end of the reactor [as can be estimated by (6a)], since beyond that point the nonstiff concentration variable is approximately constant.

As an example, (13) was solved with $Pe = 1\,000$, and $R = 10x^2$. Equations (14) and (17) give $x(0) = 0.9975124$ and $y(0) = -4.97520$. The solution obtained with the trapezoidal rule and steps of $h = 0.1$ was about 0.1% accurate over $0 \leqq s \leqq 1$. The computation time for the problem as formulated is very small compared with other TPBVP methods and is significantly easier than applying special singular perturbation methods.

We need to point out that the crux of the present concept lies in breaking an overall system into the form of (3). In other words, it is necessary to be able to identify the stiff and the nonstiff variables. When m is large (> 10 to 15), such a discrimination may not be obvious and may require an a priori analysis of the total set of differential equations. Further, a large system may contain stiff, semistiff, and nonstiff variables; current work in progress is directed toward this latter case.

NOTATION

$\mathbf{f}(\mathbf{x}, \mathbf{y})$ = general function of dependent variables $\mathbf{x}$ and $\mathbf{y}$
$F(\mathbf{z})$ = general function of dependent variable $\mathbf{z}$
$\mathbf{g}(\mathbf{x}, \mathbf{y})$ = general function of dependent variables $\mathbf{x}$ and $\mathbf{y}$
h = step size
n = the n^{th} step
m = total number of differential equations
Pe = Peclet number
R = reaction rate
s = axial distance from reactor entrance
t = independent variable
$\mathbf{x}$ = nonstiff dependent variable
$\mathbf{y}$ = stiff dependent variable
$\mathbf{Y}$ = inner stiff dependent variable
$\mathbf{z}$ = general dependent variable
λ_i = i^{th} eigenvalue

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Blending of Polymer Solutions With Different Rheological Properties

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Blending of polymer solutions with different rheological properties is a fairly frequent problem in the polymer industry. Examples include the blending of a polymer solution or melt with a stream of monomer, plasticizer, antistatic, or foaming additives. The process may be carried out either in stirred tanks or in motionless mixers. Although the components are completely miscible, at least in the range of concentrations relevant for the process, the blending takes a considerable time owing to large differences in viscosities and characteristic times of the components. In this note results are reported on the blending of aqueous solutions of two polymers in a vessel stirred by a helical screw impeller operating in a centrally positioned draught tube. An empirical correlation is then proposed for the dimensionless blending time $N\theta_B$ which takes into account the zero-shear viscosities of the initial constituent solutions and their initial orientation.

EXPERIMENTAL PART

The mixer used was comprised of a flat-bottomed vessel and a centrally located draught tube (for dimensions see Table 1) made of transparent acrylic glass. Three impellers of two different radii (see Table 2) were rotated both clockwise and anticlockwise centrally in the draught tube.

Aqueous solutions of sodium carboxymethylcellulose (CMC) made by ICI under the trade name Edifas B and of polyacrylamide (PAA) manufactured by Dow Chemicals under the name Separan AP 273 were used up to 2% concentration, thus allowing the zero-shear viscosities to vary by a factor between 10^2 and 2.10^3 and the characteristic times by a factor of about 10.

The rheological properties of all liquids used were measured by Rheogoniometer R18. In this rheometer, where the liquid sample is placed between a flat plate and a cone with large apex angle, both the torque T and the total axial thrust F between the cone and the plate are measured. The variable viscosity η of the liquid is then given by

$$\eta = 3T/2\,\pi R^3\,\dot{\gamma} \qquad (1)$$

where $\dot{\gamma} = \omega/\alpha$ is the shear rate in the conical gap (α being the complementary apex angle and ω the angular velocity), and R is the radius of the cone-and-plate setup. Two cones were used with the apex angles of 178 and 176 deg., respectively.

The axial thrust F is used to calculate the primary normal stress coefficient of the liquid σ_1 which is the measure of the liquid's elasticity:

$$\sigma_1 = 2F/\pi R^2\,\dot{\gamma}^2 \qquad (2)$$

The rheometric data were obtained in the range of $10^{-1}\ \text{s}^{-1} < \dot{\gamma} < 10^3\ \text{s}^{-1}$.

