Density and surface tension of aqueous solutions of adjuvants used for tank-mixes with pesticides

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ABSTRACT

Adjuvants are surface active agents that are added to pesticide formulations or tank-mix to facilitate the mixing, application, or efficacy of these products. Addition of adjuvants changes the physico-chemical properties of spray liquid. In this work, we have focused in particular on surface tension and density of aqueous solutions of different adjuvants registered for mixing with herbicides. Eleven different adjuvants were subject of this study under laboratory conditions. An equation which enables determination of density of aqueous solutions in concentration range of 0–15 g/kg was designed. Average difference between the experimental and calculated density values amounts to ± 0.006%. The concentration dependence of surface tension was utilized to determine the critical micelle concentration (cmc). Evidently, the cmc of most tested adjuvants was lower than the amount recommended by manufacturer, especially in case of adjuvants Dedal 90 EC and Mero 33528. For adjuvant Trend 90 EC the recommended rate is even lower than that obtained for the cmc. Maximum reduction of the surface tension of water was achieved with adjuvants Silwet L-77 and Break Superb.

Keywords: CMC; surfactants; efficacy; micelles; solubilization

Efficacy of herbicides is influenced by many factors. Efficient delivery of the active ingredient (a.i.) to the target site is generally recognised as a fundamental requirement for herbicide activity and selectivity (Knoche 1994). Delivery of a potentially lethal dose of a.i. depends upon a complex interaction of factors including the application quality, absorption, translocation, immobilisation and detoxification. The activity and selectivity of foliage-applied compounds is influenced by the efficiency of cuticle retention and penetration, tissue absorption and, in the case of phloem-systemic compounds, translocation (Kirkwood 1993).

For better application properties and intake, herbicides are often used in mixtures with other herbicides and chemicals, such as adjuvants, insecticides, fungicides, safeners, and fertilizers (DiTomaso 1999, Zhang and Somasundaran 2006, Green and Beestman 2007, Pose-Juan et al. 2009).

Adjuvant is any substance added to pesticide solution for better mixing, application, intake, etc. Tank-mix adjuvants are used in order to improve the efficacy of foliage-applied pesticides. Adjuvants can enhance ultimate biological performance: firstly, by increasing the amount of active ingredient retained by the target and, secondly, by promoting its uptake (Holloway et al. 2000). A better understanding of the factors influencing spray quality and intake of pesticides may contribute to increased efficacy and/or dose reduction. Considering that nowadays a great emphasis is put on ecology, the usage of adjuvants is of a great concern. There is no universal adjuvant for use for all herbicides and it is necessary to select the appropriate adjuvant for each application and take into account its properties and the conditions of application (Tu et al. 2001, Tadros 2005).

Most adjuvants are substances significantly lowering the surface tension of liquids. On dis-

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solving a surfactant in water its molecules tend to accumulate at the air-water interface which causes the reduction of the surface tension. The surface tension reduction causes that the wetting of the plant body (leaf area) is improved, contact angle of the spray on the plant surface is lower and adhesive power increases. Therefore the transfer (penetration and translocation) to vascular tissue of the plant (phloem) is more effective. Surfactants added to foliar sprays can act as co-solvents, ensure the adherence of droplets on leaves difficult to wet, improve coverage, remove air films between spray and leaf surface and reduce interfacial tension between polar and apolar regions of the leaf cuticle (Uhlig and Wissemeier 2000, Tu et al. 2001).

Surfactants also increase wetting ability as they reduce the surface tension and contact angle of the spray on the plant surface. On dissolving a surfactant in water its molecules tend to accumulate at the air-water interface which causes the reduction of the surface tension. With increasing surfactant concentration the reduction in surface tension continues until the interface is saturated with surfactant molecules. At this point, called the critical micelle concentration (cmc), increasing the surfactant concentration does not reduce the surface tension any more, since no more surfactant molecules can reside at the interface and they begin to aggregate to micelles (Singh et al. 1984, Tu et al. 2001).

Micelles have a particular significance in many industrial branches as agriculture, pharmacy, biotechnology etc. because of their ability to increase the solubility of sparingly soluble substances in water.

