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Liquid Phase Separation of Polar Hydrocarbons from Light Aromatics Using Zeolites

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Abstract. The liquid phase removal of low concentrations of polar compounds (acetonitrile, acrylonitrile and dioxane) from toluene by adsorption on zeolites reveals very high selectivity factors. Kinetic selectivity factors as high as 16,100 are observed. The selection of the zeolites (MFI, MWW and FAU type) allowed the study of the effects of varying aluminum content, the presence and absence of acidic centers and varying pore volumes. To assess the relative effectiveness of each adsorbent, both equilibrium and continuous flow, pseudo equilibrium, breakthrough experiments were conducted. The continuous flow experiments were carried out at 25 and 75°C. The zeolites H-ZSM-5, H-MCM-22 and Na-X are highly effective in removing the polar compounds from toluene to a concentration level down to less than 20 ppm (detection limit). The results obtained with the equilibrium batch experiments are confirmed by the continuous flow breakthrough experiments.

Keywords: zeolites, polar compounds, adsorption, adsorption isotherms, equilibrium, liquid phase, breakthrough curves, acetonitrile, acrylonitrile, dioxane, ZSM-5, MCM-22, Na-X

Introduction

Removal of trace components from liquids is a key aspect of both water and hydrocarbon purification. Hydrocarbon purification is needed to meet stringent downstream specifications designed to insure long catalyst lifetimes, efficient processing performance, and high product quality, especially for products that are polymer precursors, all factors having environmental implications. Zeolites offer the advantages of easy separation and recovery and hence will play an increasingly important role as adsorbents in this application field. Knowledge of fundamental adsorption parameters and the role of zeolite property parameters are essential for rapid progress in this area. This paper presents preliminary data obtained on the liquid phase separation of trace amounts of polar hydrocarbons from light aromatic feed streams. One commercial application could be the removal of potential catalyst poisons from process feed streams. This could be in the cleanup of either feed or product streams in processes such as xylene isomerization, toluene disproportionation, and ethyltoluene and ethylbenzene synthesis.

Extensive work (Levina et al., 1971; Lityaeva et al., 1978; Luo et al., 1998; Mingles et al., 1988; Weitkemp et al., 1991) has been done before on removal of thiophene impurities from benzene. A recent study (Luo et al., 1998) examined the removal of thiophene from benzene, produced via a coking process, by the catalytic reaction with ethanol on H-ZSM-5. The removal of thiophene and acetone from benzene by contacting with finely divided Y zeolite cracking catalyst containing rare earth metals has been patented (Gainko et al., 1992). The adsorption of pyridine and dioxane from aqueous solutions on Na-X and Mg-X zeolites, polymethylsiloxane xerogels, and mixed adsorbents such as zeolite-polymethylsiloxanes has also been reported (Slinyakova et al., 1972). Usmanova et al. (1969) have studied the adsorption on zeolite Na-X of the model liquid systems dioxane-cyclohexane, morpholine-cyclohexane, and morpholine-heptane.

The liquid phase separations of trace amounts of water from n-octane and cyclohexane from the alkali metal zeolite type A have been studied (Alexandrova et al., 1966; Sircar et al., 1970). In both of these cases only the water could be adsorbed by the adsorbent and the observed isotherms were nearly identical to single component gas phase water adsorption results.

Very recently, Boulicaut et al. (1998) reported on a liquid phase study of the sorption and diffusion of light hydrocarbons, e.g., hexane isomers, in high silica ZSM-5. They find the exchange adsorption reactions, with n-hexane, to be mildly endothermic and that the equilibrium constants and exchange energies are consistent with vapor phase data.

This study deals with removal of acetonitrile, acrylonitrile and dioxane from toluene. The selection of zeolites was made to allow the study of effects of varying aluminum content, presence and absence of acidic centers, and varying pore volumes. To assess the relative effectiveness of each adsorbent, both equilibrium and continuous flow kinetic breakthrough experiments were conducted.

Experimental

The zeolites used for this study are listed in Table 1. The Mobil Technology Company provided the H-ZSM-5 ($Si/Al_2 = 26$), H-MCM-22 and Na-X.

