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Influence of Small Amounts of Additives on Gas Hold-Up, Bubble Size, and Interfacial Area

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The gas–liquid interfacial area, which is determined by the gas hold-up and the Sauter mean bubble diameter, determines the production rate in many industrial processes. The effect of additives on this interfacial area is, especially in multiphase systems (gas–liquid–solid, gas–liquid–liquid), often not understood. The addition of a third phase can cause the gas–liquid system to become completely opaque, which means that conventional techniques to study the interfacial area cannot be used. For this reason ultrasonic spectroscopy was used in this work to study the interfacial area and the bubble size distribution in these systems. The influence of different additives on the interfacial area was studied in a stirred vessel and in a bubble column under coalescing and noncoalescing conditions. It was found that the addition of toluene to a noncoalescing electrolyte system decreased the interfacial area to a large extent by turning it into a coalescing system, due to the interaction between gas bubbles and liquid organic droplets. Furthermore, around the toluene solubility concentration, both the gas hold-up (measured using an electric conductivity technique) and the interfacial area increased to values similar to those observed in noncoalescing systems. The cause of this remarkable phenomenon lies probably in the presence of a small toluene layer around the gas bubbles, which can be formed beyond the solubility point. This layer is absent at concentrations below the solubility limit and a large surface tension gradient exists between those two situations, which can be responsible for the sharp change in coalescence behavior.

1. Introduction

In chemical engineering the rate of mass transfer between two different phases often directly determines the production rate of the process (e.g., the gas absorption rate in gas–liquid systems). This mass transfer rate is directly proportional to both the mass transfer coefficient and the specific interfacial area between the different phases, respectively. Both parameters depend mainly on the (local) hydrodynamic situation inside the system. For design purposes as well as for improvement of existing production facilities, it is very important to have a better insight into the phenomena that affect these parameters. The present study focuses on the pronounced effects of small amounts of additives on the gas–liquid mass transfer rate, with emphasis on the effects on the interfacial area. In industrial applications different kinds of additives are found in aqueous systems: electrolytes, surfactants, polar and nonpolar organic components, and solid particles (hydrophilic or hydrophobic) in slurry systems. It is known from the literature that small amounts of certain additives, typically <1%, can have substantial effects (up to a factor of 3) on the interfacial area, which is directly related to the bubble size distribution and the gas hold-up. The average bubble size and the gas hold-up depend mainly on three processes that are occurring in gas–liquid systems: bubble formation, bubble coalescence, and bubble breakup. In the case of electrolytes and surfactant added systems, the influence of these processes on the average bubble size and gas hold-up has

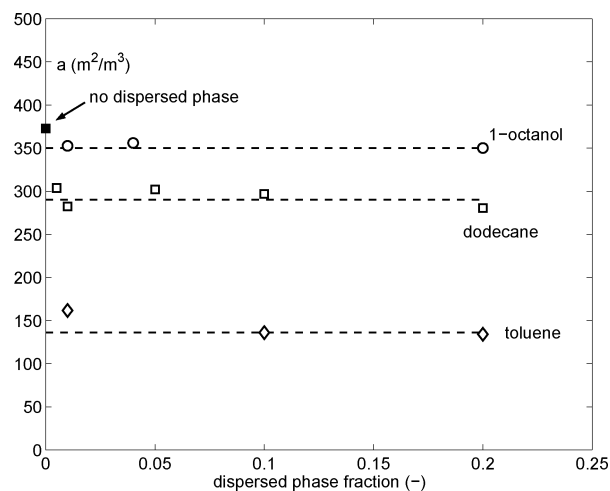


Figure 1. Effect of different organic additives on the gas–liquid interfacial area in a 0.5 M/0.5 M $K_2CO_3/KHCO_3$ solution measured using the Danckwerts plot technique.

been frequently investigated^{1–3} and the observed phenomena are relatively well understood. However, for other types of process systems this effect is not understood and thus not predictable.

An example of such an effect on the interfacial area that is still not understood is demonstrated in Figure 1. The data of Cents et al.⁴ are presented and contain interfacial areas, as measured using a chemical method (the Danckwerts plot technique⁵). It can be seen that the addition of small amounts of organic phase can have a large influence on the interfacial area in this particular 1 M electrolyte solution. Especially the large decrease (factor of 2.5) upon small additions of toluene is remarkable and cannot be explained. Also the addition

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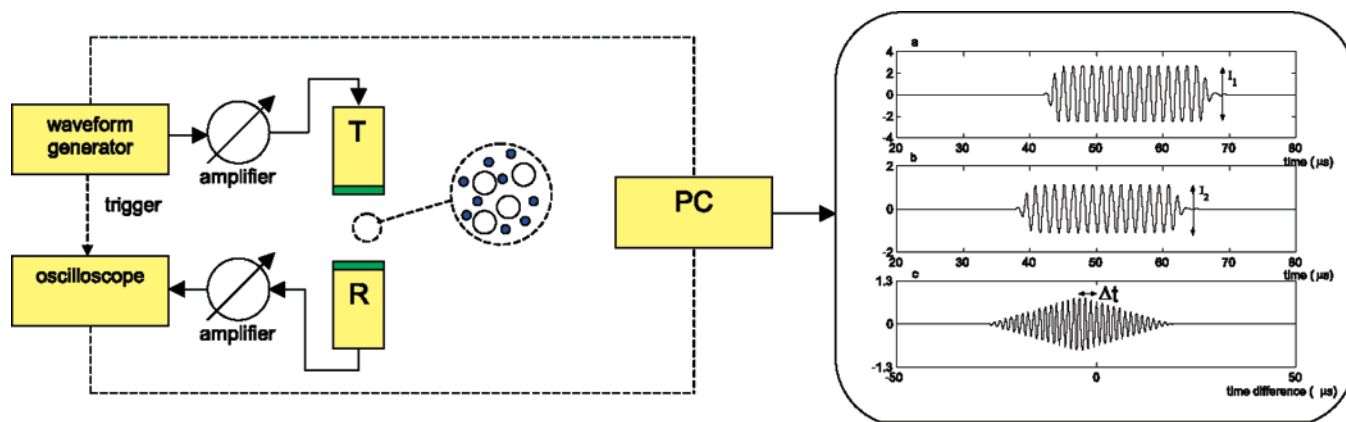


