b) The Role of Organic Molecules in Molecular Sieve Synthesis

Many similarities in the structural and chemical properties of silica and water were reviewed by Iler.[80] They both have structures which are much less dense than would be expected from close packing of the constituent atoms. They both have a temperature of minimum volume. Normally water molecules are arranged in a rather open structure like quartz and the structure of undercooled water is even more open such as is the structure of tridymite relative to quartz. Each water molecule is tetrahedrally surrounded by the oxygen atoms of four neighboring hydrogen atoms. Two of these hydrogens are near-neighbors at 1.01 angstroms and two are far-neighbors at 1.74 angstroms.[81] The entire array is likned by unsymmetrical hydrogen bonds. Pure silica only occurs in two forms; quartz and cristobalite.[82] In silica, the silicon atoms are always tetrahedrally bond to four oxygen atoms. The silicon oxygen bonds have considerable ionic character. When silica is dissolved in basic aqueous solutions, it occurs as the anion $(SiO_2\ (OH)_2)^{2-}$. Depending on the pH and concentration, tetrameric and other polymerized species are also present.[83] Because water molecules are dipolar, the addition of certain anions, and cations as well, can disturb the normal structure of water. The hydrogen end of the water molecule having a partial positive charge tends to orient itself to be pointed in the direction of an anion is solution. Similarly, the oxygen end of the water molecule having a partial negative charge will tend to point in the direction of a cation.

Information on the effect of the addition to ions to the structure of solution has been determined through neutron and X-ray diffraction studies. In pure water the molecules are oriented in a tetrahedral quasi-structure. In concentrated solutions, the water molecules tend to become more tightly packed around the ions than in the ordinary tetrahedral quasi-structure. The difference between the partial molal entropy of water in solution and that of pure water reflects the structural modification. Certain ions contribute to or enhance the structure of water by the ordering of water molecules in their hydration shell (ΔS is negative). Other ions are structure breaking and the change in entropy becomes increasingly positive as the concentration increases. Small ions which can enter the water structure through hydrogen bonding (F^-,OH^-,OH_3^+, NH_4^+) are structure-enhancing and tend to stabilize the structure of water. Large ions with decentralized charge (BF_4^-, ClO_4^-, $FeCl_4^-$) are structure-breakers and have the same effect on the quasi-structure of water as an increase in temperature. Buijs et al.measured the effect on the structural modification of water by its ions.[84] The results he obtained are summarized below:

Cations: order-producing: $La^{3+} > Mg^{2+} > H^{+} > Ca^{2+}$
order-destroying: $K^{+} > Na^{+} > Li^{+} > Cs^{+} = Ag^{+}$;
Anions: order-producing: $OH^{-} > F^{-}$
order-destroying: $ClO_4^{-} > I^{-} > Br^{-} > NO_3^{-} > Cl^{-} > SCN^{-}$

The group of structure-makers, which includes small ions which can fit into the more or less existing structure of water and thereby enhancing its stability through its charge, also includes a group of large molecules which can contribute the same affect through hydrophobic bonding. Ben-Naim[85] discussed the origin of the stabilization of the structure of water by non-electrolytes. Hydrophobic bonding occurs when the inert hydrocarbon material guards the water structure near it from disruption from thermal agitation of other water molecules. The effect of tetraalkyl ammonium ions on the structure of water has been determined.[86] Tetramethyl ammonium ions are structure-breaking. Tetraethyl and tetraethanol ammonium ions have little effect and tetrapropyl and tetrabutyl ammonium ions are hydrophic bond type structure makers. In tetrapropyl ammonium ions the hydrophobic nature of the hydrocarbon side chains enforce the structure of water about these hydrocarbon chains. The explanation given by Evans[86] suggests that water molecules that are situated at the surface of these large tetraalkyl ammonium ions will be oriented very little either by the ionic charge or the non-polar side chains on its one side. As a result of this, the water molecules can be oriented to a greater extent than normal by their nearest water molecule neighbors, and therefore can in effect be oriented into favorable positions for the formation of water cages about the inert side chains. The importance of the ability of these water molecules to be influenced by their nearest neighbors toward the production of stable water cages about these hydrocarbon side chains is that the same process appears to occur when these same chains are encased in SiO_2 cages.

"There are certain substances formed by combining one stable compound with another or with an atomic or molecular element without the existence of any chemical bonds between the two elements. This occurs when one of the compounds can crystallize in a very open structure containing cavities, holes, or channels in which the atoms or molecules of the other can be trapped."[87] Compounds of this type wherein the host lattice contains cages filled by guest molecules are called clathrate compounds from the Latin clathratus, meaning "Enclosed or protected by cross bars or grating."[87] For example, if quinol (p-dihydroxybenzene) is crystallized from water in the presence of 10 to 40 atmospheres of krypton, krypton molecules are entrapped in spherical cages approximately 4 angstroms in diameter. The appertures leading from one cage to another throughout the crystal are very small in diameter and prevent krypton molecules from being released. If, however, the crystals are redissolved in water, krypton gas is readily released.[87] In other systems the shape and size of the guest molecule can directly effect the structural properties of the host lattice which can crystallize around it. Analogies exist between the structural chemistry of water in its various clathrate hydrates and the structure of silicates. Examples of this include the comparison of the structure of ultramarine with the structure of $HPF_6 \cdot 6H_2O$. In this structure the positions of the water molecules in the clathrate hydrate are identical to the positions of the silica or alumina atoms in the framework of ultramarine.[88] The structure of the oxygen clathrate framework of tetramethyl ammonium hydroxide pentahydrate is also isostructural with $HPF_6 \cdot 6H_2O$ in that both lattices are based on the closest packed arrangement of truncated octahedra.[89,90] The structure of this tetramethyl ammonium hydroxide pentahydrate is shown in Figures 11,12, and 13

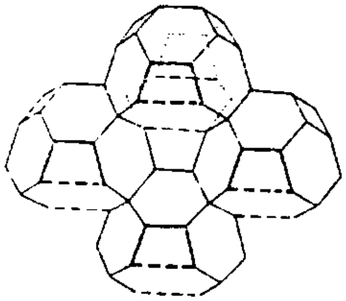


Figure 11: The framework of hydrogen-bonded OH^- ions and H_2O molecules in $(CH_3)_4N.OH.5\ H_2O$ showing distortion of the truncated octahedron in the 'Fedorov' net. The broken lines indicate O-O edges of length 4.36 A.

