

with the frequency shifts  $\Delta\nu$  (Fig. 2). As far as it would be possible to draw conclusions from so comparatively narrow interval ( $\Delta\nu = 150-210 \text{ cm}^{-1}$ ), it seems that the change in the standard free enthalpy  $-\Delta G$  is not directly proportional to but linearly dependent on, the frequency shifts. The linear relationships between  $\log K$  and  $\sigma$  and between  $\log K$  and  $\Delta\nu$  imply that also  $\Delta\nu$  vs  $\sigma$  are linearly dependent (Fig. 3). It can be therefore concluded that the association of *meta*- and *para*-substituted phenols with valeronitrile is in harmony with common concepts on formation of complexes via hydrogen bonding and further that both association equilibria and chemical reactivity of these compounds are affected by electronic effects of substituents in a similar way.

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## AXIAL DISPERSION IN A REACTOR WITH A HELICAL FLOW

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The magnitude of the axial dispersion belongs to basic problems in designing reactors for chemical reactions with reaction products of molecular masses depending considerably on time spent in the reactor. If the flow in such a reactor differs remarkably from the piston flow, a high molecular weight product of some polycondensation may for example stick on the reactor walls.

On the other hand, the reaction mixture is flowing far more quickly through the middle of the pipe and the corresponding reaction product may be converted insufficiently. It is obvious that the maximum imitation of the piston flow is an assumption necessary for obtaining a homogeneous product. This work is dealing with the determination of the axial dispersion in a reactor with the helical flow. The reactor was designed especially for performing polycondensation reactions<sup>1</sup> and the knowledge of the distribution of time spent in the reactor is quite important. According to some assumptions<sup>2,3</sup>, a helical arrangement of the pipe reactor should flatten the velocity profile. A disadvantage of this reactor type is that it consumes much space and it can be cleaned with difficulties. We have tried to remove these disadvantages in the proposed reactor.

During the flow of a liquid through a bend of a pipe or a channel, a secondary transversal flow arises in the plane perpendicular to the direction of the main flow due to the centrifugal force. The centrifugal force exerts a greater influence on liquid particles with greater velocities (*i.e.* in the centre of the stream) and pushes them towards the outer wall. Into their places, the fluid from the inner surface is coming, causing thus the double secondary flow. Both flows, *i.e.* the main and the secondary ones, add resulting in a helical flow. A detailed description of the phenomenon has been given for example by Kolář<sup>4</sup>; Koutsky and Adler<sup>2</sup> have been dealing directly with the helical flow. They have been supposing on the basis of the analysis of the axial dispersion mechanism that a proper device for the formation of secondary flows and consequently for suppressing the dispersion is a pipe coiled into a helix. According to them, the dispersion is influenced by three mechanisms: 1. nonuniformity of the velocity profile, 2. nonregularity of the mixing process due to the molecular diffusion or to turbulent vortices, 3. secondary flow.

In the laminar region, the authors were able to confirm photographically the theory of the double secondary flow. *C*-curves for *Re* in the range 300–400 are showing that the axial dispersion in coiled pipes is approaching that in straight pipes. With an increase in *Re*, the dispersion is reduced significantly as the resulting curves are narrower and higher than those for straight pipes. This trend continues up to *Re*  $\approx$  3000 to a maximum height *C* = 12. Parameters influencing considerably the axial dispersion in this region are *Re*, the pipe curvature, and the ratio of the elliptical axes of the pipe cross section. A transition region appears in the range *Re* = 3000–7000, the exact value of the critical *Re* depends on the curvature and the ratio of the elliptical axes. The transition thus begins at higher *Re* than for straight pipes and is slower, especially for small curvature radii of the helix. The height of the distribution increases up to values of *Re* lower by 1000–1500 than the critical one; then it decreases or remains constant depending on the curvature. Therefrom the authors have deduced that the beginning of the turbulence reduces the strength of the secondary flow. In the turbulent region of the flow, *i.e.* for *Re* = 7000–40000, the axial dispersion in the helix is less than in both the laminar region and a straight pipe at otherwise identical conditions. Distribution curves are sharper, more symmetrical, and more concentrated around  $\theta = 1$  than during the laminar flow. For the calculation of the dispersion number  $D/uL$ , the authors have proposed a relation in which this quantity is a relatively complicated function of geometric parameters of the reactor, of the magnitude of the Reynolds criterion, and of the friction factor.

