See Colour Plate 76.

See also: II/Electrophoresis: Capillary Electrophoresis; Capillary Electrophoresis–Mass Spectrometry; Capillary Electrophoresis–Nuclear Magnetic Resonance. III/Deoxyribonucleic Acid Profiling: Overview.

Further Reading


INTRODUCTION

The primary ingredients of a detergent are the surfactants, whereas builders provide the necessary backbone. The maximum efficiency of surfactants is achieved when the hardness in water is removed. Builders provide this essential function of water softening, primarily by means of ion exchange. Although the performance of surfactants is directly dependent on the efficacy of the builder, the consumer rarely notices the importance of the latter. The development in detergent technology during the last decade has been to improve the property of ion exchange that can lead to enhanced washing power of the detergent, while considering other factors such as environmental concerns and cost. This has been largely due to the development of ion exchange materials and molecular sieves type materials that have been used in detergent formulations as builders. Laundry detergents have a yearly $4.4$ billion market alone in the United States, shared equally by the liquid and powder detergents. A typical detergent composition is shown in Table 1. In today’s detergents, builders constitute about 6–25 wt% of liquid detergents and about 20–55 wt% of powder detergent formulations. Thus builders play a significant role in the detergents market.

Until the early twentieth century, cleaning products were essentially soaps, i.e. sodium salts of natural fatty acids. The surfactants in the first synthetic detergents were short chain alkynaphthalenesulfonates, which were followed by long chain alkylbenzenesulfonates (ABS). ABS were prepared by alkylation of benzene with propylene tetramer followed by sulfonation. Although ABS had very good cleaning properties, they were non-biodegradable and their accumulation in the environment caused foaming in sewage treatment plants and rivers. Hence ABS were replaced by their straight chain analogues, linear alkylarylsulfonates (LAS) in 1965. Surfactants can be broadly classified as anionic, cationic and non-ionic. Today’s detergent formulations contain mainly the anionic surfactants and a lesser amount of non-ionic surfactants. Cationic surfactants have very small market share compared to the anionic and non-ionic materials. The use of non-ions is increasing in liquid detergents as they offer greater stability and formulation flexibility. Whereas the main function of builders is to provide water softening capability and alkalinity, they also serve other important functions as dispersants, antiredeposition agents, and anticorrosion, bleach stabilization and processing aid. Figure 1 illustrates the various important functions played by zeolites in the washing process. Hard water, if not

<table>
<thead>
<tr>
<th>Table 1 Typical detergent composition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ingredient</strong></td>
</tr>
<tr>
<td>Surfactants</td>
</tr>
<tr>
<td>Anionic</td>
</tr>
<tr>
<td>Non-ionic</td>
</tr>
<tr>
<td>Builders</td>
</tr>
<tr>
<td>Zeolite</td>
</tr>
<tr>
<td>Citrate</td>
</tr>
<tr>
<td>Polycarboxylates</td>
</tr>
<tr>
<td>Carbonate</td>
</tr>
<tr>
<td>Sodium silicates</td>
</tr>
<tr>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>Enzymes</td>
</tr>
<tr>
<td>Peroxide bleach</td>
</tr>
<tr>
<td>Polymer stabilizer</td>
</tr>
<tr>
<td>Enzyme stabilizer</td>
</tr>
</tbody>
</table>
softerned by builders, would react with the anionic surfactants and make them insoluble, thereby rendering them inefficient.