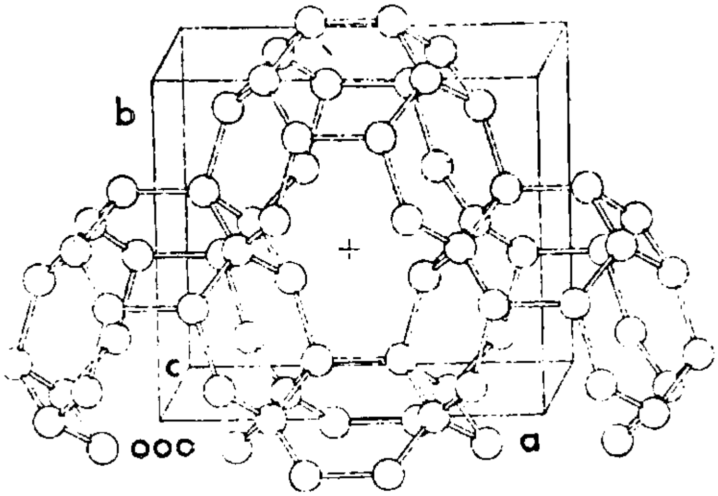


Figure 12. The polyhedral oxygen framework of hydrogen-bonded OH- ions and H_2O molecules in $(CH_3)_4N^{+}-\cdot 5H_2O$, showing three of the four distorted truncated octahedra in the unit cell.

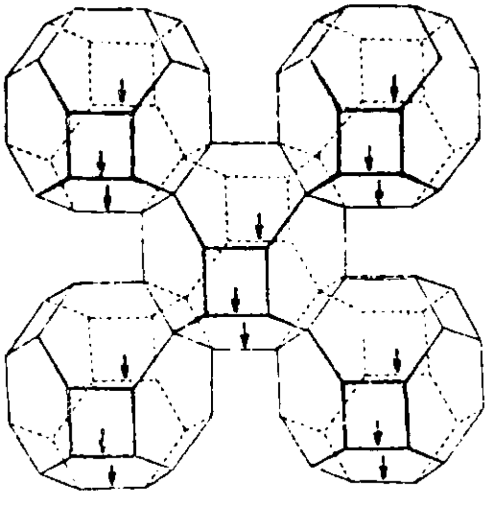


Figure 13. Idealized framework structure with closest-packed truncated octahedra. The arrows indicate edges which are expanded in the distorted structure found in $(CH_3)_4N^{+}OH^{-}\cdot 5H_2O$.

The structure of the tetramethyl ammonium ion is shown in Figure 14 TMA also forms a hydrate with a formula: $4(CH_3)_3\ N\cdot 41H_2O$. In this structure the tetramethylammine guest molecules are hydrogen bonded within the voids formed by a polyhedral host lattice of hydrogen-bonded water.[89]

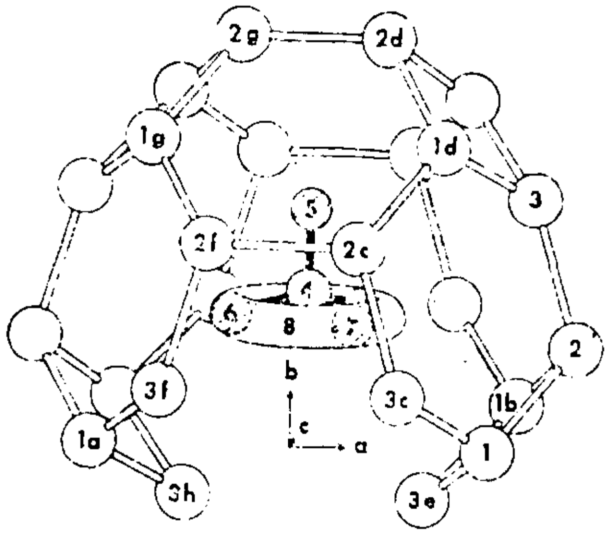


Figure 14. A distorted truncated octahedron containing an axially disordered $(CH_3)_4N^+$ ion. The disordered carbon atoms are represented by the torus; the oxygen, nitrogen, and ordered carbon atoms are differentiated by shading; the hydrogen atoms are omitted. The double and solid lines indicate the O...H-O and N-C bonds, respectively.[89]

The water molecules in this structure are shown in Figures 15 and 16; they are statistically disordered so that a hexagonal structure is observed, whereas, an ordered arrangement would have monoclinic symmetry.[90] The structure for the polyhedral clathrate hydrate of TEA $(CH_3CH_2)_2\ NH\cdot 8\ 2/3H_2O$ has been resolved. This crystal has orthorhombic symmetry.

