Linear Alkylbenzene

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Linear alkylbenzene (LAB) was introduced in the mid-1960s as a raw material for cleaning products. Since then, continuing and explosive research on its biodegradation and on its environmental and human toxicity has been performed. The efficiency of linear alkylbenzene sulfonate as surfactant is clearly established, and it is one of the safest and most cost-effective products in widespread commercial use. The aim of the present paper is to survey the most important developments and understandings of the chemistry of LAB production and of its physical and environmental properties. The expected consequence of this analytical survey is to envisage the continuous challenges for the detergents industry in catalytic production of LAB, better control of selectivity, replacement of corrosive and mineral liquid acid catalyst by heterogeneous acid catalyst and the maintenance of competitiveness of LAB with respect to natural alcohols.

KEY WORDS: Acid strength, alkylation, alkylbenzene, biodegradability, detergency, Friedel Crafts catalyst, LAB, LAS, zeolites.

The alkylbenzenes are widely used as raw materials for detergents. Two kinds of alkylates have gained industrial importance as intermediates for the production of anionic surfactants by subsequent processing to alkylarylsulfonates: The branched-chain type, referred to as "hard detergent alkylate" [known after sulfonation as ABS (alkylbenzene sulfonate), BAS (branched alkylbenzene sulfonate), tetrapropylene benzene sulfonate or dodecylbenzene sulfonate], which had a rapid growth for ten years until 1965. Its use as a raw material for domestic detergents was discontinued because of foaming in rivers and at sewage-treatment plants, caused by the low rate of biodegradation. The "linear detergent alkylates" (or soft detergent alkylates), have replaced ABS wherever high consumption and/or regulations require a more rapid and complete degradation. Replacement of ABS has taken place in almost all countries. The propylene tetramer type is still manufactured for use in countries that have not reached a high consumption and where accumulation in the environment has not yet been legislated. It is also used for specialized purposes such as agricultural emulsifiers. "Linear alkylbenzenes" are known as LAB, and after conversion by sulfonation to "linear alkylbenzenesulfonates," they are called LAS. Production of LAB, together with the detergent alcohol, has experienced continued growth as a result of increased per-capita consumption of detergents, changes in detergent formulations and the proven biodegradability of these materials. LAB is derived exclusively from benzene and petroleum- or natural gas-based feedstocks, in general paraffins derived from kerosene. Olefins derived from ethylene are sometimes used in place of paraffins. The market of LAB is expected to increase faster in developing countries as a result of the increased per-capita surfactant use and the replacement of laundry bar soap and nonbiodegradable alkylbenzenes. The worldwide supply and demand of LAB are shown in Table 1 and Figure 1 (source: DETEN Química S.A., Bahia, Brazil).

This paper presents a detailed review on LAB, with special emphasis on the chemistry of alkylation, current technologies, biodegradability, analytical methods, isomer distribution and its influence on detergent performance. Because homogeneous acid catalysts are sources of pollution, industrial hazard and corrosion, a good deal of effort has been put into research and development to find noncorrosive solid catalysts with acid properties. The last part of this paper is focused on the utilization of heterogeneous catalysis in the alkylation reaction for LAB production.

THE CHEMISTRY OF ALKYLATION FOR LAB FORMATION

The generally accepted mechanism for alkylation of arenes with alkenes involves interaction of the alkene with the

TABLE 1

Worldwide Linear Alkylbenzene Capacity/Demand

	1987 (kt/y)[a]		1992 (kt/y)		1995 (estimated) (kt/y)	
	Capacity	Demand	Capacity	Demand	Capacity	Demand
North America	305	287	384	337	380	520
South America	188	128	252	159	257	186
Western Europe	695	337	575	420	575	405
Asia/Pacific	490	492	709	675	968	932
Africa	85	52	120	92	120	115
Eastern Bloc	302	218	252	190	252	206
Total	2065	1514	2292	1873	2552	2364

[a] Kilo ton per year.

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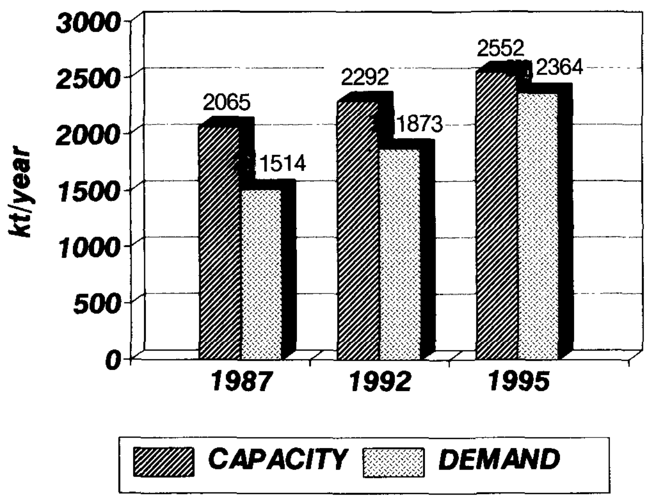

FIG. 1. Worldwide linear alkylbenzene (LAB) capacity/demand; kt, kilo ton.

acid catalyst to form an alkylcarbenium ion, a corresponding ion pair or polarized complex (1). The alkylcarbenium ion undergoes a rapid secondary to secondary rearrangement in varying degrees, followed by attack on the nucleus of the arenes in a rate-determining step to form the product (2–4). This mechanism can be represented, as shown in Figure 2, when HF (fluoridic acid) is used as a catalyst.

Side reactions can and do take place: Dimerization of the olefin, alkylation of this dimer, dialkylation of benzene, possible diphenylation of the olefin or chloroparaffin and cyclo-alkylation of the benzene (5). Thus, during the reaction, in addition to formation of the LAB, some by-products will be found. These include diphenyl alkane and dialkylbenzene, or from cyclo-alkylation, 1,3-dialkylindanes and 1,4-dialkyltetralins.

These heavy by-products are separated from LAB by distillation, and they are called "heavy alkylate." However, it is sometimes difficult to separate dialkylindanes, dialkyltetralins and branched alkylbenzenes from LAB because they have almost the same molecular weight. The heavy alkylate from chloroparaffins is similar to that from the olefin-based product and is sulfonated by either oleum or SO_3 to produce synthetic petroleum sulfonates. The natural petroleum sulfonates are produced as by-products in the production of white oils, and this "synthetic" variety is functionally almost identical, although not chemically identical. More recently, heavy alkylates have been found useful in their own right and not merely for use as substitutes for the older petroleum sulfonates. The heavy alkylates can only be partially sulfonated because here, sulfonation takes place almost invariably in the *para* position, and when it is blocked, no sulfonation occurs. The heavy alkylate normally contains 60–70% of sulfonated matter. Sulfonation can be carried out to various stages, and the type of heavy alkylate is chosen to give a final product of the desired characteristics. The choice depends on the specific balance between hydrophilic and hydrophobic characteristics required for a given application. For emulsification, products of lower- or middle-range molecular weight (more hydrophilic) are usually preferred, whereas higher-molecular weight materials are more suitable for oil system dispersal applications. The sodium salts of the heavy alkylated sulfonates are used as emulsifiers, wetting agents and dry-cleaning additives. The alkaline earth salts (Ca, Ba and Mg) are used in lubricants and greases, and their "over-based" varieties (adding surplus hydroxide or carbonate to neutralize in such a way that the base remains in colloidal suspension) are used as rust preventatives (5,6).

Secondary-to-secondary rearrangement of the alkylating agent occurs with linear alkenes, resulting in the formation of isomeric alkylcarbenium ions, which, after reaction with benzene, yield isomeric phenylalkanes. There are two major catalysts for the industrial production of LAB: $AlCl_3$ and HF. These two catalysts give different phenyl isomer distributions in the LAB produced. The $AlCl_3$ catalyst gives what is called the high 2-phenyl product: 30% 2-phenyl isomer, 20% 3-phenyl isomer, and gradually decreasing amounts (to 15–16%) of the 5- and 6-phenyl isomer. With the HF catalyst, there is a flatter distribution, with all phenyl isomers present at about the same level, approximately between 17–20%. This LAB is called low 2-phenyl product. Almost two-thirds of LAB comes from the HF process. Most of the alkylate in liquid products is probably from the $AlCl_3$ process; the situation is just the reverse in powder products. The typical composition of commercial LAB is presented in Table 2. The differences in composition markedly affect formulating properties of LAS in liquid detergents, particularly solubility and viscosity.

A large number of investigations have been performed to elucidate the most important controlling factors. As a consequence of this exhaustive work, many interesting aspects of alkylation by linear alkenes and secondary derivatives were revealed.

Alul (7) has performed many alkylation experiments to form straight-chain alkylbenzenes, with HF and $AlCl_3$ as acid catalysts and with α-olefins in the range C_{12} to C_{18}, as alkylating agents. The following reaction mixtures were employed: (i) anhydrous HF with the following molar ratios: benzene/olefin = 12.3, HF/olefin = 10. Under these

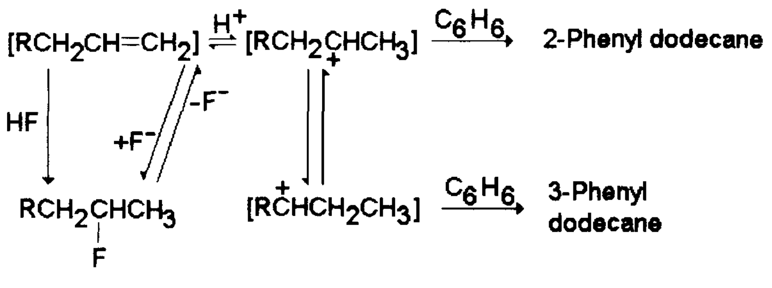

FIG. 2. Alkylation reaction.

TABLE 2

Typical Composition (wt%) of Commercial Linear Alkylbenzene Products[a]

	Catalyst								
	HF	$AlCl_3$	$AlCl_3$	HF	$AlCl_3$	HF	$AlCl_3$	HF	$AlCl_3$
	Alkylating agent								
	a	b	a	a	—	a	—	b	a
	Reference								
	14	14	14	83	83	71	71	72	72
n-Alkylbenzenes	93	88	98	99.5	83.8	92.2	82.9	—	—
2-Phenyl alkanes	18	29	29	19	30	—	—	17	28.8
Dialkyltetralins	0.5	9	0.5	0.46	16.2	0.45	13.9	0.1	11.7
Branched alkylates	—	—	—	—	—	7.04	1.83	2.5	1.2
Heavy alkylates	—	—	—	—	—	0.13	—	0.3	—
Molecular weight	240	241	240	242.3	240.3	241.9	240	241	244

[a] Alkylating agent; a = *n*-olefin; b = chloroparaffin; HF, fluoridic acid.

conditions, there is a separate liquid HF phase. (ii) Anhydrous HF with the following ratios: benzene/olefin = 13, HF/olefin = 5 (no separate liquid HF phase occurs). Under this condition, the reaction is accomplished in a limited amount of HF, which gives a total pressure slightly below the equilibrium pressure of a mixture of benzene and HF. So the HF catalyst in the system is present either in benzene solution or in the vapor phase. (iii) The same condition as 1, but in the presence of *n*-hexane. (iv) The same condition as 2, but in the presence of *n*-hexane. (v) $AlCl_3$, with ratios of benzene/olefin = 10 and $AlCl_3$/olefin = 0.12 at temperatures of 35–37°C and 0–5°C.

The generally accepted mechanism for alkylation of benzene with olefins in the presence of Friedel-Craft catalysts involves interaction of the olefin with the acid catalyst to form an alkylcarbenium ion. This alkylcarbenium ion undergoes rapid isomerization in varying degrees and finally attacks benzene, in what is considered to be the rate-determining step, to form the products (2–4).

The alkylation reaction may occur in the two liquid phases: (i) organic phase, which consists of benzene, α-olefins and HF; the solubility of HF in the organic phase, though limited, is apparently sufficient to allow formation of the intermediate alkylcarbenium ions and subsequent alkylation of benzene; (ii) inorganic phase, consisted of liquid HF, solubilized α-olefins and benzene. As mentioned above, there are two phases in mixture 1 but only an organic phase in mixture 2.

In the presence of a separate liquid HF phase (mixture 1), the amount of the 2-phenyl isomers rises from 25 to 32% as the chainlength increases from C_{12} to C_{18}. As the chainlength increases, the olefins become less soluble in HF, and greater amounts are converted into alkylcarbenium ions in the organic phase, where the concentration of benzene is much greater than in the inorganic HF phase. This results in a higher relative alkylation rate and lower isomerization across the chain as the chain increases, (32% for 2-phenyl octadecane and 25% for 2-phenyl dodecane).