Table 1. Parameters of the Vessel and of the Draught Tube

D_T	H_T	D_D	H_D	C
0.457 m	0.584 m	0.215 m	0.457 m	0.05 m

Table 2. Parameters of the Screw Impellers

D	H	h
0.190 m	0.457 m	0.152 m
0.203 m	0.457 m	0.102 m
0.203 m	0.457 m	0.203 m

Table 3. Rheological Properties of Liquids Used

Solution	η_0 $(\mathrm{gcm}^{-1}\,\mathrm{s})^{-1}$	b (—)	m $(\mathrm{gcm}^{-1}\,\mathrm{s})^{b-2}$	λ (s)
CMC approx. 0.5%	1.4-1.9	2.0-6.0	0.1-0.6	
CMC approx. 1.0%	25-45	1.7-2.5	6-12	
CMC approx. 2.0%	1,000-3,000	1.15-1.30	800-2,500	0.35
PAA approx. 0.5%	35-40	1.3-1.5	20-22	0.6
PAA approx. 1.0%	250-500	1.20-1.35	1.50-400	1.4
PAA approx. 2%	3,700-4,700	1.05-1.10	3,500-4,500	4.7

Both η and σ_1 were found to depend strongly upon the shear rate $\dot{\gamma}$ for $\dot{\gamma} > 1\ \mathrm{s}^{-1}$ but approaching a constant value when $\dot{\gamma}$ was approaching zero. The viscometric data were therefore fitted by a three-parametric empirical formula

$$\eta = \eta_o - m\,\dot{\gamma}^{b-1} \tag{3}$$

where η_o is the zero-shear viscosity. For the purpose of this work, the characteristic time λ is defined as

$$\lambda = \lim_{\dot{\gamma}\to 0} \frac{\sigma_1}{\eta} \tag{4}$$

which is consistent with other works on viscoelastic fluids.

Fresh solutions were prepared for every run at three concentration levels (approximately 0.5, 1, and 2%), and their material properties were determined before and after the mixing experiment. Their variations are summarized in Table 3. The density variation was of the order of 1%, and it was not found to be significant enough to affect the final correlation.

All experiments were carried out in a transparent vessel. The change of color intensity during the reaction of iodine with sodium thiosulfate under the presence of modified starch was used to follow the rate of mixing because it was found previously by Ford et al. (1972) that this system affects least the rheological properties of aqueous polymer solutions. The change of color intensity was monitored via a photocell which was irradiated by a ray of light coming from a 12 v quartz-iodine spot lamp through the annulus.

The amount of stray light entering the photocell was reduced by means of a collimating tube. Preliminary experiments have shown that the position of the light source and of the photocell did not affect the response curve, so that all experiments have been done with the photocell halfway between the bottom and the liquid level. The experiments were carried out in a constant temperature room (21°C) from which all daylight was excluded. In a standard experiment the iodine and starch were mixed first with the more concentrated (and thus more viscous) polymer solution and then placed in the lower half of the vessel. The sodium thiosulfate solution (approximately 30% stoichiometric excess) was mixed separately with an equal volume of the less concentrated (and thus less viscous) polymer solution or with pure water and then placed carefully into the upper half of the vessel without any visible mixing having taken place between the two liquids in the interphase. The agitation was then started by letting the screw rotate either clockwise or anticlockwise, so that the more viscous solution was oriented either upstream or downstream with respect to the flow in the draught tube.

In order to establish that this method was free from any peculiarity inherent to the procedure used, two sets of tests were run prior to the blending time measurements. In the first set of tests ordinary mixing times for solutions of corn syrup, glycerine, and CMC were measured by using the same tracing technique as for blending. The iodine was first dissolved in the bulk of the fluid, and the sodium thiosulfate was then added in a small portion (about 2 vol%) of the same solution. The mixing time data obtained in this way are represented in Figures 1, 2, and 3 by the solid line which shows a typical change from the viscous regime into the transition one at $Re = 10$ confirmed by a number of other authors and originally found by Nagata et al. (1956).

In the second set of tests, two equal volumes of the same polymer solutions were placed into the mixing vessel, and the procedure for blending was carried out. The blending times measured were found to agree with the mixing times for the same solutions. It is thus reasonable to believe that the blending time data are comparable with mixing times obtained by the same method and in the same mixer.

