Hydrodynamics and mass transfer in bubble column: Influence of liquid phase surface tension

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Abstract

According to literature, few experiments are performed in organic solvents which are mostly used in commercial gas–liquid reactors. However, it is commonly accepted that data obtained in aqueous solution allow to predict the surface tension effects, and to model the behaviour of organic solvents. In this work, we examine the validity of this approximation.

In this objective, the flows observed in two pure media having similar viscosity but different surface tension—respectively, water (reference) and cyclohexane (solvent)—are successively compared at two scales: in a bubble column and in bubble plumes.

In bubble plumes, as expected, the mean bubble size is smaller in the medium having the smallest surface tension (cyclohexane), but for this medium the destabilisation of flow is observed to occur at smaller gas velocity, due to break-up and coalescence phenomena. In bubble column, these phenomena induce the bubbling transition regime at lower gas velocity, whatever the operating conditions for liquid phase: batch or continuous. Consequently, when the two media are used at similar gas superficial velocity, but in different hydrodynamic regimes, greater gas hold-up and smaller bubble diameter can be observed in water; the interfacial area is then not always higher in cyclohexane.

This result differs from the behaviour observed in the literature for aqueous solutions. The analysis of bubble plumes in aqueous solutions of butanol shows that this difference is due to a fundamental difference in coalescent behaviour between pure solvents and aqueous mixtures: the surface tension effect is less important in pure liquid than in aqueous solutions, because of the specific behaviour of surfactants.

It is then still difficult to predict *a priori* the bubbling regime or the flow characteristics for a given medium, and all the more to choose an appropriate liquid as a model for industrial solvents.

Keywords: Bubble column; Multiphase flow; Hydrodynamics; Mass transfer; Surface tension; Bubbling regime

1. Introduction

Bubble columns are usual gas–liquid chemical reactors, especially for kinetically slow reactions such as oxidations or chlorinations. In these reactors, the gas phase dispersion and the bubble size distribution are crucial, as they define the gas–liquid interfacial area available for mass transfer and therefore the reaction efficiency. Both the column characteristics and the liquid media have a strong effect on these parameters, but the liquid media effect seems more complex and is still disputed. In fact, the bubble size strongly depends on coalescence behaviour of the liquid, but the influence of the liquid properties on bubble coalescence and break-up remains difficult to quantify, especially in industrial complex media (Deckwer, 1992). The most analysed liquid properties are viscosity and surface tension.

As we focus here on the organic solvents used in chemical industry, a particular attention is paid to surface tension, the main difference between solvents and water. Its effect is widely described in the literature, but most of these studies are limited to a comparison between water and aqueous solutions containing surfactants. Indeed, as the smallest addition of surfactant to water lowers surface tension without affecting viscosity, most engineers consider that such solutions lead to similar behaviour than poorly coalescent media such as organic media.

The observation of single bubbles shows that a decrease in surface tension (due to surfactant addition) diminishes the bubble coalescence frequency: the bubbles are then smaller,

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slower (Loubière and Hébrard, 2004; Malysa et al., 2005; Mouza et al., 2005), and also more spherical (Krzan and Malysa, 2002; Byakova et al., 2003; Gnyloskurenko et al., 2003; Mouza et al., 2005).

In bubble columns, it is commonly accepted that, depending on the gas flow rate and on the liquid phase properties, two main regimes can be distinguished. On the one hand, the homogeneous bubbly flow regime, encountered at low gas velocities (with small holes sparger), is characterised by narrow bubble size distributions and a uniform spatial dispersion of gas hold-up. In this regime, there is no interaction between bubbles; their motion is roughly vertical. On the other hand the heterogeneous (churn turbulent flow) regime, observed at higher gas velocities ($u_G > 0.05\,\mathrm{m/s}$), is defined by a large bubble size distribution and a high concentration of large bubbles on column axis, which cause macro-circulation and curved shape gas hold-up profiles. In this regime the bubble size is governed by the coalescence–break-up equilibrium.

In bubble columns, the surface tension effect is similar to what is observed for single bubbles: a decrease in surface tension decreases bubble size and bubble velocity (Camarasa et al., 1999; Dargar and Macchi, 2006); this induces higher gas hold-up (Kantak et al., 1995; Zahradnik et al., 1995, 1997; Camarasa et al., 1999; Krishna et al., 2000; Elgozali et al., 2002; Dhotre et al., 2004; Veera et al., 2004; Mouza et al., 2005) and higher mass transfer coefficient (Kantarci et al., 2005). These tendencies are confirmed by the classical correlations (Shah et al., 1982). The surface tension effect is particularly effective in homogeneous and transition regime and less in the heterogeneous regime where the reduction of coalescence is over-shadowed by the predominant effect of macro-scale turbulence (Zahradnik et al., 1995, 1997; Camarasa et al., 1999). It is also observed that in presence of surfactants in water, the transition of bubbling regimes is delayed to higher gas velocity, whereas the heterogeneous regime appears almost at the same gas velocity: the transition regime tends to disappear (Kantak et al., 1995; Zahradnik et al., 1995, 1997; Krishna et al., 2000; Camarasa et al., 1999; Thorat and Joshi, 2004; Dargar and Macchi, 2006). The homogeneous regime enlargement can be explained by the decay of coalescence and by the increase in bubble rigidity (Dargar and Macchi, 2006).

However, one may wonder if these flows, described by means of aqueous solutions, are really representative of the flows observed with organic media, as they have a lower surface tension than water. As a matter of fact, considering the few studies realised in organic media, surface tension effect seems to be more limited in pure media than in aqueous solutions (Burckhardt and Deckwer, 1975; Ozturk et al., 1987).

In order to analyse the surface tension effect in bubble columns, two pure media of different surface tension are compared: water, which is a reference as its behaviour is widely investigated, and cyclohexane, an organic solvent of similar viscosity. For a better description of bubble behaviour, this study is realised at two scales: in a bubble column and in a bubble plume.

2. Experimental set-up

2.1. Liquid media

The bubbling characteristics are compared for two liquid media of similar viscosity: water and cyclohexane. The main physicochemical difference between those two media is surface tension: the surface tension of water is three times the one of cyclohexane, as indicated in Table 1.

2.2. Pilot plants and measurements

Two experimental devices are used in this work.

2.2.1. Bubble column

The first one is a semi-industrial bubble column of 0.2 m in diameter (D_C) and of 1.6 m in liquid height (H_L) (Fig. 1a). Those dimensions are chosen so that the behaviour in this column may be representative of large scales—$D_C \geqslant 0.2\,\mathrm{m}$ (Bach and Pilhofer, 1978; Shah et al., 1982; Deckwer, 1992) and $H/D_C > 5$ (Thorat and Joshi, 2004)—without involving the manipulation of a huge quantity of solvent. Two toroidal gas spargers of 0.8% free area, pierced with different hole size (respectively, $d_0 = 0.001$ and $d_0 = 0.0005\,\mathrm{m}$), have been alternatively used. The circulation of liquid phase is possible. Large ranges of superficial gas velocity (from 0.03 to 0.20 m/s) and superficial liquid velocity (from 0 to 0.08 m/s) have been investigated. All experiments are run at atmospheric pressure and ambient temperature (around 20 °C). When organic liquid is used, a cryogenic apparatus is linked to the gas outlet so that organic vapour is fully recovered. In this case, for safety reasons, the gas introduced in the bubble column is nitrogen (N_2) instead of air.

Within the bubble column, the global gas hold-up, ε_G, has been measured by means of a differential pressure transducer (called 'DP'); this measurement includes the main part of the column, except the region lying under the sparger and the disengagement zone (Fig. 1a).

Some measurements of global mass transfer coefficient are also performed when the bubble column is operated under liquid flow conditions. In this case a steady state absorption–desorption method is used, coupled with a residence time determination method, as described by Chaumat et al. (2005a).

