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### THE VISCOSITY AND FLUIDITY OF EMULSIONS, CRYSTALLINE LIQUIDS AND COLLOIDAL SOLUTIONS.

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#### Introduction.

That viscosity and fluidity may be considered to be analogous to electrical resistance and conductance, respectively, has already been pointed out by one of us.<sup>1</sup> The well known formula of Poiseuille, for the flow of a liquid through a capillary tube, may be written

$$\frac{8l}{\pi r^4 t} \cdot V = \frac{p}{H},$$

where  $V$  is the rate of transpiration,  $p$  the pressure, and  $H$  the viscosity coefficient; or since the term  $\frac{8l}{\pi r^4 t}$  may be made a constant and equal to one, we have

$$V = \frac{p}{H} \quad (1)$$

which is the analog of Ohm's Law,  $C = E/R$ .

Let us now consider the series of conductors shown in section in Fig. 1. Suppose, for the moment, that the surface  $AC$  be maintained at a potential which is higher than the surface  $BD$ . The resistance to the flow of current between the sur-

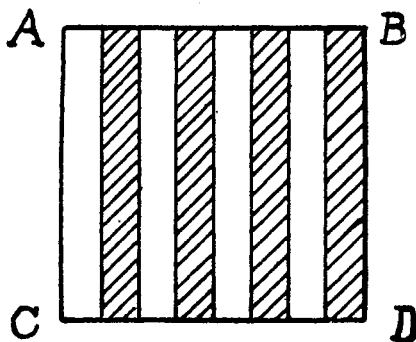


Fig. 1.

<sup>1</sup> *Am. Chem. J.*, 35, 195 (1906).



faces will be the sum of the resistances of the different lamellae, thus

$$C = \frac{E}{r_1 + r_2 + \dots}$$

or the resistance becomes

$$R = r_1 + r_2 + \dots$$

Now if we imagin the lamellae to be capable of viscous flow and that the surface  $AB$  is subjected to a shearing force toward the right, it is evident that the resistance to flow will be the sum of the separate resistances, thus:

$$V = \frac{p}{\eta_1 + \eta_2 + \dots}$$

or

$$H = \eta_1 + \eta_2 + \dots \quad (2)$$

We conclude, therefore, that *when viscous fluids are arranged in series, their viscosities are additive.*

If the surface  $CD$  is maintained at a constant potential difference above  $AB$ , the current will be the sum of the currents flowing through the separate conductors, thus:

$$C_1 = \frac{E}{r_1}$$

$$C_2 = \frac{E}{r_2}$$

and the total current is

$$\begin{aligned} C &= C_1 + C_2 + \dots = \frac{E}{r_1} + \frac{E}{r_2} + \dots \\ &= E \left( \frac{1}{r_1} + \frac{1}{r_2} + \dots \right) \end{aligned}$$

or

$$\frac{1}{R'} = \frac{1}{r_1} + \frac{1}{r_2} + \dots,$$

where  $R'$  is the resistance between  $AB$  and  $CD$ .

If again we imagine that the lamellae of Fig. 1 are capable of viscous flow and that the surface  $CA$  is sheared upward with respect to the surface  $DB$ , then the resulting viscous flow will be found by adding together those for each separate lamella. Thus:

$$V_1 = \frac{p}{\eta_1}$$

$$V_2 = \frac{p}{\eta_2}$$

and the total viscous flow is

$$V = V_1 + V_2 + \dots = p \left( \frac{1}{\eta_1} + \frac{1}{\eta_2} + \dots \right)$$



$$\frac{1}{H'} = \frac{1}{\eta_1} + \frac{1}{\eta_2} + \dots$$

or since  $\phi'$  is the reciprocal of  $H'$ ,

$$\phi' = \phi_1 + \phi_2 + \dots \quad (3)$$

*When viscous liquids are arranged in parallel, their fluidities are additive.*

The analogy is so nearly perfect that it is necessary to guard against one point of difference. In electrical flow, the conductors themselves remain stationary, while in viscous flow the substances themselves flow. Thus if we combine the two schemes referred to above, we will get a checkerboard arrangement of conductors for which the resultant resistance is intermediate between those of the two simpler patterns. Thus one might be led to suppose that in mixtures of liquids, the viscosity would always be intermediate between that given by the assumption that fluidities are additive and that given by the assumption that viscosities are additive. This might lead to serious error, for if in Fig. 1 the surface  $AB$  is sheared to the right in respect to the surface  $CD$ , the individual lamellae will tend to become inclined toward the right and very much elongated, and thus may come to assume the aspect depicted in Fig. 2. Thus although at the beginning the viscosities were strictly

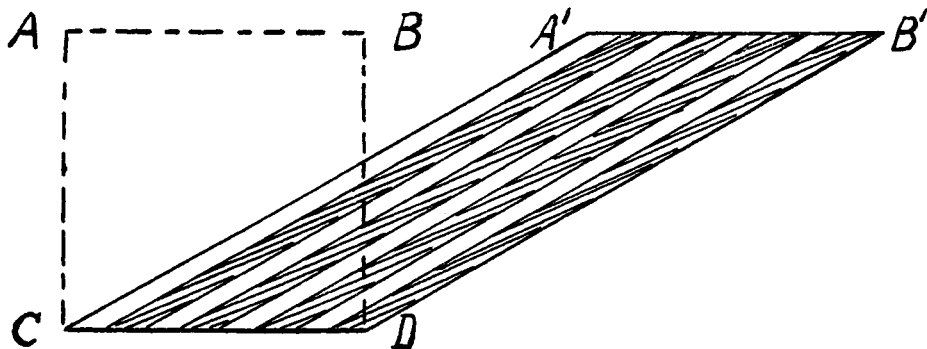


Fig. 2.

additive, as the viscous flow progresses, the conditions change more and more until the *fluidities* are additive. In miscible liquids, the condition that viscosities are additive would therefore appear to be fleeting, disappearing when the liquids are fully mixed. If the substances are immiscible, cohesion may prevent the elongation of the lamellae, in which case the viscosities may be additive as discussed below.