In the absence of a separate liquid HF phase (mixture 2), the amount of 2-phenyl produced by the alkylation reaction is larger than under the experimental conditions where a separate liquid HF phase exists because almost all the alkylcarbenium ions, once formed, react immediately with benzene (due to the high concentration of aromatics) before the hydride shift reaction in the α- olefins carbenium ions occurs.

The dilution of the reactants with *n*-hexane in reaction mixtures 3 and 4 increases the amount of internal isomers because, in the presence of the solvent, the alkylation step is apparently slowed down sufficiently to allow the intermediate alkylcarbenium ions to isomerize to the equilibrium distribution before they react with benzene. For the same reason, the alkylation of benzene with 1-dodecene and *trans*-6-dodecene diluted in *n*-hexane and in a separated HF phase (mixture 3) gives the same isomer distribution, indicating that under such conditions the position of the double bond is not critical. In general, low alkylation temperatures, the presence of a separated liquid catalyst phase and the dilution of the reactants with normal paraffins result in the greatest amounts of the internal secondary alkylbenzenes and the smallest amounts of the 2-phenyl isomers.

With $AlCl_3$ as a catalyst, the alkylation reaction proceeds in the organic phase, which contains the dissolved $AlCl_3$. In this case, the alkylation reaction competes effectively with the migration of the double bond across the chain, so that some of the initial alkylcarbenium ions form alkylate benzene without undergoing isomerization, giving a high concentration of the 2-phenyl isomers (32–44% of 2-phenyl dodecane). In addition, evidence has been obtained that the 2-alkylcarbenium ions may react faster than the internal alkylcarbenium ions because of steric factors. The isomerization reaction can also be slowed down by the presence of $AlCl_4^-$ ions in the ions pairs, compared to the more mobile F^- ions in HF alkylation.

With HF as a catalyst, isomerization of the phenyl alkane was not observed after the alkylation reaction. On the other hand, $AlCl_3$ alkylation is accompanied by product isomerization at 35°C. The latter is suppressed at 0°C, and the isomer distribution of the product differs substantially from that obtained at 35°C, which has a larger concentration of internal isomers.

Alul (8) has shown that, in the presence of catalysts with strong acidity, such as $AlBr_3$, $AlCl_3$ or HF-BF_3, the distribution of the products obtained at room temperature or higher (35–37°C) is the same, regardless of the position of the double bond in the starting alkene. Indeed, in the presence of $AlCl_3$ at 35–37°C, both 1-dodecene and *trans*-6-dodecene alkylate benzene give a nearly identical product distribution, with about 32% 2-, 20% 3-, 17% 4- and 31% 5- + 6-phenyldodecanes. This distribution was defined as 32:31. This fixed distribution, regardless of the position of the double bond in the olefin, is the result of the rapid and efficient isomerization of the alkylbenzene products themselves rather than equilibrium reactions involving the intermediate alkylcarbenium ions. This interpretation is further corroborated by the fact that 2-phenyl decane over $AlCl_3$ at 37°C isomerizes rapidly into 3-, 4- and 5-phenyl decane. Under similar conditions, but at 0–5°C, the 2-phenyldecane tracer remained unchanged for 30 min, indicating the absence of any product isomerization. It has also been shown that, at 0°C with $AlCl_3$ catalyst, the alkylation of benzene with 1-dodecene produced a rich 2-phenyl dodecane alkylbenzene with an isomer distribution ratio of 44:20, while with *trans*-6-dodecene, the isomer distribution was the 18:53. Thus, at 0°C or below, and in the absence of product isomerization, 1-dodecene and *trans*-6-dodecene give widely different isomer distributions, depending on the position of the double bond in the chain. This is similar to the alkylation with anhydrous hydrogen fluoride in the absence of *n*-hexane, where the alkylation reaction appears to be too fast to allow the intermediate alkylcarbenium ions to reach equilibrium concentration.

The alkylation becomes kinetically controlled when carried out in the presence of weak catalysts, such as HF, H_2SO_4, $AlCl_3$-CH_3NO_2, $AlCl_3$-H_2SO_4 and $EtAlCl_2$, or even in the presence of $AlCl_3$ at low temperature. Under these conditions, the distributions of the various isomers depend on factors such as chainlength, location of the double bond in the chain, nucleophilicity of the arene, type of catalyst and solvent, ratio of reactants, temperature, and homogeneity of the reaction medium (9–11).

Olson (12) has studied the effect of HF, H_2SO_4 and $AlCl_3$ as catalysts on alkylating agents and products as well as on the variation of product composition with time. Neither HF nor H_2SO_4 isomerized the phenylalkanes, indicating that the isomerization of the alkyl group occurs before the final attachment of the alkyl chain to the benzene ring. Also, the $AlCl_3$-catalyzed alkylation of benzene with 1-dodecene gave the same mixture of phenyldecane isomers as that obtained with either 2- or 6-phenyldodecane. Olson (12) concluded that the way in which the phenylalkane isomers were formed with H_2SO_4 and HF was different from that with $AlCl_3$. With H_2SO_4 and HF, the isomerization was assumed to occur by a repeated addition and elimination of a molecule of acid, giving a mixture of all possible secondary ions, which, in turn, alkylate the benzene to yield phenylalkanes. For the $AlCl_3$-catalyzed reaction, Olson (12) concluded that the isomerization may occur at one or both of the following stages: (i) before the alkylation with a π-complex between catalyst, alkene and aromatic; and (ii) subsequent to alkylation through reverse alkylation–dealkylation steps and isomerization in the catalyst–alkene–aromatic complex, and/or reverse abstraction of the hydride ions from arylalkene, followed by a series of hydride shifts and phenyl migrations. These conclusions are similar to those reached by Swisher *et al.* (13), Alul (7,8) and Alul and McEwan (9–11).

TECHNOLOGIES FOR THE PRODUCTION OF LAB

Commercial LABs are derived today by alkylation of benzene with either chloro-*n*-paraffin or linear olefins (14). In the chloro-*n*-paraffins, chlorine is attached to all the possible positions of the hydrocarbon chain. There are two principal kinds of linear olefins: Linear α-olefins or terminal olefins, and linear internal olefins in which the position of the double bond is randomly distributed in the chain. The linear olefins are produced either by dehydrogenation of *n*-alkanes, extracted from kerosene or derived from ethene by the oligomerization process, or by thermal cracking of the paraffinic wax, or obtained indirectly by chlorination/dehydrochlorination of *n*-alkanes. Hinds (15) presents alternative routes for the production of LAB as a raw material for detergents (Fig. 3).

Since the development of the process for the separation of *n*-paraffins from branched hydrocarbons and cyclic structures, *n*-paraffins have become the most widely used raw material for the production of LAB. There are two commercial processes for the separation of *n*-paraffins from petroleum fractions like kerosene. The first one and most widely used utilizes the principle of selective adsorption of *n*-paraffins onto 5 Å molecular sieves. By feeding the vaporized paraffin blend under pressure over such sieves, the *n*-paraffins are trapped (Isosiv Process). They can be recovered by desorption, with gaseous *n*-pentane. In the Molex® Process [trademark of Universal Oil Products Company (UOP), Des Plaines, IL], the adsorption and subsequent desorption with *n*-pentane occur in the liquid phase. The six most common molecular sieve adsorption processes are: (i) Molex® process, developed by Universal Oil Products Company; (ii) Isosieve process, developed by Linde Division of Union Carbide Corporation (Houston, TX); (iii) Ensorb process, developed by Esso Research and Engineering Company (Surrey, United Kingdom); (iv) TSF process of Texaco Incorporation; (v) the Shell Oil Company process (Houston, TX); (vi) the British Petroleum Company process.

An alternative method is based on clathrate complex formation of *n*-paraffins with urea. The process is based on the fact that urea forms relatively stable crystalline complexes, commonly known as clathrates, with linear paraffins, but does not with branched-chain and cyclic hydrocarbons. The crystalline complex can then be separated from the other components by filtration (Edeleanu process). The largest producers of *n*-paraffins are EniChem (formerly Chimica Augusta) and Exxon (Florham Park, NJ). Approximately 75% of the usage of *n*-paraffins serves chemical purposes, with primary utilization in the manufacture of surfactants.

The routes for the production of alkylating agents and alkylate, are discussed below.

Cracking of paraffinic petroleum fractions (wax-cracking or steam-cracking). Thermal cracking of paraffinic wax or other suitable heavy petroleum fractions is used for the production of α-olefins, for linear detergent alkylates. After maximization of the normal paraffinic content, usually made by molecular-sieve adsorption or urea complexing process, the heavier paraffinic fractions are thermally cracked to produce linear α-olefins, containing both odd and even carbon numbers from C_5-$C_{20}{}^+$. These olefins predominate in the linear α-homologues. Those falling in the range of about C_{11}-C_{18}, and particularly from about

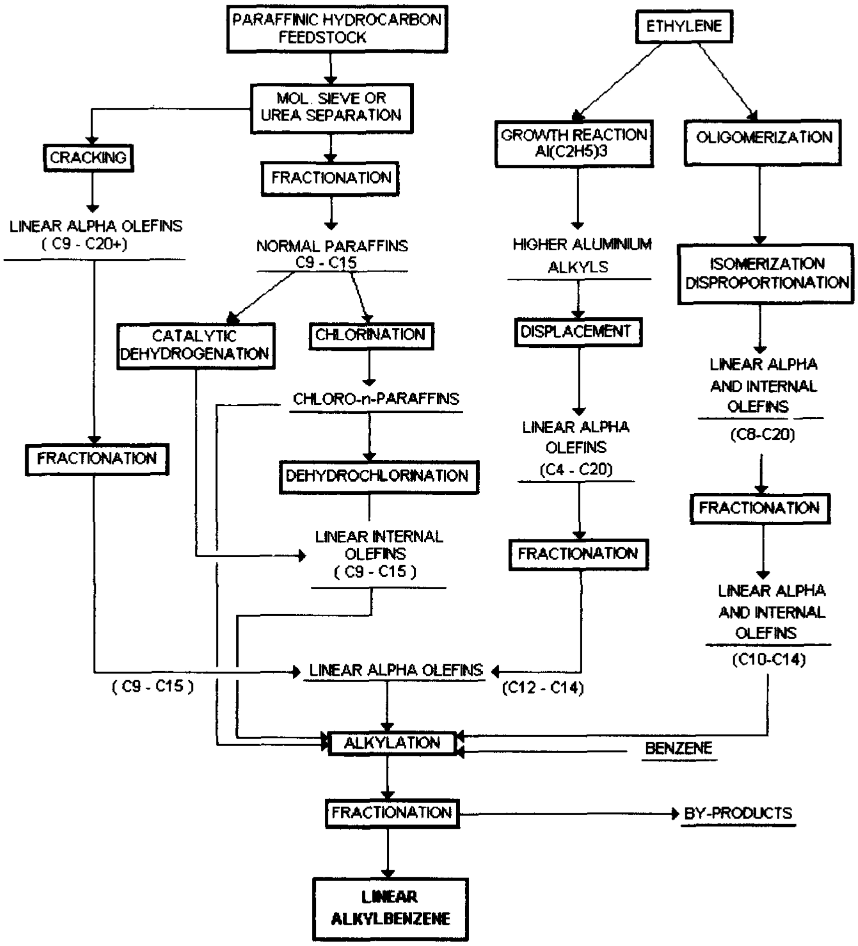

FIG. 3. Alternative routes to linear alkylbenzene.

C_{10}-C_{14}, are of greatest interest as surfactant intermediates. The carbon range desired can be obtained by fractionation (15,16).

Although higher linear α-olefins may be produced by catalytic cracking of suitable paraffinic hydrocarbon feedstocks, the catalytic process is practiced little. The yield of olefins above about C_{10} is limited, and the purity of the straight-chain α-olefins is lower than in the thermal process. Chevron (San Rafael, CA) shut down a wax-cracking olefin plant in 1984 after they acquired Gulf's (Pittsburgh, PA) ethylene-based α-olefin plant. Shell had three wax-cracking olefin plants in Europe, at least two of which are no longer operating. It is believed that the large excess of co-products was the key factor causing these plants to be replaced by ethylene-based α-olefin plants. Other factors may have been the lower quality of the olefins produced, the relatively small size of the individual units, the age of the units and difficulties in obtaining feedstocks. The wax-cracking process requires special types of high linear hydrocarbon waxes, which come from certain crude oils such as those found in Libya or Indonesia (17).

Catalytic dehydrogenation of n*-paraffins.* The catalytic dehydrogenation process was mainly developed and licensed by UOP as part of a commercial LAB complex with Pacol®, DeFine®, Olex® and HF Detergent Alkylate or Detal® (trademarks of UOP) process (3,14,16,18). The cost-effectiveness of this route and the quality of the LAB are attested to by its acceptance in the detergent industry; more than 1,7 million metric tons per year (MTA) was produced by this technology in 1992 (19).

