VISUAL BASIC APPLICATION FOR CALCULATION OF THE SUPERFICIAL TENSION OF SOLUTIONS IN THE $CuSO_4$ – H_2SO_4 – H_2O SYSTEM

Florentina NICULESCU[1], Bogdan FLOREA[2]*, Mihai BUZATU[3], Gabriel Valeriu GHICA[4], Mircea-Ionut PETRESCU[5], Gheorghe IACOB[6], Emanuel NICULESCU[7], Dragoş Florin MARCU[8], Constantin Domenic STĂNCEL[9]

The aim of this paper is to study the effect of bone glue on the superficial tension in $CuSO_4$ – H_2SO_4 – H_2O system. Aqueous solutions of sulfuric acid and cupric sulfate are usually found in cooper hydrometallurgical processes (leaching, solvent extraction, electro-refining). In the electro-deposition of cooper, it is frequently used different organic additives such as thiourea - $SC(NH_2)_2$ or bone glue. The same experimental conditions as that used in industry were applied: acidic solution composed of 40 g/l Cu^{2+}, 175, 200, 225 g/l H_2SO_4, 60ºC temperature and the bone glue concentration was between 0-3 g/l. The experiments were performed on a device consisting of stalagmometer, humidity sensor, programmable logic controller (SIMATIC S7-300), commanded by a software (written in VB 6.0) capable of calculating the surface tension of the system against the concentration of bone glue (for 3 concentrations of H_2SO_4).

Keywords: visual basic, superficial tension, acidic solution, concentration.

1. Introduction

The surface tension of solutions has a considerable influence on the transfer of mass and energy across interfaces. It is a basic thermodynamic

[1] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: flori.pereteanu@yahoo.com
[2] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: florea_b2004@yahoo.com, * - corresponding author
[3] PhD student, Materials Science and Engineering Faculty, University POLITEHNICA of Bucharest, Romania, e-mail: buzatu.mihai@yahoo.com
[4] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: gvghica@yahoo.com
[5] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: ipetrescu@yahoo.com
[6] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: iacob_gh@yahoo.com
[7] PhD student, Facylty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: emanuelniculescu@yahoo.com
[8] Lecturer, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: dragos.marcu@yahoo.com
[9] Assistant, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: stancel.constantin@yahoo.com

property that plays an important role in a multitude of processes. Accurate determination of surface tension for various liquid mixtures is important to gain insight into interfacial processes [1, 2, 3, 4, 5]. The study of superficial tension for different liquid systems is of interest in increasingly varied areas. A new direction of research for the study of superficial tension is represented by the field of high entropy alloys or multi-component mixtures [6, 7, 8, 9, 10, 11].

Aqueous solutions of sulfuric acid and copper sulfate are usually used in the cooper hydrometallurgical processes such as leaching, solvent extraction, electrolysis and electro-refining [12, 13]. Copper sulfate in distilled water solutions has been investigated for crystallization, super-saturation, solid-liquid equilibrium, and properties [14, 15]. Also, copper electro-deposition plays an important role in the electronic industry, particularly for printed circuit manufacture and for circuit interconnection. The presence of additives in the aqueous solutions produces:

- a better leveling effect at the electrodeposits surface by promoting the formation of smooth and compact deposit on cathode to reduce the loss during production;
- influence the electro-deposition rate at protrusions and recesses;
- affect the diffusion of reactants from the bulk of the solution towards the reaction front [16, 17, 18].

The superficial tension explains many phenomena characteristic of the liquid state such as: droplet formation in liquid leakage through a small opening, foam formation, adhesion of liquids, capillarity, etc. To measure superficial fluid tension, static and dynamic methods are used, as the apparent surface is immobile or moving. The most common organic agents used as surfactants in electrolytic extraction and refining processes are bone glue and thiourea. In the scientific literature are found studies which indicate the usage of different organic additives for the electro-deposition of copper such as polyethylene glycol and chloride ions [19], polyvinylpyrrolidone [20], nicotinic acid, benzotriazole, sulfonic acids [21] thiourea [22] and bone glue [23].

