

Numerical modelling of liquid-liquid flow related to countercurrent chromatography (CCC)

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Abstract

The CCC method is based on interface mass transfer between two immiscible liquids that move countercurrently. To be able to predict interface mass transfer for a CCC system accurately, the correct interface prediction is essential. In the present work, our previous numerical and experimental studies of countercurrent flow in inclined and oscillating tubes have been extended for different CCC phase systems. Furthermore the numerical models have been extended to circular and coiled tubes which are rotated centrally. The results indicate that mixing due to secondary motions is significant during the initial stages. However, their influence decreases as a quasi-steady state is approached in the cases studied.

1 Introduction

CCC is a form of liquid-liquid chromatography that allows to separate components from complex mixtures. The process takes place along a continuous length of tubing, which is wound on a drum that is rotated in planetary motion. One phase is held stationary while the other is pumped through in such a way that there is good retention of the stationary phase. As a result of the unsteady gravity field, a series of simultaneous mixing and settling zones occur along the length of the tubing. Thus a sample injected into the mobile phase will experience a number of mixing and settling steps according to the set rotor speed. This mixing and settling process and the mass transfer are key elements for successful high resolution [1].

The current development of industrial scale CCC [2,3] is supported by numerical modelling. Large scale CCC machinery will allow the continuous testing of samples of the orders of tonnes per annum. The determination of the

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optimal design parameters and driving conditions of a large scale machine are to be aided by CFD modelling. For this, the correct prediction of the interface distributions of the involved immiscible phases form the basis for realistic mass transfer modelling [4].

As a first step to investigate the influence of the gravity field on the interface between the upper and the lower phase in CCC, the flow of two immiscible liquids was investigated previously in straight, both fixed, inclined [4] as well as oscillating [5] tubes for one typical CCC phase system. Comparisons with experimental data in the former case showed that the interface motion was generally well predicted.

In the present study the model of the suddenly tilted and then fixed, inclined straight tube was extended to different CCC phase systems of different ranges of interfacial tension. In order to approach the CCC flow regime, the models were subsequently extended to circular and coiled tubes.

2 Numerical models

The unsteady fluid flow is treated as laminar, Newtonian, isothermal and buoyant. The software used in this study to solve the governing equations (CFX-4 by AEA Technology Engineering Software Limited, Release 4.4) is based on the finite volume method. (CFX-Meshbuild and CFX-View were used for pre- and post-processing, respectively.) A homogeneous two-fluid model based on mass and momentum conservation was used. Here the individual phase continuity equations are solved to determine the volume fractions. The individual transport equations are summed over all phases to give a single transport equation. The surface tension force is modeled based on the continuum surface model of Brackbill et al. [6]. To avoid a smeared interface, that may develop due to numerical diffusion in time, a surface sharpening algorithm was employed [7].

The CCC phase systems modelled, known as 4A, 4B and 4C, represent a wide hydrophobic/hydrophilic range with the 4B system being an intermediate one [8]. All three systems contain heptane, ethyl acetate, methanol and water which after mixing in their corresponding volume ratios will separate into two immiscible liquids. The phase systems property details are listed in table 1.

2.1 Straight tube model

The two-dimensional numerical model of the straight tube represents an experimental model of a square-ended, closed pipe 0.5m long with an internal diameter of 10mm. The pipe is filled with the upper and lower phase (each 50% by volume) of the phase systems 4A and 4C (for 4B, see [4]), see Table 1. The grid of the numerical model is block-structured consisting of two blocks and 64,000 cells.

2.2 Ring tube model

The numerical ring tube models are a representation of existing experimental open and closed ring glass models. Whereas the closed model, which contains a single internal separation wall, was realised only in 3D, the open model was realised in both two and three dimensions. The experimental ring models have an internal wall diameter of 100mm with a circular cross-section of 10mm diameter. Whereas the two-dimensional models consist of four blocks and 32,000 cells, the three-dimensional model was generated from 10 blocks, of which two are located centrally for an optimal grid distribution, and 688,800 cells. The grid resolution in the plane of rotational symmetry was approximately similar between the 2D and the 3D models. The three-dimensional block structure for the closed ring is shown in Fig. 1a including the grid distribution.

2.3 Coil tube model

The coil tube models representing a single, closed coil winding is of the same dimension as the ring model with a pitch of 30mm. As the 3D ring model, it consists of 5 blocks and 688,800 cells. The blocks were generated along splines that were made up from 360 points calculated along the involved block vertices. The blocks structure of the coil tube model is shown in Fig. 1b including the grid distribution.