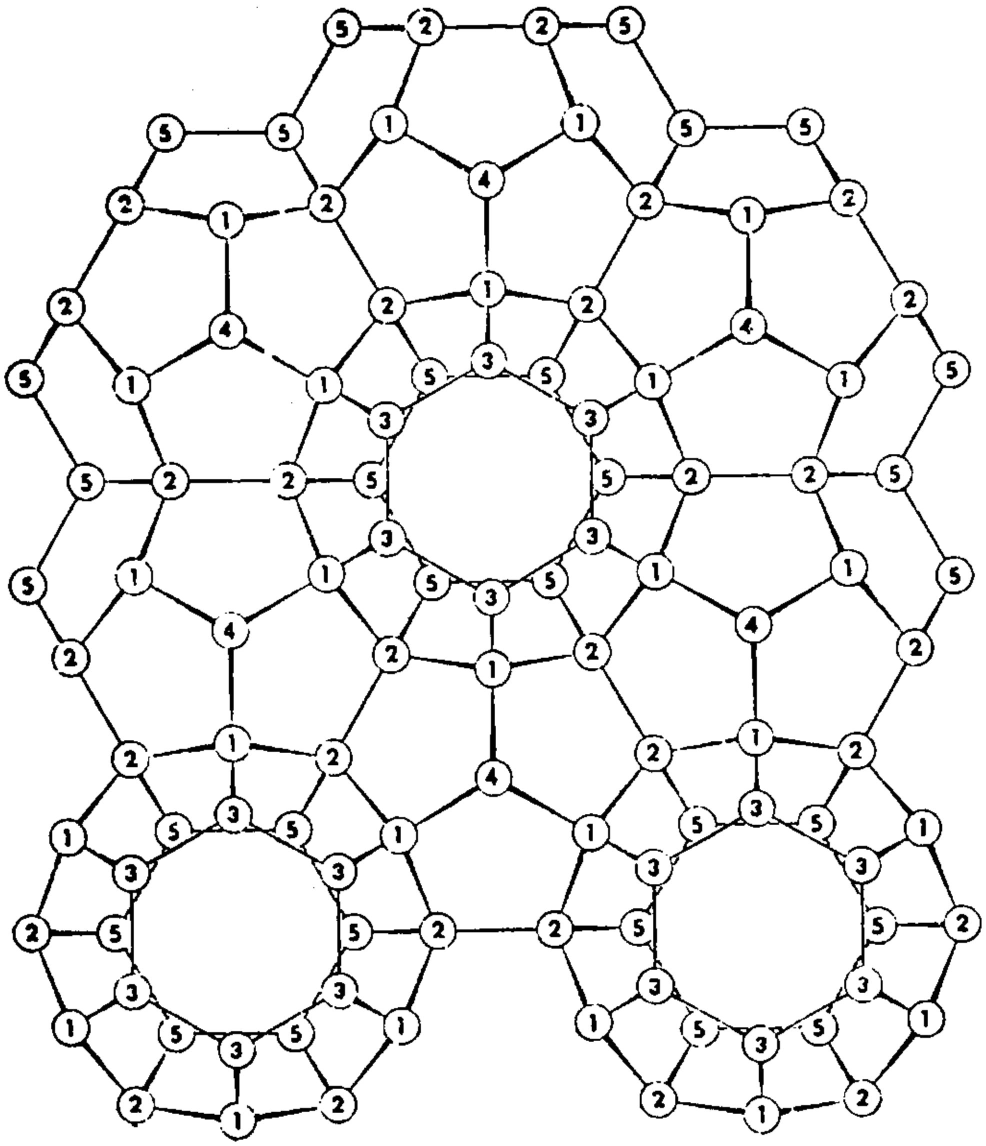


Figure 15. Ball-and-stick diagram of idealized polyhedral framework, showing three 14-hedra, one of them surrounded by six 15-hedra.

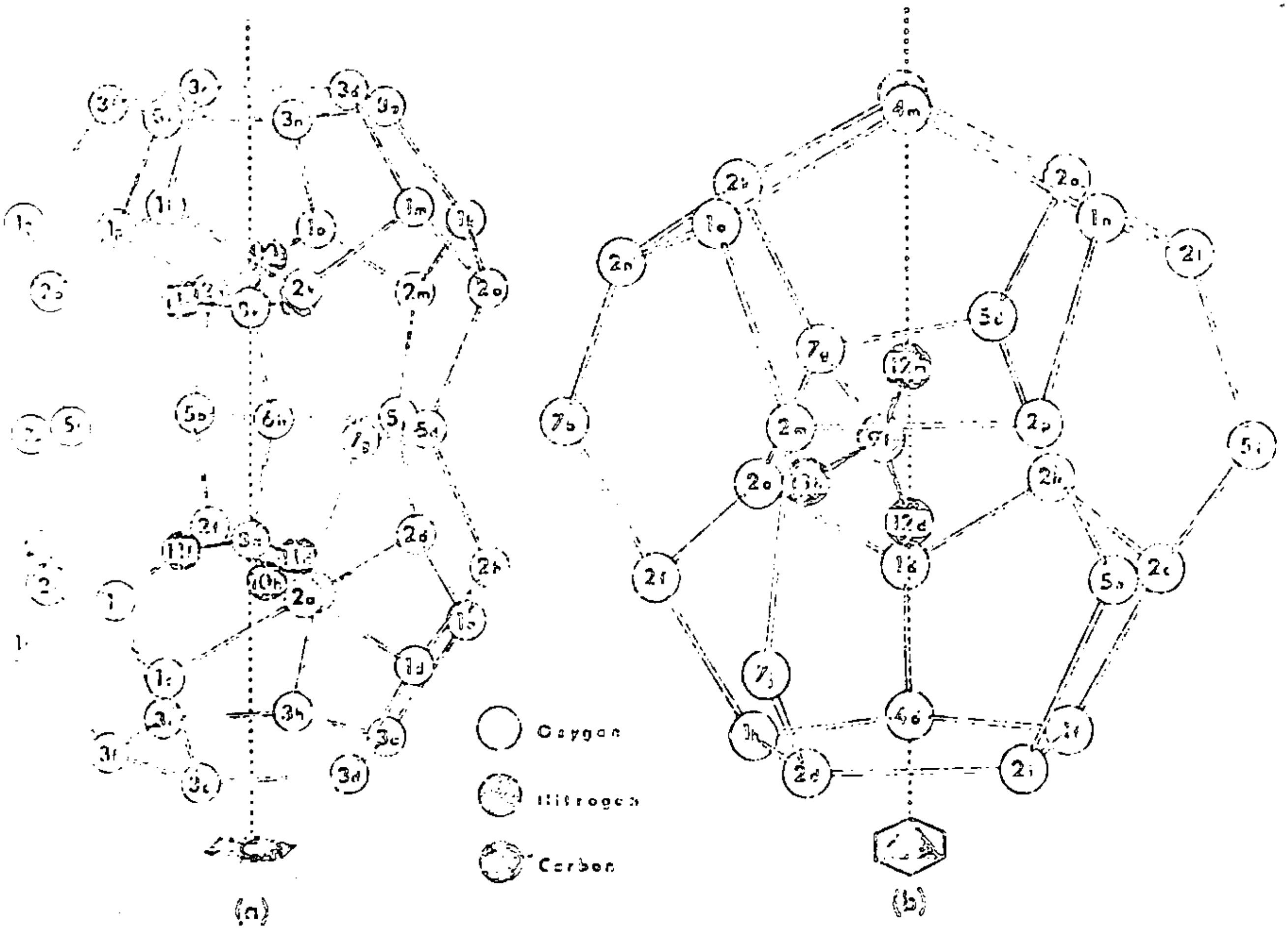


Figure 16. Ball-and-stick diagrams with atomic notation, showing the irregular cages of water molecules and the enclosed $(CH_3)_3N$ guests. Open lines indicate O···H-O and O-H···N hydrogen bonds, solid lines show C-N bonds. The symmetry axes refer to the hexagonal cell.

The hydration cage is shown in Figures 17 and 18

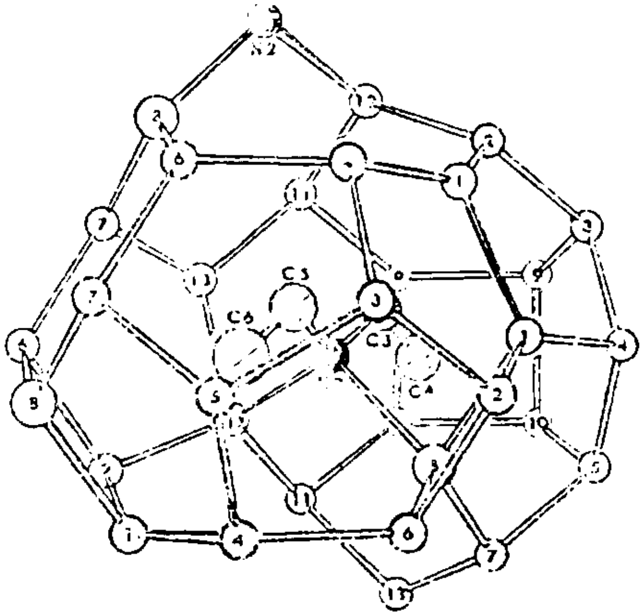


Figure 17. A perspective view of the "irregular" cage lookingdown the c axis.