Figure 2. Setup of the ultrasonic measurement system and signal analysis in the PC.

of solid particles can influence the mass transfer characteristics already at small volume fractions (see e.g. Ozkan et al.⁶). At solid contents as low as 0.1 vol %, an increase in the volumetric mass transfer coefficient as high as 3 was observed by Ozkan et al.⁶ However, it was not clear whether the increase must be attributed to the mass transfer coefficient or to the interfacial area. From these two examples, it can be concluded that it is very important to have a better understanding of these effects, especially for design purposes of gas–liquid–liquid (G–L–L) systems and gas–liquid–solid (G–L–S) systems.

The scope of this research is to validate the results from previous work⁴ using a physical measurement technique and to find the root cause of these effects (in terms of coalescence, breakup, and bubble formation). To achieve this, both the gas hold-up and average bubble size under different circumstances (for example, coalescing vs noncoalescing systems, with and without bubble breakup) will be measured, respectively.

Measurement of the gas–liquid interfacial area in three-phase systems is more difficult than in two-phase systems, because three-phase systems may become opaque at low fractions of the dispersed solid or liquid phase, due to a difference in refractive indices of the various phases. This means that conventional physical measurement techniques for determination of the interfacial area, like photography (combined measurement of bubble size distribution and gas hold-up) and laser scattering, are more difficult to operate in these systems and often cannot be used.

For this reason a technique is developed, which can measure the bubble size distribution and the gas hold-up independently in opaque media making use of ultrasonic spectroscopy. An additional advantage of this latter technique is the possibility to measure the size distribution and phase hold-up of the dispersed solid or liquid phase together with the gas-phase properties. In this way important information can be obtained for better understanding of the mass transfer mechanism in G–L–L or G–L–S three-phase systems.

2. Experimental Method

2.1. Measurement of Size Distribution. The experimental technique is based on the difference in ultrasonic wave propagation in a dispersion of particles (solid particles, gas bubbles, or liquid droplets) compared to propagation in the continuous liquid. The ultrasonic velocity (c) and attenuation coefficient (α) of a multi-phase system are directly related to the physical prop-

erties of the individual phases (e.g., density, compressibility). They are also dependent on the size and volume fraction of the particles and the frequency of the transmitted wave. The theory of ultrasonic propagation in multiphase systems with an ensemble of particles was first derived by Epstein and Carhart⁷ and Allegra and Hawley.⁸ The ultrasonic velocity and the attenuation coefficient are defined as

$$c = \frac{d}{t} = \frac{d}{d/c_w(T) + \Delta t} \quad (1)$$

$$\alpha = \frac{-\ln(I_e/I_w)}{d} + \alpha_w(T) \quad (2)$$

Both quantities are difficult to measure directly but have to be determined in reference to a single solvent, which was water in the present study (c_w and α_w). Both properties are strongly dependent on temperature, and therefore the temperature needs to be known accurately (± 0.05 K). In these equations d is the path length of the measurement, and I_w and I_e are the intensities in the continuous phase and in the dispersion, respectively. Δt is the time difference between the signal that has travelled through the dispersion and a reference signal (that has travelled the same distance through the continuous phase).

The experimental setup (Figure 2) consists of an arbitrary waveform generator (AWG), which transmits any desired electric signal to a piezoelectric transducer (T). The transducer converts the electric signal to a pressure wave that is received in a second transducer (R) where the latter is converted back into an electric signal, which is acquired with a digital oscilloscope. Simultaneously, a trigger signal is transmitted to the oscilloscope ensuring that in every measurement the starting point, $t = 0$, is known accurately. Currently the speed of the system is determined by the data acquisition system and is 33 Hz. A tone-burst signal, a limited number of cycles of a certain frequency, is used for determination of the velocity and the attenuation coefficient, which has the advantage of a low power input and the absence of signal disturbances (which may not be the case using continuous signals). The time difference between the signal in the dispersion and the reference signal can be determined using a cross-correlation function, which is also shown in Figure 2. To determine the size distribution of large bubbles as well as small droplets or particles, a frequency range of 100 kHz up to 100 MHz can be covered. The limit of

the technique in terms of measurable gas–liquid interfacial area is currently determined by the large amplifier and is around $1000 \text{ m}^2/\text{m}^3$ (at 2 cm path length). For more details of the method and the equipment used, the reader is referred to Cents et al.⁹

