

Microscale Experiments in Chemistry – The Need of the New Millenium

2. Experiments Which Bring Theory Closer to Laboratories

Shrinivas L Kelkar and Dilip D Dhavale

Shrinivas L Kelkar is a Reader in Organic Chemistry at University of Pune. After an active research career and publishing work on heterocyclic chemistry, he is now devoting his entire time and attention to propagate the small-scale experiments. On demand, he is available to conduct workshops for training teachers on microscale techniques.

Dilip D Dhavale is a Reader in Organic Chemistry at University of Pune. He is pursuing his research career in carbohydrate chemistry. He had been associated with popularizing microscale chemistry from its inception in India.

The need for and the ease of adopting the microscale experiments, particularly in the academic institutes were stressed in our earlier article¹. Microscale technologies are safe, economical and are much less damaging to the environment. In this article we show that more meaningful experiments can be performed within the time assigned for laboratory classes by the microscale method. These would further corroborate that the students can verify the theory taught in classrooms more easily in the laboratories using lesser quantities of chemicals and in a safe and clean atmosphere.

Our endeavor is to design new multipurpose experiments, which would clarify the theoretical ideas and explain the chemical principles during the scheduled hours of laboratory. This is important since laboratory classes carry about 30% of the total marks in any chemistry course, and almost 60% of the teaching time allotted for it during the academic year.

In most of the books on practical chemistry, the experiments prescribed are mainly for elaborating just one principle or technique. Besides, during most of the experiments, the students do not know how successful their experiment had been or how to assess their own performance. The need to change all this could be elaborated with a few examples.

One of the experiments normally given in any laboratory is fractional distillation of two liquids. Currently, each student takes about 15 to 20 mL of any liquid in a 100 mL round bottom (RB) flask and collects the two fractions. We modified this experiment in the following way (as in *Box 1*).

¹ Part 1. Newer Ways of Teaching Laboratory Courses with New Apparatus, *Resonance*, Vol.5, No.10, p. 24, 2000.



Experiment

Aim: To separate the given mixture of liquids and test the approximate composition of the fractions collected.

Chemicals: Mixture of cyclohexanone (5 mL) and *p*-cresol (5 mL), diethyl ether (5 mL), 2N NaOH (5 mL), conc. HCl (2 mL)

Apparatus: Test tubes, Pasteur pipettes, RB flask (5 mL with B10 joint), Hickmann head (2), suitable air condenser

Procedure:

a. Take 1 mL of the mixture in the round bottom flask and arrange the vertical distillation assembly. Add a small porcelain piece. Heat the flask slowly so that the liquid just starts boiling. Maintain the heating rate till some portion of the liquid is collected in the groove of the Hickman head. Stop the distillation, take out the liquid in the Hickman head with the Pasteur pipette and keep it in a dry sample tube. Change the Hickman head. After adding another porcelain piece, continue the distillation to collect the remaining liquid into the groove of the Hickman head. Keep these two samples of liquid separately in sample tubes D1 and D2.

b. To 1 mL of the mixture of liquids viz. cyclohexanone and *p*-cresol taken in a test tube, add about 3 mL of diethyl ether. After adding 2 mL of 3N NaOH solution, agitate the mixture thoroughly with the Pasteur pipette. For this, squeeze the rubber bulb of the Pasteur pipette when it is outside the solution, put it into the bottom layer while the bulb is still squeezed and suck the bottom layer in the pipette. From the solution, take the pipette out but it should remain still within the test tube. Squeeze the bulb quickly so that a jet of solution emerges and gushes through the top layer. Repeat this procedure at least 8-10 times. Allow the layers to separate and take out the bottom layer into a different test tube by pushing the tip of the Pasteur pipette to the bottom of the first test tube and sucking out the bottom layer as much as possible with visual observation. Add 1 mL of 2 N NaOH solution and repeat the agitation and separation twice. Collect the alkaline layer and acidify it slowly by adding conc. hydrochloric acid drop by drop till the solution is acidic. Extract the separated phenol with the help of 2 × 2 mL ether. After drying the original and the extracting ether layers with anhydrous sodium sulphate, transfer these to 2 clean test tubes and evaporate the ether to get two liquids stored in sample tubes C1 and C2.