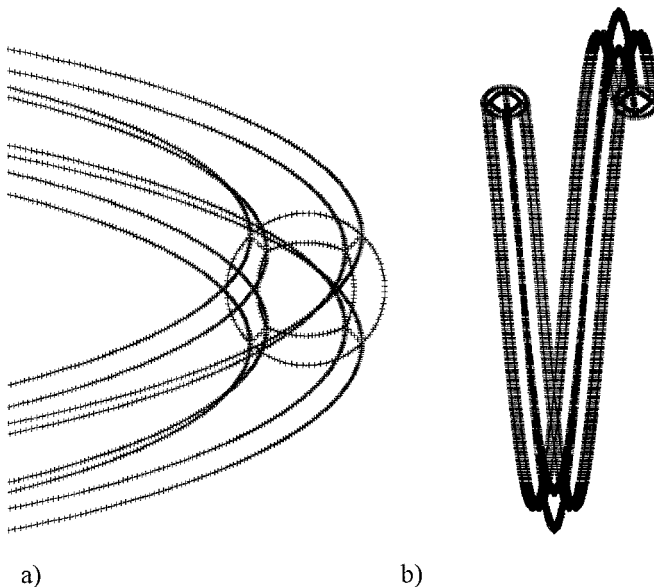


Fig. 1: The grid a) the ring model; b) the coil model

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Table 1: Heptane/Ethyl Acetate/Methanol/Water phase systems (from [9])

Phase System	Density [kg/m ³]	Density difference [kg/m ³]	Dynamic viscosity [kg m ⁻¹ s ⁻¹]	Interfacial tension [N/m]
4A Upper	679	268	$0.36 \cdot 10^{-3}$	$17.8 \cdot 10^{-3}$
4A Lower	947		$1.36 \cdot 10^{-3}$	
4B Upper	708	230	$0.35 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$
4B Lower	938		$1.35 \cdot 10^{-3}$	
4C Upper	833	98	$0.42 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
4C Lower	931		$1.35 \cdot 10^{-3}$	

3 Initial and boundary conditions

The initial phase distributions for the straight tube model were the heavier phase at the bottom and the lighter phase above within the initially horizontally positioned tube. To match the experimental inclination angle of 15° , a gravity vector of the same angle was applied to the numerical model of a horizontally positioned tube. Both the ring and the spiral models were filled radially by 50% with the heavier phase located in the outer half of the models.

For all cases the flow field had initially zero velocity in the entire domain. The no-slip boundary condition was applied to all walls.

The rotation of the computational grid was achieved using a user-subroutine. Both the circular and the spiral model were rotated centrally at a constant angular velocity of 600rpm. The latter represents a typical CCC rotational speed within the lower spectrum.

4 Computational details

Each time step uses the solution (phase volume fractions, velocities and pressure) of the previous time step as initial conditions. The pressure was obtained using the SIMPLEC algorithm. The differencing schemes used are a fully implicit backward differencing procedure for time, central differencing for pressure, upwind differencing for the phase volume fractions and hybrid differencing for the velocity variables. The under-relaxation factors were set to 0.65 for the velocity components and to 1.0 for the volume fractions and the pressure. For the phase systems 4B and 4C the runs were performed for a wall contact angle of 90° . In case of phase system 4A the wall contact angle was set to 160° . The surface sharpening level was set to 2. The computations were performed for

fixed time stepping and the results were dumped at appropriate intervals. The minimum reduction of the mass source residuals per time step was one order of magnitude. The achieved total mass source residuals were of the order of $1\text{E-}5$ kg/s. At this point in the computation the residuals for the velocity components and the volume fractions were also reduced to acceptable levels. The simulations were carried out on a SUN Blade 1000 workstation.

