February, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 585—590 (1981) 585

Studies on the Uptake of Some Complex Cations of Copper by Molecular Sieves 4A and 5A

S. S. Thantry, K. Veeramoni Iyer, and P. S. Ramanathan*

Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India

(Received September 22, 1979)

Studies on the uptake of Cu^{2+} and a few of its complex cations (*i.e.*, $[Cu(NH_3)_4]^{2+}$, $[Cu(en)]^{2+}$, $[Cu(en)_2]^{2+}$, $[Cu(pn)]^{2+}$, $[Cu(pn)_2]^{2+}$, and $[Cu(tea)]^{2+}$, where en, pn, and tea represent ethylenediamine, propylenediamine, and triethanolamine respectively) by molecular sieves 4A and 5A were undertaken using batch equilibration procedure. $[Cu(pn)]^{2+}$, $[Cu(en)_2]^{2+}$, $[Cu(pn)_2]^{2+}$, and $[Cu(tea)]^{2+}$ showed very little affinity for the zeolite phases, while the uptake of Cu^{2+} and $[Cu(en)]^{2+}$ was comparatively higher. $[Cu(NH_3)_4]^{2+}$ occupied a position in between these two sets. During the equilibration of $[Cu(en)]^{2+}$ and $[Cu(pn)]^{2+}$ some side reactions could be observed leading to the conclusion that the 1:1 complex species underwent disproportionation, generating Cu^{2+} and an equivalent amount of $[Cu(en)_2]^{2+}$ or $[Cu(pn)_2]^{2+}$. These conclusions drawn from the batch equilibration studies were confirmed by appropriate column experiments.

Ion exchange studies using zeolite exchangers of various types have been reviewed from time to time by different workers.[1-9] Scores of publications have appeared in the literature dealing with the studies on the uptake of simple cations by molecular sieves 4A(MS4). Similar studies on molecular sieves 5A-(MS5) are comparatively fewer in number. Recently Schoonheydt and coworkers[10] prepared complexes of ammonia and ethylenediamine with Cu^{2+} on zeolite A and conducted EPR and reflectance spectral studies of the various complexes. The existing literature does not appear to contain any other information on the uptake of complex cations by MS4 and MS5. It was, therefore, decided to undertake a systematic study of the uptake of a few complex cations** of Cu^{2+} (*i.e.*, $[Cu(NH_3)_4]^{2+}$, $[Cu(en)]^{2+}$, $[Cu(pn)]^{2+}$, $[Cu(en)_2]^{2+}$, $[Cu(tea)]^{2+}$, and $[Cu(pn)_2]^{2+}$) by MS4 and MS5. Studies were also carried out with Cu^{2+} for comparison.

Experimental

Chemical analyses of Anasorb MS4 and MS5 samples (40—60 mesh, supplied by Analabs Inc., U.S.A.) were carried out, following procedures given in standard books. Loading studies were carried out by the batch equilibration procedure. All reagents/chemicals used were of Analytical reagent or C.P. grade.

For studying the uptake as a function of time, 20 ml of solutions of Cu^{2+} (0.1 M), $[Cu(en)]^{2+}$ (0.05 M), $[Cu(en)_2]^{2+}$ (0.1 M), $[Cu(pn)]^{2+}$ (0.01 M), $[Cu(pn)_2]^{2+}$ (0.05 M), $[Cu(tea)]^{2+}$ (0.1 M), and $[Cu(NH_3)_4]^{2+}$ (0.1 M) were equilibrated with 0.5 g of the sieve at 30 °C for the prescribed period. The ligand to metal ratio maintained in the last 6 cases were 1, 2, 1, 2, 6, and 60 respectively. The pH values of the solutions of the first six cations used for equilibration were 2.0, 5.0, 7.0, 5.5, 7.0, and 8.0 in that order.

The quantitative and exclusive formation of the complex cation of interest, under the conditions specified above, was confirmed by comparing the spectra of their solutions with those reported in the literature.

