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Adsorptive Separations Using Zeolites: Separation of Substituted Anilines

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ABSTRACT

Separation of *N*-alkyl-substituted anilines by selective sorption on zeolites is investigated. The effects of solvent and cations on the adsorption constants are studied. Steric hindrance of alkyl groups on nitrogen affects the adsorption of anilines on zeolites.

Key Words. Substituted anilines; Zeolites; Separation; Effect of cations; Surface excess

INTRODUCTION

N-Methylation of aniline gives a mixture of *N*-methylaniline (NMA) and *N*,*N*-dimethylaniline (DMA) along with the unreacted aniline. These are important intermediates in the dye, pharmaceutical, and rubber industries. Although aniline can be removed by distillation, NMA and DMA are liquids with boiling points of 195.6 and 193°C, respectively, and they cannot be readily separated by fractional distillation.

The separation of NMA/DMA and aniline/NMA mixtures by adsorption using zeolites has been chosen for evaluation. The most important factor in improving the separation of NMA and DMA using zeolites as adsorbents is the interaction between the cations within the zeolite structure and the

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lone pair of electrons on the nitrogen atom and the pi electrons of the aromatic nucleus to form Lewis acid-base complexes superimposed on the diffusional selectivity.

The pores of the X zeolites, which are restricted by 12-membered oxygen rings, are larger, having a free aperture of about 7.4 Å. These zeolites are useful as adsorbents for relatively large molecules such as aromatics (1, 2). NaX as well as different cation-exchanged X zeolites, viz., KX, CaX, BaX, and encilite (ZSM-5 type with a pore size of 6 Å), were used in this study to explore the use of zeolites as selective adsorbents for the separation of *N*-alkylanilines.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials

The molecular sieves 13X in Na^+ form were supplied by S.D. Fine Chemicals, Bombay, in the form of pellets (1.5 mm × 2.5 mm). Powdered encilite (ZSM-5 type) crystals were supplied by United Catalyst India Limited, Bombay. *N*-Methylaniline with a purity of 98.0% was supplied by Sisco Research Laboratories Pvt, Ltd. Aniline and *N*,*N*-dimethylaniline (both with a purity of 99.0%), the *n*-heptane fraction from petroleum (LR grade), and toluene were supplied by S.D. Fine Chemicals, Bombay. *n*-Heptane was principally used as the solvent because it was not expected to adsorb significantly on the X-type zeolite in the presence of aromatic compounds.

Experimental Methods

The equilibrium adsorption experiments were conducted batchwise in a specially designed glass cell. Zeolite pellets of known weight were activated at 400°C for 7 hours in a furnace to remove any adsorbed materials and were then transferred to the cells.

Solutions of anilines in the organic phase with a concentration ranging from 2 to 20% were poured into different cells. The cells were then kept in a constant temperature water bath and periodically shaken. After 72 hours the solutions were analyzed for the residual concentration by using gas-liquid chromatography (GLC). A similar procedure was followed for the mixture of anilines. The NaX zeolite was exchanged with other cations such as K^+, Ca^{2+}, and Ba^{2+} by repeatedly treating the pellets with a boiling saturated solution of the chloride salt of the corresponding cation.

RESULTS AND DISCUSSION

Equilibrium Adsorption Studies

Figures 1 and 2 show the adsorption isotherms of aniline from heptane and toluene, respectively, at three different temperatures. It was difficult to conduct the adsorption studies of aniline from heptane because of the very low solubility in heptane (<2.5%) and because the higher volatility of heptane gave appreciable errors and poorer reproducibility. Nevertheless, the adsorption of aniline was greater from heptane than from toluene. Toluene, because of its aromatic structure, interferes with the adsorption of aniline on the zeolite and can also interact with aniline in the bulk liquid phase, thus effectively lowering the adsorption of aniline.

Figures 3 and 4 show the adsorption isotherms of *N*-methylaniline (NMA) and *N*,*N*-dimethylaniline (DMA) using heptane as a solvent. NMA and DMA both follow the Langmuir isotherm. The adsorption capacities and equilibrium constants obtained by fitting the experimental data with the Langmuir isotherm are reported in Tables 1 and 2 along with the heats of adsorption for anilines obtained using the Vant' Hoff relation. The higher heat of adsorption of aniline compared to those of NMA and DMA is an indication of the stronger adsorption of aniline. Figure 5 shows the

