PREDICTING PHASE INVERSION BEHAVIOUR USING A MONTE CARLO TECHNIQUE

Leslie Y. Yeo, Omar K. Matar, E. Susanna Perez de Ortiz, Geoffrey F. Hewitt

Department of Chemical Engineering & Chemical Technology
Imperial College of Science, Technology & Medicine
London SW7 2BY, U.K.

ABSTRACT. A stochastic model to predict phase inversion behaviour in agitated liquid-liquid dispersions is presented. The model uses a Monte Carlo technique to simulate the random motion and interactions of the drops in the dispersion taking into account the fundamental hydrodynamics of drop deformation, coalescence and break-up. Comparisons of the results with those obtained experimentally indicate good qualitative agreement with key features being captured by the model.

NOMENCLATURE

Symbols

K_1, K_2, K_3	Constants
N	Agitation speed (s^{-1})
$\lambda_1, \lambda_2, \lambda_3$	Coalescence probabilities
ϕ	Holdup
Ψ	Probability of drop translation resulting in inter-penetration
Ω	Break-up probability

Subscripts

c	Continuous phase
d	Dispersed phase
I	Impeller
i	Interfacial
inv	Inversion point

INTRODUCTION

A dispersion of two immiscible liquids can exist in the form of two general morphologies depending on the conditions governing the system. A water-in-oil (w/o) dispersion exists when the aqueous phase is dispersed in the organic phase and an oil-in-water (o/w) dispersion is one in which the organic phase is dispersed in the aqueous phase. Phase inversion occurs when these states interchange (i.e. the dispersed phase inverts to become the continuous phase and vice versa). The phase inversion point is therefore the dispersed phase holdup at which this interchange occurs.

Due to the difficulties in understanding the mechanism which is responsible for phase inversion, the ability to predict the point of phase inversion is severely limited. Studies on how phase inversion behaviour is affected by the various physical and physicochemical parameters are restricted due to the complexity in uncoupling the effects of individual parameters. Few attempts have been made to predict the phase inversion point theoretically, with emphasis being placed instead on developing empirical correlations. Nevertheless, there is a considerable amount of variation between the results predicted by these correlations [1].

Few computational models have been developed for predicting phase inversion behaviour. Juswandi [2] attempted to simulate phase inversion of a dispersion existing in a thin annular liquid film flowing around a tube wall using a Monte Carlo method. In Juswandi's model, a similar algorithm to the Metropolis Monte Carlo method [3] is used to generate a trajectory in phase space which samples from a chosen statistical ensemble.

Our work attempts to incorporate the fundamental processes of drop hydrodynamics such as deformation, coalescence and break-up absent from the model of Juswandi [2]. Since a large portion of phase inversion research has concentrated on liquid-liquid dispersions in agitated vessels, culminating in a vast amount of experimental data, our model describes a dispersion that occurs in agitated vessels. The model is being extended to flowing systems.

METHODOLOGY

General Approach

Some of the assumptions used in the algorithm by Juswandi [2] are retained: The drops assume a spherical shape, having equal sizes corresponding to the Sauter mean diameter, D_{32} (m), and distributed uniformly in a face centred cubic configuration in the dispersion lattice.

For each dispersion morphology (water-in-oil and oil-in-water), a randomly selected drop in the dispersion lattice is moved using a method somewhat similar to the Metropolis Monte Carlo method [3]. The drop is checked for the possibility of it coalescing with a neighbouring drop, subject to the limitations given by the maximum stable drop size, D_{max} (m). In the event of coalescence, the coalesced drop is placed in the position of the neighbouring drop with which the selected drop has coalesced. Another randomly selected drop is then checked for the possibility of break-up (and re-coalescence). If break-up occurs, one daughter drop is placed at the original location of the mother drop whereas the other daughter drop is randomly placed. The steady-state drop size distribution is generated after a sufficiently large number of moves [$\sim O(10^5)$] and the total interfacial energy for the dispersion is then calculated. The process is repeated for increments in the water holdup until the total interfacial energy for the oil-in-water morphology decreases below that for the water-in-oil morphology. At this point, phase inversion from a water-in-oil dispersion morphology to an oil-in-water dispersion morphology is assumed to take place.