Bone glue is a substance composed mainly of natural proteins (a mixture of amino acids). It reduces the surface tension and, as a result, it concentrates into the superficial layer from the electrolyte - cathode interface and reduces the growth rate of germination crystals, which allows the obtaining of fine and homogeneous structures. Even if organic additions also have a negative role in the fact that adsorbed organic molecules form non-conductive films that lead to the easy growth of energy consumption, the beneficial role of the cathode deposit structure and purity compensates for energy losses [24, 25, 26, 27].

In this paper the effect of the concentration of bone glue on superficial tension of $CuSO_4$-H_2SO_4-H_2O solutions was studied using an experimental system adapted with a programmable logic controller (PLC) as well as a Visual Basic application designed specifically for this equipment and used for retrieval and interpretation of all the data obtained.

The program used was developed by the research team using the Visual Basic 6.0 programming language from Microsoft, which is a free programming language.

Visual Basic uses modern programming techniques [28, 29, 30, 31, 32] as Object-Oriented Programming (OOP) and Event-Driven Programming (EDP). A simple Visual Basic program involves three steps:

- Creating the interface (creation of objects);
- Establishing the objects properties;
- Writing the code.

The major benefits for working with the Visual Basic program (and generally when working with any high-level programming language that supports database work) can be:

- Implementation of error handling;
- Creating cycles for scrolling sets of tables;
- The ability to call Windows API functions;
- Programming the various objects of a database;
- The use of constants and variables;
- Designing and troubleshooting complex processes;
- Writing reusable function libraries.

2. Materials and methods

Drop volume method (Stalagmometer method)

In the experiments, the drops of fluid flow slowly from the tube in a vertical direction. The drops hanging on the bottom of the tube start to fall when the volume of the drop reaches a maximum value that is dependent on the characteristics of the solution. At this moment, the weight of the drops is in equilibrium state with the surface tension.

The flow of a liquid through a narrow hole is not continuous but intermittent by drops. The number of drops (*N*) in which a given volume of liquid is fractionated depends on its superficial tension. At the moment of dropping, its weight (*G*) is equal to superficial force (*F*). As a result the superficial force across the contour will be:

$$F = 2 \cdot \pi \cdot r \cdot \sigma \qquad (1)$$

Where: - r is the radius of the flow orifice,
- σ coefficient of surface tension (dyn/cm^3),

If V_1 is the volume of a drop, then its weight is:

$$G = m \cdot g = V_1 \cdot \rho \cdot g \qquad (2)$$

If n is the number of droplets in which the volume V of the liquid is split between two benchmarks, and then the volume V_1 of a drop is given by the ratio:

$$V_1 = \frac{V}{n}; and\ \sigma = \frac{V \cdot \rho \cdot g}{2 \cdot \pi \cdot r \cdot m} \tag{3}$$

Determining the number of drops for a liquid with the known values of the superficial tension coefficient σ_0 and the density ρ_0, in a volume of liquid equal to the one studied, we obtain:

$$\sigma_0 = \frac{V \cdot \rho_0 \cdot g}{2\pi \cdot r \cdot n_0} \tag{4}$$

It results, as for some substance,

$$\sigma = \sigma_0 \cdot \frac{\rho \cdot n_0}{\rho_0 \cdot n} \tag{5}$$

Alternatively, since the surface tension is proportional to the weight of the drop, the fluid of interest may be compared to a reference fluid of known surface tension. We will consider the value of superficial tension for distilled water σ_0 = 78.23 dyne/cm^3 and the value of density for distilled water ρ_0 = 1g/cm^3. The average number of droplets - n_0 = 990 - measured for a volume of distilled water equal to the volume of the measuring solution.

