152. Chemical Selectivities Disguised by Mass Diffusion. VIII. Influence of pH-Gradients on the Product Distribution in Mixing-Disguised Azo Coupling Reactions[1][2]

9th Communication on the Selectivity of Chemical Processes[1]

by **Hasan Belevi, John R. Bourne** and **Paul Rys**

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, CH-8092 Zürich

Dedicated to the memory of Prof. *Norbert Ibl*

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Summary

In mixing-disguised azo coupling reactions the protons which are released during the electrophilic substitution steps cause a pH-gradient in the reaction zone. Since, owing to the acid-base pre-equilibria, these pH-gradients also determine the local concentrations of the reactants in the reaction zone, they also have an influence on the measured product distribution of such fast reactions. In the present work, the product distribution of the azo coupling of 1-naphthol with 4-sulfophenyldiazonium ion was experimentally measured and the results were compared with the distributions predicted from our mixing-reaction model developed previously [1]. Furthermore, some experimental evidence for the existence of isoselectivity points are presented, at which a change of the initial pH-value has no influence on the product distribution.

1. Introduction. - In Part VII of this series [1] a mixing-reaction model (MIRE-PH) was developed to describe the influence of pH-gradients on mixing-disguised azo coupling reactions. Calculations were carried out to simulate the influence of the diffusion of the reactants and of the proton, released during the substitution step, on the product distribution. Thereby isoselectivity points were established, where product distribution does not depend on the initial pH-value.

In the present paper the measured product distribution is compared with that predicted by the MIRE-PH model. Some experimental evidence for the existence of isoselectivity points is given.

2. The Azo Coupling Model System. - In order to investigate the pH-influence on the product distribution in mixing-disguised azo coupling reactions, the azo coupling of 1-naphthol with 4-sulfophenyldiazonium ion was chosen *(Scheme)*.

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[1] Part VII and 8th Communication *cf.* [1].

[2] Results taken from the Ph. D. thesis of *H. Belevi* [2].

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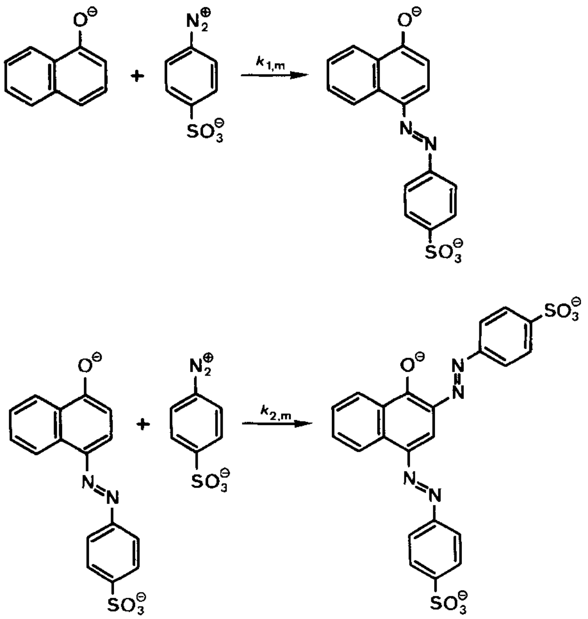
Scheme



Although one would also expect *ortho*-monoazo product, the primary azo coupling reaction occurs predominantly in *para*-position [2]. This fact facilitates the calculations by the mixing-reaction model MIRE-PH.

The pH-influence on the product distribution is enabled by the fact that there is a difference between the pK-values of 1-naphthol and 4-(4′-sulfophenylazo)-1-naphthol (*para*-monoazo product). This difference is 1.1.

From the results of *Kishimoto* [3] it can be concluded that the primary coupling reaction shows only weak general base catalysis. This is in agreement with our previous findings for the mixing-disguised azo coupling of 1-naphthol-6-sulfonic acid and phenyldiazonium salt [4]. However, the influence of general base catalysis on the predictions calculated by the MIRE-PH model can be neglected for the experimental conditions chosen in this work¹).

3. The Mixing-Disguised Selectivity Behaviour. - *3.1. Experimental Results and Calculations by MIRE-PH.* In the previous Part of this series [1], it was demonstrated, that the influence of pH-gradients on selectivity in the mixing-disguised azo coupling reactions *(Scheme)* is fully described by the parameters E, α, $\varphi^2_{B,1,m}$, $\varphi^2_{B,2,m}$, K_A, K_R, K_S, K_W, K_P, $\Pi_{A,0}$, and $H_{A,0}$ as well as by the initial and boundary conditions²).

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¹) There is no principal difficulty to consider general base catalysis in the MIRE-PH calculations. In this case, the k-values of the coupling reactions will become dependent on time and space as well as on the type and the concentration of the base. Thus considerably more computing time has to be allowed.

