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On-Line Monitoring of Drop Size Distributions in Agitated Vessels. 2. Effect of Stabilizer Concentration

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Surface-active agents play a very important role in the production of polymers by suspension polymerization. Their function is to adsorb to the monomer/water interface, thus, preventing coalescence of monomer droplets. One commonly used stabilizer is poly(vinyl acetate) partially hydrolyzed to poly(vinyl alcohol) (PVA). The degree of hydrolysis and the molar mass of PVA affect its ability to act as a stabilizer. To assess the effectiveness of PVA in stabilizing monomer drops, a model system of 1% styrene in water was selected for our experimental studies. The stabilizer had a viscosity average molar mass of 22 000 and a hydroxyl group content of 97.5–99.5 mol %. The interfacial tension of the styrene/water system was measured by the Wilhelmy plate method for various concentrations of PVA. A number of experiments were carried out to study the effect of stabilizer concentration on the evolution of drop size distribution. The minimum time required for a system to reach steady state and the corresponding average drop diameters were measured as a function of stabilizer concentration, temperature, and agitation speed. Correlations were developed to relate the minimum transition time, t_{\min} , and Sauter mean diameter, d_{32} , with the Weber number of the main flow.

Introduction

When two immiscible liquids are brought into contact in an agitated vessel, a dispersion is formed by the combined action of turbulence and surface energy. Droplet formation in the initial period of mixing and the dynamic equilibrium between breakage and coalescence of the drops are determined by the hydrodynamic conditions in the vessel and the interfacial tension between the two liquid phases. For a low-coalescing system, parameters favoring droplet breakup, such as high impeller speed or low interfacial tension, generally decrease the minimum transition time required for the system to reach steady state.

In suspension polymerization, the drops are stabilized against coalescence by the addition of water-soluble polymers called stabilizers or protective colloids. One of the commonly used stabilizers is poly(vinyl acetate) (PV-Ac) that has been partially hydrolyzed to poly(vinyl alcohol) (PVA). The function of surface-active agents is to adsorb to the monomer/water interface and prevent other drops from approaching because of steric repulsion forces. This causes a reduction of immediate coalescence due to the increasing strength of the liquid film entrapped between two colliding drops. The presence of a protective film prolongs the contact time for drop coalescence, thus, increasing the probability of drop separation by agitation. However, some of the collisions do result in adhesion of the colliding drops. In the latter case, the intervening film tends to decrease in thickness with time and finally collapses, permitting, thus, the coalescence of droplets.

Hartland (1968) investigated the effect of surface-active agents on the drainage and rupture of the film beneath a liquid drop at a deformable liquid-liquid interface. He suggested that surfactants increase the interfacial viscosity and lower the interfacial tension, thus, making the interface more rigid and more deformable.

Several investigations have been reported on the use of stabilizers in suspension polymerization (Khan et al., 1988; Hopff et al., 1964, 1965; Nilsson et al., 1985). Fundamental studies were carried out by Hopff et al. (1964, 1965) to investigate the effect of poly(vinyl alcohol) on the suspension polymerization of methyl methacrylate, styrene, and vinyl acetate. Their final particle size distributions were measured by screen analysis, and an empirical

equation was derived to correlate the "central" bead size to reactor operating conditions, including interfacial tension, impeller speed, impeller diameter, and viscosity of the continuous phase. Nilsson et al. (1985) studied by means of a dynamic drop-volume method the effect of commonly used suspension stabilizers on the interfacial tension of a vinyl chloride/water system. Trends were established in relation with the observed drop size distributions and resin porosity in PVC suspension polymerization. However, Nilsson et al. (1985) cautioned on a possible quantitative use of the determined dependence of interfacial tension with respect to time due to the constant generation of new surface during measurements. Also Church and Shinnar (1961) studied the mechanism of droplet stabilization in agitated dispersions as a function of PVA concentration and reported a decrease of 100 μm in the average drop size as the PVA concentration increased from 0.03 to 0.5 wt %.

Hence, there is still a need for systematic investigation of the effects of surface-active agents on the drop size distribution in a two-phase dispersion system. In the present study a model system of 1% styrene in water is used to investigate the effect of stabilizer concentration on the drop size distribution. Correlations are developed to relate the minimum transition time and Sauter mean diameter to the Weber number.

Experimental Details

Materials and Procedure. A model system of styrene in water was chosen for our experimental studies. The two-phase system consisted of styrene (Fluka AG) as the dispersed phase and distilled water as the continuous phase. The volume fraction of styrene was 0.01, and the continuous phase contained varying amounts of poly(vinyl alcohol) (PVA). The PVA had a degree of polymerization of 500 (molecular weight 22 000) and a hydrolysis ratio of 97.5–99.5 mol % (Fluka AG).

