

Phenolphthalein as Organic Teaching Materials: Small-scale Preparation and Modeling for Some Functional Dyes

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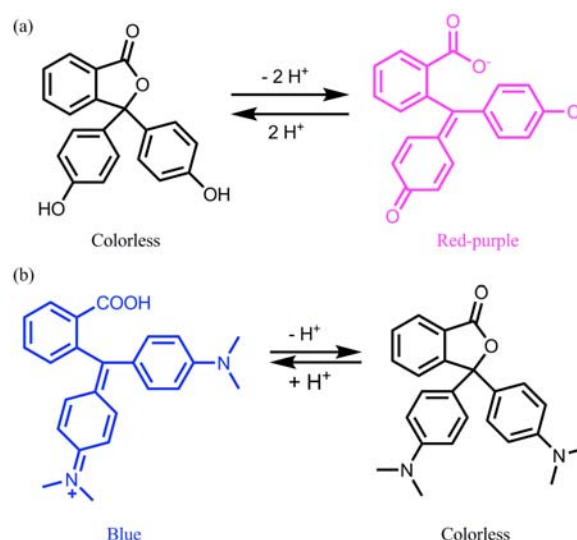
Keywords: Organic dyes, teaching materials, phenolphthalein, small-scale experiment, modeling of functional materials

Abstract

Further possibilities for utilizing phenolphthalein as the sophisticated teaching materials were reinvestigated. It was proposed to use *p*-toluenesulfonic acid as the acid catalyst for the synthesis of phenolphthalein in conventional-scale and small-scale experiments in order to increase the reproducibility and to simplify the extraction procedures. Simplified model experiments for demonstrating the functionality of organic dyes were also developed using phenolphthalein and its derivatives. The practical usefulness of these experiments in chemistry courses at high schools was discussed.

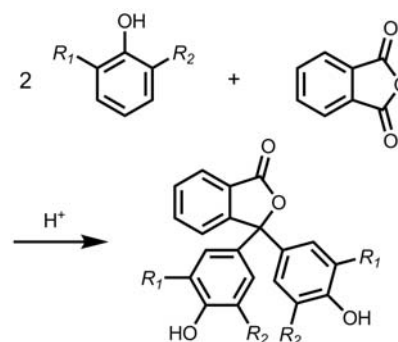
Introduction

It is generally accepted that chemical changes accompanying with dramatic color changes serve to strengthen students' enthusiasm and interest in studying chemistry. Various reaction systems which indicate such color changes have been continuously investigated for developing effective teaching materials [1-2]. The proton dissociation equilibrium of phenolphthalein (Scheme 1a), which indicates the color change between colorless and red-purple by the equilibrium shift, is one of the most popular color change phenomena for high school students, due to the utilizations as an acid-base indicator for neutralization titration, fountain of ammonia,



Scheme 1. Proton dissociation equilibrium of (a) phenolphthalein and (b) crystal violet lactone.

and so on [3-4]. Crystal violet lactone is a phthalein analogue that can make color change by shifting pH from basic to acidic condition (Scheme 1b). These color-changes are also applied to various daily necessities such as invisible inks, clear-off adhesives, and thermal papers [5-6]. In addition to the conventional experiment for preparing by acid-catalyzed condensation of phenol with phthalic anhydride (Scheme 2), it is highly expected to utilize phenolphthalein as a novel teaching material for demonstrating the functionality in relation to the application to the daily necessities.



Scheme 2. Reaction scheme for preparation of phenolphthalein derivatives.

In this work, preparation of phenolphthalein using *p*-toluenesulfonic acid as the acid catalyst was examined for improving student experiment, together with a procedure of acid-base extraction of the product phenolphthalein. On the basis of the examination, a simplified small-scale experiment of preparation and extraction of phenolphthalein was also designed. In addition, several model experiments to demonstrate the functionality of organic dyes utilizing in daily life were developed using phenolphthalein derivatives and crystal violet lactone.