**Development of Today’s Builders**

The earliest builders consisted of sodium carbonate and sodium silicate. Although inexpensive, the disadvantage of using these as water softeners is that they form sparingly soluble precipitates that deposit on fabrics and cause incrustation. In the 1950s, these builders were replaced by a complexing agent, sodium diphosphate. However, it was found that diphosphates also had similar shortcomings of forming precipitates. These drawbacks were overcome by introduction of sodium triphosphate (STP) and sodium tripolyphosphate (STPP) in the early 1960s. STP and STPP act as sequestering agents, which trap calcium and magnesium ions in the water very efficiently, forming water-soluble complexes. They also provide other functions like loosening the bond between soil and fabrics and buffering capacity. However, due to their nutrient value, the phosphates caused excessive fertilization and growth of algae in lakes and slow-flowing rivers, a phenomenon more commonly known as eutrophication. Nitrilotriacetic acid was introduced in some countries as an STPP substitute, but was withdrawn after concern about its toxicological properties. In the 1970s, the aluminosilicate zeolite A, was introduced. The aluminosilicates differ from the STPP builders in that they are water insoluble and the mechanism of removal of the calcium and magnesium ions from the water is ion exchange instead of complexation. Usually they are used in conjunction with sodium
carbonate and polycarboxylates or citrates. Today in
countries like the United States, Japan and some Cen-
tral European countries, zeolites have almost com-
pletely replaced phosphates in detergents.

Builders for Water Softening

The percentage of builders in detergents depends on
factors like water hardness, wash temperature and
wash time. The dissolved inorganic salts of calcium
and magnesium impart hardness to water. For the
washing process to proceed effectively, it is important
to remove the hardness ions in the water and replace
them with sodium ions, rendering softness to the
water. Thus the builder must exhibit high capacity for
selective removal of these ions from water. The
hardness level of water is different in different coun-
tries, leading to slight differences in detergent for-
mulations. For example, water in Japan has relatively
low hardness, typically less than 90 ppm CaCO₃,
whereas in the United States it is of low-to-intermedi-
ate hardness. The water in Western Europe has very
high hardness (greater than 270 ppm CaCO₃ in 42% of
the region) (Figure 2).

Phosphates ruled the detergent world until the in-
troduction of inorganic builders. They are still widely
used in a significant part of the world, e.g. Eastern
Europe, Southern Asia, Africa, Australia and Latin
America. We will discuss the phosphates briefly before
going into detail on zeolites as detergent builders. We
will also include some other inorganic silicate builders
that may have impact on the detergent industry of the
future. The main focus will be on the ion exchange
properties of the materials, particularly zeolites.

Phosphates

Phosphates are excellent chelating agents and work
by a sequestering mechanism, i.e. as previously men-
tioned, by trapping the calcium and magnesium ions
and forming water-soluble complexes. A chelating
agent possesses multiple sites with lone-pair electrons
that are available to interact with corresponding elec-
tron-deficient coordination sites on metal ions like
Ca²⁺ and Mg²⁺ ions. The chelation is reversible and
the strength of chelation is indicated by the equilib-
rium constant, also known as a stability constant.
The chelation proceeds in a stepwise manner between
metal ions, I, and chelating agent, C. For a divalent
cation it is a two step process given as:

\[
C + I \rightleftharpoons CI \quad K_1 = \frac{[CI]}{[C][I]} \tag{1}
\]

\[
CI + C \rightleftharpoons C_2I \quad K_2 = \frac{[C_2I]}{[CI][C]} \tag{2}
\]

The overall stability constant, \(K\), is the product of the
stability constants for each step \((K_1 \cdot K_2)\). The log
\(K\) values for stability constants of polyphosphates for
binding of Ca²⁺ and Mg²⁺ ions are fairly high (5.2
and 5.7, respectively) at > pH 9. Hence, under nor-
mal washing conditions, STPP shows excellent se-
questering capacity for both calcium and magnesium
ions in solution. The binding capacity of STPP is
fairly high, 158 mg CaO g⁻¹ at 20°C and 113 mg
CaO g⁻¹ at 90°C. As the phosphates and the calcium
and magnesium chelates formed are water soluble,
the removal is very fast. In addition to water soften-
ing, after removal of the soil, they offer the function
of suspending soil by electrostatic repulsion. They do
not provide as high buffering capacity/alkalinity as
sodium carbonate or sodium silicate. The low capa-
city of STPP to absorb non-ionic surfactants limits its
use in the new compact detergents where consider-
able amounts of the latter are used. Efficiency and
low cost are the biggest advantages of STPP. In many
countries, where phosphates are not banned for en-
vironmental reasons, STPP is still the major player in
the detergent builder market.