²) For symbols see list at the end.

For the experimental investigations the conditions are chosen in such a way, that only the parameters E, α, $\varphi^2_{B,1,m}$, $\varphi^2_{B,2,m}$ and $H_{A,0}$ change, whereby $E \cdot \alpha$, $E \cdot \varphi^2_{B,1,m}$ and $E \cdot \varphi^2_{B,2,m}$ remain constant. These conditions can be attained, when the initial naphthol concentration $[A]_0$, the buffer concentration $[P]_0$, the temperature T, the ionic strength I as well as the stirring rate remain constant and the initial diazonium salt concentration $[B]_0$, ratio of the feed volumes α and the initial pH-value vary. *Figure 1* summarizes the experimental results. X_S designates the product distribution after 100% conversion according to the relation 1.

$$X_S = \frac{2[S]_\infty}{2[S]_\infty + [R]_\infty} \tag{1}$$

For calculations using the MIRE-PH model the parameters $k_{1,m}$, $k_{2,m}$, and $\bar{R}^2/D$ must be determined. The values for the rate constants are taken from the work of *Kozicki* [5]. The ratio $\bar{R}^2/D$ can be evaluated by estimating D and $\bar{R}$. The diffusion coefficient of 1-naphthol can be calculated using the equation of *Wilke & Chang* [6],

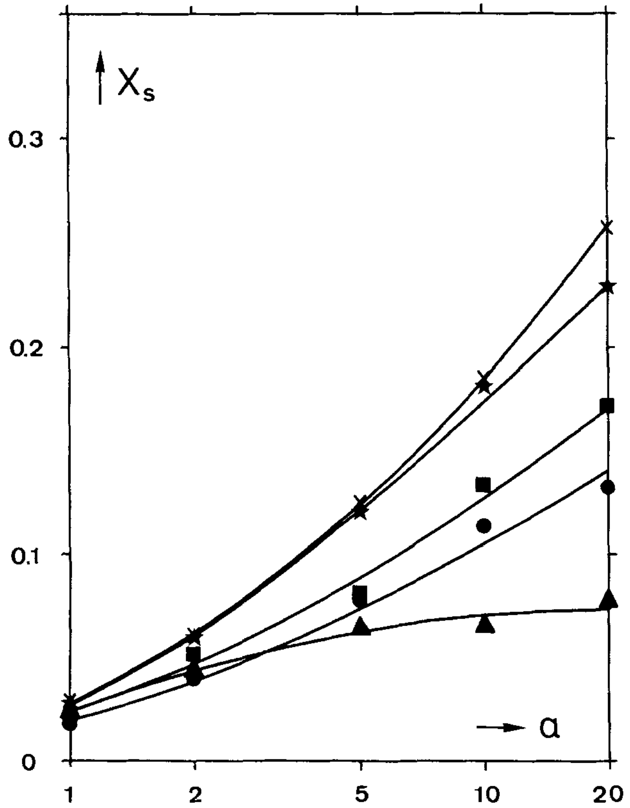

Fig. 1. *Experimental relative yields X_S as a function of α for different initial pH-values*
$[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $[P]_0 = 2.5 \cdot 10^{-3}$ mol · dm^{-3}; $I = 0.1$ mol · dm^{-3}; T = 23.0°; $E \cdot \alpha = 2.0$; stirring rate = 2.5 s^{-1}; pH = 10.05 (×); 9.30 (∗); 8.90 (■); 8.65 (●); 8.40 (▲).

where x is the association parameter, M is the molecular weight of the diffusant, T is the absolute temperature, η is the dynamic viscosity and V_D is the molar volume of the diffusing species.

$$D = 7.4 \cdot 10^{-15} \frac{(\mathrm{x} \cdot \mathrm{M})^{1/2}\,\mathrm{T}}{\eta\, \mathrm{V}_{\mathrm{D}}^{0.6}} \tag{2}$$

For the given experimental conditions $D = 0.7 \cdot 10^{-9}$ $\mathrm{m}^2\mathrm{s}^{-1}$, $\bar{R}$ can approximately be evaluated by the theory of turbulence. *Kolmogoroff* estimated the characteristic size λ_K of the smallest eddies with the relationship 3, where ε is the energy dissipated by the stirrer per unit mass of solution [7] [8].