To arrive at the '*K*' values (mmol of M^{n+} per g of the sieve/mmol of M^{n+} per ml of the solution, at any contact time '*t*'), the concentrations of the cation of interest in the original solution and in the external solution left out after equilibration were estimated spectrophotometrically. Cu^{2+} was estimated after converting it to $[Cu(NH_3)_4]^{2+}$ by adding aqueous ammonia in excess (6 M) and measuring the absorbance(E) at 600 nm(λ_{max}). In the case of the other complex cationic species (*i.e.*, $[Cu(en)]^{2+}$, $[Cu(pn)]^{2+}$ *etc.*) the 'E' values were measured at the corresponding λ_{max} (after appropriate dilution to bring the concentration within the range of the corresponding calibration graph). The concentrations were then computed. In a few cases the amount of Na^+(or Ca^{2+}) displaced from the molecular sieve was also estimated to understand the extent of uptake by ion exchange. These estimations were carried out after removing the copper from the solutions by electrolysis in the Fischer Electroanalyser.

Equilibration studies were also carried out to understand the influence of concentration on the uptake. In these cases, solutions containing different concentrations of the cation of interest were equilibrated for 24 h. The '*K*' values were then calculated as described in the earlier paragraph.

Results and Discussion

Chemical Analysis of the MS4 and MS5 Specimens. The number of AlO_2, Na, and H_2O species per unit cell of the MS4(computed from the results of chemical analysis, on the assumption that the SiO_2 content corresponds exactly to 12 SiO_2 groups) worked out to 11.60, 11.00, and 20.80 respectively. The corresponding figures for MS5 were 12.82, 1.66, and 21.52. In this case, the number for Ca was 4.34.

The results of chemical analysis speak against the possible presence of occluded $NaAlO_2$ in the MS4. The Na, H_2O, and AlO_2 figures are all smaller than those expected from the generally accepted unit cell formula ($Na_{12}(AlO_2)_{12}(SiO_2)_{12}\cdot 27H_2O$). In the MS5 specimen, there is (i) a marginal decrease in the number of Ca atoms and (ii) a significant decrease and increase in the Na and AlO_2 contents respectively(in comparison to the unit cell formula of MS4 in which 75% Na^+ has been replaced by Ca^{2+}). The results provide a measure of free Al_2O_3 and SiO_2 in the zeolite samples.

Equilibration Studies. The pH of the equilibrated Cu^{2+} solution increased from 2.0 to around 4.0 during equilibration.*** The uptake of Cu^{2+} was so slow

---

** In the subsequent sections, the symbols 'en', 'pn', and 'tea' will be used to represent ethylenediamine, propylenediamine, and triethanolamine respectively.

*** In this case, an undesirable but unavoidable side-effect of the comparatively higher acidity maintained (to keep the Cu^{2+} in solution) is the structural breakdown of a small fraction of the zeolite matrix.

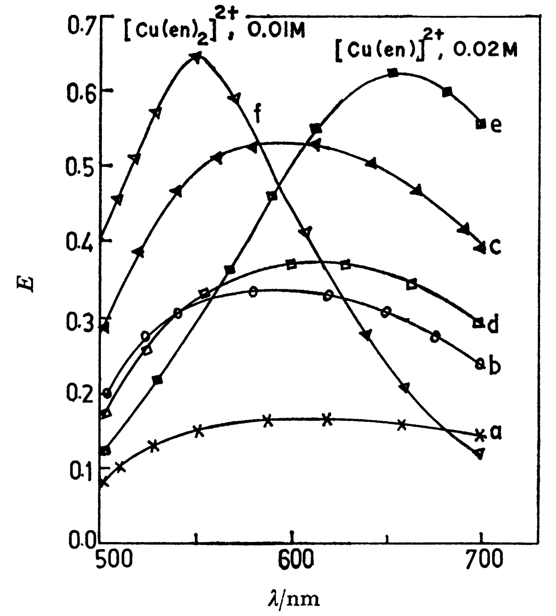

Fig. 1. Spectra of $[Cu(en)]^{2+}$, $[Cu(en)_2]^{2+}$, and the equilibrated solutions of $[Cu(en)]^{2+}$—MS4.
Concentration of $[Cu(en)]^{2+}$ before equilibration= 0.02, 0.03, 0.04, and 0.05 M for a—d.
Dilution: 2 times for d.

