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CHEMISTRY INVESTIGATION

FACTORS EFFECTING THE BOILING AND MELTING POINTS IN ORGANIC HOMOLOGOUS SERIES.

Introduction

The idea for this investigation came about when we were learning about trends in physical properties in homologous series. With regards to alkanes we saw that the boiling point increases with increasing carbon number due to stronger van der Waal's forces as the temporary dipoles increase. However according to Brown and Ford[i] "the increase is not linear, but steeper near the beginning as the influence of increased chain length is proportionally greater for the small molecules".

EX: Going towards fulfilling "The background information provided for the investigation is entirely appropriate and relevant and enhances the understanding of the context of the investigation. "

Also I have seen that for compounds of similar molar masses (so that the strength of van der Waal's forces are similar) that the addition of functional groups into the hydrocarbon chain make a very great difference to the melting and boiling temperatures. For example the permanent dipole due to the carbonyl group in aldehydes and ketones results in a stronger dipole-dipole forces and so a higher boiling or melting point. The OH group in alcohols will cause an even higher boiling and melting temperature because it causes the strongest intermolecular force, hydrogen bonding to occur. This is supported if we take three compounds of similar molar mass, propane, ethanol and ethanol and compare their boiling temperature.

EX: More relevant background information.

	Mr (g mol^{-1})	Strongest intermolecular force	Boiling Temperature [ii] (°C)
Propane	44	Van der Waal's	-42
Ethanal	44	Dipole-Dipole	20
Ethanol	46	Hydrogen Bonding	78

From these values we see that the effect on the boiling temperature of adding a carbonyl or hydroxyl group is very large. But these are small molecules and I wondered if again the effect will be reduced with increasing hydrocarbon chain length because the proportionate effect of the functional group will get less and the aldehyde, ketone or alcohol will become more "alkane" in nature as the chain length increases. Will we see the melting and boiling points of the aldehydes, ketones and alcohols converge on those of the alkanes and if so at what chain length does the effect of a carbonyl or hydroxyl group become insignificant?

PE: Evidence of curiosity arising out of their classroom learning.

When looking at the effects of carbonyl or hydroxyl group one other possible influencing factor is the position on the chain of the carbonyl or hydroxyl group. I can imagine that a functional group hidden in the middle of a long hydrocarbon chain may not be able to approach and attract a close by molecule as easily as a functional group at the end of a chain. So my second aim is to see if a

PE: Independent thinking about the research question.

functional group at the end of a chain will have a greater, lesser or the same effect on the intermolecular forces as one in the middle of a chain?

Research Questions

C: Very clearly presented and clarified research questions. Good.

(i) Will the melting and boiling points of the aldehydes, ketones and alcohols converge on those of the alkanes as we increase the carbon number and if so at what chain length does the effect of a carbonyl or hydroxyl group become insignificant?

(ii) What will be the effect on the melting and boiling points of changing the position of the functional group in the ketone of alcohol.

EX: The topic of the investigation is identified and a relevant and fully focused research question is clearly described.

Methodology

The dependent variables in this investigation are the melting and boiling points of the compounds in the homologous series: alkanes, aldehydes, 2-ketones, 3-ketones, 1-alcohols, 2-alcohols and 3-alcohols. The independent variables are the molar mass of the compound and the identity and position of the functional group

A control variable is that I will only look at compounds with linear hydrocarbon chains so there will be no added effect from branching.

When assessing the effect of the identity and position of the functional group I will be graphing the melting and boiling temperatures against the Molar Mass of the compound.

This investigation will use data available from two databases

1. CRC Handbook of Chemistry and Physics, 85^{th} Edition, CRC Press, 2004
2. The RSC Chemspider online chemical database[iii]

EX: There are other databases available through the web but this was sufficient to address research question.

The Chemspider database contains experimental data and predicted data from ACD/LABS (boiling point only) and EPISuite. The predicted data was only to be used where an experimentally determined value was not available in the CRC Handbook or the Chemspider website.

