Effect of Vertical Alignment on Continuous-Phase Axial Mixing in a Pilot Liquid/Liquid Spray Column

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Although of simple construction, spray columns have not been used extensively in industry because of high continuous-phase axial mixing, which results in low driving forces for heat and mass transfer. The experiments described in this note show that such axial mixing can be reduced markedly if the column is well aligned vertically.

EXPERIMENTAL

The spray columns (Figure 1) were basically similar to those of Henton and Cavers (1970); the most important change was that a single 2.44-m-long glass pipe, of 75 mm inside diameter, replaced an assemblage of short (0.15-m) lengths. Smoother and straighter columns resulted. The 2.44-m length was provided with 15 drilled holes fitted with Teflon plugs, many carrying a 22-gauge hypodermic needle for sampling.

The steady-state method was used for measuring axial-mixing coefficients. A sodium-chloride tracer, insoluble in the dispersed phase (technical-grade, 4-methyl-2-pentanone = 4M2P) was injected steadily into the continuous phase (water, distilled, and then deionized) at a volumetric rate equal to 0.26% of that of the continuous phase. The phases were mutually saturated.

The axially-dispersed plug-flow model applied to this case results in:

$$ln \frac{c_2}{c_1} = \frac{V_c}{\epsilon \delta_{Ec}} (Z_2 - Z_1) \qquad (1)$$

[See, for example, Henton and Cavers (1970).] In writing Eq. 1, V_c, ϵ, and δ_{Ec} are assumed constant throughout the column, and c uniform across the column at any Z. Equation 1 implies that a plot of $ln\ c$ against Z will be a straight line. The slope gives δ_{Ec}.

Tracer was prepared as a solution in 4M2P-saturated water (c = 1 kmol/m^3 of solution). A distributor A was used in earlier runs to introduce this solution at 8 points spread over the column cross-section. In later runs a distributor B introduced tracer at 4 points, all relatively near the column axis. Distributor A had the disadvantage that it had to be located at a flange at the bottom of the 2.44-m pipe section, and misalignment of the column sections could occur. Distributor B was inserted into the column, without affecting alignment, through one of the holes drilled in the 2.44-m length.

Drops were produced at the bottom of the column by passing the 4M2P-phase through sharp-edged nozzles averaging 2.6 mm I.D. at a linear velocity maintained manually close to an average value of 112 mm/s; the number of tips used was proportional to V_d. The drop-size distribution is believed to be the same as measured by Henton (1967) with d_p = 3.43 mm (Henton and Cavers, 1970). Holdup data were average values over each run, obtained by comparing, by means of a differential-pressure transducer, the pressure exerted by the fluids in the operating column, and that exerted by an equal height of continuous phase. Dynamic effects were neglected.

With the column operating at steady state, continuous-phase samples were taken at a succession of i axial positions along the column, normally at a rate less than 2.1% of the volumetric flow rate of the continuous phase. At each axial position, j radial positions were investigated. Samples were analyzed for sodium by means of an atomic-absorption spectrophotometer. Concentrations were corrected for the small sodium content of the incoming continuous phase, and normalized to the tracer concentration at the continuous-phase outlet, so that δ_{Ec} values were obtained from the slopes of straight lines fitted to

$$ln \frac{c_{i,j} - c_{\text{in}}}{c_{\text{out}} - c_{\text{in}}} = ln \text{ (reduced concentration)} \qquad (2)$$

plotted against Z_i.

Special attention was paid to the vertical alignment of the column. On the basis of measurements with respect to reference plumb lines, it was estimated that in the early runs the 2.44-m pipe was vertical overall to within about 0.012°. In Runs 9 to 20, as a result of discovering that the 2.44-m glass pipe was very slightly bent, its position was adjusted to make the *lower half* vertical, in Run 9 by measurement as described, but, for subsequent runs, by using visual observation to maximize the symmetricalness of drop movement in the lower half of the 2.44-m length, where the important tracer measurements were to be made. After this visual "tune-up" (between Runs 9 and 10), the plumb lines also indicated that the lower half was vertical to within measurement accuracy. Setup A of Figure 1 was used in Runs 1 to 9, and Setup B in Runs 10 to 20, except that in Run 9 tracer-distributor B was used in place of A.

RESULTS AND DISCUSSION

Difficulties were experienced with the stability of calibration of the atomic absorption spectrophotometer, with the result that uncertainties in the analytical results were greater than desired, and, when tracer fed to the column was compared with that measured at the outlet, agreement was poor in some runs. However, runs were made in groups, in each of which the same general operating conditions were used. In each group one or more runs have at least fair, and sometimes very good tracer balances. Furthermore, within a group there was generally fair to good agreement from run to run between the shapes of the concentration profiles, and between the values of the axial mixing coefficients, indicating that, on average, the analytical results were sufficiently accurate for present purposes.