Zeolite A

The need for a substitute for STPP led to development
of zeolites as detergent builders. Among the aluminosilicates, zeolite A is most preferred because of
its high ion exchange capacity (170 mg CaO g⁻¹)
and low cost of manufacturing. As opposed to chela-
tion by STPP, zeolite A removes hardness of water by
means of ion exchange, a process we will discuss in
more detail in further sections. Another important
difference that zeolite A exhibits from STPP is the
selectivity for removal of divalent ions. STPP simply
chelates both the Ca²⁺ and Mg²⁺ ions non-selective-
lly from water. Zeolite A being a molecular sieve,
shows higher selectivity toward Ca²⁺ ions over
Mg²⁺ ions due to high hydration of Mg²⁺ ions. This
is advantageous, as studies have indicated that the
presence of a certain level of Mg²⁺ ions in fact im-
proves the detergent performance. The ion exchange
kinetics are strongly dependent on the wash tempera-
ture, and hence zeolites tend to be more effective at
higher wash temperatures.

In addition to these properties, zeolite A offers
other functionality to the detergents. It shows adsorp-
tion characteristics that are pH dependent. At pH 10,
which is the pH during a normal wash, there is
minimal adsorption of anionic or cationic surfac-
tants, leaving them available for the soil removal. As
the pH drops during the rinse cycle, the adsorption
tendency of zeolites increases, leading to adsorption
of colloidal dispersed soil particles by hetero-
coagulation. Thus zeolites act as anti-redeposition
agents, minimizing fabric incrustation. In a mixed wash of coloured and white clothes, zeolite A suppresses the dye transfer from coloured to whites prohibiting staining. Zeolite A will ion-exchange trace metal ions such as Cu$^{2+}$, Zn$^{2+}$, etc. as well as remove them by the surface deposition of basic salts. As these metal ions are often responsible for decomposition of bleach, use of zeolite A leads to an increase in the bleach performance. The only major shortcoming of zeolite A over STPP is the slower rate of ion exchange at low temperatures. This is often overcome by use of a soluble complexation agent, like citrate or a polycarboxylate. The complexation agent acts catalytically. The soluble complexation agent binds reversibly with the Ca$^{2+}$ ions of the precipitate (either by ion exchange or by chelation), making them soluble. These solubilized Ca$^{2+}$ ions are then readily exchanged by zeolite, making the complexation agent free for more transport. Usually about 2–8% of polycarboxylates are used as co-builders to enhance the performance of zeolite A.

**Zeolite MAP**

Other than zeolite A, zeolite P and in a few cases zeolite X are the only important zeolites that have been considered for detergent applications. Zeolite MAP, the maximum aluminium P which is a synthetic gismondine, is an improved version of zeolite P. In addition to the high binding capacity (~160 mg CaO g$^{-1}$), zeolite MAP has several distinct advantages over zeolite A. First, it enhances the stability of the sensitive and environment friendly bleaching agent, sodium percarbonate. Sodium percarbonate is sensitive to moisture present in the detergent formulation. The low mobility of water in the zeolite MAP structure imparts more stability to the water-sensitive bleach. Secondly, it exchanges calcium ions more rapidly and more selectively. Especially at low temperatures, the ion exchange kinetics are considerably faster than those of zeolite A. Finally, zeolite P exhibits higher liquid carrying capacity, e.g., for carrying non-ionic liquid surfactants, allowing free-flowing powder at higher liquid loading. With all these advantages, zeolite MAP is replacing zeolite A in more and more detergent formulations.