DISCUSSION OF THE RESULTS

It is well known that the magnitudes of mixing and blending times depend strongly *inter alia* upon the selection of the end point on the response curve monitored by the photocell. It is obvious that one can never get rid of this arbitrariness and that no physical meaning can be attached to these values. Nevertheless, the mixing and blending times will serve to a good purpose if used strictly for comparison only. In this work the end point was chosen at

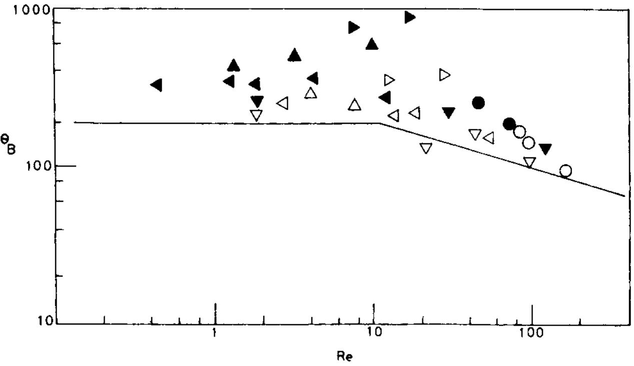

Fig 1

Fig. 1. Dimensionless blending times $N\theta_B$ of polymer solutions with different concentrations:

◀ ◁ 2% with 1% CMC
▲ △ 2% with 0.5% CMC
● ○ 1% with 0.5% CMC
▶ ▷ 2% with 0.25% CMC
▼ ▽ 1% with 0.75% CMC

The plain points refer to the upstream position and the full points to the downstream position of the more viscous fluid in the draught tube. Concentrations are given by approximate figures and serve for orientation only.

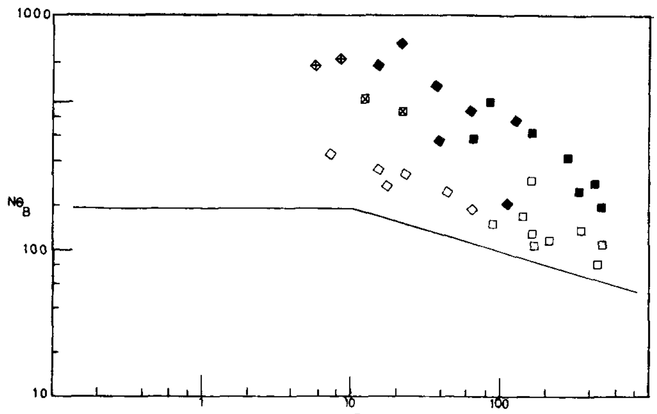

Fig. 2. Dimensionless blending times $N\theta_B$ of polymer solutions with water:
◆ ◇ 2% CMC with water
■ □ 1%CMC with water
◈ 2% PAA with water
⊠ 1% PAA with water
The plain points refer to the upstream position and the full points to the downstream position of the poylmer solution in the draught tube. The concentrations are approximate figures and serve for orientation only.

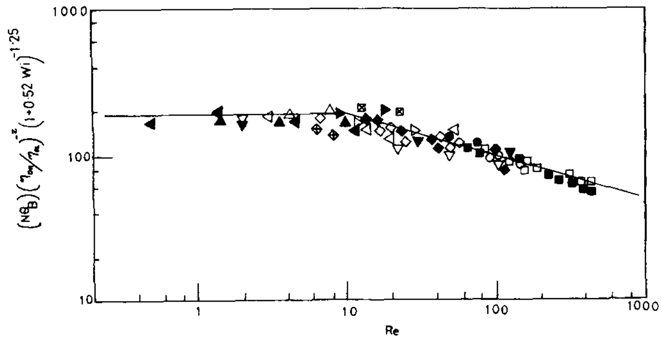

Fig. 3. Dimensionless blending time correlation. Symbols as in Figures 1 and 2.