There are some works in literature about the influence of bends in pipes on the axial dispersion. Thus for example Aunický<sup>5</sup> has studied the influence of individual bends with variable geometric parameters (curvature ratio, central angle). The influence of individual bends would be probably different from that of a helix. More important for the solved case is the work of Cassel and Perona<sup>6</sup>, who studied piping formed by several 90° bends connected by short straight parts. The respective variables were here *Re* (15400–96555), the number of bends (5 and 9), and the shape of the whole assembled system. The results are as compared with the straight pipe ones: the system with 5 bends exhibits the value of  $D/ud$  by 2.5–12% higher than the straight pipe one, the system with 9 bends changing the flow direction increases the value of  $D/ud$  by 35–61%

in comparison with the straight pipe, the helical system with 9 bends increases the value of  $D/ud$  by 8.4–22%. From the conclusions of this work it is clear that with an increase in  $Re$ , the axial dispersion decreases.

#### EXPERIMENTAL

**Apparatus.** The basic part of the apparatus was a reactor formed by a channel of a rectangular cross section, which was milled helically into a full polyamide cylinder (Fig. 1). This helix was wound round by a transparent foil closed by a wire running through fin grooves. An advantage of this method was the possibility to observe visually the behaviour of the tracing substance. Metal tubes were mounted on both ends of the reactor for the inlet and outlet of the flowing liquid. Due to its length, the polyamide helix was fixed in a metal construction by screws and in one and two thirds of its height by metal straps.

Parametres of the reactor:

Diameter of the inner (full) part	0.035 m
Diameter of the total helix	0.1 m
Lead	0.030 m
Height of the reactor (combined from 8 parts, 0.39 m each)	3.120 m
Length of the helical tube	34.080 m
Equivalent channel diameter	0.0153 m
Volume of the reactor	9.9 l

A red ink aqueous solution was used as a *tracer substance*. It was prepared by mixing 500 ml  $H_2O$  with 5 ml ink. For the sake of stability, 0.1 g citric acid was added. Water was used as the flowing liquid. It was fed to the reactor by a pump from a store reservoir through a rotameter.

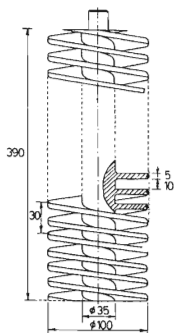


FIG. 1

Scheme of the Reactor Investigated

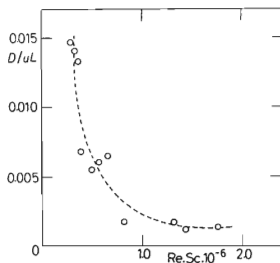


FIG. 2

Dependence of  $D/uL$  on the Product  $Re.Sc$

The pressure drop during the flow through the reactor was measured by an open U-shaped manometer connected to the reactor inlet.

*Operation procedure.* After filling the reactor with water, the desired flow rate was adjusted so that the corresponding mean residence time was 10–70 min. This range was given by the requirements of the technological procedure. When the steady state had been obtained, the tracer substance in the amount of 12.8 ml was injected as quickly as possible by a hypodermic syringe close before the reaction inlet. Samples were withdrawn at the reactor outlet in regular time intervals until the outflowing water was not colourless. The concentration of the dye was determined in the samples by a photocolimeter with two photocells using a green filter. The pressure drop was simultaneously measured at each flow rate.

The measurement was performed in the same way for two reactor positions: horizontal and vertical ones.

