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Lecture Transcripts

Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture

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Abstract:

Sulfonation of linear alkylbenzenes by reaction with sulfur trioxide is the predominant route to anionic surfactants other than soap. In the case study presented here, alkylbenzenes are contacted with sulfur trioxide in a short residence time falling film reactor following which the liquid reaction product mixture is aged. This work reviews a computational chemistry study, supported by an experimental relative rate study, on the reaction pathways occurring in the falling film reactor. It is concluded that the commonly accepted mechanism for aromatic sulfonation by sulfur trioxide does not apply, at least to alkylbenzene sulfonation, and an alternative reaction pathway consistent with the computational and experimental findings is proposed. A kinetic study on the ageing reactions is presented, indicating that there are several distinct stages leading to increase in conversion of linear alkylbenzene to linear alkylbenzene sulfonate. On the basis of these findings, process modifications leading to conversion increases ranging from 0.5 to 1% have been achieved, and conversion losses of up to 1.5% during storage have been eliminated.

Introduction

Sulfonation is the predominant route to the manufacture of anionic surfactants other than soap. Sulfonation for surfactant manufacture is usually carried out as a continuous process, typically on a scale of several tonnes per hour. However, the same basic principles of process development applicable to batch processes on the fine chemicals scale, i.e., understanding of the mechanisms and kinetics of the main reactions and side reactions so as to arrive at optimum process conditions, are equally applicable to sulfonation. This is illustrated by the present case study on linear alkylbenzene sulfonate (LAS) manufacture.

Linear alkylbenzene sulfonate (LAS) is the major anionic nonsoap surfactant used in laundry products. It is made by sulfonation of linear alkylbenzenes (LAB). LAS is presently made predominantly by sulfonation with sulfur trioxide, although in the past oleum and sulfuric acid were widely used and are still not completely obsolete in this role. Although the manufacture of LAS has been practised for many decades, new insights into the sulfonation chemistry and more stringent quality requirements continue to evolve.

General Features of Sulfonation by Sulfur Trioxide[1]

Sulfur trioxide is a liquid in the temperature range 32–44.5 °C. Below 32 °C a solid form begins to crystallise out, although this can be inhibited, down to a temperature of 16.5 °C, by small amounts of stabilising additives. Evaporation of the stabilised liquid is a useful source of sulfur trioxide for laboratory-scale sulfonation and is sometimes used on the manufacturing scale. More commonly however, production scale sulfonation plants have a dedicated sulfur burning/catalytic conversion unit to produce a gaseous mixture of sulfur trioxide and air which is fed directly to the sulfonation reactor.

Sulfur trioxide is a very reactive sulfonating agent. Accurate rate constants are rarely available, being too large to be conveniently measurable, but sulfonation reactions are often described as "instant" or diffusion-controlled. These reactions are highly exothermic, heats of reaction being of the order of 35–40 kcal/g·mol (this includes ca. 6 kcal/g·mol for the heat of absorption of gaseous sulfur trioxide in the organic substrate[2]). Sulfonation reactions, if not adequately controlled, can be accompanied by oxidation reactions, leading to color and sulfur dioxide formation.

Sulfonation Reactors[1]

Various types of reactors (e.g., batch-stirred tank reactors, continuous-stirred tank reactor cascades) can be used for sulfonation with sulfur trioxide, but presently the majority of new sulfonation reactors installed are of the falling film reactor (FFR) type.

Principles of Film Reactor Design. The basic principle of the FFR is that a stream of gaseous sulfur trioxide, diluted with air, is passed down a vertical tube, with the organic liquid feedstock flowing co-currently as a film along the tube wall. The main impetus for the flow of the organic liquid is the drag exerted by the gas on the film, the gravitational contribution being negligible. As the liquid and gas flow along the tube, sulfur trioxide is absorbed by the liquid and reacts to form the sulfonated product. The heat of reaction is removed by coolant applied to the other side of the tube wall. Because the surface-to-volume ratio of the film is high, the reaction exotherm can be efficiently removed within the short residence time (ca. 30 s) of the liquid.

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(1) Roberts, D. W. *Org. Process Res. Dev.* **1998**, *2*, 194.

(2) Roberts, D. W.; Morley, J. O. *Commun. Jorn. Com. Esp. Deterg.* **1997**, *27*, 145.

10.1021/op020088w CCC: $25.00

The hydrodynamics and thermokinetics of FFR sulfonation are complex and interlinked. The flow pattern of the liquid down the reactor is predominantly laminar rather than turbulent, and consequently, as sulfur trioxide is absorbed at the gas/liquid interface, temperature and composition gradients develop in the radial direction as well as in the vertical direction. These gradients lead to differences in mass-transfer and heat-transfer characteristics at different points. The maximum temperature is reached at the gas/liquid interface near the top of the reactor and may exceed 100 °C. The viscosity of the film, being dependent on composition and temperature, varies substantially, leading to variation of film thickness along the length of the reactor (typically from less than 0.5 mm at the top of the reactor to ca. 2 mm at the bottom) and to radial and vertical variations in the degree of turbulence in the film. These characteristics make mathematical modelling of film sulfonation far from straightforward, but several models, differing in the nature of the simplifying assumptions made, have been published.[3−8] Film reactor modelling remains an active area of current research.

A common FFR design, which is used in the case study presented here, is illustrated in Figure 1. It is based on vertical reactor tubes, arranged as in a shell and tube heat exchanger, of 25.4 mm internal diameter and 6 m in length. A single tube has a throughput of ca. 40 kg/h of linear alkylbenzene sulfonic acid (LAS) and, using a 5% solution of gaseous sulfur trioxide in air, operates with a gas velocity of ca. 30 m/s.[1] The capacity of such a reactor depends on the number of tubes—a pilot plant FFR would be based on a single tube, whilst a large commercial reactor might be based on up to 144 tubes (capacity ca. 5.5 tonnes/h).

Sulfonation conditions in a film reactor can be adjusted by modifying the throughput of the feedstock (this means a corresponding change in the sulfur trioxide throughput), changing the coolant temperature (although in practice the scope is restricted by the need to maintain the reaction mixture sufficiently fluid) and changing the molar ratio of sulfur trioxide to feedstock (the scope to do this being limited by the need to achieve high conversion and the need to avoid oversulfonation leading to excessive by-product and colour formation).

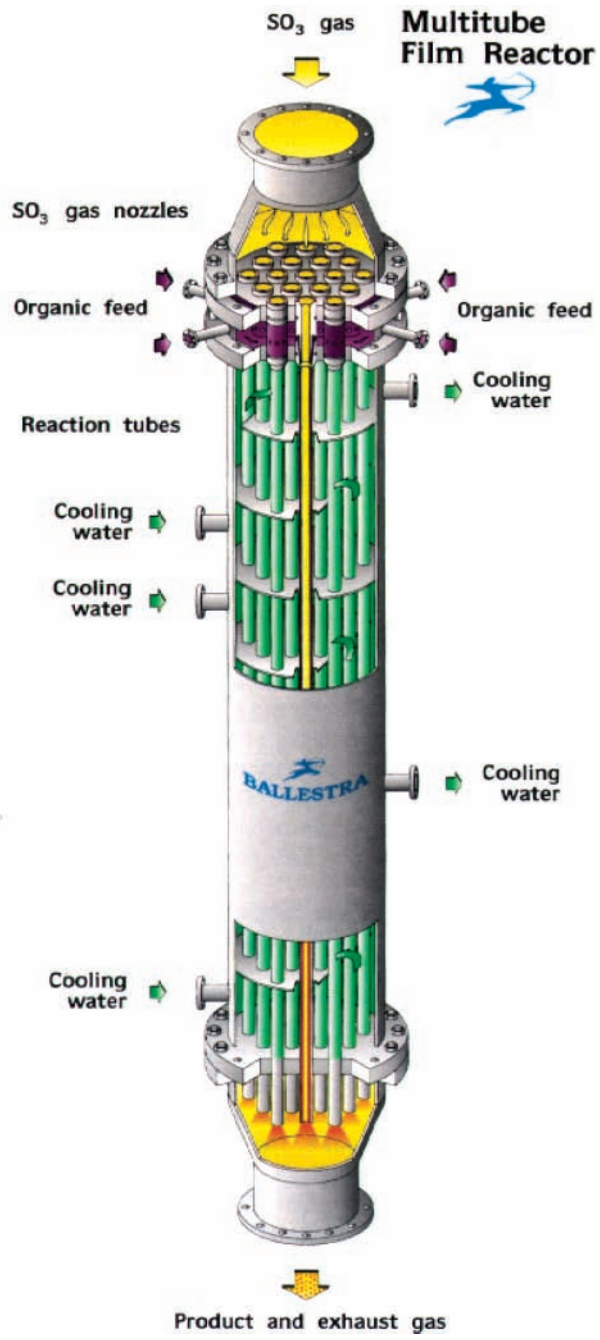

Figure 1. **Multitube falling-film reactor (19 tubes). Reproduced by kind permission of Ballestra S.p.A.**

In carrying out a continuous sulfonation run, the throughputs and temperatures of feedstock, air, sulfur trioxide, and coolant are usually set at predetermined values, and fine-tuning is done by making fine adjustments to the feedstock throughput in response to plant-side analysis of samples from the reactor outlet. Plant-side analysis for LAS production is nowadays usually done by nonaqueous potentiomentric titration of a methanolic solution of LAS acid with methanolic cyclohexylamine. This titration gives two end points: the first corresponds to neutralisation of LAS acid and the first proton of sulfuric acid while the second corresponds to neutralisation of the second proton of sulfuric acid. From these two titres, the percentages of LAS and sulfuric acid in the sample can be calculated. The titrations and the calculations are usually automated, and the analysis can be completed within about 5−10 min.

