

Studies on the Effect of Electric Field on the Viscosity of Liquids.

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Introduction. Many experiments have been done on the effect of electric field on the viscosity of liquids,⁽¹⁾ but few, on the viscosity of solutions.⁽²⁾ This paper deals with the effect of electric field on the viscosity of the following solutions. As the solutes, a homologous series of fatty acids (lauric, myristic, palmitic, and stearic acids) and an alcohol (cetyl alcohol) were used. In this homologue the number of carbon of an acid increases from the next lower one by two, or the length of the molecule increases regularly according to the number of carbon of acid. While this electro-viscose effect seems to depend upon the length of the molecule of solute, and if so, it is interesting to examine how this effect depends upon the length of molecule of solute. For this purpose the homologue of fatty acid is selected here. As the solvents, benzene and hexane, both of which are non-polar and show no electro-viscose effect, were used. The author reports here the results of the measurement, using special viscosimeter, of the viscosity of solutions which are prepared by combining these solutes and solvents. One of these solutions, i.e. benzene solution of stearic acid has been investigated and reported in the previous paper.⁽³⁾

Apparatus. The author has devised for this experiment a special viscosimeter which is similar to that of L. Herzog and S. Sokolow.⁽¹⁾ The principle of measurement is the same as Ostwald's viscosimeter, but the modified capillary part in applying electric field, is composed of two pieces of electrodes, of which the gap is very narrow and has rectangular section. The whole apparatus is shown in Fig. 1 and the section of the capillary part, in Fig. 1a. As we see in the figure, the apparatus is composed of three parts, i.e. glass bulb A, capillary C and the glass tube B. The volume of A is about 2 c.c. The electrodes are made of aluminium block, the surface of which is covered by electrolytic oxide film in order to make it a good insulator of electricity. Between two electrodes, two thin pieces of glass are inserted. Then we get a capillary of rectangular section, the dimension of which is 0.3×0.02 cm.², and the length of capillary is

(1) W. Krönig, *Wied. Ann.*, **25** (1885), 618. W. Duff, *Phys. Review*, **1896**, 23. G. Quincke, *Wied. Ann.*, **62** (1897), 1. G. Pacher and L. Finazzi, *Atti, Re 1st Ven.*, **59**, 2 (1889-1900), 389. A. Pocchettino, *Atti. D. Real. Accad. dei Linc.*, V. **12**, 2 (1903), 389. Ercollini, *Il. Nuovo Cimento*, **5** (1903), 249. Ph. Lenard, *Ann. Physik.*, (4) **61** (1920), 715. R. Herzog, H. Kudar, and E. Paersch, *Naturwissenschaften*, **21** (1933), 622., *Physik. Z.*, **35** (1934), 466. E. D. Alock, *Physics*, **7** (1936), 126. Y. Björnsthål, *Physics*, **6** (1935), 257. S. Dobinski, *Physik. Z.*, **14** (1935), 509. P. Sokolow and S. Sosinski, *Acta Physicochimica*, U. R. S. S., **5** (1936), 433, 691., *Ber. Akad. U. R. S. S.*, **4** (1935), 123.

(2) A. Passynski, *Kolloid-Z.*, **70** (1935), 180. Y. Björnsthål and K. O. Snellman, *Kolloid-Z.*, **78** (1937), 258.

(3) O. Kimura, this Bulletin, **12** (1937), 147.

6 cm. It is naturally very important to keep the apparatus at constant temperature as the viscosity of liquid is much affected even by a slight fluctuation of temperature. For this purpose, the apparatus must be set up in a thermostat. Since the liquid thermostat is inconvenient, the author has preferred air thermostat, of which the fluctuation of temperature is below 0.1°C . The time is measured by a stop-watch, which is accurate to one tenth of a second. The source of high voltage electricity is obtained by the usual means of a step up A.C. 100 volt transformer and rectifying it to direct current.

Table 1.