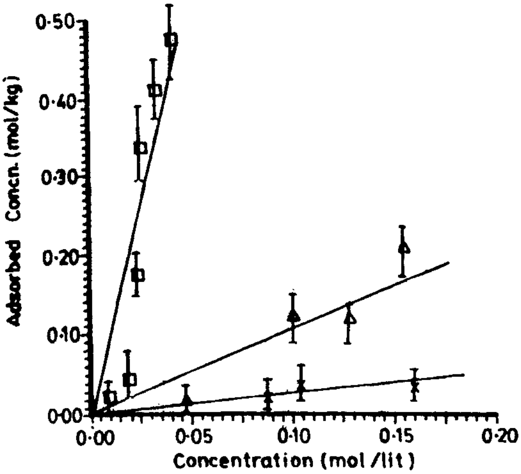

FIG. 1 Adsorption isotherms of aniline on NaX. Solvent = heptane; (□) 303 K, (△) 323 K, (×) 343 K.

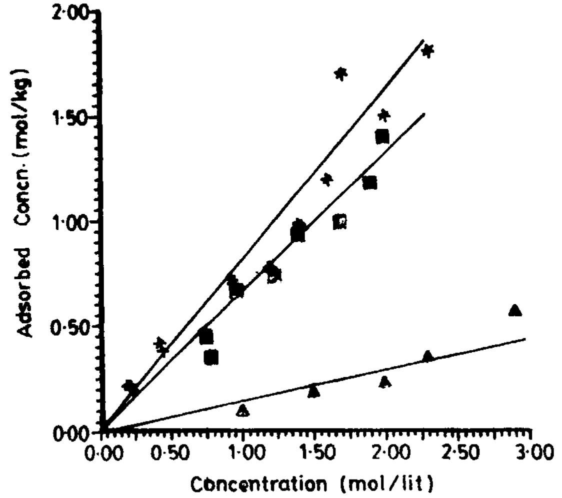

FIG. 2 Adsorption isotherm of aniline on NaX. Solvent = toluene; (*) 303 K, (■) 313 K, (▲) 323 K.

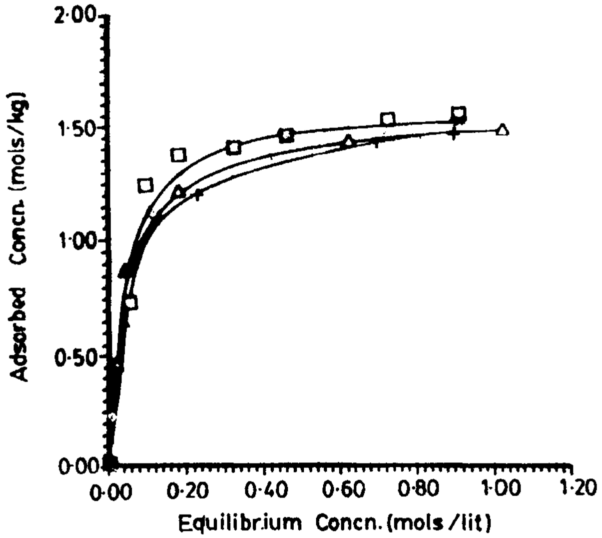

FIG. 3 Adsorption isotherms of NMA on NaX. Solvent = heptane; (□) 305 K, (△) 315 K, (+) 320 K.

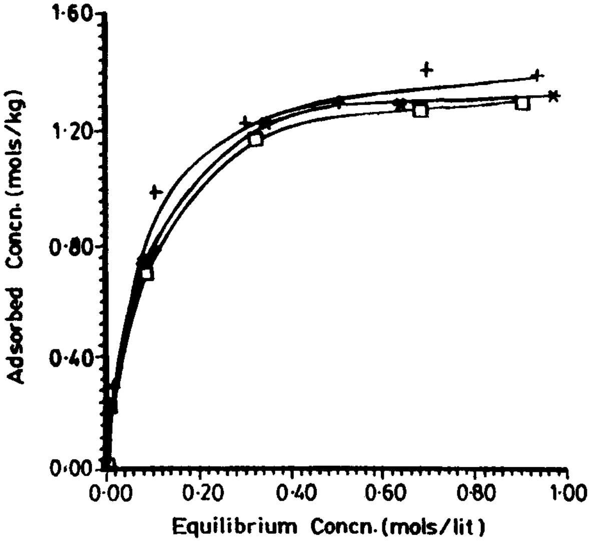

FIG. 4 Adsorption isotherms of DMA on NaX. Solvent = heptane; (□) 325 K, (∗) 315 K, (+) 305 K.

