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• Учебни опити и демонстрации •
• Teaching Chemical Experiment •

THE ECONOMIC DEMONSTRATOR: PREPARE IT ONCE, USE IT MANY TIMES. III. PHENOMENA OF DISCONTINUOUS THERMOCHROMISM[1])

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Abstract. Sealed ampoules containing solids that show pronounced thermochromism were prepared, thus continuing the series "prepare it once – use it many times" of the economic demonstrator. Two types of thermochromic solids were prepared: silver, copper(I) and thallium(I) tetraiodomercurate(II), on one hand, and diethylammo-nium tetrachlorocuprate or tetrachloronickelate, on the other.

Keywords: thermochromism, discontinuous; silver tetraiodomercurate(II); copper(I) tetraiodomercurate(II); thallium(I) tetraiodomercurate; diethylammonium tetrachlorocuprate(II); diethylammonium tetrachloronickelate(II)

Introduction

(1) Demonstrations

Demonstration experiments (demonstrations) are experiments that are performed during lectures with an intention of improving the teaching process and making it more efficient. The experiments are conducted by an instructor (professor, teaching assistant or a demonstrator), who introduces the audience to the essentials of the phenomena to be presented.

Two common obstacles might make the demonstration experiments be unattractive to teachers. These are:

- the time needed for preparation of demonstrations and their duration as well, and
- the financial background.

There is a solution to the above problems. Many demonstrations can be simplified by using sealed tubes, as shown earlier [1, 2]. This 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 or cooling 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 inside the ampoule. In this article, we continue with further examples of the method that is almost ideal for instructors: prepare the equipment for the demonstration once and then use it (practically) unlimited number of times. In order to show other ways in which sealed ampoules can be used, we continue with more examples of the phenomena of discontinuous thermochromism. In this particular case, the sealed tubes are not only used as a mean for making economic demonstrations, but also as a mean for keeping the solid thermochromic substances dry and stable (it is to be noted that some of them are very hygroscopic, i.e. deliquescent). Since the substances that show this phenomenon are often in solid state (as is the case with those dealt with), sealing can be performed easily.

(2) Thermochromism

Some basic information on the phenomenon of thermochromism were given earlier [1, 2]. Briefly, thermochromism is a phenomenon where certain substances change their colour upon changing the temperature. The colour change has to be reversible. There are two types of thermochromism: continuous thermochromism (the colour changes continuously during the temperature change) and a discontinuous one (the colour changes abruptly at some characteristic temperature). The phenomena of continuous thermochromism are usually related to chemical changes (typically changes in the equilibrium) occurring in the system [3-7], while those of discontinuous type are either due to a phase transition (usually of order-disorder type [8]) or due to isomerisation reaction (like changes in the coordination [9-12]).

Systems of Interest

The studied systems (all of which are well-known in the chemistry literature) can be presented with the formulae $M_2[HgI_4]$ and $[R_2NH]_2[MX_4]$. They were studied extensively, from both research and (many of them) from educational point of view as well (in numerous demonstrations of thermochromism). Problems appeared as to the best way of performing the demonstrations with the solids, as the compounds are subject to chemical changes after being exposed to atmosphere for a certain period.

For clarity, the symbol M refers to metals. Thus, in the formula M2[HgI4], M = Cu, Ag, Tl; and in the formula $[R_2NH_2]_2[MX_4]$, it refers to divalent transition metal. R refers to organic radical such as methyl, ethyl, i-propyl and X refers to a certain halogen element.