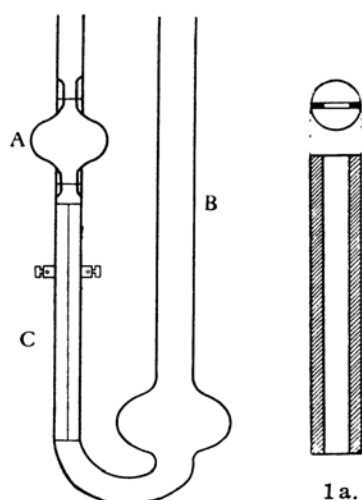


Fig. 1.

Solvent	Solute	Molar fraction	Gram %
benzene	lauric acid	0.01	2.272
"	"	0.02	4.591
"	"	0.04	9.393
"	myristic acid	0.01	2.590
"	"	0.02	5.233
"	"	0.04	10.69
"	palmitic acid	0.01	2.909
"	"	0.02	5.877
"	"	0.04	12.00
"	stearic acid	0.01	3.227
"	"	0.02	6.520
"	"	0.04	13.32
"	cetyl alcohol	0.01	2.750
"	"	0.02	5.557
"	"	0.04	11.34
hexane	"	0.04	11.72

Experiment. The solvents, benzene and hexane, were first purified and then dried by distilling them over pieces of sodium. Lauric acid and cetyl alcohol are of Takeda's pure chemical, and stearic, palmitic, myristic acid are of Merck's. As the unit of concentration, molar fraction is used. The determination was done in all cases on the solution of following three concentrations, namely; 0.01, 0.02, 0.04. The relation of molar fraction with gram percent is shown in Table 1. The temperature is kept at 20°C . throughout the experiment. The measurement of viscosity was proceeded first from pure benzene and hexane. These non-polar solvents did not show any change of viscosity in electric field, as found by the earlier investigators. Then the measurement was carried out on the above-mentioned solutions. In this case, the increase of viscosity occurs when the electric field is applied, and the reproducibility of this effect has been checked by the successive observations of the time of transpiration with or without electric field. The applied voltage varies from zero to thousand volts. The voltage per centimeter may hardly be calculated as the distribution of potential in oxide film is unknown. Therefore here is described only the applied voltage. As the distance of electrode is 0.02 cm., if we assume

the layer of oxide film very thin, the approximate voltage can be estimated by multiplying the applied voltage by 50.

The movement of liquid in a capillary tube of rectangular section is calculated by Rowell and Finlayson,⁽⁴⁾ that is

$$Q = \frac{4}{3} \cdot \frac{\Pi}{\eta} \cdot b h^3 \left(1 - x \cdot \frac{h}{b} \right) t$$

$$\text{where } x = \frac{192}{\pi^5} \cdot \sum_{n=1}^{\infty} \left(\frac{1}{n^5} \cdot \tanh \frac{\pi n b}{2h} \right) \text{ with } n \text{ odd,}$$

and Q is the volume of the transpired liquid in t seconds, the viscosity, b and h two sides of rectangle, Π pressure, x number only referring to b and h . In this apparatus since Q, Π, b and h are constant, we can get the following relation;

$$\eta \propto t$$

This is the same as found in Ostwald's viscosimeter, therefore we can assume that the time of transpiration is proportional to viscosity.

Now the results are shown in Tables 2-7 and Figs. 2-6.

Table 2. Lauric acid
($C_{11}H_{23}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	48.2	0.00
"	300	48.2	0.00
"	400	48.3	0.21
"	500	48.4	0.42
"	600	48.5	0.62
"	700	48.6	0.83
0.02	0	47.3	0.00
"	300	47.4	0.21
"	500	47.5	0.42
"	600	47.6	0.63
"	700	47.7	0.85
"	800	47.8	1.06
0.04	0	51.0	0.00
"	300	51.1	0.20
"	400	51.2	0.39
"	500	51.3	0.59
"	600	51.4	0.78
"	700	51.5	0.98
"	800	51.6	1.18