Micelles are known to have an anisotropic water distribution within their structure because the water concentration decreases from the surface towards the core of the micelle, with a completely hydrophobic (water-excluded) core. Consequently, the spatial position of a solubilized drug in a micelle will depend on its polarity: nonpolar molecules will be solubilized in the micellar core, and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions (Rangel-Yagui et al. 2005, Paria 2008).

The aim of the presented work was to compare eleven adjuvants commonly used in agricultural practice produced by various manufacturers, to determine the critical micelle concentration by measurement of surface tension and density of aqueous solutions in the dependence on solution concentration.

MATERIAL AND METHODS

The physico-chemical properties – density and surface tension of aqueous solutions of eleven frequently used adjuvants – were measured under laboratory conditions in the dependence on con-

Table 1. Adjuvants used in the study

Trade name	Registered rate of the product (kg/ha)	Active ingredient (active ingredient content)
ADIGOR	1.35	rapeseed oil methyl ester (440 g/L)
ATPLUS 463	1	paraffin oil (60%), polyoxyetylene sorbitol oleate (40%), polyoxyetylene tridecyl alcohol
BIOPOWER	1	sodium lauryl sulphate (280 g/L)
BREAK SUPERB	0.1	polyether (15–30%), silanamine, polyether siloxanes and silicones (70–85%), heptamethyltrisiloxane
DASH HC	1	palmitic acid methyl ester and oleic acid methyl ester (37.5%), oleic acid (5%), phosphoric acid polyalkyl ester (22.5%)
DEDAL 90 EC	3	rapeseed oil (90%)
MERO 33528	2	rapeseed oil methyl ester (730 g/L)
SILWET L-77	0.1	heptamethylt risiloxan modified polyalkylenoxidem (84%)
SILWET STAR	0.1	polyalkyleneoxid heptamethyl trisiloxane (80%), allyloxypolyethyleneglycol (20%)
TREND 90	0.2	isodecyl alcohol ethoxylate (900 g/L)
X-CHANGE	0.2	ammonium sulphate, polyacrylate Na(I)NH_4(I) (10%), citric acid (10%), ammonium propionate (20%), phosphate ester (5%)

Source: Agromanual (2010)

Table 2. Coefficients A_i (i = 2, 1, 0) in quadratic concentration terms of Eq. (1)

Adjuvant	A_2	A_1	A_0
ADIGOR	0	0	0
ATPLUS	1.99553×10^{-9}	-6.92721×10^{-8}	9.00447×10^{-7}
BIOPOWER	1.88575×10^{-9}	-1.21594×10^{-7}	1.44344×10^{-6}
BREAK	0	0	0
DASH	0	0	0
DEDAL	1.38762×10^{-8}	-4.07159×10^{-8}	-2.23330×10^{-6}
MERO	0	0	0
SILWET L-77	1.01377×10^{-8}	-3.71874×10^{-7}	2.92280×10^{-6}
SILWET STAR	-3.92658×10^{-9}	1.49542×10^{-7}	-1.34954×10^{-6}
TREND	5.86796×10^{-9}	-1.77152×10^{-7}	3.40515×10^{-7}
X-CHANGE	-3.72429×10^{-9}	-1.12749×10^{-7}	$-1.08284 \times \cdot 10^{-6}$

centration. The measurement of surface tension was performed at the temperature of 20°C. The density of the solutions was measured in a temperature range from 10°C to 25°C. The specifications on adjuvants tested in this study are summarized in Table 1 (in alphabetical order). Materials are given in Table 1.

Preparation of solutions. Solutions were prepared separately for each series of measurements. Tap water from locality Suchdol was used in all experiments. Because the described laboratory experiments were followed by field experiments, it was important to use water from the same source for both experimental series. Total hardness of water was (Ca + Mg) = 2.2 mmol/kg (soft); Ca content: 1.7 mmol/kg; and Mg content: 0.5 mmol/kg.

Water hardness was measured only as indicative information to characterize used water. It was not needed for the evaluation of the results of density and surface tension measurements. According to Singh et al. (1984) the influence of the water hardness on the surface tension is negligible.

All solutions were prepared by weight. The most concentrated solution in each measuring series was prepared by dissolving exactly weighed amount of solid surfactant in exactly weighed amount of tap water. Other solutions in the series were prepared by dilution: aliquots of the concentrated solution of known weight were mixed with weighed amount of water. All the solutions were prepared immediately prior to each experiment.