$$\lambda_K = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4} \tag{3}$$

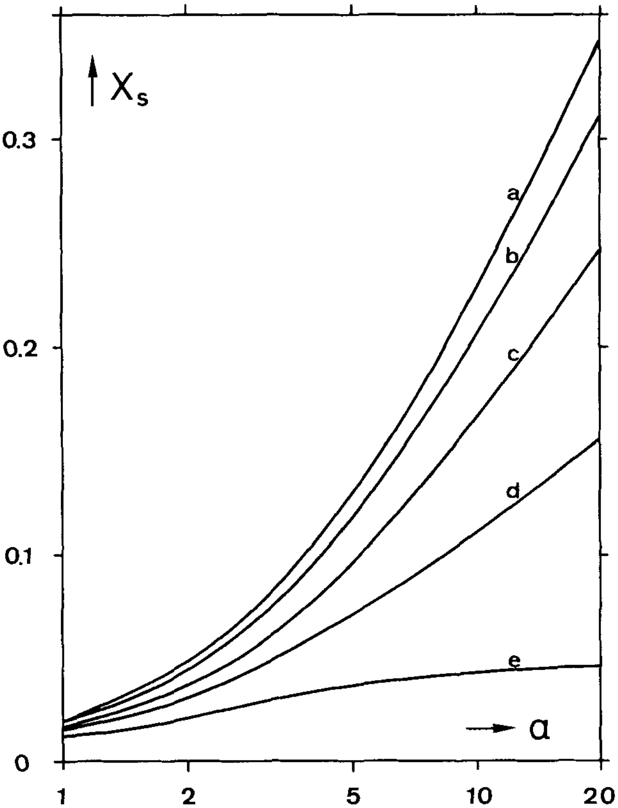

Fig. 2. *Relative yields X_S as a function of* **α** *for different initial pH-values calculated by the MIRE-PH model*

$\boldsymbol{E} \cdot \varphi^2_{\mathrm{B},1,\mathrm{m}} = 3500$; $\boldsymbol{E} \cdot \boldsymbol{\alpha} = 2.0$; $\mathrm{p}K_\mathrm{A} = 9.33$; $\mathrm{p}K_\mathrm{R} = 8.23$; $\boldsymbol{E} \cdot \varphi_{\mathrm{B},2,\mathrm{m}} = 1.23$; $\mathrm{p}K_\mathrm{S} = 7.57$; $\mathrm{p}K_\mathrm{P} = 9.14$; $\mathrm{p}K_\mathrm{W} = 14.1$; $[\mathrm{A}]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $[\mathrm{P}]_0 = 2.5 \cdot 10^{-3}$ mol · dm^{-3}; $\bar{R}^2/D = 0.7$ s; pH = 10.05 (a); 9.30 (b); 8.90 (c); 8.65 (d); 8.40 (e).

Table 1. *Experimental relative yields X_S as a function of* α *for different initial pH-values*
$[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $[P]_0 = 2.5 \cdot 10^{-3}$ mol · dm^{-3}; $I = 0.1$ mol · dm^{-3}; T = 23.0°; $\bar{R}^2/D = 0.7$ s; stirring rate = 2.5 s^{-1}.

E	α	pH initial	pH end	$X_S \cdot 100$
2	1	8.40	8.03[a])	2.5 ± 1.1[b])
1	2		7.98	4.4 ± 1.0
0.4	5		7.60	6.5 ± 2.5
0.2	10		7.60	6.6 ± 1.1
0.1	20		7.60	7.8 ± 1.2
2	1	8.65	–	1.8 ± 0.4
1	2		–	4.0 ± 1.3
0.4	5		–	7.8 ± 1.4
0.2	10		–	11.4 ± 2.7
0.1	20		–	13.3 ± 1.1
2	1	8.90	8.70	2.2 ± 0.6
1	2		8.62	5.2 ± 0.6
0.4	5		8.47	8.2 ± 2.1
0.2	10		8.40	13.4 ± 2.2
0.1	20		8.40	17.2 ± 1.4
2	1	9.30	9.15	2.8 ± 0.5
1	2		9.10	6.0 ± 1.5
0.4	5		9.00	12.1 ± 2.6
0.2	10		8.98	18.4 ± 0.8
0.1	20		8.97	23.0 ± 2.5
2	1	10.05	9.84	2.9 ± 0.4
1	2		9.82	6.1 ± 1.3
0.4	5		9.40	12.5 ± 2.1
0.2	10		9.40	18.5 ± 2.0
0.1	20		9.40	25.8 ± 2.7

[a]) The error is ≤ 0.05 pH-units.
[b]) The errors are calculated to a confidence level of 95%.

Table 2. *Relative yields X_S as a function of* α *for different pH-values calculated by the MIRE-PH model*
$[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $[P]_0 = 2.5 \cdot 10^{-3}$ mol · dm^{-3}; $pK_A = 9.33$; $pK_R = 8.23$; $pK_S = 7.57$; $\bar{R}^2/D = 0.7$ s; $pK_P = 9.14$; $pK_W = 14.1$.

