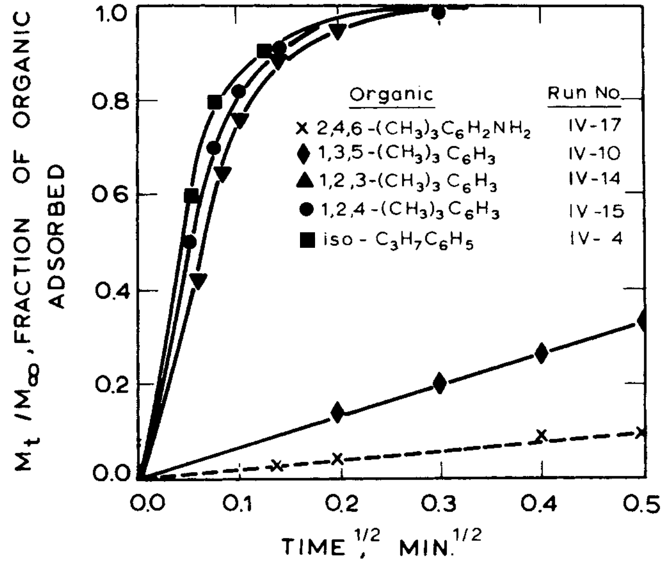

Fig. 1. Counterdiffusion of selected C_9H_{12} isomers or of mesidine (2,4,6 trimethyl aniline) into NaY saturated with cyclohexane. Adsorption measurements, 30°C.

Effect of Zeolitic Cation

The effect of the nature of the cation upon counterdiffusion rates is illustrated in Figure 2 where the value of M_t/M_∞ for mesitylene diffused into cyclohexane-saturated NaY, into HY(I) or into HY(III) is plotted against the square root of time. The initial diffusion coefficients for these runs are 0.13×10^{-13}, 2.0×10^{-13}, and 93×10^{-13} cm²/s respectively. The diffusivity increases with an increasing degree of ion exchange to convert NaY to HY. A similar increase in D_E was also observed by Satterfield and Katzer (1971) when NaY was converted to HY. This cation effect can also be explained from the viewpoint of molecule-zeolite interactions. As was shown with unidirectional diffusion, the diffusion rate of *B*-group molecules (for example, aromatics) is considerably greater in HY than in NaY while diffusion rates of *D*-group molecules (mesidine) and *A*-group molecules (1,3,5-triisopropyl cyclohexane) are more similar in the two forms of Y zeolite.

Effect of Molecule-Molecule Interactions

Because of the extremely small pore sizes in zeolites, steric hindrance, and molecule-molecule interactions between counterdiffusing species would be expected to reduce significantly the diffusion coefficient of each component relative to that observed in unidirectional diffusion. This is borne out by the data in Table 3 which compares diffusion coefficients obtained from unidirectional and counterdiffusion conditions. All the counterdiffusion results shown are, with one exception, for cyclohexane diffusing in the opposite direction. A large reduction in the diffusion coefficient is observed in most cases indicating that interactions between the incoming and outgoing molecules have a profound effect upon the diffusion rate. The nature of the molecule diffusing in the opposite direction, other than its size, also affects the diffusion rate. Thus the rate at which cumene counterdiffuses with cyclohexane (7.2 Å critical diameter in solid state) corresponds to $D_E = 150 \times 10^{-13}$ cm²/s while it is 0.33×10^{-13} cm²/s when cumene desorbs into benzene (6.8 Å critical diameter in solid state).

The counterdiffusion of benzene and cumene molecules does not occur in H-mordenite pores but readily occurs in type Y zeolites (Satterfield et al., 1971; Satterfield and Katzer, 1971). The inhibition of counterdiffusion is caused by the fact that the mordenite pore size, being 7.0 × 6.7 Angstroms, is very close to the size of benzene or cumene molecules and that these two molecules are lined-up in the tunnel-like mordenite pores and cannot freely pass each other in the main channels. A similar situation would be expected to occur here as the size of counterdiffusing molecules approaches the pore size of type Y zeolites (about 8 Angstroms minimum pore diameter). In fact this was observed in at least two cases. Mesitylene did not adsorb into NaY previously saturated with 1,3,5-triisopropyl benzene even at 120°C, although mesitylene is apparently very selectively adsorbed over 1,3,5-triisopropyl benzene (*K* estimated to exceed 2,000). Likewise, benzene did not displace mesitylene from NaY saturated with it, al-