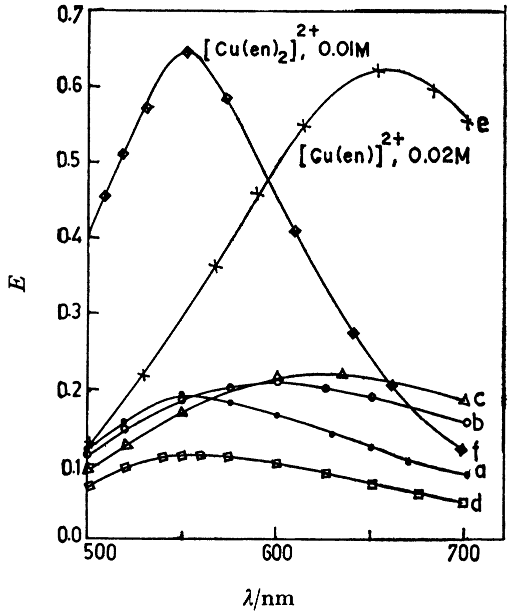

Fig. 2. Spectra of i) Equilibrated solutions, ii) $[Cu(en)]^{2+}$, and iii) $[Cu(en)_2]^{2+}$—MS5.
a=0.01 M, b=0.03 M, c=0.05 M, d=effluent from column experiment.
Dilution b: 3, c: 5, d: 10.

that final equilibrium was attained only after about 48 h. The 'K' values observed in the case of MS4 and MS5, after this time interval, were 42 and 27 respectively(when the initial concentration of Cu^{2+} solution employed was 0.1 M).

Analysis of Na^+ released during equilibration revealed that the uptake of Cu^{2+} by MS4 was predominantly by ion exchange. In the case of MS5, however, the Ca^{2+} released was only around 30% of the amount equivalent to the total Cu^{2+} taken up.

When 20 ml of water at pH 2.0 were equilibrated with 0.5 g of the sieves, the Na^+ and Ca^{2+} released were found to be 4 mg and 0.8 mg respectively in the two cases.

Spectral studies of Cu^{2+}-aqueous ammonia mixtures revealed that the formation of $[Cu(NH_3)_4]^{2+}$ was complete only when $C_{NH_3}/C_{Cu} \geq 40$(when $C_{Cu}=0.1$ M). 'K' values for this cation were lower (≈ 5 for a solution of concentration of 0.1 M) than those found for Cu^{2+}. Only marginal increases in 'K' were observed beyond 2 h. The much faster kinetics suggest that the uptake is probably restricted to the external surfaces which are in direct contact with the solution.

Increase in the concentration of aqueous ammonia (to 60 and 80 times the concentration of Cu^{2+}) produced only a marginal change in the uptake of $[Cu(NH_3)_4]^{2+}$ species. The uptake of NH_4^+ by ion exchange was then investigated in each case by equilibrating aqueous ammonia solution of the same concentration, but in the absence of Cu^{2+}. While 8 M aqueous ammonia released about 15 mg of Na^+ from MS4, the release of Ca^{2+} from MS5 was insignificant($\approx$0.2%).

The 'K' values found for $[Cu(en)_2]^{2+}$, $[Cu(pn)_2]^{2+}$, and $[Cu(tea)]^{2+}$ were extremely small($\approx$1). The uptake was also very quick, suggesting thereby, that the process involved was probably pure physical adsorption. It appears that the sizes of these ions are unfavourable for entry into the pores of the zeolites. On this basis it can be qualitatively concluded that the size of each of these three complex cations (in the hydrated form) may be greater than 5Å, the pore dimension of MS5.