Table 3. Myristic acid
($C_{13}H_{27}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	68.4	0.00
"	300	68.4	0.00
"	400	68.5	0.15
"	500	68.6	0.29
"	600	68.7	0.44
"	700	68.8	0.59
"	800	69.0	0.88
0.02	0	49.6	0.00
"	200	49.7	0.20
"	300	49.8	0.40
"	400	50.0	0.81
"	500	50.3	1.41
"	600	50.5	1.82
"	700	50.8	2.42
"	800	51.2	3.23
0.04	0	55.3	0.00
"	300	55.5	0.36
"	400	55.7	0.72
"	500	56.1	1.44
"	600	56.5	2.17
"	700	56.9	2.89
"	800	57.3	3.62
"	900	58.0	4.88

(4) *Engineering*, **126** (1928), 249, 385., see also G. Barr, "A Monograph of Viscometry", 145, (1931).

Table 4. Palmitic acid
($C_{15}H_{31}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	47.7	0.00
"	100	47.8	0.21
"	200	48.9	0.42
"	300	49.0	0.63
"	500	49.1	0.84
"	600	49.1	0.84
"	800	49.1	0.84
0.02	0	55.1	0.00
"	150	55.2	0.18
"	300	55.3	0.36
"	500	55.4	0.54
"	800	55.5	0.73

The solution of 0.04 molar fraction cannot be obtained due to its solubility restriction.

Table 6. Cetyl alcohol
($C_{15}H_{31}CH_2OH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	45.0	0.00
"	300	45.1	0.22
"	500	45.2	0.44
"	600	45.2	0.44
"	700	45.2	0.44
"	800	45.2	0.44
0.02	0	48.6	0.00
"	100	48.7	0.21
"	200	48.9	0.62
"	300	49.1	1.03
"	500	49.1	1.03
"	800	49.1	1.03
0.04	0	54.5	0.00
"	100	55.9	0.73
"	200	56.8	2.39
"	300	57.3	5.14
"	400	57.4	5.32
"	500	57.4	5.32
"	550	57.8	6.05
"	600	58.2	6.78
"	700	58.5	7.34
"	800	58.5	7.34
"	800	58.9	8.08
"	900	59.3	8.80
"	1000	60.0	10.10

Table 5. Stearic acid
($C_{17}H_{35}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	48.2	0.00
"	300	48.3	0.21
"	500	48.4	0.42
"	800	48.4	0.42
0.02	0	49.7	0.00
"	200	49.9	0.40
"	300	50.1	0.80
"	400	50.2	1.01
"	500	50.3	1.21
"	600	50.3	1.21
"	700	50.3	1.21
"	800	50.3	1.21
0.04	0	61.7	0.00
"	100	62.0	0.49
"	200	62.5	1.30
"	300	64.2	4.05
"	400	65.0	5.35
"	500	65.0	5.35
"	600	65.0	5.35
"	700	65.0	5.35
"	800	65.0	5.35

Table 7. Cetyl alcohol in hexane.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.04	0	41.0	0.00
"	100	41.1	0.93
"	200	42.2	2.93
"	300	42.2	3.42
"	400	42.4	3.42
"	500	42.4	3.42
"	600	42.4	3.42
"	650	42.4	3.42
"	700	42.7	3.14
"	750	42.7	3.14
"	800	42.8	4.39
"	850	42.9	4.64
"	900	43.1	5.12

In the earlier experiments, the remarkable electro-viscose effect was observed when the liquid touches electrodes directly; and little effect was observed when the liquid is insulated from electrode, say by glass

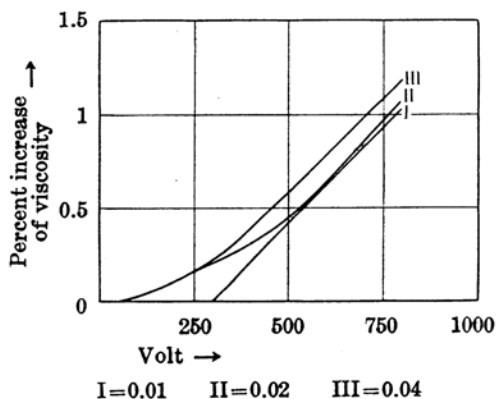


Fig. 2. Lauric acid in benzene.