General Features of Linear Alkylbenzene (LAB) Sulfonation

LAS is made by sulfonation of linear alkylbenzenes (LAB). Commercial LAB is a mixture of isomers and homologues having the general structures shown in Figure 2, which also summarises the routes used in the petrochemi-

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(3) Johnson, G. R.; Crynes, B. L. *Ind. Eng. Chem. Process Des. Dev.* **1994**, *13*, 6.
(4) Mann, R.; Moyes, H. *AIChE J.* **1977**, *23*, 17.
(5) Davis, E. J.; Van Ouwerkerk, M.; Venkatesh, S. *Chem. Eng. Sci.* **1979**, *34*, 539.
(6) Tsuto, K.; Nakayama, M.; Imamura, S.; Majima, K. *Kagaku Kogaku Rombunshu* **1985**, *11*, 369.
(7) Gutiérrez-González, J.; Mans-Teixidó, C.; Costa-López, J. *Ind. Eng. Chem. Res.* **1988**, *27*, 1701.
(8) Dabir, B.; Riazi, M. R.; Davoudirad, H. R. *Chem. Eng. Sci.* **1996**, *51*, 2553.

cal industry for LAB manufacture. The linear alkyl group typically ranges from C10 to C14 chain length.

Although the sulfonation of LAB is very rapid and for practical purposes may be treated as diffusion-controlled, paradoxically it does not go to completion in FFR sulfonation but requires a further ageing step, customarily with a residence time of about 30−50 min at ca. 45−55 °C. Typically the conversion of LAB to LAS is about 90−92% when the reaction mixture emerges from the FFR and rises to about 96−98% after ageing. The usual explanation for this paradox[9] is that accompanying the main reaction with overall stoichiometry:

$$\mathrm{ArH} + \mathrm{SO_3} \rightarrow \mathrm{ArSO_3H}$$

there is a side reaction producing LAS anhydride, with overall stoichiometry:

$$2\mathrm{ArH} + 3\mathrm{SO_3} \rightarrow \mathrm{ArSO_2OSO_2Ar} + \mathrm{H_2SO_4}$$

When the reactor is fed with sulfur trioxide and LAB in a 1:1 molar ratio, then to the extent that the side reaction occurs there will be residual LAB when all of the sulfur trioxide has been consumed. This explains why the conversion at the base of the FFR is relatively low.

However, LAS anhydride and sulfuric acid together act as a slow sulfonating agent, and in the ageing step they sulfonate the residual LAB to produce more LAS, in a reaction with overall stoichiometry:

$$\mathrm{ArSO_2OSO_2Ar} + \mathrm{H_2SO_4} + \mathrm{ArH} \rightarrow 3\ \mathrm{ArSO_3H}$$

As a final step in LAS manufacture it is customary to add a small amount of water (typically about 1%) after ageing to hydrolyze any remaining LAS anhydride. The chemistry underlying the effect of water addition does not appear to have been fully investigated, but it is usually argued that residual LAS anhydride could continue to sulfonate under uncontrolled conditions during storage, leading to color formation.

Another side reaction leads to formation of diaryl sulfones and sulfuric acid, the overall stoichiometry being:

$$2\mathrm{ArH} + 2\mathrm{SO_3} \rightarrow \mathrm{Ar_2SO_2} + \mathrm{H_2SO_4}$$

To the extent that it occurs, sulfone formation limits the maximum achievable conversion of LAB to LAS to a value below 100% and makes it impossible to completely avoid the presence of sulfuric acid (typically at levels in the range ca. 1−2%) in the final sulfonation product. Sulfone levels in the final product depend on the ratio of sulfur trioxide to LAB supplied to the reactor but are usually below 1%.

After completion of the water-addition step the reaction mixture consists predominantly of LAS and can be stored until required for further use or transported to another location for use there. This material is often referred to as LAS, LAS acid, or LASH. In other contexts the term LAS is sometimes reserved for the neutralised form (usually the sodium salt).

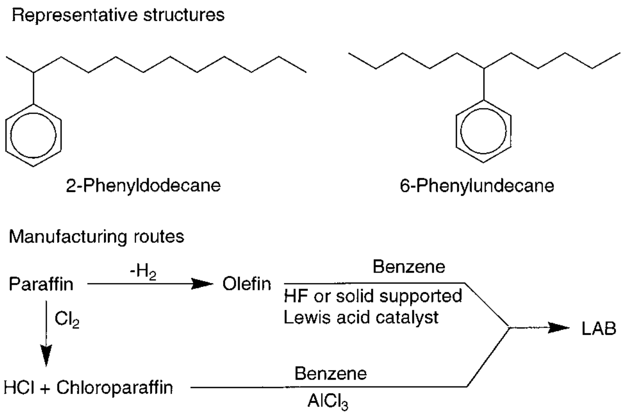

Figure 2. **LAB and its manufacturing routes.**

Table 1. **Typical LAS manufacture in multitube falling-film reactors**

FFR	
throughput per tube	40 kg/h sulfonic acid
SO_3 gas concentration	5% in air
coolant temperature	30 °C (in) − 34 °C (out)
acid exit temperature	45−55 °C
ageing	30−50 min at 45−55 °C
stabilisation	ca. 1% water added

The product manufactured as described above typically contains small quantities of sulfuric acid (in the range 1.5−2.5 wt %) and nondetergent organic material commonly referred to as free oil (FO) at a level in the range 1−2.5 wt %. The composition of the FO depends on the sulfonation conditions and the composition of the LAB used as the reaction feedstock. It consists of unreacted LAB and organic by-products such as sulfones. Any unsulfonatable organic materials such as paraffins, originally in the feedstock, are also found in the FO after sulfonation. The LAS present in the mixture is commonly referred to as active matter (AM) or anionic detergent (AD), to avoid confusion due to the term LAS being used for the whole mixture. Typical AM/AD levels in LAS produced by the method described above are in the range 95−97 wt %. To a greater or lesser extent, depending on reaction conditions and LAB feedstock quality, LAS may be colored, varying in appearance from almost water-white through yellow and brown to black, due to the presence of trace quantities of oxidation products. The color of LAS may be quantified in various ways. A very old and still widely used color parameter is the Klett value, which is the absorbance of 460 nm light of a 5% solution of the test material (usually in 2-propanol or methanol) in a 4-cm cell. Modern color acceptability criteria for LAS acid range from <30 Klett (faintly yellow as a 5% solution) to <100 Klett (pale brown as a 5% solution).

Table 1 summarises the typical conditions used in FFR sulfonation of LAB.

Scope for Optimisation

Although conversions of over 95% with acceptable colours are not difficult to achieve in LAB sulfonation, there is still scope for further optimisation. The term “optimisation” may be interpreted in different ways, depending on the requirement. Thus, it can mean:

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(9) Roberts, D. W. *Jorn. Com. Esp. Deterg.* **1995**, *26*, 369.

Maximising conversion of LAB to LAS (i.e., minimising total free-oil content): because of the large scale on which LAB sulfonation is practised, there are significant savings to be had even from a 0.5% increase in conversion.

Maximising throughput whilst maintaining acceptable-quality standards of colour and free oil content: this can avoid the need to source LAS from third parties (at a premium) when a plant operating at nameplate capacity experiences an increased demand.

Minimising unconverted LAB content on the free-oil: this can be important when the LAS is to be used in spray-dried powders—LAB, being volatile under spray drying conditions, can be emitted to the environment in the air effluent from the spray-drying tower.

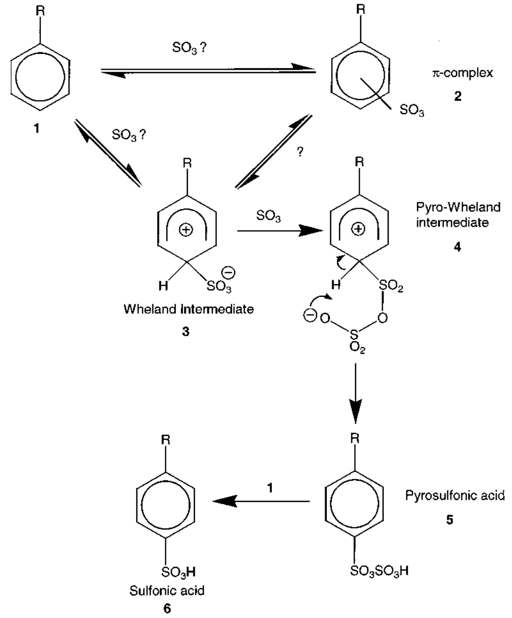
Minimising color (e.g., where the LAS is to be used in a liquid product) with minimum penalty in terms of reduced conversion or throughput.

