Effect of presorbed water and temperature on adsorption of nitrogen and oxygen in NaCaA and NaMgA zeolites

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Adsorption of N_2 and O_2 has been studied on Ca^{2+} exchanged NaA zeolites (NaCaA) and on a NaMgA zeolite using elution gas chromatography. N_2 specific retention volume and adsorption selectivity increase with increase in calcium content (0 to 97% exchange) of the zeolite. However, the increase in much higher at above 90% calcium exchange. Specific retention volumes and adsorption selectivity decrease with increase in temperature for both the adsorbates. N_2 specific retention volume decreases with presorbed water in the zeolite. For zeolite samples NaA and NaCaA having > 90% calcium exchange even 0.9 mmol/g of presorbed water suppressed the N_2 selectivity substantially. Zeolite NaMgA shows higher heats of adsorption and lower specific retention volume and selectivity compared to NaCaA with similar ion exchange for nitrogen. Pronounced decrease in N_2 specific retention volume, selectivity and heat of adsorption is observed for NaMgA even with 0.9 mmol/g of presorbed water. These results have been explained in terms of interaction of adsorbate molecules with extra-framework cations and their distribution in zeolite A.

Oxygen-enrichment of air by pressure swing adsorption (PSA) has become an alternative to the conventional cryogenic separation processes[1], particularly, in the treatment of municipal/industrial waste water, medical purposes and steel industry. The process is based on the principle of selective adsorption of nitrogen from air by an adsorbent leaving oxygen rich gas phase in equilibrium with nitrogen rich adsorbed phase. A commercial adsorption process normally consists of a cyclic sequence of adsorption and desorption steps and when desorption is achieved by decreasing the pressure, the process is called PSA. In a typical PSA process for oxygen enrichment of air nitrogen is selectively adsorbed at higher partial pressure and subsequently desorbed by lowering the partial pressure. The change in partial pressure of nitrogen can be caused either by decreasing the total pressure, by changing the composition of the gaseous mixture or by doing both simultaneously. Figure 1a shows the amount of a gas adsorbed as a function of partial pressure at a particular temperature (T_1). The amount adsorbed decreases along the curve from a point 'A' to a point 'B' with a decrease in partial pressure of the component. The adsorption capacity available for separation in a PSA process is the difference in the capacities for the given component at the two pressures. However, in practical situations, due to the heat of

adsorption, there is an associated change in the temperature of the system and hence the working capacity is slightly different (at T_2) as shown in Fig. 1b. The various adsorbents, viz., NaA, CaA, NaX, LiX, mordenite and erionite have been reported suitable for oxygen-enrichment of air by PSA. However, majority of the commercial processes employ zeolite A and X based adsorbents[1]. These zeolites which are crystalline aluminosilicates are hydrophillic in nature and adsorb substantial amounts of water and carbon dioxide usually present in ambient air, even at very low partial pressures. In our earlier study[2], we have observed that even the trace quantities of water and carbon dioxide affect the adsorption of nitrogen and oxygen in zeolite NaCaA. In continuation, the present paper describes the effect of presorbed water and temperature on the specific retention volumes and adsorption selectivities of nitrogen and oxygen in zeolites NaCaA and NaMgA.

Materials and Methods

Exchange of Ca^{2+} and Mg^{2+} with Na^+ of zeolite NaA

Zeolite NaA in the form of binderless extrudates (1/16 inch) was supplied by the CATAD division of IPCL, India. Ion exchange was carried by refluxing the zeolite samples with a 10% w/w cal-

cium/magnesium chloride solution (solid to liquid ratio of 5) followed by thorough washing with hot distilled water. The samples were dried and cal-
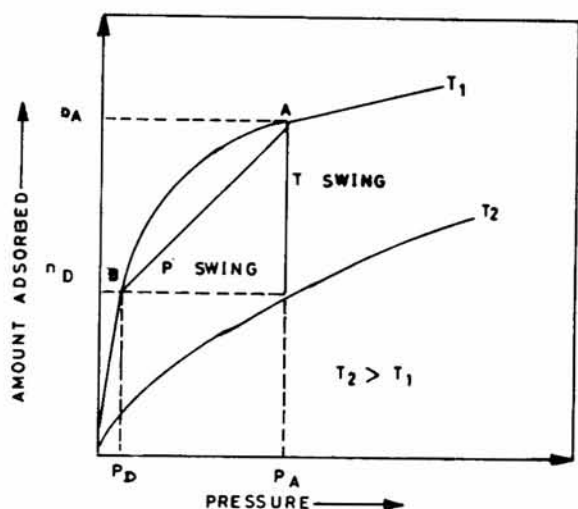

