The Chemical Engineering Journal, 15 (1978) 39 - 53

Selectivity of Benzene Sulphonation in Three Gas–Liquid Reactors with Different Mass Transfer Characteristics
II: Mass Transfer and Selectivity in a Cyclone Reactor and in a Tube Reactor

ANTONIE A. C. M. BEENACKERS and WILLIBRORDUS P. M. VAN SWAAIJ

Department of Chemical Engineering, Twente University of Technology, P.O. Box 217, Enschede (The Netherlands)

(Received 22 July 1977)

Abstract

Liquid benzene was sulphonated with gaseous sulphur trioxide in a tube reactor and in a new gas–liquid cyclone reactor. The products are benzenesulphonic acid and diphenyl sulphone (byproduct).

The observed selectivity depends on the conversion, the initial benzene concentration and the mass transfer characteristics of the reactor. Minimum diphenyl sulphone formation was obtained for a low initial benzene concentration, a low benzene conversion and with a high liquid-side mass transfer coefficient, as in the cyclone reactor.

As the actual mass transfer rate during sulphonation could not be measured, the observed selectivity was related to the mass transfer coefficient determined by the simultaneous absorption of CO_2 and O_2 in aqueous sodium hydroxide solution.

1. INTRODUCTION

For mass transfer followed by a fast chemical reaction of the type

$$A(g) \rightarrow A(l) \qquad (1)$$

$$A(l) + zB(l) \rightarrow zI(l) \qquad (2)$$

$$A(l) + I(l) \rightarrow I'(l) \qquad (3)$$

van de Vusse [1] was the first to point out that selectivity with respect to I increases with increasing mass transfer coefficient k_L. In view of this observation, we developed a new reactor of cyclonic type in which very high values of k_L have been realized [2]. We showed [3] that the kinetics of the sulphonation of liquid benzene (B) are comparable with those discussed by van de Vusse (eqns. (1) - (3)), with A equivalent to SO_3 and $z = ½$. Pyrosulphonic acid (I) and $C_6H_5(SO_3)_3H$ (I′) in the bulk of the liquid convert with benzene to, respectively, the product benzenesulphonic acid (P) and the byproduct diphenyl sulphone (X).

In Part I we presented experimental results on mass transfer and selectivity in a stirred-cell reactor, in which k_L is low (approximately 10^{-5} m s^{-1}). In the following, we report on sulphonation in a cocurrent gas–liquid tube reactor, with intermediate k_L, and in a cyclone reactor, with high k_L.

2. REACTOR DESCRIPTION

2.1. Cyclone reactor

Figure 1 is a sketch of the cyclone reactor in which the most important dimensions are indicated. The construction material is 316 stainless steel. The liquid is fed tangentially into the reactor A, as shown in Fig. 2. Part of the cylindrical wall is made of porous stainless steel (Ugine Carbone Poral ILR 20.30.30). A gas mixture of sulphur trioxide and nitrogen is introduced into the reactor via this porous section.

The liquid phase is the continuous phase in the cyclone reactor except near the cyclone axis. A gaseous core, due to the strong centripetal field generated by the rotating liquid, is present at the cyclone axis. The field causes gas bubbles to spiral from the wall to the axis. For $U_s/v_i < 5 \times 10^{-2}$, the diameter of the gas core is of the order of the diameter of the upper outlet B, which is known as the vortex [3]

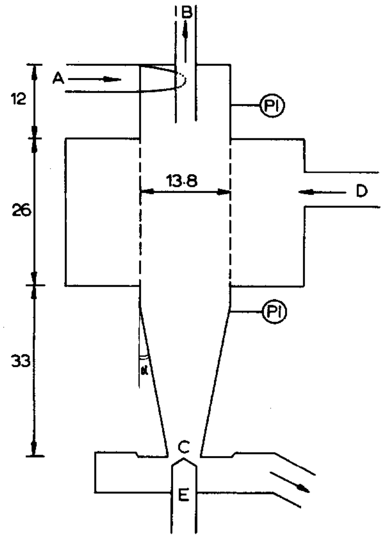


Fig. 1. Cyclone reactor: A, liquid inlet (4×10^{-3} m); B, gas outlet (vortex) (3×10^{-3} m); C, liquid outlet (apex) (8.66×10^{-6} m^2); D, gas inlet; E, cone (120 °); PI, pressure indicator; $\alpha = 8°$; unit of length, 10^{-3} m.

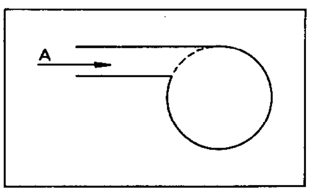


Fig. 2. Liquid inlet of the cyclone reactor.

Liquid leaves the reactor via the bottom outlet C which is referred to as the apex. The cone E prevents gas entrainment in the liquid. Gas leaves the reactor via vortex B. Liquid entrainment through the vortex varied between 12 and 20% depending on the gas and liquid velocities.

2.2. *Tube reactor*

A sketch of the tube reactor is shown in Fig. 3. After a length of 0.1 m, the mixture enters

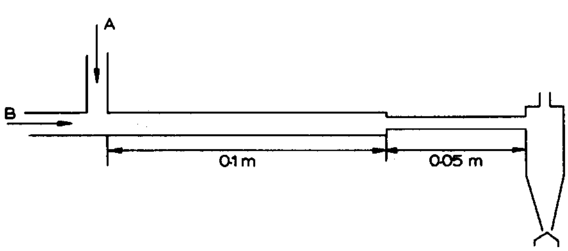


Fig. 3. Tube reactor: diameter, 8×10^{-3} m; cyclone inlet diameter, 5×10^{-3} m. A is the gas inlet and B the liquid inlet.

the cyclone inlet. For these experiments the cyclone inlet diameter was enlarged to 5×10^{-3} m.

Because of the high solubility of SO_3, absorption is expected to be practically complete within the first few centimetres of the tube reactor. The cyclone only acts as a gas–liquid separator in this set-up.

3. MASS TRANSFER CHARACTERISTICS

3.1. k_L *in the cyclone reactor*

We measured k_L, in an almost identical cyclone reactor, for simultaneous absorption of carbon dioxide and oxygen in a 2.07 M sodium hydroxide solution [2]. From the results (Fig. 4) it can be seen that k_L is extremely high and can be described to a first approximation by

$$k_L \sim U_s^{1/2} \tag{4}$$

Owing to the high solubility of SO_3, a major fraction could possibly have already been absorbed during the bubble formation period of the porous wall. This would mean that the relevant k_L for SO_3 transfer differs, at least in principle, from the k_L measured with carbon dioxide. To clarify this point, we must first consider k_L in the cyclone reactor during bubble formation.