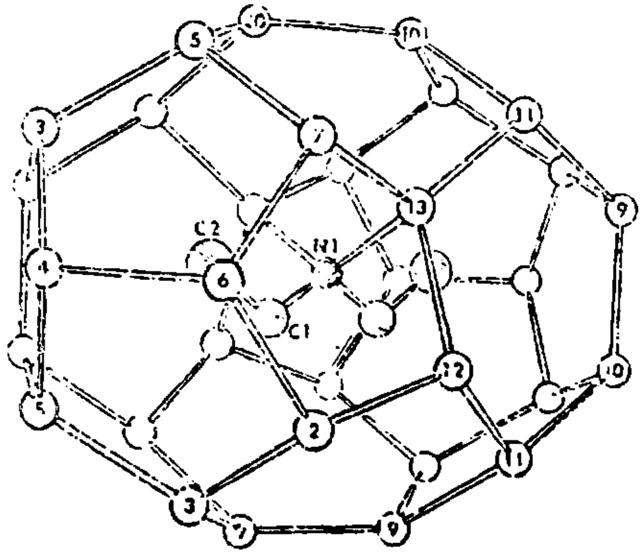


Figure 18. A perspective view of the 18-hedron looking down the c axis. The twofold axis passes through N(1) and the midpoints of 9-9 and 10-10.

Table 2 lists the various classes of clathrate hydrates giving examples and references for each structural class. Wenn[91] measured the mean molal activity coefficient of tetrapropylammonium fluoride, chloride, bromide, and iodide in aqueous solutions. The results he obtained are shown in Figure 19 which shows the activity as a function of concentration.

Clathrate hydrates

	H_2O *molecules only in framework*	H_2O *and F, N, S in framework*	*Reference*
	Polyhedral frameworks		
Class (a)			
(i)	$HPF_6 . 6 H_2O$		AC 1955 8 611
		$(CH_3)_4NOH . 5 H_2O$	JCP 1966 44 2338
(ii)	$(CH_3)_3CNH_2 . 9\frac{3}{4} H_2O$		JCP 1967 47 1229
Class (b)			
(i)	$Cl_2 . 7\frac{1}{4} H_2O$		PNAS 1952 36 112 JCS 1959 4131
	$6{\cdot}4 C_2H_6O . 46 H_2O$		JCP 1965 42 2725
		$(n\text{-}C_4H_9)_3SF . 20 H_2O$	JCP 1962 37 2231
(ii)	$CHCl_3 . 17 H_2O$		JCP 1951 19 1425
	$7{\cdot}33 H_2S . 8 C_4H_8O . 136 H_2O$		JCP 1965 42 2732
(iii)		$(i\text{-}C_5H_{11})_4NF . 38 H_2O$	JCP 1961 35 1863
(iv)	$Br_2 . 8{\cdot}6 H_2O$		JCP 1963 38 2304
	Intermediate types		
Class (c)			
(i)		$(n\text{-}C_4H_9)_3SF . 23 H_2O$	JCP 1964 40 2800
(ii)	$(C_2H_5)_2NH . 8\frac{2}{3} H_2O$		JCP 1967 47 1222
(iii)	$4 (CH_3)_3N . 41 H_2O$		JCP 1968 48 2990
	Non-polyhedral frameworks		
Class (d)			
(i)	$N_4(CH_2)_6 . 6 H_2O$		JCP 1965 43 2799
(ii)		$(CH_3)_4NF . 4 H_2O$	JCP 1967 47 414

Table 2. Structural Inorganic Chemistry, Wells, A.F., Oxford University Press, Ely House, London, 1975, pg. 544.

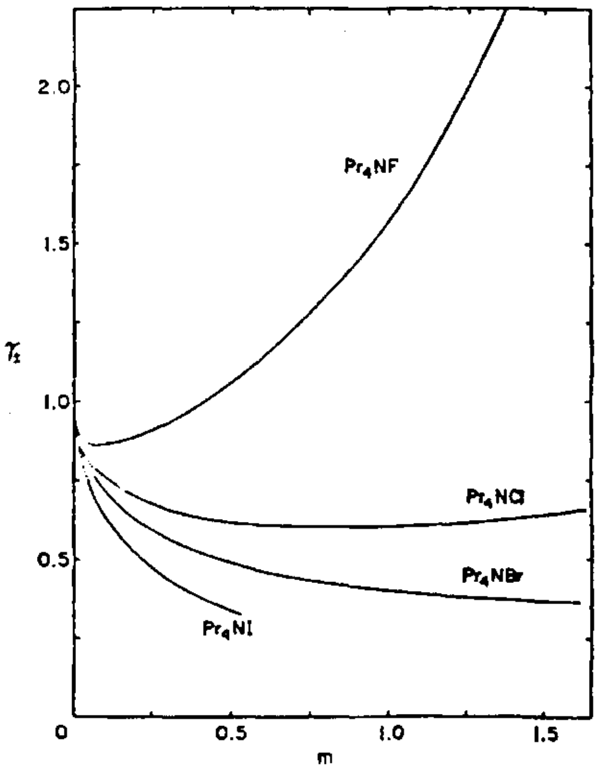


Figure 19. Mean molal activity coefficients, $\gamma \pm$, of tetrapropylammonium fluoride, chloride, bromide, and iodide in aqueous solutions at various molal concentrations, m, at 25 C.

The high activity of tetrapropyl ammonium bromide he attributes to the difference of the tetrapropylammonium and fluoride ion on the structure of solution. Although both TPA and fluoride are structure-making ions, the fluoride ion he suggests tends to immobilize water more or less in a radially dispersed pattern around it. The TPA ion favors cage-like or clathrate-like structures which he attributes to its hydrophobic properities. Because these two ions are incompatible in their modes of structure making, they compete against each other in their influence on the structure of water. As a result of this, there is a "structural salting out" of the cation and anion against each other which causes the high activity coefficient. The low activity of the tetrapropylammonium iodide he explains in a concept of "structural salting in." The I^- ion being a structure breaker contributes to the availability of water to the self-salting of the tetrapropylammonium ion.

The structure-directing effects of quaternary ammonium ions have on the structure of water suggest they might exhibit similar effects during zeolite synthesis. This effect would be to allow the silica (alumina) to polymerize into thermodynamically stable cage-like structures around these hydrophobic organic side chains. Reference has been made that hydrogen bonding might contribute to the stability of this cage arrangement. Clearly the shape and nature of the cage is likely to change with the shape, bond angle, etc. of the organic side chains.

Each particular type of organic side chain in quaternary alkyl ions can direct the syntheses of a number of different types of cages around its hydrophobic side chain. The framework structure of the zeolite can, therefore, be templated through the use of the appropriate quaternary alkyl ions. All other ions in the system also contribute to the ionic atmosphere in the hydrothermal synthesis. The nature of this contribution is complex and it is difficult to predict the effect on the crystal structure of the addition of a particular ion type.