The aim of the work described here was to provide a detailed understanding of the reaction chemistry of LAB sulfonation to be able to manipulate the process so as to achieve optimisation according to whichever of the above definitions is relevant.

The Mechanism of the Main Reaction

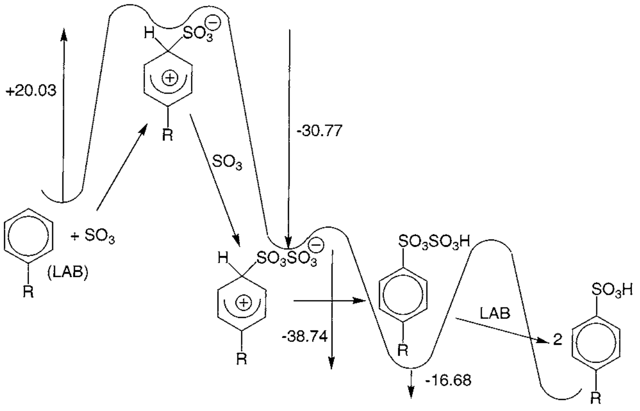
A commonly accepted mechanism for aromatic sulfonation is electrophilic attack of sulfur trioxide (SO_3) on the aromatic ring of the substrate (**1**) to produce, possibly via a π-complex (**2**), a Wheland intermediate (**3**) which reacts with more SO_3 to form, via a pyrosulfonic Wheland intermediate (**4**), a pyrosulfonic acid (**5**)[10] which can then react with **1** to produce the sulfonic acid (**6**). This mechanism is shown in Scheme 1. Kinetic studies on sulfonation of various substituted benzenes in various solvents have been interpreted in terms of this mechanism, the rate-determining step being proposed in some cases as the formation of **3** (kinetics first order in both aromatic and SO_3) and in other cases as reaction of **2** with SO_3 to form **4** (kinetics first order in aromatic and second order in SO_3).[10] Reaction of **5** with **1** to produce **6** is usually considered to be slow in comparison with the reactions leading to formation of **5**, and in most of these kinetic studies **6** is not the major product of the overall reaction.[10]

Scheme 1. **Commonly accepted mechanism for aromatic sulfonation[10]**



More recently the mechanism shown in Scheme 1 has been investigated by a molecular modelling approach.[11] Scheme 2 shows the enthalpy changes, ΔH, for each step, as obtained from ab initio calculations of the appropriate molecular orbital energies (in zero dielectric medium), using toluene as a model for LAB.[11]

Scheme 2. **Enthalpy diagram for Scheme 1**



The activation energy for this reaction pathway via the Wheland intermediates **3** and **4** would be somewhat higher than the enthalpy difference between the starting materials and the transition-state-like Wheland intermediate **3**, i.e., higher than 20.03 kcal/mol. Is this activation energy consistent with what is observed in FFR sulfonation of LAB?

Within the film residence time of about 30 s all of the SO_3 supplied is converted to stable products (mainly LAS, some anhydride, sulfone, and sulfuric acid). Assume that "all" means $>97-98\%$, corresponding to at least 6 half-lives of a first order or pseudo-first-order reaction. For 6 half-lives $= 30$ s the (pseudo) first-order rate constant k(obs) should be 0.14 s^{-1}

Assuming the sulfur trioxide concentration $[SO_3]$ to have a small steady-state value we can treat the reaction as pseudo-first-order:

$$k(\text{obs}) = k[SO_3]$$

We can make an estimate of the maximum value of $[SO_3]$ from the fact that at low (up to at least 0.9) SO_3/LAB mol ratio, when the fresh sulfonation product from the film is quenched and titrated to measure sulfonic and sulfuric acid, the sulfuric acid (which can come inter alia from "dissolved SO_3") amounts to no more than 0.3%, corresponding to about 1 mol % based on initial LAB. The molarity of LAB (neat

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(10) Bosscher, J. K.; Cerfontain, H. Aromatic Sulfonation 20. *Rec. Trav. Chim.* **1968**, *87*, 873.

(11) Morley, J. O.; Roberts, D. W. *J. Org. Chem.* **1997**, *62*, 7358.

Table 2. **Arrhenius parameters required for Scheme 1 to be applicable**

T (°C)	log A (L/mol/s) for $E_{\mathrm{Act}} = 20.03$	$\Delta S^{\ddagger\,a}$ (eu)	E_{Act} (kcal/mol) for log $A = 9$
40	14.6	+20.0	12.1
50	14.2	+18.0	12.5
60	13.8	+16.0	12.9
70	13.4	+14.2	13.3
80	13.0	+12.5	13.7
90	12.7	+10.9	14.1
100	12.4	+9.3	14.4
110	12.1	+7.9	14.8
120	11.8	+6.5	15.2

[a] $\Delta S^{\ddagger}$ calculated for standard state of 1 mol/mL.

liquid, as used commercially) is about 4 mol/L. On this basis $[SO_3] = 0.04$ mol/L at the most.

Thus, for complete reaction as defined above the second-order rate constant k should be:

$$k = 0.14/0.04 = 3.5 \text{ L/mol/s}$$

Substituting this value in the Arrhenius equation and using an E_{Act} value of 20.03 kcal/mol (the energy difference between **1** plus SO_3 and **3**, R = Me) we can calculate the required values for the preexponential factor A over the appropriate range of temperatures (Table 2). The temperature of the feedstock is initially about 40 °C, and the average temperature in film sulfonation is typically less than 70 °C, although temperatures up to about 120 °C can occur in parts of the film near the top of the reactor.

It can be seen that all of these A values correspond to entropies of activation which are large and positive. Such high positive values are completely unrealistic for reactions in which two reacting molecules form one product molecule. Typically for such reactions $\Delta S^{\ddagger}$ values are negative. Even for first-order gaseous decompositions—1 molecule forming 2—the highest $\Delta S^{\ddagger}$ value listed by Frost and Pearson[12] (p110) is +17 eu.

The log A values tabulated above may be compared with values quoted by Frost and Pearson[12] (p 104) for some typical second-order gas-phase reactions in which two reacting molecules form one product molecule:

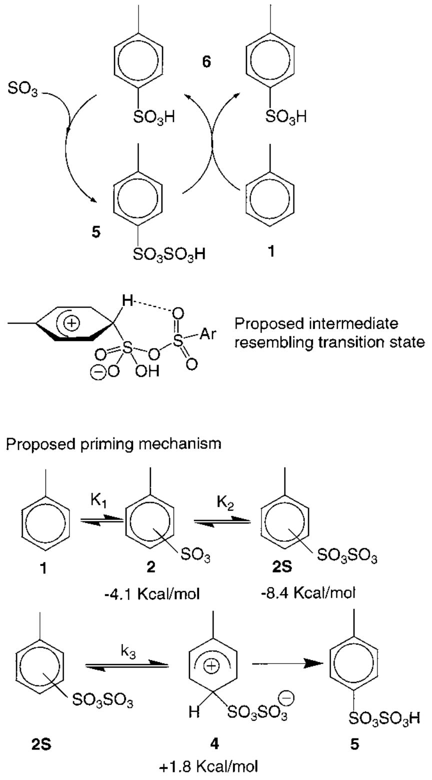
butadiene dimerisation	7.7
isoprene dimerisation	8.7
isobutene + HCl	8.0

Another way to approach this question is to calculate for each temperature the activation energy which would give the required value of 3.5 L/mol/s for the rate constant if the log A value were in the typical range. These values are shown in Table 2, based on a log A value of 9. It can be seen that the activation energy would have to be very much lower than the computed enthalpy of formation of the Wheland intermediate **3** from **1** and SO_3.

Thus, on this basis the computed enthalpy of formation of the Wheland intermediate **3** from LAB and SO_3 is not consistent with **3** being an intermediate in the major reaction pathway.

An alternative mechanism has been proposed[2,13] whereby in a first step LAS, **6**, reacts with SO_3 to form the short-lived pyrosulfonic acid **5**. It may be noted that in FFR sulfonation the liquid at the gas/film interface will be composed mainly of LAS even when the overall conversion is low, since LAS is surface active. In the second step **5** reacts with LAB, **1**, to produce 2 mol equiv of **6**. One of these mole equivalents can be regarded as replacing the one consumed in the first step, and the other can be regarded as contributing to the increase in conversion. This proposed mechanism is shown in Scheme 3. The kinetics would be first order in sulfur trioxide and first order in LAB. For this mechanism the system needs to be primed initially with a small amount of LAS **6** or pyrosulfonic acid **5**. The proposed priming sequence,[2,13] via a 2:1 SO_3/LAB π-complex **2S**, is also shown in Scheme 3.