Physical absorption during bubble formation is described by [4]

$$m(t) = 3.57\, c_{Ai} D_A^{1/2} \phi^{2/3} t^{7/6} \tag{5}$$

where

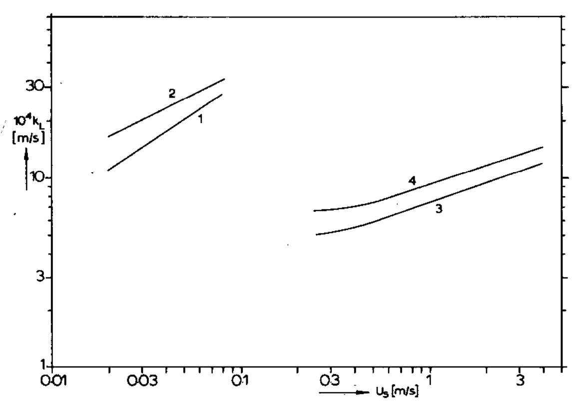


Fig. 4. k_L as a function of U_s for CO_2 in 2.07 M NaOH solution in a cyclone reactor with $v_i = 5.97$ m s^{-1} (curve 1) and $v_i = 9.15$ m s^{-1} (curve 2) and in a tube reactor for $U_L = 1$ m s^{-1} (curve 3) and $U_L = 1.75$ m s^{-1} (curve 4).

$$\phi = \text{constant} = \frac{d(\pi/6)\{d_b(t)\}^3}{dt} \quad (6)$$

and t is the age of the bubble. The absorption rate per unit area at time t follows from

$$J(t) = \frac{1}{\pi\{d_b(t)\}^2} \frac{dm(t)}{dt} \quad (7)$$

Differentiation of eqn. (5) and substitution into eqn. (7) leads, after elimination of ϕ through eqn. (6), to

$$J(t) = 1.526 c_{Ai}\left(\frac{D_A}{\pi t}\right)^{1/2} \quad (8)$$

The average value of J during the first τ seconds of bubble formation is obtained as

$$\bar{J}_{bf} = m(\tau)\left[\int_0^\tau \pi\{d_b(t)\}^2\, dt\right]^{-1} \quad (9)$$

From eqns. (5), (6) and (9) it follows that

$$\bar{J}_{bf} = 2.18 c_{Ai}\left(\frac{D_A}{\pi\tau}\right)^{1/2} \quad (10)$$

Equation (10) has been confirmed experimentally to within 20% [5]. The residence time τ of the bubble at the surface depends on ϕ and on the bubble diameter at $t = \tau$. Defining $d_b(\tau) \equiv d_b$, we obtain

$$\tau = \frac{\pi}{6}\frac{d_b^3}{\phi} \quad (11)$$

Letting n be the number of bubbles at the wall per unit area, the fraction α of surface coverage is given by

$$\alpha = n\frac{\pi}{4} d_b^2$$

and ϕ becomes

$$\phi = \frac{(1-f')U_s}{\alpha}\frac{\pi}{4} d_b^2 \quad (12)$$

Combining eqns. (10) - (12) gives

$$\bar{J}_{bf} = 1.51 c_{Ai}\left\{\frac{U_s D_A(1-f')}{d_b\alpha}\right\}^{1/2} \quad (13)$$

or

$$(\bar{k}_L)_{bf} = 2.18\left(\frac{D_A}{\pi\tau}\right)^{1/2} = 1.51\left\{\frac{U_s D_A(1-f')}{d_b\alpha}\right\} \quad (14)$$

Estimates of the parameters given in eqn. (14) are needed for an evaluation of $(\bar{k}_L)_{bf}$. The value of f_A in sulphonation experiments is typically about 0.1 and thus $1-f' \geqslant 0.9$. The diffusion coefficient of SO_3 in dichloroethane is 2×10^{-9} m^2 s^{-1} [6]. The bubble diameter d_b can be expected to be of the order of 2×10^{-4} m [3]. Although α is unknown, it must be positive and less than or equal to unity. In Fig. 5, $(\bar{k}_L)_{bf}$ is presented as a function of U_s for selected values of αd_b.

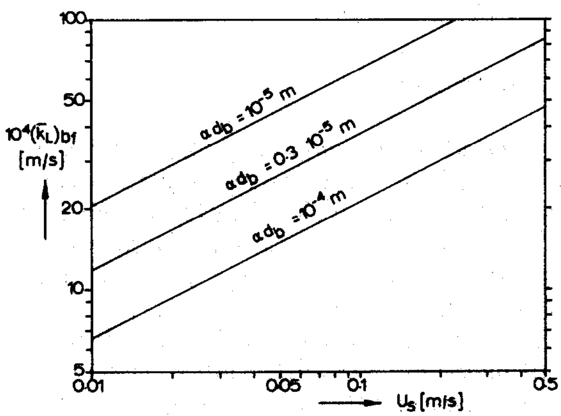


Fig. 5. Mass transfer coefficient during bubble formation at the cyclone wall, as a function of U_s for some values of αd_b; $1-f' = 0.9$; $D_A = 2\times10^{-9}$ m^2 s^{-1}.

A comparison of the k_L values given in Figs. 4 and 5 indicates that the liquid-side mass transfer coefficients before and after bubble release are of comparable magnitude.

3.2. k_L *in the tube reactor*

Different types of flow patterns can be distinguished for cocurrent gas–liquid flow in horizontal tubes [7]. Slug flow occurs (Fig. 10.3 of ref. 7) for the range of gas and liquid velocities used in our experiments. The mass transfer coefficients realized in this flow regime have been reported recently.

For the carbon dioxide–aqueous sodium hydroxide system it was found [8] that

$$k_L = 4.69\left\{\frac{(\Delta p/\Delta L)D^2}{(1-\epsilon)^2\rho d_{TR}}\right\}^{0.25} - 5\times10^{-4} \quad (15)$$

where $\Delta p/\Delta L$ is obtained from the Lockhart–Martinelli correlation and ϵ from Hughmark's relation. Equation (15) was obtained for $0.22 < U_L < 0.78$ m s^{-1} and $1.13 < U_s < 5$ m s^{-1}. Figure 4 gives the calculated values of the liquid-side mass transfer coefficient for the carbon dioxide–aqueous sodium hydroxide (2.07 M) system in our tube reactor for typical superficial gas and liquid velocities and at a total pressure of 4 bar. For these calculations eqn. (15) was assumed to remain valid for liquid velocities up to 1.75 m s^{-1}.

k_L is lower than in the cyclone reactor, but still high compared with conventional bubble contactors. As a first approximation, the relation between k_L and U_s is given by

$$k_L \sim U_s^{1/3} \tag{16}$$

4. EXPERIMENTAL

4.1. Liquid circulation system of the reactor

Figure 6 shows the complete experimental set-up. The stirred tank ST was filled with 5×10^{-3} m^3 (diluted) benzene. Liquid was pumped from the tank to the cyclone reactor CR by a variable speed gear pump P1. The liquid flow rate was measured with a displacement meter FI. Liquid that left the cyclone via the apex passed an over-designed plate-type heat exchanger HE, which maintained the temperature of the liquid section constant to within 1 °C, before it returned to the stirred tank ST. Part of the liquid was entrained in the gas which left the reactor CR via the vortex. This liquid was then separated from the gas phase in a tower 0.1 m in diameter containing a de-mister DM and was returned to the stirred tank. The flow of entrained liquid was measured with a built-in calibrated volume (LEFM). The system was continuous with respect to the gas phase. Liquid conversion per pass through the cyclone was small relative to the total liquid conversion. Therefore the system was operated batchwise with respect to the liquid. A total of about five liquid samples was taken and then the experiment was stopped. The system was emptied and washed twice with ethanol to remove all the reaction products. Afterwards the plant was washed three times with 1,2-dichloroethane to remove the ethanol.

