• Учебни опити и демонстрации •
• Teaching Chemical Experiment •

THE ECONOMIC DEMONSTRATOR: PREPARE IT ONCE, USE IT MANY TIMES. II. CONTINUOUS THERMOCHROMISM IN AQUEOUS SOLUTIONS OF TRANSITION METAL CHLORIDES

Vladimir M. PETRUŠEVSKI, Miha BUKLESKI, Marina STOJANOVSKA,
Sts. Cyril and Methodius University, Skopje, MACEDONIA

Abstract. Continuous thermochromism was studied in systems containing metal chlorides and diluted hydrochloric acid. Most of the divalent and trivalent transition metal chlorides were included. The color changes may vary from barely visible (e.g. in $MnCl_2$—HCl—H_2O), through visible (e.g. in $NiCl_2$—HCl—H_2O) to remarkable (e.g. in $MoCl_3$—HCl—H_2O). Well known examples of $CoCl_2$—HCl—H_2O and $CuCl_2$—HCl—H_2O were also included. The color changes were ascribed (as has been done many times earlier) to changes in the coordination sphere of the metal cations. The solutions were sealed in pairs of glass ampoules, thus offering the possibility to use the samples unlimited number of times.

Keywords: continuous thermochromism; transition metals; aqua complexes; aqua-chloro complexes; chemical equilibrium; economic demonstrator

Introduction

(1) The Economic Demonstrator

Demonstration experiments are experiments that are often performed as an integral part of the lectures (could be also performed later, during experimental classes), with the intention of simplifying the comprehension of the subject taught. The experiments are conducted by instructor (a demonstrator or a teaching assistant), who introduces the audience to the essentials of the phenomena to be presented.

Two very common obstacles that appear in the course of the realization of demonstration experiments are i) the time for preparation and the duration of the experiments, and ii) the financial background and the additional costs involved. In a number of cases these obstacles can be overcome by the use of sealed tubes, as demonstrated earlier [1]. The method is based on sealing the materials in glass tubes, and monitoring the changes of the optical properties of the studied materials (typically during heating the vessel). It is, however, important to avoid mechanical damage and overheating during the use of the above-mentioned tubes, in order to avoid development of high pressure in the ampoule. In the present paper, we will continue with further examples of a method that is almost ideal for instructors: prepare the equipment for the demonstration once and than use it (practically) unlimited number of times. In order to show further ways in which sealed ampoules can be used, we continue with more examples of phenomena of continuous thermochromism, in this case in systems containing solutions of transition metal chlorides. Some of the examples are well-known [2—5], others are offered for the first time.

(2) Thermochromism

Let us briefly summarize some common knowledge regarding the key-word. Thermochromism is a phenomenon where certain substances change their color upon changing the temperature. The color change has to be *reversible*. There are two types of thermochromism: continuous thermochromism (the color changes continuously during the temperature change) and discontinuous (the color changes abruptly at some characteristic temperature). The phenomena of continuous thermochromism are usually related to chemical changes occurring in the system [2—5], while those of discontinuous type are either due to a phase transition (usually of order-disorder type [6]) or due to isomerisation reaction (like changes in the coordination [7-9]). A schematic presentation of continuous and discontinuous thermochromism is shown in Figure 1:

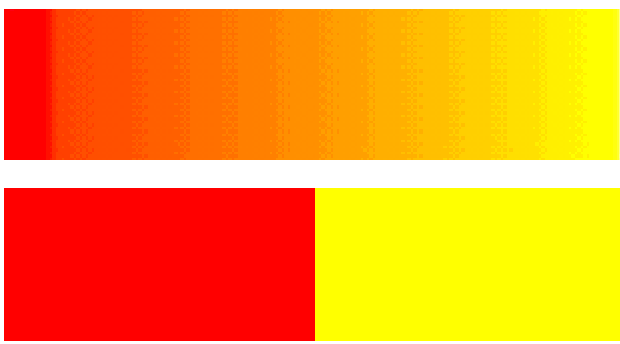

Figure 1. Thermochromism — a schematic presentation: continuous (upper) and discontinuous (lower part). One has to assume that temperature changes continuously when going from left to right.

Systems of Interest

From the numerous systems the behavior of which has already been studied in the chemical education literature [2—5] one could review the following:

$CoCl_2$(aq, HCl); $CuCl_2$(aq, HCl)

For clarity, the designation MCl_x(aq, HCl) that one meets below means a solution of the transition metal (M) chloride in hydrochloric acid of varying concentration (typically of the order of several mol/L).