Scheme 3. **Proposed mechanism for LAB sulfonation**



Kinetics for the Mechanism of Scheme 3. The computed enthalpy of formation of pyrosulfonic acid **5** from toluene-sulfonic acid **1** and SO_3 is −16.4 kcal/mol. Thus, the equilibrium between LAS **6** plus SO_3 and pyrosulfonic acid **5** should favour **5**. The forward reaction can be envisaged as proceeding via complexation of SO_3 to a sulfonyl oxygen of LAS, followed by a facile intramolecular proton transfer. The activation energy should be very low.

The pyrosulfonic Wheland intermediate **4** shown in Scheme 4 is calculated to be stabilised, relative to its non-hydrogen-bonded conformer, by 7.53 kcal/mol. This represents the degree to which the intermediate is stabilised by intramolecular hydrogen bonding. Attack of pyrosulfonic acid

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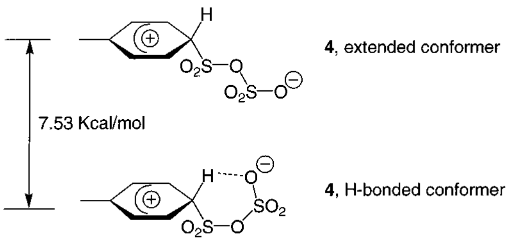
(12) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed., Wiley: New York, 1961.

(13) Morley, J. O.; Roberts, D. W.; Watson, S. P. *J. Chem. Soc., Perkin Trans. 2* **2002**, 538.

Scheme 4. **Conformers of the pyrosulfonic Wheland intermediate 4**



on an alkylbenzene to form a Wheland intermediate as shown in Scheme 3, with hydrogen bonding of the *ipso* hydrogen from the alkylbenzene, should therefore be less endothermic, by about 7.5 kcal/mol, than formation of the simple Wheland intermediate **3** from SO_3 and **1**. Thus, the activation energy for sulfonation of LAB by pyrosulfonic acid should be not much larger than 12.63 kcal/mol (the sum of 20.16, energy of formation of **3** from **1** and SO_3, and −7.53, the intramolecular hydrogen-bond stabilisation energy). Rounding up gives 13 kcal/mol as the estimated activation energy. Since the reaction is one in which two reacting molecules form two product molecules, a value of about 10^{11} $L{\cdot}mol^{-1}{\cdot}s^{-1}$ for the preexponential factor seems appropriate, and on this basis the estimated Arrhenius equation is:

$$k = 10^{11}\,e^{-13000/RT}$$

For an assumed SO_3 concentration of 0.01 mol/L the calculated reaction rates are reasonably consistent with experience in FFR sulfonation of LAB (Table 3). It may be recalled that in considering the reaction pathway of Scheme 1 the SO_3 concentration was assumed to be 0.04, not 0.01 mol/L as assumed here. This is because in the former case, where the purpose was to demonstrate the inapplicability of Scheme 1, it was appropriate to make a generous assumption. In the present case, where the purpose is to test the robustness of Scheme 3, a parsimonious assumption is appropriate.

Table 3. **Calculated rate constants and reaction times for Scheme 3**

T (°C)	k (s^{-1})	6 half-lives (s)
40	0.84	2.74
60	2.93	0.81
80	8.93	0.27
100	24.1	0.10

The 6 half-life figures are a very crude representation of the time needed for 97.5% reaction, being applicable to isothermal reaction. A better assessment of the above Arrhenius equation is obtained by using a numerical integration approach to take into account the rise in temperature as the reaction proceeds, due to the reaction exotherm. To do this, the following procedure is adopted:

(1) The heat output is calculated. This is the sum of the enthalpy of reaction (from the MO calculations, −33.1 kcal/mol) plus the molar heat of absorption of gaseous sulfur trioxide into liquid LAB. The heat of absorption would ideally be calculated as the sum of the heat of condensation of sulfur trioxide from the gas to the liquid state, plus the heat of solution of liquid sulfur trioxide in liquid LAB. The former value can easily be calculated from vapour pressure data[14] on liquid sulfur trioxide as −11.1 kcal/mol. The Trouton constant is 34.9 eu, corresponding to a high degree of association in the liquid phase. The heat of solution of liquid sulfur trioxide in liquid alkylbenzene is not known: since alkylbenzene is not an associated liquid, this heat will be positive, corresponding to the loss of the liquid sulfur trioxide association energy.

A less rigorous approximate approach is to equate the absorption enthalpy to minus the latent heat of evaporation of SO_3, calculated from the boiling point of SO_3 (318 K), and an assumed Trouton constant of 22 eu, corresponding to a nonassociated liquid.

The resulting value for the heat of absorption is −7.2 kcal/mol.

Adding this to the calculated enthalpy of reaction gives a total of −40.3 kcal/mol for the combined heat of absortion and reaction. This may be compared to the experimental value of −40.2 kcal/mol[15] often quoted for $\Delta H_a + \Delta H_r$.

(2) The specific heat of the reaction mixture is taken as 0.6 $cal{\cdot}deg^{-1}{\cdot}g^{-1}$. From this assumption it follows that, if no heat is removed, each 1% of reaction will raise the temperature by about ($670/M$) °C, where M is the molecular weight of the reaction mixture. Thus, under adiabatic conditions, to raise the temperature by 1 °C requires ($M/670$) % reaction and to raise the temperature by 2.5 °C requires ($2.5M/670$) % reaction.

(3) It is assumed that the proportion of the reaction exotherm which is not removed is linearly related to the temperature, boundary conditions being that at 40 °C none of the exotherm is removed and at 95 °C all of the exotherm is removed. Thus, the fraction of the exotherm available to raise the temperature is ($95 - T$)/55. To raise the temperature by 2.5 °C requires:

$$55 \times 2.5M/670(95 - T)\ \%\ \text{reaction}$$

(4) Spreadsheet formulae can now be used to calculate the reaction time required, starting from 40 °C with the rate constant corresponding to 40 °C, for the temperature to rise in 1° intervals. The computed % reaction is 81% when the temperature reaches 94 °C, the time being 0.20 s. The further time required at 94 °C to take the reaction the rest of the way to 97.5% completion is then calculated to be 0.11 s. Thus, the total time needed for 97.5% completion is 0.31 s. The same result is obtained if 0.5° and 0.2° temperature intervals are used, indicating that 1° intervals give a good enough approximation for the numerical integration.

Thus, the estimated 97.5% reaction time is ca. 0.3 s. Even if the estimate of A in the Arrhenius equation were off by a factor of 10, the estimated reaction time would still be only 3 s, still well within the residence time of a commercial falling-film reactor. This is consistent with the reaction being substantially complete within the residence time of a commercial falling-film reactor.

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(14) Herman de Groot, W. *Sulfonation Technology in the Detergent Industry*; Kluwer: Dordrecht, 1991.

(15) Ratcliff, G. A. PhD Thesis, Cornwell University, 1954.

Table 4. Calculated kinetic parameters for the self-priming reaction

log A	[SO3]	k (s^{-1})	t (0.1%, s)	t (1%, s)	t (97.5%) at 90°C
Activation energy E_{Act} taken as 2 kcal/mol					
3	0.01	4.0×10^{-3}	0.25	2.5	10 min
4	0.01	4×10^{-2}	2.5×10^{-2}	0.25	1 min
5	0.01	0.4	2.5×10^{-3}	2.5×10^{-2}	6 s
4	0.02	0.16	6.2×10^{-3}	6.3×10^{-2}	15 s
Activation energy E_{Act} taken as 3 kcal/mol					
3	0.01	8.0×10^{-4}	1.2	12.5	40 min
4	0.01	8.0×10^{-3}	0.12	1.25	4 min
5	0.01	8.0×10^{-2}	1.2×10^{-2}	0.13	24 s
4	0.02	4.1×10^{-2}	0.02	0.2	1 min

It should be noted that the calculations described above are purely for the purposes of testing whether the mechanism of Scheme 3 would give kinetics consistent with manufacturing experience and are not intended as a realistic model of the physicochemical processes occurring in commercial FFRs. The calculations would be directly applicable in modelling a hypothetical FFR with plug flow in the film, but in practice the hydrodynamics of commercial FFRs correspond more to laminar flow.

It is now necessary to consider the kinetics of the self-priming pathway proposed in Scheme 3. It is proposed that the π-complex **2** is formed reversibly from **1** and SO_3 and that this π-complex then reacts reversibly with more SO_3 to form the "pyro-π-complex" **2S**. This can then rearrange to form the pyrosulfonic Wheland intermediate **4** (initially as the non-hydrogen-bonded conformer), which can then form the pyrosulfonic acid **5**. The overall reaction can be represented as pseudo-first-order in which the pseudo-first-order rate constant is given by $K_1 \cdot K_2[SO_3]^2 \cdot k_3$.