E	α	$\frac{\varphi^2_{B,1,m}}{\varphi^2_{B,2,m}}$	$\varphi^2_{B,2,m}$	pH initial	pH end	$X_S \cdot 100$
2	1	2860	0.61	8.40	8.13	1.2
1	2		1.23		8.02	2.1
0.4	5		3.06		7.93	3.6
0.2	10		6.13		7.87	4.4
0.1	20		12.25		7.84	4.7
2	1	2860	0.61	8.65	8.46	1.5
1	2		1.23		8.40	3.1
0.4	5		3.06		8.34	7.0
0.2	10		6.13		8.31	11.1
0.1	20		12.25		8.29	15.7
2	1	2860	0.61	8.90	8.76	1.7
1	2		1.23		8.71	3.8
0.4	5		3.06		8.67	9.7

Table 2 (continued)

E	α	$\frac{\varphi^2_{B,1,m}}{\varphi^2_{B,2,m}}$	$\varphi^2_{B,2,m}$	pH initial	pH end	$X_S \cdot 100$
0.2	10		6.13		8.65	16.7
0.1	20		12.25		8.64	24.9
2	1	2860	0.61	9.30	9.18	1.9
1	2		1.23		9.15	4.4
0.4	5		3.06		9.12	11.7
0.2	10		6.13		9.10	20.7
0.1	20		12.25		9.09	31.5
2	1	2860	0.61	10.05	-	2.0
1	2		1.23		-	4.7
0.4	5		3.06		-	12.9
0.2	10		6.13		-	23.0
0.1	20		12.25		-	34.8

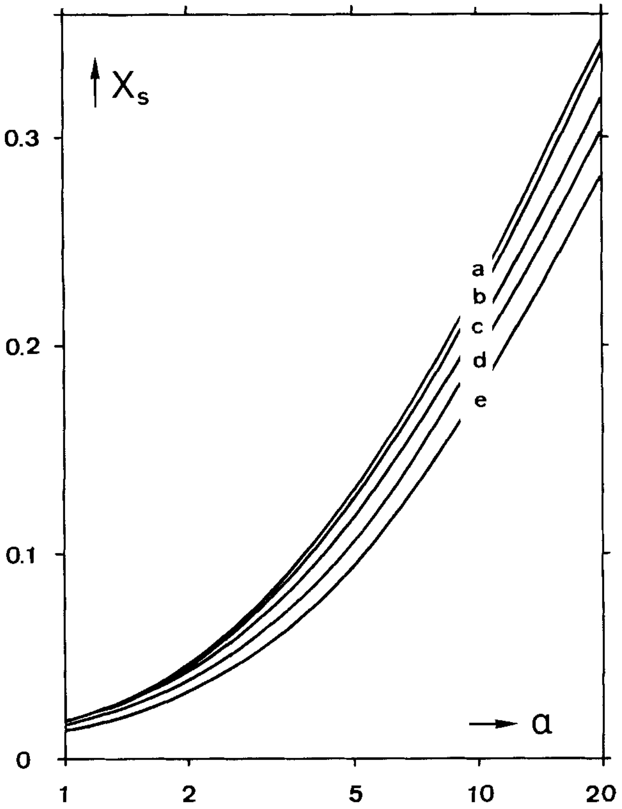

Fig. 3. *Relative yields X_S as a function of α for different (a-e) pH-values calculated by the MIRE-2 model* The pH-values correspond to the initial pH-values of the experiments. $E \cdot \varphi^2_{B,1,m} = 3500$; $E \cdot \alpha = 2.0$; $[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $E \cdot \varphi^2_{B,2,m} = 1.23$; $pK_A = 9.33$; $pK_R = 8.23$; $\bar{R}^2/D = 0.7$ s; pH = 10.05 (a); 9.30 (b); 8.90 (c); 8.65 (d); 8.40 (e).

Comparing the experimental with the calculated behaviour and taking the curve X_S *vs.* pH at pH = 8.65 as a basis, the best agreement is found for $\bar{R}^2/D = 0.7$ s. For $\lambda_K = 2\bar{R}$, this value is smaller than the estimate using *Kolmogoroff*'s equation 3 by a factor of 3.6. Thus, the assertion of *Corrsin* [9] seems to be confirmed, that $\bar{R}$ must be smaller than $\lambda_K/2$ for high *Schmidt*-Numbers ($= \nu/D$). For the experimental conditions which apply in the present work the *Schmidt*-Number is 1400.

Figure 2 shows the results of the calculations by the MIRE-PH model taking $\bar{R}^2/D = 0.7$ s. The appropriate values are listed in *Tables 1* and *2*.