Equilibrium Experiments

Solutions were prepared of 1 wt% polar compound (acetonitrile, acrylonitrile, dioxane) in toluene. A series of batch runs were carried out for each of the three polar compounds with different adsorbents. The zeolite adsorbents were activated by heating at 500°C for 2 h under vacuum. Using a glove bag to maintain dryness, 10 ml of solution was contacted with varying amounts of the activated zeolites (0–7g) in vials. After 16 h, GC analysis of the solution was carried out. As a reference material for GC analysis, 2% 2,3 dimethylbutane (DMB) was added to the starting solution. This allowed a larger injection size and hence a more accurate determination of polar adsorbate concentration. Tests were carried out to verify that there was no selective adsorption of DMB on the zeolites. A DB1 capillary column, length 60 m, was used. The GC procedure employed had a detection limit of 20 ppm of the polar hydrocarbon component.

Table 1. List of zeolite samples used in this study.

Zeolite	SiO_2/Al_2O_3 (molar ratio)
MFI (H-ZSM-5)	26
MFI (H-ZSM-5)	700
MWW (H-MCM-22)	26
FAU (Na-X)	2.7

For the equilibrium batch experiments, the H-ZSM-5 (26) and H-ZSM-5 (700) were used in pure powder form. Na-X was in pure pellet form and H-MCM-22 was in alumina bound pellet form. A correction for the dilution effect of the binder was applied in each case with an assumption that the binder does not affect the adsorption. All results are expressed on a pure zeolite basis, i.e., grams adsorbed per gram of zeolite (g/gz).

Continuous-Flow Kinetic Breakthrough Experiments

The experimental setup, shown in Fig. 1, is a fully automated system controlled via Macintosh based LabVIEW software and Kinetics System interface hardware. Three grams of 1/16″ alumina bound zeolite extrudate was packed in a column (SS pipe with inner diameter of 1/4″). The bed length was 7.5″. Prior to contacting the adsorbent with the test solution, the bed was contacted with liquid toluene. A solution of 0.25 wt% polar compound (acetonitrile, acrylonitrile and dioxane), achieved by blending streams of pure toluene and 1% polar compound in toluene, was pumped through the adsorption column at a rate of 18 g/h (WHSV = 6). Breakthrough measurements were carried out at two different column temperatures, 25 and 75°C and at a system pressure of 20 psi. The effluent from the adsorption column was vaporized and nitrogen introduced as a diluent and carrier gas. GC sampling of the effluent stream was done every 10 min by online injection. Prior to each experiment, the adsorbents were activated by ramping the temperature up to 540°C under a flow of nitrogen and then holding at that temperature under dry air flow for two hours, and then cooling down to experiment temperature under nitrogen flow. The same procedure was used for regeneration after each run.

For the kinetic flow experiments, all zeolites were in pure or 1/16″ alumina bound extrudate form; a correction for the binder was applied for the latter case. All results are expressed on a pure zeolite basis, i.e.,

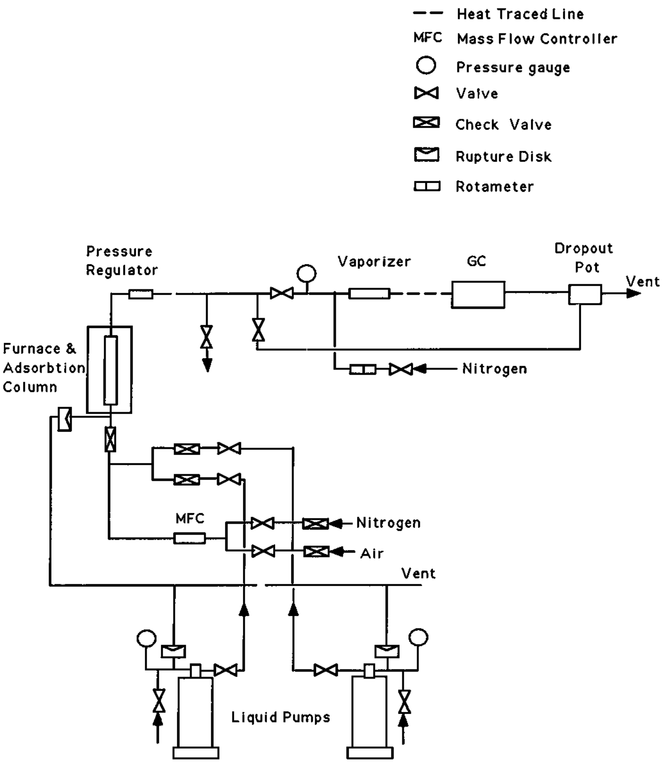

Figure 1. Continuous flow breakthrough experiment setup.

grams adsorbed per gram of zeolite (g/gz). The solid lines shown in the figures represent a least squares fit of the data and are added solely to aid in the visualization of the data.