4.2. Sulphur trioxide storage

A drum SO_3D of 0.2 m^3 stabilized liquid sulphur trioxide was stored in a separate box outside the laboratory building. The drum was placed in a sand bath and the whole box was maintained at 30 °C with hot air to

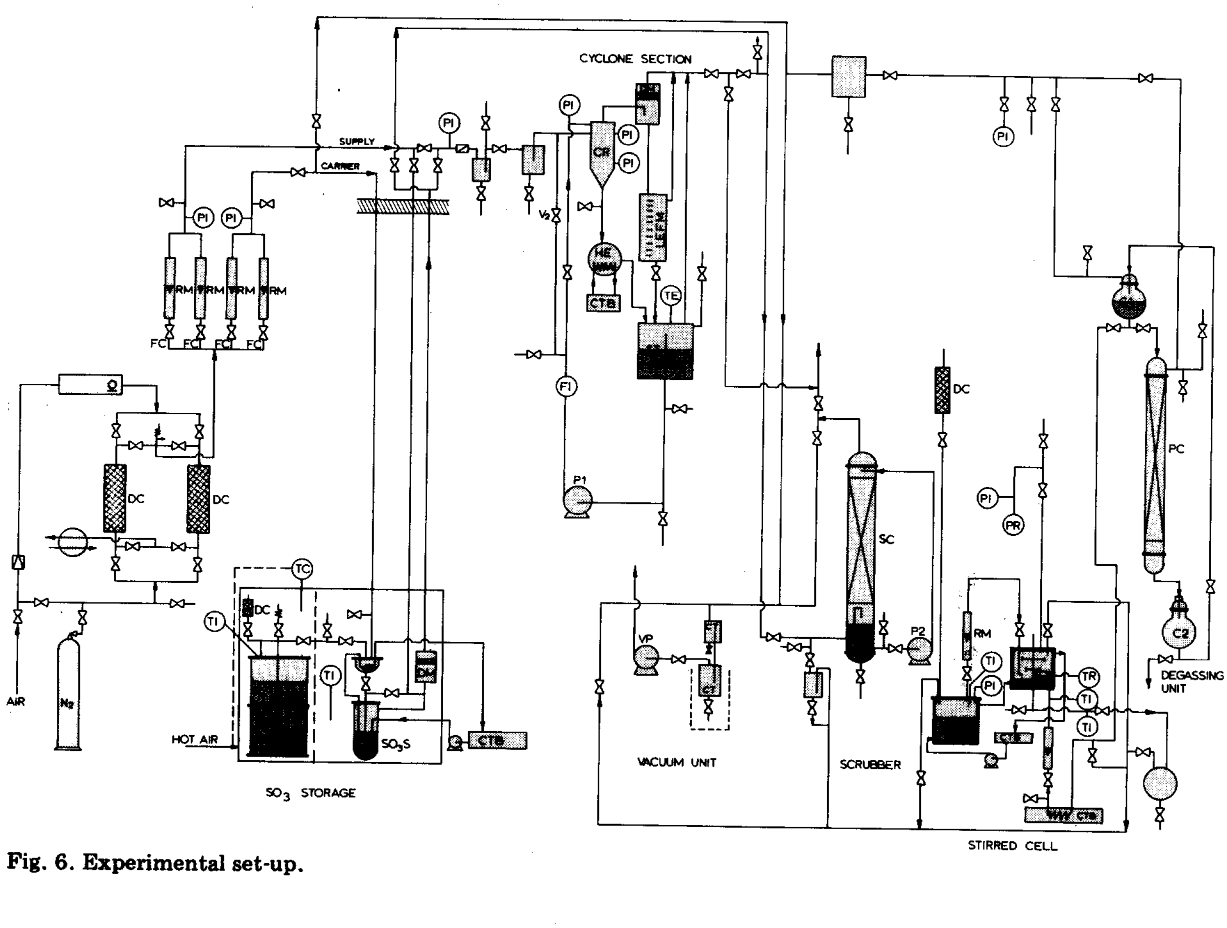


Fig. 6. Experimental set-up.

prevent polymerization of the sulphur trioxide. The container SO_3S, which was thermostatted internally with oil at 30 °C (CTB), was periodically refilled from the drum with about 0.01 m^3 liquid sulphur trioxide. This was accomplished by reducing the pressure in SO_3S using the vacuum pump VP. This pump was protected against sulphur trioxide by two cold-traps CT cooled with salt–ice–water and liquid nitrogen, respectively, and by a scrubber SC of 4 in diameter packed with Raschig rings (packing height 1 m) over which sulphuric acid was continuously recirculated to absorb the sulphur trioxide.

4.3. *Gas flow*

Nitrogen was dried in one of two parallel 5A molecular sieve beds DC. Whilst one bed was in operation the other was regenerated with hot air. Flow controllers FC were used to split the dried gas into two streams, and each flow rate was measured by rotameters RM and manometers PI. One stream (the carrier) was bubbled through the liquid sulphur trioxide (in SO_3S) and immediately thereafter diluted with the other stream (the supply) to prevent condensation and polymerization of the sulphur trioxide downstream. After passing a back-pressure valve and two back-pressure flasks, the gas entered the cyclone reactor. All the gas left the reactor via the vortex and passed through the sulphuric acid scrubber SC before leaving the system.

4.4. *Tube reactor experiments*

The experimental set-up was the same as that used for the cyclone experiments. However, in these experiments gas was not supplied to the cyclone but to the liquid inlet pipe instead, at a distance of 0.1 m from the cyclone reactor inlet.

4.5. *Stirred-cell reactor experiments*

Also shown in Fig. 6 is the set-up for stirred-cell sulphonation, which was described in Part I [9]. The reactor SCR was filled with degassed liquid from C1. SO_3 gas was obtained by the vapour pressure difference between the SO_3 container SO_3C and the reactor.

4.6. *Degassing unit*

The degassing unit consisted of two containers C1 and C2, each with a volume of 0.02 m^3, which were connected by a 4 in packed column PC (Raschig rings, 2 m packing height).

Liquid could be degassed batchwise by spraying it over the evacuated packed bed PC three times whilst continuously withdrawing gases with the vacuum pump VP. Liquid transport from C2 to C1 was pressure driven by evacuating C1 and bringing C2 to atmospheric pressure.

5. ANALYTICAL TECHNIQUES

5.1. *Benzenesulphonic acids*

The reaction mixture (10^{-4} to 2×10^{-3} kg) was diluted with 5×10^{-3} kg ethanol and titrated in duplicate with 1 M n-butylamine in dioxane. In this way H_2SO_4 and $C_6H_5SO_3H$ could be analysed separately. The variance in duplicate measurements was 10^{-6} kmol benzenesulphonic acid per kilogram of mixture. Benzenedisulphonic acid was below 1% relative to monosulphonic acid (measured by gel permeation chromatography (Sephadex LH20, 0.9 m × 0.01 m, eluant methanol)).

5.2. *Diphenyl sulphone*

Diphenyl sulphone was always analysed both chromatographically (GLC) and gravimetrically. The two methods gave the same result within 8%.

The conditions in the GLC analysis were as follows:

injector, 350 °C
column, 10% OV-17 on Chrom.W (atomic weight 60180) mesh, 2.5 m, ¼ in, 1% NaOH treated
column temperature, 225 °C
detector, katharometer, 0.155 A, 325 °C
carrier gas, helium (10^{-6} m^3 s^{-1})
amount of reaction mixture, (4–10) × 10^{-9} m^3
residence time of sulphone, about 10 min

In gravimetric analysis, the reaction mixture (2×10^{-4} m^3) was washed three times with water to extract the acids. Because of the small difference in density between the organic and the acid phase, a centrifuge was used to separate the very small aqueous drops from the organic phase. The organic phase was then mixed with water, after which benzene and dichloroethane were evaporated at about 80 °C. The water-insoluble diphenyl sulphone precipitate was filtered, dried at

50 °C in a vacuum oven and weighed. The purity of the diphenyl sulphone was verified by a melting point measurement. Gravimetric analysis in preliminary experiments showed that the precipitate contained small amounts (approximately 0.5 wt.%) of unknown heavy oil which originated from 1,2-dichloroethane. This problem was solved by first distilling the solvent before use.