The mixing vessel was a capped round-bottomed glass cylinder fitted with four vertical, equally spaced stainless steel baffles and was equipped with a stainless steel six-blade turbine impeller. Details on the reactor and impeller geometry, as well as on the sampling procedure, are discussed elsewhere (Chatzi et al., 1991).

Table I. Experimental Conditions

C_{PVA} , g/L	N^* , rpm	T , °C	$(N_{w_0})_T$	$(N_{R_0})_T$	η , μm
0.01	200	30	194	23 004	17
	300	30	436	34 506	12
	200	60	201	38 845	11
	300	60	453	58 267	8
0.05	300	30	541	34 506	12
	300	60	583	58 267	8
0.1	200	25	269	20 635	18
	300	25	604	30 953	13
	200	30	273	23 004	17
	300	30	614	34 506	12
	200	50	291	33 285	13
	200	60	301	38 845	11
	300	60	678	58 267	8
	300	60	1219	38 845	11
3	200	60	2729	58 267	8

Drop Size Measurements by Laser Diffraction. For the measurement of drop size distributions, a Malvern laser diffraction particle sizer Model 2605c connected to an Olivetti M24 microcomputer was used. The particle size analyzer was equipped with a continuous flow cell for on-line measurement of transient drop size distributions. A lens with focal length 300 mm and dynamic range 180:1 was attached to the optical measurement unit. The analyzer was capable of detecting particles and droplets in the size range of 5.8–564 μm with an accuracy of $\pm 4\%$ on the volume median diameter. The primary output of the instrument was the relative volume size distribution stored in 32 size classes uniformly spaced on a logarithmic scale. Details on the mathematical transformations of the experimental discrete distributions are discussed in part 1 (Chatzi et al., 1991). It should be pointed out that multimodal particle size distributions can be identified by the Malvern laser diffraction apparatus and associated software (Bürkholz and Polke, 1984).

Operational Conditions and Physical Properties. Several experiments were carried out at various temperatures (25, 30, 50, and 60 °C) and suspending agent concentrations (0.01, 0.05, 0.1, and 3 g/L). Two impeller speeds (200 and 300 rpm) were selected to investigate the effect of agitation rate on the droplet size distributions. The impeller speed was always above the minimum impeller speed for complete liquid–liquid dispersion while the maximum impeller speed of 300 rpm was just below the level at which air entrainment occurred. The experimental conditions are shown in Table I.

The time variation of the interfacial tension between the styrene phase and the aqueous PVA solutions was measured by a KRÜSS surface tensiometer, Model K10, using the Wilhelmy plate method. The procedure recommended by the manufacturer was closely followed for each surface tension measurement. For calibration of the instrument, the plate attached to the measuring torsion balance was initially submerged into a sample vessel containing the styrene phase. Subsequently, the plate was removed from the styrene container and carefully cleaned and annealed. Then a second sample vessel containing the water phase

was raised against the bottom edge of the plate until it became moistened. Finally, the light styrene phase was carefully poured over the heavier water phase so that the plate remained submerged at the same depth as it was during calibration. The value of interfacial tension was recorded at different times until the system reached equilibrium. It should be pointed out that in the present work interfacial tension measurements were carried out until the slope of the surface tension versus time curve became less than 0.01.

For PVA concentrations of less than 10 g/L, the physical properties of the continuous phase do not significantly vary from those of pure water. The average density and viscosity of the two-phase dispersion were calculated as weighted averages of the corresponding values of the dispersed and continuous phases (Bouyatiotis and Thornton, 1967):

$$\rho_m = \rho_d \phi + \rho_c (1 - \phi) \quad (1)$$

$$\mu_m = \mu_c / (1 - \phi) [1 + 1.5 \mu_d \phi / (\mu_d + \mu_c)] \quad (2)$$

In Table II, the calculated and measured values of the physical properties of the styrene/water system are reported.

Results and Discussion

Interfacial Tension and Evolution of Particle Size Distribution. Interfacial tension is a measure of the relative resistance of the drops to breakage as compared to coalescence. Thus a decrease of the interfacial tension results in a reduction of drop size due to both a decrease of the resistance to breakage and an increase of the resistance to coalescence. The interfacial tension between two immiscible liquids in a dispersion will depend on temperature, as well as the presence of surface-active agents. Polymeric stabilizers are commonly used as surface-active agents.

In this study, the interfacial tension of a styrene/water system was measured by the Wilhelmy plate method as a function of time in order to determine its time variation and equilibrium value over a wide range of PVA concentrations at different temperatures. The reported PVA concentrations refer to the initial concentration of PVA in the water phase. In all interfacial tension measurements it was assumed that the concentration of PVA remained constant due to the limited surface separating the two phases. However, in a two-phase dispersion, where a large number of drops exists, the equilibrium bulk concentration of PVA will generally be lower than its initial value due to the large surface area of the drops. This reduction will not be significant for systems with a low dispersed-phase volume fraction.