At last, whatever be the operating conditions, profiles of gas hold-up, bubble frequency and mean Sauter diameter are established by means of an optic double probe settled at 0.65 m above the column bottom: the profiles observed at this level are quite representative of the flow in the column core (it is

Table 1
Properties of the liquids used

Liquid	Formula	Density 20 °C (kg/m^3)	Viscosity 25 °C (mPa s)	Surface tension 25 °C (mN/m)
Cyclohexane	C_6H_{12}	778.5	0.894	24.65
Water	H_2O	996.3	0.890	71.99

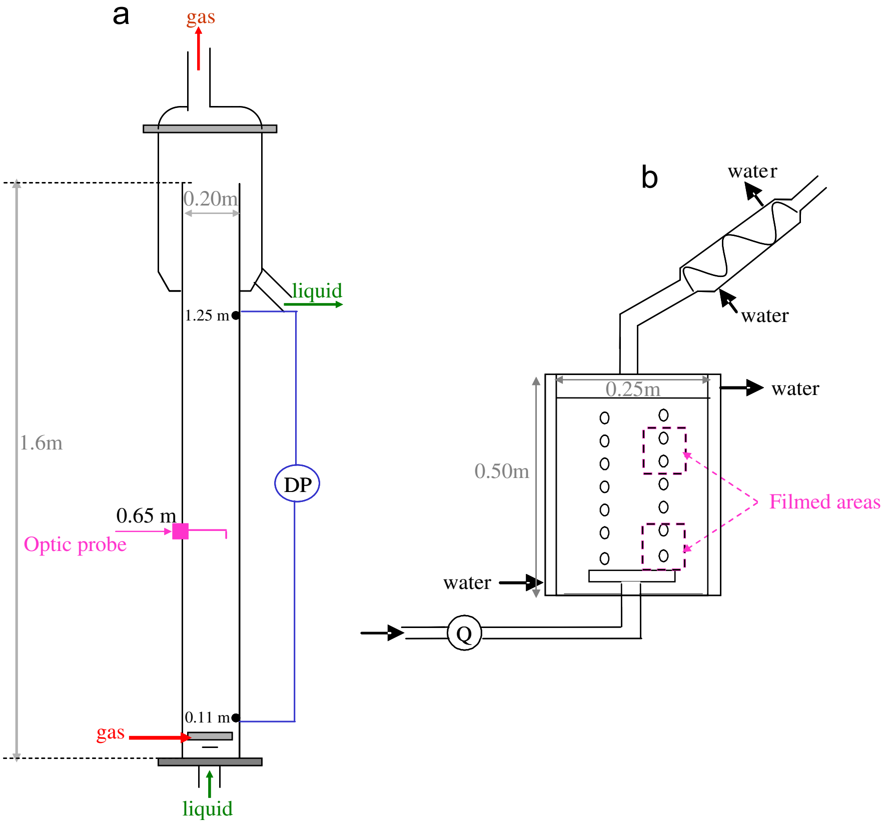

Fig. 1. Pilot plants.

neither in the sparger nor in the disengagement area; Chaumat et al., 2006). Measurement procedure and data treatment are detailed in Chaumat et al. (2007). Note that this metrology cannot give information about bubble size distributions in this work, due to the high bubble concentration and to the chaotic motion of bubbles (Chaumat et al., 2007).

2.2.2. *Small transparent tank*

To compare the bubble size distributions obtained with the two media, a specific small transparent device is used, where the bubble size distributions in bubble plumes can be reliably evaluated through image analysis technique. This second apparatus is a plane–parallel glass tank (dimensions: $0.25 \times 0.25 \times 0.50$ m), which contains around 30 L of liquid (Fig. 1b). The gas (air or nitrogen, depending on the nature of liquid phase) is injected through two rigid holes of 0.001 m in diameter (similar to the hole size used in the bubble column), spaced by 0.04 m. This device is operated at atmospheric pressure and under controlled temperature (25 °C). The injection gas velocity (u_{G0}) ranges from 1 to 22.1 m/s (note that an ejection velocity of 22.1 m/s is observed in the bubble column plant for $u_G = 0.045$ m/s); these gas injection velocities correspond to orifice Reynolds numbers ($Re_0 = \rho_G u_{G0} d_0 / \mu_G$) ranging from 60 to 1350. In order to use an organic medium, like cyclohexane, security cautions are needed: nitrogen is used instead of air to avoid explosion risks, the tank is tightly closed with an adapted cover, and the gas output flows through a condenser before being released in a hood.

In this installation, the bubble plumes are filmed with a monochrome Leutron Vision LV-95 camera as described by Chaumat et al. (2005b). The visualisation window is about 0.04×0.04 m. The images are analysed with Visilog 5.1 in order to obtain (projected) bubble size distributions, but also the average arithmetic bubble diameter ($d_{10} = \sum_{i=1}^{N} d_{\mathrm{eq},i}/N$) and the Sauter mean diameter ($d_{32} = \sum_{i=1}^{N} d_{\mathrm{eq},i}^3 / \sum_{i=1}^{N} d_{\mathrm{eq},i}^2$). The number of bubbles used to evaluate these diameters ranges between 150 and 500. Those two parameters are complementary as they give different weights to the various bubble sizes: large bubbles have a heavier weight in d_{32} than in d_{10}. Axial evolutions of those criteria are also available as two axial positions are checked in the tank: near the sparger, and at 0.20 m above the sparger (Fig. 1b).

3. Results

3.1. *Experiments performed in the bubble column*

The comparison between water and cyclohexane in the bubble column concerns successively batch and continuous liquid conditions.

3.1.1. *Liquid batch conditions*

First of all, the global data of gas hold-up are compared for both media and spargers (Fig. 2a). The hydrodynamics regimes are then deduced (Fig. 2b), as described by Chaumat et al.

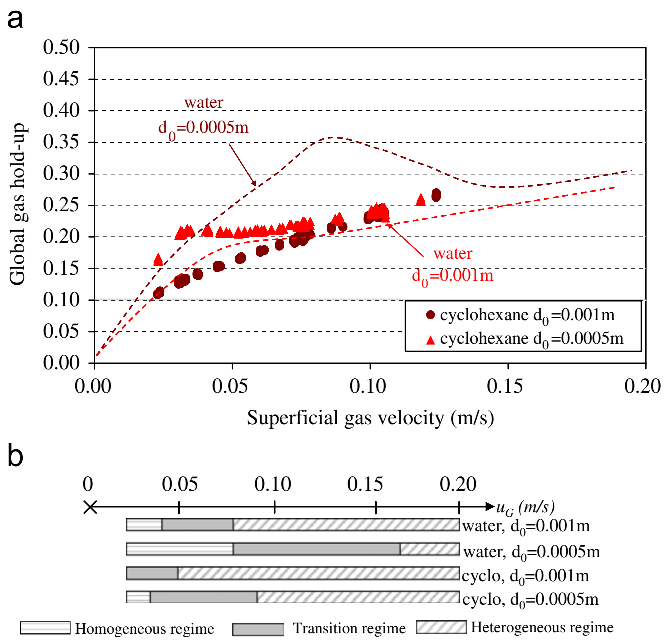

Fig. 2. Global gas hold-up and hydrodynamic regimes in liquid batch conditions.

(2005c), using among others the classical approach of Züber and Findlay (1965).

The classical sparger effect (Ohki and Inoue, 1970; Zhao et al., 1994; Zahradnik et al., 1997) can be verified: the sparger pierced with small holes ($d_0 = 0.005$ m) leads to larger or equal gas hold-up than the other one ($d_0 = 0.001$ m) because of a larger gas velocity range for the homogeneous regime (Fig. 2b).

However, the media effect is more surprising (Fig. 2a): despite a smaller surface tension for cyclohexane, the gas hold-up can be smaller in cyclohexane than in water (see the velocity range between 0.04 and 0.12 m/s for the small holes sparger and between 0.04 and 0.06 m/s for the large holes sparger). This behaviour can be directly connected to the flow regimes: in water, the homogeneous and transition regimes spread over a larger gas velocity range than in cyclohexane (Fig. 2b). Surprisingly, in the gas velocity range explored ($u_G > 0.02$ m/s), the homogeneous regime is even not observed at all in cyclohexane with the large holes sparger. To sum up, when both media are run under the same bubbling regime, the gas hold-up is, as expected, larger in the medium having the smallest surface tension (cyclohexane); but this tendency can be inverted when, at a given gas velocity, both media are not operating in the same hydrodynamic regime.