c. Determine the boiling point of each of the 4 samples thus collected, in the capillaries. From literature find out the boiling points of pure cyclohexanone and *p*-cresol. You would know which one could be which by the closeness of boiling points. Take a drop of the liquid, which could be cyclohexanone, in capillary, and add a drop of 2,4 DNP solution to get the yellow derivative. The *p*-cresol could be similarly tested by ferric chloride solution.

d. Attach a 2 cm Vigroux's column between distillation flask and Hickman head and repeat the experiment. Collect the distillates into F1 and F2.

e. Determine the refractive indices (RI) of the liquids in D1, D2, F1, F2, C1 and C2 using Abbe's refractometer. On a graph paper plot the literature values of the RI of mixtures (Y-axis) vs the composition (X-axis). From the measured values of RI of liquids from sample tubes, the percentage composition of each component in the liquid can be determined from the graph.



The students were given three test tubes containing a mixture of 1 mL each of cyclohexanone and *p*-cresol for this experiment. They used the Hickman head and performed the same experiment of fractional distillation in many ways. Initially, they heated the distillation flask containing 2 mL of mixture directly with free flame (CAUTION 1). They were allowed to cut the fractions the way they chose. For the second sample they were asked to use an oil bath for heating and record the temperature of the bath when the fractions were collected. By taking the same amounts from the third sample, they were then asked to do a chemical separation using ether extraction.

We then asked them to introduce a small Vigroux fractionating column between the RB flask along with the Hickman head for the same fractional distillation experiment. The students could do better physical separation with this. It would also demonstrate to them the importance of surface area of condensing surface and its relation to the successful separation of liquids having small difference in their boiling points.

Determination of refractive index (RI) of liquids is part of curricula at many undergraduate courses all over the country. Somehow, the use of RI for testing the purity of organic liquids has been neglected by most chemists. We tell our students to determine the purity of each physically or chemically separated fraction collected during the above distillations and compare their refractive indices (RI) against those of pure chemicals. They would then plot a graph of % composition of liquids vs RI, and determine the purity of collected fractions. They would also conduct chemical tests for each of the fractions by using capillaries [1] – FeCl_3 test for the phenol and the 2, 4 -dinitrophenyl hydrazone (DNP) derivative formation test for the ketone. They would conclude for themselves that fractional distillation is more effective only when the heating is slow or when the condensing surface is larger (the RI values of collected fractions being closer to those of the pure materials). They would confirm that the chemical separation is much more effective (almost a perfect match with the known RI values) than the physical one.



From the RI values observed for each distilled fraction they would know for themselves how successful each one of their experiment has been. They would simultaneously realise that the chemical tests are not as good when performed on impure substances while the physical tests such as RI are better from the quantitative point of view.

We are aware that in more advanced laboratories, particularly in the USA students would have easy access to GC or HPLC. These are still out of reach of even the M.Sc students in our institutions and universities. Obviously we have not considered these methods for checking the purity.

This entire experiment of chemical and physical separation of miscible liquids, involving two or three distillations can be performed in 2 to 3 hours – a typical laboratory period at the undergraduate level. Now, the students will not only do a simple fractional distillation, but also apply the relevant principles they have learnt. They will know how to assess their own results. We wish all the experiments in all the laboratories should be of this type and are done in this fashion.

Another modified experiment, which can demonstrate similar theoretical concepts, is the preparation of 2,4-DNP derivatives of aldehydes and ketones. As per the current practices prevailing in most of the laboratories all over the country the student mixes about 0.5 to 1 mL of unknown aldehyde or ketone with the 2,4-DNP reagent, filters the product, tries to dry it, determines the melting point and reports it to the teacher.