**δ-Disilicate**

Amorphous sodium silicates were among the earliest compounds that were used as builders. These compounds remove the water hardness by sequestering Ca$^{2+}$ and Mg$^{2+}$ ions, but form insoluble precipitates. Therefore amorphous silicates are used only in small proportions (0–3 wt%) mostly as a co-builder in the zeolite A builder systems. Here they provide a source of alkalinity and show selectivity towards Mg$^{2+}$ ions. In contrast with amorphous silicates, layered silicates are crystalline and work by an ion exchange mechanism. These are polymeric crystalline materials, which have a layered structure. The monovalent metal ions (Na$^+$) in the interstices can be easily exchanged with divalent ions in solution and are responsible for the ion exchange capacity of the material. δ-Disilicate, which has the empirical formula Na$_2$Si$_2$O$_5$, is an anhydrous alkali silicate that is most important for its ion exchange properties. The formation of δ-disilicate is not thermodynamically favoured over the corresponding x- and β-phases; hence production requires a specialized high-temperature crystallization process. The δ-disilicate has a very regular structure (Figure 3) as opposed to the amorphous silicates.

The δ-disilicate does not have a thermodynamically stable structure in aqueous media. It disintegrates slowly into monomeric sodium silicate, commonly known as water glass solution but this process is much slower than the ion exchange kinetics. The hardness ions of water replace the sodium ions in the δ-disilicate interstices and give stability to the framework. During the wash cycle, the pH of the solution is generally maintained at a high level, and the ion-exchanged disilicate is stable. As the pH drops in the rinsing cycle, the Ca$^{2+}$ and Mg$^{2+}$ ions are released as silicates and the disilicate disintegrates into the wash water. The size of these insoluble calcium and magnesium silicates formed is small and does not cause incrustation.

The δ-disilicate is characterized further by its multi-functionality in detergent building. It is a very good source of alkalinity and has the high buffering capacity required for the washing process. It exhibits high adsorption capacity for the non-ionic surfactants. Its mild desiccant properties and ability to combine with heavy metal ions make it compatible with unstable bleaches like sodium percarbonate. This imparts good storage stability to the detergent formulation and allows the use of environmentally friendly bleaches. Once again, due to cost considerations, δ-disilicate cannot completely replace zeolite A at this point, but it certainly has great potential to act as a supplement to the zeolite A systems.

**Figure 3** Polymetric structure of δ-disilicate. ● sodium; ▼ SiO₄ tetrahedra.
Zeolites: Synthesis, Structure and Ion Exchange

Aluminosilicates are denoted by the general formula $M_{x/n}(AlO_2)_x \cdot (SiO_2)_y \cdot wH_2O$ where $M$ is the cation of valence $n$, $w$ is the number of water molecules and $y/x$ usually has values of 1–5 depending upon the structure. The sum $(x + y)$ represents the total number of tetrahedra in a unit cell and the formula within parentheses represents the framework composition. The cation $M$, which functions as a charge balance in various solids, can be exchanged depending upon the equilibrium constant and this property finds use in several applications including catalysis, wastewater treatment, treatment of radioactive waste and in our context, detergents.

There are around 80 species of natural zeolitic minerals and about 150 types of synthetic zeolites. Of these, only a few have practical significance and a very few among them have importance in detergents. The synthetic zeolites, mainly zeolite A, and to some extent zeolite P and zeolite X are used in detergent formulations, mainly as ion exchangers.

Synthesis of Zeolites

Zeolites are normally synthesized in the sodium form. Most of the crystalline sodium zeolite is produced by crystallization from sodium aluminosilicate gels at a temperature below 150°C. The properties of the product zeolite depend greatly on the gel preparation and it is therefore a key step in zeolite preparation.

In a typical process for the synthesis of zeolite A, sodium silicate and sodium aluminate solutions are first mixed together. The resulting aluminosilicate is precipitated and crystallized hydrothermally to obtain the zeolite. Seed crystals of zeolite A are often used to obtain crystalline zeolite A in high selectivity. The crystallized zeolite is then washed, filtered and dried. The usual gel preparation temperature is 50–80°C and the temperature during crystallization is slightly higher 80–90°C. The time required for gel preparation may vary from 0.5 to 1.5 h, whereas 1–2 h is necessary for the crystallization. Optimizing the following variables controls the product quality: mixing sequence, speed of agitation, seed crystals, aging time and temperature. The desired properties for optimum detergent application are small particle size (typically < 10 μm), narrow particle size range, poor adhesive capacity (achieved by having crystalline material), high calcium binding power and good wettability.