In the catalytic dehydrogenation process, the linear paraffins are dehydrogenated to linear internal olefins in the presence of hydrogen over a selective heterogeneous platinum catalyst supported on alumina (16). This is the so-called Pacol® process (paraffin-catalytic-olefins). Hinds (15) has mentioned that the dehydrogenation catalyst needs other components that act as "attenuator," which have the function of partially poisoning the platinum to suppress its cracking activity and its tendency to promote side reactions, particularly cyclization. The "attenuator" is selected in general from elements such as As, Sb, Bi, Ge and Sn. The presence of 400–3000 ppm of water in contact with the catalyst under the dehydrogenation conditions is also required to decrease the rate of coke formation. The alumina support may be modified by Li to prevent acid reactions. Even so, the dehydrogenation catalyst has a short lifetime, 45–55 d in process conditions, due to coke formation. In addition to its short lifetime, this catalyst is considered nonregenerable, but there have been attempts to understand the causes of its fast deactivation and to achieve its regeneration (20,21).

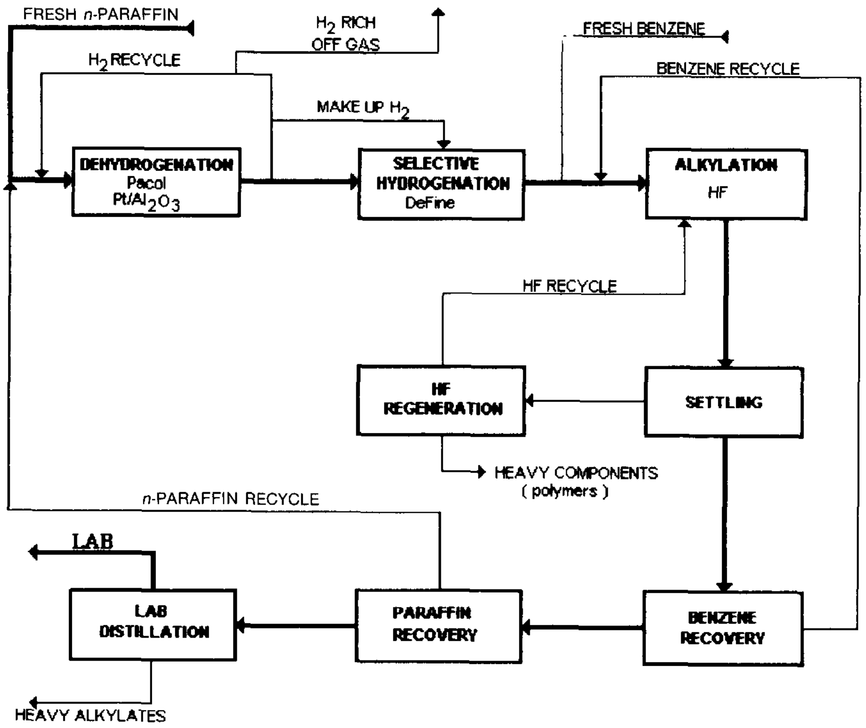

FIG. 4. Production of LAB from dehydrogenation of linear paraffins. See Figure 1 for abbreviation.

Hydrogen and some light end by-products are separated from the dehydrogenation reactor effluent, and part of this hydrogen-rich gas is recycled back to the dehydrogenation reactor. This separator liquid is an equilibrium mixture of linear internal olefins and unconverted *n*-paraffins. The conversion of *n*-paraffins to mono internal olefins is near equilibrium, and therefore, small but significant amounts of diolefins and aromatics are produced. In the alkylation process, the diolefins consume two moles of benzene to yield heavier diphenylalkane compounds, or they form polymers and even dialkylindanes and dialkyltetralins that become part of what is called heavy alkylate and HF acid regenerator by-products. Thus, formation of diolefins represents a loss of alkylate yield. The DeFine® process, a selective hydrogenation process, was developed to convert diolefins back to monoolefins by means of a heterogeneous hydrogenation catalyst called H-14 (18). The catalyst and the process conditions have been specifically developed to give high diolefin conversion and high selectivity for monoolefins. The equilibrium mixture from Pacol® is loaded onto a hydrogenator reactor. The effluent is stripped to remove dissolved light hydrocarbons. The stripper bottoms, a mixture of monoolefins, and unconverted *n*-paraffins are then loaded onto the detergent alkylate unit. From the Pacol® unit, hydrogen is also obtained as a valuable by-product and can be suitably employed for other important industrial reactions.

Since 1990, UOP has improved the existing dehydrogenation technology to increase the yield and quality of LAB. A higher selectivity dehydrogenation catalyst was conceived, designated as DeH-9 (18). This catalyst has an activity and a stability similar to the presently used DeH-7 catalyst but reduces the amount of undesired by-products (isoparaffins, cycloparaffins.and aromatics) that are produced in the dehydrogenation reaction. Commercial utilization of the new catalyst is expected to increase the LAB yield by about 3% while improving the LAB quality in terms of higher linearity and enhanced biodegradability. A new dehydrogenation moving-bed reactor has been introduced that allows for the replacement of spent catalyst without having to shut down the unit or/and without requiring a parallel swing reactor on stand-by. Considerable capital savings have resulted from the introduction of this reactor design.

In the Detergent Alkylate unit, the mixture of *n*-internal linear olefins and unreacted *n*-paraffins coming from the dehydrogenation unit is combined together with the excess of dehydrated benzene, with anhydrous HF, which acts as a Friedel-Craft catalyst. The reaction section consists of two reactor/settler units operating in series (18). The reactors are designed to maintain the acid–hydrocarbon emulsion and provide the required contact time and temperature to complete the reaction of the olefins with benzene. The effluent from the first reactor flows directly to the first-stage acid settler. The hydrocarbon and acid phase are separated in the vessel, and the hydrocarbon phase leaves the vessel from the top and flows to the second stage reactor. All the settled acid phase, except the acid regenerator charge, is recycled back to the first-stage reactor. The first-stage acid inventory is held constant by acid spillback from the second-stage settler from the discharge of the second-stage reactor circulating pump. Hydrocarbons fed to the second-stage unit combine with HF acid from the second-stage settler. The alkylation reactions are completed in the second-stage reactor. The primary function of the second-stage of alkylation (the second reactor–settler) is to solubilize the less-soluble impurities in high-purity HF acid that is

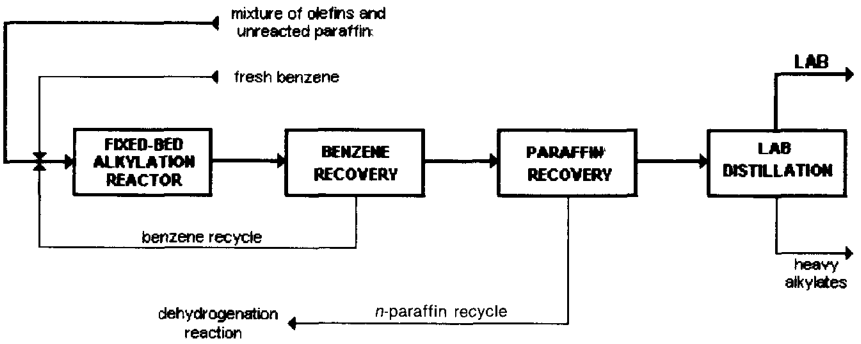

FIG. 5. Heterogeneous alkylation process. See Figure 1 for abbreviation.

returned from the acid regenerator and HF stripper. With the incorporation of the DeFine® reactor, the production of acid-soluble oil (the acid tars) was reduced by as much as 80%, and this reduction has also decreased the extent of neutralization and waste handling associated with the by-product stream. It also increases the purity of circulating HF acid and improves the efficiency of the alkylation reaction. As a result of the higher acid purity, a second stage of HF alkylation is no longer necessary to meet product specification. This change reduces capital investments of a detergent alkylation unit and reduces the HF acid inventory by approximately 40%. The HF regenerator column serves the purpose of eliminating the acid tars to maintain the required HF acid purity. The acid tars remain at the bottom of the regenerator and need to be drained periodically.

In successive sections of the plant, the HF, benzene and unconverted *n*-paraffins are recovered and recycled to the previous reaction stages. The recovered *n*-paraffins are passed through an alumina treater to remove fluorides, which can increase the acidity of the Pacol® catalyst, and then they are recycled back to the dehydrogenation unit. In the final stage of distillation, the alkylbenzene is separated from the heavy alkylates. The block diagram of an integrated complex for LAB production from dehydrogenation of *n*-paraffins is shown in Figure 4.

A new detergent alkylation process, the Detal® process, developed by UOP and Petresa, Petroquimica Espanola S.A. (Madrid, Spain), is now being introduced for the selective alkylation of detergent olefins with benzene in a fixed-bed alkylation reactor that utilizes a solid heterogeneous acidic catalyst. The block diagram of this process is presented in Figure 5. Olefin feed, combined with makeup and recycle benzene, flows through the fixed-bed reactor that contains the acidic heterogeneous catalyst. The reaction occurs under mild conditions in the liquid phase. Reactor effluents flow directly to the fractionation section, which remains the same as for the HF system, except that the HF stripper column and the alumina treater have been eliminated, as well as the entire HF reactor section, including the mixer reactors, acid settlers, HF regenerator and associated piping. In addition, all the equipment and special metallurgy required for the safe handling of HF acid, neutralization of waste streams, and disposal of fluoride neutralization products now become unnecessary. As a result, the erection cost of a Detal® unit is 30% lower than that of a comparable HF alkylation unit. The alkylation catalyst is selective and stable, and it was tested for more than eight months in the pilot plant. The expected life of this catalyst is greater than two years (19). The Detal® LAB product is similar to the typically HF-produced material (Table 3).

TABLE 3

Linear Alkylbenzene Product Characteristics

Characteristic	HF[a] Detergent alkylate	Detal® Process
Bromine index	10	10
2-Phenyl (wt%)	16	25
Linearity (wt%)	93–95	93–95
Dialkyltetralins (wt%)	0.5–1.0	<0.5

[a] Fluoridic acid.

The difference is that the 2-phenyl content is higher for Detal® LAB and is close to that LAB produced with $AlCl_3$ catalyst. Another important difference is the dialkyltetralins content. Unlike $AlCl_3$ or HF-produced LAB, the dialkyltetralin content of the heterogeneous alkylation product is consistently below the current limit of detection (0.5%). The first industrial plant with this fixed-bed alkylation technology will be used in a plant for 100,000 t/y in Becancour, situated between Quebec and Montreal, Canada. The Petresa and Canada's state-owned Societé Générale de Financement (SGF) have agreed to form a joint venture for this project. The production is expected to begin in early 1995 (22). Another project with Detal® technology is announced to be installed in Saudi Arabia by Alastra/Vista with a capacity of 50,000 t/y.

The dehydrochlorination process ("chemical dehydrogenation"). Another route for the production of internal olefins is by dehydrochlorination or "chemical dehydrogenation." By chlorination of *n*-alkanes and subsequent elimination of hydrogen chloride, a mixture of linear olefins is obtained. The double bonds are distributed over the entire chainlength (16). This process may involve a photochlorination of the C_{10} to C_{13} *n*-alkanes mixture.

The photochlorination step is carried out in the presence of ultraviolet (UV) radiation of approximately 2500–6000 Å at a temperature of 5–110°C in the liquid phase. Several photochlorination zones are used. The temperature is kept relatively low, and the amount of chlorine present in each zone is kept considerably below the stoichiometric ratio to minimize production of di- and polychlorohydrocarbons.

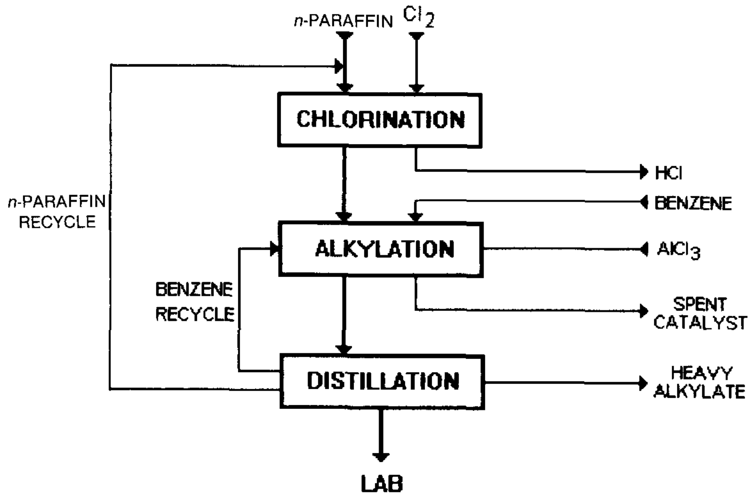

FIG. 6. Alkylation of benzene with chloroparaffins.