2.2. Determination of Phase Hold-Up. From the ultrasound measurements it is, in principle, possible to determine both the size distributions as well as the phase hold-up of the particles, bubbles, and droplets. However, Cents et al.⁹ have shown that in the case of a gas–liquid system multiple solutions can exist with different types of bubble size distributions and slightly different gas hold-ups. The interfacial area, however, determined via the ultrasonic technique, is not affected by this multiplicity and is determined very accurately. The above-mentioned complication implies that for the determination of the exact bubble size distribution the (local) gas hold-up is required. A reliable method to measure the gas hold-up uses the ratio of the electric conductivity in the continuous liquid phase and in the gas–liquid dispersion (G_ℓ/G_w), which was applied by among others Yianatos et al.¹⁰ The local gas hold-up (ϵ) can be determined with

$$\frac{G_\ell}{G_w} = \frac{1 - \epsilon}{1 - 0.5 \ln(1 - \epsilon)} \quad (3)$$

The overall gas hold-up can be measured by comparing the liquid height in the reactor with and without gas phase present, according to

$$\langle \epsilon \rangle = 1 - \frac{H_w}{H_\epsilon} \quad (4)$$

The interfacial area (a) of the bubble size distribution can be calculated from the Sauter mean diameter (d_{32}) and the phase hold-up (ϵ) according to

$$a = \frac{6\epsilon}{d_{32}} \quad (5)$$

When a nonpolar solvent is used as the continuous phase, this technique cannot be applied due to the absence of electrical conductivity in this phase, and the local gas hold-up should be determined using an alternative technique (for instance with a fiber optic probe).

The overall interfacial area (a) in the reactor can be estimated using the overall gas hold-up ($\langle \epsilon \rangle$) and the Sauter mean (d_{32}) diameter for the complete reactor. Both parameters are not necessarily the same as the locally determined values.

2.3. Experimental Setup. The experimental setup consists of a reactor vessel (15 cm diameter) with a working volume of 3.2 L, which can be operated in both a bubble column and a stirred vessel mode, respectively. The gas is distributed in the reactor through a sintered porous plate (type P1, 90–150 mm), and the gas flow rate is controlled using a mass flow controller. When the reactor is operated as a stirred vessel, a Rushton turbine with a variable stirring speed (5 cm in diameter) is placed 6 cm above the porous plate. Four baffles ensure adequate mixing in the reactor. The temperature is measured within 0.1°C using a PT-100. The ultrasonic probe was placed 11 cm above the porous plate in the center of the reactor. The path length between the transducers in the probe can be varied between 1 and 67 mm and can be adjusted to the amount of attenuation

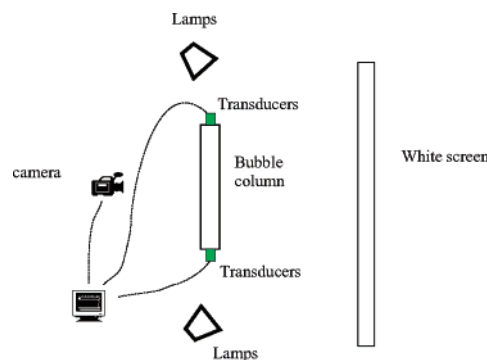


Figure 3. Setup for the comparison of the ultrasonic technique with imaging using a digital camera.

of the ultrasonic waves. It is necessary to compare this distance to the size of the measured particles, bubbles, or droplets, because the ratio of the distance between the transducers and the particles should be at least 20 to ensure a representative dispersion sample between the transducers. The conductivity probe consisted of two stainless steel electrodes and had an exactly equal shape compared to the ultrasonic probe.

After the system under investigation was replaced with another system, the system was cleaned thoroughly. Surface tension measurements were performed in order to check if all impurities were removed.

3. Results and Discussion

3.1. Validation of the Techniques. A comparison of ultrasonic spectroscopy with a digital camera technique was performed in a flat ($20 \times 3 \times 150 \text{ cm}$) bubble column using the ultrasonic technique in combination with the electrical conductivity method and using a digital camera technique with digital image analysis, simultaneously (see Figure 3). The camera was placed 10 cm in front of the column, and the ultrasonic transducers were mounted into the wall of the column (the measurement path length was 20 cm). Measurement of the exact size distribution using the ultrasonic technique was difficult, mainly due to the small attenuation and ultrasonic velocity differences. These differences were small due to low gas hold-ups that were applied ($\approx 1\%$), which was necessary for the digital camera technique to work optimally. The interfacial area could, however, be determined accurately, and together with the measurement of the gas hold-up using the electrical conductivity technique, the Sauter mean bubble diameters were calculated. As can be seen in Figure 4, a good agreement between the two methods was obtained for coalescing (air–water) and non-coalescing (air–water–0.5 g/L octanol) systems, respectively.