The bubble size data obtained on the axial position ($r = 0$) confirm this tendency (Fig. 3): due to the difference in surface tension, the bubble size is smaller in cyclohexane ($\sigma = 24.65$ mN/m) than in water ($\sigma = 71.99$ mN/m) when both media work in the same regime; when the two media work in different regimes, similar bubble size can be observed (see for example bubble size at $u_G = 0.05$–0.06 m/s for $d_0 = 0.001$ m and at $u_G = 0.08$–0.10 m/s for $d_0 = 0.0005$ m). Fig. 3 also exhibits that the mean Sauter diameter at equilibrium between

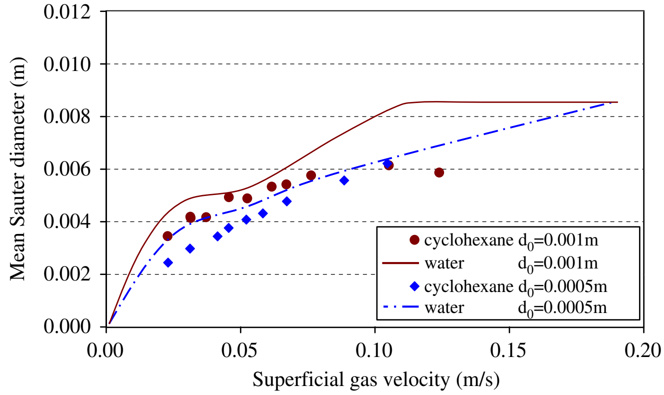

Fig. 3. Mean Sauter diameter on the axis in liquid batch conditions ($h = 0.65$ m).

coalescence and rupture (asymptotic value at high gas velocity for $d_0 = 0.001$ m) is about 0.0060 m in cyclohexane and about 0.0086 m in water. This equilibrium is reached at lower gas velocity in the case of cyclohexane (around 0.08 m/s in cyclohexane and around 0.11 m/s in water for $d_0 = 0.001$ m; for $d_0 = 0.0005$ m, the equilibrium is hardly reached in water in the studied range of gas velocity).

There is a good accordance between our different results, but they are not in agreement with the usual surface tension effect described in the literature when water is compared to liquid having smaller surface tension: as shown in Fig. 4 for similar column sizes and sparger types, ε_G is always found larger for liquids with small surface tension (mixtures of water and alcohols) when compared to the case of water. In fact, in the literature, a smaller surface tension always leads to a regime transition at higher superficial gas velocity, whereas we make the opposite observation, and this is difficult to interpret.

At last, the local gas hold-up profiles, normalised with the hold-up value measured on the axis, are plotted in Fig. 5a. They also differ from literature observations as no clear surface tension nor sparger effects were found, whereas Krishna et al. (2000), Veera et al. (2004), and Dhotre et al. (2004) notice flatter profiles in the solutions having the smallest surface tension (aqueous solutions) as shown in Fig. 5b (data from Dhotre et al., 2004).

We can then wonder if our results in water are in accordance with the literature. To verify this point, the global gas hold-up observed in our column and in column of similar geometry ($D_C = 0.1$–0.385 m, $H/D = 8$–20) and of similar spargers (pierced spargers, $\varphi = 0.2$–0.8%, identical holes diameter) are compared in Fig. 6; the gas hold-up is measured by height difference between aerated and non-aerated conditions by Zahradnik et al. (1997), by pressure difference by Camarasa et al. (1999) (as in our study), and by tomography by Veera et al. (2001). Fig. 6 shows that the accordance between our results and the literature observations is good for the sparger pierced with 0.0005 m orifices. The difference at $d_0 = 0.001$ m between our results and the results obtained by Camarasa et al. (1999) is limited to the gas velocity range between 0.04 and

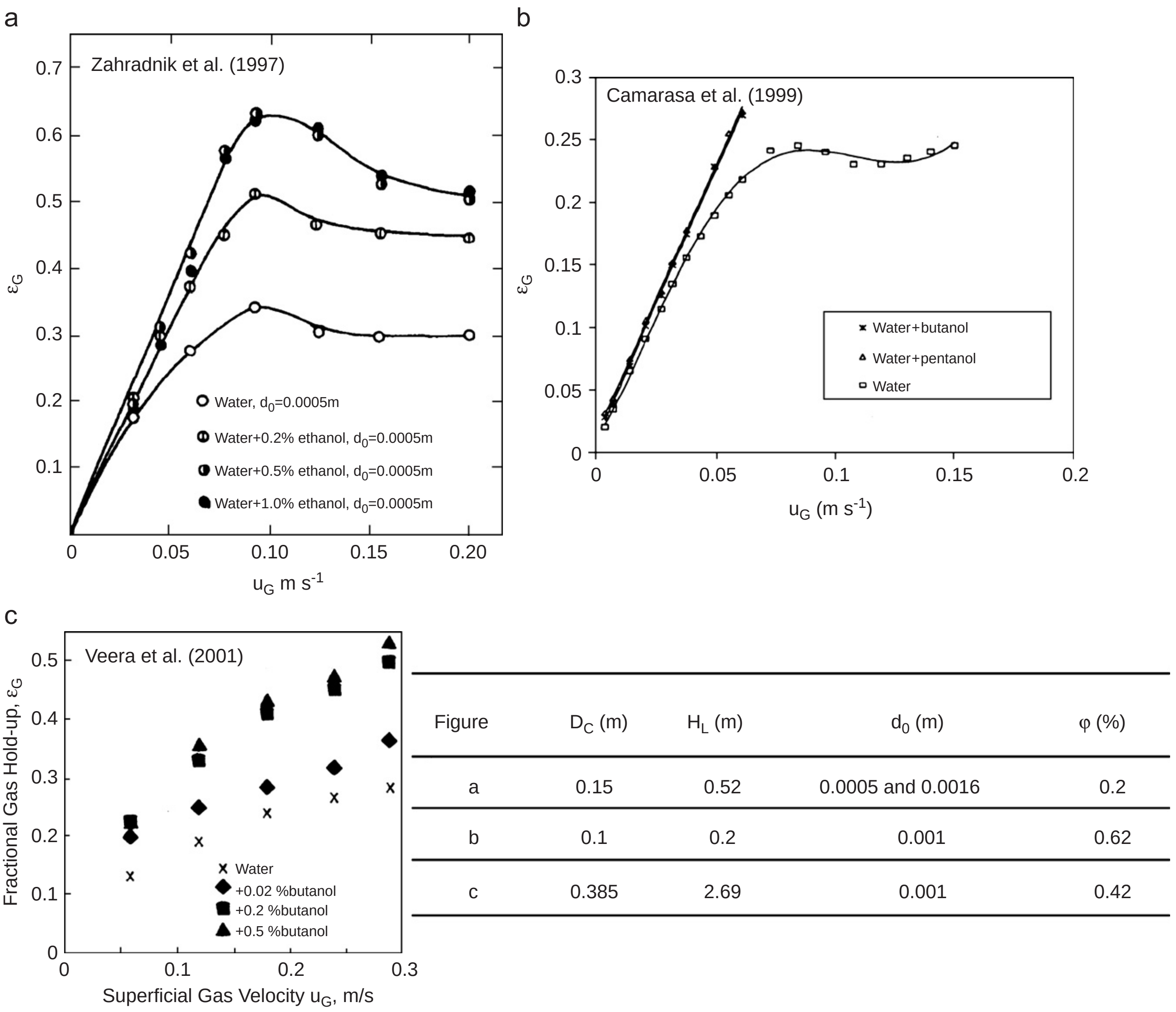

Figure	D_C (m)	H_L (m)	d_0 (m)	φ (%)
a	0.15	0.52	0.0005 and 0.0016	0.2
b	0.1	0.2	0.001	0.62
c	0.385	2.69	0.001	0.42

Fig. 4. Gas hold-up evolution observed in the literature for media having different surface tension.

0.12 m/s: it seems due to a transition at a smaller gas velocity in our case, perhaps because of different water quality (tap water in our study) and/or gas injection conditions. The gas hold-up evolution obtained by Veera et al. (2001) is exactly the same as ours, but the gas hold-up is systematically smaller (from 8% smaller to 40% smaller): it could be related to a different water quality, or to the integration of the tomography measurements made on several column sections.

As a conclusion, the gas hold-up observed in our column with water is in correct agreement with the literature: our study is reliable.

3.1.2. Liquid circulating conditions

The surprising phenomena obtained in liquid batch conditions are still observed, but to a less extent, under continuous liquid feed. For the small holes sparger (Fig. 7b), it is still verified that the bubbling regime transition appears for larger gas velocity in water than in cyclohexane, but this tendency is less pronounced for the large holes sparger (Fig. 7a).

As a consequence, the bubble size is classically smaller in cyclohexane for the whole range of operating conditions for $d_0 = 0.001$ m (Fig. 8a), whereas in the case of $d_0 = 0.0005$ m and $u_L = 0.040$ m/s, for u_G ranging between 0.07 and 0.10 m/s, the mean Sauter diameter of bubbles is obviously larger in cyclohexane (around 0.006 m) than in water (around 0.005 m) (Fig. 8b).