Experimental

(1) Preparation of the compounds

$M_2[HgI_4]$ – For preparation of these compounds, stoichiometric quantities of mercury(II) chloride, potassium iodide and M(I) salts were used. First, mercury(II) iodide was prepared by dissolving mercury(II) chloride in distilled water and adding a solution of potassium iodide. The formed precipitate was filtered through Buchner funnel and washed with distilled water (several times). The precipitate was then dissolved in small portion of concentrated solution of potassium iodide and a colourless solution of potassium tertraiodomercurate(II) was formed:

$$HgCl_2(aq) + 2KI(aq) = HgI_2(s) + 2KCl(aq)$$

$$HgI_2(s) + 2KI(aq) = K_2[HgI_4](aq)$$

This solution was used for preparation of $Ag_2[HgI_4]$, $Cu_2[HgI_4]$, $Tl_2[HgI_4]$ and $(Cu,Ag)[HgI_4]$.

$Ag_2[HgI_4]$ – in aqueous solution of potassium tertraiodomercurate(II), a solution of silver nitrate is added. Yellow precipitate of silver tetraiodomecurate(II) is formed:

$$K_2[HgI_4](aq) + AgNO_3(aq) = Ag_2[HgI_4](s) + 2KNO_3(s)$$

This precipitate is dried at atmospheric conditions, and then it is sealed in ampoule. $Tl_2[HgI_4]$ is prepared exactly in the same way as $Ag_2[HgI_4]$. The yield is about 75 %.

$Cu_2[HgI_4]$ – in aqueous solution of potassium tertraiodomercurate(II), a solution of copper(II) sulphate is added. Sulphur dioxide is passed through the system for 10-15 minutes until a red precipitate forms:

$$K_2[HgI_4](aq) + 2CuSO_4(aq) + SO_2(g) + 2H_2O(l) =$$

$$= Cu_2[HgI_4](s) + K_2SO_4(aq) + 2H_2SO_4(aq)$$

The precipitate is then dried at atmospheric conditions, and is afterwards sealed in an ampoule. The yield is □ 68 %.

$(Cu,Ag)[HgI_4]$ – in aqueous solution of potassium tertraiodomercurate(II), a solution of stoichiometric quantities of both silver nitrate and copper(II) sulphate is added. The formed orange precipitate is filtrated, washed with distilled water and then dried at room temperature. After that, the solid thermochromic compound is sealed in an ampoule. The yield is 65 %.

$[R_2NH]_2[MX_4]$ – for the preparation of this kind of compounds it is necessary to first prepare dimethylammonium chloride, diethylammonium chloride or i-propylammonium chloride. These compounds are prepared by adding stoichiometric quantities of concentrated hydrochloric acid in dimethylamine, diethylamine or i-propylamine. The solution is heated till the water evaporates and white crystals are formed.

$$R_2NH + HCl = R_2NH_2Cl$$

$[(CH_3CH_2)_2NH]_2[CuCl_4]$ – anhydrous $CuCl_2$ is mixed with diethylammonium chloride and the obtained compound (being highly deliquescent) is immediately sealed in an ampoule. During mixing the solids, the reaction mixture should be placed on a hot plate, so that absorption of water can be minimized.

$$2(CH_3CH_2)_2NH_2Cl(s) + CuCl_2(s) = [(CH_3CH_2)_2NH]_2[CuCl_4](s)$$

$[(CH_3CH_2)_2NH]_2[NiCl_4]$ is prepared in the same way as $[(CH_3CH_2)_2NH]_2[CuCl_4]$, except that anhydrous $NiCl_2$ is used, instead of anhydrous $CuCl_2$.

$[(CH_3)_2NH]_2[CuCl_4]$ is prepared analogously as $[(CH_3CH_2)_2NH]_2[CuCl_4]$, except that dimethylammonium chloride is used instead of diethylammonium chloride.

$[(CH_3)_2NH]_2[NiCl_4]$ is also prepared in the same way as $[(CH_3)_2NH]_2[NiCl_4]$, but in this case diethylammonium chloride was substituted with dimethylammonium chloride.

(2) Demonstrations

These demonstration experiments are very simple. One needs only hot plate, beaker filled with water and sealed ampoule or a set of ampoules, each containing different thermochromic compound (cf. Fig. 1). The water is heated for about 10 minutes before the demonstration. The ampoule is inserted into the hot water and changes in the ampoule are noticed.