The systems of interest that we add to the above (and we believe that most of them were not studied in this respect, at least not from an educational point of view), are all based on either trivalent transition metal chlorides, i.e.:

$TiCl_3$(aq, HCl); VCl_3(aq, HCl); $FeCl_3$(aq, HCl);

$MoCl_3$(aq, HCl)[1)]; $RuCl_3$(aq, HCl); $RhCl_3$(aq, HCl); $PdCl_3$(aq, HCl)

or divalent transition metal chlorides, i.e.:

$MnCl_2$(aq, HCl); $FeCl_2$(aq, HCl); $NiCl_2$(aq, HCl)

Experimental

(1) Preparation of solutions

The transition metal chlorides were dissolved in distilled water and concentrated hydrochloric acid was added to the solution until a color change occurred. Then few drops of water were added back, in order to restore (partly) previous color.

In the case of molybdenum, a suspension of MoO_3 in water was used, to which concentrated hydrochloric acid and metallic zinc were added. The Mo(VI) of the starting material was reduced by the generated nascent hydrogen, most probably to Mo(III). The latter was characterized by deep brown color. The intensely colored solution appeared to be air sensitive, so the further procedure with it had to be really fast one.[2)]

The prepared solutions are then put into ampoules (previously prepared from standard 160 x 16 mm test-tubes) and the ampoules are sealed.

(2) Performing the Demonstration

In order for the color change to be visible, a preparation of three ampoules is recommended. The first is the reference one (used for comparison), the second is to be cooled to temperature down to -10°C (a refrigerator can be used), and the third is to be heated (a beaker with boiling water is possibly the simplest way to achieve it). The demonstration can also be successfully performed with only two ampoules, in which case one would use two beakers filled with ice-water and boiling water, respectively.

Results

Out of the three already prepared ampoules, one is placed in a beaker with boiling water, another in a cooler with temperature down to -10°C, and the last one is left at room temperature. After ~ one minute the colors of the three ampoules are compared. A recommended way of presenting the ampoules is by making arrangement in the order in which the temperature increases/decreases. In this way one can better follow the colour change.

A color change was detected in all of the above systems. However, in some of them it is more perceptible than in others. This is seen in the forthcoming series of photographs. In all of them, we first present the color of a pair of test-tubes at room temperature, and then present the colors at high and at low temperature.

Figure 2 comprises two, so-to-say classical examples of continuous thermochromism [2—7]: the $CoCl_2$—H_2O—HCl and $CuCl_2$—H_2O—HCl systems. The color change in these systems is very remarkable. Let us mention quickly that the room temperature color in the system containing cobalt is in a way intermediate between the low- and high-temperature colors. The reason for this behavior will be explained later.

In the rest of the figures, other examples are presented. In some of them, a color change is barely visible (like in systems containing Mn, Ru, Rh), in others it is noticeable (Ni, Fe, Cr, Ti), and in some (V, Mo) it is very pronounced.

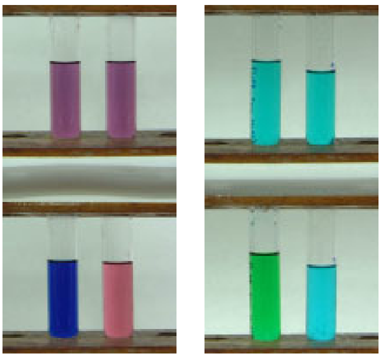

Figure 2. Remarkable color change in $CoCl_2$(aq, HCl) (left) and $CuCl_2$(aq, HCl,aq) (right). Upper row — room, lower left — high, and lower right — low temperature

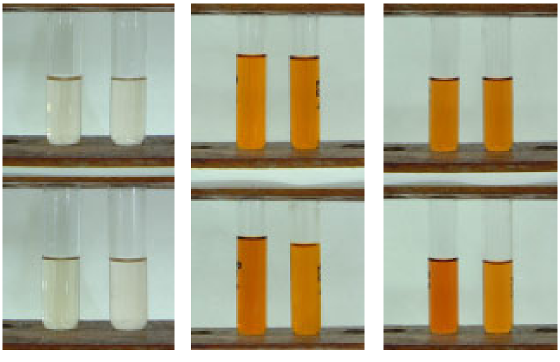

Figure 3. Barely visible color change in $MnCl_2$(aq, HCl) (left), $RuCl_3$(aq, HCl,aq) (middle) and $RhCl_3$(aq, HCl,aq) (right). Upper row — room, lower left — high, and lower right — low temperature