TABLE 1
Adsorption Equilibrium Constants of Anilines on NaX Zeolite

Component[a]	Temperature (K)	K (L/mol)	$-\Delta H$ (kcal/mol)
Aniline:			
From heptane	303	23.11 ± 10.9	
	323	1.31 ± 0.8	14.2
	343	0.88 ± 1.0	
From toluene	303	0.79	
	313	0.70	11.9
	323	0.23	
NMA:			
From heptane	303	35.36	
	315	25.25	6.67
	325	21.05	
From toluene	303	3.2	
DMA:			
From heptane	305	14.49	2.71
	315	12.82	
	325	11.0	
From toluene	303	0.15	

[a] Aniline isotherms are linear while NMA and DMA follow the Langmuir isotherm.

TABLE 2
Loading Capacities and Langmuir Equilibrium Constants of Different Zeolites[a]

Zeolite	Components	Loading capacity (mol/kg)	Equilibrium constant (L/mol)
NaX	NMA	1.54	33.56
	DMA	1.4	14.5
KX	NMA	1.47	19.7
	DMA	1.33	14.11
CaX	NMA	1.36	5.33
	DMA	1.17	4.58
BaX	NMA	0.67	6.87
	DMA	0.40	5.32
Encilite	NMA	1.16	7.17
	DMA	0.76	6.22

[a] Temperature: 303 K. Solvent: *n*-Heptane.

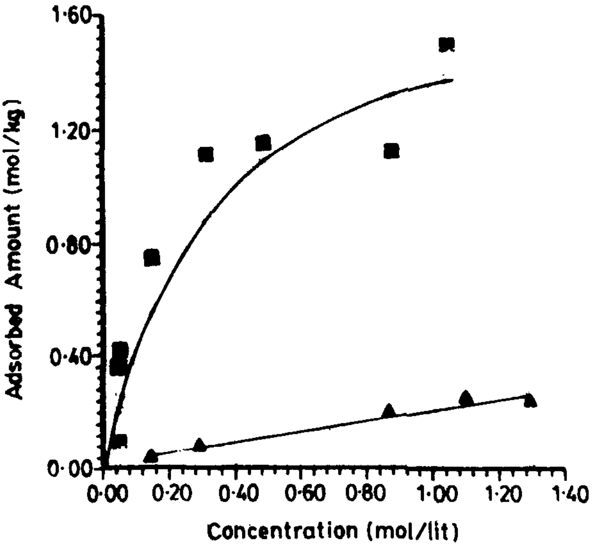

FIG. 5 Adsorption isotherms of NMA (■) and DMA (▲) on NaX. Solvent = toluene, 303 K.

adsorption of NMA and DMA using toluene as the solvent. As in the case of aniline, there is a substantial decrease in the adsorption constants; in the case of DMA the decrease in capacity is very high.

Anilines have a high affinity to adsorb on zeolites because of their tendency to form Lewis-type acid-base complexes with the cations within the zeolite structure. Both the lone pair of electrons on nitrogen and the pi electrons of the aromatic ring are capable of interacting with the cations. The lower capacities and lower adsorption constants of *N*-substituted anilines compared to those for aniline seem to result from steric hindrance to the nitrogen of the *N*-alkyl substituted anilines.

The equilibrium adsorption isotherms of NMA and DMA were obtained on different cation-exchanged X zeolites, viz., KX, CaX, BaX, and encilite. These isotherms are shown in Figs. 6 and 7 for NMA and DMA, respectively. In both cases NaX and KX have comparable adsorption

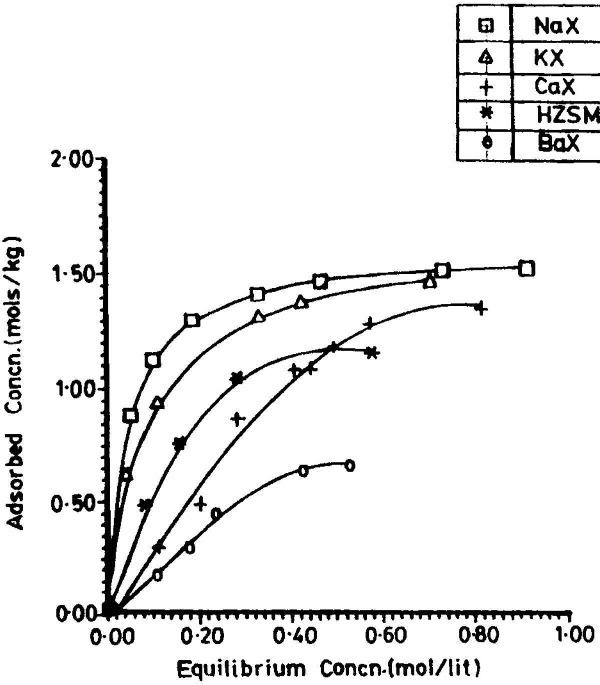

FIG. 6 Adsorption isotherms of NMA on different cation-exchanged zeolites. Solvent = heptane, 303 K.