Fig. 1a—Adsorption isotherms showing pressure and temperature swings

Fig. 1b—Adsorption isotherms showing pressure and temperature swings and PSA working capacity

cined in air oven at 673 K. The degree of ion exchange in these samples was determined by chemical analysis using a Varian Techtron Model 1200 automatic atomic absorption spectrophotometer. The percent ion exchange of the samples along with pseudo unit cell composition and equilibrium water adsorption capacity are given in Table 1. Ultra-high purity nitrogen, oxygen, and helium were used in all gas chromatographic measurements.

Adsorption of N_2 and O_2 by elution gas chromatography

The gas chromatographic (GC) method[3] used for measuring nitrogen and oxygen adsorption is described in detail elsewhere[2]. Measurements were made using Varian Vista 6000 gas chromatograph. Zeolite sample (60-80 mesh) packed in a thoroughly cleaned 6×600 mm stainless steel column was saturated with distilled water and then activated by a stepwise heating for 12 h at 423, 473, 523 and finally at 673 K under hydrogen flow (60 ml/min). After the activation at each temperature, the column temperature was brought down to 303 K and carrier gas flow was brought to 30 ml/min, a pulse (0.5 ml) of gas mixture consisting of 0.5, 2.0 and 2.0 vol% of oxygen, nitrogen and helium respectively in hydrogen was injected into the column using a gas sampling valve and the retention times of gases were measured. This procedure was repeated at 313, 323 and 333 K. The amount of presorbed water was measured by conducting a separate but similar experiment in CAHN electrobalance TGA system 113. In this experiment a saturated adsorbent was loaded and activated for 12 h at 373, 423, 473, 523 and 673 K under the flow of 60 ml/min hydrogen and weight loss at each temperature was recorded. From the weight loss the amount of water retained was calculated. The retention times were corrected by subtracting the helium retention time from
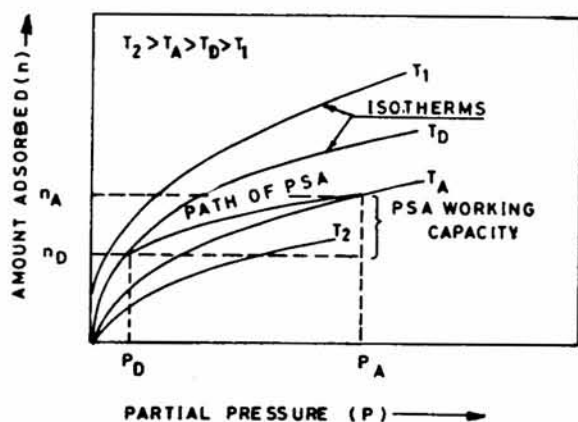
Table 1—Pseudo cell composition, equilibrium water sorption and cation locations in adsorbent samples

Adsorbent Sample	Calcium exchange %	Water sorption molecules/uc	Unit cell composition	Cations location
NaCaA-0	0	22.96	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	Na(A), Na(E)
NaCaA-24	24	22.85	$Ca_{1.5}Na_{9.0}[(AlO_2)_{12}(SiO_2)_{12}]$	Ca(A), Na(B)
NaCaA-43	43	22.88	$Ca_{2.6}Na_{6.8}[(AlO_2)_{12}(SiO_2)_{12}]$	—
NaCaA-60	60	23.02	$Ca_{3.6}Na_{4.8}[(AlO_2)_{12}(SiO_2)_{12}]$	Ca(A), Na(A)
NaCaA-75	75	23.14	$Ca_{4.5}Na_{3.0}[(AlO_2)_{12}(SiO_2)_{12}]$	Ca(A), Na(B)
NaCaA-90	90	23.82	$Ca_{5.4}Na_{1.2}[(AlO_2)_{12}(SiO_2)_{12}]$	—
NaCaA-97	97	24.25	$Ca_{5.4}Na_{1.2}[(AlO_2)_{12}(SiO_2)_{12}]$	Ca(B), Na(B), Ca(C)
NaMgA-76	76	23.39	$Mg_{4.5}Na_{3.0}[(AlO_2)_{12}(SiO_2)_{12}]$	—