The pH of $[Cu(en)]^{2+}$ solution used for equilibration was adjusted to 5.0 as the complex forms quantitatively when the reactants are mixed in stoichiometric amounts at this acidity. The pH of the external solution rose to around 6.0 after equilibration. In this case the exchange was slow(as in the case of Cu^{2+}). 0.01 M solution, when equilibrated with MS4 for 24 h became practically colourless, indicating a nearly quantitative uptake in this concentration range. The uptake was, however, not quantitative when more concentrated solutions($\approx$0.02 M and above) were employed for equilibration. Moreover, the post-equilibration spectra of these concentrated solutions were not superimposable on that of the 1:1 complex. The λ_{max} shifted from 650 nm(expected for the 1:1 complex) to a lower value. The extent of shift depended on the time of equilibration as well as the concentration of the solution used. Some typical spectra are shown in Fig. 1. The results obtained with MS5 were of the same nature except for the fact that the uptake was not quantitative at low concentrations(*i.e.*, $\approx$0.01 M). Some typical spectra obtained in the case of MS5 are shown in Fig. 2.

A careful scrutiny of the spectra of the external solutions indicated the possibility of the presence of varying amounts of the higher complex(1:2, with λ_{max} at 550 nm) in them. As both 1:1 and 1:2 complexes are known to be very stable under the experimental conditions employed, and Cu^{2+} cannot remain in/solution in the weakly acidic conditions

Table 1. Concentrations of cations in the adsorbent and external solution

Solution used for equilibration: 20 ml of $[Cu(en)]^{2+}$ at pH 5.0

λ values chosen for spectrophotometric analyses of binary mixtures: 550 and 650 nm

$(\varepsilon_1)_{550}=16$; $(\varepsilon_2)_{550}=64$; $(\varepsilon_1)_{650}=32$; $(\varepsilon_2)_{650}=24$

S. No.	Concentration of $[Cu(en)]^{2+}$ used for equilibration $\times 10^3$/M	Concentration in the external solution at equilibrium $\times 10^3$/M		Millimoles of cation taken up by 0.5 g of the sieve $\times 10^2$	
		$[Cu(en)]^{2+}$	$[Cu(en)_2]^{2+}$	Cu^{2+}	$[Cu(en)]^{2+}$
A. MS4					
1	10.0	N.D.[a)]	N.D.[a)]	N.D.[a)]	20.0
2	20.0	4.25	1.4	2.8	25.9
3	30.0	7.1	3.3	6.6	32.6
4	40.0	11.7	4.9	9.8	37.0
5	50.0	17.7	5.9	11.8	41.0
B. MS5					
6	10.0	2.1	2.45	4.9	6.0
7	20.0	8.0	3.55	7.1	9.8
8	30.0	13.8	5.2	10.4	11.6
9	40.0	21.7	5.65	11.3	14.0
10	50.0	29.1	6.0	12.0	18.0

a) N.D. means not detectable.

maintained, the possibility of the presence of free Cu^{2+} in the external solutions was ruled out. Taking the external solutions (equilibrated for 24 h) as mixtures of 1:1 and 1:2 complexes, the individual concentrations(C_1 and C_2)/of the two complexes were calculated by solving simultaneous equations. The results obtained are given in Table 1.

The above-mentioned observations may be interpreted as shown below: It appears that the MS4 phase induces the dissociation of $[Cu(en)]^{2+}$ and takes up the Cu^{2+} generated *in situ*(along with $[Cu(en)]^{2+}$, for which also MS4, shows comparable affinity). The 'en' generated by the above process combines with $[Cu(en)]^{2+}$ present in the external solution, giving rise to an equivalent amount of $[Cu(en)_2]^{2+}$. When dilute solutions($\approx$0.01 M) are employed, the uptake of all the three cationic species occurs practically quantitatively, making the external solution practically colourless. However, with increase in concentration of the external solution, a comparatively larger concentration of the 1:2 complex is formed. As it is a strong complex and it has very little affinity for the zeolite phase, the post-equilibration solution phase gradually becomes a mixture of $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$. The side equilibria represented by Eqs. 1—3 summarise the above-mentioned points.

$$[Cu(en)]^{2+} \rightleftharpoons Cu^{2+} + en \qquad (1)$$

$$Cu^{2+} + 2NaZ \rightleftharpoons CuZ_2 + 2Na^+ \qquad (2)$$

$$[Cu(en)]^{2+} + en \longrightarrow [Cu(en)_2]^{2+} \qquad (3)$$

In Eq. 2, Z stands for the zeolite anion.