a time when the regularly repeating pattern in the response curve brought about by the circulation of the locally decolorized liquid was overshadowed by the noise of the measuring system. In Figure 1, data for blending of various CMC solutions are also plotted including both the upstream and the downstream orientation of the more viscous fluid. The Reynolds number used here is based upon the apparent viscosity of the final mix η_a which in turn is related to the kinematics of flow by the formula

$$\eta_a = \eta_o - m\, N^{b-1} \qquad (5)$$

where η_o, m, and b are parameters of the flow curve of the final mix. Thus, $Re = (ND^2\rho/\eta_a)$. There is obviously no physical argument to support this choice, and, rigorously, two variable Reynolds numbers would have to be used. This would be, however, justified only if the more convenient approach based upon Equation (5) failed. Following the arguments by Coyle et al. (1970), the shear rates in a vessel stirred by a helical impeller are of the order of 5 s^{-1}, which is within the range of shear rates where the apparent viscosity was determined.

When the data in Figure 1 are inspected, it can be tentatively concluded that it takes longer to blend the two polymer solutions than to mix a single fluid. Further, the blending of pairs of liquids with widely different concentrations (and thus widely different viscosities) seems to lead to longer blending times. And, finally, longer blending times are normally observed when the more viscous fluid is placed downstream in the draught tube.

All these three conclusions are reinforced when we inspect the data in Figure 2 for blending the polymer solutions with pure solvent (water). The eminent importance of the initial orientation of the two liquids is even more apparent as the downstream and upstream data form two distinctly different sets. Within these sets the influence of the ratio of the zero-shear viscosities of the two original components remains undiminished. However, the viscoelasticity tends to lengthen the blending times as can be seen from the data points referring to the PAA solutions. Qualitatively it may be reasoned that both the viscous and the elastic forces will resist the process of dispersion of one polymer solution into another. While the elastic forces tend to reduce the tensile deformations, the viscosity will act against shear deformation of the individual liquid striations. In this context it is interesting to note that the initial orientation of the constituent solutions is superimposed only over the viscous term in the final correlation. This may be interpreted by the fact that the shear forces act across the boundaries from one liquid into another, while the elastic forces act within each individual striation. The influence of the initial orientation is, however, peculiar to the mixing system used in this work.

A simple regression will reveal (Figure 3) that the dimensionless blending time will be proportional to $(1 + 0.52\, Wi)^{1.25}$ and to $(\eta_{oM}/\eta_{oL})^z$, where the Weissenberg number $Wi = \lambda N$ is the dimensionless measure of the liquid's elasticity (λ again being the characteristic time of the final mix), and N is taken to be proportional to some characteristic shear rate in the mixer. The symbols η_{oM} and η_{oL} stay for the zero-shear viscosities of the initially more and less viscous components, respectively. The parameter z is related to the initial orientation of the two components; $z = 0.059$ for the upstream and $z = 0.17$ for the downstream position of the more viscous liquid in the draught tube. The variation of the geometrical parameters was apparently too small to appear in the correlation.

It may be thus concluded that the blending times of polymer solutions with different rheological properties will be longer than the mixing times predicted on the basis of the final mix material properties by a factor which may be as high as 10.

NOTATION

b = material parameter, Equation (3)
c = clearance between the bottom of the vessel and the lower edge of the draught tube
D = impeller diameter
D_D = diameter of the draught tube
D_T = tank diameter
F = axial thrust, Equation (2)
H = height of the screw impeller
H_T = height of the tank
H_D = height of the draught tube
h = pitch of the helical impeller
m = material parameter, Equation (3)
N = rotational speed
R = radius, Equations (1) and (2)
Re = Reynolds number, $Re = (ND^2\rho/\eta_a)$
T = torque, Equation (1)
Wi = Weissenberg number, $Wi = \lambda N$
z = parameter referring to the initial orientation

Greek Letters

α = complementary apex angle
$\dot{\gamma}$ = shear rate
ω = angular velocity
η = viscosity
η_a = apparent viscosity
η_o = zero-shear viscosity
η_{oM}, η_{oL} = zero-shear viscosity of the more and less viscous components, respectively
λ = characteristic time
σ_1 = primary normal stress coefficient
θ_M = mixing time
θ_B = blending time
ρ = density

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Probability Models in Reaction Path Synthesis

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A significant contribution has been made in the field of reaction path synthesis by Powers and his associates (1975). In employing their approach, we need to know the probability of failure in each step of the reaction path and the number of trials required to obtain the first success at each step. This note introduces a general probability model for the reaction path synthesis which can be used to predict the number of trials required to obtain the first success for sequential trials and at least one success for simultaneous tests.