Structure of Zeolite A

The structure of the crystallized zeolite A is quite unique. It is classified as a type 3 zeolite, for the interconnecting system is a double four-ring or an octahedron. The structure can be described in terms of two types of polyhedra; one is a simple cubic arrangement of octahedron or $z$-cage and the other is a truncated octahedron of 24-hedron or $\beta$-cage as shown in Figure 4. The cubic $z$-cages $(Al_4Si_4O_{16})$ are placed in the centres of the edges of a cube in the truncated octahedra. These $z$-cages connect the $\beta$-cages, creating a three-dimensional structure having pores of size 4.2 Å. Each corner of the cube ($z$-cage) is occupied by the truncated octahedra ($\beta$-cage) enclosing a cavity with a free diameter of 6.6 Å. The centre of the unit cell is a large cavity, which has a free diameter of 11.4 Å. A unit cell of zeolite A contains 24 tetrahedra; 12 each of AlO4 and SiO4. A fully hydrated zeolite A contains 27 water molecules per unit cell. The theoretical Si/Al ratio in zeolite A is 1 but in many preparations the Si/Al ratio is slightly less than 1.

Structure of Zeolite MAP (Synthetic Gismondine)

Zeolite MAP is a type 1 zeolite, meaning that the interconnecting units are single four-ring units (also known as S4R). The eight-membered rings are interconnected by S4R units as shown in Figure 5. The interconnecting chains run parallel to both X- and Y-axes, creating a three-dimensional channel system. The mean free openings of the pores are 3.1 × 4.5 Å and 2.8 × 4.8 Å. The structure is somewhat flexible, as the connecting S4R units are two-dimensional. Due to this flexibility, slight structural differences are observed by dehydration of the zeolite. MAP has a Si/Al ratio of 1. This high aluminium content leads to a higher negative charge in the crystal lattice and therefore it has the highest theoretical ion exchange capacity.

Theory of Ion Exchange in Zeolites

The ion exchange process may be represented by the following equation:

$$xB_{(s)}^{+} + yA_{(s)}^{+} \leftrightarrow xB_{(s)}^{y+} + yA_{(s)}^{y+}$$  \[3\]
Figure 5  Structure of zeolite MAP (synthetic gismondine).

where \( x \) and \( y \) are the charges of cations A and B and the subscripts \( z \) and \( s \) refer to the zeolite and solution, respectively. The equivalent fractions of the exchanging cation in the solution and zeolite are defined by:

\[
A_s = \frac{m_A^s}{x m_A^s + y m_B^s}
\]

\[
A_z = \frac{\text{number equivalent of exchanging cation A}}{\text{total equivalent of cations in the zeolite}}
\]

where \( m_A^s \) and \( m_B^s \) are the molalities of the ions A and B respectively, in the equilibrium solution; also \( (A_s + B_s) = 1 \) and \( (A_z + B_z) = 1 \). The ion exchange isotherm is a plot of \( A_z \) as a function of \( A_s \) at a given total concentration in the equilibrium solution and at constant temperature. The preference of a zeolite for one of the two ions is expressed by the separation factor, \( x_A^B \), defined by:

\[
x_A^B = \frac{A_B^z}{A_A^z}
\]

If the ions are equal valence \( (x = y) \) then:

\[
K_A^B = x_A^B
\]

If \( x \neq y \), then:

\[
[x_A^B] = K_A^B \left[ \frac{A_A^z}{A_A^s} \right]^{x-y}
\]

The corrected selectivity coefficient \( K_A^B \) includes a correction for the activity coefficient of the ions in the equilibrium:

\[
K_A^B = \frac{A_B^s A_A^z}{B_A^z A_B^s}
\]

where \( \gamma_A \) and \( \gamma_B \) are mean ionic activity coefficients of the ions in solution.

