MONITORING OF CONTAMINATION OF COAL PROCESSING PLANTS AND ENVIRONMENTAL WATERS USING BUBBLE VELOCITY MEASUREMENTS – ADVANTAGES AND LIMITATIONS

Jan ZAWALA[*], Ewa MALYSA[**], Marcel KRZAN[*], Kazimierz MALYSA[*]

[*] Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Krakow
[**] AGH University of Science and Technology, Dept. Environmental Engineering & Mineral Processing, Krakow

Abstract: The paper presents fundamentals of a simple physicochemical method (SPMD) and analysis of results obtained when the method was applied for detection of organic contaminations (surface-active substances SAS) in samples of environmental and industrial waters. The method is based on measurements of variations of air bubble local velocities, which can be significantly changed in presence of surface-active contaminants. Lowering of the bubble velocity is a consequence of a motion induced dynamic adsorption layer (DAL) formed over surface of the rising bubble. The DAL formation retards the surface fluidity and the bubble rising velocity can be lowered by over 50% when the bubble surface is completely immobilized. We showed that the SPMD is a very sensitive tool (detection limit even below 1 ppm) for detection of various kinds of surface-active substances (ionic, non-ionic) in water samples. On the basis of results obtained using precise laboratory set-up, an accuracy of the SPMD is discussed. Moreover, effect of inert electrolyte addition on the bubble velocity lowering and value of detection limit of the SPMD is discussed. Simple approach, enabling quantitative analysis of the surface-active contaminants in samples collected, based on "equivalent concentrations" determination, is proposed. Results obtained for industrial (Jankowice and Knurow coal processing plants, Jaslo Refinery channel) and environmental waters (Wisloka and Ropa river) are used for detailed analysis and critical discussion of advantages and limitations of the SPMD.

Keywords: *bubble velocity, water purity, surface-active contaminants, method of detection, adsorption layer*

Introduction

Contaminations of environmental waters are caused by different areas of human activities, mainly industrial and domestic (households). Increasing applications of various detergents, washing/cleaning powders and liquids, cosmetics, pharmaceutical

products means also an increasing volume of municipal sewages containing various surface active substances. Agriculture with growing application of fertilizers, herbicides and pesticides, and various branches of industry, such as, for example petroleum, cosmetics, pulp and paper, pharmaceutical, mineral processing industries are also large sources of organic wastes contaminating environmental waters. Generally, organic substances (pollutants) show low affinity to the aqueous phase, and therefore adsorption at the liquid/gas interface formation of adsorption layer is a typical feature of all kind of surfactants and surface active substances. Certainly, the surface activity of various organic substances (pollutants) depends on their chemical structure and can differ by orders of magnitude. Nevertheless, their adsorption at the liquid/gas interface means that their presence in waters can be detected through measurements of velocity of the rising bubble, which is highly affected by formation of the adsorption layer over the bubble surface.

The bubble velocity is very sensitive to presence of surface active substances (SAS) in water since the adsorption layer formed over surface of the rising bubble retards fluidity of the bubble surface (Levich, 1962). In clean water, devoid of any SAS, the bubble surface is fully mobile, and therefore its velocity is higher than that of a solid sphere of identical density and diameter, which surface is immobile (no-slip conditions). This is clearly seen comparing the predictions of the Hadamard–Rybczynski theory (motion of bubbles and drops in pure liquids under creeping flow conditions) and Stokes law (motion of solid particles under creeping flow conditions). Under creeping flow conditions (Reynolds number, Re < 1) the bubble and drop velocity is 50% higher than velocity of a rigid sphere of the same diameter and density difference. At higher Reynolds number the bubble surface immobilization by the SAS adsorption caused similarly high lowering velocity of the rising bubble (Clift et al., 1978; Sam et al., 1996; Bel Fdhila and Duineveld, 1996; Zhang and Finch, 1996; Ybert and di Meglio, 1998; Ybert and di Meglio, 2000; Liao and McLaughlin, 2000; Zhang et al., 2001, Krzan and Malysa, 2002ab; 2009; 2012; Krzan et al., 2004; 2007; Malysa et al., 2005; 2011).