The computed enthalpy of formation of 1 mol of **4** (non-hydrogen-bonded conformer) from 1 mol of toluene and 2 mol of SO_3 is small and negative (−3.22 kcal). The reaction steps $\mathbf{1} + SO_3 \rightarrow \mathbf{2}$ and $\mathbf{2} + SO_3 \rightarrow \mathbf{2S}$ are both computed to be exothermic, but the rearrangement of **2S** to **4** (non-H-bonded) is computed to be endothermic by 1.8 kcal/mol. The energy of the transition state seems unlikely to be much greater than that of **4** (non-H-bonded), and on that basis activation energy values of 2 kcal/mol and 3 kcal/mol are used in the illustrative calculations below.

The A value in the Arrhenius equation for the overall self-priming pathway will be in the range appropriate for a third-order reaction. Log A values quoted by Frost and Pearson[12] (pp 75 and 108) for such reactions range from 3 to 10 (A in $L^2\ mol^{-2}\ s^{-1}$ units). Assuming a $\Delta S^{\ddagger}$ value of −40 eu, which seems reasonable for three molecules combining to form one, gives a log A value of 4.26. In the illustrative calculations given below, log A values of 3, 4, and 5 are used. Table 4 shows calculated pseudo-first-order rate constants k and 0.1% and 1% reaction times at 40 °C, based on the various assumed $[SO_3]$, log A and E values.

For all of these assumed $[SO_3]$ and log A values the t (0.1%) values are low enough to enable the mechanism of Scheme 2 to be consistent with the FFR residence time. Even if it is assumed that 1% reaction is necessary for priming, then the total time (priming plus main reaction) to reach 97.5% reaction would still be well within the FFR residence time for all cases covered in Table 4.

Table 5. Sulfonation relative rate data for linear alkyl benzenes

structure[a]	relative rate constant from analysis before and after sulfonation: commercial LAB	alkylbenzenes mixed with 10 mol excess: cumene	tetralin
2−12	1	1	1
3−12	0.95		
2−13	0.98		
3−13	0.94		
2−11	1.01		
3−11	0.96		
2−10	1.02		
3−10	0.99		
1−12		1.15	1.19
1−10		1.22	1.28
1−9		1.25	1.33
1−8		1.30	1.39
1−7		1.31	1.47
1−6		1.39	1.62

[a] 2−12 = 2-phenyldodecane, etc.

The estimated 90 °C t (97.5%) values shown in Table 4 are in most cases, but not all, above the FFR residence time. Furthermore, as can be seen from comparison of Tables 3 and 4, the estimated pseudo-first-order rate constants for the proposed main reaction are in all cases larger than those for the self-priming reaction. Thus, although the formation of pyrosulfonic acid via the "pyro-π-complex" is plausible for priming the reaction pathway of Scheme 3 it seems less likely to be fast enough to serve as the main reaction pathway.

Further evidence comes from studies on the relative rates of sulfonation of the various homologues and isomers of LAB. Comparing initial LAB composition with composition of the unconverted LAB in the sulfonated product mixture, Cohen et al.[16,17] observed that the proportion of higher-molecular weight LAB homologues was higher in the recovered LAB after sulfonation than in the initial LAB and that the proportion of 2-phenyl alkanes was higher in the initial LAB than in the recovered LAB. Subsequent work at the University of Wales, Swansea, both with commercial LAB mixtures[18] and with simpler mixtures of model 1-phenyl alkanes of different chain lengths[19] confirmed and quantified the trends:

− for a given alkyl chain length, the 2-phenyl isomer is more reactive than the 3-phenyl, 4-phenyl, etc. isomers and

− for a given phenyl substitution position, the shorter the chain length, the more reactive.

These trends are illustrated by the data shown in Table 5. They indicate that the sulfonating agent must be sufficiently bulky for the reaction to be influenced by steric

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(16) Bravo, J. E.; Bengoechea, C.; Cohen, L. *Jorn. Com. Esp. Deterg.* **1989**, *20*, 301.

(17) Cohen, L.; Vergara, R.; Moreno, A.; Berna, J. L. *J. Am. Oil Chem. Soc* **1995**, *72*, 157.

(18) Roberts, D. W.; Ward, R. S.; Hughes, P. J. *J. Surf. Deterg.* **1998**, *1*, 161.

(19) Ward, R. S.; Diaper, R. L.; Roberts, D. W. *J. Surf. Deterg.* **2001**, *4*, 263.

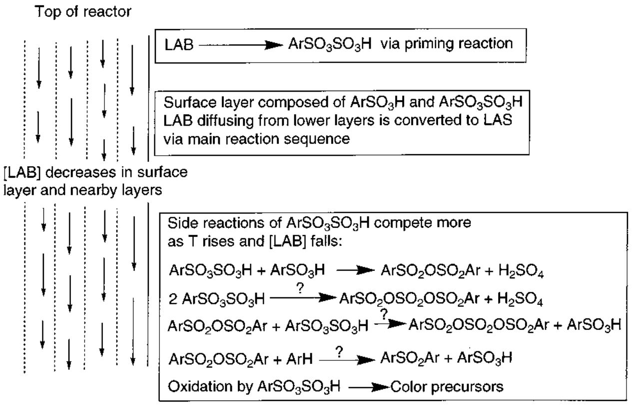

Figure 3. **Film chemistry.**

effects of the alkyl group in the para position. This is consistent with pyrosulfonic acid as the sulfonating agent, but not with sulfor trioxide as the sulfonating agent.

Furthermore, the values of the relative rate constants were found to vary, depending on the composition of the initial alkyl benzene mixture, as illustrated in Table 5. This finding is consistent with pyrosulfonic acid as the sulfonating agent: the pyrosulfonic acid compositions will be different for different alkyl benzene mixture compositions.

Thus, on the basis of the computational chemistry results and the relative rate studies it seems clear that the main reaction sequence is sulfonation of LAB by pyrosulfonic acid, which is regenerated by reaction of LAS with SO_3, the reaction being formed by initial formation of pyrosulfonic acid via the pyro$-\pi$-complex and the pyro-Wheland intermediate.

On the basis of the above, the changes in composition as the film travels down the reactor can now be described qualitatively as follows (Figure 3).

Near the top of the reactor sulfur trioxide is absorbed in the outer layer of the film and reacts with LAB, via the priming mechanism, to produce LAS, which is concentrated mainly in this outer layer of the film.

Just below this zone, the main reaction sequence takes over. Sulfur trioxide is absorbed and reacts with the LAS in the outer layer of the film to form pyrosulfonic acid. By diffusion and eddy effects, some mixing with the layer below, consisting mainly of LAB, occurs, and more LAS is formed, pyrosulfonic acid acting as the sulfonating agent.

Continuing down the reactor, successive layers of the film change in composition from mainly LAB to mainly LAS, and concentration gradients develop such that the LAS (and pyrosulfonic acid) concentration decreases from the gas$-$liquid interface to the wall and the LAB concentration decreases from the wall to the gas$-$liquid interface.

Continuing further down the reactor, although probably still much nearer the top than the bottom, the concentration of LAB in the layers of the film below the outer layer becomes so low that the pyrosulfonic acid formed in the outer layers does not encounter LAB at a rate sufficient to completely suppress competing side reactions, which are favoured by the high temperatures in the zone where the heat exchange capability of the system is most challenged. The well-known side reactions are formation of sulfone (usually considered as an inert by-product) and formation of LAS anhydride and sulfuric acid, which together act as a slow sulfonating agent in the ageing stage. The anhydride (together with sulfuric acid) probably results from reaction of pyrosulfonic acid with LAS acid, and may itself react further with pyrosulfonic acid to give pyroanhydride. Sulfones are mostly formed before ageing,[20] i.e., either in the FFR or in the separator and pipework between the FFR and the ageing reactor. They may arise by reaction of LAB with LAS anhydride via a pathway with high activation energy and hence favoured in the outer layers of the film in the upper zone of the reactor where temperatures are highest. Another possibility is that the sulfones are formed from reactions of pyroanyhdrides with LAB.

$$\mathrm{ArSO_2OSO_2OSO_2Ar + 2ArH \rightarrow ArSO_2Ar + 2ArSO_3H}$$

The fate of these by-products in the ageing stage will now be considered.

LAS Acid Ageing

The ageing step in LAB sulfonation plays an important part in the LAS acid manufacturing process. Typically in FFR sulfonation the conversion rises from below 90% on leaving the FFR to above 96% after ageing. An understanding of the kinetics of ageing is therefore essential to conversion optimisation.

Preliminary studies, in which LAS acid collected from the base of a monotube pilot-plant FFR was sampled at various time intervals and analysed by automated nonaqueous titration with cyclohexylamine, provided evidence for three stages in which the level of LAS increases and the level of sulfuric acid decreases:

(1) a fast stage which dominates for approximately the first 10 min

(2) a second, slower, stage which dominates for the rest of the normal 40$-$50 min ageing period and for a further period up to about 4 h (There is evidence (vide infra) that this stage can be further subdivided into two parts.)

(3) an even slower stage which becomes apparent when the acid is aged over a time period of several days or weeks, and which is particularly noticeable when the acid has been made under severe FFR conditions (e.g., high mol ratio, high coolant temperature, high sulfur trioxide concentration in air).