The CRC Handbook was the first choice source of data since it is a resource that has been available for many years and I would assume many people have cross checked the data. Also once I was able to find a compound e.g. hexane, it was very quick and easy to read off values for hexanal, 1-hexanol, etc, since they were adjacent in the table of physical properties. In Chemspider I had to make a separate formula search for each one which was much slower.

EX: Good consideration regarding reliability of data.

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Raw Data

C: No use of compound names and a lot of empty cells do make the data tables a little hard to follow. However they bring together a large amount of data quite concisely (better than multiple tables for each homologous series) and there is a logic to their construction with the data organised according to ascending Mr.

DATA TABLE 1 Melting Pts		Melting Point (± 1 ºC)						
Number Carbons + Oxygens	Mr (±0.5 g/mol)	Linear Alkanes	Linear Aldehydes	Linear 2-ketones	Linear 3-ketones	Linear 1-alcohols	Linear 2-alcohols	Linear 3-alcohols
1	16	-182						
2	30	-183	-92					
2	32					-98		
3	44	-188	-123					
3	46					-114		
4	58	-138	-80	-95				
4	60					-124	-88	
5	72	-130	-97	-87				
5	74					-89	-89	
6	86	-95	-92	-77	-39			
6	88					-78	-73	-69
7	100	-91	-56	-56	-55			
7	102					-47	-51	-51
8	114	-57	-43	-35	-39			
8	116					-33	-39	-70
9	128	-53		-16				
9	130					-15	-32	-45
10	142	-30	-19	-8	-8			
10	144					-5	-35	22
11	156	-26	-4	14	1			
11	158					7	-1	-8
12	170	-10	-2	15	9			
12	172					16	0	
13	184	-5	12	21				
13	186					24	19	
14	198	6	14	31	31			
14	200					32	23	32
15	212	10	30	35	34			
15	214					38	34	32
16	226	18	25	20				
16	228					44	35	39
17	240	22	35		43			
17	242					49	44	50
18	254	28	36	48				
18	256					61	54	
19	268	32	46		51			
19	270					58		
20	282	36		57				
20	284					62		

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DATA TABLE 2 BOILING PTS		Boiling Point (± 1 ºC)						
Number Carbons + Oxygen	**Mr** (±0.5 g/mol)	Linear Alkanes	Linear Aldehydes	Linear 2-ketones	Linear 3-ketones	Linear 1-alcohols	Linear 2-alcohols	Linear 3-alcohols
1	16	-161						
2	30	-89	-19			65		
2	32					65		
3	44	-42	20					
3	46					78		
4	58	-1	48	56				
4	60					97	82	
5	72	36	75	80				
5	74					118	100	
6	86	69	103	102	102			
6	88					138	119	116
7	100	98	131	128	124			
7	102					158	140	135
8	114	126	153	151	147			
8	116					176	159	157
9	128	151	171	173	168			
9	130					195	179	171
10	142	174	191	195	190			
10	144					213	194	195
11	156	196	209	210	203			
11	158					231	211	213
12	170	216	**223**	232	227			
12	172					245	230	230
13	184	235	249	247	244			
13	186					260	252	247
14	198	254	**280**	263	**260**			
14	200					274	**265**	**261**
15	212	271	260	279	275			
15	214					287	284	276
16	226	287	285	294	289			
16	228					300	284	290
17	240	302	298	318	303			
17	242					312	314	304
18	254	316	310	320	316			
18	256					324	308	318
19	268	330	321	332	328			
19	270					335	319	331
20	282	343	332	344	340			
20	284					345	330	345

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Key to Data Sources in Data Tables

Blue font – CRC Handbook **Green Font – Chemspider Experimental**

Red Font = ACD/Labs prediction **Mustard Font – EPI Suite**

Uncertainty in Raw Data

The experimental data were cited with varying precision ranging from zero to three decimal places. Also the melting temperature was sometimes cited as a range. Where a range was given I have chosen the midpoint and have rounded off to the nearest integer value.

EX: Again described methodology regarding uncertainty of data. Good.