The reaction is only driven to approximately 40% conversion. In a subsequent reaction on an iron-containing catalyst, hydrogen chloride is split off at approximately 250°C. In this dehydrochlorination reaction, a high-surface oxidized carbon or diatomite, in conjunction with a ceramic binder at higher temperatures (400–450°C), can be used. The olefin/paraffin mixture cannot be fractionated due to the similarity in boiling points. After alkylation with benzene, the unreacted paraffins can be readily removed. The leading producer is Chem. Werk Hüls (Germany) with approximately 80,000 t/y. Shell restarted its paraffin chlorination–dehydrochlorination plant in the United States in mid-1985, apparently because it was a low-cost investment and a readily available source of capacity. This unit, which had been started up in 1967, was shut down in 1981 when Shell's U.S. SHOP unit was adequate for demands (17).

*Alkylation of chloro-*n*-paraffins in presence of $AlCl_3$ as catalyst.* A process for alkylating benzene with linear chloroparaffins (containing unreacted *n*-paraffins) is described by Cavali *et al.* (14). This process was developed also by EniChem Augusta Industriale. The *n*-paraffins are partially chlorinated with chlorine gas in a multistage reactor. The mixture of *n*-paraffins and chloroparaffins is fed, with excess benzene, into a reactor with $AlCl_3$ catalyst. The catalyst suspended or dissolved in the crude alkylate is then separated. Unreacted benzene and *n*-paraffins are recovered by distillation and recycled to the previous reaction stages. This process produces a high dichloroparaffins content and, consequently, a high amount of dialkylindanes and dialkyltetralins. The LAB is separated from the heavy alkylates by distillation. This process needs to be integrated with a chlorine production unit and with industrial application for HCl (Fig. 6).

Alkylation with n*-olefins in the presence of $AlCl_3$ as catalyst.* Cavali *et al.* (14) have also described a process for the production of LAB from linear olefins with $AlCl_3$ catalyst. The process basically makes use of the same technology employed above but uses high-purity *n*-olefins obtained by the UOP processes, Pacol®, DeFine® and Olex®. The Olex® process (Olefin Extraction) is for separation of *n*-olefins from *n*-paraffins after the dehydrogenation reaction. The Olex® process uses UOP's Sorbex® technology, a continuous liquid-phase countercurrent adsorptive process. In a Sorbex® unit, countercurrent of liquid and solid is achieved without actual movement of the solid by periodically moving the positions at which the process streams enter and leave the adsorbent bed of ADS-32. If the liquid feed and withdrawal points are shifted in the same direction as the fluid flow down through the bed, the countercurrent motion of the solid in the opposite direction is simulated (18,19). The characteristic that distinguishes this alkylation process from the others is the production of a high 2-phenyl isomer content (29) without production of high concentrations of undesired dialkyltetralins (<0.5) due to the low content of diolefins in the olefin stream. A typical C_{10}-C_{13} high purity *n*-olefin cut is fed into the alkylation reactor with excess benzene and with a catalyst, made up with an active complex based on aluminum chloride. The raw alkylates go through well-known process stages that include washing to eliminate catalytic residues and fractionation to separate the LAB from benzene and light hydrocarbons, leaving some heavy alkylates as residue.

Ethylene-based α-olefins. Remarkably, less than 20% of LAB is produced from ethylene-based α-olefins. For large production, routes based on *n*-paraffins are often more attractive. The α-olefin process is a good economic choice for LAB feedstocks when the plant size is small, less than 23,000 to 46,000 MTA. A trend to lower paraffinic crude oil production worldwide may result in replacement of the latter by α-olefins. However, recent improvements made by UOP in both catalyst and process efficiencies in the paraffin route keep it still competitive with α-olefins. The *n*-paraffin route is also influenced by differences in the cost of paraffins and ethylene, the latter being more expensive. LAB is increasing in importance as a market for α-olefins as developing countries are switching to biodegradable detergents in which the propylene tetramer is gradually being replaced with C_{10}-C_{14} α-olefins. Companies in these regions may build paraffin-based plants, which tend to be more economical to operate but require significant investment to build. However, when α-olefins are used, the capital cost of conversion from propylene tetramer is lower and faster than the paraffin route.

The α-olefins are produced in ethylene-based plants operated by Ethyl, Shell, Chevron/Mitsubishi (Gulf technology). Idemitsu has an olefin plant in Japan (in operation since 1991) with a capacity of 50,000 MTA. Gulf and Ethyl licensed the original technology from Karl Ziegler of the Max Planck Institute in Germany. It was found that straight-chain alkyl groups could be polymerized from ethylene by a method involving alkylaluminum compounds as intermediates. Shell developed a unique nickel complex catalyst system that can be a solvent such as benzene or 1,4 butanediol.

The chemistry is similar for the industrial production of α-olefins from ethylene. The Ethyl, Shell, Chevron/Gulf and Idemitsu ethylene oligomerization processes require different chemistries, reactor temperatures and reactor process. The different conditions result in different reactor configurations and in different product distributions (15,17).

Biodegradability, environmental and toxicologic properties of LAB. Although ABS was successful as a synthetic detergent component, its large-volume usage soon created important problems. Large amounts of branched ABS and other hard surfactants present in water cause a number of undesirable effects due to their slow rate and incomplete biological breakdown. These effects are: (i) Residues from ABS detergents can cause foaming on rivers and other waterways—this is undesirable from an aesthetic point of view, and it presents a potential hazard to navigation. (ii) Foaming at sewage works gives rise to operation difficulties, and during windy weather, the foam may be blown away and carry with it undesirable materials, including pathogens, to areas surrounding these sewage works. (iii) Undegraded detergents constitute unnecessary pollution in surface waters—this pollution is particularly undesirable if it eventually finds its way into drinking water supplies. (iv) The presence of detergents in water reduces the rate of oxygen transfer from the air to water—this can result in a reduction in the efficiency of sewage purification plants, and when these materials enter rivers, they can affect the rate of self-purification of the rivers and their animal and vegetable life.

All these undesirable effects can either disappear or be alleviated by the use of soft detergents. As a consequence, during the 1960s, biodegradability of detergents was a key topic, and much fundamental and practical research was performed during this period, which led to an understanding of detergent biodegradability, toxicological properties and solution of the problem of environmental pollution by alkylarylsulfonates.

Biodegradability. The subject of surfactant biodegradation is well approached by Swisher (23), principally through analytical methods, chemical structure, test methods and metabolic pathways of biodegradation.

Biodegradation can be defined as any process mediated by living organisms that results in the conversion of an organic chemical into organic and/or inorganic end-products that are chemically distinct from the parent material. A more precise technical definition of biodegradation would be the metabolism of organic chemicals as sources of carbon and energy by heterotrophic microorganisms (primarily, bacteria and fungi) to form microbial mass and inorganic and organic end-products, such as carbon dioxide or methane (24).

The standard test method for biodegradability of alkylbenzene sulfonates, American Society for Testing and Materials designation D2667-82 (25), determines the degree of biodegradability of alkylbenzenes as an index of the suitability of the sulfonate for general use as a detergent, and distinguishes between sulfonates in which the alkyl side chains are linear or branched by the rate of biodegradability. At first, the surfactant is subjected to a presumptive test based on shake culture. When necessary, the sample may be subjected to a confirming test based on a semicontinuous treatment with activated sludge. The surfactant is considered to be adequately biodegradable in the presumptive test, without further testing, if the surfactant reduction is equal to or exceeds 90% within 8 d. When the surfactant reduction is between 80 and 90%, the material should be subjected to the confirming test and if is below 80%, the material is considered inadequately biodegradable. In the confirming test, the surfactant reduction must be at least 90% within 21 d for the material to be considered adequately biodegradable. In general, a good LAS may undergo more than 98% reduction within 2 d in the presumptive test (26).

Biological degradation depends on the structure of the alkylarylsulfonate as well as upon the specific organisms and the environmental conditions. As a general rule, straight-chain materials are biodegradable. A list of anionic surfactants in decreasing order of biodegradability is (15): (i) linear soaps and alcohol sulfates; (ii) linear ether sulfates; (iii) linear alkane and olefin sulfonates, (iv) LASs, (v) branched alcohol sulfates and soaps; (vi) branched ether sulfates; and (vii) BASs.

Tarring (27) has studied how the degree of branching of the lateral chain and the concentration of cyclic hydrocarbons present in the alkylating agent affect the rate and the degree of biodegradation of the ABSs derived from different petroleum raw materials. It was observed that: (i) The greater the number of methyl and dimethyl groups per molecule and the greater the concentration of saturated ring compounds in the alkylbenzene, the lower is the rate of biodegradability; and (ii) the number of dimethyl groups is even more important in retarding the biodegradation than the total number of methyl groups. In this study, the laboratory tests were confirmed in an activated sludge pilot plant. It was also observed that the degree of degradation is proportional to the residence time of the sewage in the aeration chambers.

Huddleston and Allred (28) applied desulfonation and gas-chromatographic analysis in the biodegradation of LAS mixtures and observed that the isomers with the phenyl attached near the end of the chain can be oxidized by microorganisms and disappear somewhat more rapidly than those with more central attachment. When the distance between the terminal alkyl-methyl group and the point of benzene ring attachment is five carbons or less, the oxidation rate is markedly reduced. They have also observed that the rate of oxidation decreases as branching becomes more complex, and through the identification of intermediates, they postulated that β-oxidation is one of the metabolic pathways for degradation of alkylbenzenes.

Ruschenburg (29) has found that the 2-phenyl alkanes (from C_8 through C_{16}) degraded more rapidly than the central isomer. This sort of comparison, in which the pure compounds are tested separately, is not representative because individual solutions do not represent the commercial products. However, the behavior of the commercial mixture could be at variance with that of the pure compounds. The data of Swisher (30,31) proved that not be the case.

Huddleston and Allred (28) and Allred *et al.* (32), in the comparison of C_{12}- with C_{14}-LAS, have shown that the C_{14} homolog disappears faster than the C_{12}, and this is true for each individual C_{14} isomer compared with the corresponding C_{12} isomer. Faster degradation of longer homologs has been observed from C_6 to C_{16}. The phenyl position is a more important factor than the chainlength in the acclimatization and biodegradation rate of LAS.

Swisher (30) observed that, when these homologs (from C_6 to C_{12}) were investigated individually in river water, the disappearance became progressively faster with increasing chainlength. Beyond C_{12}, however, the rates became slower again, up to around C_{14} or C_{15}. Finally, as the alkyl chain reached between C_{16} to C_{18}, the rate again increased, but did not reach the degradation rate of C_{12}. The slower degradation of C_{14} was attributed to an inhibiting action on the bacterium. The position of the sulfonate group in the LAS also influenced the degradation rate. The *para* 1-phenyldodecane sulfonate disappeared faster than the corresponding *ortho*, indicating that the distance between the sulfonate group and the most remote end of the chain played an important role in determining the rate at which degradation proceeded.

Based on his observations, Swisher (31) developed a mechanism for the biodegradation process: (i) initial oxidative attack at one end of the chain; (ii) subsequently, the chain is rapidly degraded by the β-oxidation process until a terminal carboxylic group is formed, either two or three carbons away from the phenyl group; (iii) the β- or τ-alkanoic acid thus formed is then attacked at the other end of the chain, after which complete oxidation of the molecule proceeds rapidly; and (iv) a minor fraction of the chain oxidation may involve a single one-carbon step instead of two-carbon β-oxidation process.

Kölbel *et al.* (33) have examined the aerobic biodegradability of pure sodium *p*-alkylbenzene sulfonates with a straight alkyl chain and with a quaternary carbon atom in the 1-position to the benzene ring or at the end of the alkyl chain. The effect of the position of the quaternary carbon atom has on biodegradation was studied by comparing the rate of biodegradability of isomeric alkyl benzene sulfonates under reproducible biological conditions. The surfactant degradation was tested in a dilute, nonadapted biological system of *Coli* bacteria and a culture of mixed bacteria. The degradation was determined by methylene blue activity and biochemical oxygen demand as well as by simultaneous production of UV spectra. The compound with the quaternary carbon atom at the end of the chain strongly retarded biodegradation, while the other gave only a weak retarding effect.

Many workers have shown that, under aerobic conditions, LAS is completely degraded (mineralized) in the environment. The first step in the mineralization is accomplished by microorganisms through omega and beta oxidations of the alkyl chain. The resulting sulfocarboxylic acids have a chainlength of 4–5 carbon atoms, and that step is followed by the rupture of the benzene ring and subsequent desulfonation (34).