Results and Discussion

MCM-22, ZSM-5 and X type zeolites were chosen for this study. The MCM-22 and ZSM-5 are medium pore, high silica zeolites, having two and three-dimensional channel systems, respectively (Leonowicz et al., 1994; Meier et al., 1996). The species selected were in protonic form and had identical composition (Table 1). X-type zeolite has large pores and a three-dimensional channel system (Meier et al., 1996); the material used was in the sodium form and had a 2.7 silica to alumina ratio. Thus the adsorbents covered a wide range of framework composition and were of protonic and sodium cationic forms. Diffusion of all the adsorbate components is expected to be relatively fast in these particular zeolites. Loadings shown in the figures are averages over the bed.

The adsorbates, acetonitrile, acrylonitrile and dioxane, in toluene, were selected as representative of polar aromatics and near co-boilers with light aromatics such as benzene and toluene.

Both equilibrium and continuous flow experiments were conducted. The former, where equilibration times were 16–24 h, were conducted to generate adsorption isotherms. The latter, were designed to simulate commercial type separation conditions. Equilibrium reference values were computed from the equilibrium data by estimating the throughput at which breakthrough would occur if the entire adsorbent bed had been uniformly saturated with adsorbate. The similarity of the flow results with those of the equilibration tests suggest that flow tests are at least pseudo-equilibrium in character.

Equilibrium Experiments

The isotherms for the adsorption of acetonitrile from toluene on H-ZSM-5 (26), H-ZSM-5 (700), H-MCM-22 and Na-X are shown in Fig. 2. Comparing the two isotherms for H-ZSM-5 having SiO_2/Al_2O_3

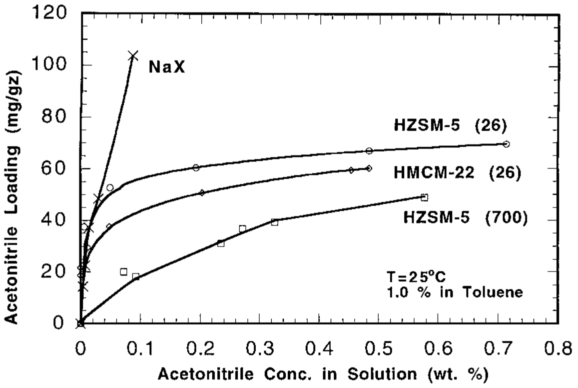

Figure 2. Adsorption isotherms: adsorption of acetonitrile in toluene by H-ZSM-5 (26), H-ZSM-5 (700), H-MCM-22 (26) and Na-X.

molar ratios of 26 and 700, respectively, shows that their effectiveness, significant adsorption at low concentrations, increases with the number of Brønsted acid sites and the polar character of the framework. The isotherms for H-ZSM-5 (26) and H-MCM-22 (26) are very similar, consistent with the similarity of their composition and pore structures, i.e., they are both 10-ring, medium pore zeolites. The Na-X, containing Na cations and the H-ZSM-5 and H-MCM-22 zeolites, containing protons as cations, allows a preliminary comparison of the effects of cation type. While both forms show good selectivity, on a per cation basis, the protonic zeolites tested, H-ZSM-5 and H-MCM-22, appear to have higher selectivity for these polar adsorbates than the sodium containing zeolite, Na-X. The high capacity and selectivity of Na-X can be attributed to its high aluminum content and pore volume. Consistent with the weakly basic character of acetonitrile, a break or inflection is not observed at the point of a 1 : 1 complex with the protons or sodium ions.

The adsorption behavior for acrylonitrile is very similar to that obtained for acetonitrile and hence has not been included. At both high and low solution concentration and zeolite loading, these adsorbents show similar acrylonitrile adsorption.

Selective adsorption of dioxane occurs in both the H and Na forms of the zeolites as demonstrated by the adsorption isotherms for dioxane adsorption from toluene on H-ZSM-5 (26), H-MCM-22 and Na-X (Fig. 3). A 1 : 1 complex, with either the protons or Na ions, is not observed in the low to moderate concentration ranges. Na-X is a standout, showing both high selectivity and capacity. Again, H-ZSM-5 (26) and H-MCM-22 give similar results.