At high concentrations, tetrapropylammonium ions tends to form dimers and large aggregates called micelles. At low concentrations they are present in aqueous solution chiefly as monomers.[92] This dimerization and polymerization of TPA ions inhibits their ability to form ion association complexes with silica and alumina ions. This reduces the ability of TPA to stabilize these ions in solution and also makes TPA, which is not involved in ion association complexes with silica and alumina, more susceptible to destruction by Hoffman degradation.

The ability of quaternary propyl, butyl, and hexal ammonium ions to form ion association complexes with transition metal ions and aluminum was studied by Maeck et al.[93] Maeck determined the effectiveness of extracting metal ions from sodium hydroxide solutions with tetrapropylammonium hydroxide. The results he obtained, showing the ability of these tetraalkyl ammonium ions to form tetraalkyl metal ammine complexes for the extraction of these metals from sodium hydroxide solution, are summarized in Figure 20. These quaternary alkyl ammonium compounds are very strong bases and are capable of forming salts with silicic acid and aluminic acid.

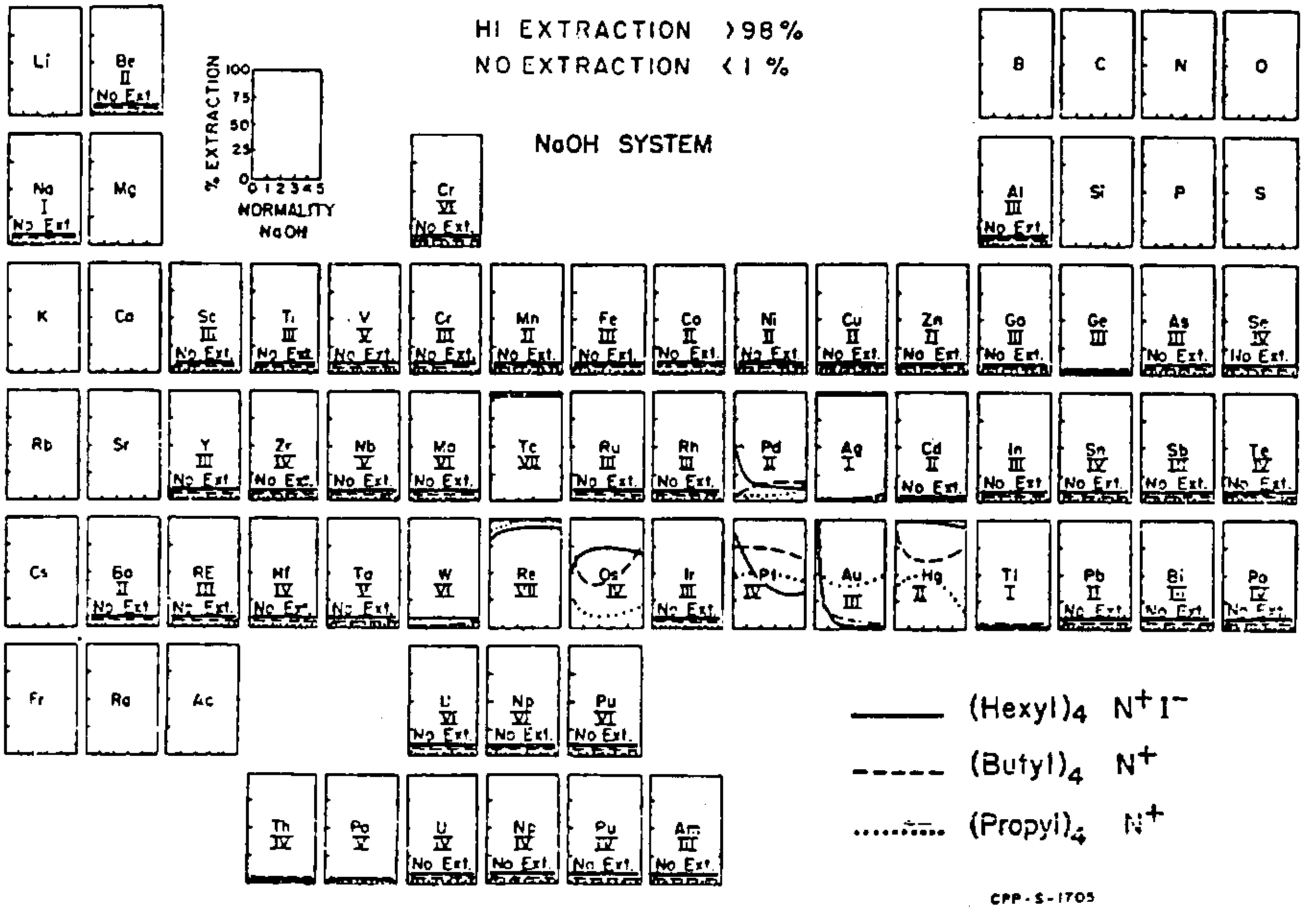


Figure 20. Extraction of elements as tetraalkyl amine complexes from sodium hydroxide.

The templating phenomenon which is thought to occur during either the gellation or nucleation process is not constrained to occur only on large organic molecules. The process whereby an ion or atom organizes oxide tetrahedra into a particular geometric topology around itself also occurs in the case of alkali or alkaline earth metal cations. Zeolite structural subunit such as the double four ring (D_4R), the double six ring (D_6R), and cancrinite, gmelinite, and sodalite cages are thought to be formed by way of clathration of an alkali cation with silica and alumina tetrahedra.[6,14,23] Sodium and hydrated sodium ions were suggested to be responsible for the formation of D4R, D6R, gmelinite and sodalite cages.[6,94] Potassium, barium, and rubidium ions were believed responsible for directing the synthesis of cancrinite cages.[6,94] R.M. Barrer[6] compiled a list of various zeolite types showing the cations which are preferred or preferentially direct the formation of each type of zeolite. The list he compiled shown in Table 3 indicates the various cationic environments from which each zeolite has been reported to synthesize and also those cations which seem to be preferred. Barrer came to the following 4 conclusions with respect to the type of zeolite structures formed under particular cationic environments.