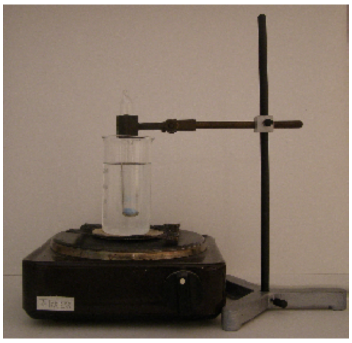

Figure 1: Discontinuous thermochromism – setup for demonstration

In order for the colour change to be clearly visible, one should fill the ampoule with the thermochromic compound to at least one quarter of its volume.

Results

Few seconds after the ampoule is placed in the hot bath, the colour of the compound changes. To achieve best results, two ampoules with the same thermochromic compound can be prepared. Only one of them will be heated and the other will be left at room temperature. The demonstration does not need to be performed in this particular way, simply because the colour changes are very noticeable. Surely, it is important to show the colour of the compound before and after the heating. A colour change was detected in all of the above mentioned systems.

Figures 2 & 3 comprise two, well-known examples of discontinuous thermochromism $Ag_2[HgI_4]$ and $Cu_2[HgI_4]$ [9]. The colour change in these systems is remarkable. It is important to stress that the thermochromism demonstrated above is not continuous even though the colour changes seemingly continuously from left to right. This is due to the temperature in the inner part of the ampoule that has not reached the point of the phase transition, followed by a discontinuous colour change.

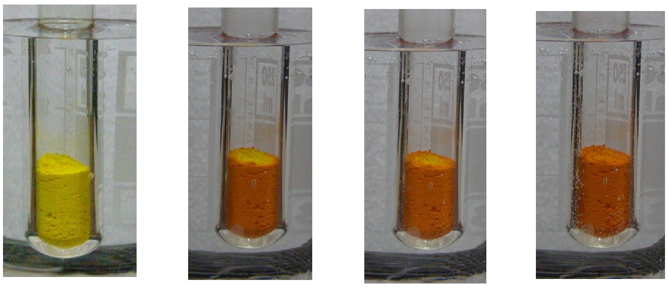

Figure 2. Remarkable colour change in $Ag_2[HgI_4]$. Leftmost photo – room temperature; the rest are at ≈ 60 °C (the longer the heating, the more complete the colour change)

Figure 3. Remarkable colour change in $Cu_2[HgI_4]$. Leftmost photo – room temperature; the rest are at ≈ 80 °C (the longer the heating, the more complete the colour change)

Figure 4. Noticeable colour change in solid solution (Ag, Cu)$[HgI_4]$.
Left – room temperature; right – high temperature

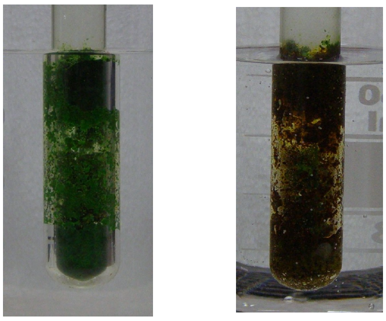

Figure 5. Very pronounced colour change in $[(CH_3CH_2)2NH]_2[CuCl_4]$.
Left – room temperature; right – high temperature

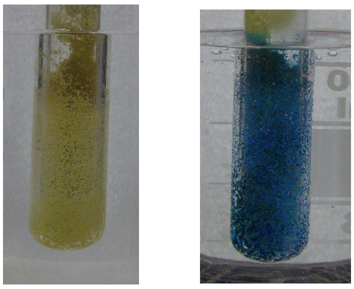

Figure 6. Very pronounced colour change in $[(CH_3CH_2)_2NH]_2[NiCl_4]$.
Left – room temperature; right – high temperature

Discussion

The colour changes in the systems mentioned above can appear as a result of:

- structural changes such as: different coordination or coordination number change,
- solid-solid phase transitions (from order-disorder type), etc.

