Boiling point and melting point of alcohol

As a result of the EU General Data Protection Regulation (GDPR). We do not currently allow internet traffic to byju's website from countries within the European Union. This page did not display any tracking or performance measurement cookies. Learning goals Explain why the boiling points of alcohols are higher than those of ethers and alkans of similar molar masses. Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water, while similar alcans are not soluble. Alcohols can be considered derivatives of water (H2O; also written as HOH). Like the H-O-H binding in water, the R-O-H band is curved, and alcohol molecules are polar. This relationship is especially visible in small molecules and reflected in the physical and chemical properties of alcohols with a low molar mass. By replacing a hydrogen atom with an alkane with an OH group, the molecules can be linked by means of hydrogen bonding (Figure \(\PageIndex{1}\)). Figure \(\PageIndex{1}\): Intermolecular hydrogen bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible. Remember that physical properties are largely determined by the type of intermolecular forces. Table \(\PageIndex{1}\) contains the molar masses and boiling points of some common compounds. The table shows that substances with similar molar masses can have very different boiling points. Table \(\PageIndex{1}\: Comparison of boiling points and molar masses Formula name Molar Mass Boiling Point (°C) CH4 methane 16 –164 HOH water 18 100 C2H6 ethane 30 –89 CH3OH methanol 32 6 5 C3H8 propane 44 –42 CH3CH2OH ethanol 46 78 C4H10 butane 58 –1 CH3CH2CH2OH 1-propanol 60 97 Alkanes are non-polar and are therefore only associated by relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with a carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of similar molar mass. The boiling point is a rough measure of the amount of energy needed to separate a liquid molecule from its closest neighbors. If the molecules interact through hydrogen bonding, a relatively large amount of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid in the gaseous state. Alcohols can also engage in hydrogen bonding with water molecules (Figure \(\PageIndex{2}\)). So, while the hydrocarbons are insoluble in water, alcohols containing one to three carbon atoms are completely soluble. However, as the length of the chain increases, the solubility of alcohols in water the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol (CH3CH2CH2CH2CH2CH2CH2CH2CH2CH2OH) is essentially insoluble in water. We often find that this borderline of solubility in a family of organic compounds occurs on four or five carbon atoms. Figure \(\PageIndex{2}\): hydrogen bonding between methanol molecules and water molecules. Hydrogen bonding between the OH of methanol and water molecules is good for the solubility of methanol in water. Alcohols have higher boiling points than ethers and alkans of similar molar masses, because the OH group allows alcohol molecules to participate in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen binding with water molecules; similar alkane molecules cannot engage in hydrogen bonding. Concept Review Exercises Why is ethanol more soluble in water than 1-hexanol? Why does 1-butanol have a lower boiling point than 1-hexanol? Answers Ethanol has an OH group and only 2 carbon atoms; 1-hexanol has one OH group for 6 carbon atoms and is therefore more like a (non-polar) hydrocarbon than ethanol is. The molar mass of 1-hexanol is larger than that of 1-butanol. Answer the following exercises without consulting tables in the text. Arrange these alcohols in order of increasing boiling point: ethanol, methanol, and 1-propanol. Which one has the higher boiling point -butane or 1-propanol? Arrange these alcohols in order of increasing solubility in water: 1-butanol, methanol and 1-octanol. Arrange these compounds in order of increasing solubility in water: 1-butanol, ethanol and pentane. methanol < ethanol < 1-propanol 1-octanol < 1-butanol < methanol Melting points are a little trickier to compare than boiling points, especially if you look at the lightest examples of a group of molecules. This graph for the undigested alkanes illustrates how the trends differ in smoothness. As you increase the weight of molecules, the observed trend depends on how you increase weight. For example, if you start with methanol and increase weight by adding more $\ce{-HCOH -}$ units (methanol, ethylene glycol, glycerol, and so on) you will find a very marked increase in both melting and cooking points. In a sense, this is a more legitimate trend to analyze, because the relative amounts of different types of intermolecular interactions remains about constant (in particular, all molecules have a hydroxyl per carbon atom, and so they all have about the same amount of hydrogen binding per atom in the molecule). In your sequence of alcohols, the strong hydrogen bond permitted by the hydroxyl group is diluted when the molecule acquires an ever-larger alkyl chain, which can only support much weaker interactions of Van der Waals. In the limit of alcohols with very large alkyl chains, the melting and cooking points of the not huge of their parent-saturated hydrocarbons. Compare the melting and boiling points of 1-hexadecanol (49°C and 344°C) and hexadecane (18°C (18°C) 287°C). Also, the temperature at which a substance freezes depends not only on the strength of intermolecular interactions, but how the solid packaging. Even substances with strong interactions can only freeze at very low temperatures if they pack very poorly when solidified. Extreme examples to which this effect contributes are ionic liquids. They tend to have very low vapour pressure at reasonable temperatures (as you would expect from many salts), but some melt even below 0°C. Freezing such large entities would entail a great deal of ordering and thus a very large decrease in entropy, so it is unfavorable (or equivalent, its melting is very entropically favored, so that the free energy of the liquid phase becomes lower than the free energy of the fixed phase, even at relatively low temperatures). The exact geometry of the molecules in the solid is also important, as some beneficial interactions in the solid state can be suppressed due to steric barriers that may be less present in the freer moving molecules of a liquid. In addition, molecules with a high degree of symmetry tend to have high melting points, because freezing is favored entropically because of molecules that fit more easily into the solid lattice. Yet another effect to consider is how large a surface each molecule