Chemistry of Colours

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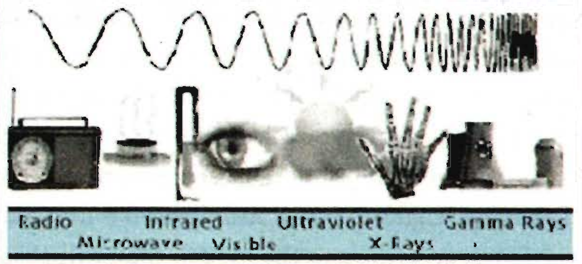
Colour provides a vital enhancement to the world in which we live. Every day materials we use – textiles, paints, plastics, paper, and foodstuffs – are especially appealing if they are colourful. Nature too presents a kaleidoscope of colours around our lives. In India as summer approaches there is a wild burst of colourful flowers and new leaves of various shades of green on trees. Elsewhere in the world in autumn, the shedding of leaves is preceded by a spectacular colour show – green leaves turn to brilliant shades of yellow, orange, and red. In this article we focus on why things have colour and what causes them to change their colour.

Light is a form of electromagnetic radiation (see *Box* 1) and delivers energy in little packets called photons. Different colours of light pack different amounts of energy in their photons. For example, photons of violet light have almost double the energy of those of red light. All materials absorb photons of some energy. But only substances that absorb photons of visible light will have colour.

The colour of a transparent object is due to the colours of light that can pass through the material. The colour of any coloured object comes from the light it doesn't absorb. For example, white light passing through a glass of red wine looks red because the wine has absorbed the other colours, and lets only the red light pass through. To see this, try looking through a piece of red cellophane at objects of different colours. All colours but red vanish. This is because the cellophane absorbs light with all other colours except red. The colour most strongly absorbed is the complement of the colour that passes through the material. A solution that appears blue green absorbs red light; a purple solution absorbs green light (see *Box* 2).

Box 1.



The electromagnetic spectrum stretches from radio waves to gamma rays

Light is a form of electromagnetic radiation. Other forms of electromagnetic radiation include radio waves, microwaves, infrared radiation, ultraviolet rays, X-rays, and gamma rays. All of these, known collectively as the electromagnetic spectrum, are fundamentally similar in that they move at 186,000 miles per second, the speed of light. The only difference between them is their wavelength, which is directly related to the amount of energy the waves carry. The shorter the wavelength of the radiation, the higher the energy.

The Molecular Basis of Colour Changes

Molecules are very selective about what photon energies they will and will not absorb. In fact, the photon energies a molecule will absorb are so characteristic that they can be used as a 'fingerprint' to identify that molecule in a mixture. This preferential absorption can be explained by assuming that molecules have quantized energies; that is, they exist only in certain allowed energy states. Quantum theory shows how quantized energies arise naturally from the wavelike behavior of confined electrons. The photon will be absorbed only if its energy is exactly what is needed to take the molecule from one allowed state to another.

Since different molecules have different colours, it follows that molecular structure has something to do with the size of the energy transitions associated with absorption of visible light. The relationship is complex, but a simple model can be used to show many essential features. An electron bound in a molecule (or part of a

Box 2. Colour Absorbed Determines the Colour Observed

A material that selectively absorbs blue light won't look blue. The colours that are not absorbed are what we see. The observed colour is said to be the complement of the absorbed colour. For example, dichromate ions absorb blue light, so their solutions appear orange. Permanganate ions absorb green light, so permanganate solutions are purple.

Colour absorbed	Colour observed
Violet	Yellow green
Blue Violet	Yellow
Blue	Orange
Blue green	Red
Green	Purple
Yellow green	Violet
Yellow	Blue violet
Orange	Blue
Red	Blue green

molecule) is treated as though it is trapped in a uniform box with walls it cannot penetrate. This 'particle in a box' model shows that confining electrons in a smaller space tends to make energy level spacings larger. The model shows that electrons restricted to a box the size of a covalent bond absorb in the ultraviolet. Therefore they appear colourless. Electrons that can spread over many atoms within a molecule absorb photons of lower energy, and if the box length is just a little over 0.6 nm, and a little less than 0.8 nm, according to the model, they will absorb visible light. This explains why many organic materials that have colour have structures with electrons that are not pinned down in single covalent bonds. A simple guideline is – colour changes can be caused by changes in electron confinement. Confining electrons to a smaller space makes the light absorbed bluer and if they move around in larger space the light absorbed is redder.

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Let us take a look at origin of colours in leaves and flowers of trees, and how nature can throw a spectacular colour show during autumn.

What Makes a Leaf Green and What Happens When it is Withered?