Prior to Run 4, concentrations were measured only at the centre line of the column. In subsequent runs tracer concentration was found to vary along a column diameter at each Z_i, a result not in accord with the model; see, for example, Danckwerts (1953). The degree of radial uniformity of concentration indeed was considerably less than that reported by Henton and Cavers (1970). Furthermore, the concentration profiles were found to be asymmetric in the present work in Runs 5 to 9.

Experiments, including rotating the column relative to distributor A, showed that the probable cause of the asymmetry was not unequal flow rates of tracer from distributor ports, but, rather, asymmetric flows of the phases caused by the 0.305-m section below the column proper (Figure 1, Setup A). At least for the 0.305-m length, the ends of the pipe were not exactly perpendicular to their axes, with the result that, when the 2.44-m section was

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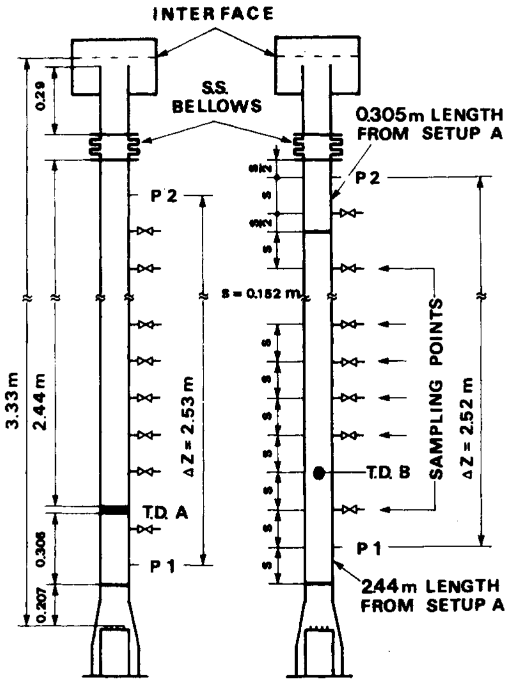

Figure 1. Column setups *A* and *B* (T.D. = tracer distributor; S.S. = stainless steel). I.D. = 75 mm

vertical overall, the 0.305-m length was not. In a non-vertical section the drops tend to move toward the higher side of the column. The result is increased upward flows of both phases on that side, and the observed asymmetric profiles. Visual observation did confirm that, relative to the column wall, the drops were moving slightly faster on one side of the column than on the other. However, in runs up to the end of 8, the effects noted were not due entirely to the 0.305-m section not being vertical.

Careful measurements with reference to the plumb lines showed that the 2.44-m-long pipe deviated from straightness by 1.8 mm measured perpendicularly to the longitudinal axis halfway between the ends. This corresponds to each half of this pipe section deviating from the vertical by 5 minutes when the overall alignment of the section is vertical. The observed asymmetric profiles presumably result from the 5-minute tilt, *and* the effects caused by the untrue pipe ends. Distributor B was used in the later runs to avoid introducing tracer at a flange, where such effects could be important.

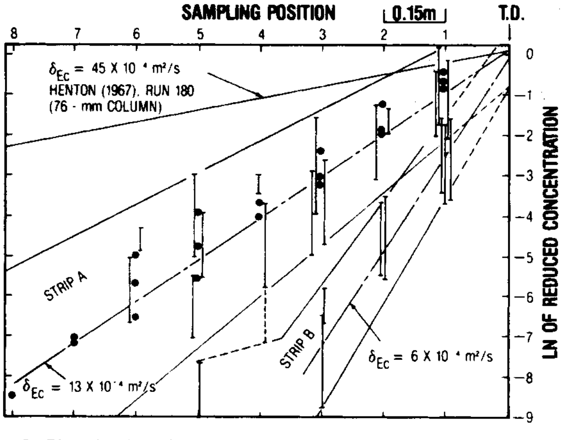

Figure 2. Plot of reduced tracer concentration vs. longitudinal position in the column. For Strip A, Runs 1 to 8; V_c = 8.75 and V_d = 3.1–3.2 mm/s; ave. $(1 - \epsilon)$ = 0.036. For Strip B, Runs 10, 11 and 14: V_c = 8.75 and V_d = 3.18 mm/s; ave. $(1 - \epsilon)$ = 0.035. For Henton's (1967) Run 180: V_c = 8.47 and V_d = 3.09 mm/s; est. $(1 - \epsilon)$ = 0.034. (T.D. = tracer distributor.)