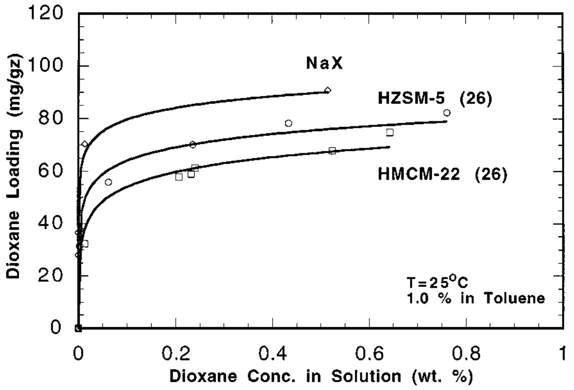

Figure 3. Adsorption isotherms: adsorption of dioxane in toluene by H-ZSM-5 (26), H-MCM-22 (26) and Na-X.

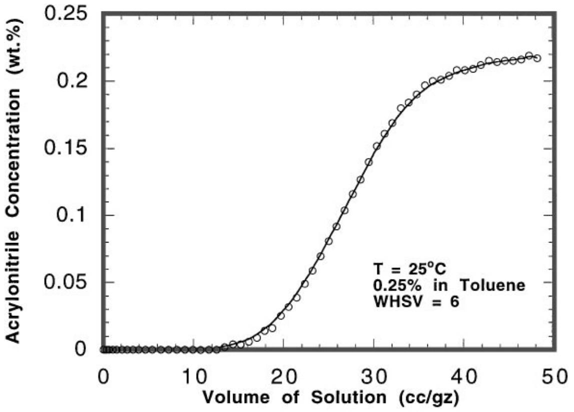

Figure 4. Adsorption of 0.25 wt% acrylonitrile in toluene by H-ZSM-5 (26): Breakthrough curve.

Continuous Flow Kinetic Breakthrough Experiments

Acrylonitrile. In a continuous flow test with a 0.25 wt% acrylonitrile in toluene feed, H-ZSM-5 (26) achieves complete removal of acrylonitrile up to 14 cm^3 of feed per gram of zeolite (Fig. 4). In these experiments breakthrough is defined as the point of first observable polar hydrocarbon. Note that in the potential applications listed above, polar hydrocarbon contaminant levels are expected to be one or more orders of magnitudes lower, with proportional extension of the breakthrough volumes expected. At breakthrough the acrylonitrile loading is 2.9 molecules of acrylonitrile per unit cell (Fig. 5) which may be compared with the 6.8, the number of protonic centers per unit cell. These loadings are averages over the zeolite bed. Since acrylonitrile is a weak base, it is not surprising that this breakthrough

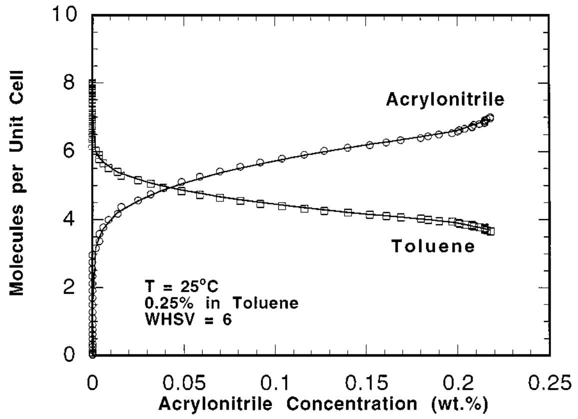

Figure 5. Adsorption of 0.25 wt% acrylonitrile in toluene by H-ZSM-5 (26): Number of molecules of acrylonitrile and toluene per unit cell as a function of acrylonitrile concentration in solution.

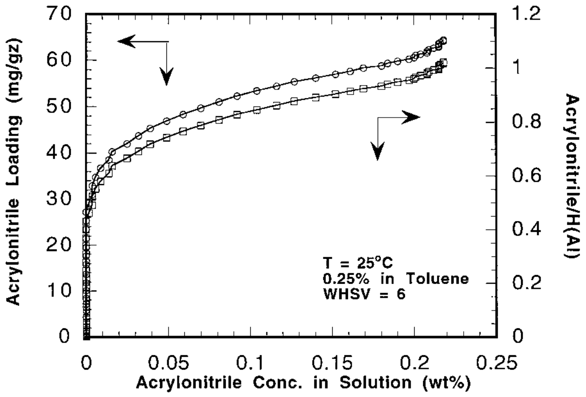

Figure 6. Adsorption of 0.25 wt% acrylonitrile in toluene by H-ZSM-5 (26): Loading of acrylonitrile in the zeolite, expressed as mg/gz and as molecules of acrylonitrile/acid site, as a function of acrylonitrile concentration in solution.

occurs at an acrylonitrile per protonic center ratio far less that the value of 1.0 which would be expected for a strong base molecule (Fig. 6).