The green pigment in leaves is chlorophyll. Chlorophyll absorbs red and blue light from the sunlight that falls on leaves. Therefore, the light reflected by the leaves is diminished in red and blue and appears green. The molecules of chlorophyll are large (Molecular formula: $C_{55}H_{70}MgN_4O_6$). They are not soluble in the aqueous solution that fills plant cells. Instead, they are attached to the membranes of disc-like structures, called chloroplasts, inside the cells. Chloroplasts are the site of photosynthesis, the process in which light energy is converted to chemical energy. In chloroplasts, the light absorbed by chlorophyll supplies the energy used by plants to transform carbon dioxide and water into oxygen and carbohydrates, which have a general formula of $C_x(H_2O)_y$.

$$x\,CO_2 + y\,H_2O \xrightarrow[\text{chlorophyll}]{\text{light}} x\,O_2 + C_x(H_2O)_y$$

In this endothermic transformation, the energy of the light absorbed by chlorophyll is converted into chemical energy stored in carbohydrates (sugars and starches). This chemical energy drives the biochemical reactions that cause plants to grow, flower, and produce seed.

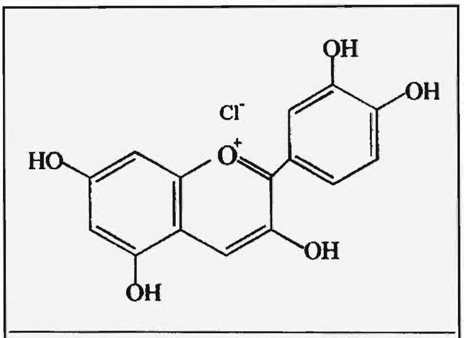
Chlorophyll is not a very stable compound; bright sunlight causes it to decompose. To maintain the amount of chlorophyll in their leaves, plants continuously synthesize it. The synthesis of chlorophyll in plants requires sunlight and warm temperatures. Therefore, during summer, chlorophyll is continuously broken down and regenerated in the leaves of trees.

Another pigment found in the leaves of many plants is carotene. Carotene absorbs blue-green and blue light. The light reflected from carotene appears yellow. Carotene is also a large molecule ($C_{40}H_{36}$) contained in the chloroplasts of many plants. When carotene and chlorophyll occur in the same leaf, together they remove red, blue-green, and blue light from sunlight that falls on the leaf. The light reflected by the leaf appears green. Carotene functions as an accessory absorber. The energy of the light absorbed by carotene is transferred to chlorophyll, which uses the energy in photosynthesis. Carotene is a much more stable compound than chlorophyll. Carotene persists in leaves even when chlorophyll has disappeared. When chlorophyll disappears from a leaf, the remaining carotene causes the leaf to appear yellow.

When carotene and chlorophyll occur in the same leaf, together they remove red, blue-green, and blue light from sunlight that falls on the leaf.

What makes Flowers so Colourful?

The blue and red pigments of flowers were isolated and extensively studied by R M Willstätter, in the early twentieth century. Willstätter later received the Nobel Prize in Chemistry in 1915 for his work on plant pigments. He found that nearly any fruit or flower that is bright red, blue, or purple contains pigment molecules that are based on cyanidin: Cyanidin-based compounds make apples, autumn leaves, roses, strawberries, and cranberry juice red. They make blueberries, cornflowers and violets, blue. They also make some grapes, blackberries, and red cabbage purple. In other words differences in flower colour are not necessarily due to differences in pigment molecules. Red roses and blue poppies both contain the same pigment (i.e. cyanidin) but have different coloured flowers. How can one molecular structure be responsible for all of these colours? It has been shown that the colour of a solution of flower pigments in a test tube depends upon the pH of the solution. As the pH is made more acidic, the colour becomes redder. Thus structure of cyanidin changes with pH.



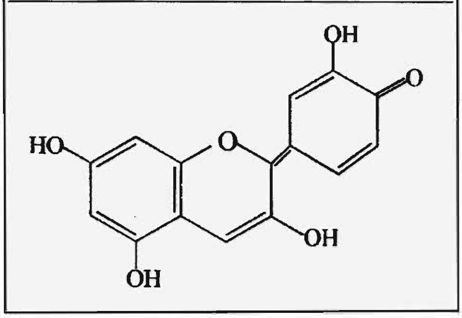


Figure 1(top). Structure of cyanidin in acidic solution (bright red).

Figure 2(bottom). Structure of cyanidin in basic solution (blue/violet).

The form shown in *Figure* 1 is found in acidic solution, and is a bright red. Notice the high formal charge on the oxygen in the structure. (It might appear that a molecule with a positive formal charge on oxygen would be rather unstable, but if the electrons are pushed around for a while, it is seen that many resonance structures can be drawn. The pi electrons are highly delocalized.)