Furthermore, the electrical conductivity technique for the measurement of the gas hold-up was compared to two types of height reading. Under conditions where standard height reading is difficult (in a turbulent vessel), an inclined tube¹¹ can be used, in which the total liquid height can be determined with a higher degree of accuracy. The experiments were performed in the small bubble column, in which a porous plate gas disperser assured a nice homogeneous flow pattern so that local and overall gas hold-up are comparable. Also standard height reading was possible due to the homogeneous flow and the nonturbulent surface. Tap water was used as the liquid phase to allow the conductivity

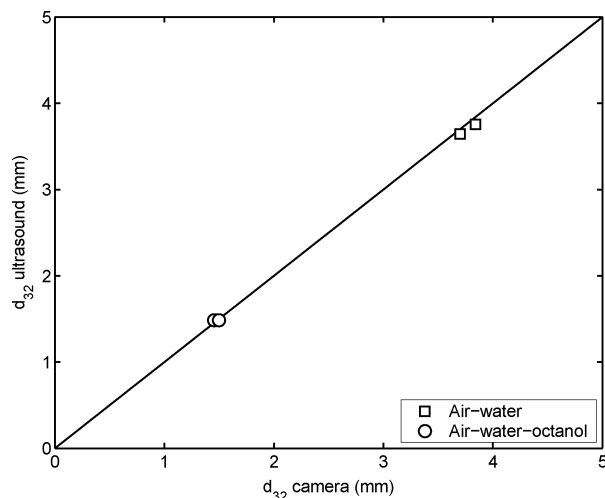


Figure 4. Parity plot of the Sauter mean diameter obtained with the ultrasonic technique and with a digital camera technique.

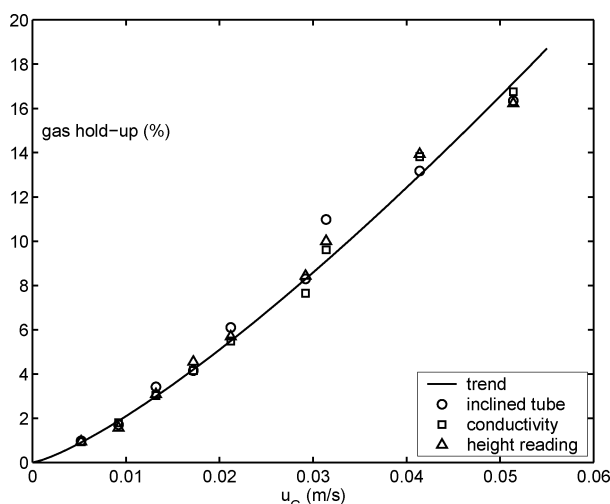


Figure 5. Cross-validation of different methods for gas hold-up measurement.

technique to work optimally. The results of the three methods are presented in Figure 5.

As is shown in Figure 5, the agreement between the three methods is very good. The maximum relative deviation from the average is 7.6%, the average relative deviation is 3.6%, and the error seems to be randomly oriented. This result shows that the conductivity method can be used for gas hold-up measurement in the stirred vessel.

3.2. Ultrasonic Velocity and Attenuation Coefficient Profiles. To be able to measure the size distribution of the dispersed phase(s) in a two- or three-phase system, the ultrasonic velocity and the attenuation profiles should contain information in the frequency region where the effect on the ultrasonic parameters is characteristic for the size of the particles. The presence of bubbles in the range of 1–4 mm affects the velocity and the attenuation mainly in the low-frequency regime (0.1–1 MHz). Particles and droplets usually are much smaller and cause large effects at higher frequencies. In Figures 6 and 7, the ultrasonic velocity and attenuation coefficient profiles are presented of an aerated dispersion of hexadecane in water. The large increase in the velocity at the lower frequencies is due to the gas bubbles present in this system, whereas the effects at higher frequencies originate from the presence of the

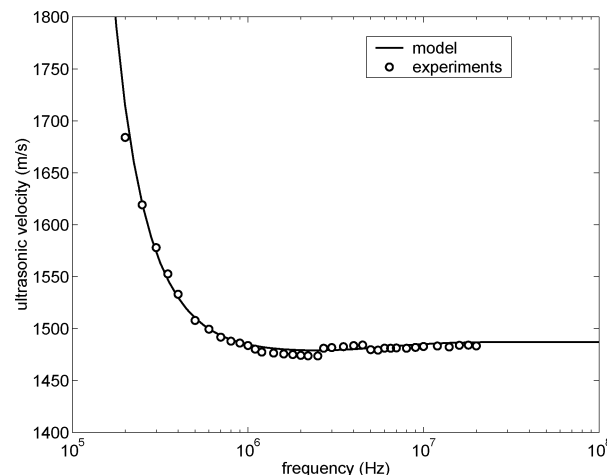


Figure 6. Ultrasonic velocity vs frequency profile of air–water–hexadecane measured in the bubble column. $u_G = 2.6$ cm/s. The gas hold-up and Sauter diameter of hexadecane and air are determined using the theory of ultrasonic propagation: $\epsilon_{\text{AIR}} = 6.6\%$, $\epsilon_{\text{HEXA}} = 6.3\%$, $d_{32,\text{AIR}} = 2.1$ mm, $d_{32,\text{HEXA}} = 0.67$ mm.

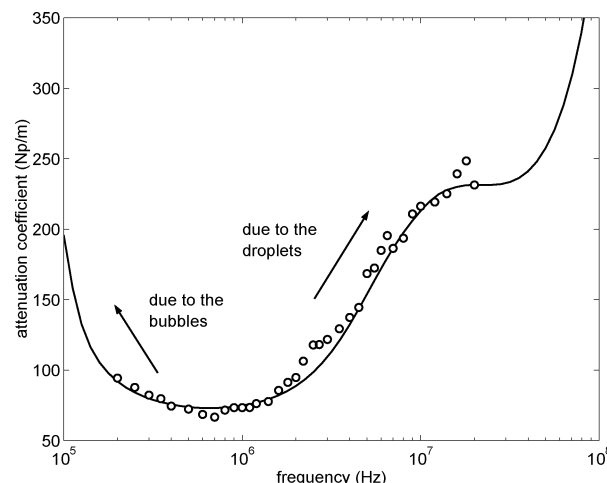


Figure 7. Attenuation coefficient vs frequency profile of air–water–hexadecane measured in the bubble column.