The *kinetic selectivity factor* for acrylonitrile/toluene is shown in Fig. 7. To distinguish the selectivities observed in these flow experiments from true equilibrium values, the term kinetic selectivity factor will be used throughout this paper. The classical selectivity factor, alpha (α), is a measure of the effectiveness of a particular adsorbent for a given separation. It is defined as

$$\alpha = (Ez_{\mathrm{A}}/Ez_{\mathrm{Tol}})/(Es_{\mathrm{A}}/Es_{\mathrm{Tol}})$$

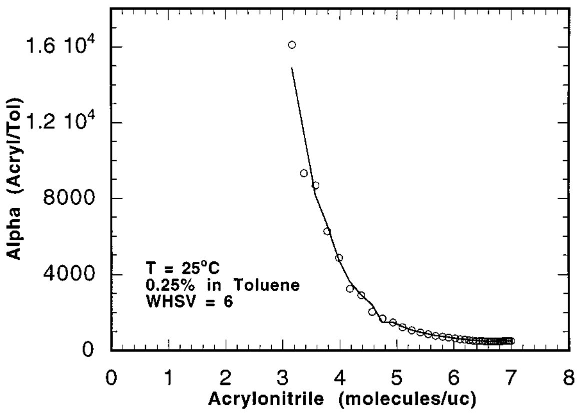

Figure 7. Adsorption of 0.25 wt% acrylonitrile in toluene by H-ZSM-5 (26): Acrylonitrile/toluene kinetic selectivity factor as a function of number of acrylonitrile molecules/unit cell.

where E_{x_i} is the equivalent fraction of component i in the x phase. Thus $Ez_{\mathrm{A}} = n_{\mathrm{A}}/(n_{\mathrm{A}} + n_{\mathrm{Tol}})$; n_{A} is the moles of A (acrylonitrile) per unit volume in the zeolite phase. The kinetic selectivity factor, used here, has the same mathematical form. At breakthrough the kinetic selectivity factor for acrylonitrile/toluene is 16,200, where the acrylonitrile concentration in solution is 0.002 wt% and there are 3.2 molecules of acrylonitrile adsorbed per unit cell of the zeolite. Alpha drops off to 510 at an acrylonitrile concentration of 0.22 wt% and 7 molecules of acrylonitrile per unit cell. Note that at breakthrough and at the end of this experiment, the toluene to acrylonitrile molar ratios in solution are 31,000 and 265 respectively, indicative of very high selectivity for acrylonitrile over toluene. Prior to breakthrough the observed solution acrylonitrile concentration is zero, making this factor indeterminate.

In the acrylonitrile/toluene/H-ZSM-5 system, the estimated loading of toluene shows a leveling off at 4 toluene molecules per unit cell (Fig. 5). In the calculation of the number of toluene molecules per unit cell, acrylontrile was assumed to replace toluene on a volumetric basis using toluene adsorption volume and liquid density for acrylonitrile. The number 4 is a crystallographically significant value and earlier work (Olson et al., 1981; Stach et al., 1984) has shown that molecules similar to toluene, e.g., p-xylene and benzene, show preferences for packing four molecules per unit cell (and at higher pressures, 8 per unit cell). In view of the smaller size and different shape of the acrylonitrile molecule it is not surprising that its loading

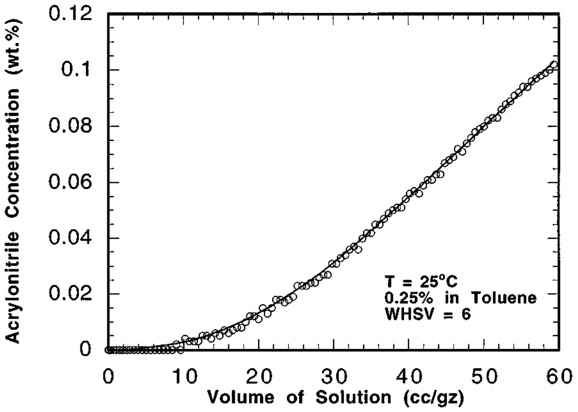

Figure 8. Adsorption of 0.25 wt% acrylonitrile in toluene by Na-X: Breakthrough curve.