In basic solution, removal of a hydrogen from the OH group on the rightmost ring results in the structure as shown in *Figure* 2. This form of cyanidin is blue or violet. So the complementary colour (red) is being absorbed. Red light carries less energy than blue, so the electrons are less confined in the base than in the acid form. In very strongly basic solutions, the hydrogens on the remaining -OH groups are also abstracted and as the electrons become even less confined, the blue colour becomes bluer because the light absorbed becomes redder.

Some flowers and berries have cyanidins with varying numbers of -OH groups on the rightmost ring, but the molecular blueprint is the same. In natural forms of the molecule, the hydro-

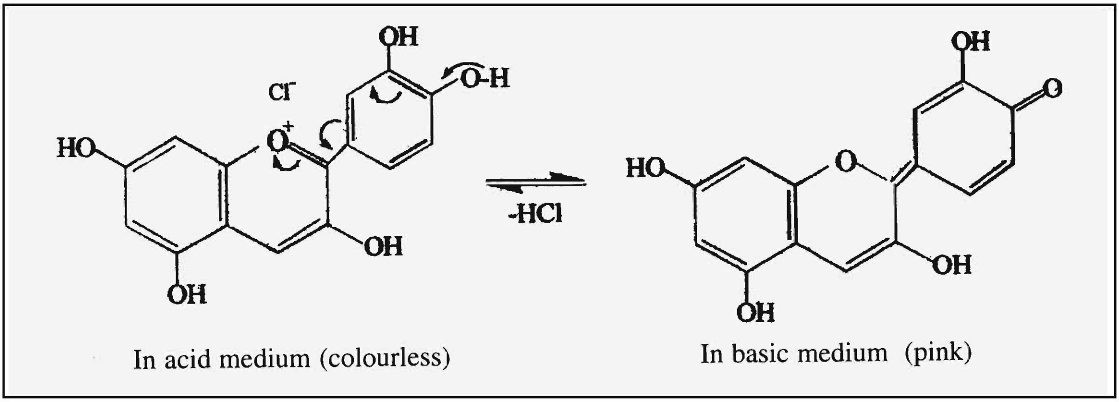
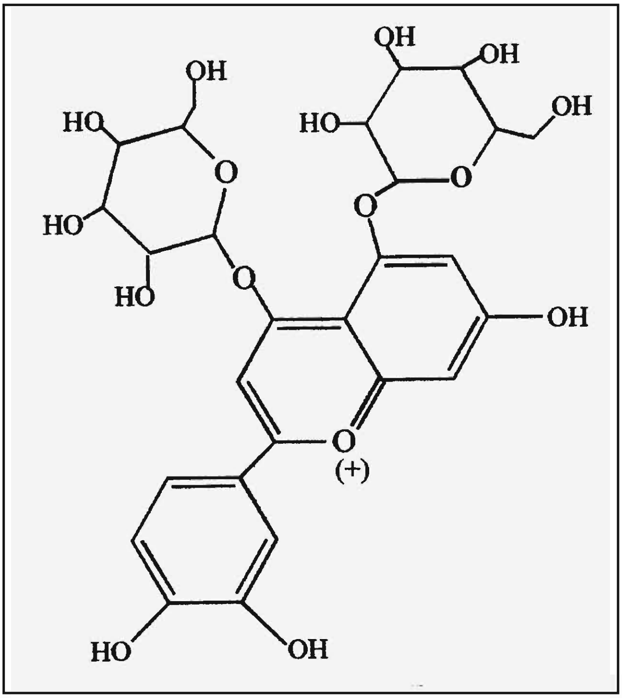


Figure 3. The rearrangement of pi electrons in basic medium.

gens on at least one of the -OH groups are replaced by a sugar molecule. A cyanidin with attached sugars is called an anthocyan or anthocyanin. For example, the anthocyan that makes roses red and cornflowers blue has the structure as shown in *Figure* 4.

Anthocyanins are not attached to cell membranes, but are dissolved in the cell sap. The colour produced by these pigments is sensitive to the pH of the cell sap. (The sugar rings bristle with -OH groups, which can hydrogen-bond to water. Their chief effect is to increase the pigment's solubility in water). If the sap is quite acidic, the pigments impart a bright red colour; if the sap is less acidic, its colour is more purple. Anthocyanin pigments are responsible for the red skin of ripe apples and the purple of ripe grapes. Anthocyanins are formed by a reaction between sugars and certain proteins in cell sap. This reaction does not occur until the concentration of sugar in the sap is quite high. The reaction also requires light. This is why apples often appear red on one side and green on the other; the red side was in the sun and the green side was in shade.

