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An Evening with Magic: Eight Colorless Liquids

Angela Aleksovska, Miha Bukleski, Igor Mavromihailov, Nikolina Mitreska, Vladimir M. Petruševski*, Monika Radevska, Marina Stojanovska and Jasmina Tanatarec

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University, Arhimedova 5, PO Box 162, 1000 Skopje, Republic of Macedonia, vladop@pmf.ukim.mk

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Abstract: The number of first-year students of chemistry in Macedonia is declining in the last few years. An informal group (both teaching staff and Ph. D. students) called The Happy Chemists Group initiated the organization of a series of evening events with spectacular experiments, hoping to 'infect' high-school students with 'the chemistry virus'. A demonstration with eight colorless liquids (based on various precipitates and complexes of lead) was introduced at the latest event that attracted students' attention.

Introduction

The number of chemistry students at the Ss Cyril and Methodius University (in Skopje, Macedonia) has been constantly declining over the years. The poor interest in the natural sciences lies (among other things) in the fact that the appropriate institutes do not use aggressive enough policies as well as marketing. Certainly, the fact that chemistry industry in our country is fading away cannot be neglected and it is another important factor for the decreasing number of students.

The really concerning fact is that if this downward trend continues, a shortage of qualified chemistry teachers will occur in the near future. This does not only impact schools, but at the same time introduces a great decline in the number of future potential scientific minds that will continue the development and research of new sciences. The small number of students affects the quality and competitiveness on the knowledge market place.

Various activities for popularization of chemistry by a group of both teaching staff and Ph. D. students (the so-called "The Happy Chemist Group", THCG) were conducted, as well as many "chemistry spectacles" in which different kinds of "magic" were presented. We believed that in this way we might increase both the students' interest in science as well as their scientific literacy, hoping that once it is done at least some of them will consider studies of chemistry as an option.

Besides the already known "magic" experiments [1–6], a contribution to the above type was introduced and will be discussed in what follows.

The Magic

The "magician" (undercovered instructor) walks before the audience, behind the demonstration desk. On the desk there is a beaker (of volume ~ 200–400 mL) placed on magnetic stirrer, with some colourless liquid in it (cf. Figure 1a). Seven smaller beakers (~ of 100 mL each) are partly filled with colorless liquids (≈ 20 mL of liquid in each of the beakers, except the last two that contain 30–50 mL).

The magician adds (part of) the colorless liquids to the beaker one at a time. After each liquid being added, one could notice the following changes:

1. The liquid in the large beaker turns foggy white (Figure 1b).
2. The entire liquid is bright yellow and opaque (Figure 1c).
3. The liquid turns milky white (Figure 1d).
4. The liquid becomes black (Figure 1e).
5. After some fizzing and foaming the liquid turns brown (Figure 1f).
6. The liquid becomes colorless and transparent (Figure 1g).
7. The liquid turns milky white (Figure 1h).

The magician bows and disappears.

Chemistry Behind the Magic

Shortly after this the instructor appears. He/she explains that, because we live in a scientific world, behind any "magic" there must be a sound scientific explanation. In this case, there is lots of chemistry (all of which is rather simple) behind the magic with the eight colorless liquids. The eight liquids (with 'a' originally in the beaker, others being subsequently added) are:

(a) Aqueous solution of lead(II) nitrate, with c = 0.2 mol/L.
(b) Aqueous solution of sodium chloride, with c = 0.4 mol/L.
(c) Aqueous solution of potassium iodide, with c = 0.2 mol/L.
(d) Aqueous solution of sodium hydroxide, with c = 1.0 mol/L.
(e) Aqueous solution of sodium sulfide, with c = 0.1 mol/L.
(f) Aqueous solution of hydrogen peroxide with w = 9–15 %.
(g) Saturated solution of EDTA (actually its disodium salt, designated as Na_2H_2Y).
(h) Diluted solution of sulfuric acid with c = 0.5 mol/L.

Depending on the particular audience present, one could give more elaborate explanations (for 11^{th} and 12^{th} grade students), an intermediate one (for 9^{th} and 10^{th} grade students) or some very basic explanation (for students of grades 7 and 8).