those of nitrogen and oxygen. The retention time values of N_2 and O_2 were precise within ± 0.01 min. Corrected retention times were used to calculate net retention volume, V_N, and specific retention volume, V_m, using the equations

$$V_N = F t_R j / (1 - p_w/p_0) T/T_R \qquad \dots (1)$$

where

$$j = (3/2)[((p_i/p_0)^2 - 1) /(p_i/p_0)^3 - 1)]$$

$$V_m = V_N/W_s \qquad \dots (2)$$

where w_s is weight of adsorbent in the column; p_i, column inlet and p_0, column outlet pressures; T_R, room temperature; T column temperature; F, carrier gas flow rate (mL/min); p_w, water vapour pressure at room temperature; j, compressibility correction and t_R, corrected retention time, (min.) Limiting nitrogen selectivity (i.e. selectivity in Henry region), α_{N_2/O_2} and initial heats of adsorption, ΔH_0 for nitrogen and oxygen were calculated from specific retention volumes using the following equations:

$$\alpha_{N_2/O_2} = V_{m(N_2)} / V_{m(O_2)} \qquad \dots (3)$$

$$-\Delta H_0 = R \, d\ln(V_m/T) /d(1/T) \qquad \dots (4)$$

where R is the gas constant ($= 82.05$ cm^3 atm/mol. K) and T is the GC column temperature in kelvin. The uncertainties in the values of V_m, α_{N^2/O^2} and ΔH_0 as calculated using the method of propagation of errors from the known errors in the experimental parameters are ± 0.8, ± 1.6 and $\pm 1.8\%$ respectively.

Results

Specific retention volume, V_m at a given temperature is a measure of the adsorption capacity of a solid for a given adsorbate. The values of V_m for N_2 and O_2 on different zeolite samples at different temperatures are given in Table 2. In general, V_m for N_2 is higher in all the cases than for O_2. It it observed from the data that there is an increase in $V_{m}(N_2)$ with an increase in calcium content of the zeolite. However, the increase is moderate for samples NaCaA-60, NaCaA-75 and NaCaA-90 and very high for NaCaA-97. However, $V_m(O_2)$ after showing initial increase from NaA to NaCaA-24 show slight decrease with increase in calcium content of the zeolite. Comparison of V_m for NaCaA-75 and NaMgA-76 at different temperatures show that $V_m(N_2)$ is 9 to 12% lower for NaMgA-76. On the other hand, $V_m(O_2)$ is 5 to

Table 2—Specific retention volume for N_2 and O_2 for different zeolite samples

	V_m (cm^3/g) at			
	303	313	323	333 K
NaA				
N_2	7.67	6.02	4.98	4.17
O_2	2.82	2.43	2.20	2.00
NaCaA-24				
N_2	10.12	7.93	6.45	5.32
O_2	3.56	3.03	2.63	2.31
NaCaA-43				
N_2	10.27	8.03	6.54	5.42
O_2	3.35	2.86	2.50	2.21
NaCaA-60				
N_2	10.53	8.07	6.52	5.41
O_2	3.25	2.79	2.44	2.18
NaCaA-75				
N_2	10.52	8.11	6.47	5.33
O_2	2.99	2.59	2.27	2.02
NaCaA-90				
N_2	11.52	8.62	6.72	5.43
O_2	2.96	2.53	2.22	2.01
NaCaA-97				
N_2	12.75	9.34	7.21	5.71
O_2	2.80	2.38	2.09	1.86
NaMgA-76				
N_2	9.68	7.26	5.77	4.70
O_2	3.13	2.85	2.65	2.42

20% higher for NaMgA-76. It is also observed that V_m for N_2 and O_2 in different NaCaA and NaMgA samples decrease with the increase in temperature.

The effect of presorbed water on the V_m values of nitrogen and oxygen at various temperatures is shown in Fig. 2. It is observed that V_m decreases with increase in presorbed water for various samples studied. Furthermore, this decrease also increases with an increase in calcium content of the zeolite. This is observed to be more for N_2 than for O_2. However, in the case of NaCaA-60 and NaCaA-75 for 0.9 mmol/g of presorbed water, almost negligible decrease in V_m (N_2) is observed. For higher calcium or NaMgA-76 samples, a substantial decrease in V_m (N_2) is seen even with 0.9 mmol/g presorbed water.

