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BRIEF COMMUNICATION

A PROBLEM FOR THE DESCRIPTION OF TURBULENT DISPERSED LIQUID–LIQUID SYSTEMS

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INTRODUCTION

Turbulent liquid–liquid dispersed flows commonly occur in chemical, biochemical and related industries in both batch and continuous stirred reactors, and in pipe flows. Usually one phase is aqueous (A) and the other organic (O). In order to control and realistically predict the flows in these systems, the influence of the hydrodynamic conditions, of the liquid properties and of the composition on the drop size distribution and mean drop size needs to be known. So too does the stability of the flow, i.e. whether the dispersion is oil-in-water (O/A) or the opposite, A/O. The detailed theoretical description of such systems is rather complicated, because the phenomena of drop breakage and coalescence, which largely control drop sizes and stability, are themselves still not well understood. Thus, they cannot be described by closed mechanistic models, i.e. by equations based on theory without constants obtained by experiments. Indeed, the systems are often so complex, e.g. in stirred vessels, that an empirical or semi-empirical approach is adopted. Recent reviews (Davies 1992; Peters 1992) make this clear whether drop sizes or phase stability are under consideration.

One unifying feature, however, whether a theoretical, empirical or semi-empirical approach is used, is the assumption of symmetry. By this we mean that, in the absence of surface modifying agents and/or electrostatic fields, when the physical properties of the two phases (A and O) are the same (theoretical) or very similar (experimental), the drop size distributions and mean sizes are the same at the same concentration and fluid dynamic conditions whether the dispersion is A/O or O/A; and that under equivalent conditions, the structure of an O/A dispersion is the same as that of an A/O one. Our recent work (Nienow *et al.* 1994) questions that assumption. In order to put this surprising finding into context, we first discuss in outline the two models mainly used for such flows and then indicate how our experiments pose problems for them. We conclude with a set of questions arising from the difference between present theory and our experiments.

A BRIEF REVIEW OF THEORIES

When a theoretical analysis is attempted, mainly two approaches are used. The first concentrates on the continuous phase and the behaviour of the dispersed phase is usually grossly simplified (we call this the continuous description). The second approach concentrates on the dispersed phase, practically neglecting the details of the continuous phase (the discrete description). We will review each of the approaches very briefly.

The "continuous description" is commonly used for pipe flow (or any one-dimensional flow) and either the drift flux model (Wallis 1969) or two-fluid model (Ishii 1975; Pauchon & Banerjee 1986) is employed. Both these models usually assume that the interaction between the drops of dispersed phase (breakage, coalescence) can be neglected or included as a correction factor in the drag coefficient. The interaction between the phases can either be included in the momentum balance equation (Pauchon & Banerjee 1986) or expressed as a jump condition on the interface (Ishii 1975) with the forces acting on the interface usually being estimated from the Stokes or the

Hadamard–Rybczynski solutions of the Navier–Stokes equation (Hetsroni 1982). Thus, the flow around the single drop is used in an averaged analysis of two-phase dispersal systems (Couët *et al.* 1991; Kowe *et al.* 1988; Pauchon & Banerjee 1986; Ishii 1975) and often extrapolated to highly-concentrated ones. The underlying assumption is that the interaction between two phases depends on the volume fraction of the dispersed phase, the densities, viscosities and average velocities of both phases, and the interfacial tension with the latter property being symmetrical (i.e. the interfacial tension for an aqueous drop in an oil is the same as that for an O/A system). The resulting set of equations has been used to analyse phase stability (Pauchon & Banerjee 1988), pressure forces (Prosperetti & Jones 1984) and the changes of pressure and void fraction (Couët *et al.* 1991) in a one-dimensional flow. The three-dimensional version of the two-fluid model is also incorporated in more complex CFD codes (e.g. CHAM 1993).

Though the CFD code of CHAM based on the "continuous description" has been used to simulate three-dimensional flow in a stirred vessel, the "discrete description" has generally been employed for such complex flows. The population balance model (Ramkrishna 1985) is commonly used, with both the continuous and dispersed phases usually treated as perfectly mixed, i.e. all spatial gradients are dropped (Coulaloglou & Tavlarides 1977) and the dispersed phase may undergo either breakage (Narsimhan *et al.* 1979) or coalescence (Tobin *et al.* 1990). Breakage is related to disruptive stresses, dependent on the density and viscosity of the continuous phase via Kolmogoroff's theory of isotropic turbulence and stabilizing forces dependent on the interfacial tension and the viscosity of the dispersed phase (Calabrese *et al.* 1986). Coalescence depends on the collision rate (Tobin *et al.* 1990) and coalescence efficiency (Chesters 1991). The latter is related to the film drainage time with different boundary conditions dependent on the drop–continuous phase interface [fully-mobile, partially mobile, immobile (Calabrese *et al.* 1993)]. Thus, coalescence is dependent on turbulent stresses, the viscosity and density of both phases and the symmetrical interfacial tension.