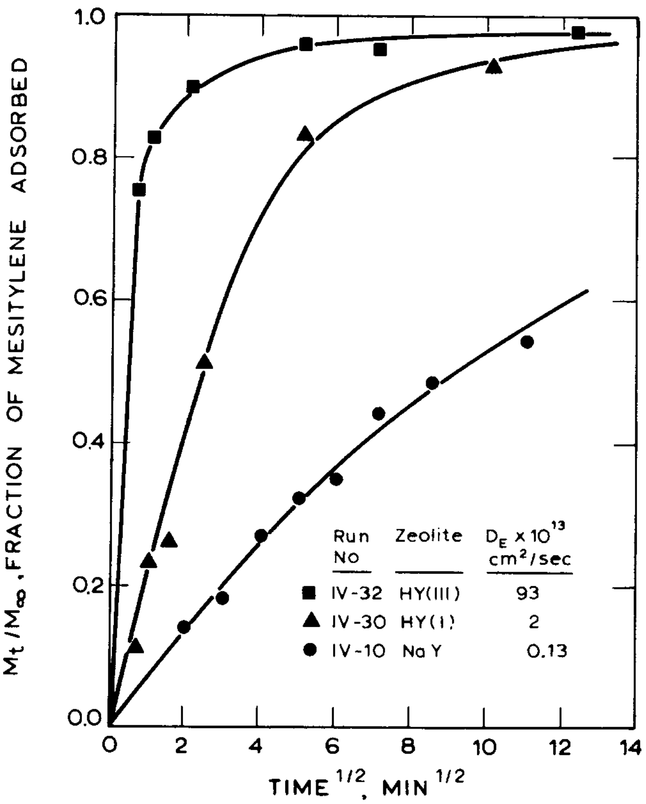

Fig. 2. Counterdiffusion of mesitylene into NaY, HY(I) (79% ion-exchanged) or HY(III) 97.7% ion-exchanged). Zeolite previously saturated with cyclohexane. Adsorption measurements, 30°C.

TABLE 3. COMPARISON BETWEEN UNIDIRECTIONAL AND COUNTERDIFFUSION COEFFICIENTS AT 30°C[1]

	Critical molecular diam., Å			$D_E \times 10^{13}$, cm²/s	
Organic compounds	In solid state	In liquid state (est.)	Zeolite	Uni-directional	D_E, unidir. / D_E, count.
Cumene	6.8	6.5-6.7	NaY	>700	- - -
Cumene[2]	6.8	6.5-6.7	NaY	>700	>2000
Mesitylene	8.4	8.4	NaY	72	72-550
Mesidine	8.4	8.4	NaY	7.1	710
1,3,5-Triisopropyl benzene	9.4	9.2-9.6	NaY	0.047	13
1,3,5-Triisopropyl cyclohexane	9.8	9-10.5	NaY	4.9	350
Mesitylene			HY (III)	>500	>5
Mesidine			HY (III)	4.1	100
1,3,5-Triisopropyl benzene			HY (III)	12.4	2.5
1,3,5-Triisopropyl cyclohexane			HY (III)	8.7	7.7

[1] Cyclohexane diffusing in the opposite direction.
[2] Benzene diffusing in the opposite direction.

though benzene is preferentially adsorbed. If counterdiffusion could occur, mesitylene should be able to displace essentially all the presorbed 1,3,5-triisopropyl benzene in NaY. On the other hand, when equilibrium permits counterdiffusion to occur in the zeolite pores, presorbed molecules with relatively small critical diameters are readily desorbed regardless of the size of the incoming molecules, provided the latter are capable of entering the pore mouths. Examples are the counterdiffusion of cyclohexane from NaY into mesitylene or into 1,3,5-triisopropyl benzene.

It appears that when molecules with critical diameters that are large relative to the zeolite pores are occluded, their mobilities in the zeolite channels are greatly reduced due to geometrical obstructions and strong interactions between the molecule and the zeolite wall. The interactions between incoming and outgoing molecules can further immobilize the presorbed molecules to the point that counterdiffusion becomes imperceptively slow.

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NOTATION

D_E = effective diffusion coefficient, cm²/s

M_t = amount of mass diffused in at time t

M_∞ = amount of mass diffused in after infinite time

t = time, s

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HI-H_2 Vapor Etch for Low Temperature Silicon Epitaxial Manufacturing

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Etching of semiconductor silicon slices at 998°C with HI-H_2 mixtures was developed to the level that practical etch rates ($\geqq$ 0.1 μm/min) and smoothness of surfaces were obtained in a manufacturing type reactor without the addition of HF or He. Such a low temperature etch is expected to lead to improved device characteristics, mainly because of more sharply defined junction surfaces.

Using deposition at 998°C on very clean slices as a testing method, two sources of impurities that cause stacking faults in the deposition layers were identified and eliminated. These were the polypropylene vessel used in the slice cleanup procedure, and the hydrogen peroxide used in conjunction with sulfuric acid in the primary cleaning step.

SCOPE

Modern electronic systems increasingly demand improvements in the performance, reliability, and cost of solid state devices. Many current limitations of systems relate directly to device limitations; of particular concern is speed of operation. The ability to produce improved devices has reached a state of the art where possibly the most significant advances will be made in the area of materials processing.

Lowering the temperature of solid state device processing would have particularly beneficial effects: more sharply defined junction interfaces would be possible, allowing higher device speeds; more freedom from crystal