The data sources were evaluated by looking at some example compounds where experimentally determined data is available as well a prediction given

EX: Once again methodology is evaluating reliability of data. Good

Table 3: Evaluation of Data Sources

Compound	CRC Handbook Experimental data		Chemspider Experimental data		Chemspider ACD/Labs Predicted Data		Chemspider EPISuite Predicted Data	
	M.Pt (ºC)	B.Pt (ºC)	M.Pt (ºC)	B.Pt (ºC)	M.Pt (ºC)	B.Pt (ºC)	M.Pt (ºC)	B.Pt (ºC)
Hexane	-95	69	-95	69	NA	69	-94	72
Pentanal	-92	103	-92	103	NA	104	-68	109
1-Pentanol	-78	138	-79	137	NA	138	-50	137

Looking at Table 3 it is clear that there is usually good agreement between the CRC Handbook and Chemspider experimentally sources.

The ACD Labs predicted values for boiling temperatures appear quite close to experimental and can be used where experimental data is not available. At higher temperatures the experimental values in the CRC handbook relate to that measured at lower than atmospheric pressure. This could be because the boiling temperature at normal atmospheric pressure is very higher and the compounds may thermally decompose before the predicted boiling temperature.

The EPISuite predicted data is not so reliable. There is some variation in the boiling points and large variation in the melting temperature data. As a result I have omitted the EPI Suite data in the analysis section below.

A: Comments on lack of reliability of the EPI Suite data and understands the impact this will have on the validity of the results and so chooses to eliminate its data from analysis

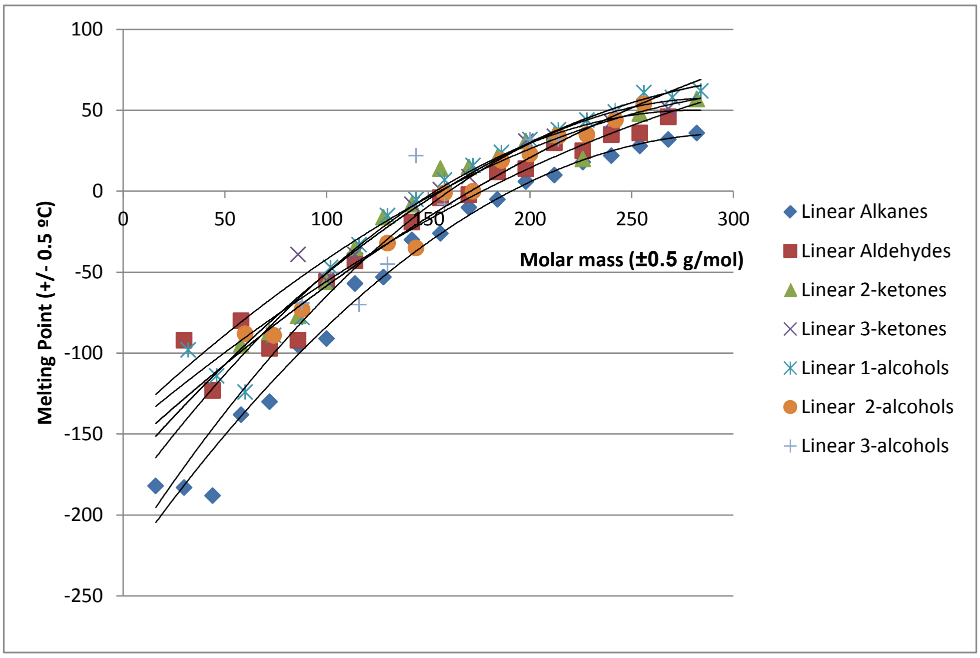
Analysis and Discussion

Part (i) Effect of chain length on the comparative melting and boiling points of the alkanes, aldehydes, ketones and alcohols.

The first two graphs below represent all the gathered data (except the discarded EPISuite predicted data).

Graph 1 – Melting points Plotted against Molar Mass for each Homologous Series

C: Trend lines are rather cramped in presentation making it hard to view individual trends, however it does enable a comparison to be seen. Graph is presented appropriately (scale, precision, units, uncertainties.)
A: Appropriate best fit line and correctly plotted points.