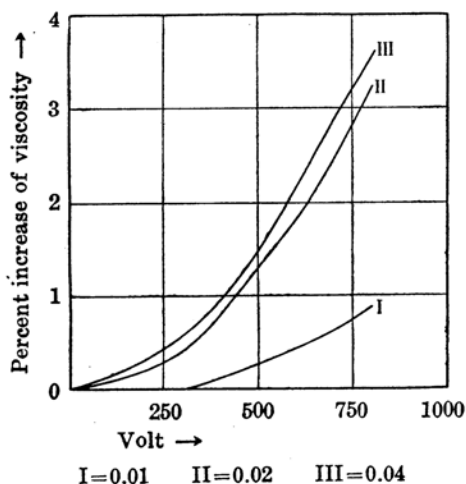


Fig. 3. Myristic acid in benzene.

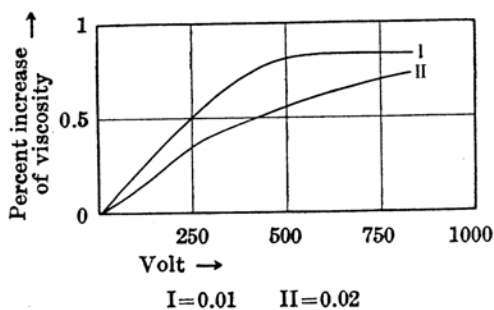


Fig. 4. Palmitic acid in benzene.

layer. This is partially due to the enormous drop of voltage in glass layer, and partially to the movement of ion in liquid. In fact, Sokolow⁽¹⁾ proved that this effect remarkably depends upon the conductivity of liquid, while electrolysis occurs at the same time when the liquid touches electrode directly, and may have some influences. Accordingly, in this case, the phenomenon is too complicated to give the proper interpretation. Therefore to minimize such disturbing influences it is necessary to insulate liquid from electrodes. It is for this reason that in the experiment the electrode was covered by oxide film to insulate it from liquid. The result of experiment clearly shows that in general the viscosity increases with voltage, but the way of increase is characteristic in each solution. This result is remarkable, considering that these substances are homologue. First, in the case of lauric acid, in which the number of carbon is least; the increase of viscosity is less noticeable than others, and is in linear relation with voltage. Next, in myristic acid in which the number of carbon is two more than that of lauric acid, the nature of curve is almost the same, but the increase is more noticeable. Although palmitic acid comes next, let us first take up the case of stearic acid. The form of curve is quite different, and viscosity increases proportionally with the increase of electric field so long as it is weak, but when it reaches a certain limiting value, the viscosity no

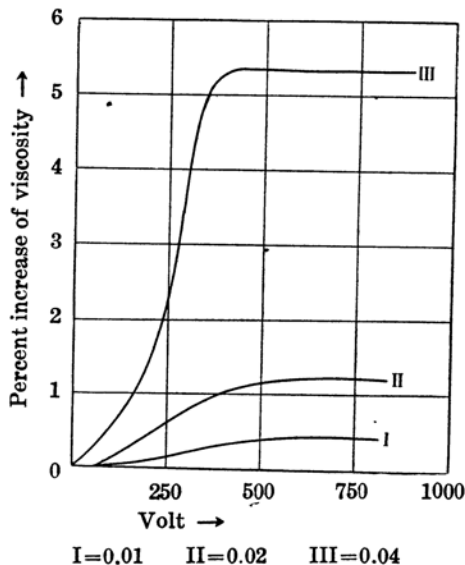


Fig. 5. Stearic acid in benzene.