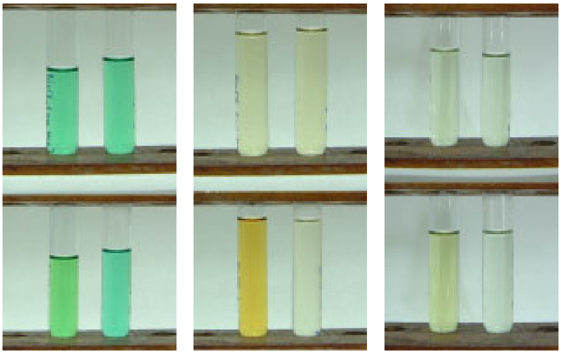

Figure 4. Noticeable color change in $NiCl_2$(aq, HCl) (left), $FeCl_3$(aq, HCl,aq) (middle) and $FeCl_2$(aq, HCl,aq) (right). Upper row — room, lower left — high, and lower right — low temperature

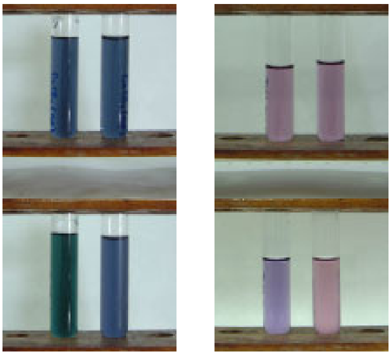

Figure 5. Noticeable color change in $CrCl_3$(aq, HCl) (left) and $TiCl_3$(aq, HCl,aq) (right). Upper row — room, lower left — high, and lower right — low temperature

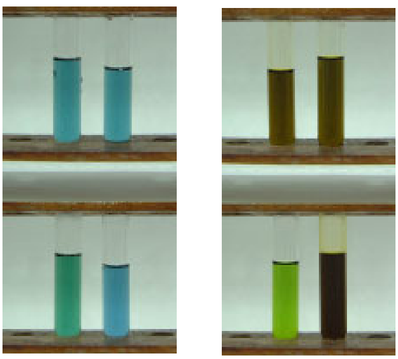

Figure 6. Very pronounced color change in VCl_3(aq, HCl) (left) and $MoCl_3$(aq, HCl,aq) (right). Upper row — room, lower left — high, and lower right — low temperature

Discussion

In order to give sound explanation to all above phenomena, it is vital to review some basic points concerning chemical equilibria. The chemical equilibrium that exists in any of the above systems can be presented with the equation (we write it in the most general form):

$$[M(H_2O)_n]^{k+} + mCl^- = [M(H_2O)_{n-m}Cl_m]^{(k-m)+} + mH_2O \quad (1)$$

We shall further assume that the complex ions on both sides of the equation have different colors. Providing this is true, the change in the equilibrium (that we say is of central importance for all presented phenomena of continuous thermochromism) can be monitored visually. Namely, in an aqueous solution, metal ions are hydrated. That is, water molecules are the ligands in the complex ion formed. If chlorine ions are present in the system (as they are in our case), part of the water molecules might be replaced by chlorine ions until equilibrium (governed by the value of the equilibrium constant, cf. Eq. 2) is reached. Of course, the equilibrium is a dynamical one. Considering Eq. 1, the quantity K_c is defined as:

$$K_c = \frac{[\{M(H_2O)_{n-m}Cl_m\}^{(k-m)+}]\cdot[H_2O]^m}{[\{M(H_2O)_n\}^{k+}]\cdot[Cl^-]^m} \quad (2)$$

K_c is therefore temperature dependent. In that case, the number of water molecules replaced with chlorine ions will depend on the temperature and concentration of the chlorine and metal ions (it should also depend on the pressure, but to a much lesser degree, as in most condensed phases). On the other hand, the chemically different complexes $M(H_2O)_n{}^{k+}$ and $[M(H_2O)_{n-m}Cl_m]^{(k-m)+}$ exhibit different colors (as mentioned above).

It may happen that at some temperature (e.g. in ice-water) $M(H_2O)_n{}^{k+}$ species are by far predominant. In such a case, the observer perceives their color. At high temperatures, $[M(H_2O)_{n-m}Cl_m]^{(k-m)+}$ might be the dominant species. However, when temperature is changed, the value of K_c will vary smoothly. That is, the color will vary *continuously* from that characteristic of $M(H_2O)_n{}^{k+}$, to that characteristic of $[M(H_2O)_{n-m}Cl_m]^{(k-m)+}$, hence the appearance of continuous thermochromism.

The above concept of equilibrium can be best presented in relation to a specific process. We shall consider the example of $CoCl_2$(HCl,aq) (as in one of the mentioned "classical" lecture demonstrations) due to the pronounced color change that can easily be perceived and offer the following simplified and tentative explanation where the basic ideas of previous works [2-5] are summarized.