## RESULTS

### *Evaluation of Measurements*

The usual procedure was used for the calculation of the dispersion number  $D/uL$ , which was described for example in Levenspiel's monograph<sup>3</sup>. With respect to the fact that it was possible in our experiments in the range of the concentrations used to express the relation transmittance-concentration by a straight line of the form

$$P = 100 - 1474 c, \quad (1)$$

the computational relations were arranged to the form

$$\sigma_{\tau}^2 = \frac{\sum (100 - P) \tau^2}{\sum (100 - P)} - \left[ \frac{\sum (100 - P) \tau}{\sum (100 - P)} \right]^2, \quad (2)$$

$$\bar{\tau} = \frac{\sum (100 - P) \tau}{\sum (100 - P)}. \quad (3)$$

For small values of  $D/uL$  it holds<sup>2</sup>

$$D/uL = \sigma^2/2, \quad (4)$$

where

$$\sigma^2 = \sigma_{\tau}^2/\bar{\tau}^2. \quad (5)$$

### Values of the Dispersion Number

Data which were described in detail in a previous work<sup>7</sup> and which correspond to both vertical and horizontal positions of the reactor are compiled in Table I. During the generalisation, the values of dispersion numbers from Table I were correlated against variables characterising physical properties of the flowing mixture and hydrodynamical conditions. Considering that we are dealing with a laminar flow, it is possible to discard the dependence on the simplex  $e/d$ ; similarly, the dependence on geometric simplexes was not taken into account as the arrangement of the reactor was fixed. We consider the dependence of the dispersion number in the form

$$D/uL = \Phi(\text{Re.Sc}). \quad (6)$$

For the calculation of the Schmidt criterion it is necessary to know the diffusion coefficient of the system tracer substance-water. The only compound that can be used in our experiments from the point of view of its colour change is according to the manufacturer's recommendation eosine. Therefore the diffusion coefficient of a dilute aqueous solution of eosine at 20°C was calculated<sup>8</sup> as  $3.68 \cdot 10^{-10} \text{ m}^2/\text{s}$ . In Table I, the values of the product  $\text{Re.Sc}$  are also given.

The dependence of  $D/uL$  on the product  $\text{Re.Sc}$  for the vertical reactor position is demonstrated graphically in Fig. 2. It is possible to approximate it by an empirical relation

$$D/uL = 7.5917 \cdot 10^5 / (\text{Re.Sc})^{1.416} \quad (7)$$

The equation holds in the range of the experimental conditions.

It is obvious that the tendency of the dependence for the horizontal arrangement is similar and we may await that the influence of the reactor axis position in the given range of flow rates would be negligible.

TABLE I  
Experimentally Determined Values of Dispersion Numbers

$u$ m/s	$\text{Re.Sc} \cdot 10^{-6}$	$D/uL$	
		vertical position	horizontal position
0.0419	1.743	0.00136	0.00177
0.0341	1.42	0.001237	—
0.0266	1.13	0.00184	0.00282
0.0196	0.807	0.001733	0.00181
0.0154	0.639	0.0065	—
0.0136	0.565	0.006137	0.00897
0.0119	0.495	0.00556	—
0.00944	0.394	0.00687	—
0.00856	0.353	0.0134	0.00476
0.00772	0.321	0.0141	0.00820
0.00692	0.288	0.0148	0.0151

TABLE II  
Comparison of the Results for the Helix with those for the Straight Pipe

$u$ m/s	Re	$D/uL$	
		this work	straight pipe <sup>9</sup>
0.00692	106	0.0148	0.675
0.0154	235	0.00613	1.324
0.042	640	0.00136	4.08

From the comparison of the results of this work with data which are valid for the straight pipe<sup>9</sup> (Table II) we may draw the following conclusions: during the laminar flow through a helix, the dispersion number  $D/uL$  decreases with an increase in  $Re$ , while for a straight pipe the reverse is true. The value of  $D/uL$  is in the whole investigated region much lower for a helix than for a straight pipe. This confirms the conception<sup>2</sup> recommending the helix as a proper arrangement for the reactor approaching the piston flow.

#### LIST OF SYMBOLS

$C$	dimensionless concentration
$D$	axial dispersion coefficient ( $m^2/s$ )
$L$	reactor length (m)
$P$	transmittance (%)
$c$	concentration of the tracer substance in the outlet flow (g/l)
$d$	diameter of the reactor pipe (m)
$u$	flow rate of the liquid through the reactor (m/s)
$\epsilon$	roughness (mm)
$\sigma^2$	variance of $C$ -curve values when the dimensionless time is used
$\sigma_\tau^2$	variance of $C$ -curve values when time $\tau$ is used (s)
$\tau$	time counted from the tracer substance pulse (s)
$\bar{\tau}$	mean residence time of the liquid in the reactor (s)
Re	Reynold's criterion
Sc	Schmidt's criterion

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