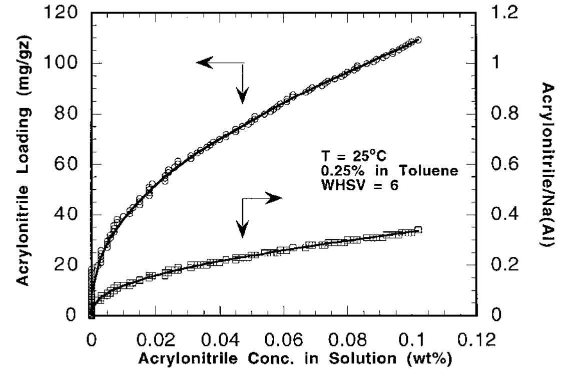

Figure 10. Adsorption of 0.25 wt% acrylonitrile in toluene by Na-X: Loading of acrylonitrile in the zeolite, expressed as mg/gz and as molecules of acrylonitrile/acid site, as a function of acrylonitrile concentration in solution.

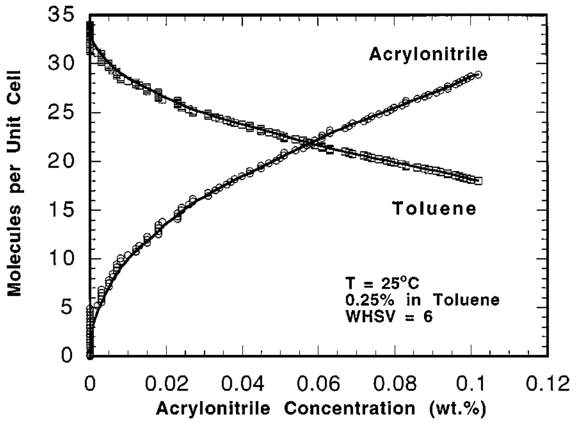

Figure 9. Adsorption of 0.25 wt% acrylonitrile in toluene by Na-X: Number of molecules of acrylonitrile and toluene per unit as a function of acrylonitrile concentration in solution.

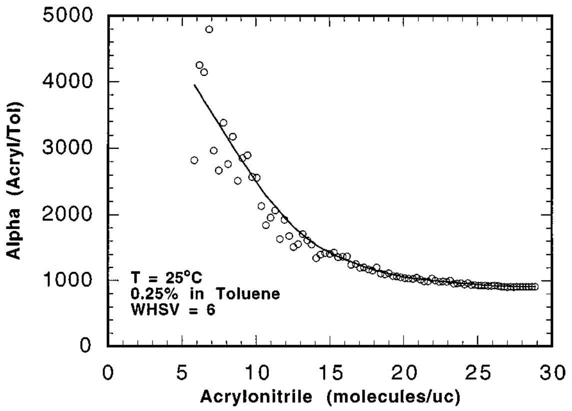

Figure 11. Adsorption of 0.25 wt% acrylonitrile in toluene by Na-X: Acrylonitrile/toluene kinetic selectivity factor as a function of number of molecules of acrylonitrile/unit cell.

does not appear to show geometric, structure specific loading numbers.

The adsorption of acrylonitrile on Na-X is shown in Figs. 8–11. As seen in Fig. 8, Na-X has a very high capacity. The saturation is not reached even up to 65 cm^3 of feed per gram of zeolite. Breakthrough occurs at 5 molecules of acrylonitrile per unit cell (Fig. 9) and at an acrylonitrile to sodium ion ratio of 0.05 (Fig. 10). The breakthrough volume is a little lower than that observed with H-ZSM-5 (26) (Fig. 8).

With H-MCM-22 the results are very similar to those obtained with H-ZSM-5 and hence the plots are not included. Table 2 compares the results obtained with different zeolites at both experimental temperatures. Increasing the temperature from 25–75°C has little effect on the breakthrough volumes but, beyond the breakthrough point, slightly lower loadings are achieved.

Acetonitrile. Results for the removal of acetonitrile from toluene are very similar to those shown for acrylonitrile and hence will not be discussed in detail. The breakthrough curve for the removal of acetonitrile from toluene using H-ZSM-5 (26) is consistent with the equilibrium experiment. As shown in the Fig. 12, the breakthrough predicted from the equilibrium experiment is very close to the observed breakthrough.

A comparison of the results obtained with different zeolites, at 25 and 75°C are presented in Table 3. Increasing the temperature from 25–75°C results in a small but measurable decrease in acetonitrile loading

Table 2. Comparison of continuous flow test results, with 0.25% acrylonitrile in toluene feed.