The rate of transfer of PVA molecules to the interface will vary with time and will be controlled by the diffusion of polymer molecules to the interface, as well as the reorganization and reformation of the adsorbed surface

Table II. Physical Properties of the Dispersed and Continuous Phases (Styrene and Water, Respectively)

T , °C	C_{PVA} , g/L	ρ_c , g/cm ³	μ_c , cP	ρ_d , g/cm ³	μ_d , cP	ρ_m , g/cm ³	μ_m , cP	σ_{eq} , dyn/cm
25	0.1	0.9971	0.890	0.9014	0.729	0.996	0.905	17.3
30	0.01	0.9957	0.797	0.8970	0.681	0.995	0.811	24.1
	0.05							19.4
	0.1							17.0
	0.1	0.9881	0.546	0.8792	0.531	0.987	0.556	15.8
60	0.01	0.9832	0.466	0.8704	0.475	0.982	0.474	22.9
	0.05							17.8
	0.1							15.3
	3							3.8

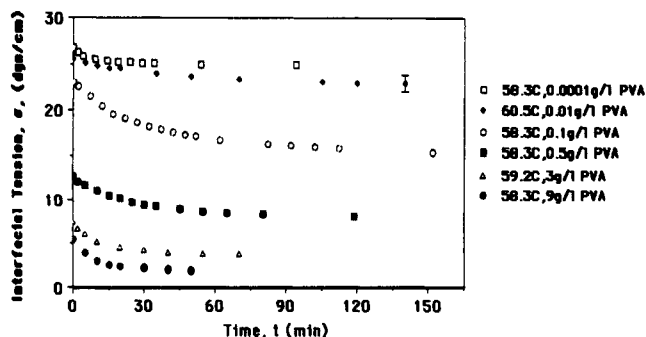


Figure 1. Evolution of interfacial tension with time for a system of styrene/water at various PVA concentrations.

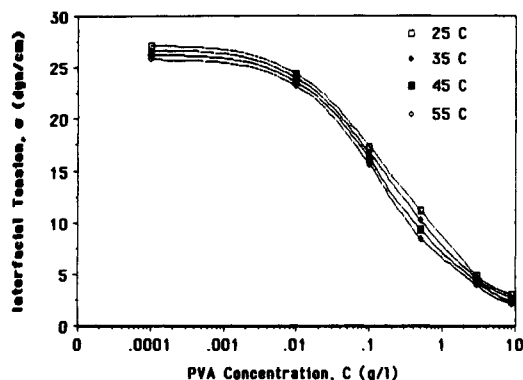


Figure 2. Dependence of interfacial tension on PVA concentration for a sequence of temperatures.

layer of PVA molecules. Nilsson et al. (1985) measured the interfacial tension of a VCM/water system in the presence of 0.1 g/L PVA. They suggested that diffusion of polymer to the interface determines the rate at which interfacial tension decreases with time. However, at higher PVA concentrations, i.e., 1 g/L for the VCM/water system, the observed reduction of interfacial tension with time cannot be simply explained by the diffusion of PVA molecules to the interface. In the latter case, Nilsson et al. (1985) suggested that PVA molecules are instantaneously transferred to the interface, though not in their most thermodynamically favorable conformation. As a result, the rate of equilibration is most likely controlled by reorganization of the PVA molecules on the surface. This may involve reconfiguration and packing of polymer molecules, as well as replacement of less surface-active groups in the interface by more hydrophobic ones. In Figure 1 experimental measurements of interfacial tension between styrene and water are plotted with respect to time for various PVA concentrations. It can be seen that as the PVA concentration increases, the time required for the system to reach equilibrium decreases.

In general, the surface tension of most liquids decreases with increasing temperature. A similar behavior was also observed for the interfacial tension of the present styrene/water system over the whole range of PVA concentrations tested. Actually, the steady-state value of the interfacial tension was found to vary approximately linearly with temperature. Figure 2 depicts the effect of PVA concentration on the equilibrium interfacial tension of a styrene/water system for various temperatures ranging from 25 to 55 °C. It appears that the surface tension is relatively independent of concentration up to about 0.01 g/L (10 ppm). For PVA concentrations higher than 10 ppm the surface tension decreases almost linearly on a semilog scale. A similar break-point behavior at 10 ppm was observed by Lankveld and Lyklema (1972) for a paraffin oil/water system in the presence of PVA with a

molecular weight of 24 000 and a degree of hydrolysis of about 98%. This transition is characteristic of "hydrophilic" PVA molecules—with a degree of hydrolysis greater than 90%—and appears between 10 and 100 ppm, depending on the molecular weight of PVA and its distribution. The shape of the interfacial tension vs concentration curve depends on the hydroxyl group content of the poly(vinyl alcohol) and especially upon the numbers of adsorbed and unadsorbed segments (Lankveld and Lyklema, 1972). For "hydrophobic" PVA in a paraffin oil/water system, the interfacial tension was shown to decrease gradually following smooth, convex curves with respect to concentration. This decrease was slightly more pronounced for a lower molar mass PVA, suggesting that the lower molecular weight PVA is more surface-active than PVA with a high molecular weight (Lankveld and Lyklema, 1972). The rather sharp transition of interfacial tension observed with respect to the concentration of hydrophilic PVA (Lankveld and Lyklema, 1972) is due to a distinct change in the physicochemical properties of solutions of PVA with a degree of hydrolysis of greater than 90% (Peter and Fasbende, 1964).