3.2. Comparison of Experimental and Calculated Reaction Behaviour. For constant pH-values the model calculations can be carried out by MIRE-2 [2] [4] [10]. *Figures 3* and *4* show calculations of X_S *vs.* $\mathbf{\alpha}$ by MIRE-2 for constant pH-values, which correspond in *Figure 3* to the initial and in *Figure 4* to the final pH-values of the experiments.

The experimental values of X_S should lie between the values in *Figure 3* and those in *Figure 4*. As *Figure 1* shows, the experimental curves lie even under the curves in *Figure 4*. This implies, that the product distribution in mixing-disguised azo coupling reactions is affected merely by local pH-gradients caused by the

Table 3. *Relative yields X_S as a function of* $\mathbf{\alpha}$ *for different pH-values calculated by the MIRE-2 model*
The pH-values correspond to the initial pH-values of the experiments.
$[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; p$K_A = 9.33$; p$K_R = 8.23$; $\bar{R}^2/D = 0.7$ s.

E	$\mathbf{\alpha}$	$\frac{\varphi^2_{B,1,m}}{\varphi^2_{B,2,m}}$	$\varphi^2_{B,2,m}$	pH	$X_S \cdot 100$
2	1	2860	0.61	8.40	1.4
1	2		1.23		3.3
0.4	5		3.06		9.3
0.2	10		6.13		17.5
0.1	20		12.25		28.0
2	1	2860	0.61	8.65	1.6
1	2		1.23		3.8
0.4	5		3.06		10.6
0.2	10		6.13		19.4
0.1	20		12.25		30.4
2	1	2860	0.61	8.90	1.8
1	2		1.23		4.2
0.4	5		3.06		11.5
0.2	10		6.13		20.8
0.1	20		12.25		32.2
2	1	2860	0.61	9.30	1.9
1	2		1.23		4.5
0.4	5		3.06		12.3
0.2	10		6.13		22.1
0.1	20		12.25		33.7
2	1	2860	0.61	10.05	2.0
1	2		1.23		4.7
0.4	5		3.06		12.9
0.2	10		6.13		23.0
0.1	20		12.25		34.8

protons released during the azo coupling reactions. The values calculated for the *Figures 3* and *4* are listed in *Tables 3* and *4*.

The agreement of the experimental results and the calculated behaviour calculated with MIRE-PH is satisfactory *(Fig. 5)*. The calculated curves spread more than the experimental curves. This fact attributes probably to the fact that the diffusion of the protons ($D_{H\oplus} = 8.7 \cdot 10^{-9} m^2 s^{-1}$) is much faster than it is assumed for the calculations where the diffusivities D of all species are assumed to be equal ($D = 0.7 \cdot 10^{-9} m^2 s^{-1}$) [11].

3.3. Existence of an Isoselectivity Point in Mixing-Disguised Azo Coupling Reactions. In a previous part of this series [1] it was established, that the product distribution does not depend on the initial pH-value for a characteristic set of parameters. Here, the question arises, whether some experimental evidence can be given for the existence of such isoselectivity points.

The calculations have shown, that for the experimental conditions applied, the isoselectivity point can be expected at $X_S = 10^{-3}$. However, at this point the