Break-up & Coalescence Probabilities

The probability of drop break-up, Ω, retained from the model of Juswandi [2], incorporates both the hydrodynamic conditions surrounding the drop and the effect of viscosity:

$$\Omega = 0.5\left[\exp\left(-\frac{1000}{Re}\right)\left(\frac{D-D_{min}}{D_{max}-D_{min}}\right)+\exp\left(-\frac{\mu_d}{\mu_c}\right)\right] \qquad (1)$$

Re is the Reynolds number [defined by $Re = \rho_c N D_I^2/\mu_c$ where ρ_c is the continuous phase density (kg/m^3), N the agitation speed (s^{-1}), D_I the impeller diameter (m) and μ_c the continuous phase viscosity (Pa.s)], D is the drop diameter (m), D_{min} the minimum stable drop diameter (m), and μ_d the dispersed phase viscosity (Pa.s).

For two approaching drops with volumes V and V' (m^3) to coalesce, the intervening continuous phase film must drain such that the film ruptures. This occurs when the contact time is sufficiently long for the film to drain to the critical film rupture thickness. In this work, two models for the coalescence probability are used:

1. Coulaloglou & Tavlarides [4] - Based on a model for film drainage

$$\lambda_I = \exp\left[-\frac{K_I\mu_c\rho_c D_I^2 N^3}{\sigma^2}\left(\frac{V^{1/3}V'^{1/3}}{V^{1/3}+V'^{1/3}}\right)^4\right] \qquad (2)$$

2. Sovová [5] - Based on the impaction of the colliding drops

$$\lambda_2 = \exp\left[-\frac{K_2\sigma(V^{1/3}+V'^{1/3})(V+V')}{\rho_d N^2 D_I^{1/3}VV'(V^{1/3}+V'^{1/3})}\right] \qquad (3)$$

where λ_I and λ_2 are coalescence probabilities. These are combined to give a single coalescence probability, λ, as proposed by Sovová [5]:

$$\lambda(V, V') = \lambda_I(V, V') + \lambda_2(V, V') - \lambda_I(V, V')\,\lambda_2(V, V') \qquad (4)$$

K_I and K_2 are constants, ρ_d is the dispersed phase density (kg/m^3), and σ the interfacial tension (N/m).

Drop Size Correlations

The correlation used for the maximum stable drop size, D_{max}, was that of Shinnar [6] whereas the Sauter mean diameter, D_{32}, is given by the correlation of Chen and Middleman [7]. The minimum stable drop size, D_{min}, below which drop break-up cannot occur was set at zero since values for D_{min} are very small compared to that for D_{max} and because the probability of drop break-up, equation (1), is relatively insensitive to D_{min}.

Accounting for Drop Deformation

At high phase volume holdups when the dispersion becomes increasingly concentrated, the translation of drops without inter-penetration becomes unfeasible. The drops are therefore allowed to inter-penetrate each other in the present model, this being interpreted as the 'deformation' of the drops into prolate spheroids. The 'deformability' of the drops is governed by a probability, Ψ, given by:

$$\Psi = \exp\left(-\frac{\sigma\Delta A_i}{K_3\rho_c N^2 D_I^{1/3}D'^{1/3}}\right) \qquad (5)$$

which restricts the random translation of the drops that result in larger degrees of inter-penetration. In equation (5), ΔA_i is the change in the interfacial area (m^2) as a result of 'deformation' and K_3 is a constant. The numerator represents the energy required to deform a drop whereas the denominator denotes the total system kinetic energy available to induce the 'deformation' of the chosen drop.