5.3. Gas phase analysis

In the relatively high gas load experiments 13–17 (Table 2), 43–44 (Table 5) and 61–65 (Tables 8, 9) the SO_3 content in the feed gas and in the off-gas was analysed by sampling 2×10^{-3} m^3 gas in a carefully dried cylinder, by adding a known amount of sodium hydroxide solution, by allowing the SO_3 to absorb for 15 min on a rolling bank, and by measuring the original SO_3 content by back-titration. The SO_3 detected in the off-gas was in all cases below 0.1 vol.%.

In the other experiments the SO_3 content in the inlet gas was calculated from the sulphur compound content of the liquid reaction mixtures.

6. RESULTS

6.1. Volumetric mass transfer coefficient (k_LS) in the cyclone reactor

The product of the liquid-side mass transfer coefficient k_L and the specific gas–liquid contact area S in the cyclone reactor was measured for 1,2-dichloroethane which contained 10 and 30 vol.% benzene, respectively.

In one set of experiments, pure methane was used as the gas phase. Methane absorption could be calculated from a gas chromatographic determination of the methane concentration in the liquid phase at the reactor inlet and at the outlet (apex).

In contrast with selectivity experiments, liquid leaving the reactor in k_LS measurement experiments was not recirculated to the stirred tank ST (Fig. 6) but instead was collected in a separate tank. Spent liquid could be re-used in a new experiment after stripping methane out of the liquid with nitrogen, in the cyclone–liquid recirculation set-up (Fig. 6). The calculation of k_LS was identical with that described in a previous paper [2].

In another series of experiments, a gas mixture containing methane, sulphur trioxide and nitrogen was used to measure k_LS under reaction conditions (vol.% $SO_3 \approx$ vol.% $N_2/4 \approx 0.1/U_s$).

The experimental results are summarized in Fig. 7. From this figure it is concluded that k_LS is nearly twice as large in a liquid phase consisting of 30 vol.% benzene in dichloroethane than in 2.07 M aqueous sodium hydroxide solution [2] (broken line in Fig. 7). This difference in k_LS is mainly caused by differences in D and σ. With sodium hydroxide as the solution we obtained [2] reasonable values for k_L and S by predicting S following van Dierendonck [10] and k_L using Calderbank and Moo Young's approach [11]. From these references, for completely mobile bubbles it is expected that

$$k_LS \sim \frac{\rho^{2/3}D^{1/2}}{\sigma^{1/2}\mu^{1/6}} \tag{17}$$

and for rigid bubbles

$$k_LS \sim \frac{\rho^{5/6}D^{2/3}}{\sigma^{1/2}\mu^{1/3}} \tag{18}$$

With $D_3/D_4 = 2.04$ [12, 13], $\mu_3/\mu_4 = 0.46$, $\sigma_3/\sigma_4 = 0.41$ and $\rho_3/\rho_4 = 1.05$, it follows that for rigid bubbles

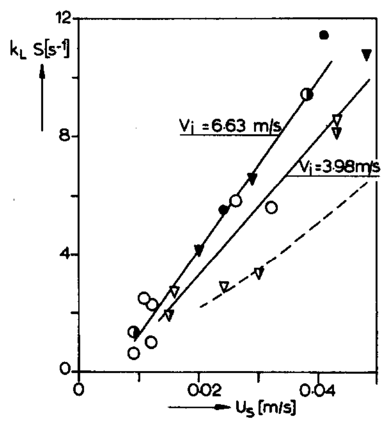


Fig. 7. k_LS as a function of U_s in benzene–1,2-dichloroethane mixtures:

	v_i = 3.98 m s^{-1}	v_i = 6.63 m s^{-1}
10 vol.% benzene	▼ (half-filled)	◑
30 vol.% benzene	▽	○
30 vol.% benzene, with reaction	▼	●

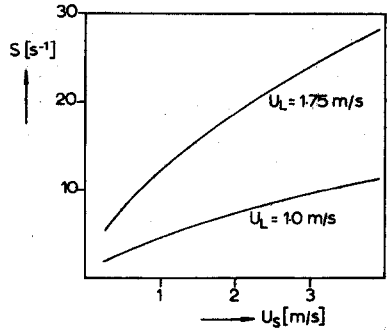
The broken line is for simultaneous absorption of CO_2 and O_2 in aqueous sodium hydroxide with v_i = 5.97 m s^{-1}.

$\text{ƙ}_LS)_3/(k_LS)_4 = 3.4$

nd for mobile bubbles.

$\text{ƙ}_LS)_3/(k_LS)_4 = 2.6$

'or comparison, Fig. 8 shows the values of $_LS$ in the tube reactor for our experimental as and liquid loads.



ig. 8. Calculated [8] values of k_LS in the tube reac-r with 2.07 M NaOH solution as the liquid phase ıd CO_2 as the gas phase (p = 4 bar, T = 25 °C).

.2. Selectivity in the cyclone reactor

'able 1 gives the scheme used for sulphona-ion experiments in the cyclone reactor. Orig-ıally, the liquid inlet velocity v_l and the ıitial benzene concentration were expected ɔ be the main parameters affecting the selec-ivity obtained. With regard to v_l, however, ur experimental results indicate that exper-nental errors alone can account for any ariation in selectivity observed for the range $< v_l < 8$ m s^{-1}.

In contrast, the superficial gas velocity had significant influence on selectivity. There-ɔre relatively high gas velocities were used in wo series of experiments (30 and 100 vol.% enzene at 20 °C) to study this effect in more etail. The experimental results are given in 'ables 2 - 6.

In principle, selectivity can be a function of liquid inlet velocity v_l, superficial gas velocity U_s, sulphur trioxide concentration $(c_A)_f$ in the gas feed, benzene concentration $\bar{c}_B$ in the bulk of the liquid, benzenesulphonic acid concentration $\bar{c}_P$ in the bulk of the liquid and reaction temperature $\bar{T}$. With the exception of the 10 vol.% benzene experiments, in which completely different selectivities were observ-ed, the series of experimental results obtained at 20 °C and at 40 °C were each correlated according to

$$1 - \eta' = CU_s^{a_1}v_l^{a_2}\bar{c}_B^{a_3}(c_A)_f^{a_4}\bar{c}_P^{a_5} \tag{19}$$

Additionally, the series of results with 30 vol.% benzene and the series with neat benzene were each correlated according to

$$1 - \eta' = CU_s^{a_1}v_l^{a_2}\bar{T}^{a_3}(c_A)_f^{a_4}\bar{c}_P^{a_5} \tag{20}$$

The regression equations (19) and (20) are logarithmically linear. Optimized sets (C, a_i) were calculated by a multiple regression analysis of the logarithmic form of the equa-tions as described by van der Grinten and Lenoir [14]. This analysis showed a signif-icant influence of U_s on selectivity in all series of experiments. Moreover, a significant decrease of η' with increasing ζ was observed in the series in which ζ was increased above ζ = 0.5 (30 vol.% benzene sulphonation at 40 °C). The effects of the remaining para-meters fell within experimental error for the range over which these parameters were varied.

However, a comparison of Tables 2 - 6 indicates that the selectivity obtained at low benzene concentration (10 vol.%) was signif-icantly higher than that at 30 and 100 vol.% benzene.