Density. The density measurements were performed using the vibrating-tube densimeter (Anton Paar DMA 5000, Graz, Austria), at the temperatures of 10, 15, 20, and 25°C. The density values were measured at five equidistant concentration intervals in the range from 0 to 15 g/kg and fitted to empirical polynomial expression:

$$\rho\ (\text{g/cm}^3) = (A_2 \times c_w^2 + B_2 \times c_w + C_2) \times t^2 + (A_1 \times c_w^2 + B_1 \times c_w + C_1) \times t + (A_0 \times c_w^2 + B_0 \times c_w + C_0) \quad (1)$$

Where: t – temperature (°C), and c_w – solution concentration expressed in grams of adjuvant concentrate contained in 1 kg of the solution.

Surface tension. The measurements of surface tension were carried out by the ring method using tensiometer Lauda TD1 (Lauda GmbH, Königshofen, Germany) equipped by a platinum ring (diameter 19.1 mm) which was cleansed by annealing in alcohol flame before each measurement. Every day before the measurement the tensiometer was calibrated. The readings of the tensiometer were corrected on the effect of liquid sticking to the ring using the correction formula reported by tensiometer manufacturer.

The measuring cell was kept at constant temperature 20 ± 0.2°C. The surface tension of each solution was measured ten times and an average value was calculated. The reproducibility of the measurements was within ± 0.1 mN/m. For each adjuvant the surface tensions of 15–20 solutions of various concentrations were determined.

RESULTS AND DISCUSSION

Density. The values of coefficients A and B obtained by linear regression of experimental data using Microsoft Excel (Redmond, USA), are given for all adjuvants in Tables 2 and 3. Coefficients C_i

Table 3. Coefficients B_i (i = 2, 1, 0) in linear concentration terms of Eq. (1)

Adjuvant	B_2	B_1	B_0
ADIGOR	-9.46270×10^{-8}	2.60760×10^{-6}	-8.14071×10^{-5}
ATPLUS	-1.04707×10^{-8}	-1.70155×10^{-7}	-8.68657×10^{-5}
BIOPOWER	-2.91844×10^{-8}	1.42331×10^{-6}	2.58049×10^{-5}
BREAK	9.78200×10^{-8}	-4.88512×10^{-6}	8.63000×10^{-5}
DASH	-7.88070×10^{-9}	-1.78170×10^{-6}	8.16000×10^{-6}
DEDAL	-1.49108×10^{-7}	1.21608×10^{-6}	-5.24561×10^{-5}
MERO	1.67743×10^{-7}	-7.55365×10^{-6}	2.90000×10^{-6}
SILWET 77	-1.10585×10^{-7}	2.88959×10^{-6}	3.65940×10^{-5}
SILWET STAR	2.04002×10^{-8}	-1.70082×10^{-6}	5.87879×10^{-5}
TREND	-4.93971×10^{-8}	5.13412×10^{-7}	5.59379×10^{-5}
X-CHANGE	3.86193×10^{-8}	-6.82408×10^{-7}	1.55015×10^{-4}

(c_w = 0) are listed in Table 4, and have the same values for all the formulations.

Eq. (1) allows calculating the density (g/cm^3) of the chosen adjuvant solution of any concentration in the range 0–15 g/kg at any temperature from 5°C to 25°C. Average difference between the experimental and calculated values was ± 0.006%.

Surface tension and critical micelle concentration. For each adjuvant, the surface tensions of 15–20 solutions of increasing concentrations were determined.

The concentrations ranged from very low values to values at which the surface tension did not change any more. As an example of the typical concentration dependence of the surface tension, the semi-logarithmic plot γ *vs.* $\ln c_w$ for Biopower is shown in Figure 1. It consists of two parts – a steep one at low concentrations and the second one at higher concentrations, the slope of which is nearly zero. The coordinates of the point of intersection of these two parts determine the values of the critical micelle concentration (cmc) and the surface tension at cmc (γ_{cmc}). Both are given in Table 5 for all adjuvants under study.