Environmental scientists are increasingly recognizing that many chemicals, including surfactants, behave differently in real-world surface waters than in laboratory "clean water" studies. Mieure *et al.* (35) present a review of recent studies about the factors that influence surfactant toxicity in aquatic ecosystems and show for LAS, the most widely tested surfactant, that the real-world margins of safety are much larger than predicted from laboratory studies. Aquatic life risk assessments for LAS, based on laboratory toxicity test data and measured real-world concentrations, overestimate real-world risk by a factor of 12 to 40.

Environmental properties. Brenner (36) has compiled abundant data about the evaluation of LAS as a biodegradable surfactant at a full-scale sewagetreatment plant in the United States. The LAS removal in these systems was most satisfactory, and it was demonstrated that, after undergoing adequate waste treatment, LAS residues would not contribute to the deterioration of water quality.

Mann and Reid (37) have evaluated a number of LASs by field trials with a trickling-filter sewage plant that serves a small community. All LAS materials showed a satisfactory order of biodegradability, and aeration of the sewage effluent resulted in further biodegradation to 96% up to 99%. The results of laboratory-scale biodegradation tests are in agreement with those obtained in the field trials. Mann and Reid (37) used LAS based on an alkylbenzene derived from paraffins and LAS based on cracked wax olefins. The first one showed markedly superior biodegradability in relation to LAS based on cracked wax olefins. Using a conventional LAB, consisting of a complex mixture of homologs and isomers, they observed that the 2-phenyl isomers degrade more rapidly than the 3-phenyl isomers, which in turn degrade more rapidly than those isomers where the point of attachment of the phenyl groups is away from the end of the alkyl chain. The alkyl chains with carbon chainlength of 12 to 14 degrade more rapidly than those of 10 to 11 carbons, and alkyl chains longer than 14 carbons are toxic to the bacterium. For those with longer alkyl chains, acclimatization is necessary, and when this acclimatization does occur, the long-chain LAS may degrade faster than the short-chain LAS.

Hon-Nami and Hanya (38) have described the percent composition of the individual components of LAS in river, estuary and bay water (Tassa River, Tokyo Bay and estuaries of rivers that discharge into Tokyo Bay). The LAS concentration was determined by combined gas–liquid chromatography and mass spectrometry (MS). In general, more than 97% of the LAS was degraded after 34 d, while in the presence of sulfuric acid, which inhibits bacterial action, no significant decrease of LAS was observed even after 41 d.

Matthijs and Stalmans (39) have established an analytical method for the selective determination of LAS in sea water and estuary samples. LAS is concentrated, and the alkyl homologs are separated by reversed-phase high-performance liquid chromatography (HPLC) and detected by fluorescence spectroscopy. The method has a detection limit of 0.4 microgram LAS/L. Analysis of North Sea water samples showed LAS concentrations around 1 microgram/L for close in-shore samples and below the detection limit of 0.4 microgram/L for samples taken more than 10 km off shore. Measured LAS concentrations in samples from the Schelde estuary were much lower than expected, based on dilution only. Perhaps this decrease may be due to biodegradation and/or adsorption upon settling of suspended solids.

Sweeney and Anderson (40) have put in perspective various questions concerning the environmental impact of BAS. It was emphasized that the use of LAS is necessary only in countries where the concentration of alkylbenzenes in the receiving waters is about 1 ppm. This situation is encountered in the United States, Europe and Japan. Studies that were made in Indonesia, India, Malaysia, Mexico, The Philippines and Thailand have shown that a switch from ABS to LAS should not produce any observable benefit.

Toxicity to fish and warm-blooded animals. The toxicological properties of alkylbenzene sulfonate were thoroughly investigated because of their widespread use and their presence in surface waters. Under certain conditions, fish are particularly susceptible to the toxic effects of alkylbenzene sulfonates. The effects of structure, size and concentration of LASs have been the subject of many interesting studies (41–44) as will be shown below.

Divo (45) has developed a method for the prediction of fish toxicity and biodegradability of industrial LASs, based on chemical analysis. The method was based on tests with pure compounds, mixtures and minor components of commercial LAS. It was concluded that the more toxic products were exactly the faster biodegradable ones. Among the minor components of LAS, the dialkyltetralins have shown markedly inferior toxicity than the LASs with almost the same molecular weight.

Divo and Cardini (46) have examined the process of primary and total biodegradation of LAS at high substrate concentration with a microorganism called "*Genus Pseudomonas*." The metabolic intermediates could be recovered in sufficient quantities and allowed characterization of their structures and their possible effects on fish. The biological breakdown of LAS begins at the end of the linear alkyl chain and proceeds, probably by a β-oxidation mechanism, up to the sulfophenylmonocarboxylic acids, characterized by the presence of 1 or 2 -CH_2 groups between the tertiary carbon atom of the chain and the carboxyl group. The second step in the degradation proceeds by attack of the aromatic ring, and its cleavage is followed by rapid metabolism of the intermediates formed. The sulfophenylcarboxylic acids are the only intermediates that can reach detectable concentrations, and some of these intermediates were tested on fish and found not to be toxic. The products that resist further degradation by the microorganism were completely degraded by mixed microbial cultures.

Schmid and Mann (47) examined changes induced in the gills of the trout by ABS and found a reduction of the epithelium, accompanied by a loss of the mucous cells on the top of the gill lamina at a concentration of 5 mg ABS/liter. An increasing destruction of epithelial cells follows a rise up to 20 mg ABS/liter. Multiple hematomes mark the destruction. The deleterious action of ABS results in a diminished uptake of oxygen by the gills, followed by death from suffocation when the concentration of ABS is high enough or even in case of prolonged action at lower levels. This can be considered a serious problem because the rate of biodegradability of ABS is low, thus resulting in the permanent presence of ABS in rivers.

Marchetti (48) has examined the toxic concentration of 17 anionic surfactants, 2 cationic and 18 nonionic upon exposure of two fish varieties, *Carassius auratus* and *Salmo irideus*, for 6 h at 15°C. Likewise, the influence of molecular structure has been evaluated on the degree of toxicity. The LASs appeared twice as toxic as the corresponding branched compounds because the lethal concentration for *Carassius* upon 6-h exposure was equal to 9.9 and 21.15 mg/L, respectively.

Hirsh (41) has studied the effects of the position of the phenyl group in LAS to fish toxicity. With C_{12}, C_{14} and C_{16}, the isomers with the phenyl groups attached to the central carbon atom were more toxic than the 2-phenyl isomers. With C_8 and C_{10} homologs, the 2-phenyl isomers were more toxic. The toxicity order of four isomers of linear dodecylbenzene was: $2 > 3 > 6 > 4$. Toxic effects were noted from a concentration range of 0.2–180 mg/L.

Kimerle (49) has analyzed the aquatic and terrestrial toxicological data bases of LAS and found that the toxicity of LAS decreases as the alkyl chain becomes shorter.

In summary, extensive biodegradation of LAS in drains, sewers, waterways and in the course of sewage treatment always occurs before they come into contact with fish. The toxicity of the biodegraded surface-active agents toward fish is the point of interest in the real environment. The acute toxicity of LAS is reduced by a factor of at least 3–5 in the course of biodegradation. Due to its biodegradability, the margin of safety in practice is really quite substantial.

A recent summary of the chronic and sublethal effects of surfactants to aquatic animals was prepared by Lewis (50). Animal test species have exhibited a moderate degree of sensitivity to several major nonionic and anionic surfactants such as LAS. From the data base of the more used surfactants, such as the alkyl sulfates (anionic), alkyl ethoxi sulfates (anionic) and several of the monoalkyl and dialkyl quaternary ammonium salts (cationic), it appears that the toxicities of the anionic compounds for aquatic animals and plants would likely parallel LAS and be relatively nontoxic.

Feeding rats with LAS and ABS indicated that the toxic dose was quite high (51,52). Oser and Morgavidge (53) have determined the acute oral toxicities and effects of subacute dietary intake of both ABS and LAS in five rats of each sex. For ABS, the acute oral toxicity is 0.52 g/kg, and for LAS it is 0.65 g/kg (fed in water dispersion). The difference between these values is not statistically significant. Rats were fed with ABS and LAS, mixed with the diet at doses of 0.05 and 0.25 g/kg/d for 12 wk. When the animals had reached maturity, the doses were 1000 and 5000 ppm, respectively. The rats developed normally and showed no changes related to ingestion of the tested material in any of the parameters examined, with the possible exception of a slight increase in liver weight. No accompanying morphologic changes were seen in their livers on microscopic examination.

Kay *et al.* (42) have studied subacute oral toxicity of commercial ABS and LAS in rats and dogs. The 90-d feeding studies in both animals at levels up to 0.5% of the diet disclosed no evidence of toxicity caused by ABS materials. The two-year dog studies with ABS revealed some evidence of degenerative changes in the livers at 0.5% in the diet while levels of 0.1 and 0.02% generated nontoxic effects. LAS was fed to rats at dietary levels of

0.02, 0.1 and 0.5% for 90 d. No adverse effects were found on growth, food congestion, survival, hematologic values, urinary analytical values and organ weights. There were no gross or microscopic tissue changes attributable to ingestion of the test material.

A complete monograph was edited by Gloxhuber (54) regarding biological properties of LAS and other anionic surfactants that affect warm-blooded animals and man. Studies about toxicological and dermatological properties and about processes of absorption, metabolism, excretion, tercetogenesis, carcinogenesis and tests of dermal and mucous irritation were compiled.

Beck *et al.* (55) have studied criteria for safety evaluation of new chemicals, and some interesting considerations were made for LAS: (i) The molecule has no characteristics that would indicate mutagenic or carcinogenic effects; (ii) no adverse effects were found on sewage treatment processes; and (iii) no adverse effects were found in home septic and aerobic systems.

The results of the "International Status Seminar of Alkylbenzene Sulfonates—LAS in the Environment" were summarized by Huber (56). The data produced at the seminar showed that LAS is basically an environmentally compatible substance, whose ecological effects with given usage quantities are transparent and controllable (57–66). It did not appear that its ecological profile should require substitution, especially because so far, no detrimental accumulation is recognizable in the various environmental compartments.

ANALYTICAL METHODS AND MINOR COMPONENTS OF LAB

Quantitative analysis of commercial LABs is generally accomplished with a mass spectrometer coupled to a gas chromatograph [gas-chromatography/MS (GC/MS)] with a capillary column. This technique provides reliable information about the homologues and about the various linear phenyl alkane isomers. Other components, such as branched alkylbenzenes, dialkylindanes and dialkyltetralins, which are minor components in LAB, are not easily identified or quantified. It is important to know their concentration, both commercially and in research work, to correlate their structures with the properties (surface activity, solubility, etc.) which determine their application, and with other important characteristics such as biodegradability and toxicity to fish.

For the determination of C_{18}–C_{20} isomer distribution in monosubstituted LABs, a GC column generally is used, either 30 m of a 0.32 nm i.d. fused-silica capillary, internally coated to a film thickness of 0.25 μm with DB-17 bonded methylphenyl-polysiloxane, or a 50-m capillary column, PONA (Hewlett-Packard, Palo Alto, CA), with cross-linked methylsilicone (HP-19091S-001). The lower limit of detection for a single component is 0.1 mass%. 6-Phenyl tridecane and 7-phenyl tridecane isomers are poorly resolved and are generally determined as one component. Apart from LABs, no other components are determined without MS.

Swisher *et al.* (13) have quantitated all six isomeric phenyl-*n*-dodecanes by capillary GC (30:60 m Apiezon L column, 240/270°C; Hewlett-Packard). The isomeric didodecylbenzene by-products formed during 1-dodecene alkylation or phenyl dodecane isomerization were tentatively identified.

Industrial LAB samples were investigated by Ötvös *et al.* (67), with a combination of GC with MS (100-m glass capillary column of 0.3 mm i.d., coated with Apiezon L). The GC/MS method has provided reliable qualitative and quantitative analytical data for linear-chain detergents. For the branched-chain products, GC/MS measurements yield only qualitative results. The dialkylindanes and dialkyltetralins could be detected.

Ötvös *et al.* (68) have desulfonated LAS with *ortho*-phosphoric acid. The desulfonated alkylbenzene (LAB) was analyzed by GC/MS, and the yield of the desulfonated alkylbenzene was nearly quantitative. Again, branched-chain mixtures could not be resolved even with capillary columns; only the type of component could be determined.