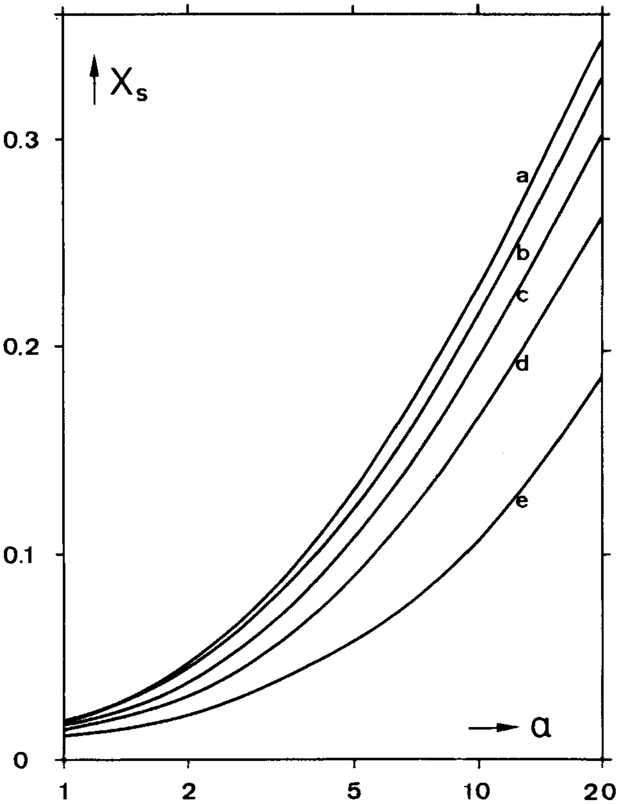

Fig. 4. *Relative yields X_S as a function of $\mathbf{\alpha}$ for different (a–e) pH-values calculated by the MIRE-2 model*
The pH-values correspond to the initial pH-value of the experiments. The calculations are made for the corresponding pH-values at the end of the experiments calculated by MIRE-PH.
$E \cdot \varphi^2_{B,1,m} = 3500$; $E \cdot \mathbf{\alpha} = 2.0$; $[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $E \cdot \varphi^2_{B,2,m} = 1.23$; $pK_A = 9.33$; $pK_R = 8.23$; $\bar{R}^2/D = 0.7$ s; pH = 10.05 (a); 9.30 (b); 8.90 (c); 8.65 (d); 8.40 (e).

Table 4. *Relative yields X_S as a function of* $\boldsymbol{\alpha}$ *for different pH-values calculated by the MIRE-2 model*
The pH-values correspond to the initial pH-values of the experiments. The calculations are made for the corresponding pH-values at the end of the experiments calculated by MIRE-PH.
$[A]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; p$K_A = 9.33$; p$K_R = 8.23$; $\bar{R}^2/D = 0.7$ s.

E	$\boldsymbol{\alpha}$	$\frac{\varphi^2_{\mathrm{B},1,\mathrm{m}}}{\varphi^2_{\mathrm{B},2,\mathrm{m}}}$	$\varphi^2_{\mathrm{B},2,\mathrm{m}}$	pH	$X_S \cdot 100$
2	1	2860	0.61	8.40	1.2
1	2		1.23		2.3
0.4	5		3.06		5.9
0.2	10		6.13		10.7
0.1	20		12.25		18.7
2	1	2860	0.61	8.65	1.5
1	2		1.23		3.3
0.4	5		3.06		8.8
0.2	10		6.13		16.5
0.1	20		12.25		26.5
2	1	2860	0.61	8.90	1.7
1	2		1.23		3.9
0.4	5		3.06		10.7
0.2	10		6.13		19.5
0.1	20		12.25		30.4
2	1	2860	0.61	9.30	1.9
1	2		1.23		4.4
0.4	5		3.06		12.1
0.2	10		6.13		21.6
0.1	20		12.25		33.1
2	1	2860	0.61	10.05	2.0
1	2		1.23		4.7
0.4	5		3.06		12.9
0.2	10		6.13		23.0
0.1	20		12.25		34.8

analytical inaccuracy is so large, that it is impossible to establish the existence of isoselectivity points by experiments. Nevertheless, there is an indication for their existence:

As shown in Part VII the product distribution X_S increases with decreasing initial pH-values at small values of $\boldsymbol{\alpha}$. For large $\boldsymbol{\alpha}$-values this dependence is opposite. Therefore, the curves X_S *vs.* $\boldsymbol{\alpha}$ measured at the several initial pH-values should intersect, probably at one point.

4. Conclusions. - The experimental results show clearly that the reaction behaviour in a mixing-disguised azo coupling reaction can be described by the mixing-reaction model MIRE-PH discussed elsewhere [1]. Unlike the previous models, this model considers the pH-gradients caused by the protons released in the azo coupling steps. A comparison of the calculations at constant pH-values and the calculations by the MIRE-PH model with the experimental results demonstrates the decisive influence of the local pH-gradients on the product distribution. Unfortunately, the experimental results can not decide definitely on the existence of isoselectivity points, which have been predicted in the previous part of this series [1].

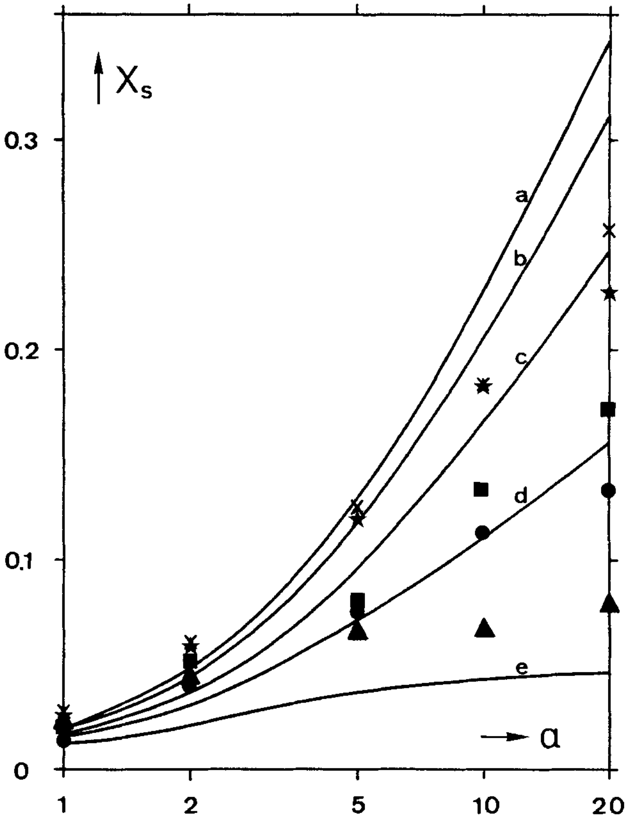

Fig. 5. *Experimental and calculated (MIRE-PH) relative yields X_S as a function of* **α** *for different (a–e) initial pH-values*

