Organic Process Research & Development **2004**, *8,* 1081–1082

Reply to Comment on "Optimisation of the Linear Alkyl Benzene Sulfonation Process for Surfactant Manufacture" and "Sulfonation Technology for Anionic Surfactant Manufacture": Falling Film SO_3 Sulfonation - Laminar or Turbulent Flow Controversy

To the Editor:

I have studied the letter by Edward Knaggs, whom I have never met but whom I "know" and respect from his massive reputation in sulphonation. I think the issue between us is mainly a matter of definition rather than of substance. I maintain that the film flow is not "pure turbulent"—if it were, then we would have plug flow and a very sharply peaked residence time distribution, and I do not think Knaggs is claiming that it is pure turbulent in that sense. Knaggs argues that the film flow is not "pure laminar", that is there is some turbulence: I would agree with that, and I do say that in the two papers he comments on. However, if I were to write these papers again, I think I would want to make it clearer that without the turbulence contribution, which is more significant than the wording of my papers might perhaps imply (particularly in the upper part of the reactor), the reaction exotherm would not be removed efficiently.

I have seen film sulphonation in glass tubes, and thus the photographs showed a picture already familiar to me, including the phenomenon of large, rolling waves and troughs moving down the tube. However, in the trials I have seen there was always a regular fluctuation in the organic feed rate due to the stroke action of the liquid feed pump, and I had attributed the waves to this effect (which would not apply in a commercial reactor).

I find it difficult to accept Knaggs's claim that the film residence time is about 1−2 s, at least for Ballestra-type reactors. De Groot[1] gives ca. 30 s and ca. 10−15 s as the film residence times for Ballestra-type and Chemithon-type reactors, respectively. However he does not state how these figures were arrived at. I have now done some estimates of my own as follows.

To estimate the average film residence time we have to know or estimate the "hold-up" H, i.e., the volume of the total film in the tube at a given moment, and the volumetric throughput V of the liquid. The residence time is then given by H/V. There is the complication that the film starts off as organic feedstock and ends up as sulphonated material, but the increase in weight as the liquid passes down the tube is largely canceled out by an increase in density; thus, it is reasonable to take the feedstock rate (weight/time) divided by the feedstock density to get the volumetric throughput V.

Table 1. **Calculated film residence times**[a]

film thickness (cm) initial	film thickness (cm) 2 m from top	film thickness (cm) bottom	calculated mean film residence time (s)
	Ballestra-type reactor[b]		
0.05[c]	0.15	0.20[c]	67
0.05[c]	0.10	0.20[c]	57[f]
0.02	0.08	0.10	36
0.02	0.05	0.10	29[f]
0.01	0.07	0.10	33
0.01	0.04	0.10	26[f]
0.01	0.03	0.04	14
0.01	0.02	0.04	12[f]
0.005[d]	0.015	0.02[d]	7
0.005[d]	0.10	0.005[d]	6[f]
	Chemithon-type reactor[e]		
0.05		0.20	12[f]
0.05		0.15	10[f]
0.03		0.15	8[f]
0.02		0.10	5[f]
0.01		0.04	2[f]
0.05		0.20	12[f]

[a] Sulfonation of linear alkylbenzene (C12, M = 240) at 40 kg/h/tube. [b] Tube length 6 m, tube i.d. 2.5 cm. [c] Values given by De Groot.[1] [d] One tenth of values given by De Groot.[1] [e] Assumed to be equivalent to a 2-m tube of i.d. 2.5 cm. Gas velocity is ca. 2−3× that for Ballestra type; thus, the film is likely to be thinner. [f] Linear increase of film thickness down the whole tube is assumed.