Cavalli *et al.* (69) have performed GC and a GC/MS on four commercial LABs. One sample was obtained from the $AlCl_3$-catalyzed alkylation of benzene with *n*-chloroparaffin. The other three different samples were all obtained by alkylation of benzene with *n*-olefins in the presence of HF. Three kinds of liquid coatings were used: Apiezon L (low-pressure hydrocarbon grease), SE-30 (methyl silicone rubber) and DC-550 (polar methylphenyl-silicone oil) on capillary columns of 50 and 100 m long. Apiezon L gives good separation, particularly for the internal isomers (7-, 6- and 5-phenyl isomers). The high-term 2-phenyl isomers are not sufficiently separated from the 7- and 6-phenyl isomers of the next higher homologue. By using SE-30, all 2-phenyl isomers are well separated at the expense of a loss in resolution of the internal phenyl isomers. DC-50 is a compromise between Apiezon L and SE-30. The minor components of the commercial LABs were detected by GC/MS, such as branched alkylbenzenes, 1,4-dialkyltetralins with linear and branched alkyl groups and 1,3-dialkylindanes with branched alkyl groups. There was no evidence of dialkylindane structures with linear alkyl groups. Dialkylbenzene and diphenylalkane compounds were not detected.

Sendem and Riermersma (70) have compared two samples of HF-catalyzed LAB, made with olefins from both cracked urea wax and the SHOP process (Shell High Olefin process). The samples were analyzed by GC/MS (50-m capillary column with methylsilicone). The first sample contained 7.1% dialkyltetralins, 1.5% branched alkylbenzenes and 0.2% diphenylalkanes. The second was free from dialkyltetralins and diphenylalkanes but contained 2.7% branched alkylbenzenes.

Bravo and Vergara (71) have performed a detailed analytical study of commercial LAB, derived from the HF and the $AlCl_3$ processes, by GC/MS, and they showed the effects of the usual impurities on the determination of the molecular weight of LAB and on sulfonation yield. The minor components appearing in LAB derived from the HF process are typically branched alkylates, while in the $AlCl_3$ process, dialkyltetralins are the most important impurities. Branched isomers of a given number of carbon atoms eluted between the corresponding linear isomers of the same number of carbon atoms and the lighter one. Dialkylindanes and dialkyltetralins of molecular weights corresponding to a given LAB homologue are eluted within the linear isomers that have a molecule weight of one carbon atom higher. The molecular weight determinations of LAB by GC/MS will therefore be different from those by the GC method. This difference affects the percentage of the active calculated ingredient and consequently the sulfonation yield.

An analytical method based on the HPLC procedure proposed by Cavalli *et al.* (69) (EniChem Augusta) for the determination of dialkyltetralins has been adopted since 1992 by an analytical task force created by ECOSOL (European Centre of Studies on LAB/LAS; Brussels, Belgium), a sector group of the European Chemical Industry Council, which represents the west European producers of LAB. This method describes a procedure for the determination of dialkyltetralins/1,4-dialkyl 2,3-dihydronaphthalene in LAB in the range between 0.5 to 10 mass%. The sample is analyzed by isocratic HPLC on a microparticulate silica stationary phase with an isooctane mobile phase and UV absorbance detection at 254 nm (71). This method is being adopted by almost all LAB producers and consumers as standard for their specifications. The target of 0.5% of dialkyltetralins by this method of analysis is expected to be mandatory from 1994 on.

COMPOSITION OF LAB AND ITS INFLUENCE IN THE PERFORMANCE OF DETERGENTS

LAB represents one-third of the active ingredients in detergents worldwide. In its sulfonated form, it is used in light-duty liquids, heavy-duty liquids, heavy-duty powders as well as in general-purpose household and various industrial cleaners. The largest LAB use is for laundry detergents, which represent over 50% of the U.S. consumption (17).

LAB's properties as a surfactant depend essentially on its structure (chainlength, position of the phenyl group, degree of branching of the alkyl chain) on the minor component content (dialkylindanes, dialkyltetralins and sulfones) and on the various inorganic and organic counterions as a sulfonate [NH_4^+, Li^+, Na^+, K^+, monoethanolammonium (MEA), diethanolammonium (DEA), triethanolammonium (TEA), etc.]. The commercially manufactured compounds are not pure, but consist of a large number of homologues and isomers of the same chemical structure type. As far as the application is concerned, this is considered an advantage because, in some cases, certain pure compounds are totally unusable. A pure linear dodecylbenzene sulfonate, for example, is nearly insoluble in water and therefore ineffective for a household detergent, whereas the soluble LAS with alkyl chainlengths in the range of 10 to 15 carbon atoms, which combine a number of homologues and isomers, are commonly used as detergent surfactants.

Higher carbon numbers in the range C_{16}–C_{24} are used as lubricant detergent additives in the form of alkylbenzene sulfonates. The alkylbenzene sulfonates derivatives of the C_{16} and higher carbon numbers have low solubility in water and are well suited for use as lubricants and cutting fluids. Household detergents must be water-soluble, so C_{16} and higher alkylbenzene sulfonates are avoided.

Light-duty liquids for use in light household chores, such as dishwashing, are produced from LAB with chainlength carbon numbers between C_{11} and C_{12}. Heavy-duty laundry applications require LAB with C_{12}–C_{14} chains. Various carbon number distributions have been studied in different liquid and powder detergents. Because the use of detergents is so diverse, producing a multi-propose formula is not always possible. However, Ethyl Company has developed a 10% C_{10}, 75% C_{12}, 15% C_{14} mixture that appears to satisfy the requirements of both light- and heavy-duty applications.

Surfactant ingredients used today in the detergent industry are either high- foaming (basically anionics) or low-foaming (nonionics, soaps). Foam has a great psychological effect, although it does not necessarily imply a direct relationship with detergency performance (73).

Rubinfeld *et al.* (74) have performed an intensive study of the mass spectral characteristics of straight-chain alkylbenzenes with their performance as sulfonates in heavy-duty formulations. This work served to support the switching from propylene oligomer-based detergents to linear alkyl-based detergents. The foam stability test used was a designed Practical Dishwashing Procedure (Colgate-Palmolive Company, Jersey City, NJ). The results with alkylates of mixed chains (made with either $AlCl_3$ or HF as catalyst) suggested that the preferred mole range is 252–266. These studies have also led to a direct relationship between foam stability characteristics and the amount of 5- and 6-phenyl isomers present. Detergency tests have shown that the low 2-phenyl mixtures were better detergents than the high 2-phenyl mixtures in the mole range of 252–266. The performance of tridecylbenzene sulfonate (ABS) can be matched in detergency and foam performance by optimizing the linear alkylate structure. This structure should be in the mole range of 252–266 with 90% of the carbon chain being C_{12}, C_{13}, C_{14} and with less than 10% of C_{11} or C_{15} and it should have approximately 40% of 5- and 6-phenyl and 20% of the 2-phenyl isomers.

Sweeney and Olson (75) have compared foam stability (dishwashing and laundry washing) and detergency of LAS in heavy-duty detergents with polypropylene ABS (based on propylene oligomers) at various mole weights, concentrations, water hardness and temperatures. The optimum performance of LAS is generally equal to ABS, except in dishwashing foam in soft water. For both LAS and ABS, a peak in performance was observed in the C_{11}-C_{17} side-chain range. The peak shifted to lower molecular weights as water hardness increased, especially at low detergent concentrations. The LAS peaks are shifted to a molecular weight one carbon number lower than that for ABS. Thus, the best overall performance for LAS is obtained with an average molecular weight corresponding to a mixture of 12- and 13-carbon side chains, whereas ABS is most effective with an average of 14 to 15 carbons on the side chain.

The results have shown that dishwashing foamability is markedly different for the different isomers contained in LAS. When the phenyl group is attached to the middle of the alkyl chain, better results are obtained. This difference is large enough to be noticeable when the isomer distribution changes in all products made with different alkylation catalysts (HF and $AlCl_3$). Detergency and washing machine foam are not affected enough to see differences between all alkylates. The solubility of LAS is greater than ABS and is influenced by isomer distribution because the high 2-phenyl LAB, made from $AlCl_3$, has better solubility than random isomer content.

Rubinfeld *et al.* (76) have established a relationship between commercial mixtures of straight-chain alkylbenzenes and their ultimate performance as sulfonates in detergent products through studies of many pure and nearly pure isomer fractions. In heavy-duty systems, the optimum performance for the 2-phenyl sulfonates occurred at chainlengths of C_{13} and C_{14} at 50–150 ppm water hardness. Sulfonates of the 5-, 6-, and 7-phenyl isomers also peaked at these same chainlengths at 50 ppm, but the optimum shifted to C_{12} and C_{13} chains at 150 ppm hardness. Within the range of optimum chainlengths (C_{12} to C_{15}), the internal isomers were substantially superior in performance at both hardnesses. For a light-duty formulation, all the phenyl isomers performed best with chainlengths in the range of C_{11} to C_{13}. The 2-phenyl isomers were most sensitive to hardness in this case, with the internal isomers giving the best results.

Anstett *et al.* (77) have established a relationship between mixtures of straight-chain ABSs and their performance in light-duty dishwashing formulations by studying pure isomers and isomer mixtures in both liquid and powder systems. The foam performance characteristics are shown to be directly related to carbon chainlength, phenyl position and water hardness. The data indicated that for the light-duty liquid dishwashing formulation, a predominance of the lower carbon chainlengths (C_{10} and C_{11}) in the LAS is desirable for maximum foam performance over a wide hardness range (50–300 ppm). When the performance of the 2-phenyl vs. internal isomers of any given chainlength at 100 ppm is compared, the preferred type of isomer distribution is the internal one. At 250 ppm, the internal isomer is also favored, but the differences are not as pronounced as at the lower hardness level. The solubility within a particular isomer series decreases with increasing carbon chainlength. This is much more marked in the internal isomer series than in the 2-phenyl series where the homologues seem to group in a small range. Because solubility effects are important in liquid formulations, the better foaming properties of the internal isomers might be overshadowed by their poor solubility. With mixtures of 2-phenyl and internal isomers (50:50%), the solubility increases. There must be a powerful solubility synergism between 2-phenyl and internal isomers in the mixtures.

For maximum foam performance, an ideal distribution for LAS in a light-duty powder formulation would be a C_{11}-C_{12} mixture with a predominance of internal isomers.

Rubinfeld and Cross (78) have shown that simply converting a detergent formulation from a branched ABS to the same-molecular-weight LAB would not give the same performance characteristics. The importance of the phenyl position was defined quantitatively as well as the carbon chain distribution in both heavy- and light-duty household formulations. In the light-duty detergents, the linear alkylate should have a molecular weight range of 231-241, with at least 50% C_{10} and C_{11} chains, at least 25% C_{12}, and have a combined minimum of 95% made up of C_{10}, C_{11} and C_{12} chains with minor proportions of C_9, C_{13} and C_{14}. The 2-phenyl content should be 15–25%. In heavy-duty applications, the linear alkylate should have a molecular weight range of 258–266, with a minimum of 70% of the carbon chain being C_{13} and C_{14}, and with a maximum of 5% being C_{11}, 20% C_{12} and the remaining 5% C_{15}. The 5- and 6-phenyl content should be above 40% with less than 20% 2-phenyl content.

Matheson and Matson (79) have determined how foam stability in dishwashing liquids or laundry powders and detergency of laundry powders are affected by changes in the carbon chainlength and phenyl isomer distribution of the LAS. Samples with chainlengths from C_{10} through C_{14} were prepared in the laboratory by both $AlCl_3$ and HF processes. All the samples were similar in salt and free-oil content. The average 2-phenyl content of the $AlCl_3$ homologues was 28–30%, while the average 2-phenyl content for the HF homologues was 17–19%. The results have shown that the carbon chainlength is the most important factor in determining foam stability and detergency performance. Differences in the performance among commercial types of LAS are primarily due to the carbon chain distribution. Optimum light-duty performance peaks between C_{11} and C_{12} for several applications under hard-water conditions. With soft water, the peak shifts to C_{13}. For heavy-duty applications, the C_{12}, C_{13} and C_{14} chain sizes are effective. Phenyl isomer distribution, within current commercial limits of the HF- and $AlCl_3$-LAS, has little effect on foam stability performance or interface tension of LAS in the light-duty liquids or on detergency performance of LAS in laundry products. Both HF- and $AlCl_3$-LAS perform equally well and can be used interchangeably in high-performance products.

LAS interact with free calcium ions to form insoluble $Ca(LAS)_2$. Formation of these complexes reduces the concentrations of the surfactant available for detergency. Several methods are available for minimizing the effect of their interaction. The most common one involves the use of builders to reduce the concentration of water hardness ions. Another is to add more surfactant to make up for the amount lost in the formation of insoluble complexes. A third method involves the use of micelle promotion agents to reduce the extent of interaction by effectively lowering the concentrations of both surfactant monomers and water hardness ions. Matheson *et al.* (80) have constructed precipitation boundary diagrams to examine the interaction of LASs surfactants with calcium ions over a range of surfactant and hardness ion levels. Three commercial LAS samples were used with carbon-chain averages of $C_{11.4}$ (28.6% of 2-phenyl isomer), C_{12} (14.5% of 2-phenyl isomer) and C_{13} (11.5% of 2-phenyl isomer). The samples were deoiled and desalted. The heavier-molecular weight-average LAS shows the greatest sensitivity to precipitation with Ca^{+2}. Both the C_{12}-average and the $C_{11.4}$- average LAS show considerably more tolerance to Ca^{+2} than the C_{13}-average LAS probably because they contain little C_{14} LAS homologues and relatively less of the C_{13} LAS homologues.

