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A MILD METHOD FOR EXTRACTING AMINES UNDER NEUTRAL CONDITIONS

Joanne M. Widom and Bruce Ganem*
Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, NY 14853

Summary: Copper (II) ion-exchanged zeolites are highly active reagents for selective complexation of amines in aqueous or organic solution.

Zeolites and other framework aluminosilicates have pores of molecular dimensions which make them widely useful in ion exchange reactions,[1] adsorption studies[1,2] and shape-selective catalysis.[3,4] Recently we needed to develop a method for anchoring complex macromolecules to the surface of an inorganic support via mono or polyamine functional groups. Although alkylammonium ions readily ion-exchange with Na or Ca-zeolites,[5] the process is too readily reversible to be of use. Copper(II), on the other hand, forms tight mono and polyamine coordination complexes. Furthermore, zeolite catalysts containing transition metal ions are easily prepared by simple exchange.[6] While Cu(II)-exchanged zeolite NaX catalyzes the decomposition of ethyl diazoacetate[7] and Cu(II)-ZSM-5 zeolites promote the decomposition of NO,[8] no one (to our knowledge) has used a Cu^{++}-zeolite for binding or extraction of soluble amines. We wish to report a simple protocol which may be particularly useful in small scale separations of amines from sensitive compounds where acid extraction is precluded.

Samples of Linde LZ-Y52 zeolite (Alfa-Ventron catalog #88767) were exchanged in saturated $CuSO_4$ as reported. [Theoretically, each gram of this zeolite could take up 3.2 mmol of $^+CuHSO_4$, thus setting an upper limit on the stoichiometry of amine sorption]. Weighed amounts of the resulting pale blue powders were stirred or vortexed for 15 min with solutions of pyridine, triethylamine or spermidine in the appropriate solvent. Samples were then either centrifuged or filtered through a 0.45µm Millipore filter and aliquots were assayed by UV-visible absorbance to determine the concentration of remaining soluble amine. Control experiments using the Na^+-form of the zeolite showed no absorption of these amines by the gel either in aqueous or organic solution. Results are given in the Table. Clearly, the method is more successful in extracting amines from water (Entries 1-3 and 6-10) than from ether solution. As expected, successive extraction with additional portions of zeolite (Entries 7-9) is most effective in removing triethylamine from aqueous solution. The triamine spermidine was most effectively adsorbed, the striking deep-blue color of the interstitial Cu(II)-zeolite-polyamine complex (λ_{max} = 582 nm) indicative of the bicyclic Cu^{++}-spermidine chelate.[9]

TABLE

RUN	AMINE (mmol)	SOLVENT (conc.)	CU-ZEOLITE (mg)		% AMINE BOUND
1	pyr (.062)	water (.025M)	40[a]		73
2	pyr (.062)	water (.025M)	100[b]		86
3	pyr (.124)	water (.041M)	100		83
4	pyr (.062)	ether (.025M)	40		61
5	pyr (.062)	ether (.012M)	40		33
6	Et_3N (.072)	water (.025M)	100		93
7	pyr (.062)	water (.048M)	100		78
8	----second extraction of Run 7 ------		100	total 7 + 8 =	94
9	------third extraction of Run 7-------		100	total 7 + 8 + 9 =	98
10	spermidine (.050)	water (.030M)	100		99

(a) Theoretical max = .128 mmol Cu(II); (b) Theoretical max = .320 mmol Cu(II).

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