In summary, whichever of these approaches is used, the assumptions briefly discussed above imply that if two liquids have the same density and the same viscosity and the velocity field is the same, there should not be any difference between the structure of the flow at the same dispersed phase volume fraction regardless of which liquid is continuous and which is dispersed.

REVIEW OF EXPERIMENTS

We have developed a video system able to give sharp images of drops as small as 25 μm every 1/50th second by synchronizing strobe lighting to the camera framing rate and linking the camera to a stereo-microscope as described in detail elsewhere (Pacek *et al.* 1994). We have used this system to study the structure of two-phase liquid–liquid dispersed flows in a stirred vessel using the wide

Table 1. Liquids used in the experiments at 20°C and their physical properties

(a)

Oil phase (with water)	Density (kg/km^3)	Viscosity (mPas)	Interfacial tension† (N/m)
Chlorobenzene	1106	0.75	0.033
Benzene	879	0.65	0.025
Toluene	867	0.59	0.028
Cyclohexane	779	1.02	0.044
Silicon fluid 200/1cS	814	0.80	0.039
Silicon fluid 200/20 cS	941	18.90	0.047
Silicon fluid 200/50 cS	960	48.00	0.037

(b)

Aqueous phase (with CLB)	Density (kg/m^3)	Viscosity (mPas)	Interfacial tension‡ (N/m)
Water	998.2	1.00	0.033
1% glycerol in water	999.2	1.02	0.025
10% glycerol in water	1026.1	1.23	0.025
25% glycerol in water	1063.1	2.02	0.027
36% glycerol in water	1085.0	3.10	0.026
0.5% NaCl in water	999.1	1.00	0.031

†With water; ‡with chlorobenzene.

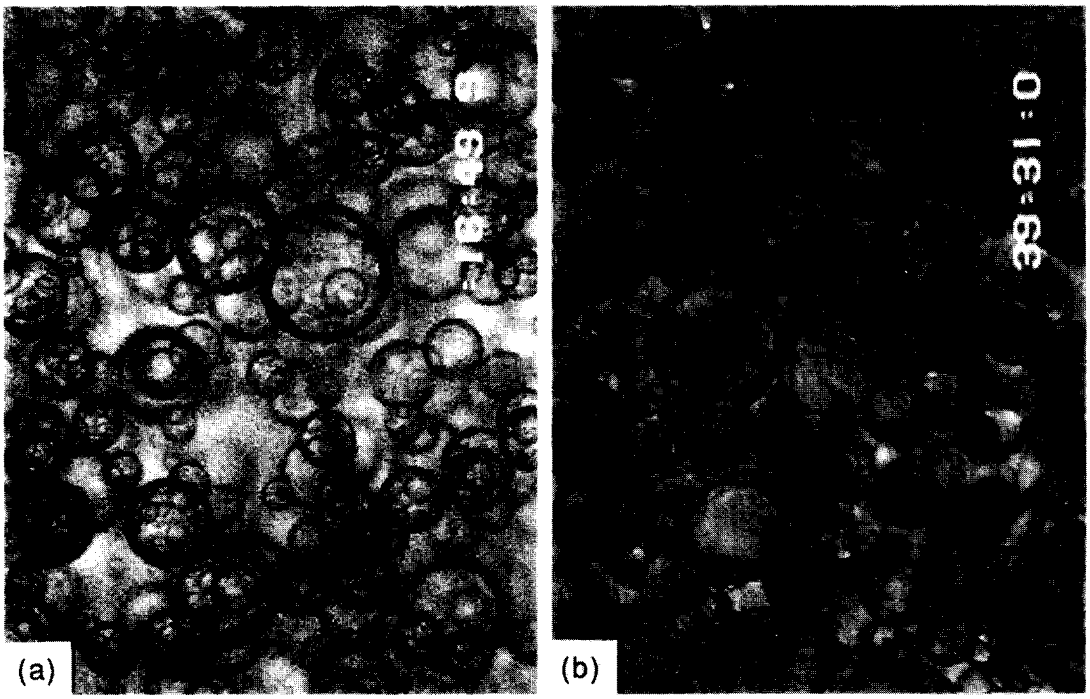

Figure 1. (a) A dispersion of 30% by volume of water in benzene showing droplets of benzene in drops of water; (b) a dispersion of 30% by volume of benzene in water.