Any agent that promotes micelle formation improves detergency performance of LAS in hard water. Lowering the critical micelle concentration (CMC) performs two functions: LAS monomer concentration is reduced due to incorporation of surfactant into micelles, and the concentration of free hardness ions is also reduced through counterion binding of the cations with micellar surfaces. Effectively, micelles act as a sink for both surfactant and water hardness ions. Less surfactant is lost due to formation of insoluble $Ca(LAS)_2$ and $Mg(LAS)_2$ because less surfactant monomer and water hardness ions are available to interact. This results in an improvement in hard-water detergency. There are two main types of micelle promotion agents, salts and cosurfactants. Cox and Matheson

(81) have investigated the ability of inorganic salts and co-surfactants to act as micelle promotion agents. Sodium sulfate and a 55% C_{12}/45% C_{14} linear alcohol with 70% (10.6 moles) ethylene oxide—1214/70—were used as the salt and nonionic (NI) co-surfactant, respectively, to help solubilize Ca/Mg$(LAS)_2$. The results have shown that the addition of sodium sulfate lowers both CMC and surface tension of LAS. These effects result from a decrease in the repulsion of head groups in the micelle and by a reduction in surfactant solubility (82). Lowering CMC and surface tension improves detergency performance. The addition of surfactants can be effective in improving the hard-water performance of LAS as well. However, in comparison to increasing ionic strength, the effect of adding a co-surfactant is complicated by interactions that can occur between the co-surfactant and other species in solution.

LAS and NI surfactant (1214/70) interact to produce the nonlinear decrease in CMC observed when NI is substituted for LAS. It is this interaction that produces a substantial reduction in CMC with only a small amount of NI surfactant.

A greater ethylene oxide content increases the ability of the surfactant to interact with (and solubilize) $Ca(LAS)_2$.

The appearance and detergency properties of LAS solution were compared either in the presence or absence of a micelle promotion agent (83).

Free oil content (unsulfonated matter) in LASs has a considerable influence on the physical properties (viscosity and solubility—cloud point) of sulfonate slurries. Using a combination of MS and SO_2 fluorometry, Moreno *et al.* (84) have identified another set of by-products in the sulfonation process called sulfones. A mechanism for their formation by reaction of pyrosulfonic acid with alkylbenzene was postulated. The presence of this kind of product causes drastic modifications in the physical properties of LAS. The higher the sulfone/LAB molar ratio, the higher the viscosity and the lower the solubility. Sulfone formation is favored by increasing acidity. At the end of the sulfonation process, the SO_3/alkylate molar ratio is substantially higher than at the beginning because of the excess SO_3 normally used. This excess SO_3 increases the acidity. Therefore, careful control of the final aging step in commercial plants is important to minimize sulfone formation. LAB-derived from the $AlCl_3$ alkylation process gives slurries with higher solubilities than those of LAB derived from the HF process. This effect has been explained in the past as a function only of the higher 2-phenyl alkane isomer content of the $AlCl_3$ derivative. Although the external isomers (2- and 3-phenyl) of a given homologue have different solubilities than the internal ones (4-, 5- and 6-phenyl), the fact that $AlCl_3$ derivatives give lower cloud points than those from the HF process is also related to the higher dialkyltetralin content of the former (85). The adverse effect of the presence of sulfones on the solubility may be made up for by the presence of dialkyltetralins in a similar molar fraction as in the LAB produced by $AlCl_3$.

Moreno *et al.* (85) have conducted a detailed study on several physicochemical parameters of sulfonated slurries to evaluate their behavior by using pure isomers and homologues derived from commercial LABs. They came to the following conclusions: (i) Solubility: For homologues of the same molecular weight, the optimum solubility is reached with a symmetric isomer distribution, sodium salts of external isomers are less soluble than internal isomers salts, and calcium salts of external isomers are more soluble than internal-isomer salts. For homologues with different molecular weight, the higher the molecular weight, the lower the solubility. (ii) Viscosity: For homologues of the same molecular weight, the higher the tetralin content, the lower the viscosity, and for homologues with different molecular weight, the higher the molecular weight, the higher the viscosity. (iii) Detergency: LAS–Na derived from HF–LAB shows more superior detergency performance than the corresponding $AlCl_3$–LAB derivative at zero water hardness an unbuilt formulation. No significant differences were observed between both derivatives when different degrees of water hardness and built formulations were used. (iv) Foaming power: At 0 ppm water hardness, the higher the molecular weight, the better the foaming power; at 100 ppm, the optimum is around the C_{11} homolog, and at 300 ppm, the higher the molecular weight, the lower the foaming power. (v) Foam stability: For homologues with the same molecular weight, the greatest stability is reached for the highest content of external isomers. For homologues with different molecular weight, stability is a function of water hardness. At 0 ppm, the higher the molecular weight, the better the stability; at 100 ppm, the optimum is reached by C_{11}, and at 300 ppm, stability decreases with increasing molecular weight. (vi) Stability to water hardness: For homologues with the same molecular weight, stability increases with increasing content of external isomers. For homologues with different molecular weight, stability to water hardness decreases with increasing molecular weight.

LAS salts are produced *via* neutralization by organic or inorganic bases. Moreno *et al.* (86) have studied the effects of different inorganic and organic counterions on the physicochemical behavior of three commercial LAS products. For the inorganic ions, the larger the ionic radius of the counterion, the lower the solubility, ($NH_4 < K < Na < Li$ for solubility increase). The presence of dialkyltetralins increases the solubility of LAS. The solubility decreases with the length of the alkyl chain. For the organic ions, the solubility increases in this order: MEA < DEA < TEA. Viscosity follows the opposite direction of solubility, the larger the counterion size, the more viscous the sulfonate solution ($Li < Na < K < NH_4$). Dialkyltetralins act as a viscosity depressor. The molecular weight has also an important role on viscosity—The lower the molecular weight of a similar type of LAB, with the same dialkyltetralins content, the lower the viscosity. With organic salts, the higher the number of ethanol groups in the molecule, the lower the viscosity. In relation to detergency performance, no significant differences have been found among the various counterions used.

Cohen *et al.* (87) have investigated foam properties of a commercial-grade LAS over a wide range of surfactant and Ca-ion levels. The foam height determination was carried out according to the Ross–Miles Test (ASTM-D-1173) at 49°C and LAS concentration of 0.5 g/L. The foam stability index is given by the difference between foam height measured at $t = 0$ and $t = 5$ min. In the presence of Ca and Mg ions, at equilibrium conditions, both the composition and the concentration of dissolved LAS are

TABLE 4

Variation of Activity and Selectivity with Zeolite Structures

				Selectivity (%)		
Catalyst	T (°C)	P (bar)	Conversion (%) (olefin C_{12})	pHC_{12}	Linear pHC_{12}	$2\text{-}pHC_{12}$
HZSM-4	205	14	92	73	90	57
BETA	250	41	38	47	53	57
HZSM-20	250	41	26	33	100	51
Linde L	195	14	72	72	88	40
HZSM-38	200	15	94	73	78	37
REY	200	15	89	85	92	25

significantly different from the initial levels. For LAS/Ca solutions, the maximum foam height is always reached in the neighborhood of the CMC of dissolved LAS. Contrary to what happens in soft water, foam stability does not decrease beyond the surfactant CMC. The foam height is almost independent of Ca concentration until a "critical" Ca concentration is reached, where the amount of precipitated LAS is substantial, resulting in a dramatic decrease of foam height. The critical Ca concentration increases when LAS concentration increases. As far as foam stability is concerned, as was described earlier, foam stability is independent of the Ca concentration in the premicellar zone. In the post-micellar zone, however, the higher the Ca concentration, the greater is the foam stability, until critical Ca concentrations are reached, beyond which the foam stability remains constant.

Cohen *et al.* (88) have studied the effect of the concentration of LAS on soil removal efficiency at various levels of water hardness. This investigation indicates that for each LAS concentration, a Ca-ion concentration interval exists, where the detergency reaches a maximum. The solutions that have been prepared 24 h before present either clear solutions (water appearance), milky solutions (without precipitate in the bottom of the bottle) or clear solutions with precipitate in the bottom of the bottle. The milky solutions correspond to the defined interval where the ratios of LAS/Ca are located, surprisingly, in a precise zone of the LAS–Ca solubility diagram. The addition of electrolyte moves the maximum detergency performance interval to higher Ca-ion concentrations.

HETEROGENEOUS CATALYSIS IN THE LAB SYNTHESIS

The processes for alkylation of aromatics with long-chain alkenes in the presence of Friedel-Craft catalysts ($AlCl_3$, H_2SO_4, HF, etc.) are known and used commercially. However, the above-described catalysts have the disadvantage of causing corrosion of equipment as well as waste production. Due to the hazardous nature of this kind of catalyst, a good deal of effort has been devoted to finding noncorrosive solid catalysts with similar catalytic performance.

Highly acidic faujasites, including rare-earth-exchanged X and Y, and hydrogen Y, issued from thermal decomposition of ammonium Y, are potentially useful for alkylation of benzenes with long-chain alkenes, as reported by Venuto *et al.* (89). In this work, benzene and 1-decene were used, in the presence of faujasites, in the liquid phase at temperatures of 150–230°C. With REX catalyst at 160°C and 3 h on stream at 27.4 bars pressure, 90% conversion of 1-decene to a mixture of decylbenzenes occurred. Good catalyst life was observed at 160°C, and some alkylation activity was even observed at 100°C. Side-chain cracking was not observed under these relatively mild conditions. GC and spectroscopic analyses showed that there were at least three major monoalkylation products, namely, 2-, 3- and 4-phenyl decane. Likewise, in the sealed-tube reaction of 1-hexene and benzene at 80°C, the monoalkylate consisted almost exclusively of 2- and 3-phenyl hexane. The general conclusions of this work are: (i) Liquid-phase operation is usually essential because catalyst aging and many side reactions are more rapid in the vapor-phase. With materials where a sufficiently rapid reaction rate can be maintained at temperatures near or below their boiling point, a liquid phase is assured. With more volatile reactants, however, pressure increase is necessary. (ii) With low-molecular weight species, such as ethylene, a high molar ratio of aromatic to alkylating agent is required to minimize unfavorable interaction of the reactive alkylating agent with the catalyst surface intermediates and to favor monoalkylation. With higher-molecular weight (C_6-C_{16}) alkylating agents, however, lower ratios may be employed. (iii) Temperatures in the range of 150–230°C are generally required for efficient alkylation of simple aromatics with C_2-C_{16} olefins. (iv) For the same or similar reactants, the highly acidic faujasites catalyze alkylation at significantly lower temperatures than the silica–alumina-type catalysts, thus eliminating many of the undesirable side reactions encountered at higher temperatures. Lewis acids, such as $AlCl_3$, and BF_3 and protonic acid, such as H_2SO_4 or HF, generally show significant activity at much lower temperatures than the acidic faujasites.

Sebulsky and Henke (90) have performed a bench-scale study to evaluate supported silicotungstic acid as a catalyst for alkylation of benzene with 1-dodecene. The experiments were conducted in a continuous-flow fixed-bed stainless-steel reactor, 38 inches long by 1 inch i.d., at 66–120°C and 14–34 bars with a benzene/1-dodecene molar ratio of 4:1 to 15:1. Silicotungstic acid is active for the alkylation of benzene with 1-dodecene; the activity of supported silicotungstic acid depends greatly upon the choice of support. Silica gel is superior to alumina and silica–alumina as a support, and the activity of this silica-gel-supported catalyst is a linear function of silicotungstic acid content. A sulfonated LAB prepared from the silicotungstic acid-catalyzed linear alkylate had the same detergency and biodegradability properties as other commercial LASs. Control of selectivity depends largely on the ratio of benzene to 1-dodecene in the feed, selectivities of 90 to 94% to phenyldodecane being readily achievable. A

TABLE 5

Variation of Activity and Selectivity with Pore Diameter of Various Zeolites

					Selectivity (%)		
Catalyst	T (°C)	P (bar)	diameter (Å)	(olefin C_{12})	pHC_{12}	Linear pHC_{12}	2-pHC_{12}
HZSM-12	200	13	—[a]	54	63	78	92
Mordenite[b]	200	14	7	98	80	95	85
Offretite	250	42	6.4	97	73	75	79
HZSM-4	205	14	7.4	92	73	90	57
Beta	250	41	—[a]	38	47	53	57
Linde-L	195	14	7.1	72	72	88	40
HZSM-38	200	15	—[a]	94	73	78	37
REY	200	15	7.4	89	85	92	25

[a] Pore size unknown.
[b] Dealuminized.

model based on second-order kinetics can be used to predict the effects of temperature, mole ratio, catalyst composition and space time on conversion and selectivity, considering as principal products the phenyl dodecane isomers and as by-products the dodecene dimers (polymer) and heavy alkylate. An apparent activation energy of 14 kcal/mol was found.