droplets. As indicated in Figure 7, the attenuation coefficient profile contains influences of both dispersed phases. Examples of velocity and attenuation profiles of G–L, S–L, and G–L–S systems can be found in Cents et al.⁹

3.3. Air–Aqueous Systems. To study the effects of different additives on the interfacial area, measurements are performed in a stirred vessel and in a bubble column. In both cases the gas (air) was distributed through a porous plate, which means a similar initial bubble size can be assumed. In the stirred vessel both coalescence of bubbles as well as breakup are important, due to the high energy dissipation especially in the impeller region. The bubble column is operated in the homogeneous regime, because of the low superficial velocities ($0.2 < u_G < 3$ cm/s) as indicated by Deckwer.¹² In this regime breakup of bubbles is relatively unimportant due to the low energy dissipation and the bubble size is mainly determined by coalescence phenomena just above the gas distributor (chain bubbling). After this initial coalescence region, the bubbles are rising with an approximately constant velocity. In this section results are presented of coalescing (air–tap water) and noncoalescing systems (0.5 M KCl and 0.5 M/0.5 M $\text{K}_2\text{CO}_3/\text{KHCO}_3$ buffer solutions). Tap water was used to improve the accuracy of the gas hold-up mea-

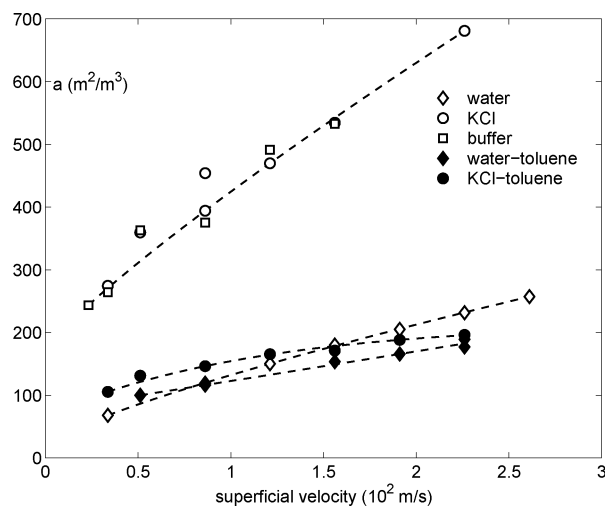


Figure 8. Gas-liquid interfacial area of different systems as a function of the superficial velocity in the stirred vessel.

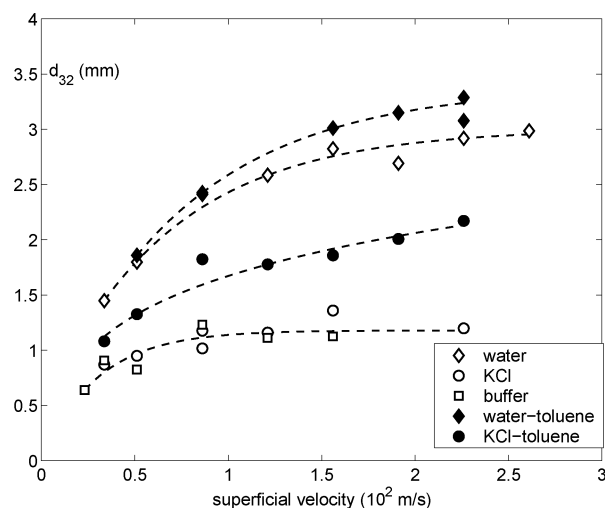


Figure 9. Sauter mean diameter of different systems as a function of the superficial velocity in the stirred vessel.

surement using the electrical conductivity technique. It was verified that the use of tap water did not significantly influence the determination of the interfacial area, when compared to measurements with deionized water. Although the measured quantities are the interfacial area (using the ultrasonic method) and the gas hold-up (using the conductivity technique), the interfacial area, defined by eq 5, and the Sauter mean diameter, which is a very characteristic parameter, are presented.

The results for the stirred vessel are shown in Figures 8 and 9. As expected from the work of Craig et al.¹³ the applied electrolyte concentration seems high enough to prevent coalescence of the gas bubbles. In the electrolyte systems the interfacial area is a factor of 3–4 higher compared to the coalescing air–water system. In the calculation of the Sauter mean diameter in the electrolyte solutions, the overall gas hold-up was applied instead of the local hold-up, because the conductivity technique failed due to the low resistivity in the solution. This did not affect the results to a large extent, owing to the homogeneous nature of the systems. The bubble size distribution was narrow (variance < 0.1 mm) in the electrolyte solutions and the Sauter mean diameter was around 0.8–1.2 mm, which was considerably lower compared to the air–water system (1.5–3 mm).