**Ion Exchange by Zeolites**

The cation exchange properties of zeolites were observed some one hundred years ago. It was this property and the ease with which it was happening that led to an early interest in ion exchange materials for use as water-softening agents. The cation exchange behaviour of zeolites depends upon the following:

- Si/Al ratio;
- nature of the cation species, cation size (both anhydrous and hydrated) and cation charge;
- temperature;
- concentration of the cation species in solution;
- anion species associated with the cation in solution;
- solvent (most of the exchange is carried out in aqueous solution although some work has been done in organic solvents); and the
- structural characteristic of the particular zeolite.

The cations that contribute towards the hardness of water are calcium and magnesium ions. It is therefore evident that the property of zeolite should be such that it has a large ion exchange capacity and should be selective towards the exchange of these ions. Zeolite A, zeolite MAP, and to a certain extent zeolite X, have been shown to exhibit this property and consequently are the favourable candidates of choice towards being incorporated in the detergent formulation.

Ion exchange in zeolite A seems to be possible only with univalent and divalent counterions. Exchange of higher valence ions fails with zeolite A. The order of decreasing selectivity for univalent ions in zeolite A is as follows: Ag > Ti > Na > K > NH₄ > Rb > Li > Cs. For divalent ions, the order of decreasing selectivity is: Zn > Sr > Ba > Ca > Co > Ni > Cd > Hg > Mg.

The ion exchange kinetics depends on the zeolite structure and cation properties. As zeolite A has
a small pore diameter of 4.1 Å, the exchange of ions like Mg$^{2+}$ is slow due to its high hydration at low temperatures. At higher temperatures, the hydration shell is reduced, making the effective ion size smaller. Thus the diffusion kinetics and in effect, exchange kinetics of Mg$^{2+}$, are enhanced at higher temperature. Ions like Ca$^{2+}$ diffuse easily at room temperatures as they exhibit smaller hydration. This sieving action is responsible for the selectivity of zeolite A towards Ca$^{2+}$ ions as compared to Mg$^{2+}$ ions.

Zeolite MAP is more selective than zeolite A towards calcium exchange. The plot of calcium selectivity constant log $K$ versus the calcium loading (Kielland plot, Figure 6) shows peculiar behaviour for zeolite MAP. For zeolite A, as expected, the selectivity constant decreases with increase in calcium loading. In case of zeolite MAP, the opposite behaviour is observed, which indicates a cooperative exchange process. The insertion of some calcium ions in the structure causes a structural change in zeolite MAP, predisposing the framework to accept further calcium ions more readily. Its flexible structure, which was explained earlier, allows this phenomenon.

The ultimate base exchange capacity of a zeolite depends on the Si/Al ratio; it increases as the Si/Al ratio approaches unity (Table 2). This is the primary reason for the dominance of zeolite A among other zeolites as far as builder applications are concerned. The table indicates that the exchange capacity of zeolite MAP approaches that of zeolite A as the Si/Al ratio approaches unity. The exchange kinetics and total exchange capacity are also dependent on the Si/Al ratio. Table 2 shows comparison of time required to reduce concentration of 2 mmol L$^{-1}$ Ca$^{2+}$ ions in a solution to the level specified. Although zeolite MAP with a Si/Al ratio approaching unity shows high capacity and faster kinetics, it becomes increasingly difficult to prepare an aluminosilicate material with a zeolite MAP structure at lower Si/Al ratios. In many cases the measured exchange capacities deviate from theoretical values due to impurities or variation in chemical composition. The specific exchange capacity also varies with the exchange cation.