Based on the outcome of the previous analysis, $1 - \eta'$ was regressed once more on

'ABLE 1

ulphonation experiments in the cyclone reactor

C)	*Initial vol.% benzene in the liquid phase*	U_s (m s^{-1})	v_l (m s^{-1})	f_A	ζ
0	10	0.02 - 0.04	3.5 - 6.8	0.09 - 0.11	0.13 - 0.46
	30	0.01 - 0.38	3.3 - 7.9	0.06 - 0.13	0.07 - 0.42
	100	0.01 - 0.21	2.8 - 6.6	0.08 - 0.13	0.01 - 0.05
0	30	0.01 - 0.08	2.7 - 7.9	0.09 - 0.12	0.04 - 0.51
	100	0.01 - 0.02	2.4 - 7.6	0.11 - 0.12	0.01 - 0.05

TABLE 2

Sulphonation of 30 vol.% benzene in 1,2-dichloroethane in a cyclone reactor at ± 20 °C

Exp. no.	U_s (m s^{-1})	v_i (m s^{-1})	f_A	ζ	η'	$\bar{T}$ (°C)	p_w (bar)
11	0.014	3.23	0.134	0.083	0.955	22.0	1.12
				0.134	0.965		
12	0.017	5.27	0.080	0.069	0.953	23.3	1.31
				0.132	0.970		
13	0.040	5.38	0.096	0.162	0.964	21.5	1.52
14	0.095	3.56	0.093	0.266	0.982	20.8	1.28
15	0.159	6.42	0.066	0.174	0.988	22.5	1.83
				0.417	0.962		
16	0.202	7.92	0.064	0.203	0.983	22.0	2.64
17	0.384	3.61	0.072	0.298	0.980	22.5	1.60

TABLE 3

Sulphonation of 30 vol.% benzene in 1,2-dichloroethane in a cyclone reactor at ±40 °C

Exp. no.	U_s (m s^{-1})	v_i (m s^{-1})	f_A	ζ	η'	$\bar{T}$ (°C)	p_w (bar)
21	0.011	6.63	0.109	0.070	0.953	40.5	1.60
				0.103	0.954		
22	0.013	4.02	0.117	0.043	0.961	40.0	1.22
				0.075	0.967		
				0.106	0.967		
23	0.019	2.75	0.122	0.045	0.961	40.3	1.096
				0.087	0.958		
				0.186	0.955		
24	0.041	7.17	0.095	0.098	0.980	40.5	1.78
				0.169	0.973		
				0.254	0.969		
25	0.042	7.88	0.098	0.147	0.983	41.5	1.94
				0.249	0.972		
26	0.053	2.94	0.118	0.042	0.983	40.5	1.18
				0.104	0.983		
				0.240	0.978		
27	0.079	3.34	0.095	0.132	0.987	40.9	1.25
				0.296	0.967		
				0.509	0.886		

the parameters that were found to have a significant influence (U_s) and a partially significant influence ($\bar{c}_P$), according to

$$1 - \eta' = C U_s^{a_1} \bar{c}_P^{a_5} \tag{21}$$

Table 7 lists the values thus obtained for C, a_1 and a_5.

6.3. *Selectivity in the tube reactor*

Tables 8 and 9 show the experimental results obtained in the tube reactor for sulphonation of 30 vol.% benzene in 1,2-dichloroethane and of neat benzene, respectively. The ranges for U_s and U_L are such that the gas and liquid loads in cubic metres per second are comparable with those in the cyclone experiments. From Table 8 it follows that the influence of

TABLE 4

Sulphonation of neat benzene in a cyclone reactor at 40 °C

Exp. no.	U_s (m s^{-1})	v_i (m s^{-1})	f_A	ζ	η'	T (°C)	p_w (bar)
31	0.012	7.58	0.119	0.008	0.954	40.8	1.58
				0.017	0.955		
				0.028	0.943		
				0.049	0.950		
32	0.014	4.30	0.119	0.022	0.960	40.2	1.19
				0.035	0.959		
				0.046	0.947		
33	0.019	2.37	0.106	0.013	0.961	40.0	1.094
				0.024	0.968		
				0.043	0.962		

TABLE 5

Sulphonation of neat benzene in a cyclone reactor at ±20 °C

Exp. no.	U_s (m s^{-1})	v_i (m s^{-1})	f_A	ζ	η'	T (°C)	p_w (bar)
41	0.012	6.37	0.111	0.013	0.945	19.0	1.39
				0.022	0.960		
				0.035	0.952		
42	0.014	2.83	0.134	0.012	0.965	20.0	1.10
				0.024	0.964		
				0.036	0.959		
				0.051	0.973		
43	0.211	6.03	0.078	0.012	0.972	20.5	1.73
				0.054	0.981		
44	0.213	6.63	0.083	0.023	0.978	19.5	1.70
				0.038	0.979		

TABLE 6

Sulphonation of 10 vol.% benzene in 1,2-dichloroethane in a cyclone reactor at ±20 °C

Exp. no.	U_s (m s^{-1})	v_i (m s^{-1})	f_A	ζ	η'	T (°C)	p_w (bar)
51	0.025	6.80	0.105	0.128	0.995	23.0	1.77
				0.187	>1.00		
				0.259	1.00		
52	0.030	3.46	0.107	0.138	0.995	20.0	1.23
				0.234	>1.00		
				0.327	1.00		
53	0.042	5.89	0.088	0.222	0.998	20.6	1.58
				0.320	0.995		
				0.459	0.995		

the superficial gas velocity on selectivity is analogous to the results obtained in the cyclone reactor, *i.e.* higher gas velocities result in less byproduct formation.

TABLE 7

Values of the optimized parameters in the regression eqn. (21)

Regressed experiments	C	a_1	a_5
20 °C (30 + 100 vol.% benzene)	0.0142	−0.21 ± 0.10	−0.09 ± 0.18
40 °C (30 + 100 vol.% benzene)	0.0062	−0.53 ± 0.21	0.30 ± 0.20
30 vol.% benzene (20 + 40 °C)	0.0086	−0.45 ± 0.16	0.43 ± 0.23
100 vol.% benzene (20 + 40 °C)	0.0140	−0.23 ± 0.09	−0.07 ± 0.17

TABLE 8

Sulphonation of 30 vol.% benzene in 1,2-dichloroethane in a tube reactor at ± 20 °C

Exp. no.	U_s (m s^{-1})	U_L (m s^{-1})	f_A	ζ	η'	$\bar{T}$ (°C)	p (bar)
61	0.266	1.13	0.078	0.016	0.913	20.6	1.51
				0.050	0.929		
62	0.258	1.05	0.078	0.015	0.908	19.0	2.61
				0.037	0.915		
				0.062	0.949		
63	3.88	1.51	0.052	0.114	0.977	20.8	4.05
				0.326	0.971		

TABLE 9

Sulphonation of neat benzene in a tube reactor at ± 20 °C

Exp. no.	U_s (m s^{-1})	U_L (m s^{-1})	f_A	ζ	η'	$\bar{T}$ (°C)	p (bar)
64	3.83	1.76	0.048	0.040	0.943	20.0	3.95
				0.106	0.948		
65	4.07	1.78	0.046	0.047	0.954	19.5	3.82
				0.120	0.936		

7. DISCUSSION

As shown in Table 6, sulphonation of 10 vol.% benzene in 1,2-dichloroethane resulted in 100% selectivity, within experimental error. However, Figs. 9 - 11 indicate that lower selectivities were obtained for the sulphonation of 30 vol.% benzene in 1,2-dichloroethane and of neat benzene.

