Example 3

Explain the following phenomenon.

(a) The density of ice is smaller than water.

(b) Boiling points of hydrides tend to increase down a group due to an increase in relative molecular masses. However, the hydrides of the first member of Group V, VI and VII are higher than expected.

(c) The viscosity of a diol (alcohol with two OH groups) is greater than that with a single OH group.

(d) 4-nitrophenol has a higher boiling point that 2-nitrophenol.

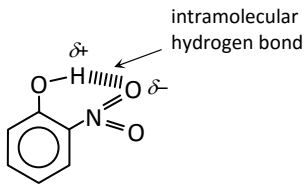
Solution:

(a) In ice the hydrogen bonds hold the molecules together in a rigid but open structure. As ice melts, only a small number of hydrogen bonds are broken. This allows the water molecules to be more compactly arranged, accounting for the decrease in density when ice melts. The property is what allows a layer of ice to form on top of water surfaces in winter, while the water below remains unfrozen so that aquatic animals can survive. (ans)

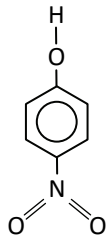
(b) The hydrides of groups V, VI and VII, ammonia, water and hydrogen fluoride respectively, have higher than expected boiling points due to the ability of these molecules to form hydrogen bonds. Hydrogen bonding occurs when a small, highly electronegative atom is attached to a hydrogen atom. More energy is required to overcome the hydrogen bonds as compared to molecules with only Van der Waals' forces. (ans)

(c) A diol with two OH groups can form more hydrogen bonds and thus have stronger intermolecular forces. As such, the diol is expected to flow slower than an alcohol with a single OH group. (ans)

(d) Hydrogen bonding accounts for the difference in boiling points of the two isomers, 4-nitrophenol and 2-nitrophenol. Strong intramolecular hydrogen bonds are formed between the atoms in 2-nitrophenol, while interactions between the molecules are weak. This leads to 2-nitrophenol having a lower boiling point.



2-nitrophenol



4-nitrophenol

4-nitrophenol cannot form intramolecular hydrogen bonds as the hydrogen atom is too far from the oxygen atom. It can only form intermolecular hydrogen bonds with another molecule. This results in greater stability and thus higher boiling point. This causes the boiling point of 4-nitrophenol to be higher than that of 2-nitrophenol. (ans)