Degree of adsorption coverage of the bubble, formed in SAS solutions at a capillary orifice, is determined by the adsorption kinetics and velocity of the bubble surface growth. The equilibrium adsorption coverage over the bubble surface is attained only, when the adsorption kinetics is faster than the rate of bubble surface growth. Nevertheless, independently if there was or was not the attained equilibrium adsorption coverage, the adsorption coverage over surface of the detaching bubble is uniform. When the bubble starts to float then a non-uniform distribution of the adsorbed molecules, called dynamic adsorption layer (DAL), starts to be formed over surface of the rising bubble (Levich, 1996; Dukhin et al., 1995; Dukhin et al., 1998, Zholkovskij et al., 2000; Malysa et al., 2005 and 2011; Krzan et al., 2007) as a result of the viscous drag exerted by fluid on the moving bubble. Formation of this dynamic structure of the adsorption layer means that the adsorption coverage is much lower at the upstream pole of the moving bubble than at the rear pole. This difference in

adsorption coverage means induction of the surface tension gradients over the bubble surface, which - depending on degree of adsorption coverage (Dukhin et al. 1995; Levich, 1996; Dukhin et al., 1998: Zholkovskij et al., 2000; Krzan and Malysa, 2002ab) cause either partial or a complete immobilization of the bubble surface. As showed elsewhere (Krzan and Malysa, 2002ab; 2009; 2012; Krzan et al., 2004; 2007; Malysa et al., 2005; 2011) the degree of adsorption coverage needed for complete immobilization of the bubble surface varies for different surface active substances, but generally is rather low, a few percent in the case of non-ionic surfactants and up to ca. 30% for ionic SAS. On the other hand, the time of the DAL formation depends on concentration of SAS solutions. It needs to be underlined here that, as even traces of surfactant can lower the bubble velocity, monitoring the bubble motion in waters can be used as sensitive tool for detection of surface active contaminations. Loglio et al. (1989) were probably the first who applied measurements the time of bubbles rising at different heights of the column for detection surfactants presence in water. They pointed out that the velocity of the rising bubbles (2–3 mm diameter) decreased when an amount of surfactant increased. Recently, Zawala et al. (2007) carried out systematic studies on influence of various contaminants on the bubble rising velocity and proposed a simple physicochemical method (SPMD) for detection of organic contaminations in water. The details of the SPMD are described below.

The paper analyses possibilities, advantages and limitations of application of the bubble velocity measurements in monitoring presence and concentration of organic contaminants in environmental and industrial waters. Influence of ionic and nonionic surface active substances on motion of the rising bubble and the experimental data obtained for samples collected in two polish rivers (Zychowska, 2012) and in water circulating system of the coal processing plants (Malysa et al., 2009) are presented and discussed.

Experimental

The bubble velocity measurements were carried out using the precise laboratory set-up, called here Moticam-2000 and the SPMD set-up elaborated, described in details by Zawala et al. (2007). The Moticam 2000 set-up described in details by Krzan and Malysa (2002a) consists of the following main elements (Fig. 1, right): i) a square glass column of cross section 40x40 mm with the capillary of inner diameter 0.075 mm, ii) syringe pump for gas supply with high precision control of the flow rate, iii) stroboscopic illumination system, and Moticam-2000 CCD camera coupled with PC computer for the images recording, and iv) image analysis software. The bubble local velocity was determined as

$$U = \frac{\sqrt{(x_{i+2} - x_{i+1})^2 + (y_{i+2} - y_{i+1})^2}}{\Delta t} \, , \tag{1}$$

where (x_{i+2}, y_{i+2}) and (x_{i+1}, y_{i+1}) are the coordinates of the subsequent positions of the bubble bottom pole and Δt is the time interval between stroboscopic lamp flashes. In majority of the experiments Δt is equal to 0.01 s. The bubble terminal velocity was calculated as an average for distances, where values of the bubble local velocity started to be constant. In distilled water, the bubble formed at the capillary used in the experiments had the radius of 0.74 mm.
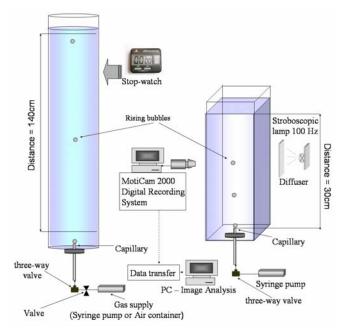