If the surface tension of distilled water is known which are 78.23 dyne/cm^3, we can calculate the surface tension of the specific fluid from the equation. The more drops we weigh, the more precisely we can calculate the surface tension from the equation. The stalagmometer must be kept clean for meaningful readings.

The stalagmometric method was improved by S. V. Chichkanov and colleagues [33], who measured the weight of a fixed number of drops rather than counting the drops. This method for determining the surface tension may be more precise than the original method, especially for fluids whose surface is highly active. The experimental equipment shown in Figure 1 is composed of:

- Traube stalagmometer fixed on a stand;
- Programmable Logic Controller (PLC) from Siemens;
- Sensor for humidity;
- Software for the calculation of superficial tension (Visual Basic).

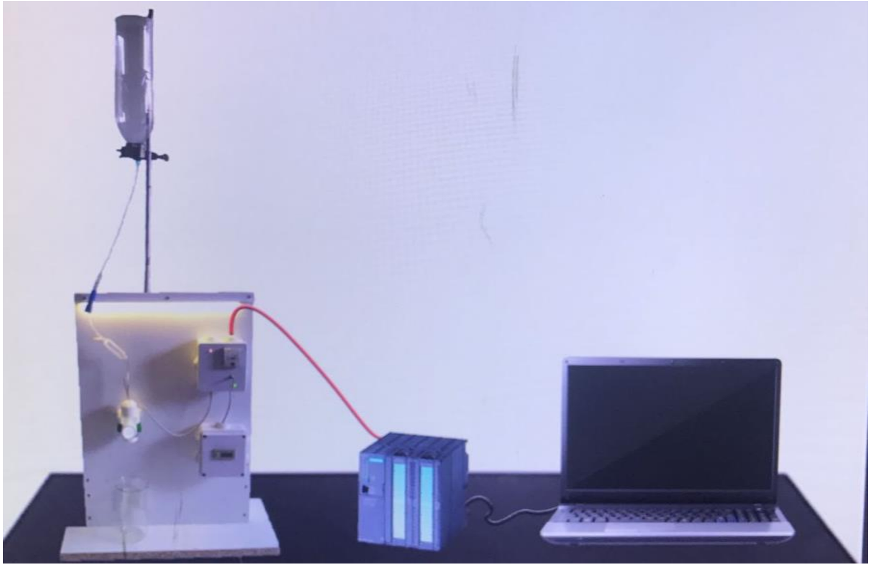

Fig. 1. Experimental equipment

Due to the use of the PLC that can perform record-breaking cycles at the milliseconds level, the experimental equipment allows for the elimination of possible reading errors compared to other methods. At the same time, the software created for this installation allows real-time recording and visualization of the values obtained for each experiment by recording the number of droplets as soon as the humidity sensor detects their presence on its surface and stopping the count immediately that their presence is no longer detected.

When an experiment is run, the recorded values are stored in a database with which later interpretations of experimental data can be made. The created program allows the calculation of the superficial tension for each experiment and making graphs.

The PLC used is a Siemens product, the SIMATIC S7-300 model, CPU 314 with MPI, 16DI/16DO, 4AI/1AO, 2 X 40 PIN, integrated 24V DC power supply, 24 Kbytes working memory. The S7-300 series is a line of micro-programmable logic controllers (Micro PLCs) that can control a variety of automation applications. Compact design, low cost, and a powerful instruction set make the S7-300 a perfect solution for controlling small applications. The wide variety of S7-300 models and the Windows-based programming tool give solutions for many automation problems [34, 35].

This program is designed to run on PCs that do not require special configurations. An Aspire E1-571G laptop with Intel Core I3-2348 processor (2.3GHz), RAM - 4GB was used in the tests. The humidity sensor used in the installation was designed by the research team. The electrolytic solutions were prepared using the following analytical grade reagents: H_2SO_4 (175, 200, 225 g/l); $CuSO_4 \times 5H_2O$ (40, 45, 50 g/l copper); bone glue (0.00; 0.50; 1.00; 1.50; 2.00; 2.50; 3.00). The mass of $CuSO_4$ was 159. The experiments were made at the temperature of 60^0C. The values were chosen due to the industrial use of these parameters for the electrolytic refining process of copper.