range of systems given in table 1. When the aqueous phase was distilled water, the oil phase covered pure organic liquids whose density and viscosity straddle those of water, and silicone oils of viscosity up to 50 mPas. Additionally, 0.5% NaCl solution and a range of glycerol solutions in water were used as the aqueous phase with chlorobenzene as the organic. Because of the findings

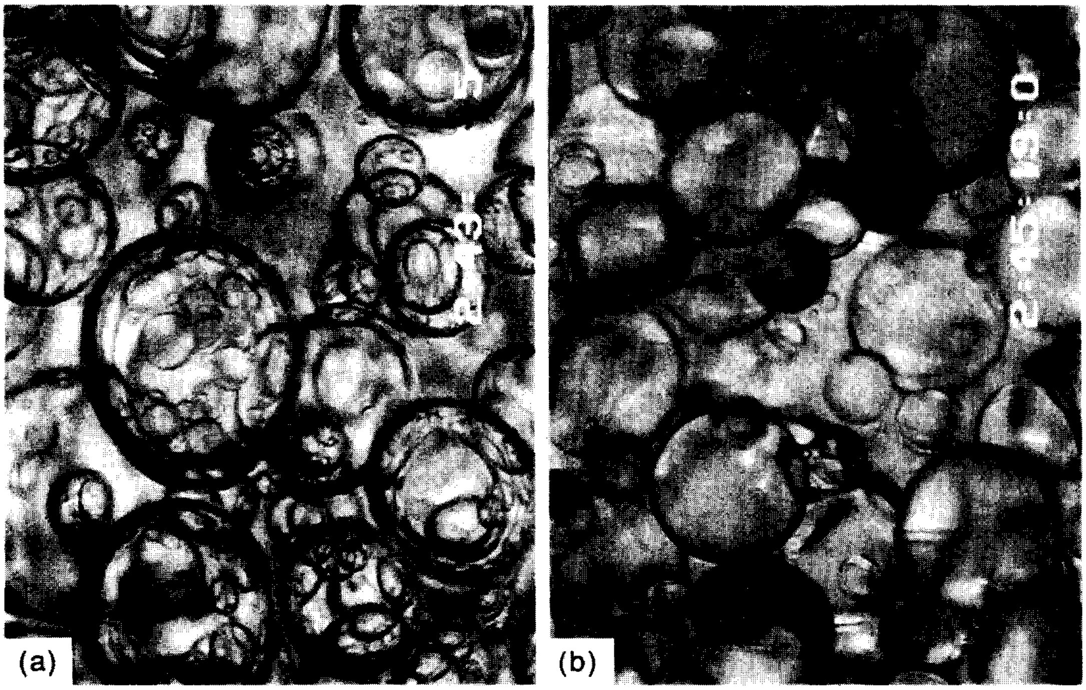

Figure 2. (a) A dispersion of 54% by volume of water in benzene just before phase inversion; (b) the same system 2 min later after phase inversion.