The data concerning mass transfer, obtained with liquid circulation, are in good agreement with these observations (Fig. 9): for $d_0 = 0.001$ m, the liquid side mass transfer coefficient is greater in cyclohexane than in water, as the mean Sauter diameter is smaller (Fig. 8a) and the gas hold-up greater (Fig. 7a). This tendency is less pronounced at small gas velocity when gas hold-up and bubble size values are less different between the two media (Figs. 7a and 8a). For the other sparger

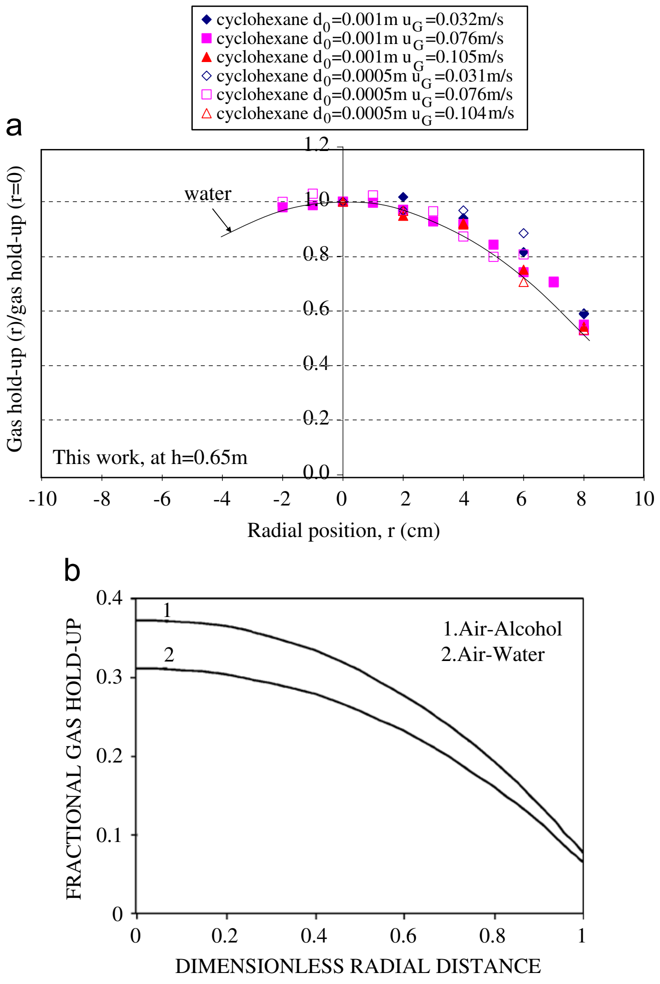

Fig. 5. Normalised gas hold-up profiles in liquid batch conditions.

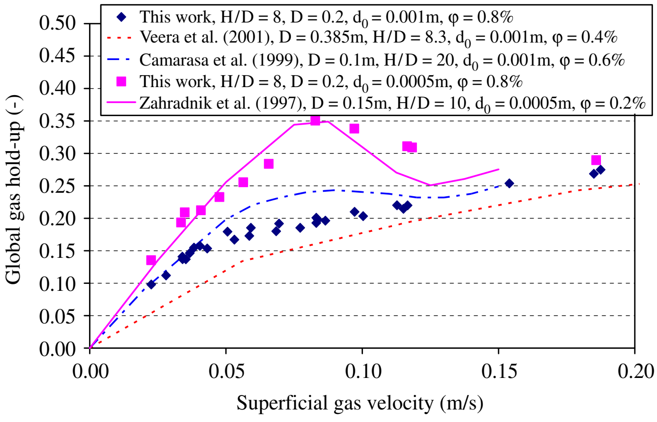

Fig. 6. Comparison in water between global gas hold-up observed in the literature and results obtained in this work.

($d_0 = 0.0005\,\mathrm{m}$), the mass transfer coefficient is greater in cyclohexane at high gas velocity ($u_G \sim 0.15\,\mathrm{m/s}$), but k_La values in water reach the same order of magnitude for $u_G \sim 0.1\,\mathrm{m/s}$, due to the longer extent of homogeneous and transition regimes.

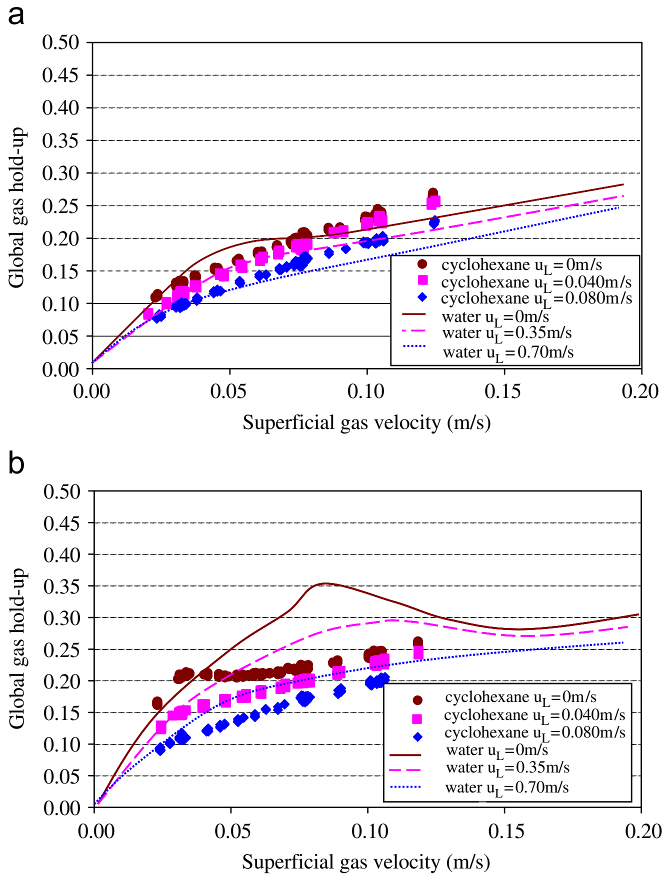

Fig. 7. Global gas hold-up evolution versus superficial gas velocity for both media (cyclohexane and water) in case of liquid circulation (both spargers): (a) $d_0 = 0.001\,\mathrm{m}$ and (b) $d_0 = 0.005\,\mathrm{m}$.

As a consequence, depending on operating conditions, the bubble column contactor can be more efficient either in cyclohexane or in water. As a matter of fact, due to surface tension difference, in a given hydrodynamic regime, the bubble size is smaller in cyclohexane than in water, but the transitions in bubbling regimes occur at smaller gas velocity in cyclohexane. This observation is very surprising and not yet described in the literature, where decreasing the surface tension always results in enlarging the homogeneous regime. In order to elucidate this behaviour, bubble size distributions are considered in a smaller installation.

3.2. Experiments performed in the glass tank

In this apparatus, the surface tension effect is analysed in terms of bubble size distributions in plumes.

The measurements of average arithmetic diameter d_{10}, mean Sauter diameter d_{32}, minimum and maximum diameters ($d_{\min}$ and $d_{\max}$), standard deviation of the distribution, and also of the number of analysed bubbles are reported in Table 2.

Of course, the bubble size distributions in this small tank cannot be exactly the same than in the pilot plant, but they may be similar, at least in the sparger area. As a matter of fact, the mean Sauter diameter observed at 0.2 m above the

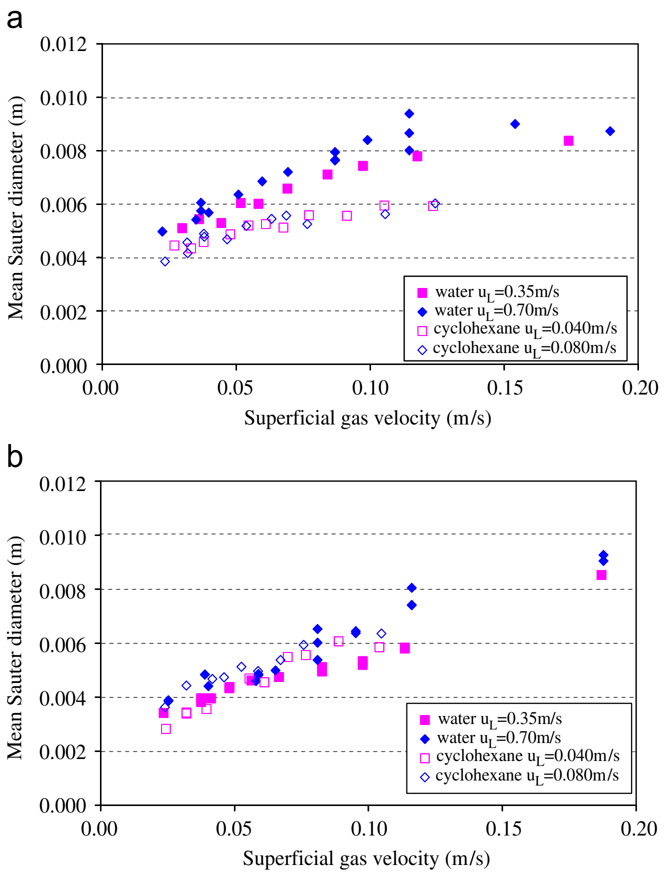

Fig. 8. Mean Sauter diameter observed on column axis with liquid circulation (both spargers): (a) $d_0 = 0.001$ m and (b) $d_0 = 0.005$ m.