3. Experimental results and discussion

After the experimental research performed in the *Laboratory of hydro/ electrometallurgical processes and operations* from the *Department of Engineering and Management of Metallic Materials Elaboration* were obtained the following results, presented in Tables 1 and 2. Using the Visual Basic program the graphs presented in the paper based on the experimental results were made.

Table 1.

Experimental results on the number of droplets and their average in the $CuSO_4$-H_2SO_4-H_2O system

Exp. no.	Bone glue	Cu, 40g/l		Cu, 40g/l		Cu, 40g/l	
		Sulfuric acid,175g/ l		Sulfuric acid, 200g/l		Sulfuric acid, 225g/l	
		Density, g/cm^3	1.1646	Density, g/cm^3	1.3309	Density, g/cm^3	1.4973
		N	**n_1**	**N**	**n_2**	**N**	**n_3**
1	0.00	1456	1459.33	1292	1290.66	1171	1169
		1459		1289		1169	
		1463		1291		1167	
2	0.50	1714	1716.33	1570	1569.66	1253	1251.33
		1723		1568		1250	
		1712		1571		1251	
3	1.00	2097	2094.33	1863	1867.66	1490	1514.66
		2099		1871		1496	
		2087		1869		1558	
4	1.50	2598	2601.33	2310	2311.66	1616	1619
		2601		2314		1622	
		2605		2311		1619	
5	2.00	2902	2900.33	2589	2597.66	1897	1897
		2900		2603		1899	
		2899		2601		1895	
6	2.50	3352	3354	2608	2608.66	2069	2069
		3359		2611		2071	
		3351		2607		2067	
7	3.00	3820	3818.33	3011	3008.33	2231	2231
		3816		3008		2228	
		3819		3006		2235	

Table 2.

Experimental results on the surface tension of solutions in the $CuSO_4$-H_2SO_4-H_2O system

Exp. no.	σ_1, dyne/cm	σ_2, dyne/cm	σ_3, dyne/cm
1.	61.80602	79.86194	99.19798
2.	52.55132	65.66689	92.67110
3.	43.06649	55.18926	76.55971
4.	34.67283	44.58910	71.62596
5.	31.09835	39.7989	61.12938
6.	26.89194	39.51257	56.04757
7.	23.62171	34.26320	51.97002

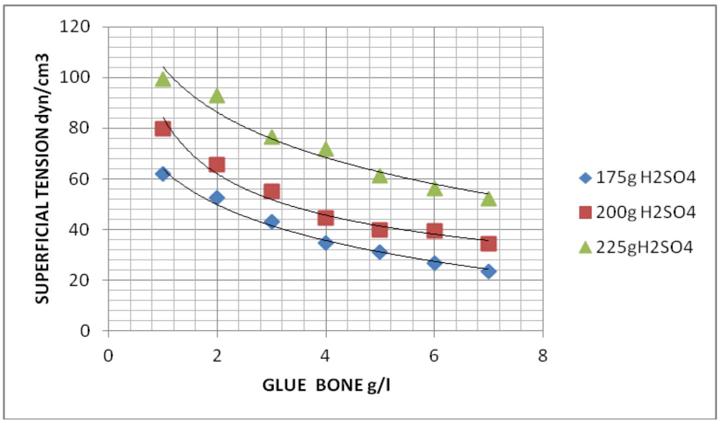

Fig. 2. The variation of superficial tension depending on the concentration of bone glue at 40 g /l Cu, different concentrations of H_2SO_4 and a temperature of 60°C