A possible explanation of the observed variation of interfacial tension with respect to PVA concentration (Figure 2) has been proposed by Lankveld and Lyklema (1972) based on the dependence of interfacial tension on (i) the number of adsorbed segments per unit area of the liquid-liquid boundary, (ii) the interaction free energy per segment in the loops of the adsorbed polymer molecules, and (iii) the average loop length. The combined effects of segmental adsorption, as well as loop interaction, tend to decrease the interfacial tension due to the appearance of steric repulsion forces. These effects contribute to the surface activity of PVA. In the region of low PVA concentration, Zwick (1965) suggested that there might be a complete and rapid unfolding of the very flexible PVA molecules, resulting in an extended conformation of PVA with a large number of segments per molecule in the interfacial region. The break point marks the onset of almost complete coverage of the interface and its saturation with molecules having an extended conformation. The rather steep decrease of interfacial tension at higher concentrations is probably due to increased adsorption of molecules and the appearance of strong loop repulsive forces. The conformation of adsorbed molecules will be initially random. However, as the number of adsorbed segments increases, the packing of the molecules in the surface layer increases up to the formation of a monolayer. In the present study, the monolayer formation appeared at concentrations higher than 3 g/L (Figure 2). Above this PVA concentration, no significant changes of the drop size distribution are expected.

Samaritan et al. (1986) measured the interfacial tension of a styrene/water system in the presence of various grades and concentrations of poly(vinyl alcohol). The molecular weight of PVA varied in the range of 25 000–80 000 and its degree of hydrolysis from 86 to 100 mol %. At a PVA concentration of 1 g/L with a degree of polymerization of 1600 and a blocky distribution of hydroxyl groups, they found that the interfacial tension decreased from 23.4 to 6.4 dyn/cm as the -OH content decreased from 99.5 to 86.5%. At the same concentration of PVA with a degree of hydrolysis of 86.5%, they observed only a slight increase of interfacial tension from 6.4 to 7.3 dyn/cm as the degree of polymerization changed from 1600 to 500. It is interesting to notice that corresponding measurements of interfacial tension in the presence of PVA having a random distribution of hydroxyl groups were substantially higher

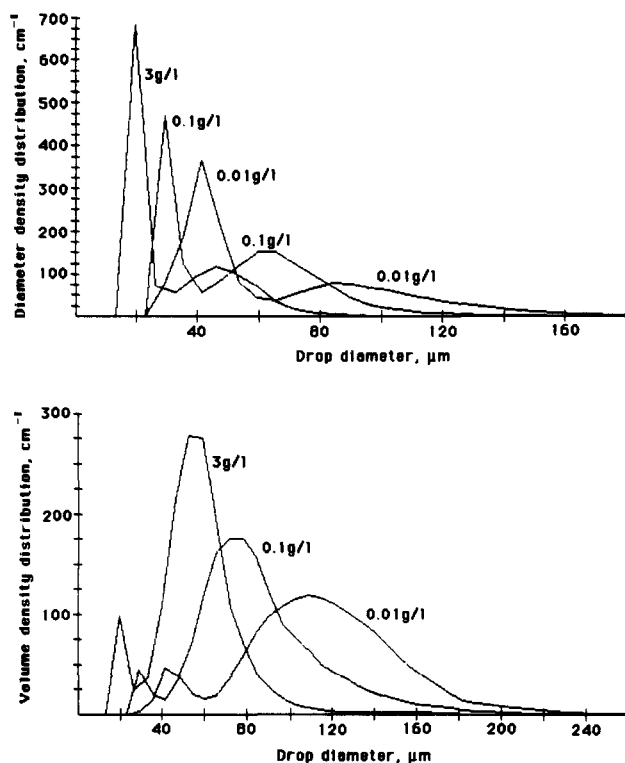


Figure 3. Steady-state diameter and volume density distributions for a system of 1% styrene in water at 60 °C and 300 rpm for different PVA concentrations.

than those obtained with PVA having a blocky distribution of hydroxyl groups. The same investigators reported that PVA with a degree of hydrolysis of 1600 and a blocky distribution of hydroxyl groups showed a decrease of the interfacial tension from 23.4 to 21.3 dyn/cm as the PVA concentration increased from 1 to 10 g/L. In the present work, the interfacial tension of a styrene/water system varied from 27 to 5 dyn/cm as the PVA concentration with a degree of polymerization of 500 changed from 0.0001 to 3 g/L (Figure 2).