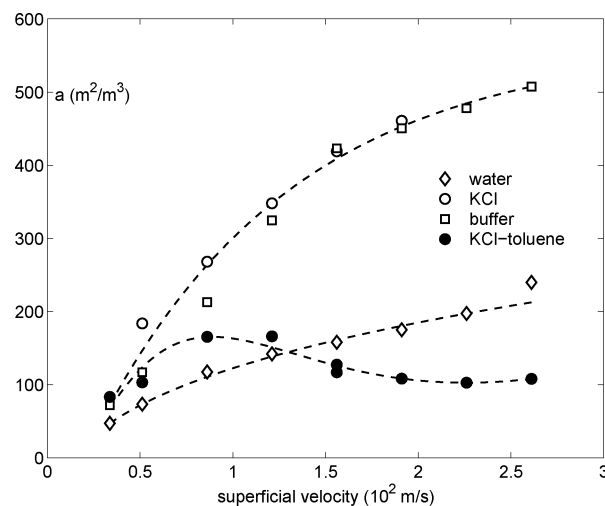


Figure 10. Gas-liquid interfacial area of different systems as a function of the superficial velocity in the bubble column.

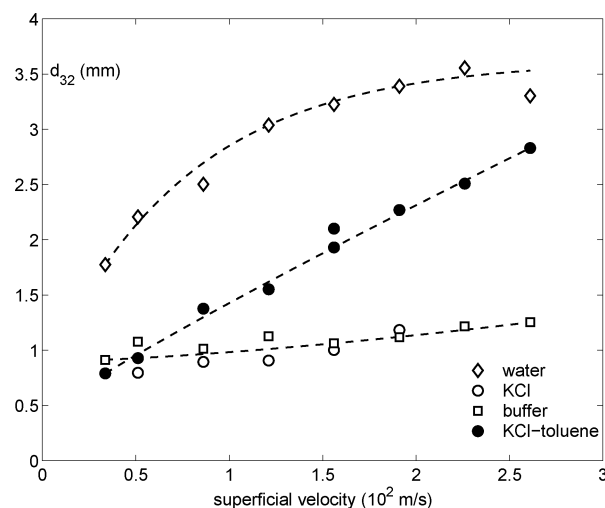


Figure 11. Sauter mean diameter of different systems as a function of the superficial velocity in the bubble column.

These bubble sizes are in the range of values commonly observed in coalescing and noncoalescing aqueous systems. In the bubble column similar trends are observed, as is shown in Figures 10 and 11.

3.4. Air–Electrolyte–Toluene System. The influence of toluene on the interfacial area and bubble size distribution was studied in the stirred vessel and in the bubble column under coalescing and noncoalescing conditions using a toluene volume fraction of 2.5% and is visualized in Figures 8–11. The addition of toluene to an electrolyte solution in the stirred vessel reduced the interfacial area to values of the same order of magnitude as in the coalescing air–water system. The hydrodynamic conditions in the tank, however, are in the presence of toluene completely different compared to the coalescing system. A very broad size distribution was obtained in this case, and the presence of very large (2–3 cm) bubbles rising very fast through the reactor was observed visually. Furthermore, a certain fraction of microbubbles was required to be present in the bubble distribution, to be able to get a reasonably good fit with the scattering model on the experiments. This was also observed in an air–water–toluene system and is described more extensively by Cents.¹⁴ This indicates that the ultrasound technique can be used to quantify

different shapes of distributions, but further study is necessary to determine the exact shape of the distributions.

The interfacial areas measured using this physical measurement technique are in good qualitative agreement with the results obtained in our previous work (in a comparable stirred vessel with the gas distributed from a single orifice) using the Danckwerts plot technique (Figure 1). Two possible mechanisms for this change are now suggested:

(a) The additional mass transfer of the organic phase from the liquid to the bubble can cause a change in the coalescence rate, as indicated in the review article by Chaudhari and Hofmann.¹⁵

(b) The dissolved or dispersed toluene is present at the bubble surface, either as a monolayer or as a film with a certain thickness, which causes a repression of the electric double layer and thus a reduction of the inhibition of coalescence.

To study the effect of toluene mass transfer, experiments were performed with 2.5 vol % toluene in the stirred vessel and using a gas stream that was pre-saturated with toluene and water, so no (net) mass transfer occurred between the liquid and the gas phase. Pre-saturation had no effect on the interfacial area, which means that it is unlikely that toluene mass transfer changed the coalescence properties of the dispersion. This result suggests that toluene is present at the surface, but it remains unknown whether interaction of the bubble with the organic droplets or the dissolved toluene is responsible for this effect.

To study this effect, the interfacial area in an initially toluene-free 0.5 M KCl solution was determined, while the gas stream was saturated with toluene. In this way the toluene is absorbed in the electrolyte solution, but no toluene droplets are formed, as the concentration in the liquid phase cannot pass the solubility limit. In these experiments, and in contradiction to the experiments described previously with 2.5% toluene present as droplets, no decrease in interfacial area was observed. This observation strongly supports the hypothesis that the interaction of the gas bubbles with toluene droplets is responsible for the decrease in interfacial area.

This hypothesis was further supported by experiments with 2.5% toluene in an air–KCl-solution in the bubble column mode at homogeneous bubble flow conditions. The use of 2.5% toluene ensured that the continuous phase was completely saturated with toluene, although the toluene was poorly dispersed through the reactor content and the value of the superficial gas velocity determined the amount of toluene dispersion in the reactor. From Figure 10 it can be concluded that two different phenomena occurred when the superficial velocity is increased. An initial increase in interfacial area is obtained due to the higher gas content of the bubble column, but above a certain gas velocity (around 1 cm/s) the interfacial area is decreased, which is likely to be caused by the presence of the droplets in the more turbulent reactor. These combined effects resulted in a linear increase in the Sauter mean diameter with the superficial gas velocity (Figure 11).