Graph 1 (the melting temperatures) showed a trend but it is not very well defined. The trend-lines of the different homologous series do not converge as clearly as with the boiling temperatures below. This is not something that I was expecting at first and I cannot easily explain the fact that melting temperatures of aldehydes, ketones and alcohols remain significantly above the melting temperature of the alkane of similar molar mass. From the data sources the melting temperatures were not so well defined as boiling temperatures and were often given as a range of temperatures. This could be an area for further study.

A. Graph clearly represents data but importantly the student has not over interpreted the graph. There is not a clear convergence and the student has not unduly claimed so which is quite insightful.

EV: Recognizing impact of uncertainty on the possible conclusion.

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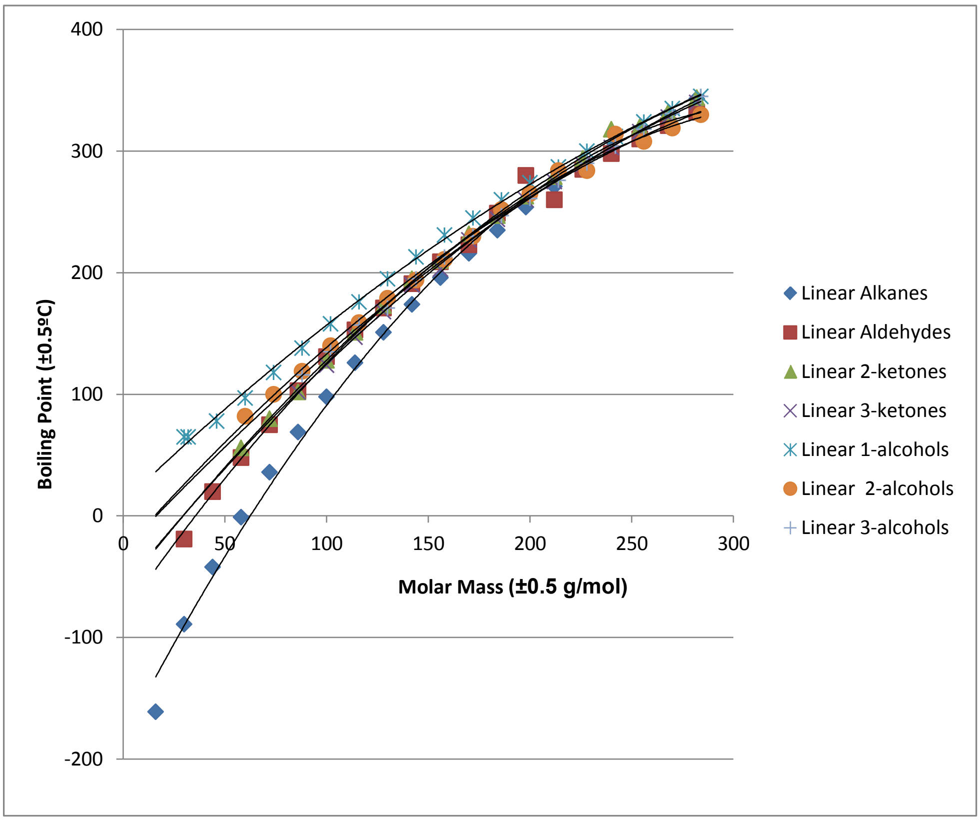
Graph 2 – Boiling points Plotted against Molar Mass for each Homologous Series

C: Again trend lines are rather cramped in presentation making it hard to view point of convergence. Graph 3 with just the experimental data reveals this more clearly. Graph is presented appropriately (scale, precision, units, uncertainties.)



From Graph 2 we see that the boiling temperatures are well defined and the smooth trend-lines do indicate the boiling temperature values for the alkanes, aldehydes, ketones and alcohols do appear to converge at molar mass values above 220 gmole^{-1}. This is not surprising since the influence on the intermolecular forces of the carbonyl and hydroxyl groups reduces as the hydrocarbon chain increases and dominates the character of the molecule.