DISCUSSION OF RESULTS

Effect of Drop Initial Conditions

Simulations using different drop initial conditions such as the initial mean drop sizes, the initial number of drops, the polydispersity and the initial packing state of the system indicate that the total interfacial energy per unit volume tends to a stationary value after a significantly large number of random translations [8]. This indicates that the energy states of the system are largely insensitive to the initial drop conditions. The drop size distributions however, have been found to be slightly sensitive to initial conditions [8]. These are due to the effects of the different initial states on the coalescence and break-up probabilities which tend to have a permanent effect on the final drop size distributions. Nevertheless, as phase inversion holdups in this model are governed mainly by the relative interfacial energies of each dispersion morphology, it can be concluded that the inversion holdup itself is insensitive to the drop initial conditions.
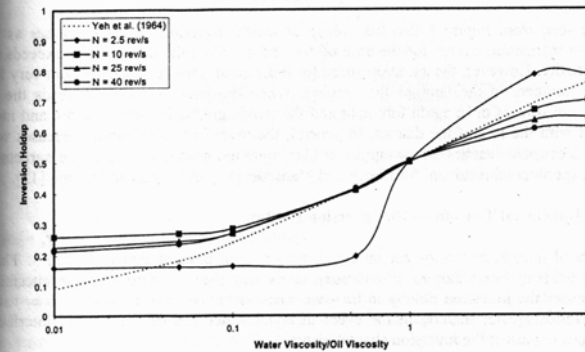
Effect of Viscosity on the Inversion Holdup

Figure 1. Inversion holdup as a function of the water to oil viscosity ratio (equal density system). Note that the trendlines are added for clarity rather than on a theoretical basis.

Figure 1 shows that as the dispersed to continuous phase viscosity is increased, the inversion holdup, ϕ_{inv}, increases as observed by Selker and Sleicher [9]. These results are also in good qualitative agreement with the scaling law of Yeh et al. [10] although it should be noted that their experiments were carried out by shaking the dispersion manually. In the absence of viscosity differences, the system inverts at a holdup of 0.5, in agreement with the predictions of McClarey and Mansoori [11]. As the ratio of dispersed to continuous phase viscosity is increased, the coalescence probability increases for the w/o dispersion and decreases for the o/w dispersion as a direct result of the increase in film drainage times. On the other hand, from equation (1), the break-up probability, proportional to $[\exp(-\mu_d/\mu_c)]$, decreases for w/o dispersions and increases for o/w dispersions. These result in larger mean drop sizes and lower interfacial energies. Thus there is an overall downward shift in the energy curve of the w/o dispersion and a corresponding upward shift in the energy curve of the o/w energy curve leading to a higher inversion holdup as illustrated in Figure 2. The reverse is true if the dispersed to continuous phase viscosity is decreased.
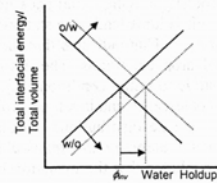

Figure 2. Effect of increasing the water to oil viscosity ratio
on the w/o and o/w interfacial energies

It can be seen from Figure 1 that the holdup at which inversion occurs decreases as the agitation is intensified except for the case of $N = 2.5$ s^{-1} when the oil viscosity exceeds the water viscosity. However, the agitation speed for these conditions corresponds with very low Reynolds numbers in the laminar flow region. When the water viscosity exceeds the oil viscosity, the flow is once again turbulent and the trends gradually become more and more consistent with the rest of the dataset. In general, the inversion holdup thus decreases with agitation speed and reaches an asymptote at high agitation speeds in qualitative agreement with the experimental results of McClarey and Mansoori [11] and Quinn and Sigloh [12].

Effect of Interfacial Tension on the Inversion Holdup

The effect of interfacial tension for an equidensity system is illustrated in Figure 3. Three cases are evident: For water to oil viscosity ratios less than 1, increasing the interfacial tension causes the inversion holdup to increase whereas the reverse is true for water to oil viscosity ratios greater than 1; In the event of equal water and oil viscosities, interfacial tension does not affect the inversion characteristics.