In the case of MS5, the results(Table 1) were qualitatively of the same type(*i.e.*, as described above in the case of MS4). The notable differences were: (i) The uptake was not quantitative in low concentrations. (ii) The quantity of $[Cu(en)]^{2+}$ taken up was smaller and the uptake of Cu^{2+} was greater than those found in the case of MS4. (iii) The total uptake (as Cu^{2+} and $[Cu(en)]^{2+}$) was, however, much lower. Equation 2 takes the following form in this case, while (1) and (3) continue to remain applicable.

$$0.5Cu^{2+} + Ca_{0.5}Z \rightleftharpoons Cu_{0.5}Z + 0.5Ca^{2+} \qquad (4)$$

In this context it is worth mentioning that a significant part(>60%) of Cu^{2+} and $[Cu(en)]^{2+}$ going to the MS5 phase is by physical adsorption. Irrespective of whether the uptake is by ion exchange or by physical adsorption, the arguments presented earlier concerning the apparent disproportionation of $[Cu(en)]^{2+}$ (giving Cu^{2+} and an equivalent amount of $[Cu(en)_2]^{2+}$) will hold good.

To understand the nature of the results obtained in a column experiment, a MS4 column(5 g packed in a column of i.d. 1.2 cm) was fed with 100 ml of $[Cu(en)]^{2+}$ solution of concentration 0.05 M(pH=5.0). The flow rate was 0.5 ml per min. The effluent solution was colourless. When 50 ml of 0.05 M $[Cu(en)]^{2+}$ solution were passed through a column containing 2 g of MS4, the effluent contained about 5% of the total copper as the 1:2 complex, while the effluent was colourless when 25 ml of 0.01 M solution were passed through the same column. All these observations point out that the disproportionation reaction does take place in the column experiment as well. When dilute solutions are employed, copper is not found in the effluent as $[Cu(en)]^{2+}$, as well as the small amount of Cu^{2+} and $[Cu(en)_2]^{2+}$, formed by the disproportionation reaction, are all retained by the column. On increasing the concentration, a small amount of the 1:2 complex leaks out as its affinity for the adsorbent is low.

In the case of MS5, the effluent contained around 50% of the copper as a mixture of 1:1 and 1:2 complexes(in approximately equal concentrations) when 20 ml of 0.05 M $[Cu(en)]^{2+}$ solution at pH 5.0 were passed through a column containing 2 g of the sieve. The higher extent of disproportionation and the comparatively lower affinities for the cations seem

TABLE 2. CONCENTRATIONS OF CATIONS IN THE ADSORBENT AND EXTERNAL SOLUTION

Solution used for equilibration: 20 ml of $[Cu(pn)]^{2+}$ at pH 5.5

λ values chosen for spectrophotometric analyses of binary mixtures: 550 and 650 nm

$(\varepsilon_1)_{550}=16$; $(\varepsilon_2)_{550}=66$; $(\varepsilon_1)_{650}=33$; $(\varepsilon_2)_{650}=28$

S. No.	Concentration of $[Cu(pn)]^{2+}$ used for equilibration $\times 10^3$/M	Concentration in the external solution at equilibrium $\times 10^3$/M		Millimoles of Cu^{2+} taken up by 0.5 g of the sieve $\times 10^2$
		$[Cu(pn)]^{2+}$	$[Cu(pn)_2]^{2+}$	
A. MS4				
1	5.0	N.D.[a]	1.95	3.90
2	10.0	0.66	4.25	8.50
3	15.0	1.55	6.37	12.74
4	20.0	3.17	8.02	16.04
B. MS5				
5	5.0	0.4	2.3	4.6
6	10.0	1.3	4.3	8.6
7	15.0	2.8	6.0	12.0
8	20.0	6.5	6.7	13.4

[a] N.D. means not detectable. The calculations reveal that 0.022, 0.017, 0.014, and 0.016 millimoles of Cu-pn complex species go to the MS4 phase in the four cases respectively. The uptake is negligible in the case of MS5.

to be responsible for this situation.