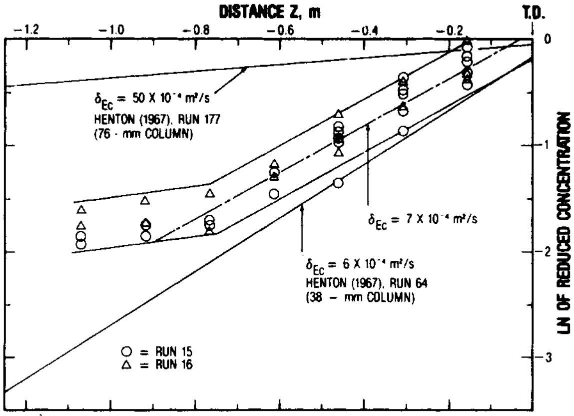

Figure 3. Plot of reduced tracer concentration vs. longitudinal position in the column. For strip shown, Runs 15 and 16: V_c = 1.59 and V_d = 3.18 mm/s; $(1 - \epsilon)$ = 0.032. For Henton's (1967) Runs 64 and 177: V_c = 1.54 and V_d = 3.09 mm/s; $(1 - \epsilon)$ = 0.028 and (est.) 0.030 resp. (T.D. = tracer distributor.)

Figure 2 is a plot of the kind mentioned earlier, used in determining δ_{Ec}. Strip *A* contains the measurements of Runs 1 to 8, and Strip *B* those of Runs 10, 11, and 14. The vertical lines represent the range of c_j found at a particular cross-section i, and the single points in Strip *A* the centre-line samples of Runs 1 to 3. The strips show the approximate range of possible lines drawn through the data. The strip boundaries were drawn by eye, and a value of δ_{Ec} has been recorded for a line placed half way (vertically) between the top and bottom of each strip. The Strip-*A* results indicate a reduction of axial mixing by a factor of about three, from that measured by Henton (1967) for similar conditions.

It seems likely that this decrease is due to a combination of three factors. Perhaps the most important, judging from the results of later runs, is that the lower half of the 2.44-m section was only 5.2 minutes from the vertical. Henton's column probably was overall at a larger angle from the vertical than this. Unfortunately, in his work the angle was not measured because the importance of *exact* verticality was not appreciated at that time. The other two factors reducing the axial mixing probably are the smooth walls of the 2.44-m length, and increased straightness of the column walls. The short (0.15-m) column pieces used by Henton and Cavers (1970) did not all have ends truly perpendicular to their longitudinal axes. The result must have been a column with a certain amount of zigzag in the general vertical direction, with the additional problem of some lack of smoothness at successive flanges. Henton and Cavers (1970) comment on the marked large-scale mixing seen in their column; this was considerably greater than what was observed in any runs of the present work.

After the "tuning-up" between Runs 9 and 10, the measured concentration profiles above the tracer distributor were more symmetrical, although the concentration still was not uniform with radius at a given Z_i; each profile showed a maximum at the centre [consistent with the velocity profiles shown by Wijffels and Rietema (1972) and Anderson and Pratt (1978)]. Henton (1967) did not find such a maximum. However, this result presumably was due to a much greater radial mixing in his column, associated with the much higher level of axial mixing which existed there.

Strip *B* in Figure 2 shows the effect of the tuning operation described earlier. The level of axial mixing was much reduced from that of any of the previous runs; ϵ_{Ec} is roughly one seventh of the value measured by Henton for similar operating conditions.

Run 9 (omitted from Figure 2) gave results intermediate between those of Strips *A* and *B*.

Figure 3 shows a similar strip for runs at flow rates chosen to permit comparison of the results with those of Henton (1967) for a 38-mm column. The value of δ_{Ec} obtained in the present column was about one seventh that obtained by Henton (1967) in his 76-mm column, and almost equal to his value in his 38-mm column.

Above the slight bend in the column, where, with the new alignment, the column was not perfectly vertical, visual observation indicated asymmetrical flow of the dispersed phase. The drops were seen clearly to move faster on one side of the column than on the other. Correspondingly, Figure 3 shows a change in the slope of the strip about halfway up the 2.44-m length [reminiscent of results of Deckwer et al. (1973) for bubble columns]. This indicates an increase in axial mixing, presumably due to asymmetrical flow of the continuous phase induced by that of the dispersed phase. [Values of δ_{Ec} reported here for runs numbered 9 or higher are those obtained for the *vertical* (lower) part of the column.] The suggestion of Valdes-Krieg et al. (1975), that tilting the axis of a bubble fractionation column away from the vertical causes greater backmixing, is consistent with the present results.

