

Similarities in the Viscosities of Polyhydric Alcohols

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The purpose of this project was to discover what similarities might exist between the viscosities of various polyhydric alcohols and what specific factors influenced the viscosities.

METHOD

Theory—Comparisons of the viscosities of the polyhydric alcohols were made by calculating the energy barrier to viscous flow. This energy barrier is analogous to the energy barrier which governs the rate of any chemical reaction found through the equation (Rogers, 1967):

$$\ln k = - [(E_a/R) (1/T)] + \ln A$$

where E_a = energy of activation, which determines the energy barrier for the reaction

k = the reaction rate constant

R = 1.98 calories per degree mole

T = temperature, in degrees Kelvin

A = a constant

Consequently the energy barrier to viscous flow can be found through the analogous equation:

$$\ln v = 2.303 \log v = - [(E_{v,i}/R) (1/T)] + C'$$

where v = velocity of a sphere falling through a viscous liquid.
In performing the calculations, the velocity is a constant at a constant temperature.

$E_{v,i}$ = the energy barrier to viscous flow

R = 1.98 calories per degree mole

T = temperature in degrees Kelvin

C' = a constant which includes all constant factors and consistent errors

Both equations 1 and 2 are in the form of the equation for a straight line, $y = b(x) + b$, and by plotting either $\ln k$ or $\ln v$ against $1/T$, the slope of the line can be found, and consequently E_a or $E_{v,i}$ can be found. From the plots of the lines and from the $E_{v,i}$ values, similarities and contrasts can be observed in the polyhydric alcohols.

Experimental Procedure—In performing the project, the following apparatus was used for each alcohol:

1. 1 large test tube, 25 × 200 mm
2. 1 Centigrade thermometer, -100 to +50 C
3. 1 two-hole stopper
4. A supply of BB's
5. 1 stopwatch, graduated to 1/10 sec
6. 1 beaker, at least 200 mm deep

The following is a list of the polyhydric alcohols used:

1. Ethylene glycol — $\text{CH}_2\text{OHCH}_2\text{OH}$
2. Diethylene glycol — $\text{O}(\text{CH}_2\text{CH}_2\text{OH})_2$
3. Propylene glycol — $\text{CH}_2\text{OHCHOHCH}_2$
4. Glycerol (1,2,3-propanetriol) — $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$

To start the experiment, the test tube was prepared by making two marks (a starting line and a finishing line), exactly 100 mm apart, on the outside of the test tube. Afterwards, the test tube was filled with one of the alcohols to within $\frac{3}{4}$ inch of the top of the tube. The thermometer was then inserted in one of the holes of the stopper and the thermometer and stopper were placed in the test tube. This entire assembly was then placed in a beaker of water. The fluid level in the test tube had to be below the level of the water in the beaker to insure a uniform heating of the fluid.

Finally, a Bunsen burner was used to slowly heat the water bath. As the temperature rose, BB's were dropped through the unoccupied hole of the two-hole stopper and the stopwatch was used to determine the time of fall between the starting and finishing marks. Timings were taken at 5 C intervals over a temperature range of about 50 C.

From each timing taken, a unique velocity was found, using the equation:

$$\text{velocity} = \text{distance}/\text{time}$$

These velocities were then substituted into equation 2 to calculate the E_{\dots} values.

In making the timings, temperatures below room temperature (+25 C) were needed to provide the desired temperature range, since glycerol was the only alcohol used which could be accurately tested above +25 C. Since viscosity varies inversely with temperature, lower temperatures would increase the viscosity of the liquid and a greater range of accurate timings could be taken.

To produce these low temperatures, a bath of ice and salt was first used. But the lowest observed temperature was -17 C, which was not low enough to provide a wide temperature range. A bath of dry ice and acetone was finally used and it provided the temperature needed, dropping as low as -78 C. Temperatures this low were not needed, however, because all of the fluids either congealed or began to congeal above -45 C.