LAS acid ageing is a far from ideal reaction system for kinetic studies. Kineticists prefer to carry out reactions in dilute solution and to monitor the early period of the reaction, when the changes in composition are substantial and the slopes of the kinetic plots are not significantly affected by error in the infinity values. In the case of LAS acid ageing the reaction mixture is undiluted, and the reaction product concentration is typically almost 90% at the start of ageing and is not usually above 98% at the end. With such a small range available, if the sampling intervals are selected to be sufficiently frequent to produce enough data points for meaningful regression analysis, then the change in composition between successive sampling intervals is hardly greater

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(20) Cohen, L.; Moreno, A.; Berna, J. L. *Tenside* **1996**, *33*, 441.

Table 6. **Fast ageing reaction**

t (s)	LASH	H_2SO_4	ln(LASH − 91.5)	ln(H_2SO_4 − 1.46)
30	85.96	2.30	1.71	−0.17
45	86.46	2.23	1.62	−0.26
60	86.28	2.17	1.65	−0.34
90	87.68	2.04	1.34	−0.54
105	87.30	2.01	1.44	−0.60
120	88.30	1.98	1.16	−0.65
150	88.01	1.87	1.25	−0.89
180	88.31	1.90	1.16	−0.82
210	88.79	1.87	1.00	−0.89
240	88.51	1.84	1.10	−0.97
270	89.20	1.90	0.83	−0.82
300	89.78	1.76	0.54	−1.20
330	90.47	1.69	0.03	−1.47
360	91.23	2.09	−1.31	−0.46
390	90.25	1.92	0.22	−0.78
420	91.06	1.59	−0.82	−2.04
450	90.44	1.73	0.06	−1.31
480	90.30	1.73	0.18	−1.31
510	90.41	1.58	0.09	−2.12
540	90.86	1.57	−0.45	−2.21
570	90.68	1.50	−0.20	−3.22
600	90.65	1.55	−0.16	−2.41
19 h	98.18	0.47	colour (Klett, 5%)	21

than the analytical error limits. Because of these difficulties, substantial scatter in the rate plots is inevitable. To get the best possible estimates of the rate constants under these circumstances, the approach adopted was to obtain as many data points as possible for the kinetic plots, to ignore any points obviously off-line, and where possible, to do several repeat kinetic runs. Since the LASH and sulfuric acid levels both change in the ageing reactions, and since both are easily measured by nonaqueous titration, it is usually possible to get two rate plots from one kinetic run.

Kinetics for Stage 1. The early part of the ageing reaction proved to be too fast to follow by ageing a batch of acid and sampling it at selected time intervals. Instead, a main-plant FFR production run was used as a continuous source of unaged acid of constant initial composition, as follows.

Acid was sampled from the base of the FFR during a normal production run at Lever Europe, Port Sunlight, on 6/11/96. A stopwatch was used when taking samples, to time the delay period between taking the sample and diluting it with methanol ready for potentiometric titration with cyclohexyamine. This was done with a range of delay periods between 0 and 10 min. The results are shown in Table 6.

Stoichiometry of the Reaction. The LAS increase over 10 min is 4.69%, corresponding to 14.59 mmol per 100 g. The sulfuric acid decrease in this time period is 0.75%, corresponding to 7.65 mmol/100 g. Within experimental error, this corresponds to two new molecules of LASH produced for each molecule of sulfuric acid lost.

For the subsequent reaction between t = 10 min and 19 h, the LASH increase is 23.42 mmol/100 g, while the sulfuric decrease is 11.02 mmol/100 g—the same stoichiometry as above. Over the whole period the quantities (mmol/100 g) are LASH gain, 38.01, sulfuric loss, 18.67, ratio 2.04, insignificantly different from 2.

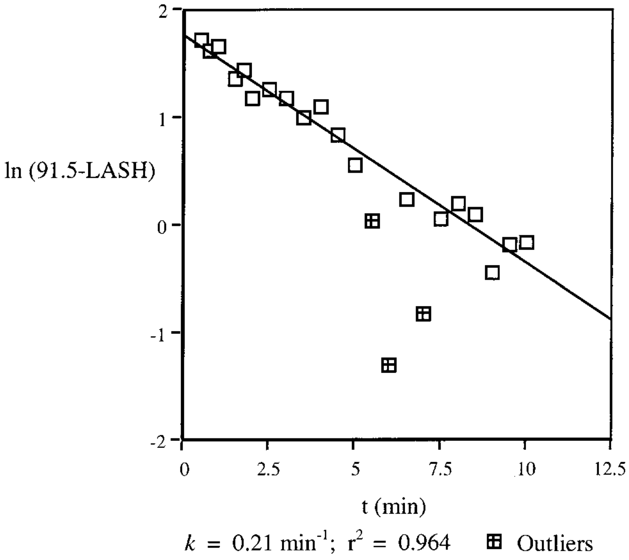

Figure 4. **Fast ageing reaction. LASH plot. T = 40−45 °C.**

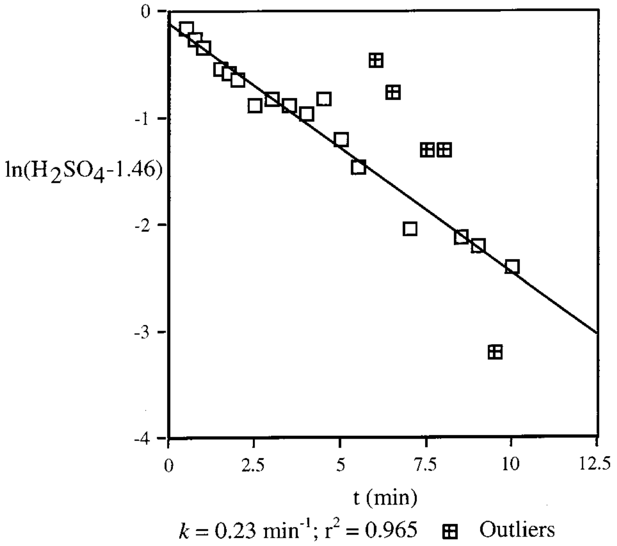

Figure 5. **Fast ageing reaction. H_2SO_4 plot. T = 40−45 °C.**

Kinetics. For LASH formation, an infinity value of 91.5 is chosen, on the basis of a plot of LASH vs t. On the basis of the 2:1 stoichiometry, a corresponding infinity value of 1.46 is calculated for sulfuric acid. First-order rate plots based on these infinity values are shown in Figures 4 and 5. The rate constants agree within experimental error.

A similar kinetic run was carried out on a separate occasion, again using a main-plant production run as the source of unaged LAS acid. Figures 6 and 7 show kinetic plots based on the LASH and sulfuric acid analyses.

Overall these four plots obtained from two separate kinetic runs indicate that the rate constant for the reaction is, to one significant figure, 0.2 min^{-1}.

Kinetics for Stage 2. Several runs, all giving similar results, were carried out to follow the ageing kinetics over the normally used ageing time period and somewhat beyond. One of these runs, using acid produced on a pilot-plant monotube FFR, is described below.

Table 7 shows the results of analyses on samples taken after ageing for various times at 40 °C.

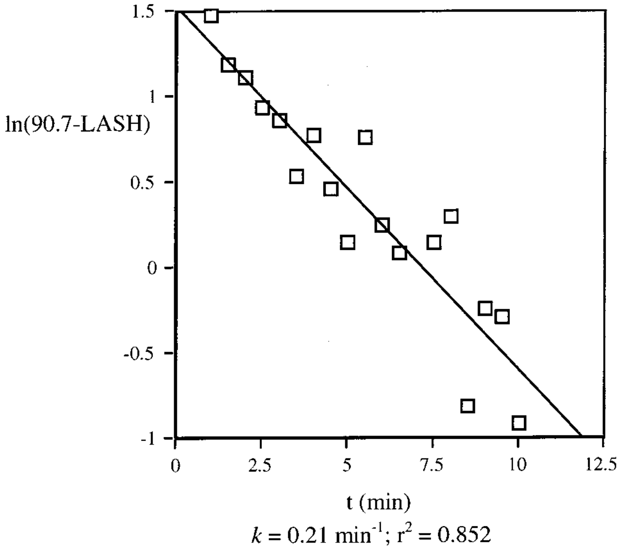

Figure 6. **Fast reaction, repeat, LASH plot.**

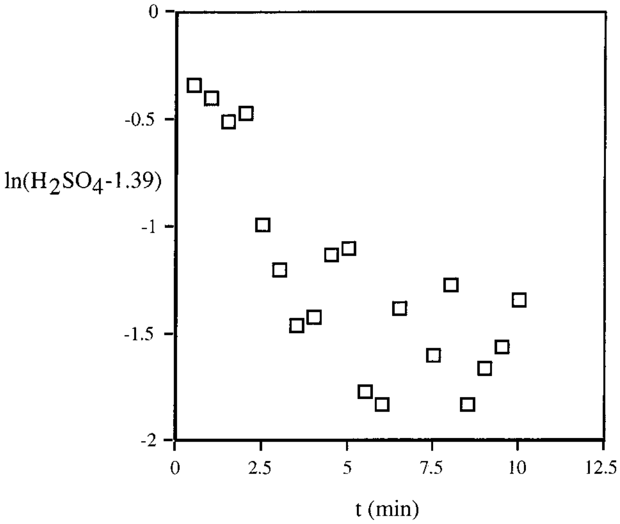

Figure 7. **Fast reaction, repeat, H_2SO_4 plot. The extent and nature of the scatter on this graph make it inappropriate to carry out regression analysis or to select outliers to be omitted before carrying out a regression analysis on a reduced data set. However, it can be seen by inspection that the general trend of the graph is not substantially different from those in the preceding figures.**

Rate plots, using the overnight LASH and H_2SO_4 data as infinity values, are shown in Figures 8 and 9.