5 Results and discussion

5.1 Straight tube model

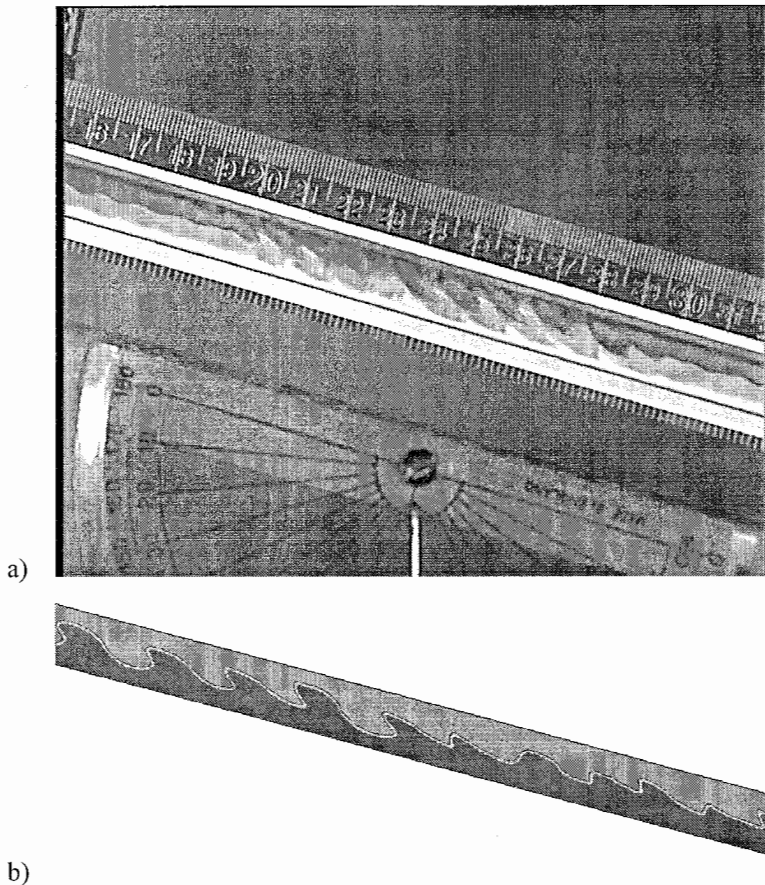


Fig. 2: Straight tube model for phase system 4C: a) experiment; b) simulation

The numerical results for the phase systems 4A and 4C compared generally well with experimental results. The details of the experimental set-up are given in [4].

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In the center of the tube the flow, starting from rest, is initially parallel to the tube walls. After a short period, the onset of instability can be observed in form of a distinct wave pattern along the interface for both phase systems. As for the phase system 4B [4], the timing and the wave shape were predicted well for the phase system 4C, however, the numerical wave length was slightly over-predicted compared to the one seen experimentally, see Fig. 2. Also, whereas the waves were seen along the entire interface in the prediction, they were seen predominantly in the central region in the experiment.

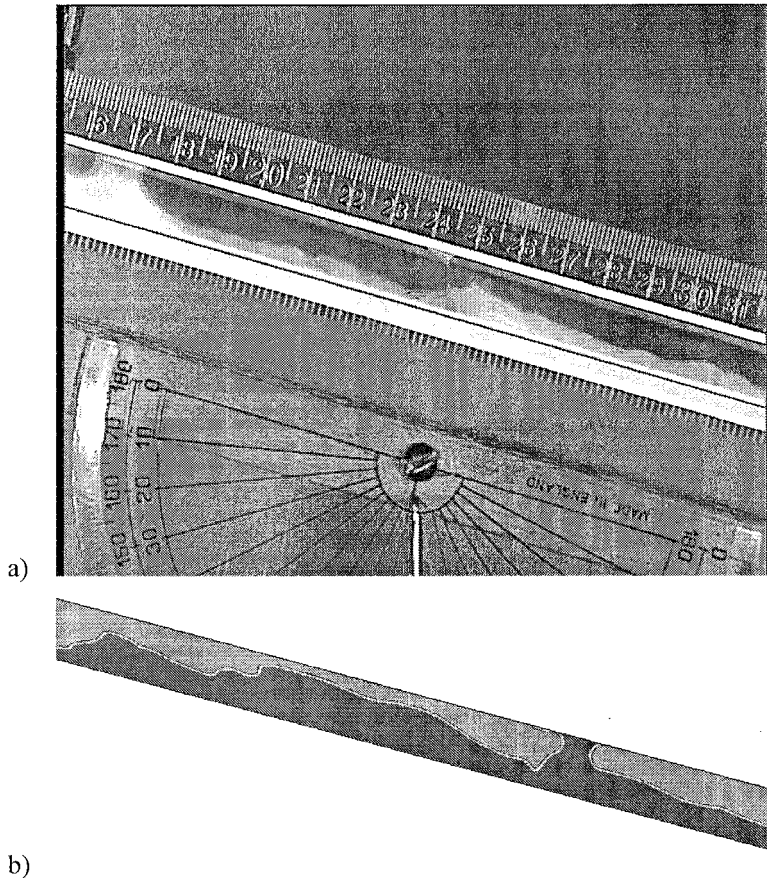


Fig. 3: Straight tube model for phase system 4A: a) experiment; b) simulation

For the high interfacial tension phase system 4A the agreement was found to be less good. Also to achieve convergence proved to be more difficult in this case. This agrees with findings in [10]. As a result the time steps were reduced by one order of magnitude. However, characteristic features like the liquid bridges of the lower phase between the upper and lower wall, also known as plug or slug

flow, were predicted, though not necessarily in the same location nor at the same time, see Fig. 3.