A: Graph allows for valid interpretation.

C: Use of correct convention for representing unit. Should be 220 gmol^{-1}, but not sufficient to hamper understanding.

EV: Student has described AND justified a valid conclusion.

If we look only at the CRC Handbook experimental data and not use any predicted data then the convergence is even more clear (and removes the anomalous linear aldehyde data points at 198 and 212 gmol^{-1}) as shown in Graph 3 below.

A: This was an excellent step to remove the predicted data. Fine reflective thinking while processing.

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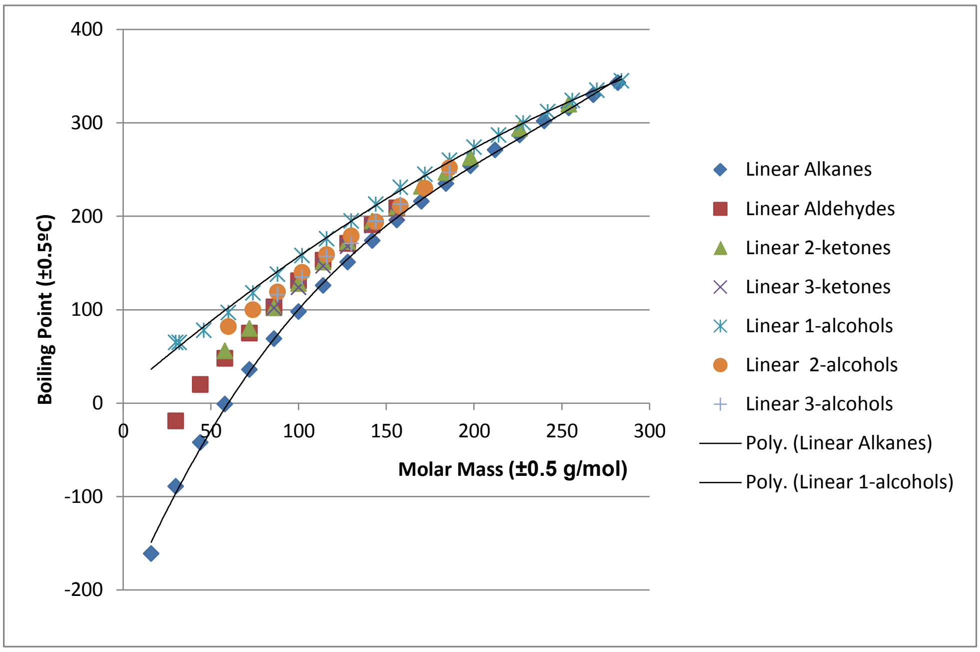
Graph 3: CRC Handbook Experimental Data Only



Graphs 2 and 3 also show that at low molar masses that the trend in boiling points is

alcohols > aldehydes/ketones > alkanes

which agrees with hydrogen bonding being stronger than dipole-dipole forces which are stronger than van der Waal's forces. At higher molar masses the difference gets much less.