	Breakthrough volume (cm^3/gz)			Breakthrough loading (mg/gz)		Maximum loading (mg/gz)	
Zeolite	25°C	75°C	Predicted[a]	25°C	75°C	25°C	75°C
H-ZSM-5 (26)	13.4	12.3		29.1	26.5	64.4	53.9
H-MCM-22 (26)	11.6	12.8	11.5	25	27.6	56.8	53.8
Na-X (2.7)	9.7	9.83		20.9	21.3	108.4[a]	105[b]

[a] Breakthrough volumes predicted from the equilibrium experiment. There is uncertainty in these numbers because of a limited number of data points in the low concentration region.

[b] These are the loadings corresponding to 0.1% acrylonitrile concentration in effluent solution (the 0.25% acrylonitrile concentration was not reached within the duration of the experiment).

Table 3. Comparison of continuous flow test results, with 0.25% acetonitrile in toluene feed.

	Breakthrough volume (cm^3/gz)			Breakthrough loading (mg/gz)		Maximum loading (mg/gz)	
Zeolite	25°C	75°C	Predicted[a]	25°C	75°C	25°C	75°C
H-ZSM-5 (26)	11.3	13.6	10.8	24.3	29.3	50.2	43.7
H-MCM-22 (26)	13.2	11.6	11.8	28.5	25	51.7	44.5

[a] Breakthrough volumes predicted from the equilibrium experiment. There is uncertainty in these numbers because of a limited number of data points in the low concentration region.

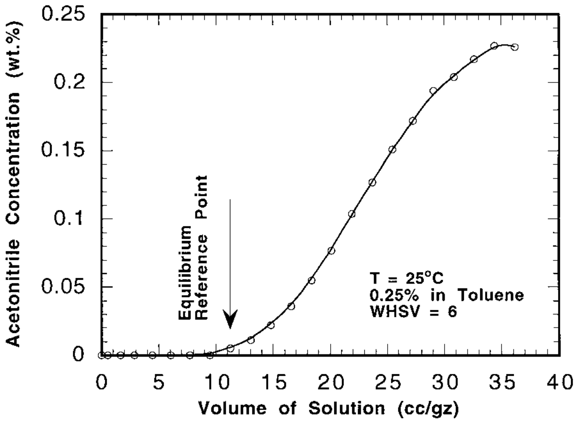

Figure 12. Adsorption of 0.25 wt% acetonitrile in toluene by H-ZSM-5 (26): Breakthrough curve.

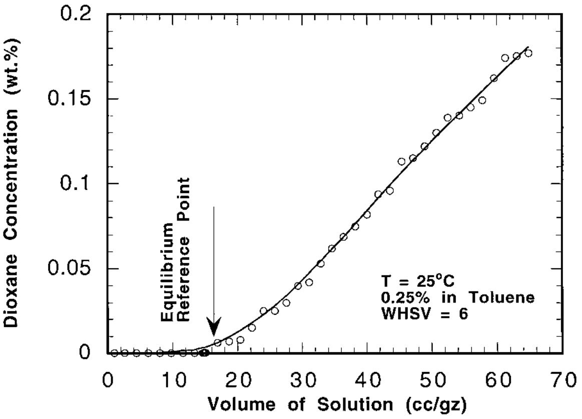

Figure 13. Adsorption of 0.25 wt% dioxane in toluene by H-ZSM-5 (26): Breakthrough curve.

just as increasing temperature decreases loading in single component gas phase adsorption experiments.

Dioxane. The results for the continuous flow test with H-ZSM-5 (26) at 25°C are presented in Figs. 13–16. Dioxane shows breakthrough at 0.42 molecules per H(Al) (Fig. 15). If dioxane acts as a dibasic molecule with respect to protons then 0.5 would be the equivalence point; if it acts as a monobasic molecule then the equivalence point would be 1.0. Fig. 13 shows that the predicted and the observed breakthrough volumes are almost the same. In the calculation of the number of toluene molecules per unit cell (Fig. 14), because of their similar sizes, dioxane was assumed to replace toluene on a one for one molecular basis. Again, the plots for results obtained with H-MCM-22 have not been included because they are very similar to those for H-ZSM-5 (26).

Results from the continuous flow tests using other zeolites have been presented in Table 4. Higher temperature gives lower loadings beyond the breakthrough point.

Table 4. Comparison of continuous flow test results, with 0.25% dioxane in toluene feed.