In view of the above-mentioned side reactions, 'K' values, as defined earlier, cannot be given for $[Cu(en)]^{2+}$ uptake by MS4 and MS5. One can, however, arrive at 'K_{av}' and 'K^*' values, defined as shown below:

$$K_{av}=\frac{\text{mmol of Cu}^{2+}\text{ in all forms per g of sieve}}{\text{mmol of Cu}^{2+}\text{ in all forms per ml of the solution}}$$

$$K^*=\frac{\text{mmol of }[\text{Cu(en)}]^{2+}\text{ per g of sieve}}{\text{mmol of }[\text{Cu(en)}]^{2+}\text{ per ml of the solution}}.$$

These values are tabulated in Table 3.

From the earlier sections it becomes obvious that Cu^{2+} and $[Cu(en)]^{2+}$ exhibit good affinity for the zeolite phase. Uptake of these preferred cationic species, with the consequential breakdown of the less favoured $[Cu(en)_2]^{2+}$, is not observed because of the very high stability of the 1:2 complex.

In this context it is worth pointing out that Schoonheydt *et al.*[10] recently reported the preparation of the following complexes (by gas phase adsorption) on the A type zeolite surface:

(i) $[Cu(NH_3)_4]^{2+}$ and a small amount of tetrahedrally coordinated Cu^{2+} ions by adsorption of NH_3 on a dehydrated CuA zeolite,

(ii) $[Cu(en)]^{2+}$ by the adsorption of 'en' on a dehydrated CuA zeolite and

(iii) $[Cu(en)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ by adsorption of 'en' on CuA in the presence of water.

They also found that $[Cu(en)]^{2+}$ could be loaded on NaA by ion exchange from aqueous solution, but the bis-complex could not be loaded in this way. The impossibility of loading the bis-complex has been attributed by them to the fact that its dimensions (0.47 × 0.77 nm) exceed the free diameter of the 8-membered windows (≈0.44 nm). Another factor was the instability of the bis-complex in the supercage of zeolite A. They found that the bis-complex could be synthesised *in situ* by equilibrating either the Cu^{2+} or the mono-complex loaded zeolite with excess of 'en'. They also observed the uptake of both Cu^{2+} and $[Cu(en)]^{2+}$ by the zeolite when the solution of the latter was equilibrated with NaA at pH 6. The above-mentioned conclusions were drawn by them from EPR and reflectance spectral studies of the various complex loaded zeolites. Our findings reported in the earlier paragraphs have been obtained by the spectrophotometric investigations of the solutions prior to and after equilibration with the zeolite. They are thus complementary to those reported by Schoonheydt *et al.*[10]

Results of equilibration studies using $[Cu(pn)]^{2+}$ were somewhat similar to those described in the case of $[Cu(en)]^{2+}$. In this case also computations were made to arrive at the distribution of the different cationic species between the aqueous and zeolite phases. The results are tabulated in Table 2. As discussed in the case of $[Cu(en)]^{2+}$ the affinity of Cu^{2+} for the zeolite phase stimulates the dissociation of $[Cu(pn)]^{2+}$ also. Essentially, the zeolite phase gets loaded with Cu^{2+}, leaving behind a mixture of $[Cu(pn)]^{2+}$ and $[Cu(pn)_2]^{2+}$ (formed by the combination of $[Cu(pn)]^{2+}$ and free 'pn' released during the migration of Cu^{2+} to the zeolite phase) in the external solution. In other words, the side equilibria of the type represented by Eqs. 1—4 apply for the case of $[Cu(pn)]^{2+}$ as well. The low uptake of $[Cu(pn)]^{2+}$ compared to $[Cu(en)]^{2+}$ is to be attributed to the larger size of the former (>0.5 nm). Moreover, even this small uptake may be due to physical adsorption.