The last observation is in agreement with Yeh et al. [10] who suggested that the inversion holdup is 50% in systems in which forces other than interfacial tension are absent. Both Clarke and Sawistowski [13] and Norato et al. [14] have shown that lowering the interfacial

tension tends to increase the difficulty of inversion. However, both Clarke and Sawistowski [13] and Norato et al. [14] used liquids which have aqueous phase to organic phase viscosity ratios greater than 1. Our model predictions are therefore in good agreement with these results. On the other hand, it is not known as yet whether there are any experimental evidence to verify the predictions for the case where the water to oil viscosity ratios are less than 1.
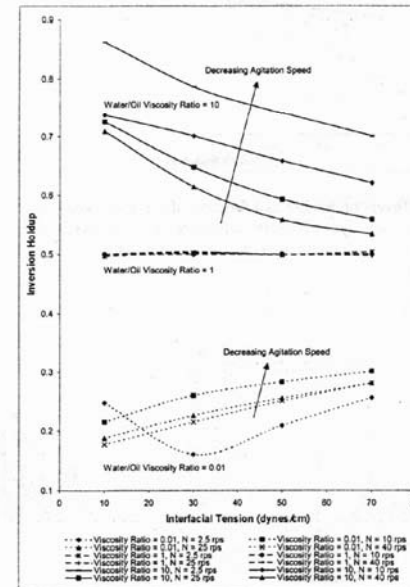

Figure 3. Effect of interfacial tension on the inversion holdup
for various water to oil viscosity ratios (equal density system)

Effect of Density on the Inversion Holdup

Figure 4 shows the effect of varying liquid densities in an equal viscosity system. Inverting the water-in-oil dispersion becomes increasingly difficult with increasing water to oil density ratios. This is in agreement with the results of Chiang and Chen [15] who observed an increased difficulty in inversion for water dispersed systems in which large density differences are evident. It can also be seen that there is no effect of agitation speed on the inversion holdup, an observation consistent with the study of Selker and Sleicher [9] on the effect of kinematic viscosity on the ambivalence limits for an equal viscosity system.
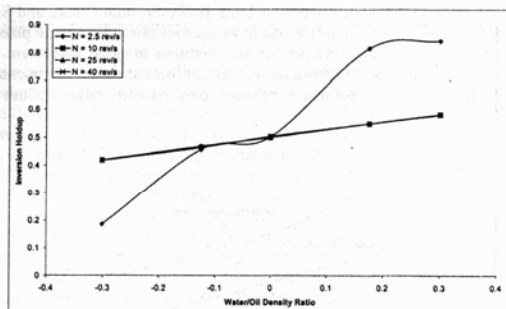
Figure 4. Inversion holdup as a function of the water to oil density ratio
(equal viscosity system). Note that the trendlines are added for clarity
rather than on a theoretical basis
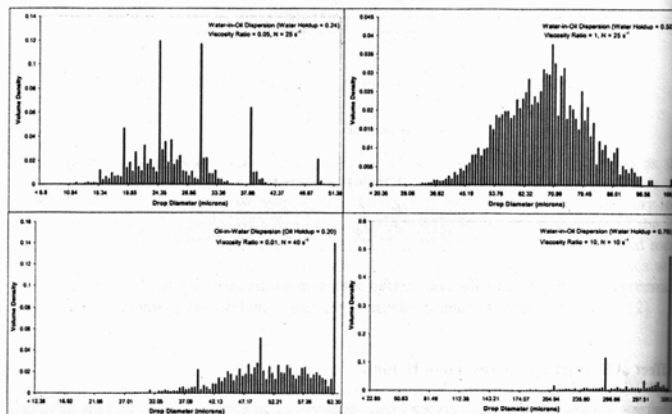
Drop Size Distributions

Figure 5. Typical drop size distributions at phase inversion

Figure 5 illustrates typical distributions obtained at phase inversion for various system conditions; we have found no single general shape for the drop size distributions near the inversion point. The lack of data for drop size distributions near the phase inversion point,

however, makes comparisons of our model predictions with experimental observations difficult.

