Shorter communication

A simple predictive tool for modelling phase inversion in liquid–liquid dispersions

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1. Introduction

Phase inversion is the process in which the dispersion morphology of a system of two immiscible liquids spontaneously interchange under the influence of system properties, volume fraction and energy input. For example, phase inversion occurs when a water-in-oil dispersion inverts to become an oil-in-water dispersion and vice versa. This phenomenon occurs widely, whether desirably or undesirably, in industrial processes ranging from mixing and contacting equipment to pipeline flows.

The prediction of the holdup at which phase inversion occurs is an important factor in the design of these systems. Although various empirical correlations have been proposed to determine the phase inversion point, the complexities that accompany the phenomenon motivate the need for more theoretical work (Yeo, Matar, Perez de Ortiz, & Hewitt, 2000a). Among the most complex phenomena of phase inversion is the existence of a hysteresis effect manifested by a so-called 'ambivalent' region wherein there is a range of volume fractions over which either component can be the stable dispersed phase (Selker & Sleicher, 1965); the extent of this range depends on the previous history of the system. The physical phenomena defining these limits are equally as complex: Any factor influencing the inversion process will affect the limits of ambivalence.

A stochastic model to predict the inversion holdup using a Monte Carlo technique has been reported by the authors (Yeo, Matar, Perez de Ortiz, & Hewitt, 2000b, 2001). While this model is capable of predictions that are qualitatively in good agreement with experimental trends, it is limited by its inability to capture hysteresis effects that so often accompany the phase inversion phenomenon.

In this brief note, we attempt to do so by using a simple analysis, limited to the case of phase inversion occurring in agitated vessels. Nevertheless, it will become apparent that this analysis can be easily extended to other systems.

2. Model

As phase inversion is a spontaneous process, both Luhning and Sawistowski (1971) and Tidhar, Merchuk, Sembira, and Wolf (1986), have suggested the minimisation of the total system energy content at the point of inversion. Since no measurable change in the power delivered to the system is observed and as there is always a reduction in the interfacial energy at the point at which phase inversion occurs (Fakhr-Din, 1973), the minimisation of the total system energy would, therefore, arise when the interfacial energy and the total system kinetic energy are redistributed. As the magnitude of the change in the interfacial energy is comparable to that of the total system energy (Fakhr-Din, 1973), the change in kinetic energy would be small compared to the change in the interfacial energy upon inversion and hence the modelling of phase inversion by minimising the interfacial energy satisfies the criterion that the total system energy has to be minimised.

At the phase inversion point, we can write (Tidhar et al., 1986)

$$E_{w/o} + E_{o/s} = E_{o/w} + E_{w/s}, \qquad (1)$$

where the subscripts o and w referring to the organic and aqueous phases, respectively, and the subscript s referring to the solid wall. $E_{w/o}$ and $E_{o/w}$, therefore, denote the total interfacial energies of the water-in-oil dispersion morphology and the oil-in-water dispersion morphology, respectively. Similarly, $E_{o/s}$ and $E_{w/s}$ are the interfacial energies between the organic phase and the solid wall and that between the aqueous phase and the wall, respectively. In terms of the

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drop Sauter mean diameter, d_{32}, and the interfacial tension, σ, Eq. (1) may be reexpressed as

$$\frac{6\sigma_{o/w}(1 - \phi_{o,i})}{d_{32_{w/o}}} + \frac{S\sigma_{o/s}}{V} = \frac{6\sigma_{o/w}\phi_{o,i}}{d_{32_{o/w}}} + \frac{S\sigma_{w/s}}{V}, \qquad (2)$$

where $\phi_{o,i}$, S, and V represent the organic phase holdup at inversion (i.e. the critical holdup), total surface area of the solid, and the volume, respectively. It is not unreasonable to assume that the interfacial tension of the oil-in-water dispersion and that of the water-in-oil dispersion is constant as the phases invert and hence we drop the subscript o/w henceforth from the aqueous–organic interfacial tension term. From Young's equation,

$$\sigma_{o/s} = \sigma_{w/s} + \sigma \cos \theta. \qquad (3)$$

Eq. (2) can be written as

$$\frac{6(1 - \phi_{o,i})}{d_{32_{w/o}}} + \frac{S}{V} \cos \theta = \frac{6\phi_{o,i}}{d_{32_{o/w}}}, \qquad (4)$$

where θ is the liquid–solid contact angle.