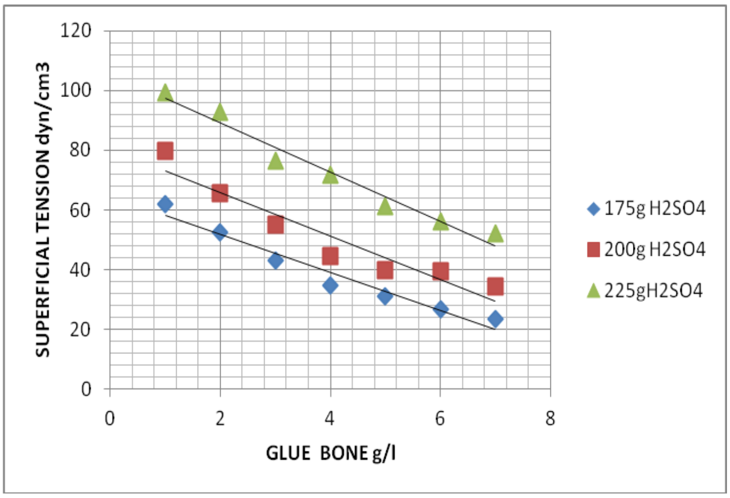

Fig. 3. Variation of superficial tension logarithm depending on the concentration of bone glue at 40 g /l Cu, different concentrations of H_2SO_4 and a temperature of 60°C