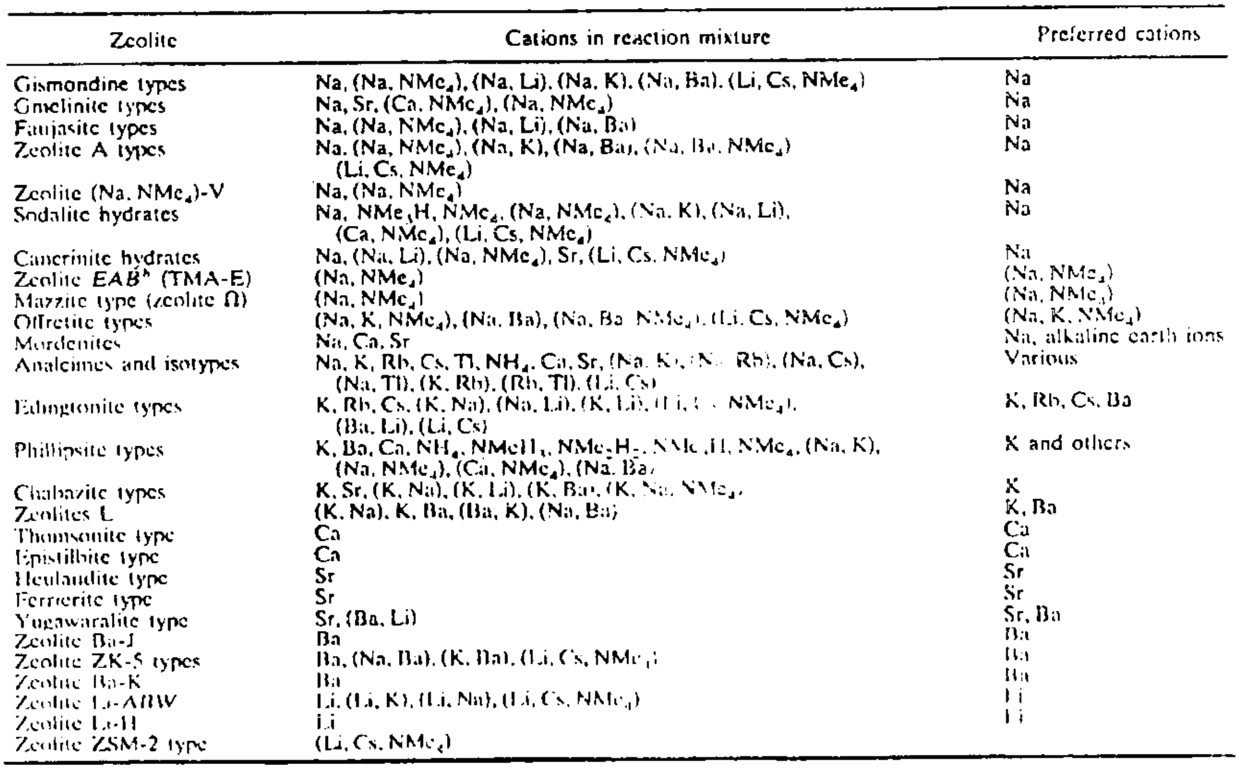
1) Sodalite and cancrinite hydrates, gismondine-types (Na-P), gmelinites, faujasites, and zeolite A are all favored by sodic environments.

2) Mordenite analcime, edingtonite, and phillipsite type zeolites can be synthesized in a variety of cation environments, the later favoring sodic, calcic, and strontium

containing environments.

3) In potassic environments chabazite and zeolite L are favored. Lithic environments favors zeolites Li-ABW and Li-H. Alkaline earth metal cations were constituents in the gel magnama from which thomsonite, epistillbite, heulandite, ferrite, yugawaralite, Ba-J and Ba-K were formed.

4) Certain zeolites require or prefer the presence of two or more cations in the system. Zeolite EAB, offretite and mazzite are examples of zeolites formed in a binary cation system which in this case is sodium plus TMA.[95]



Zeolite	Cations in reaction mixture	Preferred cations
Gismondine types	Na, (Na, NMe$_4$), (Na, Li), (Na, K), (Na, Ba), (Li, Cs, NMe$_4$)	Na
Gmelinite types	Na, Sr, (Ca, NMe$_4$), (Na, NMe$_4$)	Na
Faujasite types	Na, (Na, NMe$_4$), (Na, Li), (Na, Ba)	Na
Zeolite A types	Na, (Na, NMe$_4$), (Na, K), (Na, Ba), (Na, Ba, NMe$_4$) (Li, Cs, NMe$_4$)	Na
Zeolite (Na, NMe$_4$)-V	Na, (Na, NMe$_4$)	Na
Sodalite hydrates	Na, NMe$_3$H, NMe$_4$, (Na, NMe$_4$), (Na, K), (Na, Li), (Ca, NMe$_4$), (Li, Cs, NMe$_4$)	Na
Cancrinite hydrates	Na, (Na, Li), (Na, NMe$_4$), Sr, (Li, Cs, NMe$_4$)	Na
Zeolite *EAB*^{b} (TMA-E)	(Na, NMe$_4$)	(Na, NMe$_4$)
Mazzite type (zeolite Ω)	(Na, NMe$_4$)	(Na, NMe$_4$)
Offretite types	(Na, K, NMe$_4$), (Na, Ba), (Na, Ba, NMe$_4$), (Li, Cs, NMe$_4$)	(Na, K, NMe$_4$)
Mordenites	Na, Ca, Sr	Na, alkaline earth ions
Analcimes and isotypes	Na, K, Rb, Cs, Tl, NH$_4$, Ca, Sr, (Na, K), (Na, Rb), (Na, Cs), (Na, Tl), (K, Rb), (Rb, Tl), (Li, Cs)	Various
Edingtonite types	K, Rb, Cs, (K, Na), (Na, Li), (K, Li), (Li, Cs, NMe$_4$), (Ba, Li), (Li, Cs)	K, Rb, Cs, Ba
Phillipsite types	K, Ba, Ca, NH$_4$, NMeH$_3$, NMe$_2$H$_2$, NMe$_3$H, NMe$_4$, (Na, K), (Na, NMe$_4$), (Ca, NMe$_4$), (Na, Ba)	K and others
Chabazite types	K, Sr, (K, Na), (K, Li), (K, Ba), (K, Na, NMe$_4$)	K
Zeolites L	(K, Na), K, Ba, (Ba, K), (Na, Ba)	K, Ba
Thomsonite type	Ca	Ca
Epistilbite type	Ca	Ca
Heulandite type	Sr	Sr
Ferrerite type	Sr	Sr
Yugawaralite type	Sr, (Ba, Li)	Sr, Ba
Zeolite Ba-J	Ba	Ba
Zeolite ZK-5 types	Ba, (Na, Ba), (K, Ba), (Li, Cs, NMe$_4$)	Ba
Zeolite Ba-K	Ba	Ba
Zeolite Li-ABW	Li, (Li, K), (Li, Na), (Li, Cs, NMe$_4$)	Li
Zeolite Li-H	Li	Li
Zeolite ZSM-2 type	(Li, Cs, NMe$_4$)	

Table 3. Zeolite syntheses in relation to cation environments.[96]

The utilization of quaternary ammonium compounds and their inherent capacity to "template" the formation of zeolite structures had two major impacts to zeolite science. The first of these relates to the larger size of the organic cation. Large cations cannot be placed as close together in the zeolite pore system as their alkali or alkaline earth counterparts. Preservation of charge neutrality, therefore, forced the anionic aluminum sites to be equivalently spaced at larger intervals. This provided the mechanism by which zeolite synthesis could be extended to high silica to alumina ratios ($SiO_2/Al_2O_3 \geqq 20$). Because the thermal and hydrothermal stability of zeolites vary in direct proportion to the silica to alumina ratio ultrastable species could therefore, be formed by direct synthesis. Previous to this, zeolites such as ultrastable Y could only be prepared through a dealuminization procedure.