In a two-phase dispersion system, the drop size distribution is determined by the relative contribution of breakage and coalescence mechanisms. Both processes are related to the drop surface energy, which is proportional to the interfacial tension. For a low-coalescing system, a decrease of the resistance to breakage by means of a reduced surface tension results in smaller drop sizes. The effect of stabilizer concentration on the steady-state drop size distributions at 60 °C and an agitation rate of 300 rpm is shown in Figure 3. The drop diameters vary from 15 to 240 μm , and the diameter density distribution follows a bimodal form. As the interfacial tension decreases from its maximum value of 22.9 dyn/cm to a minimum of 3.8 dyn/cm, both peaks of the distribution shift to smaller sizes. Actually, the large-diameter peak changes from 90 to 50 μm and the small-diameter peak from 40 to 20 μm . Bimodal drop size distributions have been scarcely reported in the literature (Ward and Knudsen, 1967; Hong and Lee, 1985; Laso et al., 1987). This may be attributed to errors resulting from the photographic method typically used for measuring the drop size distributions (Mlynek and Reshnick, 1972; Chatzi et al., 1991) and the tendency of the observer to preferentially count larger drops while neglecting smaller ones (Laso et al., 1987). The laser diffraction technique used in this study shows increased sensitivity in measuring the small-size portion of the drop size distribution, which is more pronounced in the diameter density distributions.

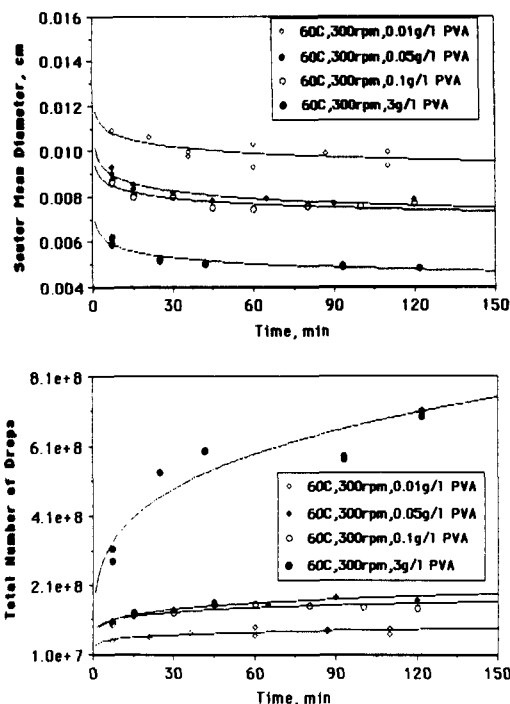


Figure 4. Effect of PVA concentration on the evolution of the Sauter mean diameter and the total number of drops with agitation time.

For low-coalescing systems the observed bimodality of the drop size distributions is generally attributed to the drop breakage process. Ward and Knudsen (1967) obtained drop size distributions characterized by two peaks from photographs of a flowing dispersion. As circulation proceeded, the position of the peaks remained relatively constant with respect to diameter but their relative frequency changed. The median volume of the low-diameter peak was found to vary only from 0.03 to 4% of the median volume of the high-diameter peak. As a result, they suggested that drop breakage was of an erosive type, according to which a droplet breaks off a much larger drop, leaving it virtually unchanged. For a noncoalescing liquid-liquid system Brown and Pitt (1972) measured photographically drop size distributions of a bimodal form that were affected by the dispersed phase holdup. The bimodality was attributed to a breakage process that involves an orderly removal of small elements from drops whose sizes are approaching the maximum stable value. Hong and Lee (1983) observed bimodal distributions by a microphotographic technique. The multimodality was more pronounced at short agitation times, and the peaks exhibited a shift to smaller diameters as the agitation time increased. Thus, the production of a bimodal distribution from a break-up process has to be attributed to erosive breakage involving removal of a number of small drops from a larger one. This gives rise to two superimposed distributions with the modes corresponding to the daughter or satellite drops, depending on their volume ratio (Brown and Pitt, 1972; Chatzi et al., 1989). There seems to be no indication that bimodality is a result of an increasing breakage resistance due to a membranelike structure developing at the drop surface. In fact, bimodal distributions were observed even at the low PVA concentration of 0.01 g/L (Figure 3), reaching an equilibrium loose arrangement of PVA molecules with an extended conformation in the interfacial region.