An interpretation is even more speculative for the results presented here than for the previously discussed sulphonation in a stirred-cell reactor [9]. In the stirred-cell reactor direct information on k_L was obtained from the measured absorption rate J, and gas phase resistance was known to be negligible. Such direct information is not available from the experiments conducted with the tube and the cyclone reactors. Therefore indirect information must be used to deduce:

(1) whether absorption takes place mainly during bubble formation;

(2) whether k_L is lowered by an interfacial viscosity increase;

(3) whether the reaction can still be considered as instantaneous;

(4) whether gas phase resistance prevails.

Two arguments can be presented, both of which indicate that in these reactors the mass transfer coefficient k_L during sulphonation is possibly lower than that observed experimentally for carbon dioxide and oxygen absorp-

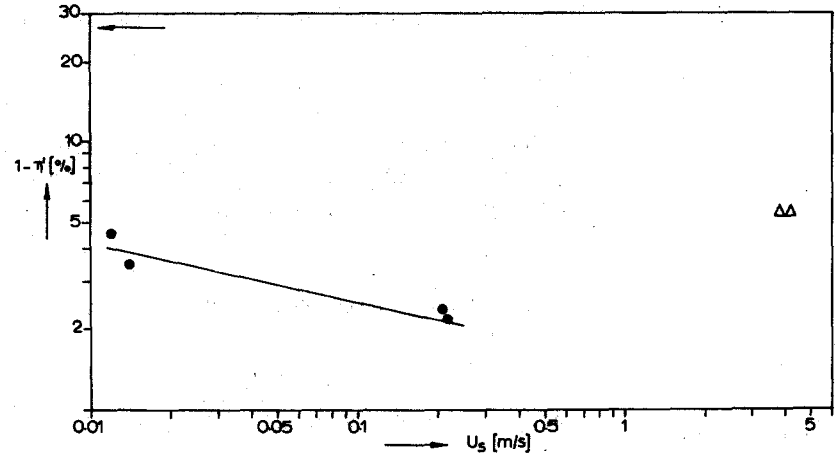


Fig. 9. Byproduct formation in the sulphonation of neat benzene at ±20 °C with gaseous SO_3 in different reactors: ●, average $1-\eta'$ in the cyclone reactor; ——, regression eqn. (21) (Table 7) for $\bar{c}_P = 0.33$ kmol m^{-3}; △, average $1-\eta'$ in the tube reactor; ←, average $1-\eta$ in the stirred-cell reactor ($\zeta \approx 0.05$; $T = 25$ °C).

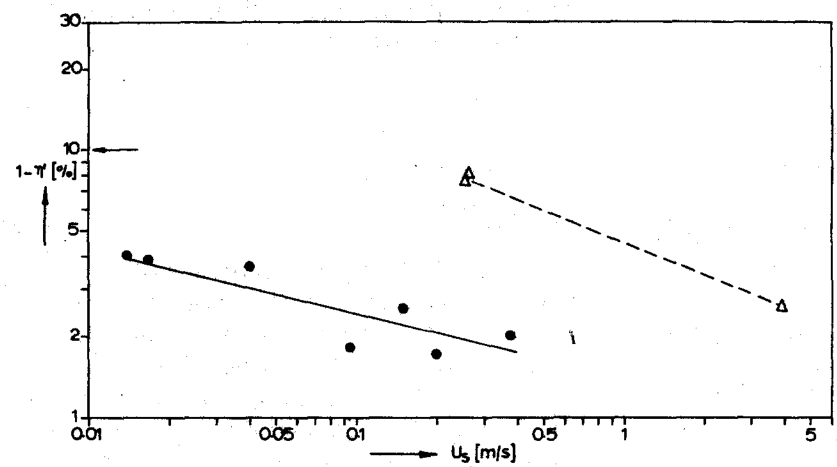


Fig. 10. Byproduct formation in the sulphonation of 30 vol.% benzene in 1,2-dichloroethane at ±20 °C with gaseous SO_3 in different reactors: ●, average $1-\eta'$ in the cyclone reactor; ——, regression eqn. (21) (Table 7) for $\bar{c}_P = 0.33$ kmol m^{-3}; △, average $1-\eta'$ in the tube reactor; ←, average $1-\eta$ in the stirred-cell reactor ($\zeta \approx 0.1$, $T = 25$ °C).

tion in hydroxide solution. Such an effect has in fact already been noted in the stirred-cell reactor, as reported in Part I of this work [9].

The first argument begins with a crude estimate of the fraction of SO_3 that is absorbed during bubble formation at the cyclone wall. For a given value of k_G, this fraction is a maximum if the resistance to mass transfer is completely in the gas phase. Then

$$m(\tau) = \int_0^\tau k_G(t)\bar{c}_A(t)\pi\{d_b(t)\}^2\,dt \tag{22}$$

where $\bar{c}$ is the bulk concentration in the gas bubble. On approximating $\bar{c}_A(t)$ by an effective mean constant concentration $\bar{c}_A$ and assuming the Sherwood number to be a constant, we obtain

$$k_G(t) = \mathrm{Sh}_G(D_A)_G/d_b(t) \tag{23}$$

With eqns. (6), (11), (12) and (23), eqn. (22) can be integrated to yield

$$m(\tau) = \frac{\pi \mathrm{Sh}_G(D_A)_G \alpha d_b^2 \bar{c}_A}{2(1-f')U_s} \tag{24}$$

An integral SO_3 balance over a bubble during the τ seconds of bubble formation gives

$$\frac{(c_A)_f - (1-f')\bar{c}_A}{(c_A)_f} = \frac{m(\tau)(1-f')}{\phi(c_A)_f\tau} \tag{25}$$

After substituting $m(\tau)$ from eqn. (24) and $\phi\tau$ from eqn. (11) we obtain

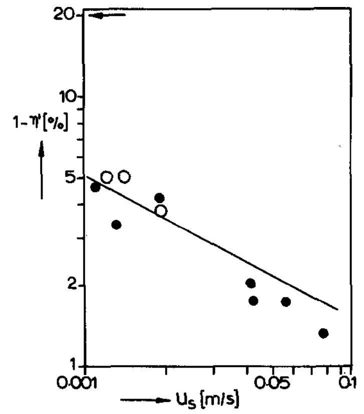


Fig. 11. Byproduct formation in the sulphonation of benzene with SO_3 at approximately 40 °C: ○,●, $1 - \eta'$ in the cyclone reactor; ●, 30 vol.% benzene, $\zeta \approx 0.1$; ——, regression eqn. (21) (Table 7) for $\bar{c}_P = 0.33$ kmol m^{-3}; ○, neat benzene, $\zeta \approx 0.04$; ←, average $1 - \eta$ in the stirred-cell reactor for $\bar{T} = 45$ °C and 30 vol.% benzene at $\zeta \approx 0.15$.

$$\frac{(c_A)_f}{\bar{c}_A} = 1 - f' + 3\mathrm{Sh_G}\,\frac{(D_A)_G}{d_b}\,\frac{\alpha}{U_s} \qquad (26)$$