At the very least, the instructor should explain the appearance of the colors that result from chemical changes in the system, upon mixing the colorless and transparent solutions. Thus, in terms of chemical equations related to the corresponding reactions:

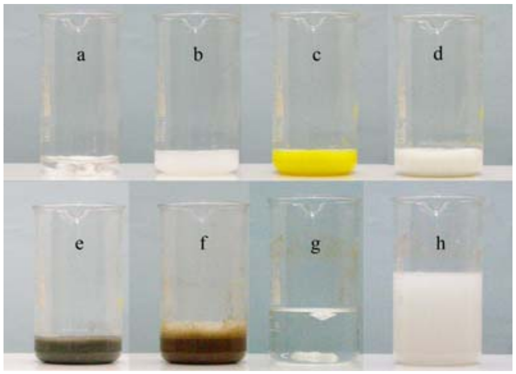

Figure 1. The color changes upon successive addition of the colorless liquids

(a) The first beaker contains the original colorless aqueous solution of $Pb(NO_3)_2$.

(b) Upon addition of 'b' to 'a' a foggy white color is seen:

$$Pb(NO_3)_2(aq) + 2NaCl(aq) = PbCl_2(s, white) + 2NaNO_3(aq)$$

(c) Addition of 'c' gives the opaque yellow color:

$$PbCl_2(s, white) + 2KI(aq) = PbI_2(s, yellow) + 2KCl(aq)$$

(d) With strong base ('d') milky white color appears:

$$PbI_2(s, yellow) + 2NaOH(aq) = Pb(OH)_2(s, white) + 2NaI(aq)$$

(e) With 'e' black lead(II) sulfide forms:

$$Pb(OH)_2(s, white) + Na_2S(aq) = PbS(s, black) + 2NaOH(aq)$$

(f) With 'f' the sulfide is oxidized in (at least) two parallel reactions:

$$PbS(s, black) + 4H_2O_2(aq) = PbSO_4(s, white) + 4H_2O(l)$$

$$PbS(s, black) + 5H_2O_2(aq) + 2NaOH(aq) = PbO_2(s, brown) + 6H_2O(l) + Na_2SO_4(aq)$$

The fizzing results from another reaction (of hydrogen peroxide decomposition), catalyzed by the presence of Pb(IV) [7]:

$$2H_2O_2(aq) = 2H_2O(l) + O_2(g)$$

(g) Upon addition of 'g' the content is transparent again:

$$PbSO_4(s, white) + Na_2H_2Y(aq) = Pb^{II}H_2Y(aq) + Na_2SO_4(aq)$$

$$PbO_2(s, brown) + Na_2H_2Y(aq) = Pb^{IV}Y(aq) + 2NaOH(aq)$$

(h) Finally, with 'h' the content is milky white once again, due to:

$$Pb^{II}H_2Y(aq) + H_2SO_4(aq) = PbSO_4(s, white) + H_4Y(aq)$$

Qualitative and Quantitative Explanations

One could say that the reactions represented by the above equations are possible due to the fact that the solubility of the four precipitates – $PbCl_2$, PbI_2, $Pb(OH)_2$ and PbS – decreases in that order, and it is a general rule in chemistry that a chemical reaction will go in the direction of formation of the least soluble precipitate (as this, in the same time, ensures the minimum number of ions of a given type in the solution). The formation of $PbSO_4$ and PbO_2 is enabled via redox reactions, and their dissolution is a consequence of a complex formation (both $Pb^{II}H_2Y$ and $Pb^{IV}Y$). Finally, in acidic medium the first complex ($Pb^{II}H_2Y$) is destroyed and $PbSO_4$ precipitate reappears with its characteristic white color (upon oxidation of PbS with H_2O_2 the white color of $PbSO_4$ is masked by the PbO_2 present). It is not clear what happens to $Pb^{IV}Y$ when in H_2SO_4 solution. One might speculate that it oxidizes the EDTA, the lead being reduced to Pb(II) that also gives $PbSO_4$, as there is no trace of a brown color in the acidified solution. This detail remains to be uncovered in future.

In order to give a more quantitative background for these assertions, one should look at the equilibrium values for the concentration of Pb^{2+} ions (calculated from K_{sp} values for the precipitates or from K_s value of $Pb^{II}H_2Y$, taken from the literature [8–10]) presented in Table 1.