The variation of the average drop size and total number of drops with agitation time is shown in Figure 4 for different stabilizer concentrations. It can be seen that an

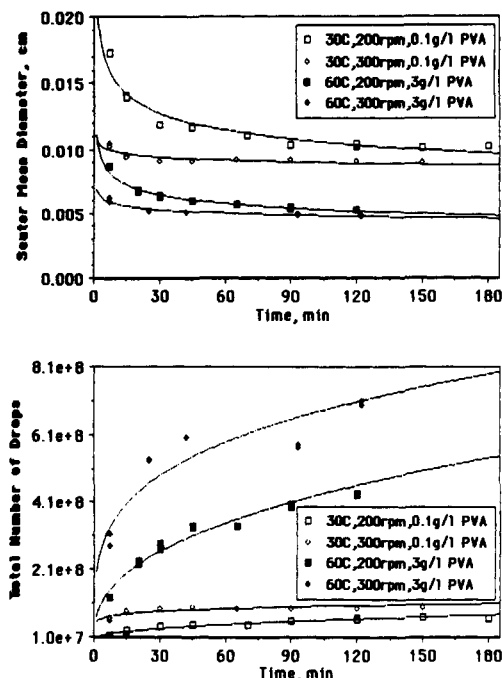


Figure 5. Effect of impeller speed on the evolution of the Sauter mean diameter and the total number of drops with agitation time.

increase of PVA concentration from 0.01 to 3 g/L results in a decrease of the Sauter mean diameter from 100 to 50 μm . On the other hand, the total number of drops in the system is increased by 1 order of magnitude. The average drop size and the total number of drops calculated at PVA concentrations of 0.05 and 0.1 g/L are almost identical. This can be explained in view of the small difference in the corresponding interfacial tension values (about 5 dyn/cm), as shown in Figure 2.

The effect of agitation rate on the average drop size and the total number of drops is shown in Figure 5. Notice that at lower agitation rate the reduction of the Sauter mean diameter with time is more gradual. This can be attributed to the larger rate of primary breakdown at higher impeller speeds (Bajpai et al., 1975). The evolution of drop size distribution with time is shown in Figures 6 and 7 for a temperature of 60 °C, a PVA concentration of 3 g/L, and agitation rates of 300 and 200 rpm, respectively. At 300 rpm (Figure 6), the large-size peak shifts from 60 to 50 μm and the small-size peak from 30 to 20 μm as the agitation time increases. A similar behavior is observed at 200 rpm, as illustrated in Figure 7. However, a more gradual reduction of drop size is experienced at the lower agitation rate, especially during the initial period. In this case, the large-size peak shifts from 70 to 50 μm and the small-size peak from 30 to 25 μm as the agitation time increases. A similar behavior was observed for all other transient experiments. At both agitation levels (200 and 300 rpm) the system assumed its characteristic bimodal shape of the size distribution in less than 5 min. Further stirring caused a reduction of the drop size without substantially altering the shape of the distribution.

Correlations for the Steady-State Mean Drop Size and Minimum Transition Time. Droplets in a turbulent flow field are exposed to inertial forces due to velocity fluctuations, as well as to viscous shear forces. Breakage in agitated vessels may occur in regions of high shear stress near the agitator blades or may be caused by turbulent velocity and pressure variations along the surface of a single droplet (Shinnar, 1961).

For local isotropic turbulent flow and if the droplet is much larger than the microscale or turbulence, η , the

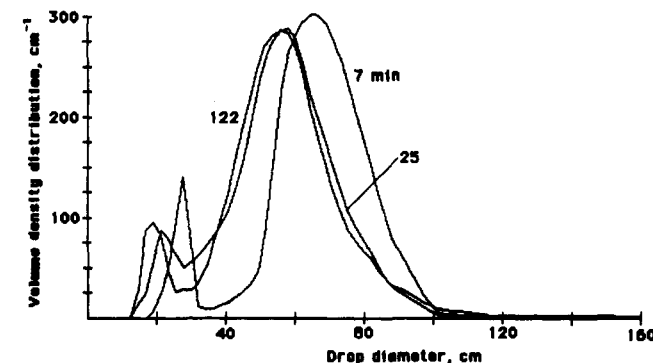
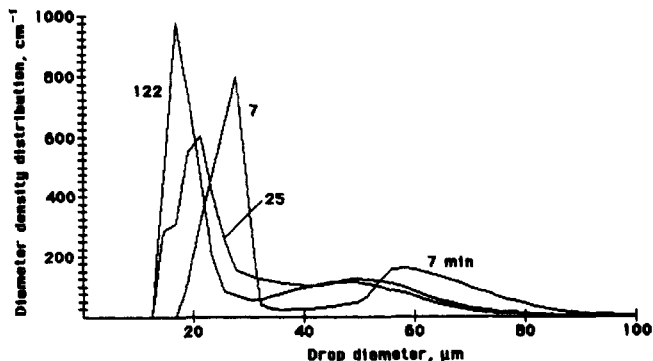


Figure 6. Transient diameter and volume density distributions for a system of 1% styrene in 3 g/L aqueous PVA solution at 60 °C and 300 rpm and for agitation times of 7, 25, and 122 min.