5.2 Circular tube model

Due to the centrifugal action the greater density fluid is subjected to a higher centrifugal force which causes it to move away from the centre of curvature while the lighter fluid goes towards the centre of the curvature. When comparing the general differences of the flow between the open and the closed ring it is most notable that instability occurs much earlier in the closed ring. In the open ring, as a result of the differential velocities between the inner and the outer wall and the different inertia and viscosity of the two liquids, the resulting shear at the interface triggers the onset of instability. In 2D numerical tests it was observed that variation of the rotational speed will result in different rotation angles for the instability to start but the extent of the instability appeared to be independent of this variable. Higher rotational speeds result in a higher differential between the inner and outer wall velocities and hence a higher disturbance at the interface can be expected. However, the increased Coriolis force will have the reverse effect and will tend to stabilise the interface and, as a result of both, the observed interfacial instabilities are generally small and similar for different rotational speeds, see Fig. 4a.

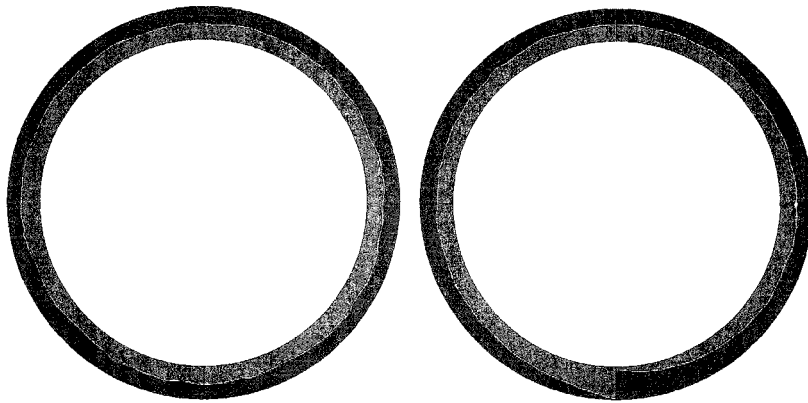


Fig. 4: Phase volume fractions at $t=0.2s$ for the 2D models: a) open ring; b) closed ring

In the closed ring due to the internal separating wall instability occurs very early on, both in the two- and in the three-dimensional model. In three dimensions the two-phase Couette flow will initiate pronounced, complex secondary motions normal to the main flow during the start of the rotation. As a result the

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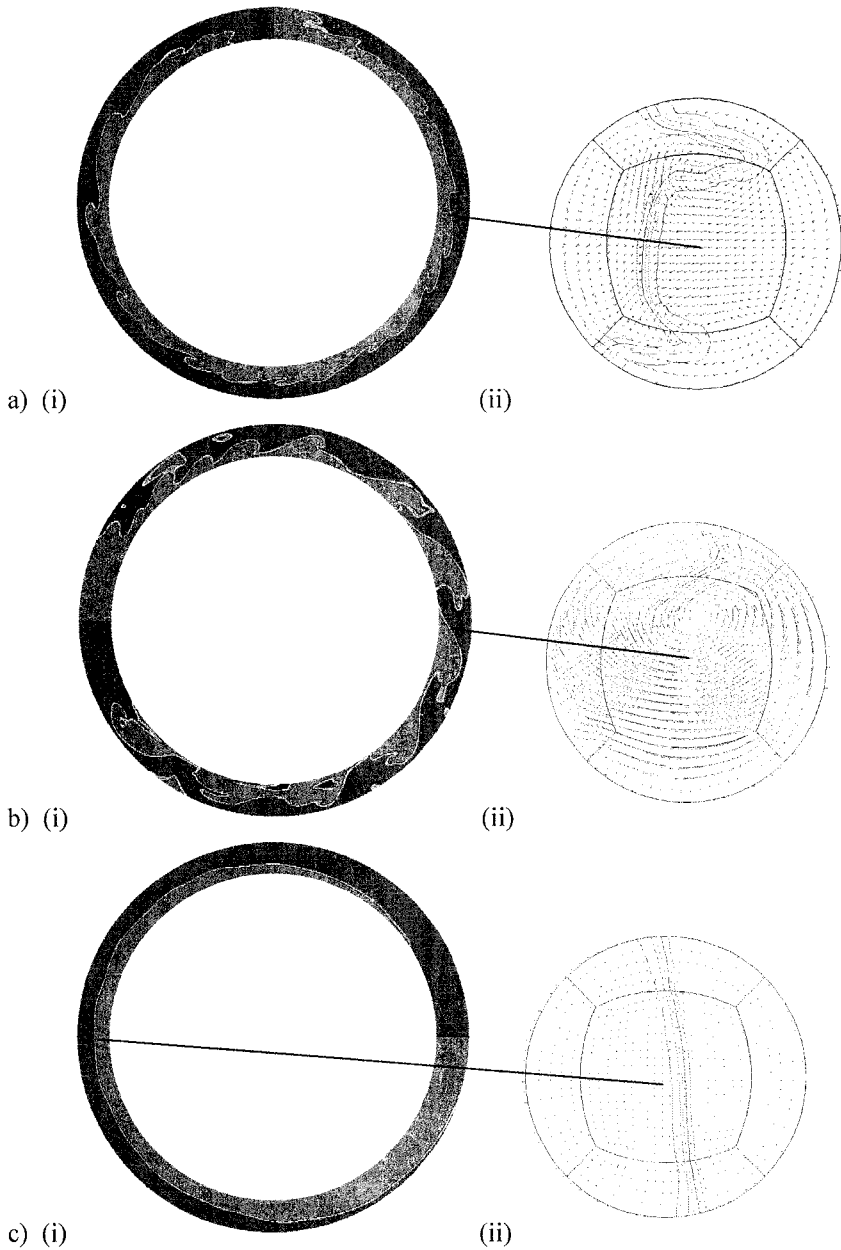