In general, the Sauter mean diameter can be described in terms of the impeller Weber number, We_I,

$$d_{32} = C_1 We_I^{-n} D_I, \qquad (5)$$

where

$$We_I = \frac{\rho_c N^2 D_I^3}{\sigma}. \qquad (6)$$

Here, ρ_c is the continuous phase density, N is the agitation speed, and D_I is the impeller diameter. In Eq. (5), C_1 is a constant and n is a parameter.

However, correlations described by Eq. (5) apply for dilute systems only. Since phase inversion often occurs at very high dispersed phase holdups, drop size correlations which account for the influence of larger holdups are required. For concentrated dispersions, a modified form of Eq. (5) has been proposed (see, for example, the review by Godfrey, Obi, & Reeve, 1989) to take into account the increase in drop size due to turbulence damping and the coalescence of drops:

$$d_{32} = C_1(1 + C_2\phi_d^m)We_I^{-n} D_I, \qquad (7)$$

where ϕ_d is the dispersed phase holdup, C_2 is the turbulence damping factor, and m is a parameter.

To extend the drop sizes to liquid–liquid systems over a wider range of viscosities, a viscosity correction factor has been introduced by Calderbank (1958) and later by Godfrey et al. (1989):

$$d_{32} = C_1(1 + C_2\phi_d^m)We_I^{-n} D_I \left(\frac{\mu_d}{\mu_c}\right)^p, \qquad (8)$$

where μ_c and μ_d are the continuous and dispersed phase viscosities, respectively, and p is a parameter. For dilute systems, the turbulence damping factor is omitted to give

$$d_{32} = C_1 We_I^{-n} D_I \left(\frac{\mu_d}{\mu_c}\right)^p. \qquad (9)$$

In order to account for the hysteresis that is described by the ambivalent range which so often accompanies the phase inversion phenomenon, we note that if one phase is concentrated, then the other phase at the same corresponding holdup must be dilute. For example, an oil-in-water dispersion generally inverts when the organic phase holdup, $\phi_{o,d}$, is large and so Eq. (8) is used. However, in order to determine the phase inversion point for the oil-in-water dispersion inverting to a water-in-oil dispersion, we require the corresponding interfacial energy for the water-in-oil dispersion at the same holdup. In this case, the aqueous phase holdup, $1 - \phi_{o,d}$, is small and hence Eq. (9) is used. However, when calculating the reverse inversion process, i.e. inversion from the water-in-oil dispersion to an oil-in-water dispersion, the reverse is true, i.e. the water-in-oil dispersion generally inverts when the aqueous phase holdup is large. Therefore, Eq. (8) is used to calculate the water-in-oil interfacial energy and Eq. (9) is used to calculate the corresponding oil-in-water interfacial energy.

The effects of hysteresis are further accentuated by the wetting effects since the solid surface is wetted by the organic phase for a water-in-oil dispersion and by the aqueous phase for an oil-in-water dispersion. Therefore, the wetting of the surface is not just a function of the tank material but also of the configuration history of the system. However, the effect of wetting is only significant when the drops are large or if there is a significant amount of surface area per unit volume. In the case of agitated vessels, the drop interfacial energy ($E_{w/o}$ or $E_{o/w}$) is usually several order of magnitudes larger than the interfacial energy associated with the solid surface ($E_{w/s}$ or $E_{o/s}$) and hence the latter terms can be neglected; these terms only become significant for example in pipeflow when S/V is large or the velocities small enough for the drop sizes to be large (Tidhar et al., 1986).

Since this study is limited to agitated vessels, we neglect the terms $E_{w/s}$ and $E_{o/s}$. In this limit, Eq. (2) can be simplified to

$$\frac{\phi_{o,i}}{1 - \phi_{o,i}} = \frac{d_{32_{o/w}}}{d_{32_{w/o}}}. \qquad (10)$$

In this study, we solve for the organic phase holdup at phase inversion $\phi_{o,i}$ using the correlation proposed by Calderbank (1958) (Eq. (8)) where $C_1 = 0.06$, $C_2 = 0$ (for dilute dispersions) or $C_2 = 3.75$ (for concentrated dispersions), $m = 1$, $n = 0.6$ and $p = 0.25$.