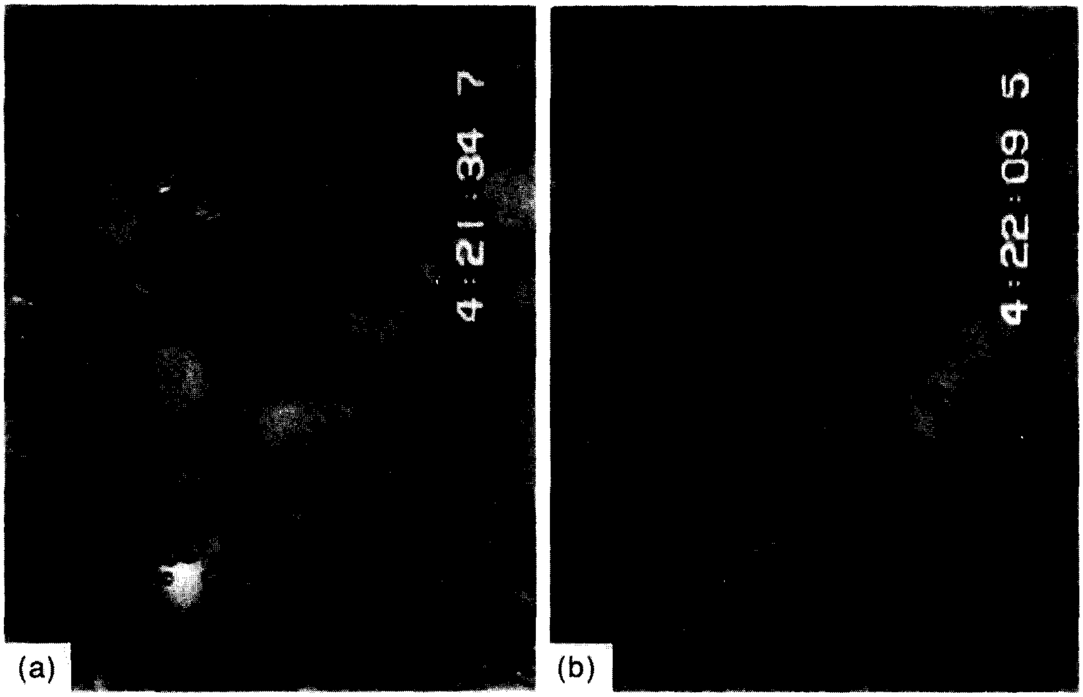

Figure 3. (a) A dispersion of 72% by volume of benzene in water just before phase inversion; (b) the same system 35 s after phase inversion.

reported below, the interfacial tension was measured by the drop weight method which confirmed that it was the same whichever phase was used to form the drop.

The vessel was 150 mm in diameter, closed to avoid any air introduction and agitated by a four-bladed, 60°-pitch turbine of half the vessel diameter. The speeds used were from 400 to 700 rpm, well above the minimum required to produce a visually-homogeneous dispersion. Fuller details are given elsewhere (Nienow *et al.* 1994). In all cases, for systems with water dispersed, droplets of oil in the drops of water have been observed for volume fractions of water greater than about 20% up to that at which phase inversion occurred. Conversely, droplets of water in the drops of oil have never been seen. Examples, for the water–benzene system at a volume fraction of 30% of dispersed phase are shown in figure 1(a) and (b). The phenomenon of droplets-in-drops intensifies as the system approaches phase inversion from W/O to O/W and disappears just after phase inversion. Figure 2(a) and (b) for the benzene–water system illustrates this latter point. On the other hand, when the system approaches inversion from O/W to W/O, droplets-in-drops are not seen up to inversion and appear immediately afterwards [figure 3(a) and (b)]. A more detailed description of the same phenomenon is set out elsewhere (Nienow *et al.* 1994).

Some preliminary experiments in pipe flow using the kerosene–water system have shown the same two-phase structure; namely oil droplets in water drops in an oil-continuous system and the absence of droplets of water in drops of oil for a water-continuous one.

Clearly, these systems do not behave symmetrically. Regardless of the physical properties of each of the phases (which in some cases are very similar and some cases quite different) or the value of the interfacial tension, the structure of the dispersion is the same over a wide range of concentrations if the dispersion is A/O (droplets-in-drops) and different from that when the dispersion is O/A (no droplets-in-drops).

We have also measured the concentration of the dispersed phase (ϕ_d) at which inversion occurs from A/O to O/A and for O/A to A/O. The values and the associated agitator speeds are given in table 2 for the systems where the physical properties of the organic phase are close to and straddle those of water. Thus, there is no indication from the physical properties that would suggest that inversion should occur at a higher concentration for A/O going to O/A or vice versa. Yet, in each case, it can be seen that the volume fraction of dispersed oil at inversion to water dispersed is much higher than when water is dispersed in oil. This finding suggests that, under the same hydrodynamic

Table 2. The concentration at the phase boundaries and speeds used

Oil phase (with water)	ϕ_d from O/A to A/O	ϕ_d from A/O to O/A	Impeller speed (rpm)
Chlorobenzene	0.680	0.545	400
Benzene	0.717	0.541	500
Toluene	0.705	0.528	500
Cyclohexane	0.843	0.521	500

conditions and similar physical properties, O/W dispersions are more stable than W/O. This observation again indicates a lack of symmetry.

DISCUSSION AND CONCLUSIONS

These experimental observations give rise to several questions:

(a) what causes droplets of oil to enter drops of the aqueous phase whereas under the same hydrodynamic conditions, drops of aqueous phase do not enter drops of oil, i.e. these aqueous–oil systems are clearly non-symmetrical even when the density and viscosity of both phases are practically the same? Indeed, the phenomenon seems to be independent of which phase is the more viscous or the more dense;

(b) what property or phenomenon other than viscosity, density and interfacial tension is necessary at the fluid dynamic level to explain and/or quantify this non-symmetrical behaviour?

(c) what is the maximum volume fraction of dispersed phase at which the equations for the forces acting on the interface taken from the flow around a single entity of the dispersed phase can be applied realistically in the description of a multi-drop, two-phase system?