Experimental

Conventional-scale Preparation of Phenolphthalein. A mixture of phenol (2.0 g: 21 mmol), phthalic anhydride (1.5 g: 10 mmol), and *p*-toluenesulfonic acid monohydrate (190 mg: 1 mmol) was placed in a 30-mL round-bottom flask fitted with a magnetic stirring bar, an air-cooled head, and an oil bath with a thermometer. The reaction mixture was heated at 150°C for 3 hours with continuous stirring. After cooling to room temperature, 10 mL of water and 10 mL of dichloromethane were added into the

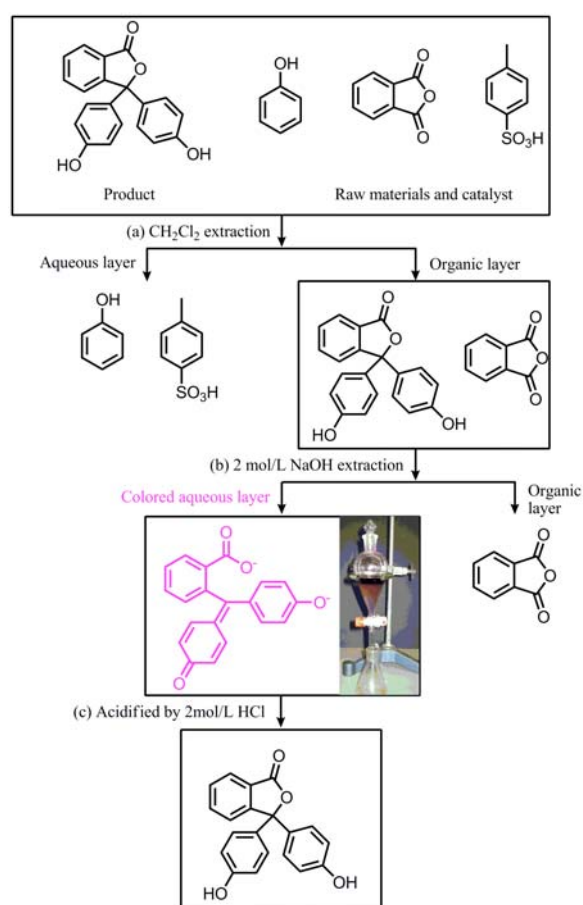


Figure 1. Flow chart for a purification protocol of phenolphthalein.

flask, and then the resulting solution was transferred to a 50-mL separatory funnel. The extraction of product phenolphthalein follows the scheme shown in Figure 1. The lower organic layer was drawn off into a 50-mL Erlenmeyer flask. The remaining aqueous layer was further extracted with 10 mL of dichloromethane and the separated organic layer was drawn off into the same Erlenmeyer flask (Figure 1a). The combined organic layer was returned to the separatory funnel and made alkaline by addition of 5 mL of 2 mol/L NaOH solution (Figure 1b). After the extract was diluted with 10 mL of water, the lower organic layer was drawn off and the upper aqueous layer was taken from the top of the separatory funnel and transferred into another 50-mL Erlenmeyer flask. The aqueous solution was acidified with 5 mL of 2 mol/L HCl solution to isolate phenolphthalein as white mossy fibers (Figure 1c), which were separated by suction-filtration. Yield: 735 mg (22%).

Simplified Small-scale Preparation of Phenolphthalein.

The typical snapshot of each stage is shown in Figure 2. In a 10-mL sample vessel was placed a mixture of phenol (190 mg: 2 mmol), phthalic anhydride (150 mg: 1 mmol), and *p*-toluenesulfonic acid monohydrate (19 mg: 0.1 mmol), which was heated at 150°C for 5 minutes on the hot plate fitted with a digital thermometer (Figure 2a). After cooling to room temperature, 2 mL of water was added into the vessel, in which a part of the reaction mixture was solidified (Figure 2b). The supernatant was removed using a Pasteur pipet and discarded. The remaining solid was treated in 2 mL of 2 mol/L NaOH solution to give the colored solution (Figure 2c). The insoluble matter was

separated by pressure filtration using a cotton-loaded Pasteur pipet and a pipet bulb. The filtrate was received in another 10-mL sample vessel and acidified with 2 mL of 2 mol/L HCl solution, in which precipitation took place (Figure 2d). Filtration under suction afforded the desired product as white crystalline fibers (Figure 2e). Yield: 27 mg (8.5%).

Demonstration 1: Invisible Ink. The dye solution was prepared by mixing of 10 mg of phenolphthalein, 1 mL of 10% poly(vinyl alcohol) aqueous solution, and 1 mL of ethanol. The basic solution was used as a color developer, in which 1 mL of 2 mol/L NaOH solution was added into 1 mL of 10% poly(vinyl alcohol) aqueous solution. On the other hand, the acidic solution was used as a bleaching reagent, in which 1 mL of 2 mol/L HCl solution was added into 1 mL of 10% poly(vinyl alcohol) aqueous solution. The dye solution was applied over a