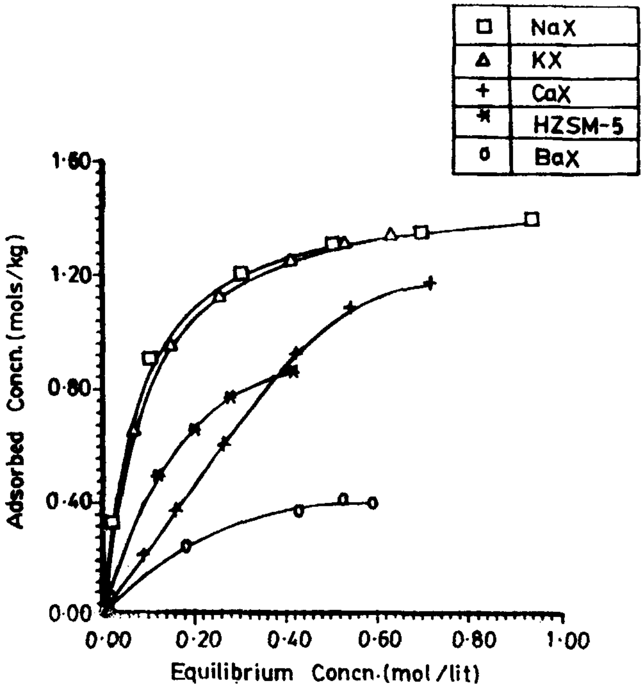

FIG. 7 Adsorption isotherm of DMA on different cation-exchanged zeolites. Solvent = heptane, 303 K.

constants and capacities. However, for divalent cation-exchanged zeolites, the adsorption constants as well as capacities were found to be lower than those for univalent cation-exchanged zeolite (Table 2).

For all the zeolites the saturation adsorption capacity for NMA is higher than that for DMA. The larger size of DMA molecules produces a steric restriction, and the two bulky —CH_3 groups on the nitrogen atom also reduce the Lewis acid-base interaction between the cations in the zeolite structures and the lone pair of electrons on the nitrogen atom of the aniline.

The capacity of zeolites can be estimated by considering a cavity-filling mechanism for adsorption, knowing that the volume of each cavity of the NaX zeolite is 822 $Å^3$ and knowing that there are 2.17×10^{20} cavities per gram (2). The estimated capacities for aniline, NMA, and DMA are 1.6, 1.64, and 1.41 mol/kg, respectively. Assuming a 15% reduction in capacity due to the presence of binder, the capacities for NMA and DMA on NaX would be expected to be 1.4 and 1.2 mol/kg, respectively. Since the experimental adsorption capacities are somewhat higher than the estimated values, it appears that the binder clay may also adsorb the anilines.

The larger K^+ cation compared to the Na^+ cation [sizes of Na^+ and K^+ are 1.96 and 2.66 Å, respectively (3)] is responsible for the lower saturation capacity of KX than that of NaX. The lower adsorption capacities of CaX and BaX can be explained by considering the replacement of two sodium ions by one divalent cation, thereby decreasing the number of cations in a cavity available to interact with the anilines. The saturation capacity of BaX is lower than CaX, primarily because of the larger size of the barium ion. [Sizes of Ca^{2+} and Ba^{2+} ions are 2.12 and 2.86 Å, respectively (3).] Again, a smaller pore size (6 Å) and less interaction of the zeolite structures with the adsorbate molecules due to a lower cationic charge of the zeolite structure are responsible for the lower adsorption capacity and equilibrium constant of encilite.

Separation of Mixtures of Alkylanilines

Knowing the selectivity of the zeolite toward the less-substituted aniline batch, experiments were conducted on the separation of aniline/NMA and NMA/DMA mixtures. For an ideal behavior in liquid and adsorbed phase, the experimental separation factor (α) is defined as

$$\alpha_{12} = \frac{x_1^s/x_2^s}{x_1^l/x_2^l} \tag{1}$$

where x is the mole fraction of the components 1 and 2 in the adsorbed (s) and liquid (l) phases. The mole fractions are given on a solvent-free basis. Component 1 is preferentially adsorbed on the zeolite. Figure 8 shows the variation of the separation factor for aniline/NMA mixtures as a function of the concentration of aniline. Aniline was preferentially adsorbed on the zeolites despite the higher adsorption constant of *N*-methylaniline. This is apparently caused by the higher diffusivity of aniline. If that is the case, the data may not reflect true equilibrium conditions. In both cases with heptane and toluene as solvent, separation was higher at lower concentrations of aniline in the mixture. However, with an increased concentration of aniline, the separation factor decreased for both solvents.

