Recrystallisation of benzoic acid and determination of its melting point

(a) Recrystallisation
Theory

An impure solid may be purified by first dissolving it in the minimum quantity of a boiling solvent. Insoluble impurities are then removed by rapid filtration of the hot mixture. The filtrate is next allowed to cool slowly. Since the solubility of the solid decreases as the temperature falls, crystals will form. The soluble impurities mostly remain dissolved in the solvent as the crystal structure "re-grows" in a regular pattern.

Procedure

Boil about 100 cm^3 deionised water in a 250 cm^3 beaker and keep the water just at its boiling point. Weigh out about 1 g of the benzoic acid sample in a 100 cm^3 beaker.

Flute a filter paper – your teacher will show you how to do this. Place the fluted filter paper in the funnel, and secure it by wetting it. Prepare for hot filtration by standing a 250 cm^3 conical flask containing about 20 cm^3 of boiling water on a hotplate or over a low Bunsen flame. Sit the funnel with fluted filter paper in the neck of the flask.
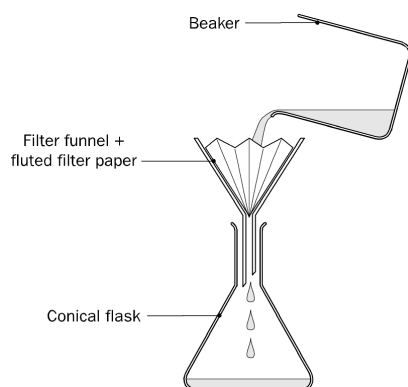
Using a dropping pipette, add 25 cm^3 of boiling water to the beaker containing the sample, with constant stirring. Heat the mixture gently to keep the solution near its boiling point. Any remaining crystals should be dissolved by adding the minimum extra amount necessary of boiling water.

When ready to filter, empty the conical flask, replace the funnel quickly, and stand the flask on a heat resistant mat. Working quickly but carefully, pour the boiling solution through the filter paper (Fig.1) in small portions. (It may be necessary to reheat the beaker periodically.) If any crystals form in the filter paper, add a little boiling water to dissolve them.

Empty the filtrate into a warm 100 cm^3 beaker. Heat the filtrate until traces of crystals begin to appear on the sides of the beaker. You now have the minimum amount of solvent required. Place the beaker on a heat resistant mat and allow the filtrate to cool to room temperature.

To recover the crystals, carefully filter the recrystallised mixture, by vacuum filtration if possible. If some crystals remain in the beaker, transfer the filtered liquid back to the beaker and filter again. Repeat this procedure until all the crystals have been transferred to the funnel.

Wash with 2 cm^3 of ice cold deionised water and dry the crystals using vacuum filtration for ten minutes.

Using the spatula, remove the crystals from the funnel and transfer them to a previously weighed dry clock glass. Dry the crystals by placing the clock glass in an oven set at 80 ^{0}C, or on top of a radiator for 24 hours.

(b) Melting point determination
Theory

One of the physical properties of a pure substance is its melting point, or, more correctly, its melting point range. The melting point range of a substance is the narrow band of temperatures between the temperature at which melting begins and the temperature at which all the solid has liquefied. The solid state and the liquid state of the substance co-exist across this small temperature range.

The melting point range of an impure substance is lower and broader than that recorded for a pure sample of the same substance. Comparing the melting point ranges of the benzoic acid sample before and after recrystallisation with the melting point range of pure (Analar) benzoic acid will therefore indicate the success of the recrystallisation process in improving the sample purity. It will also indicate whether it is as pure as an Analar sample.

Melting point determination using an aluminium block

Sprinkle a thin layer of the substance to be melted on the surface of a clean aluminium block into which a thermometer has been placed.

Heat the block slowly using a Bunsen burner or on a hot plate.

Observe the melting point range i.e. the temperature at which liquid first appears and the temperature at which no solid remains.
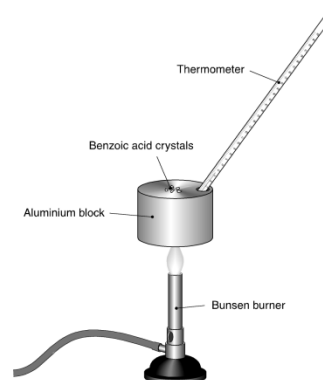
Specimen Results

Melting point of impure benzoic acid = 116 - 118 ^{0}C
Melting point of purified benzoic acid = 118 - 119 ^{0}C
Melting point of pure (ANALAR) benzoic acid = 118 - 119 ^{0}C

Student Questions

Why is it important to use the minimum amount of hot solvent at the crystallisation stage?

It is necessary to use hot solvent in order to produce a solution that will be supersaturated at room temperature. On cooling, the substance recrystallises from solution. The minimum amount of solvent is used because this reduces the quantity of the substance that can remain dissolved when the hot filtered solution is allowed to cool. The yield of recovered crystals would be very low if too much solvent were used.

What action could you take if some of the crystals formed on the filter paper or in the leg of the funnel during the hot filtration?

Boiling water would have to be dropped on to the crystals using a dropping pipette to dissolve them. The filtrate would then contain more than the minimum quantity of boiling solvent to keep the substance dissolved. In order to avoid low yields due to the substance remaining dissolved after cooling, it would be necessary to boil off most of the extra solvent before allowing the filtered solution to cool.

Suggest a way of obtaining a second crop of crystals from the solution obtained after filtering off the crystals. Would these be as pure as the first crop? How would you confirm this?

Heat the filtered solution to boiling. Allow its volume to reduce by half. Do not boil to dryness. Allow the solution to cool slowly to room temperature and place it in an ice- water bath to cool further. A small second crop of crystals is obtained, and may be filtered off with a Hirsch funnel and dried.

This crop of crystals will not be as pure as the first since the soluble impurities are now more concentrated in the partially evaporated mother liquor and will be incorporated into the crystalline structure of the second batch of crystals more than they were in to the first.

What would you expect a forensic scientist to observe about the melting point if two samples of the same substance both equally pure were mixed and the melting point recorded?

Since these samples are chemically identical and of equal purity, there will be no lowering of melting point when they are mixed.

What would you expect the scientist to observe about the melting point if pure samples of two different substances with the same melting point were mixed and the melting point recorded?

The two substances when mixed will act as impurities present in one another and so a lowering and broadening of the original melting point will be observed.

This procedure is used to test whether two substances with the same melting point are in fact the same substance or not.

Two samples have melting points 115 - I18 ^{0}C and 120 – 121 ^{0}C. Could they be the same substance? How would you check your answer?

Yes, they could be the same substance. The first one is lower and broader than the second and this difference could be due to impurities. Purify the first sample by recrystallisation and record its melting point again. If it increases and narrows to the same melting range as the second sample they could be the same substance. Carry out a mixed melting point test as referred to in Question 5 to check.

Industrial, Environmental & Social Links

Recrystallisation is widely used in the bulk chemical and pharmaceutical industries to purify products.

Recrystallisation is used in sugar production to obtain sugar crystals from syrupy sugar solutions. Seeding is carried out to speed up the process. Several crops are obtained from the mother liquor, the white sugar crystals first and darker sugar from later crops. Activated charcoal is also used to remove coloured impurities.

Salt is extracted from sea water by allowing the water to evaporate in large pools. The salt crystallises when this is done.