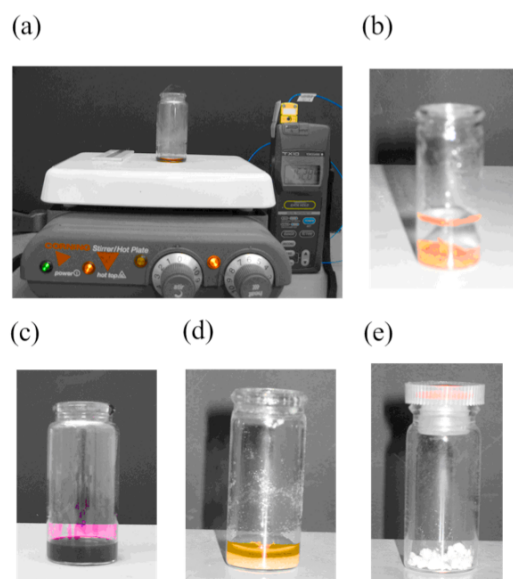


Figure 2. Snapshots of experimental steps for small-scale preparation of

paper with a brush, on which the basic solution was traced to develop vivid red color. When the acidic solution was retraced on the line, the color was erased.

Demonstration 2: Clear-off Adhesive. The blue-colored adhesive was prepared by mixing of 10 mg of 2,2'-dimethoxyphenolphthalein, 1 g of starch paste, 1 mL of 10% poly(vinyl alcohol) aqueous solution, 1 drop of triethylamine, and 1 mL of ethanol. The blue adhesive was applied over a paper with a brush, the color-fading in the course of time was checked with naked eyes.

Demonstration 3: Thermal Paper. The gel particles containing of phenolphthalein analogue were prepared as follows: 0.5 g of gelatin was swollen in 2 mL of 50% aqueous ethanol, in which 10 mg of crystal violet lactone was added with mechanical stirring. After stirring at room temperature for 1 hour, the mixture was stored in refrigerator. The gel was suspended in 10 mL of cyclohexane with vigorous stirring to form gel particles, which were allowed to stand until they were precipitated. The supernatant was removed by decantation and the gel particles were washed twice with ethanol. The obtained gel particles were spread over an acid paper with a brush to prepare a gel-coated paper. The coloration of this paper with heat treatment was checked with naked eyes.

Hazards. Phenol, triethylamine, and dichloromethane are irritant and carcinogenic. *In order to avoid a contact with phenol, the preparation of phenolphthalein should be carried out in a hood.* The acid and alkaline solutions are also corrosive. It is required to wear safety glasses, protective gloves, and lab coat for all experiments. Organic solvents such as ethanol and cyclohexane are flammable, and should be handled in a safe place where there are no flames. The chemical wastes are sure to be disposed in appropriate residue containers.

Results and Discussion

Improved Preparation of Phenolphthalein. In the conventional method, a large excess of phenol is reacted with phthalic anhydride over a small flame and a few drop of concentrated H_2SO_4 is used as an acid catalyst [7], but this harsh condition often causes undesirous over-reactions such as carbonization and oligomerization, which are difficult to accomplish high yields and an easy isolation of the product. For improving these practical difficulties as well as introducing the concept of contemporary chemistry, researchers have attempted to find zeolites as solid acid catalysts [8] and to accelerate the condensation reaction by microwave irradiation [9]. Although these modifications are available in the specialized organic

Table 1. Yields of phenolphthalein derivatives prepared in this study

R_1	R_2	Yield (%)
H	H	22
CH_3	H	30
CH_3	CH_3	40
OCH_3	H	24
Cl	H	18

laboratory, there is much room for further improvements as applying to student experiments in views of the access of zeolites catalysts, the condition of microwave irradiation, the reproducibility of the reaction, and so on. We found that benzenesulfonic acid derivatives that students encounter in chemistry textbooks can be utilized as the acid catalyst for preparation of phenolphthalein. *p*-Toluenesulfonic acid is a good choice because of ease to handle and the reproducibility of the experimental results. The optimum amount of *p*-toluenesulfonic acid is about 10 mol%, with lower amounts resulting in decreased product yields. We also found that the control of the reaction temperature was particularly important in preventing over-reactions. By regulating the temperature so as to be at about 150°C, the product was produced with the reasonable yield, although it took a prolonged time of 3 hours for completing the reaction. In this procedure a stoichiometric amount of phenol is used to prevent sub-reactions of phenol, which causes the disadvantage that the yield is limited to be relatively low. On the other hand, it also has the advantage that the isolation process is free from the tedious treatments for elimination of excess phenol and by-products such as steam-distillation and chromatography used in the conventional method. This reaction condition can be also applied to other phenolphthalein derivatives, whose yields are summarized in Table 1.