Figure 2 compares the critical micelle concentration values with concentrations recommended by the manufacturers. The heights of the black columns, read on the left vertical axis, represent the cmc values of single adjuvants, the heights of the grey columns, read on the same vertical axis, stand for the recommended concentrations.

Table 4. Coefficients C_i (i = 2, 1, 0) in zero-degree concentration terms of Eq. (1)

C_2	C_1	C_0
-5.40×10^{-6}	1.22×10^{-5}	1.00065

Evidently, the cmc is achieved at lower doses than those registered by manufacturers of adjuvants, which should ensure the micelles formation. The highest difference between the recommended dose and the dose at which the cmc is reached was found for products MERO 33528 and Dedal 90 EC – the recommended rate is several times higher. In the case of Trend however, the rate of the adjuvant is lower than its cmc (cmc = 1.24 g/kg; registered rate is 1 g/kg) and therefore the rate is not sufficient for the formation of micelles.

All tested adjuvants reduced substantially the surface tension even though not in the same extent. Maximum reduction in the surface tension of water was caused by adjuvant Silwet L-77 and Break Superb (from approx. 72 to approx. 21 mN/m); it means that recorded values for the product with

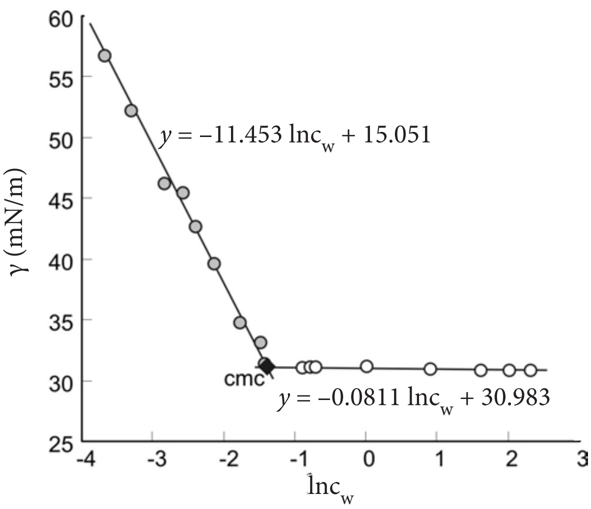

Figure 1. The determination of the critical micelle concentration of Biopower from the semi-logarithmic plot of the surface tension. ▪ – experimental points below the cmc; ○ – experimental points above the cmc, ♦ – cmc

Table 5. The critical micelle concentrations and the surface tensions (cmc)

Adjuvant	cmc (g/kg)	γ_{cmc} (mN/m)
ADIGOR	1.71	32.4
ATPLUS 463	0.52	36.2
BIOPOWER	0.25	31.1
BREAK SUPERB	0.30	21.5
DASH HC	0.24	39.1
DEDAL 90 EC	0.33	36.5
MERO 33528	0.23	35.6
SILWET L-77	0.05	21.1
SILWET STAR	0.03	22.6
TREND 90	1.24	26.6
X-CHANGE	1.91	37.2

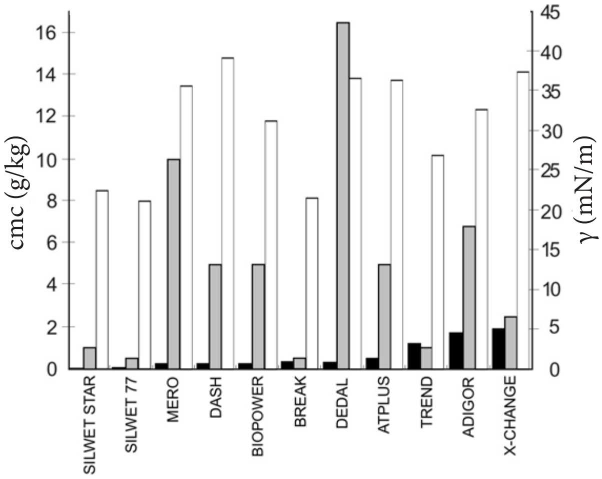

Figure 2. Critical micelle concentration (black columns), recommended concentration (grey columns), surface tension at cmc (white columns)

the highest tension (Dash HC) are twice as high as for Silwet L-77 with the lowest tension. Presented values can be used for selection of the proper product if the surface tension is the crucial factor for ensuring the spray performance.

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