Fig. 1. Sketch of the Moticam 2000 and SPMD set-ups

Simplicity of measurements and low cost of the experimental set-up were the main aims of elaboration of the simple physicochemical method for detection (SPMD) of organic contaminants in water (Zawala et al., 2007). The SPMD set-up (Fig. 1, left) consists of: i) a long (ca. 1600 mm) glass tube with the glass capillary sealed at the bottom, ii) a stop-watch, and iii) air supply system with a controlled flow rate. We used either a compressed air container with a precise valve or the syringe pump. Single bubbles were formed at the capillary orifice with time interval above 10 s between each subsequent bubble. The time of bubble passage of the distance 140 mm (t_i) was measured manually using stop-watch. The choice of this measurement distance is a compromise between a convenience of the bubble observation and compactness of the set-up. When the time intervals are determined manually using the stop-watch, then we should have long distance of the bubble passage to measure the time values with a satisfactory accuracy and precision. To increase the precision of determination, the measurements were repeated at least 20 times (the passage time of

20 bubbles was measured and the average value was calculated for every sample). The time interval (t_i) was started to be measured when the bubble was passing the point marked 60 mm above the capillary orifice, i.e. after acceleration period of the bubble motion (Krzan et al., 2007; Zawala et al., 2007) and the bubble velocity (U_i) was determined as:

$$U_i = \frac{140}{t_i}.$$ (2)

Results and discussion

Sequences of images of the bubbles rising in $3 \cdot 10^{-5}$, $1 \cdot 10^{-4}$ and $3 \cdot 10^{-3}$M sodium n-dodecyl sulfate (SDDS) solutions are presented in Fig. 2. Figure 2 shows the bubbles motion immediately after detachment (acceleration stage of the rising bubble motion) and at the distance L=30 cm from the capillary. The experiments were carried out under identical frequency of stroboscopic illumination (100 Hz), therefore the photos clearly illustrate the following features of the bubble motion: i) the detached bubble increases rapidly its rising velocity, ii) at distance L = 30 cm the bubble velocity seems to be constant (does not change with distance), iii) with increasing the SDDS concentrations the bubble velocity decreases, iv) spherical bubbles formed at the capillary orifice started to be deformed immediately after their detachment, and v) degree of the bubble shape deformation was decreasing with the SDDS concentration.

Figure 3 (left) presents quantitative data on influence of the SDDS concentration on the bubble local velocities. A similar data for Persil (a popular washing powder used in Polish households) as an comparison are given in Fig. 3 (right). It needs to be underlined, that the washing powder Persil is a commercial product and similarly as all commercial detergents it is not a well-defined surfactant but a "formulation", that is a mixture of ionic and non-ionic surfactants containing many different additives. We carried out measurements to check if the bubble velocity is changing in similar way in Persil solutions as in solutions of well-defined ionic and non-ionic surfactants. The general features of the bubble local velocity profiles (Fig. 3) show that variations of the bubble local velocities with distance are similar for the SDDS and Persil solutions. Immediately after detachment, the bubbles velocity monotonically increases and far away from the capillary, a tendency to attain a constant value (terminal bubble velocity) can be noted for all concentrations of SDDS and Persil solutions. Moreover, at low concentrations of SDDS and Persil there are maxima on local velocity profiles. As it was already showed before (Krzan et al., 2004; Malysa et al., 2005 and 2011; Krzan et al., 2007), the occurrence of the maximum on the local velocity profile indicates that dynamic architecture of the adsorption layer (DAL), causing immobilization of the bubble interface as a result of the surface tension gradients inducement, was not established during the acceleration stage of the bubble motion.
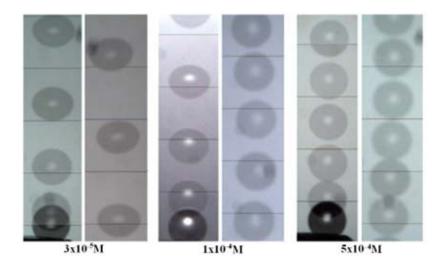
Fig. 2. Sequences of photos (3 pairs) showing rising bubbles in SDDS solutions, immediately
after detachment (left side sequences) and far away (30 cm) from the capillary.
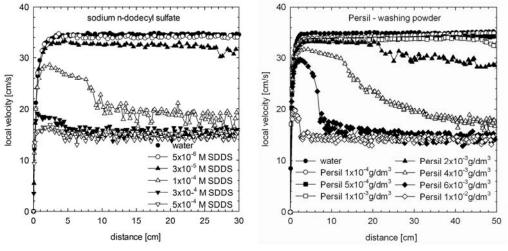Time interval between the stroboscopic lamp flashes Δt = 0.01 s

Fig. 3. Bubble local velocities as a function of distance in SDDS (left)
and Persil washing powder (right) solutions of different concentrations