With 10 vol.% SO_3, as was typical for our experiments, $f' \leqslant 0.1$. The bubble diameter is probably of the order of 2×10^{-4} m [3] and $D_A = 1.25\times10^{-5}$ m^2 s^{-1} [9]. While the fractional surface coverage α is unknown, it is likely to be a function of U_s and is always less than unity. Assuming a linear relation between α and U_s and letting $\alpha = 0.5$ for $U_s = 0.5$ m s^{-1} gives

$$\frac{(c_A)_f}{\bar{c}_A} \approx 1 + 0.2\mathrm{Sh_G} \qquad (27)$$

No published data are available at present on mass transfer in the gas phase during bubble formation. However, the relation [15] for a rising bubble given by

$$\mathrm{Sh_G} = 6.6 + \frac{1}{6}\,\mathrm{Re_G Sc_G} \times \times \left\{1 - 0.61\exp\left(-\frac{39.5}{\mathrm{Re_G Sc_G}}\right)\right\} \qquad (28)$$

suggests that $\mathrm{Sh_G}$ is not much above 6.6 for $d_b \approx 2\times10^{-4}$ m [3]. Because an increase in surface area induces at maximum an increase of k_G by a factor of 2, we expect that during bubble formation

$$\mathrm{Sh_G} \approx 10 \qquad (29)$$

From eqns. (27) and (29) it follows that for the case in which gas phase limitation prevails SO_3 absorbs mainly during bubble formation:

$$\frac{(c_A)_f}{\bar{c}_A} \approx 3 \qquad (30)$$

The determination of whether mass transfer limitation is by k_G or by k_L follows from the ratio k_G/mk_LE. From

$$k_G \approx \mathrm{Sh_G}(D_A)_G/d_b \qquad (31)$$

and using k_L from eqn. (14), this ratio becomes

$$\frac{k_G}{mk_L} = \frac{\mathrm{Sh_G}(D_A)_G}{1.5m\{d_b(D_A)_L(1-f')U_s/\alpha\}^{1/2}} \qquad (32)$$

Assuming that $m \approx 10^3$ [9], taking $(D_A)_L$ as the diffusivity of SO_3 in 1,2-dichloroethane, *i.e.* $(D_A)_L = (D_A)_S = 2\times10^{-9}$ m^2 s^{-1} [9], and with the other parameter values as used in deriving eqns. (27) and (29), we obtain by substitution into eqn. (32)

$$\frac{k_G}{mk_L} = 0.15 \qquad (33)$$

Thus, since $E \gg 1$,

$$k_G/mk_LE \leqslant 0.15 \qquad (34)$$

Although the above analysis is very crude, eqn. (34) suggests that the absorption rate is limited by k_G and eqn. (30) implies that nearly all the SO_3 is absorbed during bubble formation. However, experimental results on the selectivity in 10 and 30 vol.% benzene sulphonation exclude the possibility of completely gas phase limitation. Byproduct formation was found to be much lower in the 10 vol.% than in the 30 vol.% benzene sulphonation, while the reverse should have been observed if complete gas phase limitation existed. Apparently, eqns. (30) and (34) do not agree with these experimental results. One explanation may be that the approximations used in deriving these two equations are too crude. However, a more likely possibility is that k_L is lower than we estimated because of an increase in viscosity at the interface. Such a decrease in k_L has been observed previously in benzene sulphonation in a stirred-cell reactor [9].

The second argument in support of k_L being lower than that observed for carbon dioxide and oxygen absorption in a hydroxide solution is based on a comparison of the selectivities obtained in the cyclone and in the stirred-cell reactors. A maximum relative rate of byproduct formation is found in the instantaneous reaction regime. For $1 - \eta' \ll 1$, we derived [9] that byproduct formation is approximated by

$$1 - \eta' = \frac{k_{15} D_A (D_B \bar{c}_B / D_I + \bar{c}_I)}{(k_L E_\infty)^2} \tag{35}$$

For an identical value of $D_B \bar{c}_B / D_I + \bar{c}_I$, it follows from eqn. (35) and from the observed instantaneous reaction in the cell reactor [9] that

$$\frac{(1-\eta')_{CT}}{(1-\eta')_{SCR}} \leqslant \frac{(D_A)_{CT} (k_L E_\infty)^2{}_{SCR}}{(D_A)_{SCR} (k_L E_\infty)^2{}_{CT}} \tag{36}$$

The inequality sign has been included in eqn. (36) to cover the case of a non-instantaneous reaction in the cyclone or in the tube reactor. It should also be noted that, owing to possible gas phase limitation in the cyclone or the tube reactors,

$$\frac{(E_\infty)_{SCR}}{(E_\infty)_{CT}} \leqslant 1 \tag{37}$$

for identical $\bar{c}_B$ and $(\bar{c}_A)_G$. Thus

$$\frac{(1-\eta')_{CT}}{(1-\eta')_{SCR}} \leqslant \frac{(D_A)_{CT} (k_L)^2{}_{SCR}}{(D_A)_{SCR} (k_L)^2{}_{CT}} \tag{38}$$

Typical k_L values in the absence of an interfacial viscosity increase are $(k_L)_{CR} \approx 10^{-3}$ m s^{-1} and $(k_L)_{SCR} < 10^{-4}$ m s^{-1} [9]. With diffusivities equal in both reactors, it follows from eqn. (38) that

$$\frac{(1-\eta')_{CR}}{(1-\eta')_{SCR}} \leqslant 10^{-2} \tag{39}$$

The observed increase in interfacial viscosity in the stirred-cell reactor lowers the value of $(k_L)^2{}_{SCR}/(D_A)_{SCR}$. Therefore eqn. (39) should certainly hold if k_L in the cyclone reactor is not lowered by an increase in viscosity near the interface. For the sulphonation of neat benzene and of 30 vol.% benzene, it was found experimentally that

$$7.5 \times 10^{-2} < \frac{(1-\eta')_{CR}}{(1-\eta')_{SCR}} < 25 \times 10^{-2} \tag{40}$$

Apparently eqn. (39) does not hold for these experiments. This observation also suggests that k_L in the cyclone reactor, and therefore also in the tube reactor, is lower during sulphonation than without reaction.

A possible decrease of k_L has been attributed to an increase in viscosity at the interface caused by pyrosulphonic acid accumulation. The accumulation of pyrosulphonic acid was approximated [9] by

$$c_{II} - \bar{c}_I = \tfrac{1}{2}\eta c_{Ai} E \tag{41}$$

The product $c_{Ai} E_\infty$ is not very dependent on c_{Ai} if $E_\infty > 2$, *i.e.* for 30% benzene and for neat benzene sulphonation (Table 3 in ref. 9). Thus for cases in which the reaction is instantaneous the interface pyrosulphonic acid concentration is the same in all three reactors if bulk concentrations are also equal. In principle, this analysis indicates that a decrease in k_L can also occur in the cyclone and in the tube reactors. However, it is still possible for the value of the mass transfer coefficient, as measured in the cyclone and in the tube reactors with the $(O_2-)CO_2-$aqueous NaOH system, to remain a relative measure of the actual k_L in those reactors during sulphonation, provided that gas and liquid loads are similar in both types of experiment.

Figure 12 presents average values of $1 - \eta'$ as a function of the liquid-side mass transfer coefficient for the absorption of CO_2 in hydroxide solution in both the cyclone and the tube reactors (from Fig. 4, partly by extrapolation). From Fig. 12, it is readily apparent that the experimental differential selectivities obtained in both reactors fall on a single line, within the experimental error of these measurements. However, the relation for the case of an instantaneous reaction as given by

$$1 - \eta' \sim k_L^{-2}$$

is not observed; a power varying between 0.5 and 1 is more appropriate.