Adsorption from a binary mixture can be plotted as a composite isotherm in terms of surface excess as shown in Fig. 9 for mixtures of NMA and DMA with heptane as solvent. The surface excess (n^e) is defined as the difference between the amount of solute adsorbed and the hypothetical amount adsorbed when the composition of the adsorbed phase is equal to the composition of the bulk liquid phase (4). The surface excess thus

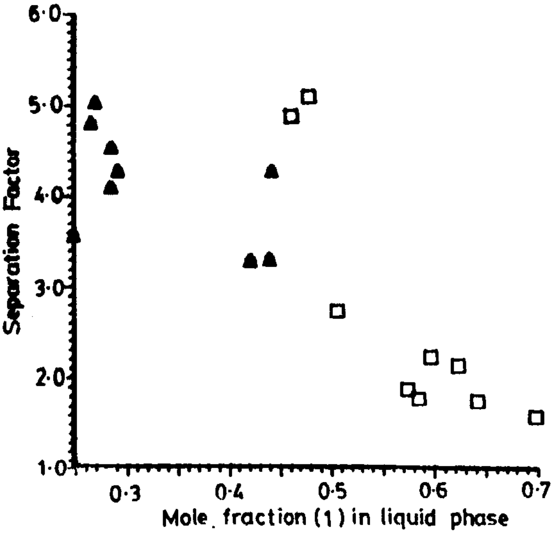

FIG. 8 Variation of separation factor with concentration of aniline in aniline (1)/NMA(2) mixtures at 303 K. Solvent: (▲) toluene, (□) heptane.

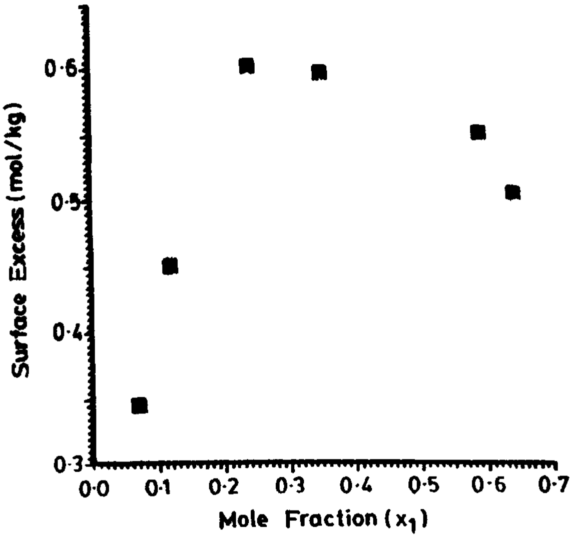

FIG. 9 Composite adsorption isotherm of NMA(1)/DMA(2) mixtures. Solvent = heptane, 303 K.

signifies the preferential sorption of the component. In terms of the experimental parameters, it can be obtained as

$$n_1^e = n^t(x_1^0 - x_1^1) \tag{2}$$

where n^t is the initial total moles in the mixture and the superscripts 0 and 1 indicate the initial and final concentrations of the component in the liquid phase, respectively. The surface excess composite isotherm (Fig. 9) shows the selective adsorption of NMA from its mixture with DMA. If the adsorption isotherm is of the Langmuir type, then the surface excess can also be analyzed by the Everett model (5).

$$\frac{x_1 x_2}{n_1^e} = \frac{x_1}{n_1^s} + \frac{1}{n_1^s(\alpha_{12} - 1)} \tag{3}$$

A plot of (x_1x_2/n_1^e) vs x_1 thus gives a straight line. The slope and intercept of the line can be used to estimate the separation factor (α_{12}). The separation factor evaluated at 32°C by means of the Everett model is 2.04, and the separation factor calculated as the ratio between the equilibrium constants of the Langmuir isotherms is 2.44. This agreement between the experimental separation factor evaluated by means of the Everett model and the calculated separation factor confirms the validity of the Langmuir isotherm for NMA and DMA mixtures.

CONCLUSIONS

Steric restrictions to the interaction between the zeolite active sites and anilines are responsible for the selective adsorption of the less-substituted aniline. The cation size and the charge also affect the extent of adsorption and the strength of interaction. Monovalent cations show higher adsorption capacities than do divalent cations, while increasing the size of the cation decreases the adsorption constant as well as the adsorption capacity of the zeolite.

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