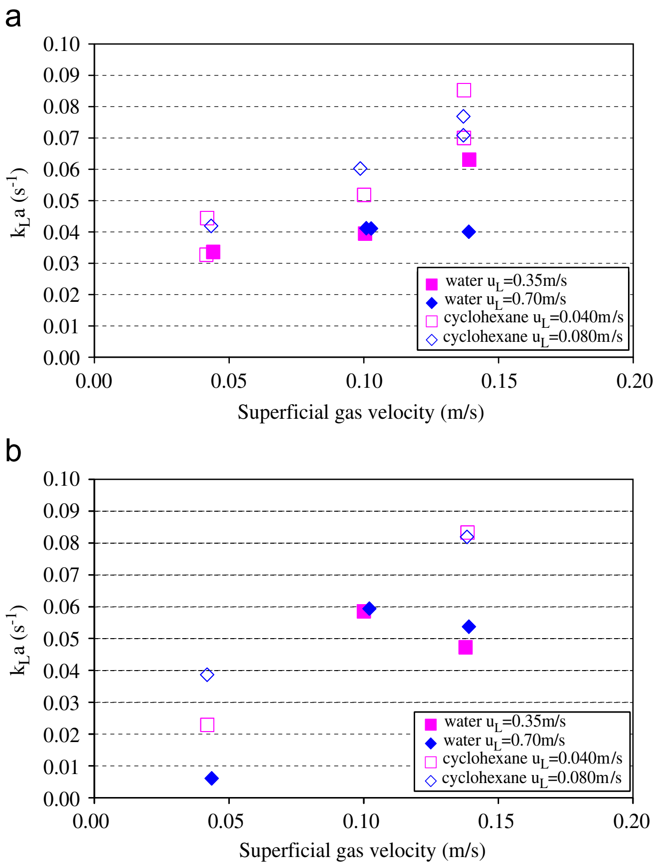

Fig. 9. Mass transfer coefficient observed with liquid circulation (both spargers): (a) $d_0 = 0.001$ m and (b) $d_0 = 0.005$ m.

sparger in the glass tank is close to the value measured in bubble column (around 0.006 m at the equilibrium for cyclohexane and around 0.0085 m for water). The measurements realised in the glass tank are then coherent and complementary with the results obtained in the bubble column.

In the area of bubble formation, three regimes can be distinguished, depending on the injection velocity and on the media properties. When increasing the gas flow rate, the observed regimes are successively: the separate bubble formation regime, the chain bubbling regime, and the jet regime (Fig. 10, Heijnen and Van't Riet, 1984; Camarasa et al., 1999). The first two regimes are here brought together, as they present similar characteristics, and are called bubble regime. In this study, the bubble and jet regimes are visually distinguished (Fig. 11): in both media (water and cyclohexane), the transition between bubble regimes and jet regime occurs for u_{G0} lying between 10 (bubble regime) and 22.1 m/s (jet regime), that is to say around $Re_0 \sim 1000$. Note that bubbles are not spherical even at small gas ejection velocity (Fig. 11).

The bubble size distributions in cyclohexane are first discussed (Fig. 12):

- At the two levels studied ($h = 0$ and 0.2 m), at $u_{G0} = 1$ m/s, the bubble size distribution is quite homogeneous (for instance around 0.0035 m at sparger level, Fig. 12a). This distribution spreads with increasing gas velocity; the mean bubble diameter becomes so large that bubbles become unstable and break-up into a new population of tiny bubbles (characteristic diameter: 0.001 m, appearing up from $u_{G0} = 5$ m/s).
- Comparing distributions at $h = 0$ and 0.2 m at small gas velocity, we observe that the bubble size tends to increase with h ($d_{32} = 0.0038$ m at $h = 0$ m to 0.0056 m at $h = 0.2$ m) and that the smallest bubbles observed near the sparger are not observed at $h = 0.2$ m any more (Fig. 12a): the smallest bubbles may coalesce and induce an increase with h of the mean bubble size and also of the maximum bubble diameter. At high gas velocity, very large bubbles are observed in the injection area (up to 11.5 mm), and the small bubbles population fraction increases with h (15% at $h = 0$ m and 20% at $h = 0.2$ m for $u_{G0} = 22.1$ m/s): these small bubbles probably result from the break-up of the large unstable bubbles and rise slowly. In water (Fig. 13), some tendencies are similar:
- At small gas velocity ($u_{G0} = 1$ m/s), only one population is distinguishable. During their rise, the smallest bubbles formed at the sparger coalesce with other bubbles, but the effect on the mean Sauter diameter is smaller than in

Table 2
Results obtained in the glass tank for cyclohexane and water

Liquid	Height (m)	u_{G0} (m/s)	d_{32} (mm)	d_{10} (mm)	$d_{\min}$ (mm)	$d_{\max}$ (mm)	Std deviation (%)	Treated bubbles
Cyclohexane	0.2	1	5.76	5.31	0.30	9.36	21.10	180
Water	0.2	1	5.64	5.32	2.04	8.43	17.14	156
Cyclohexane	0.2	5	8.50	4.61	0.24	13.24	70.86	346
Water	0.2	5	7.78	6.99	0.88	10.68	26.05	168
Cyclohexane	0.2	10	7.68	4.22	0.11	11.71	71.48	434
Water	0.2	10	8.65	6.04	0.57	13.26	51.77	363
Cyclohexane	0.2	22.1	7.18	1.77	0.23	14.70	117.37	497
Water	0.2	22.1	9.07	3.76	0.13	16.70	92.31	447
Cyclohexane	0	1	3.76	3.18	0.44	5.45	33.66	230
Water	0	1	4.50	4.03	1.38	5.89	26.24	223
Cyclohexane	0	22.1	7.80	3.22	0.23	11.49	93.51	394
Water	0	22.1	15.63	9.45	0.38	20.08	67.51	207

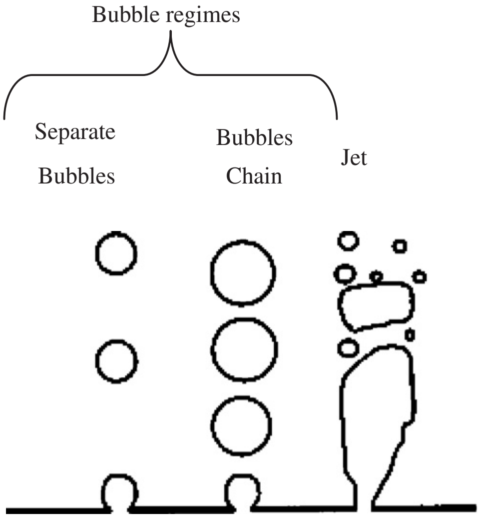

Fig. 10. Formation regimes (Heijnen and Van't Riet, 1984; Camarasa et al., 1999).

cyclohexane ($d_{32} = 0.0045$ m at $h = 0$ m to 0.0056 m at $h = 0.2$ m), as there are less small bubbles in the injection area in water than in cyclohexane. Note that, at $h = 0.2$ m, the bubble size is roughly the same for both media (around 5.7 mm).

- When the gas velocity increases, the bubble diameter tends to increase (around 0.007 m at $u_{G0} = 5$ m/s). At high gas velocity a population of small bubbles appears, but this occurs at higher gas velocity in water ($u_{G0} > 10$ m/s) than in cyclohexane ($u_{G0} \sim 5$ m/s) and its bubble fraction is always greater in cyclohexane (see also Fig. 14). Moreover, in water this population is not visible at sparger level; the small bubbles appear between $h = 0$ and 0.2 m.

In order to have a global view of the phenomena, the Sauter diameter and the average arithmetic diameter are compared and plotted versus the ejection velocity at $h = 0.2$ m (Fig. 15). In the case of cyclohexane, it appears that those diameters differ; even at small gas velocity there is a wider bubble distribution up from $u_{G0} = 5$ m/s. Moreover Table 2 shows that, at 5 m/s, there are both larger bubbles and smaller bubbles in cyclohexane than in water. It confirms that the tiny bubbles appear at smaller gas velocity in cyclohexane and that they come from bubble break-up: they are stripped off the largest bubbles. At higher gas velocity, both media present large distributions and bubble sizes are systematically smaller in cyclohexane.