Note that we could find no data on the stability of $Pb^{IV}Y$ in the literature, but the experimental evidence, i.e. complete dissolving of the PbO_2 precipitate [11] in EDTA shows its K_s value must be very large. Actually, it must be large enough as to completely compensate the low value for the solubility of PbO_2 as calculated from the K_{sp} value ($K_{sp} \approx 10^{-66}$ mol^3 dm^{-9}, according to the literature value [12]).

For best results, the exact values for the volumes should be found empirically. Often it is enough that the yellow and the black colors just appear. Thus, one can safely use only part of the liquid in the beaker, meaning that only part of the present lead will be converted into PbI_2, i.e. PbS.

Possible Extensions of the Demonstration

As pointed by the reviewer, given that lead is the key topic in this demonstration one possible extension would be to mention common lead pigments: basic lead carbonate – $Pb(OH)_2{\cdot}2PbCO_3$ (lead white); minium – Pb_3O_4 (red lead); lead chromate – $PbCrO_4$ (lead yellow), lead molybdate – $PbMoO_4$ (red orange) etc. It is also possible to reorganize the demo and show how easy could some of the mentioned pigments be synthesized.

Conclusions

This chemistry "magic" can achieve its goal not only at the scientific fairs or chemistry spectacles; it can be very helpful in the classroom – the lesson is expected to become more interesting and impressive to students. This experiment ("magic") can be used during lectures when discussing reactions that go to completion, solubility product of precipitates or even when explaining the stability of the complexes versus solubility (and stability) of precipitates. This experiment can also find its place in the inorganic chemistry courses when discussing the properties of lead compounds. Finally, such experiments can always reveal something the instructor was not aware of [13].

Table 1. Solubility product constants and solubilities of various lead salts

Compound	K_{sp} or K_s	Units	$c_{eq}(Pb^{2+})$ / mol dm^{-3}	Reference
$PbCl_2$ (K_{sp})	$1.70 \cdot 10^{-5}$	mol^3 dm^{-9}	$1.62 \cdot 10^{-2}$	8
PbI_2 (K_{sp})	$9.8 \cdot 10^{-9}$	mol^3 dm^{-9}	$1.35 \cdot 10^{-3}$	8
$Pb(OH)_2$ (K_{sp})	$1.43 \cdot 10^{-20}$	mol^3 dm^{-9}	$1.53 \cdot 10^{-7}$	8
PbS (K_{sp})	$3 \cdot 10^{-28}$	mol^2 dm^{-6}	$1{,}73 \cdot 10^{-14}$	9
$PbSO_4$ (K_{sp})	$2.53 \cdot 10^{-8}$	mol^2 dm^{-6}	$1.59 \cdot 10^{-4}$	8
$Pb^{II}H_2Y$ (K_s)	$2 \cdot 10^{18}$	mol^{-1} dm^3	$2.24 \cdot 10^{-10}$	10

Safety Tips and Disposal

Lead(II) nitrate (also acetate, and all other water soluble lead salts), causes lead poisoning. It is a harmful substance and can cause serious damage to health by prolonged exposure if swallowed. There is, also, danger of cumulative effects. When working with lead(II) salts protective gloves, safety goggles and protective clothing should be used. Hands and face should be thoroughly washed after working with the material. Soluble lead salts are also harmful environmental pollutants. Dispose the solutions of lead salts according to local safety regulations.

In high concentrations, hydrogen peroxide is an aggressive oxidizer and will corrode many materials, including human skin. In applications where high concentrations of hydrogen peroxide are used, suitable personal protective equipment should be worn. Hydrogen peroxide vapor is a primary irritant, primarily affecting the eyes and respiratory system.

Solid sodium hydroxide and solutions of more than 2 % by weight (0.5 mol/dm^3) should be labeled as corrosive. Solid sodium hydroxide or its solutions may cause chemical burns, permanent injury or scarring if it contacts unprotected human or other animal, tissue. It may cause blindness if it contacts the eye. Protective equipment such as rubber gloves, safety clothing and eye protection should always be used when handling the material or its solutions.

References and Notes

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12. Switzer, J. A., Rajasekharan, V. V., Boonsalee, S., Kulp, E. A., Bohannan, E. W. *Environ. Sci. Technol.* **2006**, *40*, 3384–3387.
13. The present demonstration showed clearly that iodide anions (they are present in the solution, see the chemical equation explaining step 3) cannot be oxidized with H_2O_2 in a basic medium. We were not aware of this fact, but it seems that it is also missing in the literature devoted to educational experiments.