It is clear from these two figures that at some time between 50 and 100 min there is a change of slope and the rate of change in composition is reduced significantly. A rough estimate of the rate constant for this slower reaction, from Figure 9, is ca. 0.004 min^{-1}. This relatively slow process has not previously been detected.

Kinetics for Stage 3. LAB was sulfonated in a pilot-plant monotube FFR under "severe" high throughput conditions, with continuous ageing (residence time ca. 30−40 min). After ageing, four batches were stored at a temperature of 40−45 °C:

(A) acid collected from the ageing reactor outlet,

(B) acid as above, to which 0.1% water was added,

Table 7. **LAS acid ageing, normal ageing period**

time (min)	LASH	H_2SO_4	colour (Klett, 5%)
0	86.55	2.09	2
10	92.44	1.38	2
20	94.45	1.00	3
30	94.97	0.92	2
40	95.17	0.83	3
50	95.37	0.82	10
60	95.70	0.79	11
120	96.28	0.76	12
180	96.30	0.72	14
overnight	97.50	0.60	20
Δ 10 min-overnight	33.6 mm	−15.2 mm	

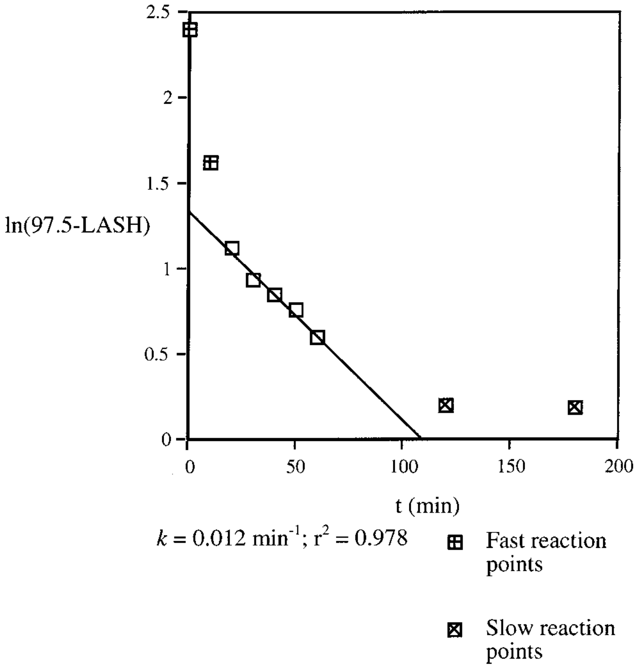

Figure 8. **LAS ageing reaction, normal ageing period. LASH plot.**

(C) acid to which 0.1% water had been continuously added in the stabilisation mixer, and

(D) acid to which 1% water had been added continuously in the stabilisation mixer.

Samples were taken at various time intervals, over a period of about four weeks. The samples were added to methanol and analysed by potentiometric titration with methanolic cyclohexylamine to determine the levels of LASH and sulfuric acid.

Plots of ln(LASH_{inf} − LASH_{t}) and ln($\text{Sulfuric}_{\text{inf}}$ − $\text{sulfuric}_{\text{t}}$) against time *t* were made and the rate constants were estimated by regression analysis (in some cases after eliminating obvious outliers attributable to experimental scatter). In most cases the final LASH or sulfuric acid reading was taken as the infinity value. In cases where experimental scatter made this inappropriate a "guesstimated" infinity value was used.

Table 8 shows the rate constants obtained, with some details of the regression analyses. Table 9 shows the raw data from one of these runs (C above) and Figures10 and 11 show the kinetic plots from run C above.

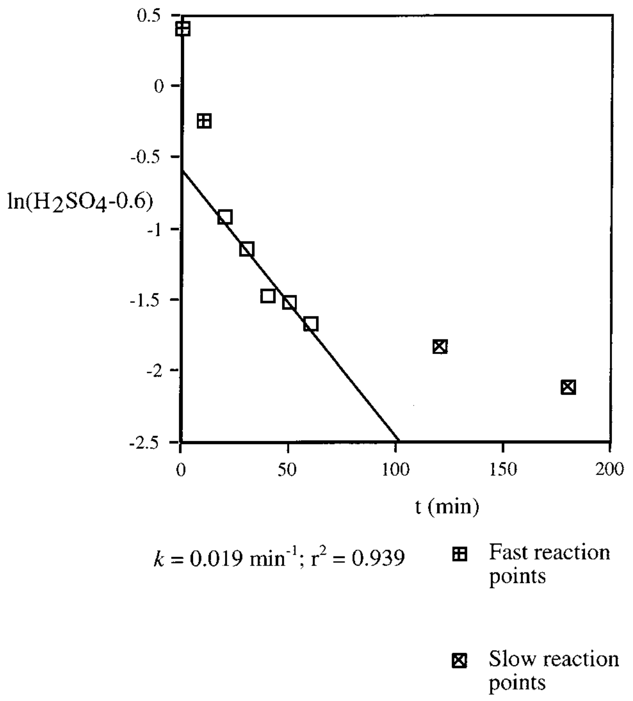

Figure 9. **LAS ageing reaction, normal ageing period. H_2SO_4 plot.**

Table 8. **LAS ageing**[a]

run	n	outliers	k (h^{-1})	r^2
A (LASH plot)	8	1	0.012	0.984
A (H_2SO_4 plot)	7	3	0.007	0.992
B (LASH plot)	7	1	0.012	0.987
B (H_2SO_4 plot)	Excessive scatter, rate constant not estimated			
C (LASH plot)	9		0.011	0.960
C (H_2SO_4 plot	9		0.013	0.970
D (LASH plot)	8		0.010	0.990
D (H_2SO_4 plot)	7	3	0.010	0.998

[a] Rate constants estimated for stage 3.

Table 9. **LAS ageing**[a]

time[b] (h)	LASH	H_2SO_4	colour (Klett, 5%)
0	91.58	2.12	46
1	91.82	2.11	61
16	92.45	2.01	259
40	93.81	1.98	630
90	95.37	1.78	1800
117	95.85	1.68	1900
162	96.57	1.68	1960
185	96.28	1.61	2000
258	96.74	1.59	
498	97.21	1.57	
666	97.09	1.57	

[a] Stage 3 data (run C). [b] Times quoted are after collection of the acid from a continuous ageing reactor (30−30 min residence time).

As illustrated by Figures 10 and 11, the kinetic plots show good linearity, and as shown in Table 8 the rate constants from the kinetic runs are all in very close agreement.