The influence of electrolyte concentration on the bubble velocity in solutions of ionic and nonionic surface active substances is compared in Figs. 4 and 5. Sequences of photos presented in Fig. 4 illustrate that addition of inert electrolyte (NaCl) had practically no influence on the bubble velocity (L = 30 cm) in $2 \cdot 10^{-4}$ M n-hexanol solution (non-ionic surface active substance) and caused a significant lowering the bubble velocity in $3 \cdot 10^{-5}$ M SDDS solution (anionic surfactant). It needs to be underlined that without ionic surfactant presence, the bubble velocity in 0.05 M NaCl

solution is identical as in distilled water (Krzan and Malysa, 2012). Thus, the electrolytes affect the bubble velocity in solutions of ionic surfactants through variation of their adsorption at the bubble surface and /or their surface activity and dissociation degree.
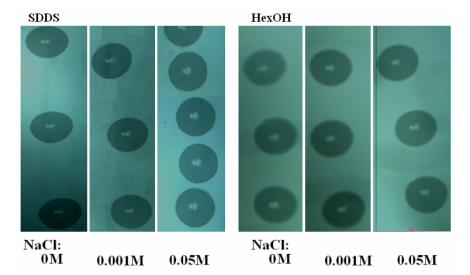

Fig. 4. Sequences of photos (2 sets) showing the influence of electrolyte
on bubble motion in $3 \cdot 10^{-5}$ M SDDS and $2 \cdot 10^{-4}$ M n-hexanol solutions far away (30 cm)
from the capillary. Time interval between the stroboscopic lamp flashes $\Delta t = 0.01$ s
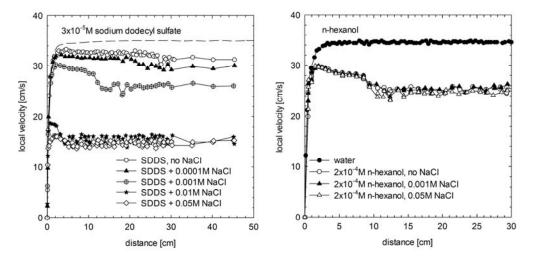

Fig. 5. Influence of electrolyte on the bubble local velocity profiles
in $3 \cdot 10^{-5}$ M SDDS and $2 \cdot 10^{-4}$ M n-hexanol solutions

Figures 5 shows influence of NaCl concentration on profiles of the bubble local velocity in $3 \cdot 10^{-5}$ M sodium dodecyl sulfate SDDS (left) and $2 \cdot 10^{-4}$ M n-hexanol (right) solutions. It can be seen that the bubble local velocity profile in n-hexanol solution does not depend on concentration of the electrolyte added. The picture is completely different in the case of the $3 \cdot 10^{-5}$ M SDDS solution. Addition of 0.05 M NaCl resulted in lowering of the bubble terminal velocity by ca. 50%, from 31.4±0.6 (no electrolyte) to 14.6±0.5 cm/s (0.05 M NaCl). The bubble velocity profiles in $3 \cdot 10^{-5}$ M SDDS solution were significantly affected even in the presence of much smaller (0.01 and 0.001M) NaCl concentrations (Fig. 5 left). Influence of inert electrolyte and pH on parameters of the rising bubble motion in solutions of sodium n-alkylsulfates of different hydrocarbon chain length was studied earlier by Krzan and Malysa (2009, 2012) and it was concluded that electrolyte affected the bubble motion through its influence on state of the dynamic adsorption layer formed over surface of the rising bubbles. It is rather well known and documented in the literature (Kalinin and Radke, 1996; Warszynski et al., 1998, 2002; Adamczyk et al., 1999ab; Para et al., 2005; Jarek et al., 2010) that addition of electrolyte can increase adsorption of ionic surfactant. For example in the case of the SDDS solutions, the surface tension isotherm can be shifted towards lower concentrations by more than order of magnitude (Warszynski et al., 1998). This effect is related to neutralization of the surface charge of adsorbed ionic surfactant molecules by counter ions adsorbed in the stern layer. In other words, the electrolyte presence caused that the SDDS adsorption coverage at the bubble surface was increased, and therefore fluidity of the bubble surface was retarded in a higher degree. It should be added here, that at more concentrated SDDS solutions the influence of electrolyte presence is much smaller and disappears, when the SDDS adsorption coverage is high enough for a complete retardation of the bubble surface mobility (Krzan and Malysa, 2009, 2012). We would like to underline here that data presented in Fig. 5 clearly show a possibility of checking and distinguishing if samples of the contaminated waters contained ionic, nonionic and/or mixtures of ionic and nonionic surfactants and/or formulations. For this purpose the appropriate experiments and analysis of influence of the electrolyte and/or pH on the bubble velocity would have to be carried out.