Even at the low temperatures of the dry ice and acetone bath, ethylene glycol and diethylene glycol did not show any signs of measurable viscosity and consequently timings could not be taken for these two alcohols. However, diethylene glycol was noticeably more viscous than ethylene glycol.

Glycerol, when tested, was found to be viscous over a wide temperature range (-30 to $+55$ C). Because viscosity varies inversely with temperature, glycerol reached a point ($+60$ C) at which its fluidity began to resemble that of ethylene glycol at room temperature.

Propylene glycol, at $+10$ C, was barely viscous enough to allow accurate timings to be taken. Timings were then taken at lower temperatures until, somewhere between -40 and -45 C, propylene glycol began to congeal.

DISCUSSION

The most apparent result was that the degree of viscosity depends

DATA AND TREATMENT

<i>Glycerol</i>				
K°	Time (sec)	ν	$\log \nu$	$\ln \nu$
323°	0.3	333.3	2.523	5.810
318°	0.4	250	2.398	5.522
313°	0.5	200	2.301	5.299
308°	0.65	153.9	2.187	5.037
303°	1.00	100	2.000	4.606
298°	1.66	65.24	1.815	4.189
293°	1.71	58.48	1.767	4.069
288°	2.78	35.84	1.554	3.579
283°	3.75	26.67	1.426	3.284
278°	5.8	17.24	1.237	2.847
273°	18.65	5.362	0.729	1.681
268°	23.31	4.29	0.633	1.457
263°	41.25	2.422	0.384	0.885
258°	69.08	1.433	0.156	0.360

<i>Propylene glycol</i>				
K°	Time (sec)	ν	$\log \nu$	$\ln \nu$
283°	0.3	333.3	2.523	5.810
278°	0.41	243.9	2.387	5.498
273°	0.69	144.9	2.161	4.977
268°	0.8	125.0	2.097	4.829
263°	1.25	80.00	1.903	4.383
258°	2.00	50.00	1.699	3.913
253°	3.00	33.33	1.523	3.506
248°	4.25	23.53	1.372	3.159
243°	14.55	6.872	0.833	1.918
238°	21.32	4.690	0.671	1.545
233°	43.00	2.326	0.366	0.844

primarily upon the number of hydroxyl groups in the molecule and then upon the length of the uninterrupted carbon chain. For example, ethylene, diethylene, and propylene glycol were all similar in viscosity and each contained two hydroxyl groups per molecule. However, the viscosity of diethylene glycol, with its carbon chain interrupted by an oxygen atom, was not as great as that of propylene glycol, even though it had a heavier molecular weight.

The difference between the E_{∞} value of glycerol and that of propylene glycol was approximately 0.9×10^5 . This difference could only have been caused by one of the hydroxyl groups at either end of the glycerol molecule, since this one hydroxyl group is the only difference between glycerol and propylene glycol.

One very interesting phenomenon appeared in the graphs for the E_{∞} values of glycerol and propylene glycol. This phenomenon was the sudden drop of the E_{∞} line at a low temperature. For glycerol, the line dropped between 278 and 273 K. For propylene glycol, the line dropped between 248 and 243 K. If a graph for glycerol is superimposed upon a graph for propylene glycol an abrupt drop appears at approximately the same point on the two lines. The drop-off points are in the same area because both glycerol and propylene glycol have a three-carbon length chain. However, there is no readily apparent reason for the drop-off point itself, which might indicate the point at which the liquid *actually* begins to congeal.

CONCLUSION

Final results of the project show that there are similarities between the viscosities of polyhydric alcohols. These similarities can be classified in two ways:

1. Excepting high polymers, those alcohols with the same number of hydroxyl groups will have similar viscosities.
2. Polyhydric alcohols with the same unit length carbon chains (e.g., ethyl, propyl, butyl, etc.) will either have similar viscosities or else they will behave in a similar manner. Also, the graphs for the E_{∞} values of these alcohols will be similar.

LITERATURE CITED

- Rogers, Donald W. 1967. Dependence of viscosity on temperature. Chemistry. 40(5).
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