FORMULATION

As shown in Figure 1, n sequential trials are conducted in the horizontal direction in synthesizing a reaction path. At the i^{th} trial the reagent is divided into l_i portions, M_{i1}, M_{i2}, ..., M_{il_i}, distributed in the vertical direction, which can be used either simultaneously or sequentially. Several specific cases can be considered.

Case 1. Sequential both in the horizontal and vertical directions. The probability for the first success to occur at the $M_{ij}{}^{\text{th}}$ test (the j^{th} test at the i^{th} trial) can be expressed as (Parzen, 1960)

$$Pr\,\{\text{the first success to occur at the } M_{ij}{}^{\text{th}} \text{ test}\}$$
$$= (1-P_s)^{l_1}(1-P_s)^{l_2}\ldots\ldots(1-P_s)^{l_{i-1}}(1-P_s)^{j-1}P_s$$
$$= (1-P_s)^{\sum\limits_{r=1}^{i-1}(l_r)+j-1}\,P_s \qquad (1)$$

where P_s is the probability of success in a single test. Equation (1) is the geometrical probability density function. The expected number of tests to obtain the first success, according to this probability density function, is (Parzen, 1962; Appendix 1)*:

$$E\left[\sum_{r=1}^{i-1}(l_r)+j\right]=\frac{1}{P_s} \qquad (2)$$

If we have

$$l_1 = l_2 = \ldots = l_i = 1$$

and consequently $j = 1$, we have from Equation (1)

$$Pr\,\{\text{the first success to occur at the } i^{\text{th}} \text{ trial}\}$$
$$= (1-P_s)^{i-1}P_s$$

which is the geometrical probability density function in a simple form (Parzen, 1960). Of course, the expected number of trials to obtain the first success can still be calculated by Equation (2).

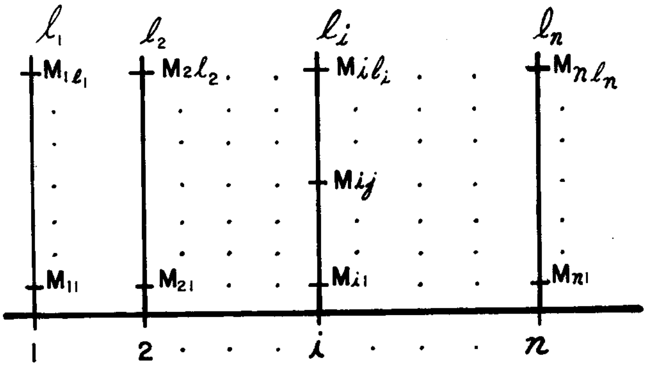

Fig. 1. A probability model for the reaction path synthesis.

Case 2. Sequential in the horizontal direction and simultaneous in the vertical direction. For this case, we may have more than one success at any given trial because l_i tests are carried out simultaneously at the i^{th} trial. The probability for at least one success to occur at the i^{th} trial can be expressed as (Feller, 1950; Parzen, 1962)

$$Pr\,\{\text{at least one success in } l_i \text{ simultaneous tests to occur at the } i^{\text{th}} \text{ trial}\}$$
$$= (1-P_s)^{\sum\limits_{r=0}^{i-1} l_r}\{1-(1-P_s)^{l_i}\} \qquad (3)$$

where

$$i \geqq 1$$
$$l_0 \equiv 0$$

Let

$$Q_i \equiv (1-P_s)^{l_i} \quad \text{where} \quad Q_0 \equiv (1-P_s)^{l_0} \equiv 1$$

Q_i is the probability that the i^{th} trial is a failure. Thus

$$R_i = 1 - Q_i$$

is the probability that the i^{th} trial is a success. Then Equation (3) can be rewritten as

$$Pr\,\{\text{at least one success to occur at the } i^{\text{th}} \text{ trial}\}$$
$$= \left(\overset{i-1}{\underset{r=0}{\pi}} Q_r\right)\cdot R_i \quad i \geqq 1 \quad Q_0 \equiv 1 \qquad (4)$$

Thus the expected number of trials to obtain at least one success at the i^{th} trial is (Appendix II)*