Figure 6 presents the bubble velocities in samples of waters from rivers in Jaslo region and the Jaslo Refinery Channel (JRC). The bubble velocity in the Wisloka river, upstream of the Jaslo Refinery Channel (JRC) inlet was 32.5±0.5 cm/s, that is practically identical as in Krakow tap water. Waters in the Jaslo Refinery channel contained a lot surface active substances (organic contaminants) since the bubble average velocity was only 15.4±0.2 cm/s in these waters. Therefore, in the Wisloka waters sample collected below the JRC inlet, the bubble velocity decreased to 31.3±0.5 cm/s. As the waters of the Ropa river were of similar quality so the bubble velocity in water samples from Wisloka below the Ropa inlet did not change.
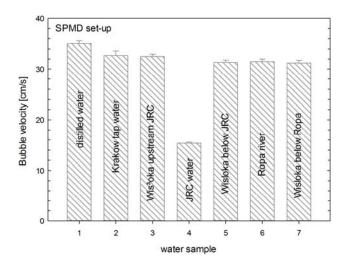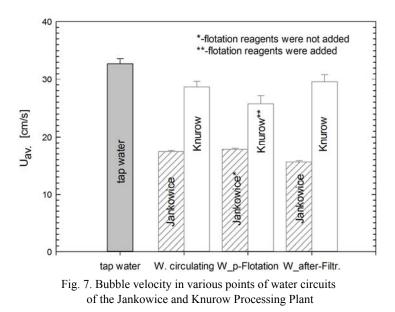
Fig. 6. Bubble velocity in samples of waters
from Jaslo region – Wisloka and Ropa rivers, Jaslo Refinery Channel

Figure 7 presents the bubble velocities in samples collected at different points of the water circulation systems in Knurow and Jankowice Coal Processing Plants (Malysa et al., 2009). The bubble terminal velocity in Krakow tap water as comparison is also given. The bubble velocities in all samples from Knurow and Jankowice Coal Processing Plants were significantly lower than in tap water. The bubble velocities in samples from the Jankowice Plant were systematically much

Fig. 7. Bubble velocity in various points of water circuits
of the Jankowice and Knurow Processing Plant

lower than in the Knurow samples. It shows that waters of the Jankowice water circulating system contained more surface active substances (flotation reagents used in the plant). The water prior flotation sample (Fig. 7, W_p-flotation) was collected in the Jankowice Plant before the flotation reagents were added to the flotation feed, while in the case of the Knurow Plant after the reagents addition. This is immediately reflected in the bubble velocities measured. In the case of the Knurow samples the bubble velocity was the lowest in water prior flotation because of addition of the flotation reagents. These data clearly show that the bubble velocity measurements can be used as a simple method for monitoring presence and variations of the flotation reagents concentration in industrial water circulating systems.

The bubble velocity is highly dependent on concentration of surface active substances, especially at their lowest concentrations. It is very advantageous since it makes possible detection of even traces of surface active substances in environmental and industrial waters. On the other side, however, there is no a unique dependence and for different the SAS the bubble velocity variations with solution concentration can be quite different (Malysa et al., 2005, 2011) and this is the main difficulty in converting the bubble velocity variations into contaminants concentration. Therefore, a reagent "X" or commercial products "Y", "Z", etc. needs to be chosen as a "model pollutant" and used for calibration. Then, the concentration of waters contaminants can be expressed as the "equivalent concentration of "X", "Y" or "Z". Zawala et al. (2007) proposed to use the commercial detergents "Ludwik" (washing liquid) and "Vizir" (washing powder), widely used in Polish household, as the "reference detergents" for environmental waters. Montanol and Flotanol, which are mixtures of higher alcohols and esters (Malysa et al., 2009) are the flotation reagents used in Polish coal processing plants therefore, they were chosen as the "reference reagents" for the Knurow and Jankowice water circulation systems.