The colour change in the $M_2[HgI_4]$ – systems is due to a phase transition of an order-disorder type. The β (low-temperature) form is tetragonal and the á (high-temperature) form is cubic. Both forms have different colour. Some basic information will be given below. More details may be found elsewhere [13-15]. Sometimes, the information about the colours differ [16].

$Ag_2[HgI_4]$ – A colour change from yellow to orange is evident at 50°C (phase transition from β to á form).

$Cu_2[HgI_4]$ – At 68°C, the colour changes from red to dark brown as a result of the transition from β to á form.

$(Ag,Cu)_2[HgI_4]$ – The change in colour occurs at 34°C. This is actually a solid solution with $x(Ag_2[HgI_4])$ = 57 % and $x(Cu_2[HgI_4])$ = 43 % where silver, copper and mercury ions become disordered simultaneously by increasing the temperature. This solid solution corresponds to the eutectoid composition where the metal ions go from ordered to a disordered state and there is no change in the chemical composition.

In $[R_2NH_2]_2[MX_4]$ – systems the colour change appears as a result of changes in coordination geometry and coordination number. Other changes (like the change of the crystal system) depend on the chemical nature of the metal ion – M.

$[(CH_3CH_2)_2NH]_2[NiCl_4]$ – At 72-73°C, the colour changes from yellow to blue. At this thermochromic temperature, the coordination around M changes from octahedral into one consisting of two-dimensional infinite polymeric sheets.

$[(CH_3CH_2)_2NH]_2[CuCl_4]$ – The change in colour occurs at 52-53°C. This results from a structural change: upon heating, the low-temperature phase (with square-planar coordinated Cu) transforms into a high-temperature one (tetrahedral coordination of Cu, cf. Fig. 7).

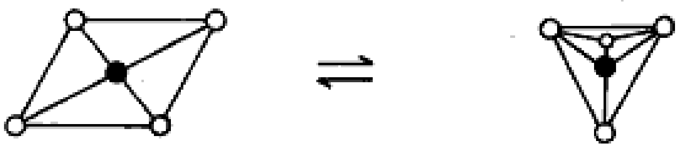

Figure 7. Low-temperature phase (square-planar, left) due to heating transforms into the high-temperature one (tetrahedral, right)

Conclusions

- This is yet another example of prepare-it-once, use-it-many-times experiment for chemistry instructors;

- the experiment deals with examples of discontinuous thermochromism;
- the syntheses of the compounds are relatively easy and can be maintained in most chemistry laboratories;
- solid-solid phase transitions and structural changes can be represented with this kind of demonstration;
- the fastest and simplest way for conducting this experiment is to use only one ampoule and have boiling water prepared in advance;
- in all compounds dealt with, the colour change is easily detected.

Safety tips

Concentrated hydrochloric acid (used for preparation of some samples) is highly corrosive substance. Ammonia and its alkyl derivatives are toxic and corrosive substances. Always wear safety goggles and gloves during syntheses.

The salts of all transition metals are toxic and must be handled with care.

Overheating the ampoules should be avoided, especially overheating the $M_2[HgI_4]$ type of compounds simply because they may disintegrate, thus producing elemental mercury. Ampoules containing $[R_2NH_2]_2[MX_4]$ type of compounds should never be heated with open flame or overheated because gases are produced during thermal decomposition (pyrolysis) of the compounds, and dangerously high pressure may develop in the ampoule.

NOTES

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ДЕМОНСТРАЦИОННИ ЕКСПЕРИМЕНТИ ВЪРХУ ЯВЛЕНИЯТА НА ТЕРМОХРОМИЗЪМ

Резюме. Приготвени са запоени ампули с твърди вещества, с които могат да се демонстрират явления на термохромизъм. Два типа твърди вещества са предложени: сребро, мед (I) и талиев (I) тетрайодмеркурат (II), от една страна, и диетиламониев тетрахлоркупрат или тетрахлорникелат, от друга страна.

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