$\boldsymbol{E} \cdot \varphi^2_{\mathrm{B},1,\mathrm{m}} = 3500$; $\boldsymbol{E} \cdot \boldsymbol{\alpha} = 2.0$; $\mathrm{p}K_\mathrm{A} = 9.33$; $\mathrm{p}K_\mathrm{R} = 8.23$; $\boldsymbol{E} \cdot \varphi^2_{\mathrm{B},2,\mathrm{m}} = 1.23$; $\mathrm{p}K_\mathrm{S} = 7.57$; $\mathrm{p}K_\mathrm{P} = 9.14$; $\mathrm{p}K_\mathrm{W} = 14.1$; $[\mathrm{A}]_0 = 5 \cdot 10^{-4}$ mol · dm^{-3}; $[\mathrm{P}]_0 = 2.5 \cdot 10^{-3}$ mol · dm^{-3}; $I = 0.1$ mol · dm^{-3}; T = 23.0°; stirring rate = 2.5 s^{-1}; $\bar{R}^2/D = 0.7$ s. pH = 10.05 (×) (a); 9.30 (∗) (b); 8.90 (■) (c); 8.65 (●) (d); 8.40 (▲) (e).

Experimental Part

General remarks. The preparative and the thin layer chromatography (TLC.) were performed on precoated silica gel plates (*Merck* F_{254}). The UV./VIS. spectra were determined using a *Beckman-Acta II* spectrophotometer. The pH-values were measured using a digital pH-meter (*Philips* PW 9414, CA 11). The product distribution was analysed by high pressure liquid chromatography (HPLC.) (*Waters Associates* 6000B, U6K) with a UV./VIS. detector (*Perkin-Elmer* LC 55). The column was a self packed column (*Spherisorb* 55 W) of 250×4 mm filled with *spherisorb* S5W, 5 (*Separations Ltd.*). As solvent system *n*-butanol/ethanol/water 7.2/1/1.8 with 0.25% sodium acetate-solution was used. The flow rate was 6 · 10^{-5} m^3 s^{-1}. The measurements are performed at the wave-length $\lambda_{\max} = 368$ nm.

Materials. 1-Naphthol. Commercial product was purified by sublimation i.V.

4-Sulfophenyldiazonium tetrafluoroborate. The synthesis was performed according to the procedure described elsewhere [12].

2-(4′-Sulfophenylazo)-1-naphthol. This *ortho*-monoazo product was synthesized from 1,2-naphthoquinone by the method of *Noelting & Grandmougin* [13].

4-(4′-Sulfophenylazo)-1-naphthol. This *para*-monoazo compound was synthesized according to the procedure described elsewhere [14]. The purification was carried out by chromatography on silica gel

Table 5. *pK- or (pK_1+pK_2)/2-values, respectively, of the reactants and products*

Substance	pK	Ref.
1-Naphthol	9.33	measured [2]
4-(4'-Sulfophenylazo)-1-naphthol	8.23	measured [2]
2,4-Bis(4'-sulfophenylazo)-1-naphthol	7.57	measured [2]
	$\frac{(pK_1+pK_2)}{2}$	
4-Sulfophenyldiazonium ion	10.48	[42]

Table 6. *Composition and pH of the Buffer Systems*
(T=23.0°: I=0.1 mol · dm^{-3})

Buffer No.	pH	Volume 0.1N HCl/cm^3	Volume 0.1N NaOH/cm^3
1	8.40	76	-
2	8.65	46	-
3	8.90	-	-
4	9.30	-	52
5	10.05	-	120

plates using the solvent system chloroform/acetic acid/water 6/5/1 (*v*/*v*). - VIS. (water, pH=10, [R]=2.5 · 10^{-5} mol · dm^{-3}): λ_{max}=516 nm (32430).

2,4-Bis(4'-sulfophenylazo)-1-naphthol. This disazo compound was synthesized by the method of *Krohn* [15]. It was purified by chromatography on silica gel plates using the solvent system: *n*-butanol/methanol/acetic acid/chloroform/water 2/2/1/2/1 (*v*/*v*). - VIS. (water, pH=10, [S]=5 · 10^{-5} mol · dm^{-3}): λ_{max}=560 nm (24770).