Figure 4. Cyanidin diglucoside, the colour in roses and cornflowers. (The sugar groups vary in structure and point of attachment for different species of plants).



The Colour Show in Autumn

If the leaf contains carotene, as do the leaves of birch and hickory, it will change from green to bright yellow as the chlorophyll disappears.

During summer, the leaves of trees are factories producing sugar from carbon dioxide and water by the action of light on chlorophyll. Chlorophyll causes the leaves to appear green. (The leaves of some trees, such as birches and cottonwoods, also contain carotene; these leaves appear brighter green, because carotene absorbs blue-green light.) Water and nutrients flow from the roots, through the branches, and into the leaves. The sugars produced by photosynthesis flow from the leaves to other parts of the tree, where some of the chemical energy is used for growth and the rest is stored. The short days and cool nights of autumn trigger changes in the tree. One of these changes is the growth of a corky membrane between the branch and the leaf stem. This membrane interferes with the flow of nutrients into the leaf. Because the nutrient flow is interrupted, the production of chlorophyll in the leaf declines, and the green colour of the leaf fades. If the leaf contains carotene, as do the leaves of birch and hickory, it will change from green to bright yellow as the chlorophyll disappears. The membrane between branch and leaf stem also inhibits the flow of sugar from the leaf. In some trees, as the concentration of sugar in the leaf increases, the sugar reacts to form anthocyanins. These pigments cause the yellowing leaves to turn red. Red maples, red oaks, and sumac produce anthocyanins in abundance and display the brightest reds and purples in the autumn landscape. The range and intensity of autumn colours is greatly influenced by the weather. Low temperatures destroy chlorophyll, and if they stay above freezing, promote the formation of anthocyanins. Bright sunshine also destroys chlorophyll and enhances anthocyanin production. Dry weather, by increasing sugar concentration in sap, also increases the amount of anthocyanin. So the brightest autumn colours are produced when dry, sunny days are followed by cool, dry nights.

Colour Change due to Acid-base Indicators

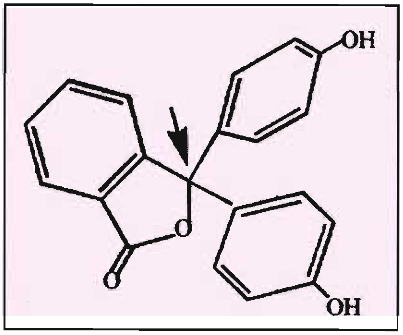
Indicators are weak acids or bases exhibiting different colours in acids and bases. Thus, as we have seen in the case of anthocyanin, the indicator reaction is also pH dependent because it involves either the release or capture of hydrogen ions:

$$\underset{\substack{\text{acid}\\ \text{(colour A)}}}{\mathrm{HIn\,(aq)}} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \underset{\substack{\text{conjugate base}\\ \text{(colour B)}}}{\mathrm{In^-\,(aq)}}$$

In the above, 'HIn' and 'In$^-$' stand for the indicator molecule with and without an attached hydrogen ion. The two forms of the indicator molecule have noticeably different colours. For example, bromocresol green has a yellow HIn form and a blue In$^-$ form. When there are equal amounts of HIn and In$^-$, the solution looks bright green. Adding a drop of acid adds H$^+$ ions, which react with the In$^-$ ions to form HIn, and the solution becomes more yellow. Adding a drop of base converts HIn to In$^-$, and the solution becomes more blue.

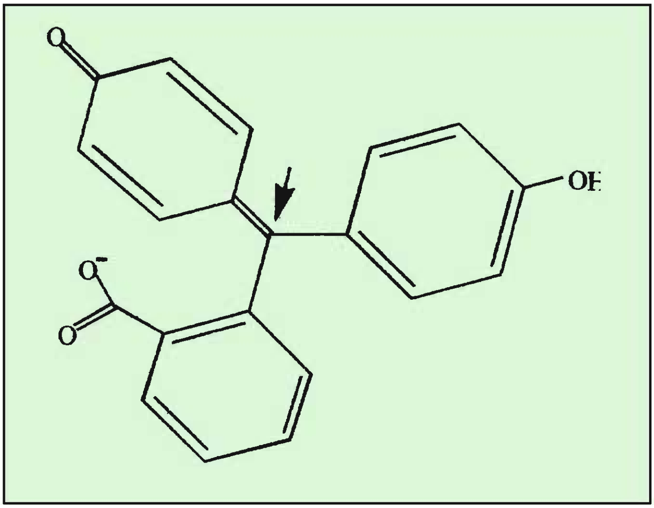
When a hydrogen ion combines with the base form of an indicator molecule, it will confine two formerly mobile electrons to a single covalent bond with the hydrogen, shifting the light that is absorbed towards the blue end of the spectrum. Indicator structures often undergo additional changes that amplify the change in electron confinement. Let us take phenolphthalein as an example to understand the changes. Phenolphthalein is colourless in acid medium and pink/red in basic medium. *Figure* 5 illustrates the colourless form of phenolphthalein.