We changed this in the microscale laboratory. The 2,4-DNP reagent is now stored in Beral pipettes [1]. The students were given a free hand to take out substances, which they think would give the positive 2,4-DNP test. Some would even wrongly select esters and anilides along with aldehydes and ketones. They took a few crystals or microlitre quantity of each of these substances into different capillaries and added just a drop of 2,4-DNP reagent to each from Beral pipette [2]. The derivative would obviously be formed instantaneously only for aldehydes and



Suggested Reading

- [1] S L Kelkar, D D Dhavale and B G Mahamulkar, *J. Chem. Ed.*, 387, 2000.
- [2] B Osterby, G Rausch and R Roskos, *Laboratory Handbook for Course CH103*, University of Wisconsin at La Crosse, 1997.

ketones and not for esters and amides. The students could now also see for themselves that the derivatives formed are of different colours ranging from yellow to deep red. They were then asked to write the structures of the starting aldehydes and ketones and the colour of the derivative. They would now immediately comprehend that the 2,4-DNP derivatives of aliphatic substrates such as acetone, methyl ethyl ketone and cyclohexanone are yellow; while those of aromatic ones such as benzaldehyde, acetophenone etc. are orange or red. It is then made clear to them that the colour deepened as the conjugation increased. When experiments are performed on large scales, it is usually not possible for the students to perceive these ideas.

Another similar experiment on a small scale further corroborates the idea of 'structure-property relationship'. The students can be asked to prepare hydrazone, phenylhydrazone and 2,4-DNP derivatives of the same substrate such as acetophenone using just 100 mg each time. They would then compare not only the colours but also the melting points of the derivatives. Once again they can confirm the more conjugated the substance is, the deeper is the colour. So while the oxime is white the 2,4-DNP derivative is orange in color. The relationship between the molecular weights and the melting points can now be verified and they will realise that higher the molecular weight, higher will be the melting point. It is difficult to illustrate this during the laboratory hours if the experiments are done by the conventional methods and on large scales.

Since considerable time is saved in doing the experiments on microscale, several such experiments could be sought from literature and given to the students during the laboratory hours. We are trying quite a few of these. These include preparation and separation of *E* and *Z* oximes of some ketones and subjecting each to rearrangement. When successful, it would demonstrate that the product would be mainly with only the *anti* group migration. This is taught to students but never validated in the laboratory. We are also looking at the possibility of prescribing a microscale photolysis of isoxazole at two different wavelengths



to get two different products, illustrating the basic principles of photochemistry.

Similar experiments can be introduced in the inorganic chemistry laboratory also. An example is an experiment in which metallic copper undergoes various chemical changes and is recovered back again in metallic form [2]. During the experiment, a student is asked to record all the changes that he detects *viz.* change in the colour of the reactants, dissolution, precipitate formation, facile nature of the reactions, evolution of gases etc. He weighs just 0.5 g of copper wire and puts it in 6 N nitric acid. The red copper reacts and forms copper(II) nitrate with the colour of the liquid turning deep green with the evolution of brown fumes of NO_2 gas (TOXIC !). The difference between 'dissolution' and 'reaction' should be clarified at this stage. It should be reiterated that copper has now *reacted* and formed a soluble salt and so 'dissolved' is a wrong word to describe the observation. After the reaction subsides, sodium bicarbonate is added to the same solution. The deep bottle-green colour of copper (II) nitrate changes to light green as less soluble copper carbonate precipitates partially. The evolution of CO_2 gas during the reaction is noted. After the reaction is complete, concentrated sulfuric acid is added to this solution. Now the colour changes from light green to deep blue with the evolution of carbon dioxide gas. Finally zinc powder is added portionwise so that a solution of colourless zinc sulfate is formed and copper is re-precipitated. The student can weigh the regenerated copper and know that there is hardly any material lost. The entire experiment can be performed in just about 90 minutes, but clarifies and verifies many principles learnt in theory.

The experiments described by us are of course well known. We are simply using the same well-established experiments with a different purpose. It should be noted that many experiments of this kind need to be introduced in our curricula. We hope that in the near future an increasing number of teachers will come forward with newer ideas of using microscale experiments for the benefit of students.

Address for Correspondence

Shriniwas L Kelkar
Department of Chemistry
University of Pune
Pune 411 007, India.
Email:
skelkar@chem.unipune.ernet.in
or
skelkar@vsnl.com