Adsorption selectivities, α_{N_2/O_2} at different temperatures are plotted as a function of presorbed water in Fig. 3. The values of α_{N_2/O_2} decrease with increase in temperature. Further, the percent decrease in α_{N_2/O_2} also increases with
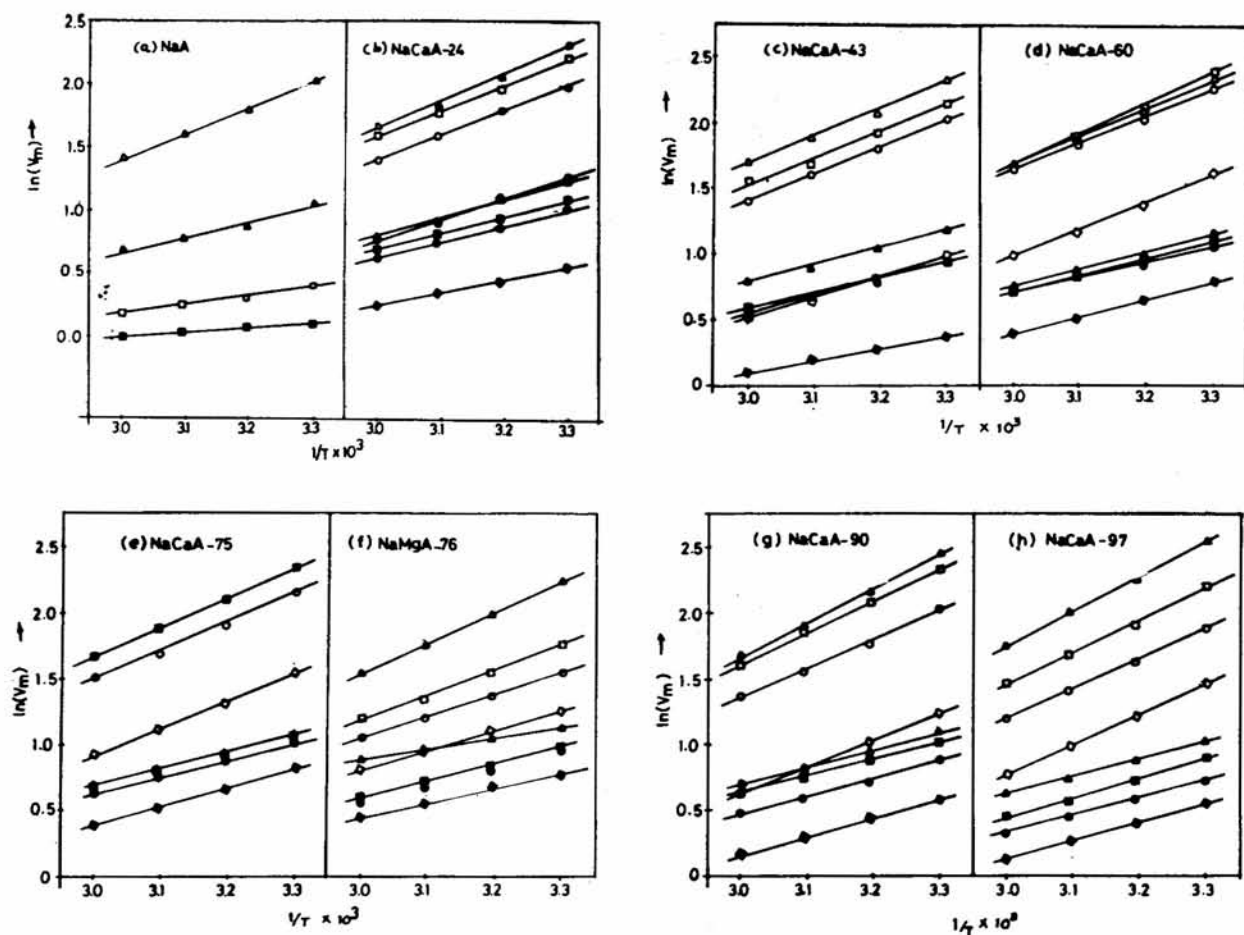
Fig. 2—Specific retention volumes of nitrogen (open symbols) and oxygen (filled symbols) at different temperatures on various zeolite A samples with presorbed water. ($\triangle$) no presorbed water, ($\square$) with 0.9 mmol/g, ($\bigcirc$) with 1.6 mmol/g, and ($\Diamond$) with 3.5 mmol/g of presorbed water