At present, it does not seem possible from our knowledge of the physics of interfaces to answer these questions or explain the above results. In addition to the fundamental interest of this finding, it has important practical consequences for the process engineering of liquid–liquid systems, e.g. food structure, liquid–liquid extraction, bioseparations, etc.

REFERENCES

Calabrese, R. V., Chang, T. P. K. & Dang, P. T. 1986 Drop breakup in turbulent stirred-tank contactors—Part I: effect of dispersed-phase viscosity. *AIChE Jl* **32,** 657–666.

Calabrese, R. V., Pacek, A. W. & Nienow, A. W. 1993 Coalescence of viscous drops in a stirred vessel. *The 1993 Inst. Chem. Engrs Research Event*, Birmingham, January; Inst. Chem. Engrs, Rugby, pp. 642–644.

CHAM 1993 Introduction to two phase flow. In *Introduction to Pheonics*, Chap. 11. TR/300 Course Notes, London.

Chesters, A. K. 1991 The modelling of coalescence processes in fluid–liquid dispersions: a review of current understanding. *Trans. I. Chem. Engrs* **69A**, 259–270.

Couët, B., Brown, P. & Hunt, A. 1991 Two-phase bubbly-droplet flow through a contraction: experiments and unified model. *Int. J. Multiphase Flow* **17,** 291–307.

Coulaloglou, C. A. & Tavlarides, L. L. 1977 Description of interaction processes in agitated liquid–liquid dispersions. *Chem. Engng Sci.* **32,** 1289–1297.

Davies, G. A. 1992 Mixing and coalescence phenomena in liquid–liquid systems. In *Science and Practice of Liquid–Liquid Extraction* (Edited by Thornton, J. C.), Vol. I, pp. 245–342. Clarendon Press, Oxford.

Hetsroni, G. 1982 *Handbook of Multiphase Systems.* Hemisphere, Washington, DC.

Ishii, M. 1975 *Thermo-fluid Dynamic Theory of Two-phase Flow.* Eyrolles, Paris.

Kowe, R., Hunt, J. C. R., Hunt, A., Couët, B. & Bradbury, L. J. S. 1988 The effects of bubbles on the volume fluxes and the pressure gradients in unsteady and non-uniform flow of liquids. *Int. J. Multiphase Flow* **14,** 587–606.

NARSIMHAN, G., GUPTA, J. P. & RAMKRISHNA, D. 1979 A model for transitional breakage probability of droplets in agitated lean liquid–liquid dispersions. *Chem. Engng Sci.* **34,** 257–265.

NIENOW, A. W., PACEK, A. W., MOORE, I. P. T. & HOMER, J. 1994 Fundamental studies of phase inversion in a stirred vessel. *8th European Mixing Conferene*, Cambridge, September. Inst. Chem. Engrs, Rugby, pp. 171–178.

PACEK, A. W., MOORE, I. P. T., NIENOW, A. W. & CALABRESE, R. V. 1994 A video technique for the measurement of the dynamics of liquid–liquid dispersion during phase inversion. *AIChE Jl.* **40,** 1940–1949.

PAUCHON, C. & BENERJEE S. 1986 Interphase momentum interaction effects in the averaged multifield model, Part I: void propagation in bubbly flows. *Int. J. Multiphase Flow* **12,** 559–573.

PAUCHON, C. & BANERJEE, S. 1988 Interphase momentum interaction effects in the averaged multifield model, Part II: kinematic waves and interfacial drag in bubbly flows. *Int. J. Multiphase Flow* **14,** 153–264.

PETERS, D. C. 1992 Dynamics of emulsification. In *Mixing in the Process Industries* (Edited by HARNBY, N., EDWARDS, M. F. & NIENOW, A. W.), 2nd Edn, Chap. 14, pp. 294–321. Butterworth–Heinneman, Oxford.

PROSPERETTI, A. & JONES, A. V. 1984 Pressure forces in disperse two-phase flow. *Int. J. Multiphase Flow* **10,** 425–440.

RAMKRISHNA, D. 1985 The status of population balances. *Rev. Chem. Engng* **3,** 49–95.

TOBIN, T., MURALIDHAR, R., WRIGHT, H. & RAMKRISHNA, D. 1990 Determination of coalescence frequencies in liquid–liquid dispersions: effect of drop size dependence. *Chem. Engng Sci.* **45,** 3491–3504.

WALLIS, G. B. 1969 *One-dimensional Two-phase Flow.* McGraw–Hill, New York.