Figure 5. Phenolphthalein in acidic solution.



How are electrons confined in this molecule? Every atom involved in a double bond has a p-orbital, which can overlap side-to-side with similar atoms next to it. The overlap creates a 'pi bond' which allows the electrons in the p-orbital to be found on either bonded atom. These electrons can spread like a cloud over any region of the molecule that is flat and has alternating double and single bonds. The atom marked by the arrow does not have a p-orbital available for pi-bonding, and it confines the pi electrons to the rings. The molecule

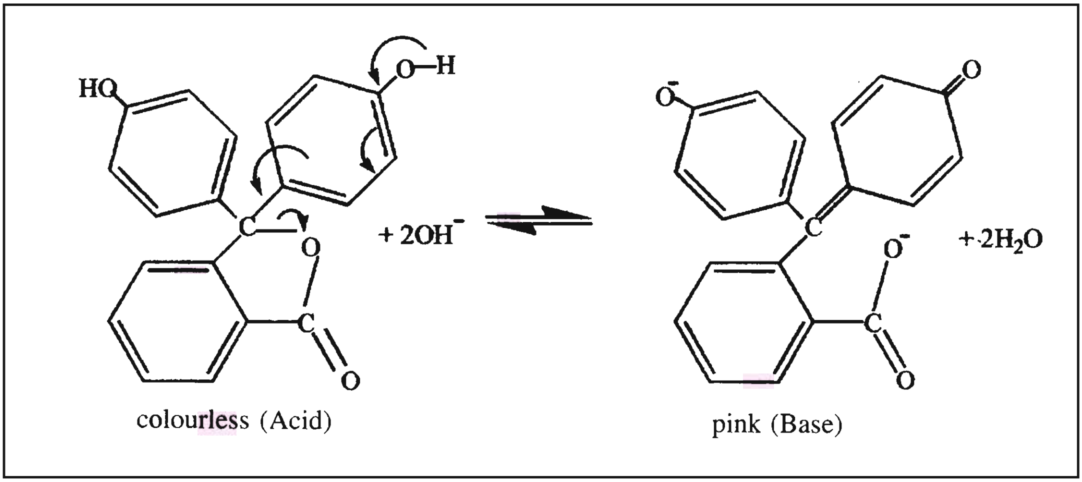
Figure 6. Phenolphthalein in basic solution.



absorbs the ultraviolet, and this form of phenolphthalein is colourless.

In basic solution, the molecule loses two hydrogen ions (*Figure* 6). Almost instantly, the five-sided ring in the center opens and the electronic structure around the carbon atom (marked by arrow) changes. The pi electrons are no longer confined to one ring alone. Notice that it is almost flat compared to the acidic form, which allows the pi cloud to extend over most of the molecule. The absorption shifts from the ultraviolet to the blue-green region of the spectrum, which makes this form of the molecule red (see *Box* 2).

Figure 7. The rearrangement of pi electrons in basic medium.



Many other indicators function in essentially the same way. For example, azo indicators (like methyl orange) are structurally quite different from the phthaleins, but again, a shift in electron structure around a key atom results in a change in electron confinement.

Universal indicator is a mixture of indicators which gives a gradual change in colour over a wide pH range – the pH of a solution can be approximately identified when a few drops of universal indicator are mixed with the solution. Indicators are used in titration solutions to signal the completion (end point) of the acid-base reaction.

To summarise, it is indeed remarkable that a lone hydrogen ion plays such a significant role resulting in different pH and hence different colours. In Nature, many plant pigments act as acid-base indicators. Two different species with different flower colours have exactly the same molecules for pigmentation. The difference between the flowers is the pH of the fluid in pigment-bearing tissues; alkaline for cornflowers, and acidic for roses. Studies have revealed that tampering with genes that regulate the pH in flowers has shifted petunia colours from red to blue. So it need not be always that roses are red and violets are blue, in future, roses can be blue and violets can be red.

Suggested Reading

[1] *Indicators*, Ed. Edmund Bishop, Pergamon Press, 1972, Chapter 2. Theory and principles of visual indicators by E Bishop, Chapter 3. Acid-base indicators by Éva Bányai.

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