Bakhshi-zade (91) has studied the alkylation of benzene with 1-dodecene in the presence of Ca, Na-Y zeolites as catalysts in a batch reactor, at 210–240°C and 2 bars pressure. The maximum conversion reached was 45% after 50 min. with a selectivity of 98% to phenylalkanes. The distribution of isomers found was 83% 2-phenyldodecane, 6% 3-phenyldodecane, 4% 4- and 5-phenyldodecane and 3% 6-phenyldodecane.

Young (92) (Mobil Oil Corporation, Princeton, NJ) has patented a process for selective alkylation of benzene compounds with long-chain alkylation agents, principally olefins, to produce phenylalkanes with an improved yield of the more external phenyl isomers. The reaction is carried out in the presence of crystalline zeolite catalyst, such as ZSM-4, ZSM-20, ZSM-38, REY, Linde Type L and zeolite β. The invention was illustrated by the alkylation of benzene with 1-dodecene, at an aromatic/olefin molar ratio of 4:1 and WHSV (water hourly space velocity) 30 h^{-1}. A summary of the results and reaction conditions is presented in Table 4. The table shows clearly that, among all the phenyl dodecane isomers, 2-phenyl dodecane is less favored with REY, which has a faujasite-like structure. The results suggest that shape selectivity plays a role, the relatively less bulky 2-phenyl product being favored. This was again evidenced in a subsequent study by the same author, Young (93). A process for the selective alkylation of benzene compounds with long-chainlength alkylation agents to produce a high 2-phenyl isomer content has been developed. In Table 5, results of runs are shown in which various zeolite materials were used that were characterized by channels or networks of pores having openings with a major dimension of 6–7 Å. The feed stream was a 4:1 molar mixture of benzene and 1-dodecene, which was passed across each of the catalysts at WHSV of 30 h^{-1}. The HZSM-12, Mordenite and Offretite selectively produce the 2-phenyl dodecane isomer in high yields with little or none of the other isomers. In contrast, the larger-pore size zeolites produce a relatively broader spectrum of phenyl dodecane isomers, making the 2-isomers difficult to isolate in significant amounts.

The use of various types of zeolites as catalysts in alkylation reactions, as described above, can produce a high proportion of the alkyl aromatic isomer in which the aromatic group is attached to the second carbon of the alkyl side chain. However, a substantial proportion of the alkylaromatic material produced has nonlinear side chains, that is, either the linear olefin and/or the alkyl aromatic product has undergone skeletal isomerization. These by-products are undesirable as alkylaromatic sulfonate detergents because they are nonbiodegradable. Bouncer (94) has patented a process for the production of alkylated aromatic hydrocarbons, in the range of detergent products, in the presence of large-pore noncrystalline amorphous acidic silica–alumina catalysts that results in phenyl alkanes of which only a small proportion has nonlinear alkyl side chains. The major product of the reaction is monoalkyl aromatic. Little poly-alkylation or olefin polymer co-production occurs. The catalyst is characterized by channels or networks of pores from about 50 to 500 Å. The reaction conditions are reactor temperature of 100–150°C and aromatic/olefin molar ratio of 3:1 to 7:1. The olefin conversion is 50 to 87%, with 73 to 84% selectivity to monoalkylation product, 98 to 100% selectivity to linear product and 25 to 46% selectivity to 2-phenyl isomer.

Ming-Juan *et al.* (95) have studied the alkylation of benzene with 1-octene and 1-dodecene on dried Al-pillared montmorillonite samples (Al–PM). The reaction was performed in a continuous stirred-batch reactor at 80°C and atmospheric pressure for a period of 0.5 h. The conversion of 1-dodecene correlates well with the amount of Brönsted acid sites, which depends on the pretreatment temperature of the samples. The conversion of Al–PM with respect to 1-octene and 1-dodecene was 56.3 and 99.2%, respectively. Al–PM with a basal spacing of 1.8–1.9 nm exhibited shape selectivity for reactions in which large molecules were involved.

Bouncer (96) has patented a process for producing alkylaromatic hydrocarbons by contacting an aromatic hydrocarbon with an alkylating agent, such as long-chain linear olefins (both alpha or random internal) containing from 10 to 20 carbons, in the presence of catalysts that consist solely of low-crystallinity, partially collapsed HY

TABLE 6

Alkylation of Benzene with a Commercial Olefin Mixture[a]

Selectivity	%
Linear alkylbenzene	92.4
Branched alkylbenzene	5.7
Heavy alkylbenzene	1.9

[a] Conversion = 97%, catalyst life = 182 h.

TABLE 7

Isomer Distribution (%) upon Alkylation of Benzene with 1-Dodecene

Alkylbenzene isomer	MCM-22	Beta
2	59.2	53.7
3	36.5	20.3
4	2.5	9.4
5	0.9	5.8
6	0.4	5.3
7	0.5	5.5

and HX zeolites that have from 30 to 80% retained crystallinity. Example B of the patent application shows that the feed stream, consisting of toluene and α-*n*-hexadecene (molar ratio 5:1), was passed upflow over the catalyst at a total LHSV (liquid hourly space velocity) of 1.67 h^{-1}, at 12 bars pressure, with H_2 (gas flow rate 0.04 m^3/h) at a temperature of 104°C. Gas-chromatographic analysis of the product stream indicated a conversion of 94.5%. After 179 h on stream, a catalyst sample was regenerated and reused and gave practically the same performance as the fresh catalyst.

Berna Tejero and Moreno Danvila (97) (Petroquimica Espanola S.A.–Petresa) has patented a process for the alkylation of benzene with long-chain olefins in the presence of an aluminum-magnesium silicate catalyst, to give LABs of detergent range. The process is of the continuous type and is carried out in a fixed-bed reactor in the liquid phase. As is shown in example 5 of the patent, benzene is alkylated with C_{10}-C_{14} linear olefins to produce monoalkylbenzenes. The alkylation reaction is carried out in a carbon steel tubular reactor, down flow, 330 mm long, with a height/inner diameter ratio of 7.45, with 540 g (500 cm^3) of catalyst. The catalyst consists of an aluminum silicate with a silica content of 61% and an alumina content of 16% by weight. It is shaped in a granular form and the particle size of the catalyst was in the 0.4–1.0 mm range. The reaction conditions were benzene/olefin molar ratio 20:1, 35 bars pressure, reaction temperature of 170°C and space velocity of 4 h^{-1}. The results are summarized in Table 6.

The regeneration of the catalyst is performed in a semicontinuous manner, by washing alternatively and successively the waste catalyst with a stream of paraffin and then a stream of alcohols.

Le *et al.* (98) have patented a process for the manufacture of long-chain alkyl aromatic compounds by alkylating an aromatic with a long-chain olefin in the presence of the zeolite MCM-22. The results of the alkylation of benzene with α-C_{14} olefin over MCM-22 and zeolite β are shown in Table 7. The alkylation was carried out in a one-liter autoclave with 2.02 moles of olefin, 1.01 moles benzene and 38 g catalyst. The reaction time was 5 h at 204°C under 27 bars nitrogen. The zeolite MCM-22 produced a significantly higher yield of 2- and 3-alkyl isomer varieties than a Lewis acid such as HF or zeolite β under identical or similar conditions.

TABLE 8

Alkylation of Benzene with 1-Dodecene

Catalyst	Product distribution 2 pH	3 pH	4 pH	5 pH	6 pH	2 pH/6 pH ratio
SiO_2–Al_2O_3	33.4	21.9	14.8	15.6	14.2	2.4
H-Montmorillonite[a]	26.0	19.1	16.7	19.1	19.1	1.4
Amberlyst	34.5	20.2	14.3	15.9	15.1	2.3
H-Y	29.5	20.2	17.1	16.9	16.3	1.8
RE-Y	17.6	19.1	19.8	22.0	21.5	0.8
H-BETA	39.1	26.4	18.9	10.8	4.80	8.2
HM[b]	63.7	35.4	0.90	trace	—	70.7[c]
HF	16.7	16.4	17.5	24.1	25.3	0.70

[a] WHSV set to 0.5 to obtain 100% conversion.
[b] Incomplete conversion.
[c] 2 pH/4 pH ratio, 6 pH not detected.

San Gil *et al.* (99) have studied acidic Brazilian clays, bentonites, as catalysts for the alkylation of benzene with 1-dodecene. The acid bentonite samples showed good activity for the alkylation reaction, and among all the samples tested, the most active catalysts were those with the highest Si/Al molar ratio.

Araújo (100) has studied the influence of lanthanides (La, Ce, Nd, Eu and Gd) in rare earth-exchanged Y zeolites in the alkylation reaction of benzene with 1-dodecene. The reaction was carried out in a batch reactor, at 80°C, for 120 min with a benzene/1-dodecene molar ratio of 8. The major product was the 2-phenyl isomer. The catalysts' activities were in the following order: La,Ca/NaY > Ce,Ca/NaY = Nd,Ca/NaY > Gd,Ca/NaY, and the selectivities to 2-phenyl isomer were Ce,Ca/Na > Nd,Ca/NaY = Gd,Ca/NaY > La,Ca/NaY. No transalkylation, polymerization or cracking reactions were observed.

Sivasanker and Thangaraj (101) have reported a comparative study of alkylation of benzene with 1-dodecene and with a commercial olefin mixture over a number of amorphous and zeolite catalysts. The reaction was performed in a vertical isothermal reactor, 19 mm i.d. A 50 g charge of catalyst (14–18 mesh) was used. The length of the catalyst bed was between 30 and 40 cm. The general reaction conditions were temperature = 135°C, WHSV = 0.8 h^{-1}, pressure = 7 bars and a benzene/olefin molar ratio of 10:1. These reaction conditions were chosen to keep the benzene in the liquid state and to achieve 100% conversion of olefin. The results are given in Table 8.

The H-β, H-M and H-Y catalysts are classified as wide-pore zeolites. H-M has unidirectional pores (0.67 × 0.70 nm); H-β has a complicated 3-D pore system (0.73 and 0.55 nm), while the faujasites (Y-type) have large cavities (1.3 nm diam.), along with a 3-D system (0.73 nm). H-M and H-β produce much more 2-phenyl isomers than H-Y or RE-Y. In H-M and H-β, shape selectivity appears to play a key role, with the relatively nonbulky 2-phenyl product being favored. H-M is so shape selective that the 5- and 6-phenyl isomers are not formed at all. The similarities in product distribution between RE-Y and HF suggest the absence of shape selectivity in the Y (Faujasite) system. The results of alkylation with a commercial mixture olefin feed (C_{10}-C_{13}), were similar to those reported for the alkylation of benzene with 1-dodecene.

Sivasanker *et al.* (102) have studied the alkylation of benzene with 1-hexene, 1-octene, 1-dodecene and a mixture of C_{10}-C_{13} olefins (alkylation feed used in industrial manufactured LAB) over a number of wide pore zeolites (H-Y, H-β, H-M, H-L, HZSM-12) and medium-pore zeolites (EU-1 and ZSM-5). Zeolite Y does not exhibit shape selectivity effects in the alkylation of benzene with long-chain alkenes with C-number as large as 13. Mordenite and zeolite β exhibited more pronounced shape selectivities with increasing C-number of the alkene. The shape selectivities observed are attributed to both product and transition-state types.

A new detergent alkylation process, the Detal® process, developed by UOP/Petresa is being introduced for the selective alkylation of benzene with olefins in a fixed-bed alkylation reactor (liquid phase) as we have previously mentioned.

The available data clearly show that heterogeneous catalysts indeed may be taken seriously as a potential substitute for the current processes of LAB manufacture. As is normal, the pioneer studies in this field have mostly been of the catalyst screening type to afford a reasonable basis for both practical and fundamental research in this field.

The future work in this area will be devoted at least partly to the stability of the various catalyst formulations against ageing. The relationship between activity and selectivity of a catalyst and its porous nature will no doubt attract considerable attention from investigators of both industrial and academic background. Focus will also be placed on the possible relationship between acidic strength and/or density and the desired LAB structure.

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