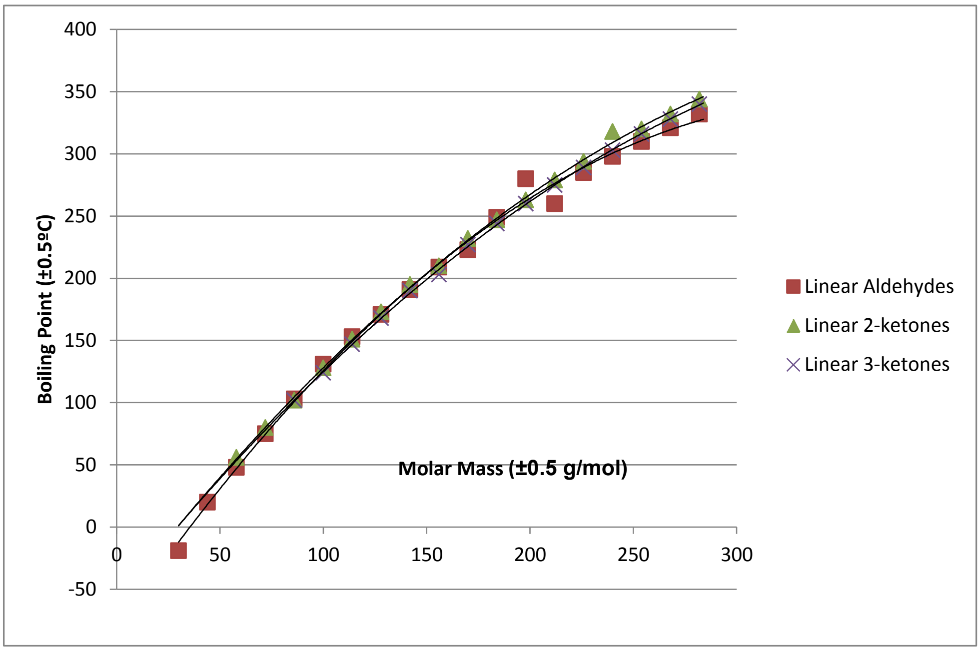
EV: Again justifying the conclusion.

Part(ii). Effect on the boiling points of the functional group position in the aldehyde/ketones and alcohols.

Because the boiling points are so much clearer than the melting points the rest of my analysis will be based only on the boiling points.

A: A sensible decision.

Graph 3 Effect on the Boiling Points of the carbonyl position in the aldehyde and ketones



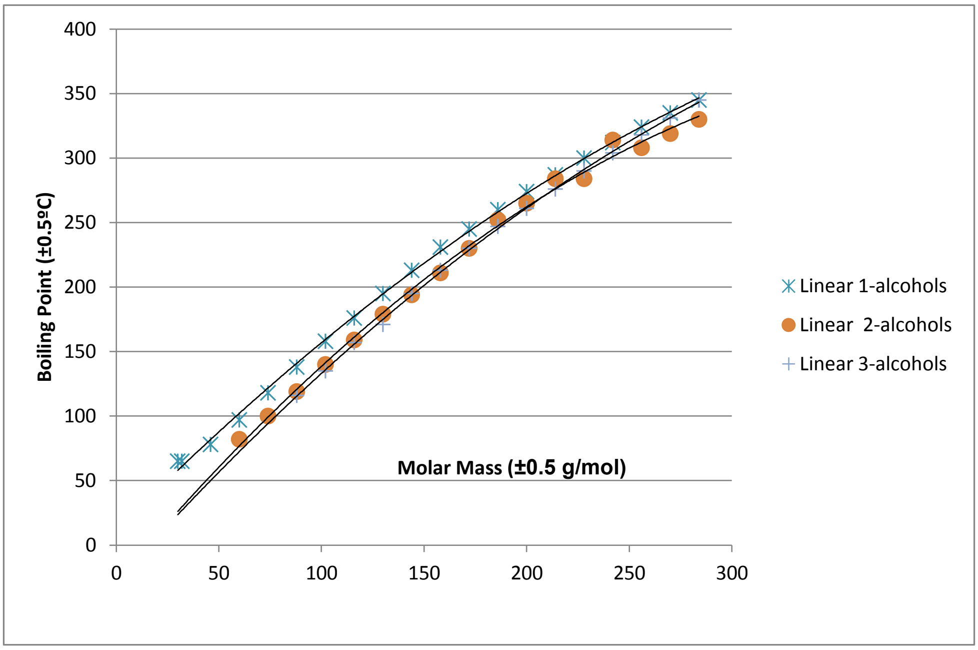
There is very little difference in the melting points between the aldehyde, 1-ketone and 2-ketone isomers at each molar mass and the graph lines are very similar. There is a strange anomaly with the data for the aldehydes $C_{13}H_{18}O$ and $C_{14}H_{30}O$ where the respective boiling points of 280°C and 260ºC seem to be swapped around. I have checked again the experimental data on ChemSpider and those are the values given. The values are not available in the CRC Handbook to double check and this means that I am not very confident in their correctness.