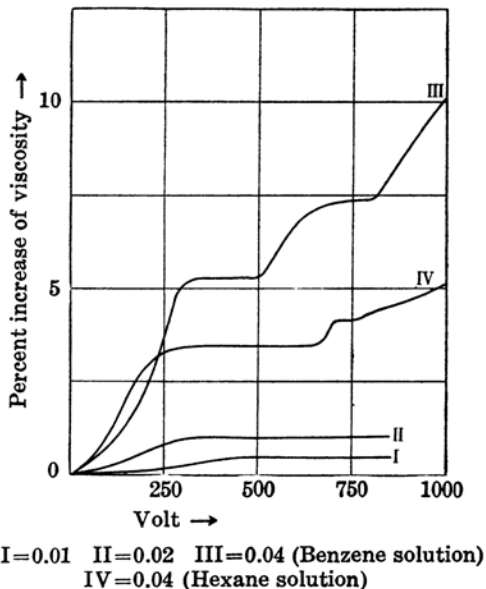


Fig. 6. Cetyl alcohol in benzene and hexane.

longer increases. This phenomenon is common in three different concentrations. The break point in the curves practically coincides with one another. Now let us consider palmitic acid, which lies between myristic and stearic acid in their number of carbon. The nature of curve again seems to be similar with those of two acids and lie between those of two acids. Now the curve of cetyl alcohol is the most characteristic as compared to the rest; in this case, as we see in the figure, the viscosity increases stepwise, and in the horizontal part of the curve for benzene solution corresponds with that of hexane solution, which shows that electroviscose effect is almost independent of the nature of solvent. Thus we can say that in homologue series, the longer the molecule of solute and the more concentrated a solution is, the greater the effect appears.

In general, if the solute has a dipole moment, the electric field will tend to orient the solute molecule in a direction which is parallel to the field. If F be the field strength and μ the electric dipole moment of the molecule, the energy of the molecule due to the electric field will be $\mu F \cos \alpha$, where α is the angle between the dipole axis and the direction of the electric field. There are also thermal energy and energy due to viscous flow associated with molecule. Thermal energy does not depend upon angle between the dipole axis and the direction of the electric field, hence it will cause no orientation of the molecules. Neglecting the viscous stress, we can compare the magnitude of electrical energy with that of thermal energy, as mentioned in the previous paper,⁽³⁾ and obtain the following result that the number of molecules, which orients to the direction of electric field, is very few at the voltage which is realized in this experiment, and so if we raise the field intensity, the number of oriented molecules must increase, and also the viscosity. The above interpretation agrees with experimental results of lauric and myristic acids, and the

results for palmitic acid slightly deviates from the theory, while in stearic acid much more deviation is observed; hence it may be stated that longer the chain, the greater the deviation. This suggests us that the phenomenon may be influenced by some other additional factors. It is more complicated in the case of cetyl alcohol. The reason of this discrepancy from the theory is that the above-mentioned assumption is too simple to be applied in this case. The association of the molecule of solute may be an explanation. The fact that the greater the molecular weight, the easier to form associated molecules, agrees with these experimental results; and that in the case of cetyl alcohol the effect is independent of solvent also supports this theory.

Summary.

- (1) A capillary viscosimeter is made, to which electric field can be applied.
- (2) By means of this viscosimeter, the viscosity of benzene and hexane solution of lauric, myristic, palmitic, and stearic acid and of cetyl alcohol is measured in the presence of electric field.
- (3) The viscosity of these solutions generally increases in electric field, and the stronger the field the greater the increase. The acid with longer chain shows much more effect than one with the shorter. In a solution the effect is proportional to concentration.
- (4) In lauric acid, the increase of viscosity shows a linear relation. In stearic acid, the increase ceases at a certain voltage.
- (5) In cetyl alcohol the viscosity increases stepwise and the form of the viscosity-field intensity curve is independent of the nature of solvent.
- (6) This electro-viscose effect is due to the orientation of molecules of solute.
- (7) The irregularity of curves in stearic acid and cetyl alcohol seems to be the result from association.

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