Additional runs, not shown in the figures, were made at a higher holdup; e.g., for Runs 19 and 20 [$V_c = 1.59$, $V_d = 6.35$ mm/s, and $(1 - \epsilon) = 0.074$], $\delta_{Ec} = 3 \times 10^{-4}$ m^2/s. Notice the reduction from δ_{Ec} of 7×10^{-4} m^2/s in Figure 3. A similar reduction occurred from a δ_{Ec} of 7×10^{-4} m^2/s in Run 12 [$V_c = 4.20$; $V_d = 3.18$ mm/s, and $(1 - \epsilon) = 0.032$] to an (ave.) δ_{Ec} of 4×10^{-4} m^2/s in Runs 17 and 18 [$V_c = 4.20$; $V_d = 6.35$ mm/s, and $(1 - \epsilon) = 0.075$]. Reduced axial mixing at higher holdup is in accord with earlier findings: Henton and Cavers (1970), Hupfauf (1973), Perrut et al. (1973), and Horvath et al. (1978), but is at odds with the results of Wijffels and Rietema (1972), Zheleznyak and Landau (1973) and Erving and Chen (1976). The lowered axial mixing in the present work is due presumably to the presence of a flatter velocity profile in the continuous phase at the higher holdup. Flatter velocity profiles would be expected to be accompanied by flatter concentration profiles. Such were observed in the present work, when holdup was increased.

As mentioned earlier, the axially-dispersed plug-flow model has, as one of its assumptions, uniformity of concentration in the radial direction, at a fixed axial position. Although this situation did not exist in the present experiments, the authors believe that the results reported here are valid. Figures 2 and 3 show that the range of concentrations at a given axial position is not so large as to prevent drawing a reasonably straight line on the semi-logarithmic plot. It follows that useful statements can be made about the magnitude of axial mixing despite the nonuniform concentrations across the column cross-sections, in the radial direction. Knowing the maximum and minimum concentrations of tracer at a given height, one can construct strips, such as those shown on the figures. The slope of a strip (rather than the slope of a line) then can be used to find the axial-mixing coefficient for practical purposes. Supporting the view that the results are correct is the fact that the observations made visually of column behavior, by the present authors and by Henton and Cavers (1970), correlate qualitatively with the values measured for the axial-mixing coefficients. At the higher holdup, with concentration of tracer more uniform in the radial direction, the dispersion model becomes more adequate.

CONCLUSIONS

The results show that a spray column of the diameter studied is extremely sensitive to vertical alignment. In a nonvertical column the phases flow asymmetrically, with the result that continuous-phase axial mixing is relatively high due to nonuniformity of velocity.

By carefully adjusting the axis of the present 75-mm I.D. column to the vertical position, the continuous-phase axial-mixing coefficients could be reduced markedly from the results measured by Henton and Cavers (1970) in a column of the same size. In fact, values measured in the present study approach those of Henton and Cavers for a 38-mm tower. In addition, to keep axial mixing low, the walls of the column should be as smooth and straight as possible. Perhaps at least some of the discrepancies between the axial-mixing coefficients reported by various workers [e.g., see Henton and Cavers (1970)] are due to minute differences in column alignment.

Except for a few data obtained by Wijffels and Rietema (1972) almost all results reported in the literature for axial mixing in spray columns, including those described here, refer to towers of relatively small diameter. More data for larger columns are needed to provide further clarification. However, the present data show that the increase in continuous-phase axial mixing with diameter for truly vertical columns probably is much less than indicated by earlier results, although further data, in, for example, truly vertical 38-mm columns (as well as in large-diameter columns) are needed to reinforce this conclusion. The present work points to at least the possibility that truly vertical, large-diameter spray columns may not be as seriously subject to axial mixing as previously believed, and, therefore, increases the potential attractiveness of such columns for industrial use.