To conclude, the comparison between the two media shows that in cyclohexane the bubbles are globally smaller (as expected, due to smaller surface tension). The axial effect depends on the gas velocity. In fact, as for both media the population of small bubble diminishes with h (coalescence) at small gas velocity but increases with h (break-up) at high gas velocity, and as there are always a larger concentration of small bubbles near the injection in cyclohexane than in water, the axial variations are more visible in cyclohexane at small gas velocity and in water at high gas velocity. Besides, in cyclohexane, the population of small bubbles appears at smaller gas velocity; this easy destabilisation of gas dispersion in cyclohexane could be responsible for the early transition of bubbling regime observed in bubble column with cyclohexane.

This analysis of bubble size distributions in a glass tank explains the global behaviour in bubble column; but so far it cannot explain the differences between our results obtained with cyclohexane, and those described in the literature for aqueous mixtures of low surface tension.

4. How to explain the differences between our results and literature?

As described previously, the main difference between our work and literature is the use of pure solvent instead of aqueous solution with surfactant. It could be responsible for the observed differences, as the studies performed with solvents by Burckhardt and Deckwer (1975) and Ozturk et al. (1987) also exhibit a moderate surface tension effect compared to the case of water with additives. On the other hand it is well known that mixtures have specific behaviour (Burckhardt and Deckwer, 1975; Bach and Pilhofer, 1978; Ozturk et al., 1987).

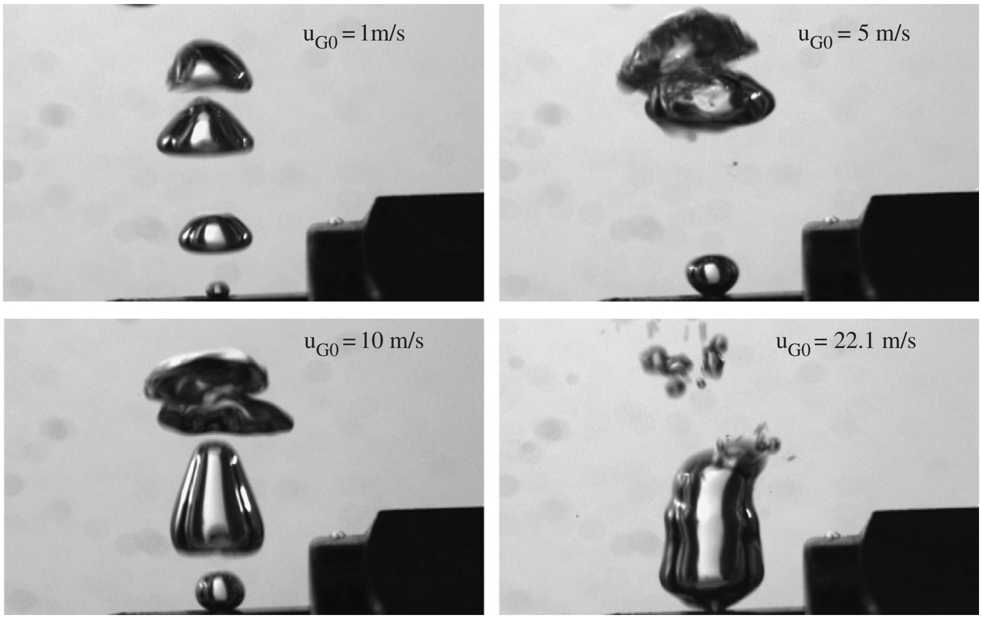

Fig. 11. Pictures of injection area in cyclohexane.

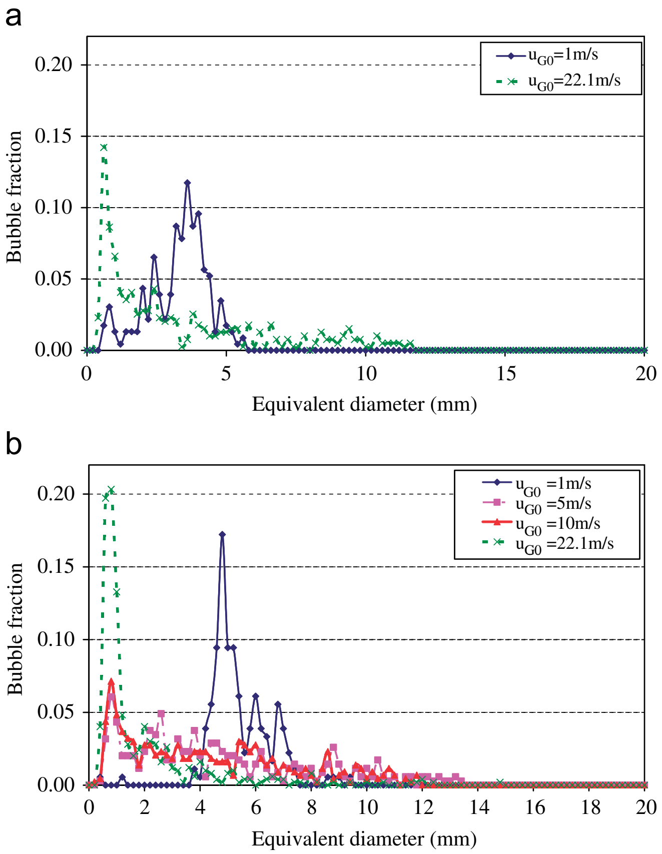

Fig. 12. Bubble distributions in cyclohexane at two levels: (a) cyclohexane, $h = 0\,\mathrm{m}$ and (b) cyclohexane $h = 0.2\,\mathrm{m}$.

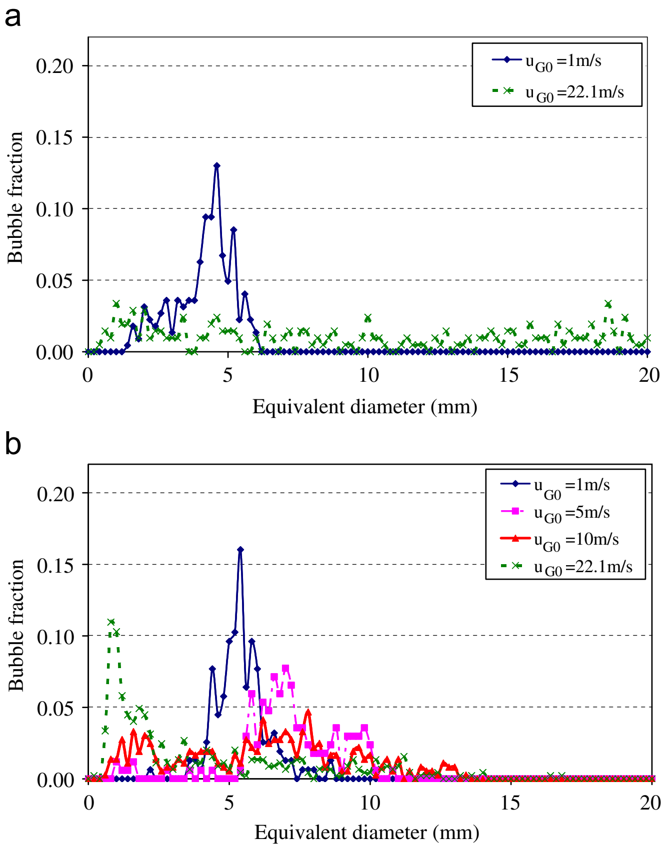

Fig. 13. Bubble distributions in water at two levels: (a) water, $h = 0\,\mathrm{m}$ and (b) water, $h = 0.2\,\mathrm{m}$.