is available for intermolecular interactions. This is often brought up to explain differences between melting and cooking points of branched and undetected organic compounds; when comparing structural isomers, branched compounds have a lower available space for interaction than undigested compounds, so the latter tend to have higher melting and boiling points (branching can sometimes create a combination of opposing packaging and surface effects, though). So why is your sequence of alcohols behaving the way it does? The fact that the trend is monotonous at boiling point, while the melting point does not suggest that although there is a relative shift in the importance of types of intermolecular interaction as the alkyl chain increases (from hydrogen bonding to Van der Waals interactions), it is unlikely to be the source of the melting point decline. Hence, it probably has to do with geometric factors in the solid. The alcohol alkyl chain is likely to disrupt the hydrogen bonding network from the solid to the solid as it grows from methyl to propyl in a very serious way, by making the solid packaging less good or by partially impeding the number or strength of hydrogen bindings in the geometry of the solid. Perhaps viewing the crystalline structures of the fixed provide further insight. Edit: I wrote the wrong answer at first. I've updated it, but now I realize that I'm still not quite sure it's right. I originally intended to write just one comment, and as I kept writing more I forgot that my first thought was actually incorrect, so the whole text wasn't as well built as if should be. Everyone is free to take apart or reuse what I wrote! Edit 2: User Uncle Al posted an interesting list of compounds and their melt/boiling points, showing the importance of molecular symmetry and solid packaging. Physical properties: Water Alcohol solubility is water-soluble. This is due to the hydroxyl group in the alcohol that is able to form hydrogen coupons with water molecules. Alcohols with a smaller hydrocarbon chain are highly soluble. As the length of the hydrocarbon chain increases, solubility in water decreases. With four carbon in the hydrocarbon chain and higher, the decrease in solubility becomes apparent as the mixture forms two indispensable layers of liquid. The reason why solubility decreases as the length of the hydrocarbon chain increases is because more energy is needed to overcome the hydrogen fissions between the alcohol molecules because the molecules are more firmly packed together as the size and mass increase. In the image above, the partially negative oxygen atom in the ethanol molecule forms a hydrogen bond with the partially positive hydrogen atom in the water molecule. Boiling pointThis graph shows the comparison of boiling points of methane with methanol, ethane with ethanol, propane with propanol and butane with butanol. From the graph we can see that the boiling point of an alcohol is always much higher than the boiling point of the corresponding alkane with the same hydrocarbon chain. The boiling point of alcohols also increases as the length of the hydrocarbon chain increases. The reason why alcohols have a higher boiling point than alkanen is because the intermolecular forces of alcohols are hydrogen bindings, as opposed to alkanen with van der Waals forces as their intermolecular forces. The image below shows ethanol molecules with a hydrogen bond. Alcohol changes from liquid to solid at room temperature and pressure (rtp) as the length of the hydrocarbon chain in the alcohol increases. The boiling points of the first 11 alcohols are as follows:The factors that influence the cooking/melting points of alcohols are not only hydrogen bindings, but also van der Waals dispersion forces and dipole dipole interactions. The hydrogen bindings and dipole dipole interactions will remain relatively the same throughout the range of alcohols. Van der Waals' dispersal forces increase as the length of the hydrocarbon chain increases. This is due to the increase in the number of electrons in the molecules, which in turn increases the strength and size of the temporarily induced dipole-dipole attraction. Therefore, more energy is needed to overcome the intermolecular forces, resulting in the increase in cooking/melting points. ViscosityViscosity is the property a liquid that is resistant to the force that makes the liquid flow. The viscosity of alcohols increases as the size of the molecules increases. This is because the power of the forces, which makes the molecules more firm. PolarityAmide > Acid > Alcohol > Ketone ~ Aldehyde > Amine > Ester > Ether > AlkaneAmide is the most polar, while alkane is the least. Alcohol ranks third in terms of polarity due to its hydrogen bonding potential and the presence of a single oxygen atom in an alcohol molecule. Carboxyacids are more polar than alcohols because there are two oxygen atoms present in a carboxy acid molecule. FlammabilityThe flammability of alcohols decreases as the size and mass of the molecules increases. Combustion breaks down the covalent bonds of the molecules, so as the size and mass of the molecules increases, there are more covalent bonds to break to burn that alcohol. Therefore, more energy is needed to break the bonds, therefore the flammability of alcohols decreases as the size and mass of molecules increase. Chemical properties: CombustionAlcohols burns in oxygen to produce carbon dioxide and water. Alcohols burn clean and easy, and do not produce soot. It becomes increasingly difficult to burn alcohol as the molecules get bigger. The general molecular equation for the reaction is:CnH2n+1OH + (1.5n)O2 → (n+1)H2O + nCO2e.g. combustion of ethanol: C2H5OH (l) + 3 O2 (g) → 2 CO2 (g) + 3 H2O (g); (ΔHc = −1371 kJ/mol) Dehydration - alcohol to alkeneDehydration of alcohols is done by heating with concentrated sulphuric acid, which acts as the dehydrating agent, at 180°C. This reaction uses alcohols to produce corresponding alkenes and water as a by-product.b.v. dehydration of ethanol: Oxidation - alcohol to carboxy acid Alcohols can be oxidized into carboxyacids. e.g. oxidation of ethanol:C2H5OH + [O] → CH3COOH + H2O Oxidation can be done using oxidising agents such as acidified potassium didichromate (VI), acidified potassium permanate (VII)...... or atmospheric oxygen. Ethanol, if exposed to air, can oxidize and become ethanic acid. An example is wine that turns acidic because the alcohol content, which is ethanol, is oxidized by atmospheric oxygen. EsterificationAlcohols can be reacted with carboxylic acid to form esters. More of this will be explained under Formation of esters esters