**Environmental Aspects of Detergent Building**

STPP is a very efficient and cost-effective builder. As it is water soluble, and the hardness removal is by chelation, the process is very fast even at low temperatures.Irrespective of these advantages, many countries have stopped using STPP in detergents as it causes environmental problems. Phosphates, being essential nutrients, cause excessive fertilization in stagnant waters and slow-flowing rivers, which leads to excessive growth of algae. These problems can be avoided by employing a wastewater treatment system that removes the phosphorus. However, as aluminosilicates made an entry, it was preferred to limit the use of phosphorus compounds in detergents. Aluminosilicates are environment friendly materials. Aluminosilicates are produced by combining silica and alumina (from bauxite ore). After use in detergents, they are returned to the environment, where they decompose back to silica and alumina. The only concern about the aluminosilicates arises from their insoluble nature. There are some reports of zeolites leading to enhanced sludge in the wastewater. As long as the particles are larger than 1 μm, they can be

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**Figure 6** Kieelland plots for zeolite MAP and zeolite A calcium-sodium exchange, 25°C, 0.1 mol L$^{-1}$ solution.

**Table 2** Ion exchange capacity and rate of removal of Ca$^{2+}$ from aqueous solutions by zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Effective ion exchange capacity (mg CaO g$^{-1}$ zeolite)</th>
<th>*Time required to achieve 0.5 mmol L$^{-1}$ Ca$^{2+}$ (s)</th>
<th>*Time required to achieve 0.01 mmol L$^{-1}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite MAP</td>
<td>1.46</td>
<td>123</td>
<td>1</td>
<td>Ineffective</td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>146</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.12</td>
<td>155</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1.005</td>
<td>159</td>
<td>2</td>
<td>11.5</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>1.0</td>
<td>152</td>
<td>14</td>
<td>95</td>
</tr>
</tbody>
</table>

*Initial Ca$^{2+}$ concentration 2 mmol L$^{-1}$, 1.48 g dm$^{-3}$ zeolite, 25°C.
easily removed by sedimentation. The δ-disilicate, though insoluble during the wash process, dissolves when the solution becomes dilute during the rinse cycle.

**Future Trends**

The builder development for detergents is now more and more driven by environmental issues. Zeolite A was a major breakthrough over the conventional phosphates. An ideal builder would be one combining the efficacy of STPP and the environment friendly nature of (alumino) silicates. At this point, combination of builders and co-builders is the way detergents are being formulated. The new materials zeolite MAP and δ-disilicate, are the future; though more efficient, they still have to cross the cost barrier to become major players in the detergent industry. As efforts are constantly underway to come up with more and more efficient builder and detergent formulations, the challenge is to achieve compatibility, environment friendliness, and low production cost, all at the same time.


**Further Reading**


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**DNA**

*See III/DEOXYRIBONUCLEIC ACID PROFILING: Overview; Capillary Electrophoresis*

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**DRUGS AND METABOLITES**

**Liquid Chromatography–Mass Spectrometry**

R. P. W. Scott, Avon, CT, USA

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The tandem analytical instrument, comprising a liquid chromatograph and a mass spectrometer is ideally suited for identifying drug metabolites and for following their metabolic pathways. The segregation of each drug metabolite from the sample matrix, and its subsequent identification, firstly requires a very efficient separation technique. As the metabolites are often chemically very similar to the parent drug, this exigency is adroitly furnished by the liquid chromatography (LC) column (usually microbore) packed with very small particles. Secondly, the materials of interest are inevitably present in the biological system in very small quantities and thus, despite the use of sample concentrating techniques, a very sensitive detection technique is essential. The required high sensitivity is effectively supplied by the ion multiplier of the mass spectrometer sensor. Thirdly, in order to identify the individual metabolites, structural information is required which must be highly specific and contain adequate detail at high resolution. Such data is readily provided by the mass spectrum of each eluted solute, which can either be compared with standard spectra or identified by using well-established interpretation procedures. In some cases, the liquid chromatograph can be coupled to a MS/MS instrument that will provide mass spectra of each fragment ion, from each eluted solute, should more detailed information be needed.

For the effective use of LC/MS, special sample preparation techniques are necessary and suitable LC/MS interfaces should be employed. Both these subjects are discussed in detail in other parts of the Encyclopedia, and it will be sufficient here to give the sample preparation details of each typical application that is discussed. In addition, the general interface systems that are used, such as thermospray, electrospray, atmospheric pressure chemical ionization devices, transport interfaces etc., are also described in