	Breakthrough volume (cm^3/gz)			Breakthrough loading (mg/gz)		Maximum loading (mg/gz)	
Zeolite	25°C	75°C	Predicted[a]	25°C	75°C	25°C	75°C
H-ZSM-5 (26)	16.9	16.9	16.2	36.5	36.5	102.6	83.2
H-MCM-22 (26)	15.7	15.2	14	34	32.9	90.8	71.5

[a] Breakthrough volumes predicted from the equilibrium experiment. There is uncertainty in these numbers because of a limited number of data points in the low concentration region.

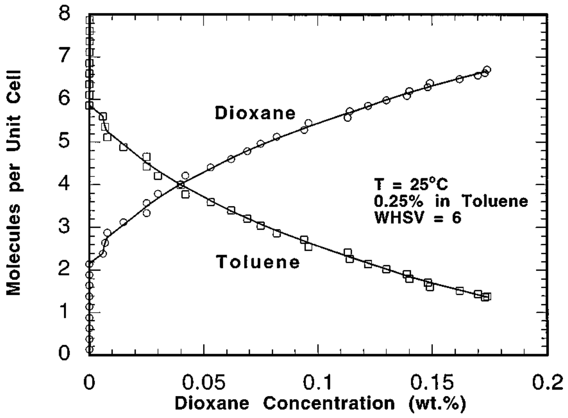

Figure 14. Adsorption of 0.25 wt% dioxane in toluene by H-ZSM-5 (26): Number of molecules of dioxane and toluene per unit cell as a function of dioxane concentration in solution.

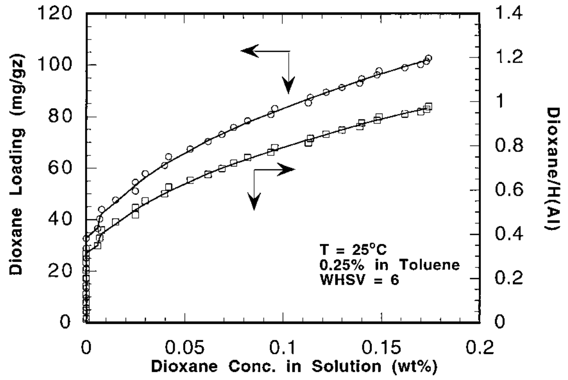

Figure 15. Adsorption of 0.25 wt% dioxane in toluene by H-ZSM-5 (26): Loading of dioxane in the zeolite, expressed as mg/gz and as molecules of dioxane/acid site, as a function of dioxane concentration in solution.

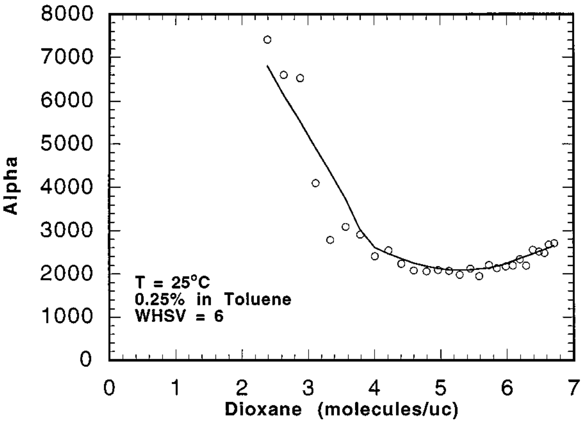

Figure 16. Adsorption of 0.25 wt% dioxane in toluene by H-ZSM-5 (26): Dioxane/toluene kinetic selectivity factor as a function of the number of dioxane molecules/unit cell.

Conclusions

H-ZSM-5, H-MCM-22 and Na-X are effective in removing acetonitrile, acrylonitrile and dioxane from toluene to a concentration level down to less than 20 ppm (detection limit). The results obtained with the equilibrium, batch experiments are consistent with those obtained from the continuous flow breakthrough experiments. The high aluminum content Na-X is a standout. It shows high selectivity as well as capacity. H-ZSM-5 and H-MCM-22 show higher selectivity but have a lower capacity. Also, increasing temperatures from 25–75°C had no detectable effect on breakthrough volume while the lower temperature, 25°C, shows somewhat higher adsorption capacity and selectivity following breakthrough. The continuous flow technique is a highly effective and versatile method to measure adsorbent performance and adsorption isotherms.

Further work involving investigation of other high alumina zeolites such as H-Mordenite is underway. Study of the fundamentals of the adsorption process (effect of cation type and concentration, and structural factors), evaluation of diffusional restrictions (the effect of WHSV on removal), adsorption at higher temperatures, and the adsorbent effectiveness from more dilute solutions, are among the proposed future work.

Acknowledgments

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