The phenomena observed in the presence of surfactant can be related to the surface tension gradient around the bubble that limits the interface mobility, and as a consequence its velocity (Malysa et al., 2005; Prince and Blanch, 1990). Note that, as the surfactant migration to the bubble interface may take some time at small surfactant concentration, it could be interesting to

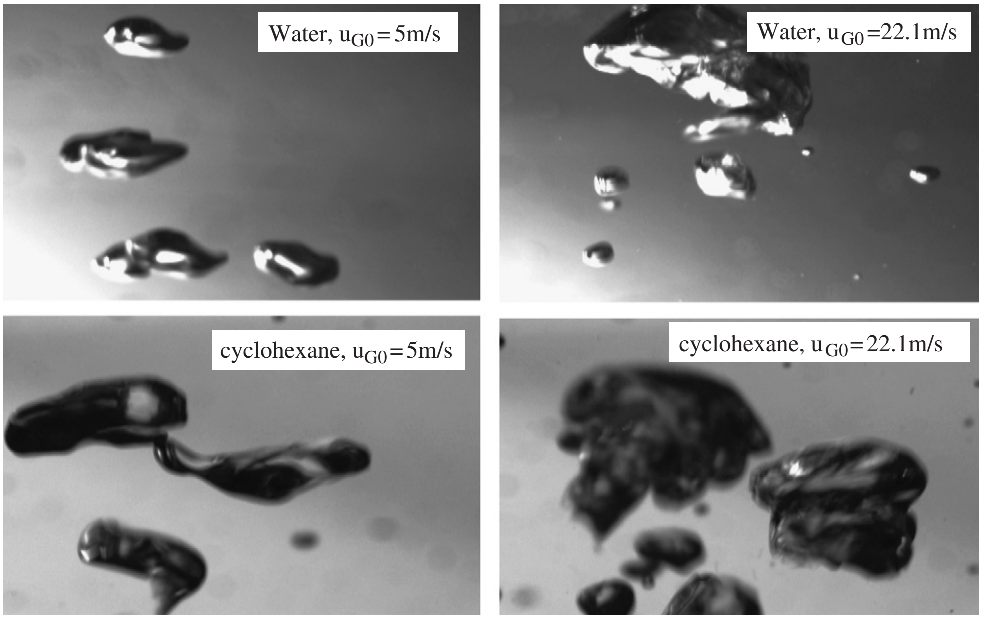

Fig. 14. Pictures taken at $h = 0.2$ m for both media at $u_{G0} = 5$ and 22.1 m/s.

determine the dynamic surface tension. This kind of investigation provides surface tension values for different surface ages (Loubière and Hébrard, 2004).

In order to check whether the observed differences between our results and those of literature are due to the use of pure solvent, the bubble distributions obtained in aqueous solution with surfactants are measured in the glass tank, as previously. The chosen surfactant is butanol, as alcohols are often used in literature (Kantak et al., 1995; Zahradnik et al., 1995, 1997; Camarasa et al., 1999; Krishna et al., 2000; Dhotre et al., 2004; Mouza et al., 2005; Dargar and Macchi, 2006); butanol is added to water at different concentrations from 0.01%’ to 0.1% vol.

First, the dynamic surface tension is determined thanks to the bubble pressure method, as described by Loubière and Hébrard (2004). This method is adequate for bubble interface ages from 0.05 to 50 s. The results for all the used liquids are reported in Fig. 16 . Note that the dynamic surface tension tends to the static surface tension at long formation times. The static surface tension is almost the same whatever be the butanol concentration used: this confirms the limit of this parameter to describe the observed phenomena. Fig. 16 also exhibits that the decrease in surface tension with bubble formation time is the steepest in cyclohexane, probably because it is the purest medium, that is to say the medium where the impurities migration is the less observed.

Now, the butanol concentration effect is analysed (Table 3 and Fig. 17). In the range studied, the butanol concentration has no clear effect, neither on arithmetic and Sauter diameters (Table 3, Fig. 17a), nor on bubble size distributions (Fig. 17b). As a matter of fact, there is a critical concentration above which the surfactants effect is independent of its concentration. Camarasa et al. (1999) estimate this critical

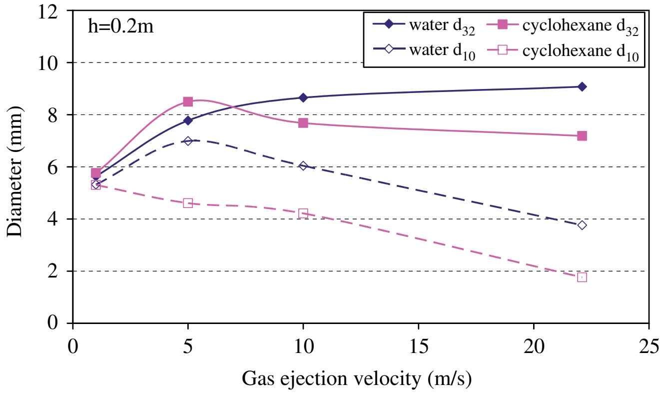

Fig. 15. Comparison of the evolution of the Sauter diameter and of the arithmetic average diameter versus gas ejection velocity (cyclohexane and water).

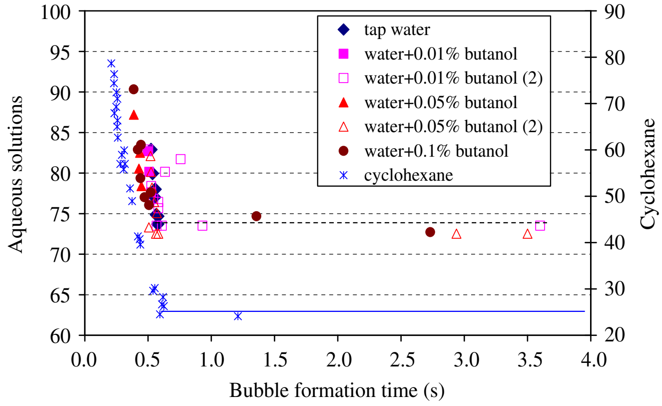

Fig. 16. Dynamic surface tension of different used liquids (mN/m).

Table 3
Results obtained in the glass tank for aqueous solutions of butanol

Liquid	Height (m)	u_{G0} (m/s)	d_{32} (mm)	d_{10} (mm)	$d_{\min}$ (mm)	$d_{\max}$ (mm)	Std deviation (%)	No. of treated bubbles
Water	0.2	1	5.64	5.32	2.04	8.43	17.13	156
Water + butOH 0.01%	0.2	1	4.05	3.61	0.89	5.38	26.55	286
Water + butOH 0.05%	0.2	1	4.42	3.88	0.84	5.86	29.64	226
Water	0.2	5	7.78	6.99	0.88	10.68	26.05	168
Water + butOH 0.01%	0.2	5	5.64	4.71	0.58	7.42	36.35	289
Water + butOH 0.05%	0.2	10	8.65	6.04	0.57	13.26	51.77	363
Water + butOH 0.01%	0.2	10	5.72	4.78	1.04	9.42	34.34	410
Water	0.2	22.1	9.07	3.76	0.13	16.70	92.31	447
Water + butOH 0.01%	0.2	22.1	6.18	4.07	0.58	9.13	56.39	421
Water + butOH 0.05%	0.2	22.1	6.41	4.31	0.54	10.28	55.15	347
Water + butOH 0.1%	0.2	22.1	6.40	3.86	0.29	10.98	62.64	456
Water	0	1	4.50	4.03	1.38	5.89	26.24	223
Water + butOH 0.01%	0	1	4.35	3.82	0.79	8.56	27.98	227
Water	0	22.1	15.63	9.45	0.38	20.08	67.51	207
Water + butOH 0.01%	0	22.1	9.22	5.65	0.52	13.22	65.30	329

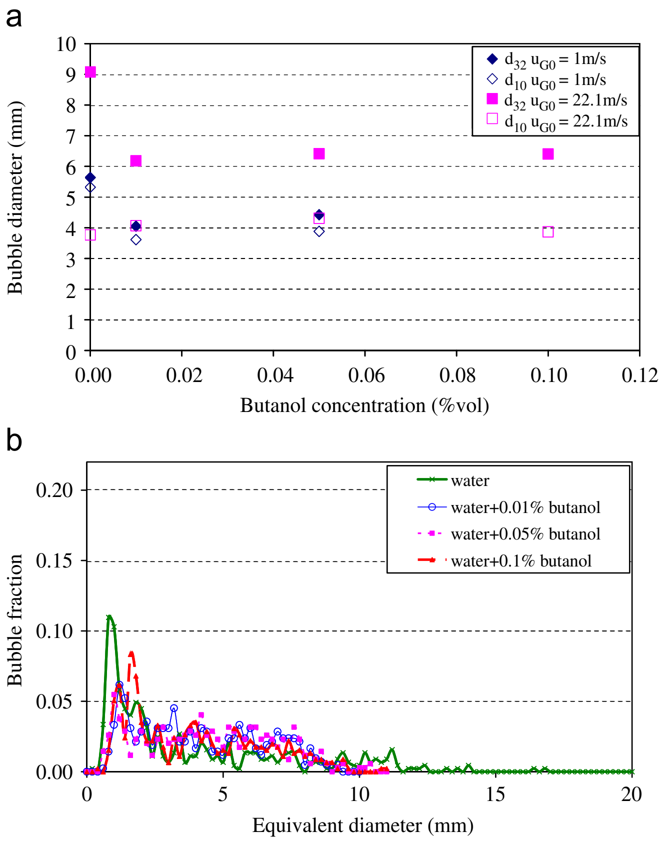

Fig. 17. Butanol concentration effect: (a) $h = 0.2\,\mathrm{m}$ and (b) $h = 0.2\,\mathrm{m}$, $u_{G0} = 22.1\,\mathrm{m/s}$.

concentration to about 10^{-3} mol/L of butanol in water; this is in accordance with our results as the lowest concentration we used (0.01% vol.) corresponds to 0.1 mol/L, i.e., a concentration largely greater than the critical concentration. In the following the presented results are then restricted to the results obtained for 0.01% vol. butanol solutions.