The conclusions concerning the disproportionation reaction were confirmed further by carrying out column experiments. The spectrum of the effluent was that of the 1:2 complex. The copper content was found to be slightly less than 50% of that present in the initial solution. These results indicate that the disproportionation reaction is practically complete in this case (*i.e.*, 1 mol of the 1:1 complex gives 0.5 mol

TABLE 3. VARIATION OF 'K', 'K_{av}', AND K^* AS A FUNCTION OF CONCENTRATION

S. No.	Concentration $\times A$/M	Cu^{2+}		$[Cu(NH_3)_4]^{2+}$		$[Cu(en)]^{2+}$				$[Cu(pn)]^{2+}$	
						K_{av}		K^*		K_{av}	
		I	II	I	II	I	II	I	II	I	II
1	0.03	—	80	—	—	—	—	—	—	—	—
2	0.05	103	45	—	—	—	—	—	—	40	34
3	0.10	38	19	—	—	a)	48	a)	57	35	31
4	0.15	—	—	—	—	—	—	—	—	32	27
5	0.20	—	10	—	—	102	29	120	25	29	20
6	0.25	—	—	69	—	—	—	—	—	—	—
7	0.30	10	6	—	31	75	23	92	17	—	—
8	0.40	6	—	—	—	56	19	63	13	—	—
9	0.50	5	—	24	16	45	17	46	12	—	—
10	1.00	—	—	5	6	—	—	—	—	—	—

$A=1.0$ for Cu^{2+}; 10.0 for all other cations. a) The values are very high (as the solution left out after equilibration was practically colourless and did not show any measurable E value at 550 and 650 nm). I and II are data for MS4 *and* MS5 *respectively.*

of Cu^{2+} and 0.5 mol of the 1:2 complex). As a small amount of the 1:2 complex is retained on the sieves, besides Cu^{2+}, the concentration of copper in the effluent turns out to be slightly less than 50% of the total amount taken.

Because of the above-mentioned disproportionation reactions, 'K' values for $[Cu(pn)]^{2+}$ also cannot be calculated. In view of the low uptake of $[Cu(pn)]^{2+}$ by the sieves, K^* values were not computed. The 'K_{av}' values were, therefore, the only set computed in this case. These are included in Table 3. These 'K_{av}' values can be considered as an indirect measure of the influence of 'pn' on the uptake of Cu^{2+}.

Interestingly enough, 20 ml of a solution of 'pn' (0.22 M), when equilibrated for 3 h with 0.5 g of 75% Cu^{2+} substituted MS4, eluted about two thirds of Cu^{2+} as $[Cu(pn)_2]^{2+}$. The MS4 phase ceased to have the green colour characteristic of Cu^{2+} form, but attained the blue colour characteristic of $[Cu(pn)]^{2+}$. From this experiment it was qualitatively concluded that 'pn', taken up by the MS4 phase, complexed $Cu_2{}^+$ present there (to give 1:1 complex *in situ*), even though $[Cu(pn)]^{2+}$ itself was not taken up (inside the pores) by MS4 because of its larger size.

It would be quite fruitful to refer here once again to the earlier work of Schoonheydt *et al.*[10] According to them $[Cu(en)_2]^{2+}$ is unstable in the supercage of zeolite A. The bis-complex can be synthesized in aqueous suspensions by first exchanging Cu^{2+} or the monocomplex and then adding large excess of 'en' to the suspensions ($pH\geq 11$). The instability of the bis-complex was further substantiated by the observation of Schoonheydt and others that Cu^{2+} moved out of the zeolite phase into the 'en' solution upon standing overnight.