At the very start of the experiment, the system in the sealed tube consists of $CoCl_2$ dissolved in water and HCl. The salt is dissociated:

$$CoCl_2 = Co^{2+} + 2Cl^- \quad (3)$$

the metal ions being hydrated almost instantaneously:

$$Co^{2+} + 6H_2O \ \Phi \ [Co(H_2O)_6]^{2+} \quad (4)$$

Due to the chloride ions present in the system (both from the salt itself, as well as from the added HCl), a chemical equilibrium is established. Consequently, part of the water molecules is replaced with chloride ions, the first step being:

$$[Co(H_2O)_6]^{2+} + Cl^- = [Co(H_2O)_5Cl] + H_2O \quad (5)$$

As the temperature changes, there is a gradual replacement of the water molecules with chloride ions (consequence of changes in K_c) and a continuous change in colour occurs (cf. Fig. 2, left). The pink color of the system is a result of the $[Co(H_2O)_6]^{2+}$ ions present (these are by far predominant when the solution is cold). The purple color comes from the $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_2Cl_2]$ ions (both are present at room temperature). Finally, the heated solution contains $[Co(H_2O)_2Cl_2]$, $[Co(H_2O)Cl_3]^-$ and $[CoCl_4]^{2-}$ ions, and the color turns blue. In principle, analogous explanations could be offered in all studied cases.

Why are the colors at different temperatures sometimes markedly different, and sometimes almost identical? At least two reasons could be offered as an explanation. It may happen that the colors of the aquacomplex ions and of the chloro(aqua)complex ions are practically identical. Alternatively, it may happen that with certain metal ions, only one of the above complexes is of high-enough stability. In both cases, the observer sees a barely varying (or even a single) color (cf. Fig. 3).

Conclusion

- this is another example of prepare-it-once, use-it-many-times experiment for instructors of chemistry;
- the experiment deals with examples of continuous thermochromism;
- changes of chemical equilibrium in solutions can be represented with this kind of demonstration;
- the fastest and simplest way for conducting this experiment is to use only two ampoules and have boiling- and ice-water prepared in advance;
- the color change may vary from very pronounced to a barely detectable, depending on the chemical nature of the system.

Safety tips

Concentrated hydrochloric acid is highly corrosive substance. The salts of all transitional metals are toxic and must be handled with care. In case of breaking the ampoule and leaking of its contents, the first step is to precipitate the metal ions and neutralize the solution before it is disposed. The best way to perform this is by adding Na_2CO_3 solution. In case of eye contact, flush eyes with water and ask for medical advice if necessary. For other types of accident, call for physician immediately.

NOTES

1. We are not certain that the stoichiometry of the product formed by reduction is indeed $MoCl_3$, as we did not check this. Fortunately, for the purposes of the present paper this not of crucial importance.

2. We also tried to prepare an analogous solution of tungsten, from WO_3. Indeed, a deep blue solution was obtained, upon reduction with atomic hydrogen. On heating in a sealed tube, however, the color disappears irreversibly. We suspect that the product (trivalent tungsten?) is a strong reducing agent, capable of reducing the water to hydrogen gas. If this is true, the behavior of the product resembles that of Ta(III), but also Cr(II), etc [10].

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ХИМИЧНИ ДЕМОНСТРАЦИИ: ТЕРМОХРОМИЗЪМ ВЪВ ВОДНИ РАЗТВОРИ НА ПРЕХОДНИ МЕТАЛНИ ХЛОРИДИ

Резюме. В системи, съдържащи метални хлориди и разредена солна киселина, се наблюдава термохромизъм. В изследването да включени повечето от хлоридите на дву- и тривалентните преходни метали. Промените в цвета варират от едва видимо (например в $MnCl_2$-HCl-H_2O), през видимо (например в $NiCl_2$—HCl—H_2O), до подчертано видимо (например в $MoCl_3$—HCl—H_2O). Разгледени са още случаите на $CoCl_2$—HCl—H_2O и $CuCl_2$—HCl—H_2O. Промяната в цвета се приписва на промяната на координационната сфера на металните катиони. Разтворите почифтно са запечатани в стъклени ампули, което осигурява многократната употреба на образците.

✉ **Prof. Dr. Vladimir M. Petruševski**,
Institute of Chemistry,
Faculty of Natural Sciences and Mathematics,
Sts. Cyril and Methodius University,
Arhimedova 5, PO Box 162
1001 Skopje, Republic of Macedonia,
E_Mail: vladop@iunona.pmf.ukim.edu.mk