Our results also show that bubble mean diameters (d_{10} and d_{32}) are smaller in mixtures than in water (Fig. 17a) and that the bubble distributions are narrower, especially at high ejection velocity: at h=0.2 m, the maximal bubble size decreases (Table 3) and the population of tiny bubbles diminishes (Fig. 17b).

In fact, the butanol is already active in the sparger area and migrates quickly towards the bubble interfaces (see the dynamic surface tension, Fig. 16); this is in agreement with the work of Loubière and Hébrard (2004): these authors observe a particularly fast migration for the butanol.

To check whether the aqueous solution of butanol can model the behaviour of solvents and whether the evolution in respect to water is similar for both media, the distributions in water, aqueous solution, and cyclohexane are compared for $h = 0.2\,\mathrm{m}$ (Fig. 18). It appears that the addition of butanol in water leads to similar tendencies than in cyclohexane: the population of large bubbles moves towards smaller bubble size (4 mm in water + butanol instead of 5.5 mm in water at $u_{G0} = 1\,\mathrm{m/s}$). Nevertheless, at high gas velocity, the population of tiny bubbles is clearly smaller than in cyclohexane (and water): the bubble interfaces, stabilised by butanol, undergo less deformation due to shear stress and consequently do not easily break-up. In aqueous solution of butanol, the minimum bubble size is systematically higher and the maximum bubble size is smaller than in other media: bubble distributions are narrower. As a consequence, even if the butanol addition in water decreases the mean bubble size, which approaches the value obtained in cyclohexane, it does not lead to similar bubble size distribution: in aqueous solution, the width of bubble size distribution is smaller and the population of tiny bubbles is not observed. The bubble interface is rigidified by butanol hindering bubble coalescence, whereas the coalescence is less reduced in solvent.

The bubble distributions obtained in aqueous solution with butanol are then in accordance with the literature observations, but they cannot properly model the bubble distributions in pure solvent.

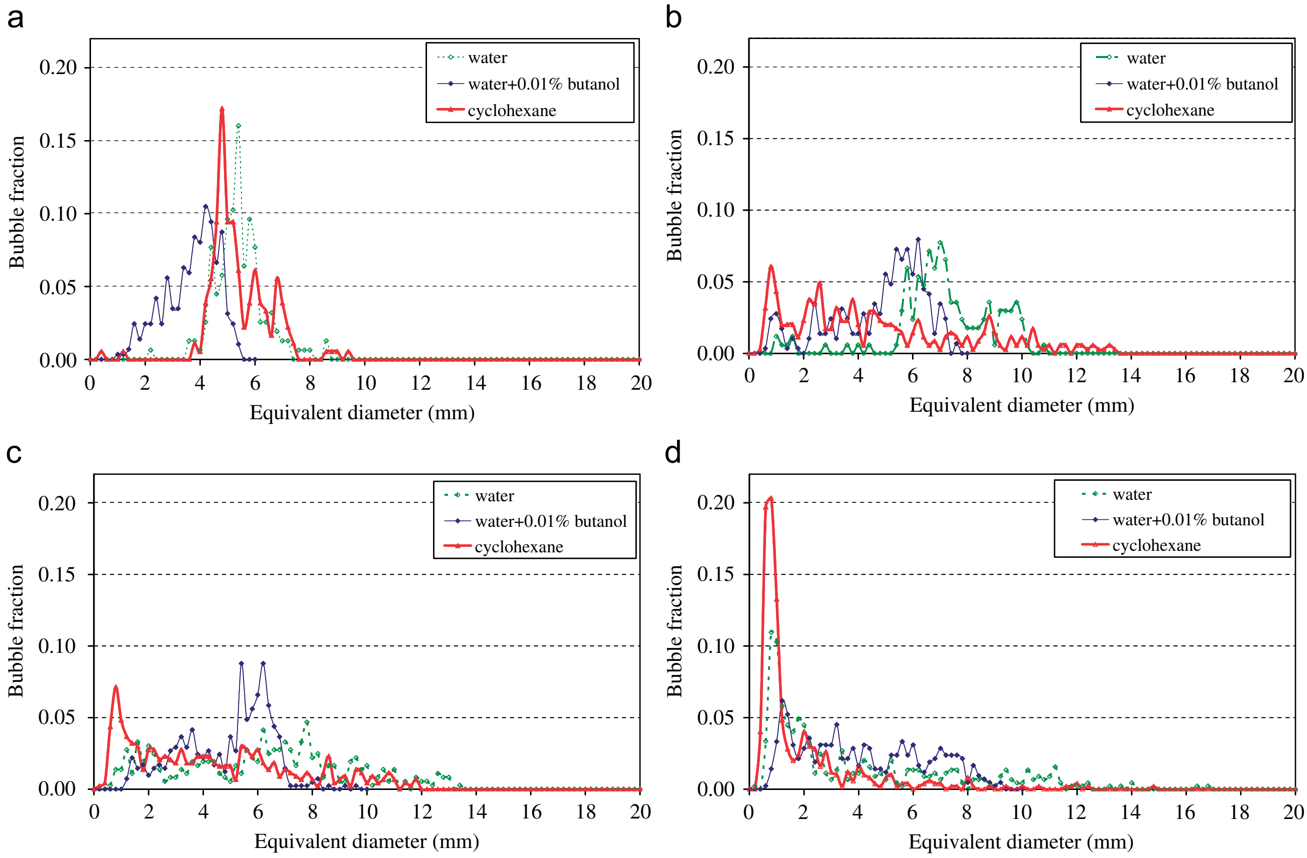

Fig. 18. Comparison of bubble distribution at $h = 0.2$ m for different liquid media: (a) $u_{G0} = 1$ m/s; (b) $u_{G0} = 5$ m/s; (c) $u_{G0} = 10$ m/s and (d) $u_{G0} = 22.1$ m/s.

5. Conclusions

The comparison between water and cyclohexane, two media having similar viscosity but different surface tension, is performed in bubble column and in bubble plumes. It appears in both cases that the bubble size is globally smaller in cyclohexane, because of smaller surface tension. However, the opposite trend can be observed in bubble column as the homogeneous regime is destabilised at smaller gas velocity in cyclohexane, probably because of the early apparition of the coalescence-break-up phenomena, as shown in the small tank. This behaviour concerns both batch and continuous liquid conditions, and has some consequences on mass transfer, as $k_L a$ coefficient may be lower in cyclohexane, when both media do not operate in the same hydrodynamic regimes.

These observations are not in agreement with the classical surface tension effect related in the literature. The observed differences can be explained by the use, in this study, of a pure liquid instead of classical aqueous solutions of surfactant (widely mentioned in the literature). In aqueous solution of butanol, the bubble size distribution in bubble plumes is more stable and the coalescence is more inhibited than in cyclohexane, where the bubble size distribution is less stable.

To conclude, the bubble size distributions in solvents cannot be experimentally modelled by means of aqueous solutions of surfactants, as their coalescence behaviour, a crucial parameter for bubble size distribution, is not the same. Consequently, the isolated effect of the surface tension is less important in solvent than in aqueous solutions. On the other hand, the easy destabilisation of bubbling regime in cyclohexane cannot be explained on the only basis of the physicochemical properties. Therefore, there is still some progress to do in order to better understand and predict the effect of liquid nature. It is then recommended to use the real medium in pilot studies as often as possible.

Notation

Symbols

a	interfacial area, m^2/m^3
d_0	sparger hole diameter, m
$d_{eq,i}$	equivalent diameter of i bubble, m
d_{10}	arithmetic mean diameter, m
d_{SM} or d_{32}	Sauter mean diameter, m
D_C	column diameter, m
h	axial position of measurements in small tank, m
H_L	liquid height, m
$k_L a$	volumetric mass transfer coefficient, s^{-1}
N	number of treated bubbles for image analysis, dimensionless
r	radial position in column, m
Re_0	Reynolds number at the orifice, dimensionless

u_L	superficial liquid velocity, m/s
u_G	superficial gas velocity, m/s
u_{G0}	gas velocity through the sparger hole, m/s

Greek letters

ε_G	global gas hold-up, dimensionless
μ_G	gas viscosity, Pa s
μ_L	liquid viscosity, mPa s
ρ_G	gas density, kg/m^3
ρ_L	liquid density, kg/m^3
σ	surface tension, N/m
φ	free area of sparger, dimensionless

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