The other advantage of this preparation is that the isolation of the product is simply performed by the acid-base extraction accompanied by color change. At the initial stage, phenol and *p*-toluenesulfonic acid are easily removed by solving in water. When 2 mol/L NaOH solution is added into the organic layer containing the product and phthalic anhydride, only the product can react with hydroxide to form the red-purple species which dissolves in the aqueous layer. When the red-colored aqueous layer is acidified by 2 mol/L HCl solution, the solution turns off-white suspension and then phenolphthalein is precipitated as white solid.

Small-scale Preparation for the Student Experiment. The above experiment takes about 4 hours and requires an usual laboratory set-up for organic synthesis. On the basis of the above work, we arranged a small-scale preparation of phenolphthalein which can be applied to the student experiment. A 10-mL sample vessel is enough to establish the reaction apparatus for this small-scale experiment. The reaction is carried out by heating on a hot plate at 150°C for only 5 minutes, and the purification by the acid-base extraction is easily done in the sample vessel without a separatory funnel. Although there is one disadvantage that the yield by the small-scale preparation is lower than that by the conventional-scale procedure because of the shorter reaction time and the absence of an appropriate condenser, this method includes three merits for student activity as follows: (1) it can be finished within one hour including cleaning up, (2) no organic solvents for extraction such as CH₂Cl₂ are needed, and (3) the limited use of phenol makes an exposure of toxic phenol to student's skin minimize.

Modeling of Dye Materials. As the daily necessities using phenolphthalein derivatives and crystal violet lactone, three types of model experiments are featured for demonstrating

invisible ink, clear-off adhesive, and thermal paper. The typical snapshots are shown in Figure 3. In the invisible ink, the colorless solution of phenolphthalein in neutral (Figure 3a) turns vivid pink by applying the alkaline solution (Figure 3b). The generated color can be erased by applying the acidic solution (Figure 3c). In the clear-off adhesive, 2,2'-dimethoxyphenolphthalein is used as blue-coloring dye in alkaline (Figure 3d). As the glue dries, the color of the dye is disappeared due to neutralization among the acid component of the paper (Figure 3e). In the thermal paper, crystal violet lactone is used as blue-coloring dye in acidic situation (Figure 3f). When the gelatin is molten by heating and the dye appears on the paper, the dye can react with the acid component on the paper to develop blue color (Figure 3g).

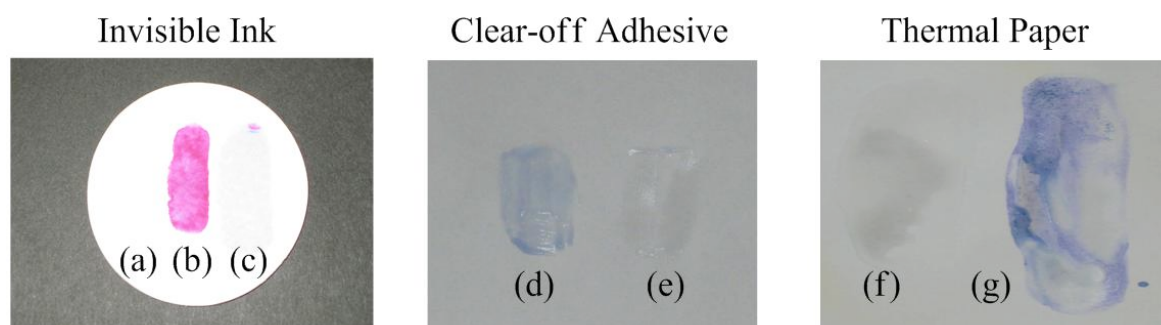


Figure 3. Snapshots of modeling for some daily necessity using phenolphthalein analogues.

Conclusion

The conventional-scale preparation of phenolphthalein can be improved by replacing sulfuric acid catalyst with *p*-toluenesulfonic acid and by regulating temperature to be 150°C for 3 hours, in which the acid-base extraction of product phenolphthalein can be applied as a suitable experiment to laboratory activity at high school. By reducing the scale of the improved preparation method, students can finish the preparation and extraction of phenolphthalein within one hour with limited use and exposure of harmful reagents. The functionality of organic dyes utilizing in the daily necessities can be demonstrated by simple model experiments using phenolphthalein derivatives and crystal violet lactone, which may provide visual impacts and promote students' interest in chemistry in daily life.

Acknowledgment

The present work is supported partially by a grant-in-aid for scientific research (B) (No. 18300267) from Japan Society for the Promotion of Science.

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