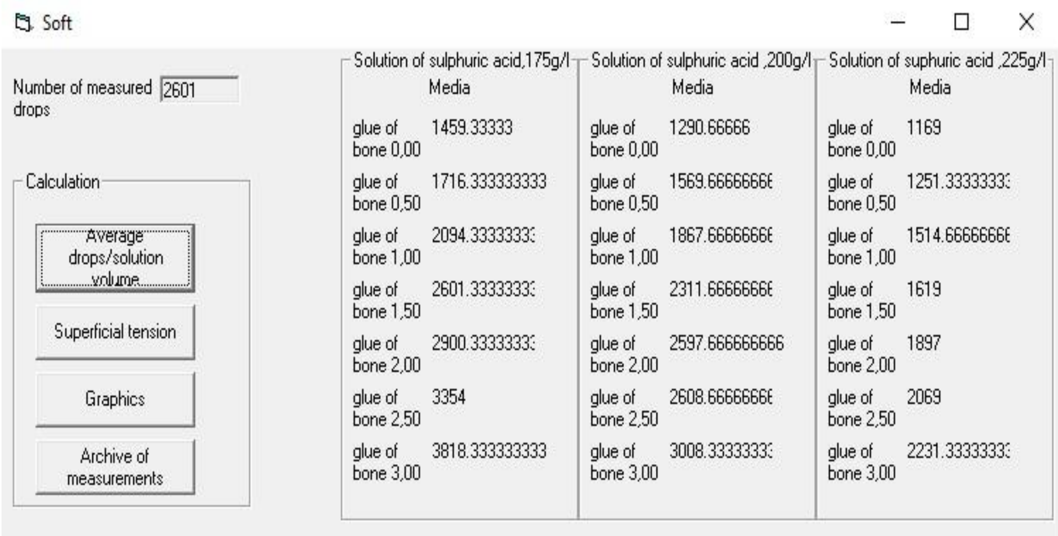

Fig. 4. Screen capture of average drops calculations using the program

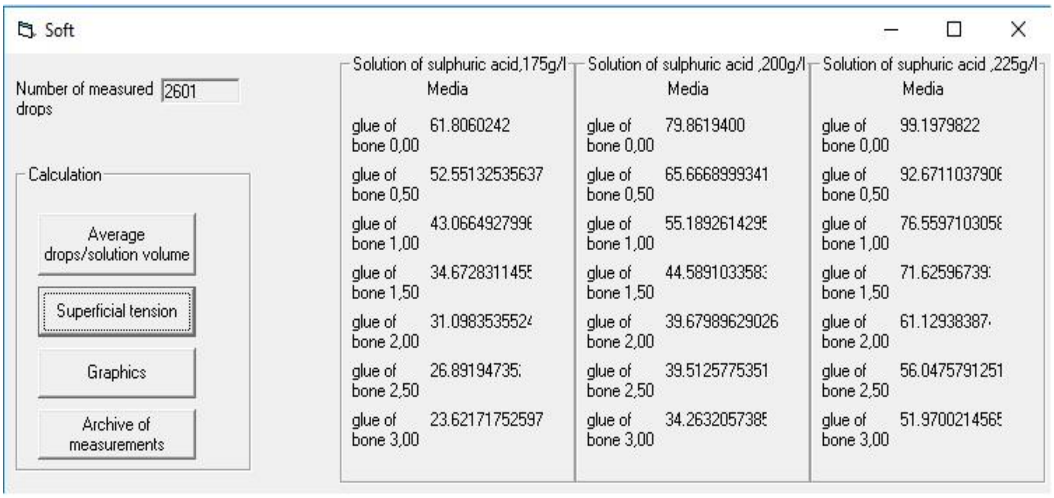

Fig. 5. Screen capture of superficial tension calculations using the program

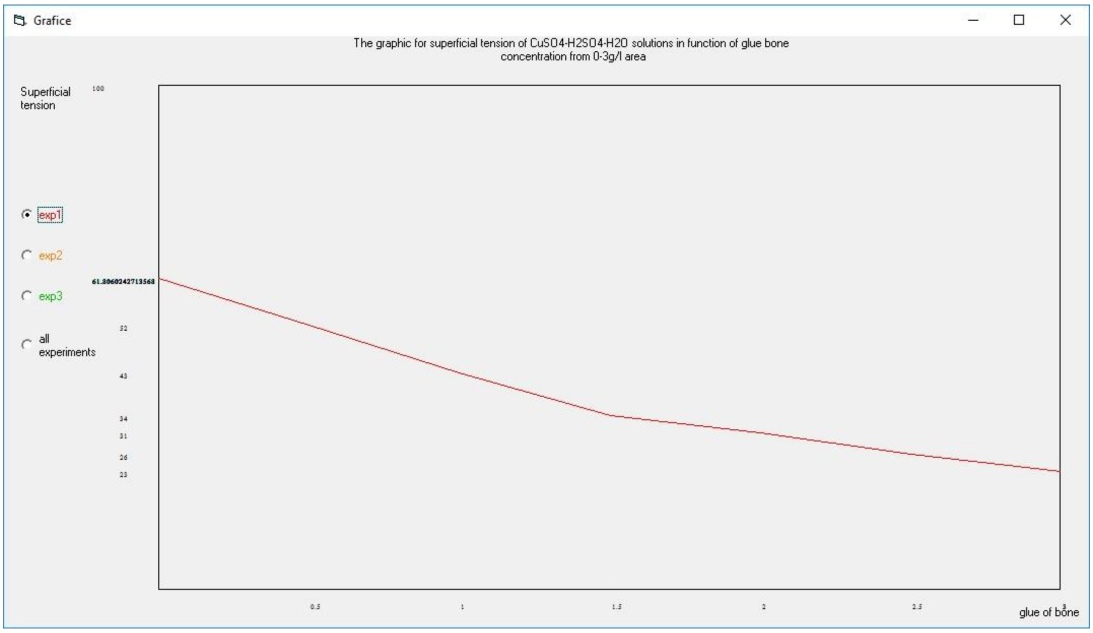

Fig. 6. The variation of superficial tension of $CuSO_4$-H_2SO_4-H_2O solutions depending on the concentration of bone glue in the range 0-3g/l, the first set of experimental values (n_1)