EV: Clear evidence of appreciating limitations in data and understanding methodological implications.

If the data in the table is looked at in Data table 2 we can see that where experimental values are are available the 3-ketone has a slightly lower boiling point by between 1 and 6 °C. But the predicted values are often higher than the corresponding aldehyde and 2-ketone. I suggest that 3 ketones have a lower melting point than the aldehydes and 2-ketones but the effect is not large enough to state confidently.

EV: Once again student gets it right by not overstating their interpretation.

Graph 4 Effect on the Boiling Points of the OH group position in the alcohols



Graph 4 shows that the boiling points of the 1-alcohols are significantly higher than the corresponding 2-alcohols and 3-alcohols. Where we have the CRC Handbook experimental data available for all three series (up until the dodecanol $C_{12}H_{26}O$ isomers) the 2- and 3- alcohols have similar boiling temps which are significantly below the 1-alcohols. I can make the hypothesis that this is because the OH group at the end of the chain in the 1-alcohols can more easily approach from a variety of angles another OH group from another 1-alcohol molecule. If the OH group is in the middle of a chain (like a 3-alcohol) then there are less ways that two molecules can align and attract each other. I have shown these possibilities in Figure 1 and 2 below with Chemsketch 3D images of 1-hexanol and 3-hexanol. It can be seen that there are more possible orientations where the 1-hexanol molecule OH groups can approach and H-bond

EV: Clear conclusion supported by the data is given. The student then goes on to try to justify within a relevant scientific context.

PE: This personal hypothesis shows some real original thinking. Shame that the student hasn't found any literature support for the hypothesis. That would then have been close to perfect! As it is this is an outstanding effort.

Figure 1: 1-Hexanol

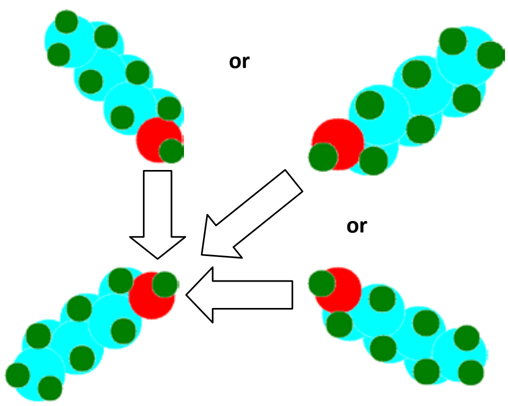


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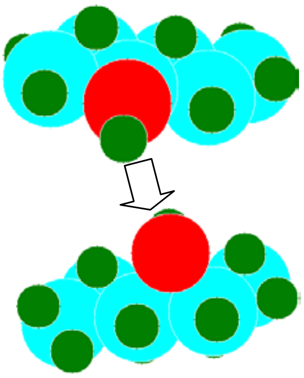
Figure 2. 3-Hexanol



Conclusion

The main conclusions to this research are the answers to the two parts of the research question given earlier

(i) The boiling points of the aldehydes, ketones and alcohols do converge on those of the alkanes as we increase the carbon number and above 200gmol^{-1} the differences become minimal. The melting points were less well defined and although there is some convergence it is not so clear as for the boiling points

(ii) The effect of boiling point on changing the position of the functional group in the alcohol is significant. 1-alcohols with the OH group at the end of the chain have a higher boiling temperature than the 2- and 3-alcohols.

C: Clearly restated main conclusions.

There were other interesting findings such as the significant differences in how well defined the melting and boiling temperatures were and the fact that some predicted values available in the web-based databases were very unreliable. These can be the basis for further study.

EV: Not very strong suggestions and no real suggestions for modifications.

[i] C. Brown and M. Ford, Higher Level Chemistry, p 367, Pearson Baccalaureate, 2009
[ii] CRC Handbook of Chemistry and Physics, 85th Edition, CRC Press, 2004
[iii] http://www.chemspider.com, last accessed on 11/3/2012