3. Results and discussion

Fig. 1 illustrates the plot of the ambivalence limits given as a function of the ratio of the oil-to-water kinematic viscosities, denoted by v_o and v_w, respectively. It can be seen that the simple model presented in this work provides reasonable agreement with the results of Selker and Sleicher (1965). In general, the inversion holdups are slightly underpredicted for viscosity ratios below 1 and slightly
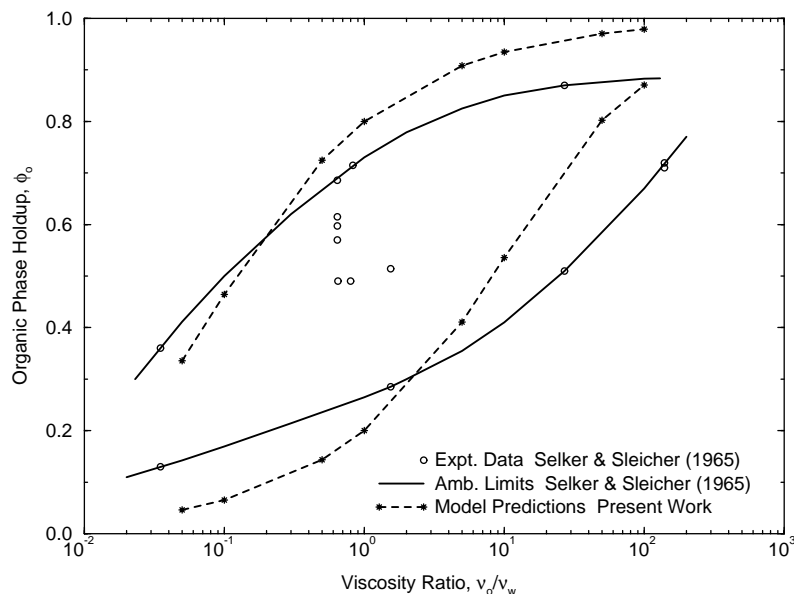
Fig. 1. Ambivalence limits predicted by the present model compared to the results of Selker and Sleicher (1965).

overpredicted for viscosity ratios above 1. Salient features observed by Selker and Sleicher are captured: For example, the tendency for a phase to be dispersed as its viscosity increases and the lack of symmetry between the upper and lower ambivalence curves.

One interesting observation is the independence of the curves of the agitation speed, N, which is obvious when the effect of wetting is negligible as in the case of agitated vessels (Eq. (10)). It was also found by solving for the inversion holdup, $\phi_{o,i}$, from the unsimplified equation where the term for N is still present (Eq. (4)) that the effect of agitation speed is negligible. Selker and Sleicher (1965) noted in their experiments that the agitation speed appeared to have no effect on the ambivalence limit given that the agitation was sufficient to prevent settling of the liquids. This was also observed in other studies (Quinn & Sigloh, 1963; Luhning & Sawistowski, 1971). In addition, Groeneweg et al. (1998) also reported no observable effects of the agitation speed on the ambivalence curves. Nevertheless, they admitted the possibility of their experiments being conducted in conditions which prevent creaming or sedimentation, similar to Selker and Sleicher. The inability of the model to capture the dependence of the ambivalence limits on the agitation speed, therefore, imposes a limitation on its predictive capabilities, thereby restricting the model to large agitation speeds where the phase inversion holdup asymptotes to a constant value when the agitation is intense enough to prevent settling (Selker & Sleicher, 1965; Luhning & Sawistowski, 1971).

4. Concluding remarks

In this short communication, we present a simple tool based on the criterion of interfacial energy minimisation to predict the limits of the ambivalence region of a phase inversion process. In order to model hysteresis, the observation that different drop sizes are obtained when the dispersion is dilute or concentrated is utilised, and hence different drop size correlations must be used, a fact that is obvious but has a tendency to be overlooked. By taking these geometrical considerations into account, we are thus able to compare the interfacial energy of both morphologies on either side of the inversion process and also to capture hysteresis by considering the history of the system. Thus, this hybrid method brings together two separate approaches upon which theoretical explanations for the critical dispersed phase holdup had hitherto been based (Yeo et al., 2000a): The surface energetics approach discussed earlier (Luhning & Sawistowski, 1971; Fakhr-Din, 1973; Tidhar et al., 1986) and the geometrical approach in which phase inversion is taken to occur when the limit of the packing efficiency of the dispersion is reached (Nädler & Mewes, 1997). Despite the simplicity of the model, we find that the predictions agree reasonably well with the results of Selker and Sleicher (1965) and are able to capture certain features observed in their experiments. Refinement of the model to achieve greater agreement with experimental results is possible by using different drop size correlations. It is hoped that this simple model could be the basis for the development of more accurate models to predict the hysteresis effects of phase inversion in various systems.

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