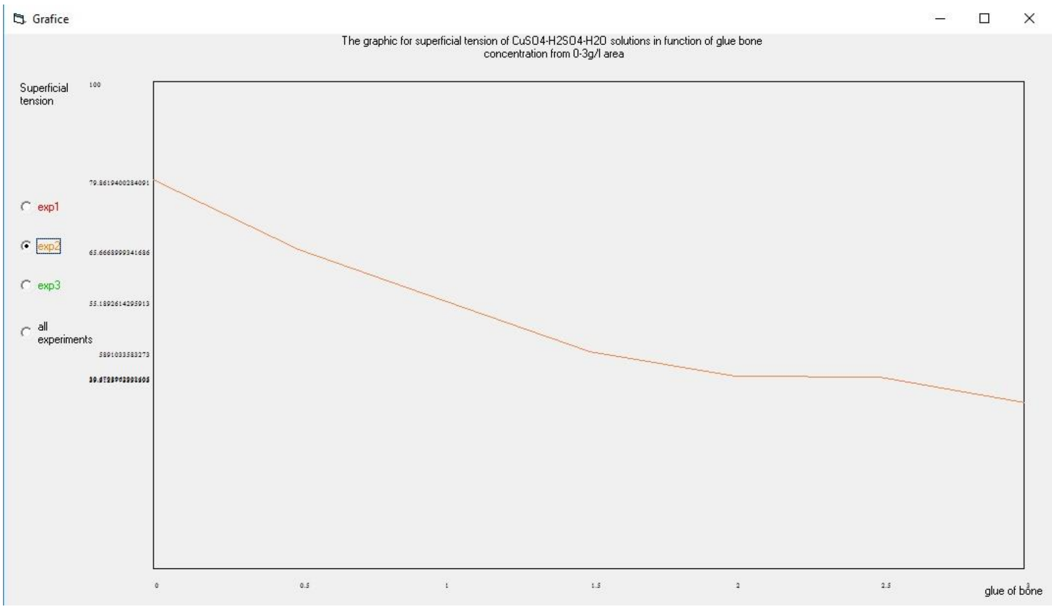

Fig. 7. The variation of superficial tension of $CuSO_4$-H_2SO_4-H_2O solutions depending on the concentration of bone glue in the range 0-3g/l, the second set of experimental values (n_2)

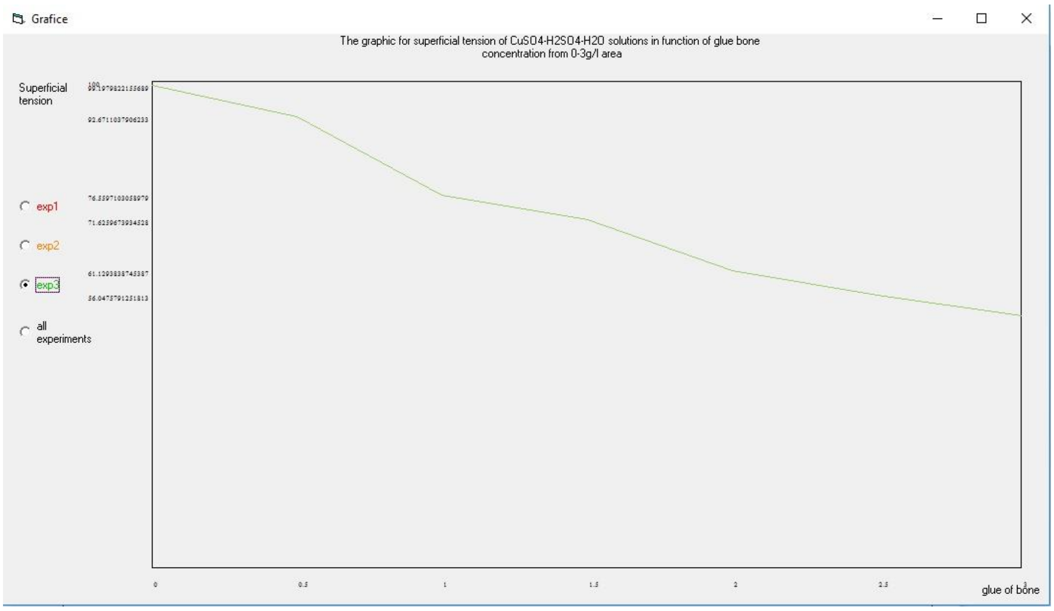

Fig. 8. The variation of superficial tension of $CuSO_4$-H_2SO_4-H_2O solutions depending on the concentration of bone glue in the range 0-3g/l, the third set of experimental values (n_3)