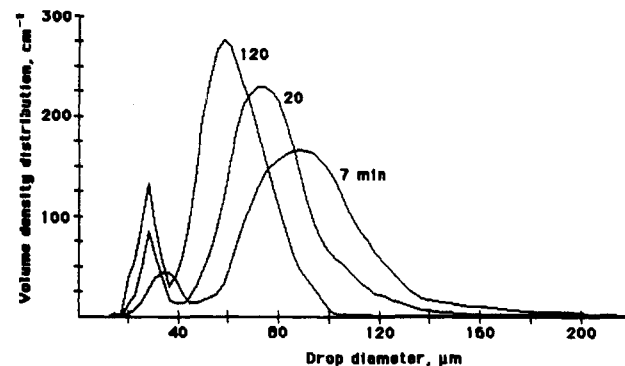
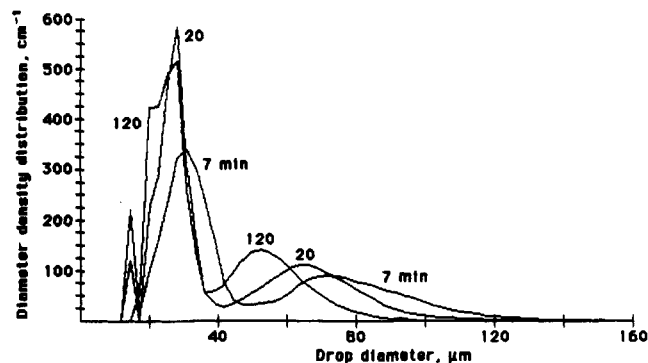


Figure 7. Transient diameter and volume density distributions for a system of 1% styrene in 3 g/L aqueous PVA solution at 60 °C and 200 rpm and for agitation times of 7, 20 and 120 min.

viscous forces can be neglected (Shinnar, 1961). Local isotropy for this system has been shown previously (Chatzi et al., 1989). The microscale of turbulence is given by

$$\eta = (v_c^3/\bar{\epsilon})^{1/4} \quad (3)$$

where v_c is the kinematic viscosity of the continuous phase

and $\bar{\epsilon}$ is the average energy dissipation per unit mass, that is, the power input per unit mass in the volume swept by the impeller, P_{MI} . For turbine or flat-bladed impellers the volume swept out by the impeller as it rotates is $(\pi/4)D_1^2W_1$, where D_1 and W_1 are the impeller diameter and blade width, respectively (McManamey, 1979). Therefore, the power input per unit mass into this region is

$$P_{MI} = 4P/\pi\rho_c D_1^2 W_1 \quad (4)$$

where P is the power input to the impeller and ρ_c is the density of the continuous phase of the dispersion. P can be calculated as

$$P = P_0 \rho_c (N^*)^3 D_1^5 \quad (5)$$

where P_0 is the power number of the six-blade turbine impeller. For sufficiently large Reynolds numbers, the power number is constant. For the system used in this study (a six-blade turbine impeller with $D_1/W_1 = 5$), P_0 was found to have a constant value of 5 (Uhl and Gray, 1966; Nienow and Miles, 1971). Thus, the average energy dissipation per unit mass, $\bar{\epsilon}$, can be expressed as

$$\bar{\epsilon} = \frac{100}{\pi} (N^*)^3 D_1^2 \quad (6)$$

As calculated by using eqs 3 and 6, for the experimental conditions used in this study, the microscale of turbulence, η , ranges from 8 to 18 μm , as shown in Table I. Therefore, for the large-size breaking drops the viscous forces may be neglected in comparison to the inertial forces, and droplet breakage is predominately a result of turbulent pressure or velocity fluctuations.

Various equations have been proposed in the literature for the maximum and average drop size in a dispersion, depending on the drop breakage mechanism and the relative importance of breakage as compared to coalescence. Leng and Quaderer (1982) derived equations for an idealized cylindrical agitator and drop dispersion based on shear stresses, as well as on turbulent forces, predicting a $(N^*)^{-0.8}$ dependence of the maximum stable drop diameter for breakage caused by turbulence. For fully baffled vessels equipped with a turbine impeller and if breakage is due to turbulent velocity fluctuations, Shinnar (1961) derived the following expression for the dependence of the Sauter mean diameter on the vessel geometry and physical properties of the dispersion system:

$$d_{32}/D_1 = k_1 (N_{We})_T^{-0.6} \quad (7)$$

where $(N_{We})_T = \rho_c (N^*)^2 D_1^3 / \sigma$ is the Weber number of the main flow. The equation has been derived for low-coalescing systems based on the assumption of local isotropy and the Kolmogoroff theory of universal equilibrium (Shinnar and Church, 1960; Shinnar, 1961) and was verified by a large number of investigators (Tavlarides and Stamatoudis, 1981).