increase in calcium content of the zeolite. For example, with an increase of 30 K in temperature, decrease in α_{N_2/O_2} for NaCaA-24, -43, -60, -75, -90 and -97 is 19, 20, 23, 25, 32 and 33% respectively. Adsorption selectivity data on various adsorbents having presorbed water as given in Fig. 3 show that for NaA and high calcium NaCaA, viz., NaCaA-90 and NaCaA-97, α_{N_2/O_2} starts decreasing even with 1 mmol/g of presorbed water in zeolite. However, for other samples NaCaA-24, -43, -60 and -75 there is slight increase in nitrogen adsorption selectivity upto 1 mmol/g of presorbed water after which progressive decrease is observed with increasing amount of presorbed water at all temperatures.

As shown in Table 3, NaMgA-76 exhibits less α_{N_2/O_2} and $V_m(N_2)$ compared to NaCaA-75 at all temperatures. However, ΔH_0 values of N_2 in NaMgA-75 are higher than in NaCaA-75. Effect of presorbed water is more pronounced for NaMgA-76 as seen from values of V_m, α_{N_2/O_2} and ΔH_0 given in Table 3. Unlike NaCaA-75, where upto 1 mmol/g of presorbed water slight increase in selectivity is observed, NaMgA-76 shows a sharp decrease.

Discussion

The major interactions between a zeolite and adsorbed molecules of N_2 and O_2 include electrostatic, induction, dispersion and short range repulsive forces. The extra-framework zeolitic cations Na^+, Ca^{2+} and Mg^{2+} act as the principal sites for these interactions. The increase in V_m for N_2 with calcium content of a zeolite is due to enhanced electrostatic interactions (Table 4) of quadrupole moment (4.3029×10^{-40} C.m^3) of N_2 molecules with bivalent Ca^{2+} compared to Na^+. However, the difference in the adsorption behaviour of ni-

trogen with increasing calcium content is not along the lines of expected increased interaction on Na^+ replacement by Ca^{2+}. Similarly, owing to higher charge density of Mg^{2+} compared to Ca^{2+} ions, N_2 molecules are expected to have higher interactions with the former cations. On the basis of these interactions, the value of $V_m(N_2)$, which is equivalent to thermodynamic equilibrium constant, for NaMgA is expected to be higher than for NaCaA. However, the data given in Table 2 show

Fig. 3—Adsorption selectivity of nitrogen as a function of presorbed water at various temperatures. (O) 303 K (□) 313 K (△) 323 K (●) 333 K