The second major attribute of the addition of quaternary ammonium and other organic ions to hydrothermal synthesis was that the structure directing functions contributed by these ions could such influence the polymerization procedure that many unique zeolite structure types were observed. Barrer summarized the zeolite structure types which were found to occur in the presence of certain organic bases and in combination of alkali and/or alkaline earth salts with organic bases.[96] The tabularized results he reported are shown in Table 4.

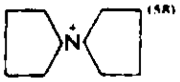
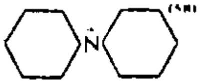
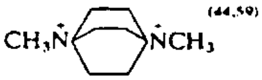
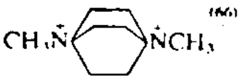
Cations	Zeolite type	Cations	Zeolite type
TMA [49,50]	Sodalite	$Li^+ + Cs^+ + TMA$ [41]	Cancrinite
	Gismondine		Li-ABW
$Na^+ + TMA$ [25,42,51,52,53,54,55]	Sodalite		Zeolite A
	Cancrinite		Edingtonite (K-F)
	Gismondine		Analcime
	Zeolite A (isotypes N-A, α, ZK-4)		Offretite (O)
	Faujasite		Zeolite ZK-5 (KF
	Zeolite TMA-E (*EAB*)		Zeolite ZSM-2
	Mazzite (zeolites Ω, ZSM-4)		Gismondine
	Zeolite (Na, TMA)-V (isotypes N and Z-21)		Sodalite
		$Na^+ + K^+ +$ benzyltrimethylammonium [57]	Erionite
	Zeolite Nu-1 Zeolite Fu-1	$Na^+ +$  (58)	Losod
$Ca^{2+} + TMA$ [44]	Sodalite	$Na^+ +$  (58)	Losod
	Gismondine		
	Gmelinite	$Na^+ +$ neopentyltrimethylammonium [58]	Losod
$Ba^{2+} + TMA$ [56]	Erionite	$Na^+ +$  (44,59)	Zeolite ZK-5 (KF
	Zeolite L		Levynite
$K^+ + Na^+ + TMA$ [23]	Erionite	$Na^+ +$ primary n-alkylamines (C_2 to C_{12}) [60]	Zeolite ZSM-5 (M
	Offretite	$Na^+ +$ isopropylamine, dipropylamine or dibutylamine [60]	Zeolite ZSM-5
	Chabazite		
$Na^+ + NH_2(CH_2)_nNH_2$ [61]	Zeolite ZSM-5 (*MFI*)		
$NH_4^+ +$ tetrapropylammonium [62]	Zeolite ZSM-5		
$Na^+ +$ tetrapropylammonium [60,63]	Zeolite ZSM-5		
$Na^+ +$ tetraethylammonium [64]	Zeolite ZSM-8		
$Na^+ +$ tetrabutylammonium [65]	Zeolite ZSM-11 (*MEL*)		
$Na^+ +$ benzyltriphenylammonium [65]	Zeolite ZSM-11		
$Na^+ +$ tetrabutylphosphonium [65]	Zeolite ZSM-11		
$NH_4^+ +$ tetrabutylammonium [62]	Zeolite ZSM-11		
$K^+ +$  (66)	Zeolite ZSM-10		
$Na^+ + K^+ +$ tetraethylammonium (with $(Cr(OH)_3, Fe(OH)_3, Al(OH)_3)$ [67]	Zeolite ZSM-12		

Table 4. Some zeolite syntheses in presence [96] of organic bases

The structure directing role of a particular quatenary ammonium compound appears to influence the variety of secondary building units present in the hydrothermal magma. The result of this is that a particular organic base does not cause the formation of a specific zeolite structure type but rather a variety of zeolite structure types, which can be compiled from the various combinations of secondary building units. An example of this is evident in systems employing TMA as the quatenary amine. Table 5 shows the various zeolite structure types and secondary building units incorporated in those structure types for systems synthesized in the presence of TMA.[25] It is evident from Table 5 that a large number of zeolites can be formed in the presence of TMA cations. Certain zeolite structures tend to be preferentially crystallized in the presence of certain organic bases. Table 6[25] lists various organic bases which have been employed and the numerous zeolite structure types which have been observed to occur in the presence of the aforementioned bases.

In addition to the structural modifications to aluminosilicate zeolites made possible through the incorporation of structure directing organic bases. Compositional variations have also been explored. The substitution of iron, boron, chrome, and silica for the aluminum of zeolite aluminosilicates has resulted in the formation of ferrosilicates, borosilicates, chromosilicates and silicalite species of the molecular sieve type. The final generation

Cations	Structure-type	Secondary building units
TMA	Gismondine[29]	S4R
	Sodalite[29]	Sodalite cage
Na$^+$ + TMA	Zeolite P[10]	S4R
	Sodalite[10]	Sodalite cage
	S (Gmelinite-type)[10]	Gmelinite cage D6R
	R (Faujasite-type)[10]	D6R, sodalite cage
	Zeolite E[10]	Cancrinite cage D6R
	N-A[2,3] (ZK-4, α)	D4R Sodalite cage
	N-X, N-Y[2,3]	D6R Sodalite cage
	N[33]	?
	Ω[33] (ZSM-4)	Gmelinite cage
	Nu-1[34]	?
	Fu-1[35]	?
	Holdstite[14]	Pentagonal dodecahedron Hexakaidecahedron?
K$^+$ + TMA	Zeolite O[10]	Gmelinite and cancrinite cages D6R
Na$^+$ + K$^+$ + TMA	TMA-'offretite'[36].	Gmelinite and cancrinite cages D6R
	Zeolite Ω[30]	Gmelinite cage
	Zeolite E[30]	Cancrinite cage D6R
	L[30,37]	Cancrinite cage D6R
	G (Chabazite-type)[38]	D6R
Na$^+$ – TMA	ZSM-47[18]	?
Na$^+$ – TMA	ZSM-6[38]	?
Na$^+$ – TMA – TEA	ZSM-39[14]	Pentagonal dodecahedron
Na$^+$ – TMA + n-propylamine	ZSM-39[14]	Hexakaidecahedron
	ZSM-48[10]	ZSM-12?