Consider a horizontal slice across a single tube of a Ballestra-type reactor, internal diameter 2.5 cm. Let the film thickness be T (cm). Then the area of film in the horizontal slice is:

$$\pi(2.5^2 - (2.5 - T)^2) \tag{1}$$

The simplest, albeit rather unrealistic, assumption is that the film is the same thickness throughout the length of the reactor. If so, then the hold-up H is given by:

$$\pi L(2.5^2 - (2.5 - T)^2)$$

where L is the length of the reactor tube. Consider sulphonation of linear alkyl (C12) benzene, at nameplate capacity, i.e., 40 kg of sulphonic acid per hour per tube. This corresponds to a feedstock rate of 30 kg/h. The density is ca. 0.85 so that the volumetric throughput is 35.3 L/h, i.e., 9.8 cm^3/s. Thus, for a film residence time of 2 s:

$$2 = 9.8\pi(2.5^2 - (2.5 - T)^2) \tag{2}$$

Solving eq 2 for T gives 0.013 cm as the film thickness corresponding to a film residence time of 2 s, based on the assumption of constant film thickness throughout the length of the reactor. This figure is much lower than figures given by De Groot,[1] who states that in a Ballestra reactor (L = 600 cm) the film thickness ranges from ca. 0.05 cm at the top to ca. 0.2 cm at the bottom.

A somewhat more realistic assumption is that the film thickness increases linearly down the length of the reactor. Rather more complex, although probably a better simulation of reality, is to assume that the film thickness is linearly

---

* To whom correspondence should be addressed. E-mail: david.w.roberts@virgin.net.

(1) Herman de Groot, W. *Sulphonation Technology in the Detergent Industry*; Kluwer: Dordrecht, The Netherlands, 1991.

10.1021/op040209n CCC: $27.50 © 2004 American Chemical Society
Published on Web 09/24/2004

related to the extent of sulphonation. In what follows it is assumed that two-thirds of the total increase in film thickness occurs linearly in the top one-third of the reactor (200 cm), and the other one-third of the increase occurs linearly in the lower two-thirds of the reactor (400 cm). Let the film thickness be T_t and T_b for the top and bottom, respectively, of the section of reactor under consideration. For the upper one-third (200 cm), we can write:

$$T_L = T_t + L(T_b - T_t)/200 \tag{3}$$

where L is the distance from the top of the upper reactor section. Similarly for the lower two-thirds (400 cm) of the reactor:

$$T_L = T_t + L(T_b - T_t)/400 \tag{4}$$

where this time L is the distance from the top of the lower reactor section, T_t (= T_b for the upper section) is the film thickness at the top of the lower section (= T_b for the upper section) and T_b is the film thickness at the bottom of the reactor.

Substituting the right-hand side of eq 3 for T in eq 1, the volume dV of an element between L and L + dL is given by:

$$\mathrm{d}V = \pi(2.5^2 - (2.5 - (T_t + L(T_b - T_t)/200))^2)\,\mathrm{d}L \tag{5}$$

The film hold-up H in the top section of the reactor is obtained by integrating the right-hand side of eq 5 between the limits $L = 200$ and $L = 0$:

$$H\text{ (top section)} = 200\,\pi\,(1.25^2 - (1.25 - T_t)^2 + (1.25 - T_t)(T_b - T_t) - (T_b - T_t)^2/3) \tag{6}$$

H (lower section) is found similarly. Adding H (top section) to H (lower section) and dividing by the volumetric throughput V gives the residence time.

These calculations are conveniently carried out using a spreadsheet so that sensitivity analyses can be carried out. Some results of these calculations are shown in Table 1.

For the Ballestra-type reactor, film thickness values given by De Groot[1] correspond to residence film times rather more than the 30 s value which he gives. The residence time is quite sensitive to the figure assumed for the film thickness at the bottom of the reactor, but even when the film thickness values are taken as being only one-tenth of the values given by De Groot, the residence time is still well in excess of 2 s. For the Chemithon-type reactor the calculated residence times are lower, but the film thickness values would need to be 5 times lower than the figures De Groot[1] gives (albeit for the Ballestra-type reactor) for the film residence time to be as low as 2 s.

David W. Roberts

C. Chem. Eur. Chem., FRSC, Manufacturing Chemistry and Toxicology Consultant, 63 Poulton Road, Bebington, Wirral, Merseyside CH63 9LD, UK

OP040209N