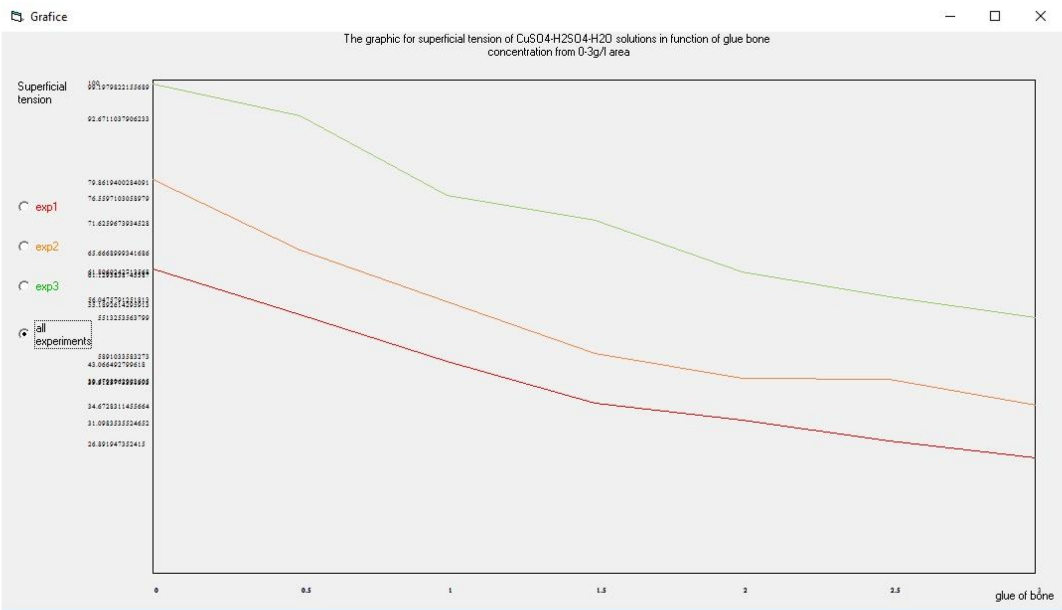

Fig. 9. The variation of superficial tension of $CuSO_4$-H_2SO_4-H_2O solutions depending on the concentration of bone glue in the range 0-3g/l for all experimental values

4. Conclusions

Through this experimental equipment adapted to digital software, we were able to record and view in real time the experimental values obtained by recording the drops as soon as the humidity sensor detected their presence. With the same software, all experimental data was stored in a database that allows for various thermodynamic analyzes and interpretations.

Also, due to the program, the values of superficial tensions were calculated automatically for each experiment, and the superficial tension variations of the solutions from the $CuSO_4$-H_2SO_4-H_2O system were graphically plotted depending on the concentration of glue in the 0 - 3 g/l range.

Experimental researches on the influence of bone glue concentration at different concentrations of Cu and H_2SO_4 shows the following:

The superficial tension decreases exponentially with increasing the concentration of bone glue to a value of about 3 g/l when the bone glue concentration no longer influences the superficial tension;

The superficial tension of the solutions from the $CuSO_4$-H_2SO_4-H_2O system decreases as the concentration of H_2SO_4 decreases;

The superficial tension of the solutions increases with the concentration of Cu in the $CuSO_4$-H_2SO_4-H_2O system.

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