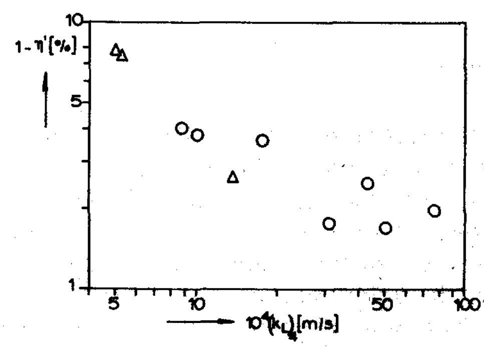


Fig. 12. Byproduct formation $1 - \eta'$ in the sulphonation of 30 vol.% benzene in 1,2-dichloroethane at 20 °C, as a function of $(k_L)_4$: ○, in the cyclone reactor; △, in the tube reactor.

As shown earlier, sulphonation of 10 vol.% benzene in 1,2-dichloroethane results in 100% selectivity (Table 6). Compared with 30 vol.% benzene sulphonation, the term

$$1+\frac{D_B\bar{c}_B}{zD_A m\bar{c}_{AG}}$$

decreases from 2.4 to 1.4 (Table 3 in ref. 9). Apparently this is sufficient to produce a substantially higher k_L, by lowering c_H (eqn. (41)), and also a far better selectivity. Comparison of the 10 vol.% benzene cyclone experiments with the 5.3 vol.% benzene sulphonation in the stirred-cell reactor [9] shows that minimum byproduct formation is found in the cyclone reactor even though the higher benzene concentration favours sulphone formation. At these low $\bar{c}_B$ values eqn. (39) may possibly hold.

An unequivocal theoretical explanation of the observed effects of reaction conditions on selectivity requires a detailed knowledge of c_{Ai} and of $k_{15}D_A/k_L^2$ (eqn. (35)) as a function of $\bar{c}_B$ and $\bar{T}$. However, such knowledge is not available at present.

The observed values of k_LS in the cyclone reactor with reaction do not differ significantly from the values measured without reaction (Fig. 7). This is not in conflict with the previous analysis because nearly all the SO_3 is absorbed at a distance of a few bubble diameters from the gas inlet and therefore k_LS is in fact measured without reaction in the major part of the reactor volume.

8. CONCLUSION

In the sulphonation of liquid benzene with gaseous sulphur trioxide in a cyclone reactor and in a tube reactor, the observed selectivities depend on conversion, on the initial benzene concentration and on the mass transfer characteristics of the particular reactor. Minimum diphenyl sulphone formation was obtained with a low initial benzene concentration, a low benzene conversion and the high liquid-side mass transfer coefficient realized in the cyclone reactor.

NOMENCLATURE

A	sulphur trioxide
B	benzene
c	concentration, kmol m^{-3}
d	diameter, m
D	diffusion coefficient, m^2 s^{-1}
E	enhancement factor, *i.e.* factor by which the rate of absorption is increased by reaction
E_∞	enhancement factor when reaction (2) is controlled entirely by diffusion, *i.e.* when reaction (2) is instantaneous
f	mole fraction in the gas feed
f'	volumetric gas fraction absorbed during bubble growth at the porous wall (with respect to the total gas flow into the bubble)
g	gas phase
I	pyrosulphonic acid (benzenesulphonic acid, monoanhydride with sulphuric acid)
I'	$C_6H_5S_3O_9H$ (benzenesulphonic acid, monoanhydride with disulphuric acid)
J	absorption rate per unit area, kmol m^{-2} s^{-1}
k_{15}	reaction rate constant of reaction (3), m^3 $kmol^{-1}$ s^{-1}
k_G	gas phase mass transfer coefficient, m s^{-1}
k_L	liquid phase mass transfer coefficient, m s^{-1}
l	liquid phase
m	$(c_{Ai})_L/(c_{Ai})_G$, solubility
$m(t)$	total number of kilomoles absorbed in the liquid during the first t seconds of bubble age at the porous wall for the case of physical absorption, kmol
p	pressure, bar, N m^{-2}
$\Delta p/\Delta L$	pressure drop per unit length, N m^{-3}
Re	$\rho v d/\mu$, Reynolds number
S	specific interfacial area, m^{-1}
Sc	$\mu/\rho D$, Schmidt number
Sh	k_Ld/D or k_Gd/D, Sherwood number
t	time; age of a bubble at the porous wall, s
T	temperature, °C
U_L	superficial liquid velocity, m s^{-1}
U_s	superficial gas velocity, in the cyclone reactor defined at p_w and related to the porous wall area; in

	the tube reactor as usual, m s^{-1}
v	velocity, m s^{-1}
z	stoichiometric coefficient from eqn. (2)

Greek symbols

α	defined above eqn. (12)
ϵ	gas holdup per cubic metre of reactor
ζ	conversion of benzene
η	selectivity, fraction of benzene that is converted into benzenesulphonic acid
η'	(differential) selectivity, fraction of converted benzene that is converted into benzenesulphonic acid during the period $\zeta(i) - \zeta(i-1)$, where i is the sample number
μ	viscosity, Pa s
ρ	density, kg m^{-3}
σ	surface tension, N m^{-1}
τ	residence time of a bubble at the porous cyclone wall, s
ϕ	growth rate of a bubble, m^3 s^{-1}

Subscripts

A	sulphur trioxide
b	bubble
B	benzene
bf	during bubble formation
CR	cyclone reactor
CT	cyclone and tube reactors
f	in the feed
G	gas phase
i	at the interface; in the inlet
I	pyrosulphonic acid
L	liquid phase
P	benzenesulphonic acid
S	solvent
SCR	stirred-cell reactor
TR	tube reactor
w	at the porous cyclone wall
3	methane–30 vol.% benzene in 1,2-dichloroethane system
4	oxygen–2.07 M sodium hydroxide solution system

A bar over a variable indicates the value in the bulk of the liquid.

REFERENCES

1 J. G. van de Vusse, *Chem. Eng. Sci., 21* (1966) 631.
2 A. A. C. M. Beenackers and W. P. M. van Swaaij, *Chemical Reaction Engineering, Proc. 6th Europ., 4th Int., Symp.*, Dechema, Frankfurt am Main, 1976, p. VI-260.
3 A. A. C. M. Beenackers, *Ph.D. Thesis*, Twente University of Technology, Enschede, 1977.
4 W. J. Beek and H. Kramers, *Chem. Eng. Sci., 16* (1962) 90.
5 P. H. Calderbank and R. P. Patra, *Chem. Eng. Sci., 21* (1966) 719.
6 K. A. Reddy and L. K. Doraiswamy, *Ind. Eng. Chem. Fundam., 6* (1967) 77.
7 G. W. Govier and K. Aziz, *The Flow of Complex Mixtures in Pipes*, Van Nostrand–Reinhold, New York, 1972.
8 G. A. Gregory and D. S. Scott, in E. Rhodes and D. S. Scott (eds.), *Cocurrent Gas–Liquid Flow*, Plenum Press, New York, 1969.
9 A. A. C. M. Beenackers and W. P. M. van Swaaij, *Chem. Eng. J., 15* (1978) 25.
10 L. L. van Dierendonck, *Ph.D. Thesis*, Twente University of Technology, Enschede, 1970.
11 P. H. Calderbank and M. B. Moo Young, *Chem. Eng. Sci., 16* (1961) 39.
12 C. R. Wilke and P. Chang, *A.I.Ch.E. J., 1* (1955) 264.
13 R. A. T. O. Nijsing, R. H. Hendriksz and H. Kramers, *Chem. Eng. Sci., 10* (1959) 88.
14 P. M. E. M. van der Grinten and J. M. H. Lenoir, *Statistische Procesbeheersing*, Spectrum, Utrecht, 1973.
15 F. H. H. Valentin, *Absorption in Gas–Liquid Dispersions*, Spon, London, 1967.