The most likely form of droplet–bubble interaction to occur is complex formation¹⁶ in which a droplet and a bubble “coalesce” to form a bubble covered by an organic layer. The spreading of an organic liquid over an aqueous solution is favorable when the final spreading coefficient (at mutually saturated conditions, $S^* =$

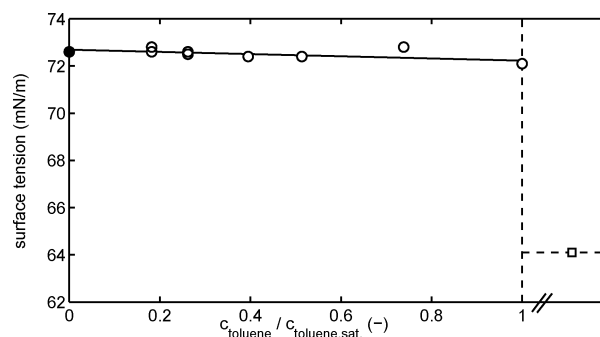


Figure 12. Effect of the normalized toluene concentration (c/c_{sat}) on the surface tension. The data point beyond the point of maximum solubility was measured with different organic layer thicknesses (1.2 μm –3 mm), and the x -coordinate for that point is therefore in arbitrary units.

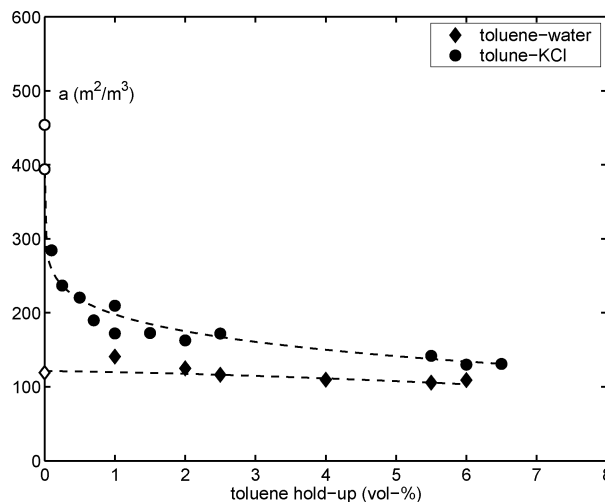


Figure 13. Gas–liquid interfacial area of air–water–toluene and air–electrolyte–toluene systems as a function of the toluene fraction in the stirred vessel (u_G : 0.86 cm/s).

$\sigma_{\text{WG}}^* - \sigma_{\text{OG}}^* - \sigma_{\text{OW}}^*$) is positive, which is the case in the air–toluene–electrolyte system (+8 mN/m¹⁴).

According to the work of Bartell et al.¹⁷ a positive spreading coefficient cannot exist in a system at equilibrium. In that case a small toluene layer will be formed spontaneously on the gas–liquid interface, and the final spreading coefficient will go to zero. Measurements of the surface tension of water with a small layer of toluene on top (see Figure 12) showed that at the point of maximum toluene solubility a sharp decrease of the surface tension occurred and the spreading coefficient decreased to approximately zero. The origin of the molecules that are required to form the layer around the bubbles is, however, not clear. Toluene droplets might be required to act as small toluene supplies and facilitate the formation of the small organic layers.

If toluene is present as a film around the bubble (by one of the two proposed mechanisms), the toluene layer determines the coalescence properties and no coalescence inhibition is expected. This can explain the coalescing nature of the air–electrolyte–toluene system.

3.5. Air–Water–Toluene System. From Figure 13 it seems that the addition of toluene (1–6%) to an air–water dispersion does not influence the gas–liquid interfacial area, in contrast to the addition to the electrolyte solution. The bubble size distribution is, however, much wider in the presence of toluene, and similar to the experiments with the electrolyte solutions, large gas bubbles are observed.

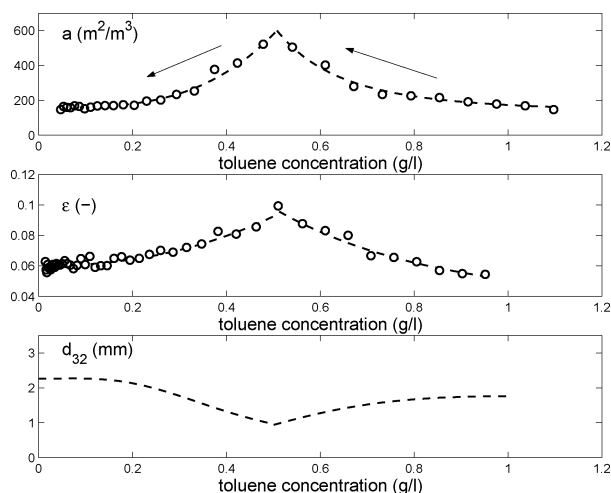


Figure 14. Gas–liquid interfacial area, gas hold-up, and Sauter mean diameter at low toluene fractions in an air–water system (u_G : 0.86 cm/s).