The calculated values of the Weber and Reynolds numbers for the present study are shown in Table I. Please note that the equilibrium value of interfacial tension was used for the Weber number calculation, as measured by using the Wilhelmy plate method. The Reynolds number of the main flow is defined as $(N_{Re})_T = N^* D_1^2 / \nu_m$ and, in all cases, is larger than 20 000. This value is well above the limit of 10 000 proposed by Rushton et al. (1950) for local isotropy. At high Reynolds numbers ($(N_{Re})_T > 10\,000$) droplet diameters satisfy the condition $L \gg d \gg \eta$, where L and η are the macroscale and microscale of turbulence, respectively.

The parameter k_1 in eq 7 was calculated by fitting the experimentally determined steady-state Sauter mean diameters to the Weber number using a least-squares al-

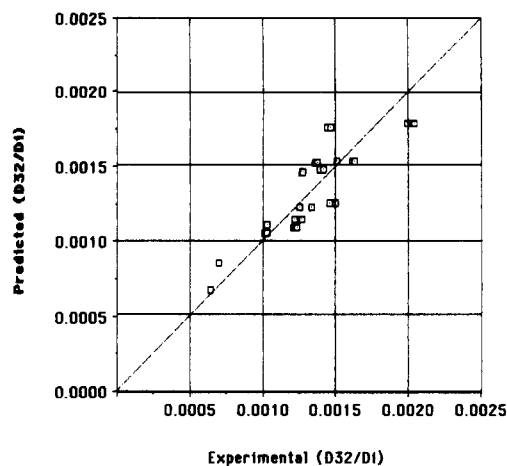


Figure 8. Comparison between experimental and predicted values of the Sauter mean diameter according to eq 7.

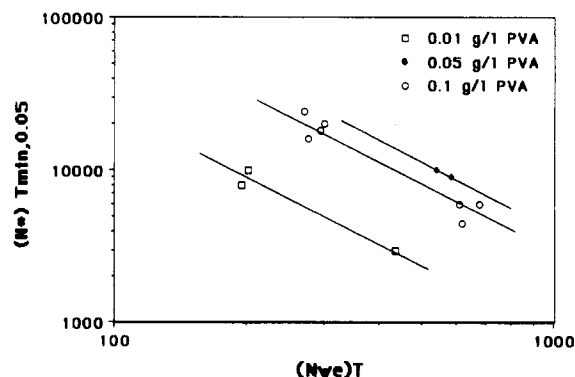


Figure 9. Dependence of the dimensionless minimum transition time, $N^*t_{\min,0.05}$ on the Weber number of the main flow, $(N_{We})_T$.

gorithm. The estimated value of k_1 was 0.046 ± 0.002 with a correlation coefficient of 0.80. A comparison between the predicted and experimental values of the Sauter mean diameter is shown in Figure 8. The estimated value of parameter k_1 in eq 7 is smaller than the values reported in the literature ($k_1 = 0.051\text{--}0.081$). This might be due to the fact that values of average diameters obtained by the present laser diffraction technique are generally smaller than those measured photographically. As discussed in part 1 (Chatzi et al., 1991), the laser diffraction technique shows higher sensitivity to the small-size droplets. It should be mentioned that, at low PVA concentrations (0.01 g/L), the measurement of d_{32} was less reliable due to inefficient stabilization of the suspension and difficulties in handling the sample.

The minimum transition time required for the system to reach steady state is important for design purposes. During the initial period of mixing, the Sauter mean diameter approximately follows an exponential decrease (Figures 4 and 5) to its final equilibrium drop size, d_{32}^* . The minimum transition time, $t_{\min,0.05}$, is defined as the time required for the average drop size to reach 95% of the d_{32}^* value.

The dimensionless minimum transition time, $N^*t_{\min,0.05}$ was found to depend on the Weber number according to the equation

$$N^*t_{\min,0.05} = k_2 (N_{We})_T^{-1.5} \quad (8)$$

as shown in Figure 9. Determination of the exact dependence of parameter k_2 on the interfacial tension and possibly other physical properties, as well, requires a more extensive set of on-line experimental data. Also, a Levenberg-Marquardt algorithm was used in an attempt to

relate $N^*t_{\min,0.05}$ with various dimensionless groups, according to a general correlation obtained by Hong and Lee (1985):

$$N^*t_{\min} = k_2(\mu_d/\mu_c)^a N_{Fr}^b N_{We}^c N_{Re}^d \quad (9)$$

where D_I and D_T are the impeller and tank diameters, respectively, and N_{Fr} is the impeller Froude number defined as $N_{Fr} = D_I(N^*)^2/\rho_c(g\Delta\rho)$. $\Delta\rho$ is calculated as $|\rho_c - \rho_d|$, and g is the acceleration due to gravity. However, it was not possible to estimate the parameters that appear in eq 9 within satisfactorily narrow confidence limits.

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