otherwise. This observation can be explained in terms of cation sites occupied by Na^+, Ca^{2+} and Mg^{2+} in these zeolites. It is known[4,5] that with increasing Ca^{2+} exchange there is a variation in locations of the cations inside zeolite cavities. Further, these cationic sites vary in the degree of their accessibility to N_2/O_2 molecules. The distribution of Na^+ and Ca^{2+} cations at different locations in zeolite A for different samples as determined from Far IR spectroscopy[4,5] is as shown in Table 1. Unit cell of zeolite A illustrating the common cation positions denoted by Mortier's notation[6] is shown in Fig. 4. The cation positions in this figure are exaggerated for the sake of clarity. In $Na_{12}A$ zeolite, 8 Na^+ per pseudo unit cell are located in site A (in the plane of the six-ring), $3Na^+$ in site E (in the plane of eight-ring) and 1 Na^+ in site H (inside sodalite cage). On the other hand in the case of Ca_6A zeolite 4.4 Ca^{2+} are located at site B (in the six-ring but displaced into the α-cage) and the remaining Ca^{2+} at site C (in the six-ring but displaced into the β-cage). Depending on their location in the zeolite framework, certain cations are not accessible or are less accessible to adsorbate molecule such as N_2. For example cations located in site H are not accessible to N_2 molecule. On the other hand, all the extraframework cations are accessible to water molecules as these can enter β-cages also. From bond valence method[7], it is calculated that Ca^{2+} and Na^+ in a three-fold coordinated site such as six-ring site in most frame work types, require $M^{n+} - O$ distances of 2.06 and 2.14Å for valence matching. However, these distances are not attained. As a result, these sites will possess a local excess of positive charges. It is further, reported from Far IR that in Ca_6A zeolite, Ca^{2+} cations are located at site B with $Ca^{2+} - O$ distance of 2.27Å. Thus, Ca^{2+} cations at site B will possess higher positive charge than those at site A. As the cations present at site B are 0.28Å projected out of the six-ring plane, these are steri-
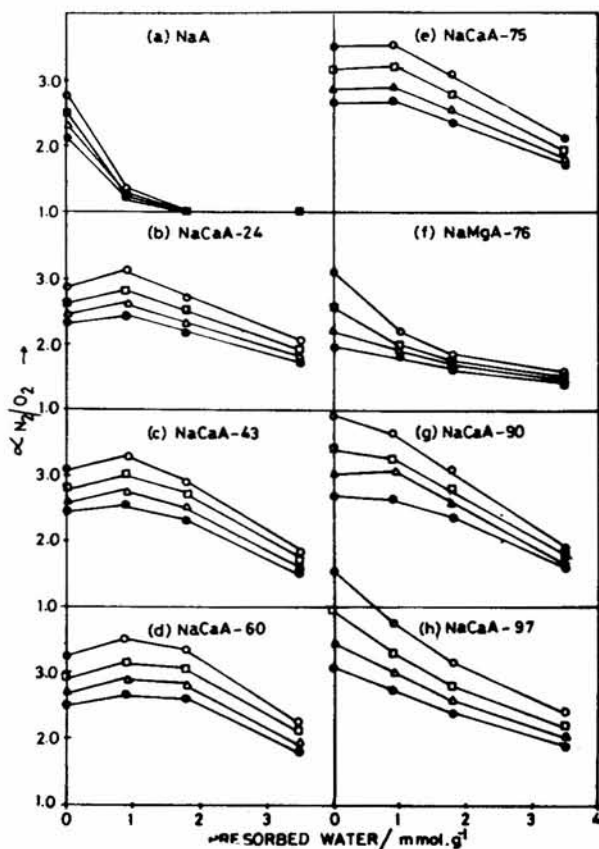
Table 3—Effect of presorbed water on ΔH_0 (kJ·mol⁻¹) and $\alpha_{N_2O_2}$ in NaCaA-75 and NaMgA-76

Presorbed water	NaCaA-75					NaMgA-76				
	V_m (cm³·g⁻¹)		α_{N_2/O_2}	$-\Delta H_0$ (kJ·mol⁻¹)		V_m (cm³·g⁻¹)		α_{N_2/O_2}	$-\Delta H_0$ (kJ·mol⁻¹)	
(mmol·g⁻¹)	N_2	O_2		N_2	O_2	N_2	O_2		N_2	O_2
0.0	10.52	2.99	3.5	21.8	14.0	9.68	3.13	3.1	22.8	12.3
0.9	10.41	2.95	3.6	21.5	13.8	5.86	2.71	2.2	18.5	13.2
1.6	8.59	2.78	3.1	21.1	13.8	4.76	2.59	1.8	16.7	13.1
3.5	4.70	2.26	2.1	20.0	13.5	3.54	2.20	1.5	15.3	12.1

Table 4—Calculated interaction energies between isolated cation and adsorbate molecule

Cation	Adsorbate	Interaction energies $(kJ \cdot mol^{-1})$		
		E_{F-Q}	E_I	E_D
Na^+	N_2	-13.2	-18.6	-0.9
	O_2	-1.9	-21.0	-0.9
Ca^{2+}	N_2	-22.2	-112.7	-6.33
	O_2	-3.8	-124.0	-6.98
Mg^{2+}	N_2	-33.6	-195.7	-3.66
	O_2	-5.8	-221.7	-4.18

Note: Properties of cations and adsorbate molecules

Property	N_2	O_2	Ca^{2+}	Mg^{2+}	Na^+
Ionic/van der Walls radii[a] (Å)	1.54	1.40	0.99	0.65	0.95
Quadrupole moment[b] $(C \cdot m^2 \times 10^{40})$	4.3029	0.6338			
Polarizability[b] $(cm^2 \times 10^{24})$	1.76	1.57	0.53	0.12	0.19
Ionisation energy[a] (ev)	14.534	13.618	50.908	80.143	47.286

[a]Reference 10; [b]Reference 11; E_{F-Q}, field-quadrupole interaction energy; E_I, induction energy and E_D, dispersion energy.
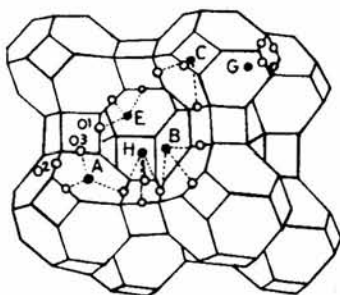