CONCLUSIONS

We have developed a Monte Carlo technique to predict phase inversion of liquid-liquid dispersions in agitated vessels. This model, which takes into account drop deformation, coalescence and break-up, shows good agreement with observations obtained experimentally. Although the hysteresis effects which are normally present in systems undergoing phase inversion cannot be captured by the model, this model is nevertheless a promising basis which can be developed further to study phase inversion behaviour.

REFERENCES

1. Yeo, L. Y., Matar, O. K., Perez de Ortiz, E. S., Hewitt, G. F., Phase Inversion and Associated Phenomena, *Multiphase Science & Technology*, Vol. 12, pp. 51-116, 2000.
2. Juswandi, J., Simulation of the Oil-Water Inversion Process, *M.S. Thesis*, Oklahoma State University, 1995.
3. Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H., Teller, E., Equation of State Calculations by Fast Computing Machines, *J. Chem. Phys.*, Vol. 21, No. 6, pp. 1087-1092, 1953.
4. Coulaloglou, C. A., Tavlarides, L. L., Description of Interaction Processes in Agitated Liquid-Liquid Dispersions, *Chem. Eng. Sci.*, Vol. 32, pp. 1289-1297, 1977.
5. Sovová, H., Breakage and Coalescence of Drops in a Batched Stirred Vessel - II. Comparison of Model and Experiments, *Chem. Eng. Sci.*, Vol. 36, No. 9, pp. 1567-1573, 1981.
6. Shinnar, R., On the Behaviour of Liquid Dispersions in Mixing Vessels, *J. Fluid. Mech.*, Vol. 10, pp. 259-275, 1961.
7. Chen, H. T., Middleman, S., Drop Size Distribution in Agitated Liquid-Liquid Systems, *AIChE J.*, Vol. 13, No. 5, pp. 989-995, 1967.
8. Yeo, L. Y., Matar, O. K., Perez de Ortiz, E. S., Hewitt, G. F., Simulation Studies of Phase Inversion in Agitated Vessels Using a Monte Carlo Technique, submitted to *Chem. Eng. Sci.*
9. Selker, A. H., Sleicher, Jr., C. A., Factors Affecting which Phase will Disperse when Immiscible Liquids are Stirred Together, *Can. J. Chem. Eng.*, Vol. 43, pp. 298-301, 1965.
10. Yeh, G. C., Haynie, Jr., F. H., Moses, R. A., Phase-Volume Relationship at the Point of Phase Inversion in Liquid Dispersions, *AIChE J.*, Vol. 10, No. 2, pp. 260-265, 1964.
11. McClarey, M. J., Mansoori, G. A., Factors Affecting the Phase Inversion of Dispersed Immiscible Liquid-Liquid Mixtures, *AIChE Symposium Series*, Vol. 74, No. 173, pp. 134-139, 1978.
12. Quinn, J. A., Sigloh, D. B., Phase Inversion in the Mixing of Immiscible Liquids, *Can. J. Chem. Eng.*, Vol. 41, pp. 15-18, 1963.
13. Clarke, S. I., Sawistowski, H., Phase Inversion of Stirred Liquid/Liquid Dispersions Under Mass Transfer Conditions, *Trans. IChemE*, Vol. 56, pp. 50-55, 1978.
14. Norato, M. A., Tsouris, C., Tavlarides, L. L., Phase Inversion Studies in Liquid-Liquid Dispersions, *Can. J. Chem. Eng.*, Vol. 76, pp. 486-494, 1998.
15. Chiang, C. L., Chen, C. M., Characteristics of Phase Inversion in a Turbine-Type Agitator, *J. Chinese Inst. Chem. Eng.*, Vol. 25, No. 6, pp. 367-374, 1994.