Fig. 5: 3D ring models at a) $t=0.025s$; b) $t=0.05s$; c) $t=0.3s$: i) volume fractions in z-plane; ii) velocity vectors and iso-contours of volume fraction in y-plane

instability is seen occurring even sooner in three dimensions and also the interface disturbance is significantly more pronounced, see Fig. 5a as an example. It is therefore anticipated that until the flow has developed into a quasi-steady state there will be enhanced mixing and that the increased interfacial area will aid mass transfer. Subsequently, the interface undergoes even more significant disturbance as a result of the heavier fluid wanting to flow to the bottom of the ring. However, the increasing acceleration of the core flow will subsequently result in the Coriolis force dominating gravity and the heavier fluid will move away from the centre of curvature again. It is anticipated that continuing the simulation will result in the heavier fluid being more homogeneously distributed away from the centre of curvature, similarly to the volume fraction distribution seen in Fig. 4a. Although the secondary motions tend to decrease in strength as the flow is to approach quasi-steady state they are still pronounced and will aid mixing, see e.g. Fig. 5c.

5.3 Coil tube model

Overall the initial flow development in the coil is very similar to the one in the closed circular model. Notable is that kind of fluid pockets develop in same areas of the coil in the early stages, see the arrows in Fig. 6. As a result of the different inertia of the phases and the Archimedian screw effect there is a trend for the heavier phase to go to the end of the coil and the lighter fluid to the start of the coil. As a result of the complex secondary motions developing (not shown) one can see a larger cross-sectional area of the lighter phase contained in the zone of heavier fluid and vice versa (Fig. 6). As time progresses these pockets disappear and a similar phase distribution as in the closed circular ring develops.

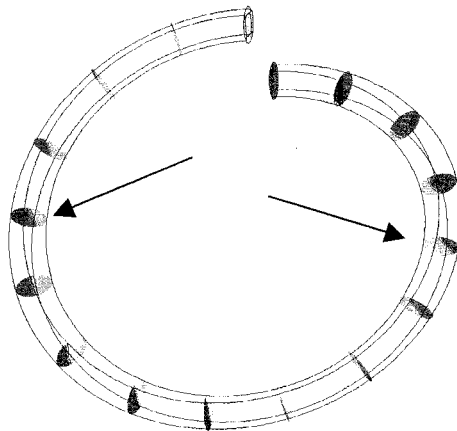


Fig. 6: Volume fractions in 3D coil model at $t=0.2s$

6 Conclusions and future work

Generally good agreement between the numerical and the experimental models was seen for the straight, inclined tube. However, the agreement was reduced in case of the very high interfacial tension system. It is anticipated that modelling such systems in a CCC set-up will be problematic.

To validate the three-dimensional ring model results experimental verification is in progress. This is to be extended by other modelling techniques such as application of perturbation theory.

As a result of what is seen in the studied three-dimensional ring and coil models in form of developing secondary flows it is concluded that here mixing is supported only to a small degree. It is anticipated though that the influence of secondary motions will increase once one of the phases is actively pumped through the system. Their influence in mixing and mass transfer may further increase once the flow is subjected to the cycloidal gravity field.

The numerical ring and coil models are currently extended to include the coil's planetary motion as present in CCC as well as the inclusion of mass transfer.

Acknowledgements

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