Fig. 4—Pseudo unit cell of zeolite A (LTA) and the cation positions denoted as per Mortier's[6] (1982) classification

cally more accessible to adsorbate molecules. Hence, interaction of Ca^{2+} cations at site B with nitrogen or in that way even with water molecules are going to be higher than those at site A. That is why unexpectedly high values for $V_m(N_2)$ (Table 2) and α_{N_2/O_2} (Fig. 3) are observed for NaCaA-97 sample.

Effect of presorbed water on N_2 adsorption is also explained in terms of interactions of adsorbate molecules with zeolite cation. Water molecules due to their strong polarity (dipole moment $= 6.1376 \times 10^{-30}$ C.m) will preferentially interact with the cations present in the zeolite. This in turn weakens cations interactions with adsorbate molecules. Since interactions of nitrogen are expected to be higher with the zeolite cations than oxygen, presorbed water affects nitrogen adsorption more

than oxygen adsorption. However, on certain samples (particularly NaCaA-60 and -75) presorbed water upto 0.9 mmol.g^{-1} showed negligible effect on N_2 adsorption. This indicates that presorbed water molecules upto 0.9 mmol.g^{-1} are hydrating Na^+/Ca^{2+} cations present at those sites in the zeolite which are inaccessible to nitrogen molecules. In the case of NaA the initial presorbed water might be interacting with Na^+ present at site E, as these are present at the pore openings and thus completely suppressing N_2 adsorption. On the other hand, in the samples NaCaA-90 and NaCaA-97 even the initial water seems to interact with more accessible cations present at site B thus affecting nitrogen adsorption even at very small amount of presorbed water.

The low values of $V_m(N_2)$ for NaMgA-76 compared to that for NaCaA-75 may be due to fewer Mg^{2+} ions present at sites which are accessible to adsorbate molecules than Ca^{2+} or due to higher interaction of Mg^{2+} ions with zeolite framework oxygen atoms which make them less available to N_2 molecules. Because of its higher charge density Mg^{2+} is expected to have more interactions with framework oxygen atoms than Ca^{2+} ions. Though the precise data on the site locations of Mg^{2+} ions in zeolite A are still not available in the literature it has been suggested[8] that the distribution of Mg^{2+} ions in zeolite A is similar to that of Ca^{2+} ions. Higher heat of adsorption of N_2 in NaMgA-76 (Table 3) suggests that N_2 molecules interact strongly with Mg^{2+} ions than with Ca^{2+} reflecting

the absence of interaction of Mg^{2+} with framework oxygen atoms. The lower values for $V_m(N_2)$ in zeolite NaMgA is due to less number of Mg^{2+} present at sites accessible to N_2 molecules. This implies that the site locations of Ca^{2+} and Mg^{2+} are not similar in zeolite A even at equivalent ($\approx 75\%$) ion exchange.

Adsorption of oxygen due to its lower quadrupole moment is less dependent on its interactions with ions. As a result, its V_m is expected to depend more on the pore volume available to its molecules. This explains the higher $V_m(O_2)$ for NaMgA as compared to NaCaA because pore volume is higher in the former due to smaller size of Mg^{2+} ions and their fewer number in super cage.

The effect of presorbed water on the adsorption of N_2 in NaMgA-76 is very pronounced. For example, the decrease in $V_m(N_2)$ observed for NaMgA-76 as a result of 0.9 mmol.g^{-1} presorbed water is around 40% compared to 1% for NaCaA-75. This strongly indicates that initial water hydrates magnesium cations present at those sites which are accessible to nitrogen molecules. Further, Mg^{2+} ions are reported[9] to coordinate water molecules stronger than other bivalent cations like Ca^{2+} and it has also the larger hydrated radius than Ca^{2+} ion. Because of its higher charge/size ratio, Mg^{2+} ions fulfil their coordination sphere with the mobile water molecules in the zeolite cage. Consequently, Mg^{2+} ions will be more effectively screened by presorbed water molecules

than Ca^{2+}. This is further reflected in the effect of presorbed water on α_{N_2/O_2} and ΔH_0 in NaCaA-75 and NaMgA-76 (Table 3).

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