Determination of the pK-values. The pK-values of the reactants were determined by the method of *Hammett* [16] *(Table 5).*

The buffer systems. The buffer solutions were sodium borate/hydrochloric acid- or sodium borate/sodium hydroxide-solutions. In all experiments the concentrations of H_3BO_3 and $H_2BO_3^{\ominus}$ were 2.5 · 10^{-3} mol · dm^{-3}. For the buffer solutions 0.625 · 10^{-2} mol $Na_2B_4O_7$ are dissolved in 500 cm^3 water, the volumes of the solutions of 0.1N HCl or 0.1N NaOH, which are given in *Table 6,* were added and diluted with water to 1 dm^3 [17].

Mixing experiments. The reaction vessel consisted of a two-necked flask of 0.05 dm^3 volume and 50 mm diameter, equipped with a symmetrical three-wing propeller (height: 15 mm, diameter: 9 mm). The blades of the stirrer were arranged at an angle of 35° with respect to the rotational axis. The buffered solution of diazonium salt (I=0.1 mol · dm^{-3}) was added quickly to the buffered solution of 1-naphthol (I=0.1 mol · dm^{-3}) in the reaction vessel by means of a pipette (2-5 s). Before the start of each experiment the pH-values of the reactant solutions were measured. The accuracy was within ±0.03 ±0.03 pH-units.

After completion of the reaction the products were analyzed by high pressure liquid chromatography. The UV./VIS. detector was fixed at 368 nm, since at this wave length the diazo compound has a high and the monoazo compound has a low extinction coefficient. This enables the analysis of small product distributions (X_S=0.005). No *ortho*-monoazo product could be detected.

Appendix

List of Symbols

	A	Coupling component, 1-naphthol
	B	Diazonium ion, 4-sulfophenyldiazonium ion
	D	Diffusion coefficient [m^{2}s^{-1}]
	E	Ratio of initial concentration of A and B, $[A]_0/[B]_0$

	$H^{\oplus}$	Hydronium ion and higher hydrated proton
	$\boldsymbol{H}_{A,0}$	Initial concentration of $H^{\oplus}$ normalized with respect to $[A]_0$
	I	Ionic strength $[mol \cdot dm^{-3}]$
	$k_{1,m}, k_{2,m}$	Intrinsic second-order rate constants $[dm^3 mol^{-1} s^{-1}]$
	$K_A, K_R,$	Acidity constants of the species A, R, S
	K_S, K_P	and P $[mol \cdot dm^{-3}]$
	$\boldsymbol{K}_A, \boldsymbol{K}_R,$	Acidity constants of A, R, S and P normalized
	$\boldsymbol{K}_S, \boldsymbol{K}_P$	with respect to $[A]_0$
	K_W	Ionisation constant of water $[mol^2\, dm^{-6}]$
	$\boldsymbol{K}_W$	Ionisation constant of water normalized with respect to $[A]_0$
	M	Mol. weight of the solvent $[g \cdot mol^{-1}]$
	P	Buffer
	$\boldsymbol{\Pi}_{A,0}$	Initial concentration of buffer normalized with respect to $[A]_0$
	R	Monoazo product, 4-(4′-sulfophenylazo)-1-naphthol
	$\bar{R}$	Radius of spherical eddy [m]
	S	Disazo product, 2,4-bis(4′-sulfophenylazo)-1-naphthol
	T	Temperature [°C or °K]
	V_A	Volume of surrounding solution $[m^3]$
	V_B	Volume of eddies $[m^3]$
	V_D	Mol. volume of diffusing species $[cm^3\, mol^{-1}]$
	x	Association parameter
	X_S	Measure of product distribution defined in equ. 1
	$\boldsymbol{\alpha}$	Ratio of eddy volume to surrounding solution volume, $\boldsymbol{\alpha} = V_A/V_B$
	ε	Density of energy dissipation $(m^2 s^{-3}]$
	η	Dynamic viscosity of the solvent $[kg\, m^{-1}\, s^{-1}]$
	λ	Wave length [nm]
	λ_K	*Kolmogoroff* velocity microscale [m]
	ν	Kinematic viscosity $[m^2 s^{-1}]$
	$\boldsymbol{\varphi}^2_{B,1,m}$ $\boldsymbol{\varphi}^2_{B,2,m}$	Rate constants normalized with respect to $[B]_0$
Special notation	$[i]$	Concentration of species i $[mol\, dm^{-3}]$
	$[i]_0$	Initial concentration of species i $[mol\, dm^{-3}]$

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