Figure 8 shows dependences of the bubble velocity on concentration of Ludwik, Vizir, Montanol and Flotanol solutions. From Fig. 8 it can be seen that the dependences of the bubble velocity on Montanol and Flotanol solution concentration are almost identical and quite different from that ones for Ludwik and Vizir. The highest surface activities were observed for Flotanol and Montanol, while the lowest for the Vizir washing powder. The relation between the average bubble velocity U_{av}, concentration of surface active reagent c was used to fit experimental data obtained for Ludwik, Vizir, Flotanol and Montanol solutions:

$$U_{av} = P \exp\left(\frac{Q}{c+R}\right), \tag{3}$$

where P, Q and R are fitting parameters (Fig. 8). The values of fitting parameters obtained for these "reference reagents" are collected in Table 1. The values of these parameters are very similar for Montanol and Flotanol since these reagents lower the bubble velocity in a similar way and at similar concentrations.

Rearrangement of Eq. 3 gives relation:

$$c = \frac{Q - R(\ln U_{av} - \ln P)}{\ln U_{av} - \ln P},\qquad(4)$$

which can be used to express the degree of environmental and industrial waters contaminations in a concentration scale (as equivalent concentration of either Ludwik, or Vizir, or Montanol, or Flotanol). When the bubble velocity measured in industrial and/or environmental waters is 15–16 cm/s, the samples should be diluted in the controlled manner, because such low velocity value means that the bubble surface was completely immobilized, and therefore the bubble velocity stopped to be dependent on SAS (contaminants) concentration (Malysa et al., 2011). Thus, to determine real concentration of contaminants in such samples, the bubble velocity measurements should be carried out as a function of the sample dilution.
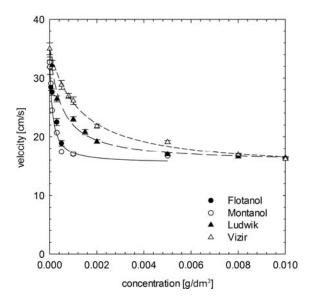

Fig. 8. The bubble velocity as a function of Ludwik (▲),Vizir (△), Montanol (◊) and Flotanol (♦) concentration. Lines are the exponential function (Eq. 3) fitted to Ludvik, Vizir and Montanol experimental data

Table 1. Values of the parameters *P*, *Q*, *R* obtained from fitting Eq. 3 to experimental data

Surfactant	P [cm/s]	Q [g/dm^3]	R [g/dm^3]
Montanol	15.4	$1.97 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$
Flotanol	15.4	$1.3 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
Ludwik	15.6	$6 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$
Vizir	14.2	$1.8 \cdot 10^{-3}$	$2 \cdot 10^{-3}$

Figure 9 shows dependences of the bubble velocity on dilution of the Jaslo Refinery Channel (JRC) and Jankowice waters after filtration. Table 2 presents contaminations degree of the environmental and industrial waters calculated using the fitting parameters collected in Table 1. The results clearly illustrate possibilities and some limitations of application of the bubble velocity for monitoring presence and concentration of surface active contaminants in environmental waters. The proposed method is very sensitive and enables detection even traces of organic contaminants in environmental and industrial waters.
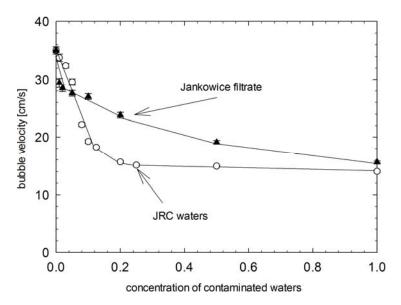

Fig. 9. The bubble velocity in diluted samples of JRC waters
and Jankowice waters after filtration (lines added to guide the eye)

Table 2. Concentration of contaminants in environmental and industrial waters expressed in units
of equivalent concentrations of Ludwik, Vizir and, Flotanol and Montanol

Sample	Ludwik mg/dm^3	Vizir mg/dm^3	Flotanol mg/dm^3	Montanol mg/dm^3
Distilled water	0,00	0,00	0,00	0,00
Tap water	0,07	0,16	0,00	0,00
Wisloka r. before oil renifery	0,08	0,17	0,00	0,00
Wisloka r. after oil renifery	0,12	0,28	0,01	0,02
Ropa	0,11	0,26	0,01	0,02
Knurow coal mine – water circulating	0,25	0,57	0,04	0,06
Knurow coal mine – water prior flotation	0,46	1,03	0,08	0,12
Knurow coal mine – water after filtration	0,20	0,46	0,03	0,04
Jankowice coal mine – water circulating	4,75	6,86	0,89	1,35
Jankowice coal mine – water prior flotation	3,81	5,97	0,73	1,10