From considerations of electroneutrality, reactions of the type discussed above (in which about two-thirds of Cu^{2+} is eluted out by the amine) cannot be classified as regular ion exchange processes. As the loss of Cu^{2+} from the solid phase occurs without the uptake of an equivalent amount of another cation, a change in the nature of the solid phase becomes an inevitable consequence. It would then be logical to conclude that structural alterations may have to occur to satisfy electroneutrality conditions in the solid phase left out after equilibration.

Table 3 includes the following parameters obtained as a function of concentration: (i) 'K' values of Cu^{2+} and $[Cu(NH_3)_4]^{2+}$, (ii) 'K_{av}' values of $[Cu(en)]^{2+}$ and $[Cu(pn)]^{2+}$ and (iii) K^* values of $[Cu(en)]^{2+}$. The data for the other cations are not being included as they are too small to deserve any consideration.

A scrutiny of the data included in Table 3 reveals that the 'K', K^*, and 'K_{av}' values decrease with increase in concentration of the cation equilibrated. This is to be attributed to the fact that the uptake tends to reach a saturation value with increase in concentration of the equilibrated solution.

From a comparison of the data given in Table 3 one can understand the relative affinities of the different cationic species for the two sieves. The 'K', K^*, or 'K_{av}' (as the case may be) for the same ion on MS4 and MS5 reveal that the uptake on the latter sieve is considerably less in the case of all the cations included in the Table. One possible reason for this may be the fact that the Ca^{2+} ions preferentially occupy a more stable site in the A type zeolites. (The difficulty encountered in displacing the Ca^{2+} is further illustrated by equilibration experiments with water at pH 2.0 and 8 M aqueous ammonia discussed earlier). In addition to this, the influence of cation valency on the ion exchange process cannot be ignored. The cation to be displaced in the case of MS5 has the same charge (+2) as the displacing (simple or complex) one, while the displacement of a univalent ion (Na^+) by bivalent ones is involved in the case of MS4. Though the larger pore dimension of MS5 is a favourable factor for migration of ions into the zeolite phase, the occupation of preferential sites by Ca^{2+} and its higher charge turn out to be unfavourable factors (from the point of view of ion exchange).

As already stated, dilute solutions of $[Cu(en)]^{2+}$ give colourless effluents when passed through a MS4 column. Solutions of $[Cu(pn)]^{2+}$, however, give around 50% of the total copper in the effluent (as the 1:2 complex). These differences can be fruitfully used to estimate (with some limitations) the amounts of 'en' and 'pn' in their mixture. In principle, this type of estimation can be extended further to cover mixtures of 'en' and other higher homologues of 'pn' as well. Experimental data substantiating this expectation have been obtained by the authors.

The authors are grateful to Dr. M. Sankar Das, Head, Analytical Chemistry Division and Dr. Ch. Venkateswarlu for their constructive suggestions.

References

1) S. P. Zdhanov, *Neorg. Ionoobmen. Mater.*, **1**, 124 (1974).

2) L. V. C. Rees, *Ann. Rep. Progr. Chem., Sect. A.*, **67**, 191 (1970).

3) F. S. Stone, *Acta Cient Venez.*, Suppl., **24**, 32 (1973).

4) H. S. Sherry, Phy. Chem. Sci. Res. Rep. 1975, 1 (Nat. Sea Water, Rep. Dahlem Workshop, 1975), 523.

5) K. Wacks, *Fette, Seifen., Anstrichm.*, **77**, 366 (1975).

6) V. Grba, Z. Soljic, and I. Dican, *Nafta(Zagreb)*, **26**, 520 (1975).

7) J. H. Lunsford, A. C. S. Symp. Ser, **40** (Mole. Sieves—2, Int. Conf., 4th), (1977) 473.

8) A. Cremers, A. C. S. Symp. Ser., **40** (Mole. Sieves—2, Int. Conf., 4th), (1977) 179.

9) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).

10) R. A. Schoonheydt, P. Peigneur, and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2550 (1978).