Table 5. Structure-types synthesized using TMA.[25]

Organic	Structure	Structure type	Reference
TEA	β	?	6
	ZSM-8	ZSM-5	10
	ZSM-12	?	41
	ZSM-20	Faujasite	42
	Mordenite	Mordenite	43
	ZSM-25	?	44
Methyltriethyl-ammonium	ZSM-12	?	45
TPA	ZSM-5	ZSM-5	9
n-Propylamine	ZSM-5	ZSM-5	46
TBA	ZSM-11	ZSM-11	11
Choline	ZSM-38	Ferrierite	47
	ZSM-34	Erionite–offretite	48
	ZSM-43	?	49
	CZH-5	?	50
TMA + TEA	ZSM-39	ZSM-39	39
TMA + n-propylamine	ZSM-39	ZSM-39	39
	ZSM-48	ZSM-12?	40
Pyrrolidine	ZSM-35	Ferrierite	51
	ZSM-21	Ferrierite	47
	ZSM-23	?	52
1,2-Diaminoethane	ZSM-5	ZSM-5	53
	ZSM-21	Ferrierite	47(b)
	ZSM-35	Ferrierite	51
1,3-Diaminopropane	ZSM-35, ZSM-5	Ferrierite, ZSM-5	53, 54
1,4-Diaminobutane	ZSM-35, ZSM-5	Ferrierite, ZSM-5	53, 54
1,5-Diaminopentane	ZSM-5	ZSM-5	53, 55
1,6-Diaminohexane	ZSM-5	ZSM-5	53, 55
1,7-Diaminoheptane	ZSM-11	ZSM-11	56
1,8-Diaminooctane	ZSM-11, ZSM-48	ZSM-11	56, 57
1,9-Diaminononane	ZSM-11	ZSM-11	56
1,10-Diaminodecane	ZSM-11	ZSM-11	56
UDO	ZSM-10	?	58
	ZK-5	?	7
MDO	ZK-20	Levynite	8
MQ	LZ-132	Levynite	59
	Nu-3	Levynite	60
TOA	ZSM-18	?	61
BP	LOSOD	LOSOD	62
Dihexamethylene-triamine	ZSM-30	?	63
Neopentylamine	Mordenite	Mordenite	39

Table 6. Organic zeolite structure relationships.[25]

of molecular sieve materials generated by such substitutions are the organic - $AlPO_4$ molecular sieves. In this family phosphate is substituted for the silica of aluminosilicates resulting in an aluminophosphate molecular sieve. Table 7[25] reveals the aluminophosphate type structures which were synthesized in the presence of the organic bases listed in the Table. More than 20 unique 3-dimensional aluminophosphate molecular sieve structures were formed from the more than 45 amines and quatenary ammonium ions tested.[25]

The purpose for this review of literature relevant to the synthesis of zeolites was to point out two important concepts. The first of these is that zeolite synthesis represents a most complex area of crystallization phenomenon. The myriad of processes simultaneously occurring in the hydrothermal magma have to date prevented any success in attempts to model the overall process. The major aspects of the condensation - polymerization process in which zeolites are formed including those theories which have best stood the test of time have been presented. The second important concept relates to the breadth of this field and the dynamics of its growth over the past decade. The three generations of molecular sieve synthesis were reviewed by Lok et al.[25] The number of combinations possible of the various alkali alkaline earth and organic cations coupled with the number of alternatives of metals which can be incorporated with or substituted for aluminum in the formation of metal silicates

Quaternary ammonium	
TMAOH	$AlPO_4$-20
TEAOH	$AlPO_4$-5, $AlPO_4$-18
TPAOH	$AlPO_4$-5
TBAOH	$AlPO_4$-8
TPeAOH	$AlPO_4$-8
Choline-OH	$AlPO_4$-5, $AlPO_4$-7
DDO	$AlPO_4$-22
Trialkylamines	
Me_3N	$AlPO_4$-21
Et_3N	$AlPO_4$-5
Pr_3N	$AlPO_4$-5
$(CH_2CH_2OH)_3N$	$AlPO_4$-5
Dialkylamines	
n-Pr_2NH	$AlPO_4$-11, $AlPO_4$-31
iso-Pr_2NH	$AlPO_4$-11
n-Bu_2NH	$AlPO_4$-8, $AlPO_4$-11
n-PeNH	$AlPO_4$-8, $AlPO_4$-11
Dicyclohexylamine	$AlPO_4$-5
N-methylcyclohexylamine	$AlPO_4$-5
n-butyldimethylamine	$AlPO_4$-5
Monoalkylamines	
n-$PrNH_2$	$AlPO_4$-21
iso-$PrNH_2$	$AlPO_4$-14
Tert-$BuNH_2$	$AlPO_4$-14
neo-$PeNH_2$	$AlPO_4$-17
CHA	$AlPO_4$-5, $AlPO_4$-17
DMBA	$AlPO_4$-5
Alkylethanolamines	
Diethylethanolamine	$AlPO_4$-5
Aminodiethylethanolamine	$AlPO_4$-5
Dimethylethanolamine	$AlPO_4$-5, $AlPO_4$-21
Methyldiethanolamine	$AlPO_4$-5, $AlPO_4$-7
Methylethanolamine	$AlPO_4$-5, $AlPO_4$-21
Cyclic amines	
Pyrrolidine	$AlPO_4$-21, $AlPO_4$-23
2-picoline	$AlPO_4$-5
3-picoline	$AlPO_4$-5
4-picoline	$AlPO_4$-5
Pyridine	$AlPO_4$-5?
Piperidine	$AlPO_4$-5, $AlPO_4$-17
N-methylpiperidine	$AlPO_4$-5
3-methylpiperidine	$AlPO_4$-5
Diamines	
Dimethylpiperazine	$AlPO_4$-5, $AlPO_4$-21
EDA	$AlPO_4$-12
Ethylene urea	$AlPO_4$-12
Tetramethylethylene diamine	$AlPO_4$-21
Tetramethylpropylene diamine	$AlPO_4$-21
Bicyclicamines	
DABCO	$AlPO_4$-5, $AlPO_4$-7, $AlPO_4$-9
Quinuclidine	$AlPO_4$-7, $AlPO_4$-16, $AlPO_4$-17
Polyamine	
$[(C_{14}H_{32}N_2)Br_2]_x$	$AlPO_4$-26

Table 7. Organic - $AlPO_4$ molecular sieves structure relationships [25]

coupled with those variations possible in the substitution of phosphate for silica are so massive that we have only scratched the surface in the synthesis of molecular sieves. It is possible, if not probable, that the thousands of systems which have not been explored will result in hundreds of new structures of the molecular sieve type. As the number of new zeolite structures crystallized over the past decade is expanding faster than the investigations which adequately reveal the properties and potential uses of these molecular sieves. This field is clearly in its infancy.