In the case of nonionic surface active substances the detection limit can be even below 0.1 ppm (Table 2 for Flotanol and Montanol equivalent concentrations). When waters are contaminated by unknown mixtures of the ionic and non-ionic surface active substances, then the detection limit is shifted to higher concentrations, but this is still within the concentration range below 1 ppm, as can be observed in Table 2 (equivalent concentrations of Ludwik and Vizir). Moreover, the method is reliable, quite simple and non-expensive. In the measurements there is no need to add or use any additional reagents, and this is a big advantage of the simple physicochemical method SPMD. The SPMD can be especially useful for quick and direct controlling of variations of reagents concentration in different points of the industrial water circulating systems. On the other side, one should remember that the method can express a contamination degree only by means of the units of equivalent concentrations of some reference detergent after careful calibration.

Conclusions

The measurements of velocity variations of the rising bubbles was successfully applied for detection of organic (surface active) contaminants presence in environmental and industrial waters. The simple physicochemical method (SPMD) elaborated is based on measurements of variations of rising bubble average velocity. It was shown how highly dependent is the bubble velocity on presence of surface active substances (SAS), especially at their lowest concentrations. The bubble velocity is a very sensitive tool for detection of even traces of organic contaminant, because its detection limit of the SAS presence is lower by over order of magnitude than in the case of the surface tension measurements. The SPMD set-up is simple and non-expensive and easy to operate even under field conditions. It was shown that the SPMD method enables, when applied properly, to detect the SAS presence in concentrations, even below 1 ppm. The method can be especially useful for quick and direct controlling of variations of reagents concentration in different points of the industrial water circulating systems. Additionally, it was shown that by addition of inner electrolyte, the type of the surface active contaminant (ionic, non-ionic) can be distinguished.

The bubble velocity is highly sensitive to presence of any surface active substance and this is simultaneously a big advantage of the SPMD and difficulty in converting the bubble velocity variations into a contaminant concentration. The method of converting the bubble velocity variations into contaminants concentration expressed in terms of "equivalent concentrations of a "model contaminant" is described and it advantages and limitations are evaluated.

References

ADAMCZYK Z., PARA G., WARSZYNSKI, P., 1999, *Influence of ionic strength on surface tension of cetyltrimethylammonium bromid*, Langmuir 15, 8383–8387.

ADAMCZYK Z., PARA G., WARSZYNSKI P., 1999, *Surface tension of sodium dodecyl sulphate in the presence of a simple electrolyte*, Bull. Pol. Ac. Sci. 47, 175–186.

BEL FDHILA R., DUINVELD P.C., 1996, *The effect of surfactant on the rise of spherical bubble at high Reynolds and Peclet numbers*, Phys. Fluids A 8, 310–321.

CLIFT R., GRACE J.R. and WEBER M.E., 1978, *Bubbles, drops and particles*, Academic Press, New York, San Francisco, London.

DUKHIN S.S., KRETZSCHMAR G., MILLER R., 1995, *Dynamics of adsorption at liquid interfaces. Theory, Experiments, Application*, Elsevies, Amsterdam-Laussane-New York- Oxford-Shannon

DUKHIN S.S., MILLER R., LOGLIO G., 1998, *Physicochemical hydrodynamics of rising bubble*, in: Studies in Interface Science, Elsevier, 367–432.

JAREK E., JASINSKI T., BARZYK W., WARSZYNSKI P., 2010, *The pH regulated surface activity of alkanoic acids*, Colloids Surf. A. 354, 188–196.

LEVICH V.G., 1962, *Physicochemical hydrodynamics*, Prentice-Hall, Inc., Engelwood Clift, N.J.

LIAO Y., MCLAUGHIN J.B., 2000, *Bubble motion in aqueous surfactant solutions*, J. Colloid Interf. Sci. 224, 297–310.

KALININ V.V., RADKE C.J., 1996, *A ion-binding model for ionic surfactant adsorption at aqueous-fluid interfaces*, Coll. Surf. A. 114, 337–350.

KRZAN M., MALYSA K., 2002, *Profiles of local velocities of bubbles in n-butanol, n-hexanol and n-nonanol solutions*, Colloids and Surfaces A: 207, 279–291.

KRZAN M., MALYSA K., 2002, *Influence of frother concentration on bubble dimension and rising velocities*, Physicochemical Problem of Mineral Processing 36, 65–76.