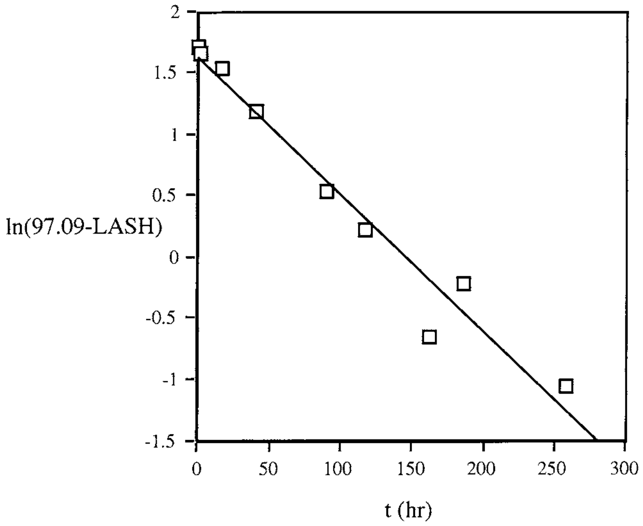

Figure 10. **Stage 3 ageing reaction. LASH plot.**

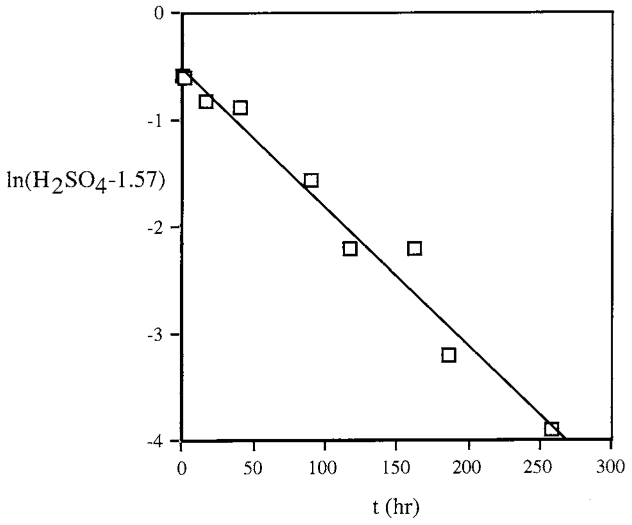

Figure 11. **Stage 3 ageing reaction. H_2SO_4 plot.**

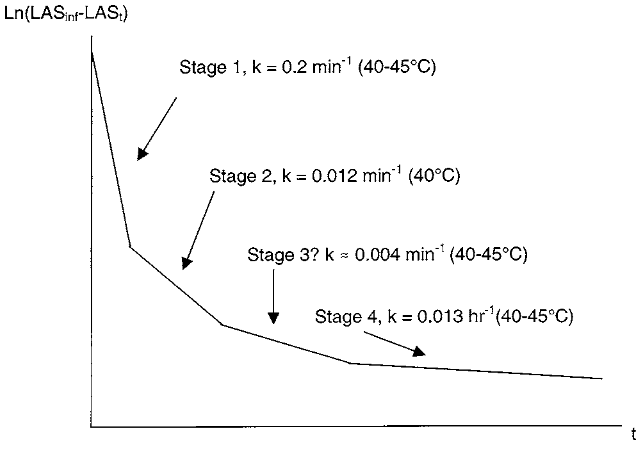

Figure 12. **Overall kinetic profile for LAS acid ageing.**

The Nature of the Ageing Reactions. Figure 12 summarises the kinetic course of the ageing reactions. It should be noted that, although the rate constants are expressed in first order units and are derived from first order rate plots, this does not necessarily mean that the reactions are first order. To establish the true orders would require much more precise analytical techniques and a much more elaborate experimental procedure than has been used in the present work. From consideration of the possible chemical reaction mechanisms at the molecular level it seems likely that the rate-determining steps will be bimolecular and that the reaction orders will be more complex than first order. The *k* values reported here are therefore best considered as pseudo-first-order rate constants, which are applicable over the composition range normally found in LAS acid.

It seems clear from Figure 12 that at least three and possibly four distinct conversion-increasing reactions can occur in ageing. The magnitude of the differences between the rate constants is consistent with different classes of reacting species rather than with differences in reactivity amongst different isomers/homologues of the same species. Starting from the assumption that the second part of the graph corresponds to reaction of LAS anhydride, the following reactions seem reasonable.

The first stage, which dominates for the first ca. 10 min of ageing, may involve a pyroanhydride or an anyhydride/sulfur trioxide complex, together with sulfuric acid, as the sulfonating species, e.g.:

$$\mathrm{ArSO_2OSO_2OSO_2Ar + 2ArH + H_2SO_4 \xrightarrow[\substack{k\,=\,\text{ca. } 0.2\ \text{min}^{-1}\\ \text{at } 40-45\ ^\circ\text{C}}]{} 4ArSO_3H}$$

The second, slower stage, which dominates over the rest of the normal ageing period, probably involves mainly the reaction of anhydride/sulfuric acid with LAB to produce LASH:

$$\mathrm{ArH + ArSO_2OSO_2Ar + H_2SO_4 \xrightarrow[\substack{k\,=\,\text{ca. } 0.012\ \text{min}^{-1}\\ \text{at } 40\ ^\circ\text{C}}]{} 3ArSO_3H}$$

The slower reaction which becomes apparent at some time between 50 and 100 min could involve the action of sulfuric acid as a sulfonating agent:

$$\mathrm{ArH + H_2SO_4 \xrightarrow[\substack{k\,=\,\text{ca. } 0.004\ \text{min}^{-1}\\ \text{at } 40\ ^\circ\text{C}}]{} ArSO_3H + H_2O}$$

An alternative possibility which cannot be excluded is that the change of slope after the second stage is a numerical artefact of an incorrect choice of infinity values rather than an indication of a separate reaction.

The final very slow reaction, which occurs over several days, involves sulfone cleavage by sulfuric acid, a reaction which has recently been demonstrated in experiments with ditolyl sulfone:[21]

$$\mathrm{ArSO_2Ar + H_2SO_4 \xrightarrow[\substack{k\,=\,\text{ca. } 0.013\ \text{h}^{-1}\\ \text{at } 40-45\ ^\circ\text{C}}]{} 2ArSO_3H}$$

All of these reactions, except for the one involving sulfuric acid as the sulfonating agent, should behave, when followed by the nonaqueous titration method, as having the stoichiometry that for each mole of sulfuric acid consumed two moles of LASH are produced. This is obvious for the sulfone cleavage reaction but not immediately apparent for the reactions involving pyroanhydride and anhydride, until the fates of pyroanhydride and anhydride in the analysis are considered. In the former case, each mole of pyroanhydride will react with methanol, the solvent for the titration, to give one mole of LASH, one mole of LAS methyl ester (LASMe), and one mole of methyl hydrogen sulfate. The methyl hydrogen sulfate, being a monobasic strong acid, will behave as LASH in the titration. Thus, in the ageing reaction two "apparent moles" of LASH and one of sulfuric acid will disappear with formation of four moles of LASH. In the case of anhydride/sulfuric acid as the sulfonating agent, one mole of anhydride will react with methanol to produce one mole each of LASH and LASMe. Thus, in the ageing reaction one "apparent mole" of LASH and one mole of sulfuric acid will disappear with formation of three moles of LASH.

Implications and Implementation of the Findings

The findings reported here have proved useful in setting optimum FFR conditions for our sulfonation plants around the world. A major development resulting from this work is in the ageing step.

From the rate constant observed (ca. 0.012 min^{-1}), the half-life for the main ageing reaction (attributed to LAS anhydride/sulfuric acid as the sulfonating agent) is calculated to be about 1 h at 40 °C. The activation energy for this reaction is unlikely to be more than about 13 kcal/mol, and on the basis of that figure the half-life at 50−55 °C is estimated at 20−30 min. Thus, it seems clear that the conventional ageing step in LAS manufacture (ca. 30−45 min at 45−55 °C) is insufficient to give maximum conversion, corresponding to at the most two half-lives. This conclusion applies even if the slow reaction, which we attribute to sulfone cleavage, is neglected as a source of conversion increase. It follows from the above argument that there is a conversion benefit to be had from extended ageing, provided colour can be kept within acceptable limits (this is dependent on feedstock quality and FFR conditions).

Accordingly, many of our plants have now been modified to provide extended ageing for up to 4 h. The design of the extended ageing reactor is not critical; in some cases vessels originally acquired for other purposes have been adapted to serve as bottom-fed continuous reactors to extend the ageing residence time, and in other cases bottom-fed cylindrical nonagitated vessels with several take-off points, offering the option of residence times up to 4 h, have been commissioned.

Another implication concerns the stabilisation step in which water is added, after ageing, to hydrolyse any residual anhydride. From the kinetic data we can estimate how much water is required for this purpose as follows. Taking the data in Table 5 as representative of a typical "mild" sulfonation and assuming that the % LASH increase over the period from 10 min to overnight (92.44−97.50, ca. 5%) is all due to reaction of anhydride and bearing in mind that for each mole of anhydride which reacts two new moles of LASH are formed, we can estimate that the initial amount of anhdyride present would have been no more than about 3%. Even if the normal ageing time is taken as only 1 half-life, the amount of water required to hydrolyse the residual anhydride after normal ageing would be less than 0.1%. Even if we allow a further 0.2% water to hydrate the sulfuric acid

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(21) Ward, R. S.; Diaper, R. L.; Roberts, D. W. J. *Surf. Deterg.* **2001**, *4*, 185.

present, it seems clear that addition of 0.3% water should be sufficient for stabilisation.

Hydrolytic desulfonation of aromatic sulfonic acids has been well-known for many years:

$$ArSO_3H + H_2O \rightarrow ArH + H_2SO_4$$

The reaction is acid-catalysed, the rate being proportional to the hydrogen ion activity of the reaction mixture, and is reversible.[22] Bearing in mind that the acidities of sulfuric acid and LAS acid are unlikely to be the same and that the system under consideration is far from an ideal solution, it is not currently possible to be specific about how the tendency to loss of conversion through hydrolyis will vary according to the composition of the LAS and the amount of water added. However, it was found empirically that for LAS made under mild sulfonation conditions with addition of 1% water, between 1 and 1.5% conversion could be lost after a few days storage. Accordingly, our plants now control the water addition in the stabililisation step so as to add only 0.3%.

With these modifications, conversion increases ranging from 0.5 to 1% have been achieved and conversion losses of up to 1.5% have been eliminated.

Current work is focused on the use of feedstock additives to moderate the FFR reactions so as to suppress subsequent color formation and to minimise sulfone levels while achieving high conversions through extended ageing.

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(22) Baddeley, G.; Holt, G.; Kenner, J. *Nature* **1944**, *3907*, 361.