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NOTATION

c = concentration of tracer, kmol/m^3 or ppm
d_p = drop size at the peak for larger-sized drops in the drop-size distribution (Henton and Cavers, 1970), mm
ln = natural logarithm
V = superficial velocitiy, m^3/m^2·s
Z = axial distance, m; positive downward

Greek Letters

δ_E = axial-mixing coefficient, m^2/s; $\epsilon\delta_E$ = superficial axial-mixing coefficient
ϵ = (1 − holdup) = volume fraction of continuous phase, dimensionless

Subscripts

c = continuous phase
d = dispersed phase
i = sampling position in axial direction
in = inlet value
j = sampling position in radial direction
out = outlet value
1,2 = in Eq. 1, example values of i

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Generalized Correlations of Mean Activity Coefficients of Polyelectrolytes with Monovalent Gegenions in Aqueous Solutions

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In recent years, correlations have been presented whereby the mean ionic activity coefficients of many types of electrolytes can be estimated in both pure and mixed aqueous solutions at temperatures of 0 to 100°C, and at concentrations up to saturation (Meissner and Tester, 1972; Meissner and Kusik, 1972; Meissner et al., 1972; Kusik and Meissner, 1973; Meissner and Peppas, 1973; Kusik and Meissner, 1975; Kusik and Meissner, 1978). These correlations have been applied to monobasic acids, their neutral mono- and polyvalent salts, polybasic acids and their salts. It is desirable to extend these simple correlations to more complex ionic solutions, and especially to polyelectrolytic solutions.

Natural and synthetic polyelectrolytes are macromolecules with ionizable groups on their backbone chains. When dissolved in water they show characteristics of linear polymers and of electrolytes. Because of the combination of both features, their thermodynamic and hydrodynamic behavior in solution may be complicated. Typical synthetic polyelectrolytes include poly(styrene sulfonates), poly(acrylates) and poly(ethylene sulfonates). Their thermodynamic properties are of great importance in applications for ion-exchange resins, surfactants, etc. In addition, the study of polyelectrolytes can provide valuable information towards the understanding of the physicochemical behavior of biological molecules in solution, since polyelectrolytes are simplified models for these biomacromolecules.

The significance of the mean activity coefficient of polyelectrolytes in aqueous solutions was not fully recognized until the first contribution on the direct determination of this thermodynamic parameter was published (Ise and Okubo, 1965). Previously, attention had been paid only to the single-ion activity of gegenions or of ions of coexisting simple electrolytes. However, the single-ion activity can neither be a substitute for the solute activity nor represent physical phenomena correctly.

Determination of thermodynamic properties such as osmotic pressure of a mixed solution of a polyelectrolyte and a neutral salt, and ionic mobility, and analysis of polyelectrolytic transport phenomena such as viscosity, sedimentation, diffusion, electrophoresis and swelling call for preliminary knowledge of the mean activity coefficient, $\gamma_\pm$, at various temperatures and concentrations (Nagasawa, 1975). Indeed, the present work was undertaken because of the need to quantify thermodynamic phenomena related to the diffusion of polar solutes through novel resins of poly(styrene sulfonates) (Peppas et al., 1981).

Most of the experimental data available for $\gamma_\pm$ of polyelectrolytes in aqueous solutions at various temperatures and concentrations are well summarized in a standard reference (Ise, 1971). These data are frequently presented in graphical form by curves of $\gamma_\pm$ at 25°C for several electrolytes plotted against concentration, expressed as molality (moles of macromolecule per 100 g water). Inspection of these graphs (Ise, 1971) indicates that the variation of $\gamma_\pm$ with molality differs widely from one electrolyte to the next, and that considerable crossing of the curves occurs, so that no generalized graphical representation of all the data can be achieved.

Here the objective is to present a simplified graphical method for representation of activity coefficients of polyelectrolytes in aqueous solutions, applicable from low concentration to saturated solutions; and to show how this method can be used to determine the mean activity coefficient, $\gamma_\pm$, at any concentration if a single value of this parameter at a single concentration is known.

THEORY

In the proposed correlation, use is made of the reduced activity coefficient Γ, defined as

$$\Gamma \equiv \gamma_\pm{}^{1/z_+z_-} \tag{1}$$

Here z_+ and z_- are the charges of the cation and anion of the polyelectrolyte in question. For example, in the case of poly(styrene sulfonate), z_- denotes the charge of the macroion poly(styrene sulfonate), and z_+ denotes the charge of the gegenion.

Concentrations in the aqueous solution are expressed by the ionic strength, μ, defined as:

$$\mu = \frac{1}{2} m(\nu_+ z_+^2 + \nu_- z_-^2) \tag{2}$$

where ν_+ and ν_- are the g-equivalents of gegenions and macroions respectively, which are formed upon dissociation of one mole of polyelectrolyte, and m is the molality of the polyelectrolyte expressed as mol/100 g H_2O.

To understand the thermodynamic behavior of polyelectrolytic solutions, it is important to understand the conformation of a macroion in solution. The macroion chain (polymer) attains a more or less randomly coiled conformation and it is surrounded by a cylindrical ionic atmosphere. It may be reasonable to assume that the macroion is represented by a rod which has smeared charges

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