KRZAN M., MALYSA K., 2009, *Influence of solution pH and electrolyte presence on bubble velocity in anionic surfactant solutions*, Physicochemical Problems of Mineral Processing 43, 43-58.

KRZAN M., MALYSA K., 2012, *Influence of electrolyte presence on bubble velocity in solutions of sodium n-alkilsulfates (C8, C10 and C12)*, Physicochemical Problems of Mineral Processing, 48, 49–62.

KRZAN M., LUNKENHEIMER K., MALYSA K., 2004, *On the influence of the surfactant's polar group on the local and terminal velocities of bubbles*, Colloids and Surfaces A: 250, 431–441.

KRZAN M., ZAWALA J., MALYSA K., 2007, *Development of steady state adsorption distribution over interface of a bubble rising in solutions of n-alkanols (C_5, C_8) and n-alcyltrimethylammonium bromides (C_8, C_{12}, C_{16})*, Colloid & Surfaces A: 298, 42–51.

LOGLIO G., DEGLI INNOCENTI N., TESEI U., CINI R., WAND Q.-S., 1989, *Il Nuovo Cimento* Della Socieraie Italiana di Fisica C. 12, 289.

MALYSA E., IWANSKA A., HANC A., MALYSA K., 2009, *Metoda monitorowania stężenia odczynników flotacyjnych w wodach obiegowych zakładów przeróbczych węgla przez pomiar prędkości pęcherzyków powietrza*, Gospod. Surowcami Mineralnymi, 25 (3) 109–120.

MALYSA K., KRASOWSKA M., KRZAN M., 2005, *Influence of surface active substances on bubble motion and collision with various interfaces*, Adv. Colloid Interface Sci. 114–115C: 205–225.

MALYSA K., ZAWALA J., KRZAN M., KRASOWSKA M., 2011, *Bubbles Rising in Solutions; Local and Terminal Velocities, Shape Variations and Collisions with Free Surface*, in: R. Miller, L. Liggieri (Eds.) Bubble and Drops Interfaces, 243–292.

PARA, G., JAREK, E., WARSZYNSKI, P., 2005, *The surface tension of aqueous solution of cetyltrimethylammonium cationic surfactants in presence of bromide and chloride counterions*, Colloids Surf. A. 261, 65–73.

SAM A., GOMEZ C.O., FINCH J.A., 1996, *Axial velocity profiles of single bubbles in water/frother solutions*, Int. J. Miner. Process. 47, 177–196.

WARSZYNSKI, P., BARZYK, W., LUNKENHEIMER, K., FRUHNER, H., 1998a. *Surface tension and surface potential of Na n-dodecylsulfate at the air solution interface: Model and experiment*, J. Phys. Chem. B 102, 10948–10957.

WARSZYNSKI, P., LUNKENHEIMER, K., CICHOCKI, G., 2002, *Effect of counterions on the adsorption of ionic surfactants at fluid−fluid interfaces*, Langmuir 18, 2506–2514.

YBERT C. and DI MEGLIO J.-M., 1998, *Ascending air bubbles in protein solutions*, Eur. Phys. J. B 4, 313-319.

YBERT C. and DI MEGLIO J.-M., 2000, *Ascending air bubbles in solutions of surface active molecules: influence of desorption kinetics*, Eur. Phys. J. E 3, 143-148.

ZAWALA J., SWIECH K., MALYSA K., 2007, *A simple physicochemical method for detection of organic contaminations in water*, Colloids & Surfaces A, 302, 293.

ZHANG Y., FINCH J.A., 1996, *Terminal velocity of bubbles: approach and preliminary investigation*, Column 96, 63–69.

ZHANG Y., FINCH J.A., 2001, *A note on single bubble motion in surfactant solution*, J. Fluid Mech. 429, 63-66.

ZHANG Y., MCLAUGHIN J.B., FINCH J.A., 2001, *Bubble velocity profile and model of surfactant mass transfer to bubble surface*, Chem. Eng. Sci. 56, 6605–6616.

ZHOLKOVSKIJ E.K., KOVALCHUK V.I, DUKHIN S.S., MILLER R., *Dynamics of Rear Stagnant Cap Formation at Low Reynolds Numbers: 1. Slow Sorption Kinetics*, J. Coll. Interf. Sci., 226 (2000), 51–59

ZYCHOWSKA P., *Monitorowanie stanu czystości wód poprzez pomiary prędkości pęcherzyków gazowych*, M.Sc. Thesis (in Polish), Jagiellonian University, Krakow, 2012.