During the stripping of toluene from the aqueous solution, a strong increase of both the interfacial area and the gas hold-up is observed at toluene fractions around the maximum concentration at the solubility limit in water (0.53 g/L). Both a and ϵ were measured on-line and the toluene concentration was determined from the stripping speed of toluene (Figure 14). The observed increase is remarkable, because the coalescing air–water–toluene system ($a = 150 \text{ m}^2/\text{m}^3$, $\epsilon = 5.7\%$, $d_{32} = 2.3 \text{ mm}$) is altered in a noncoalescing system ($a = 550 \text{ m}^2/\text{m}^3$, $\epsilon = 9.9\%$, $d_{32} = 1.1 \text{ mm}$) around the maximum toluene concentration at the solubility limit.

This remarkable effect was not only observed during stripping, but also (up to the saturation point) when saturating an initially toluene-free water–air system, using a gas stream which was presaturated with toluene (thus like in Figure 14, but then coming from the left-hand side). The changing behavior of the system going from toluene-free water (“coalescing system”) to water saturated with toluene (“noncoalescing system”) to a coalescing system of water containing toluene droplets is not completely understood. It is clear that coalescence is the dominating phenomenon determining the interfacial area obtained as the gas bubbles formed at the porous plate sparger are very fine. Coalescence between two neighboring gas bubbles involves the drainage of the liquid film separating the two bubbles.^{18,19} Such a liquid film can be stabilized, and hence coalescence can be hindered, by surface tension gradients, caused by a gradient in concentrations. Around the saturation point such a steep surface tension gradient can be present if the bubble is covered with a small layer of toluene (see Figure 12). This figure shows that there is a large difference in the surface tension when a small toluene layer is present on the gas–liquid interface compared to the surface tension of the saturated solution (64 and 72 mN/m, respectively). These observed surface tension gradients might explain that coalescence is slowed down or even inhibited completely around the saturation point.

The fact that this increase and decrease is not instantaneous but somewhat gradual may be understandable when realizing that for newly created bubbles the probability of coalescence before arriving at the measurement cell is dependent on the (local) conditions in the vessel (droplet fraction, concentration). Further

Table 1. Gas–Liquid Interfacial Areas (m^2/m^3) of Water and 0.5 M KCl Solutions with Different Additives (2.5%) in the Stirred Vessel^a

additive	tap water	0.5 M KCl solution
none	115	394
toluene	116	146
hexadecane	109	378
heptane	77	375
1-octanol	670	691

^a $N = 550 \text{ rpm}$, $u_G = 0.86 \text{ cm/s}$.

research on this topic is, however, required to support this hypothesis.

3.6. Other Three-Phase Systems. The gas–liquid interfacial area in air–water and in air–electrolyte (0.5 M KCl) systems was also measured in the presence of different organic phases; heptane, hexadecane, and 1-octanol. From the results, presented in Table 1, it can be concluded that the mechanism accounting for the strong effects on the interfacial area is very sensitive to the type of the organic additive. The large decrease of the interfacial area in air–electrolyte systems is only observed in the presence of toluene. Heptane ($S^* \approx 0$) and hexadecane ($S^* < 0$) show no significant effect, and the addition of 1-octanol actually increased the area to a large extent. This large increase was also observed in the air–water–octanol system and is probably the result of a smaller initial bubble size, due to a lower air to water surface tension ($\sigma_{A/W(O)} = 30 \text{ mN/m}$) or due to a more decreased coalescence rate compared to the electrolyte system. The interfacial area in the air–water–heptane system was measured several times and was significantly lower compared to the air–water system, and similar to the systems with toluene some large bubbles were observed visually. Spreading of heptane around the bubbles might have caused this, but further research must be performed to study the spreading behavior of the organic phases.

4. Conclusions

Ultrasonic spectroscopy was used to study the gas–liquid interfacial area in gas–liquid and gas–liquid–liquid systems, while the gas hold-up was measured separately using an electrical conductivity technique. The ultrasonic spectroscopy technique applied has proven to be a valuable tool in analyzing gas absorption effects in multiphase systems.

The addition of toluene to a noncoalescing air–electrolyte system reduced the interfacial area to a large extent and the formation of large gas bubbles is observed, thus effectively transforming it into a coalescing system. It was found that interaction between gas bubbles and toluene droplets (like bubble–droplet coalescence or the spontaneous formation of a small toluene layer around the gas bubble) causes this effect; effects of dissolved toluene are negligible. Another, possibly related, interesting phenomenon was observed around the solubility concentration of toluene in a coalescing air–water system. The interfacial area at this point increased by a factor of 3–4, and the system changed into a noncoalescing system. The cause of this remarkable phenomenon lies probably in the presence of a small toluene layer, which forms beyond the solubility point. This layer is absent at concentrations below the solubility limit and a large surface tension gradient

exists between those two situations, which can be responsible for the sharp change in coalescence behavior. In general, it was found that the influence of different additives on the gas–liquid interfacial area is very sensitive to the nature of the added components, and further investigation (e.g., on the spreading behavior of these phases) is required to be able to predict beforehand whether certain additives will affect the gas–liquid interfacial area.

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Notation

a = interfacial area, m^2/m^3
 c = ultrasonic velocity, m/s
 d = distance between the transducers, m
 d_{32} = Sauter mean diameter, m
 G = conductivity, S
 H = liquid height, m
 I = signal intensity, V
 S^* = final spreading coefficient, N/m
 T = temperature, K

Greek

α = attenuation coefficient, Np/m
 Δt = time difference, s
 ϵ = phase hold-up
 σ^* = mutually saturated surface/interfacial tension, N/m

Subscript

ϵ = dispersed phase
 G = gas phase
 O = oil phase
 W = water phase

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