The stream lines around the openings of a capillary tube may be readily observed in the case of emulsions. They are shown in Fig. 3. It is seen that after flowing through the capillary, the liquid continues on for a considerable distance before its velocity is checked, thus apparently prolonging the capillary in this direction. As the liquid flows into the



capillary, no such action is noticed. In other words, the liquid is drawn from a hemisphere around the opening, the result being that any portion

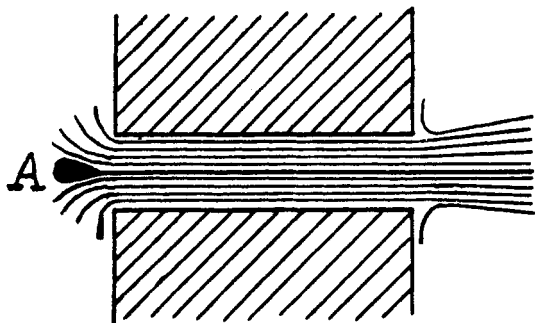


Fig. 3.

of liquid, A in the figure, near the entrance of the capillary, considered as a sphere, suffers great elongation in passing into the capillary. The work of Osborne Reynolds, using colored liquids, should be mentioned as confirming this view. Hence we believe that the conditions in

*homogeneous mixtures are always such that the fluidities are additive.* Dr. B. B. Turner has suggested to one of us the possibility of investigating this point on the basis of the kinetic theory. It is greatly hoped that this may be done.

From the analogy between viscosity and electrical resistance, it appears possible that there may be conditions under which viscosities are additive, according to equation (2). As a result of correspondence with Dr. A. H. Sabin in regard to a problem in viscosity in heterogeneous mixtures, it occurred to one of us that the simplest case of the kind might be obtained by employing two liquids which form an emulsion, particularly such as show a critical-solution temperature. A little reflection showed that this was a case where the viscosities of the components would be additive. The viscosities of suspensions of finely divided solid matter in liquids will be considered in detail in a subsequent paper.

The hypothetical appearance of an emulsion as it flows through a capillary tube is represented in section in Fig. 4. Due to the friction against

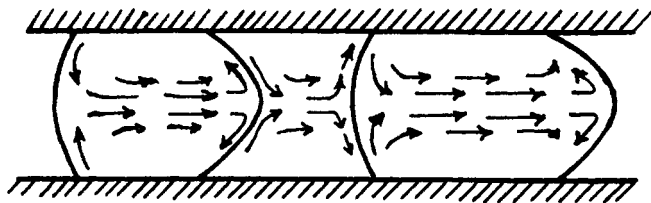


Fig. 4.

the walls, the front end of each drop tends to become abnormally convex and the rear end concave. It is to be specially noted that when the drops are small in diameter as compared with the diameter of the tube and yet large enough to occupy the whole cross-section of the tube, the



motion of the liquid is by no means entirely linear, being transverse as well as longitudinal as indicated by the arrows. The effect of this transverse motion is to increase the apparent viscosity of the liquid. If, however, the drops are very large in comparison to the diameter of the tube, the importance of this transverse motion may be diminished to zero. It is self-evident from what has been said above that *if the drops of an emulsion are large enough to fill the cross-section of the tube, the viscosity, as measured by the method of Poiseuille, will be at least as great as the sum of the component viscosities.* It may be greater due to transverse motion. In the case of miscible liquids where the mixing is excessively imperfect, the resultant viscosity may also approach the sum of the component viscosities but it can never exceed it, because there can then be no transverse motion under the conditions for linear flow.

For liquids of limited solubility, it follows that above the critical-solution temperature, the fluidity of the homogeneous solution will be the sum of the component fluidities; but below the critical-solution temperature, the fluidities are no longer additive, but the viscosities may be. It remains now to determine whether the resulting fluidity will be uniformly greater or less when the viscosities are additive than it is when the fluidities are additive. We start from the equations representing these two assumptions:

$$H = a\eta_1 + b\eta_2 \quad (2')$$

and

$$\Phi' = a\varphi_1 + b\varphi_2, \quad (3')$$

where  $a$  and  $b$  represent the percentages of each of the components, assuming that only two are present. Since  $\Phi$  is the reciprocal of  $H$ ,

$$\frac{1}{\Phi} = \frac{a}{\varphi_1} + \frac{b}{\varphi_2}$$

or

$$\Phi = \frac{\varphi_1\varphi_2}{a\varphi_2 + b\varphi_1}.$$

When  $a = 0$  or  $1$  and  $b = 1$  or  $0$ ,  $\Phi'$  must be equal to  $\Phi$ . For all other values of  $a$  and  $b$ , we propose to prove that  $\Phi'$  must always be greater than, equal to, or less than  $\Phi$ . Multiplying equation (3)' by unity, we have

$$\begin{aligned} \Phi' &= \frac{(a\varphi_1 + b\varphi_2)(a\varphi_2 + b\varphi_1)}{a\varphi_2 + b\varphi_1} \\ &= \frac{(a^2 + b^2)\varphi_1\varphi_2 + ab(\varphi_1^2 + \varphi_2^2)}{a\varphi_2 + b\varphi_1} \begin{matrix} > \\ < \end{matrix} \frac{\varphi_1\varphi_2}{a\varphi_2 + b\varphi_1}. \end{aligned}$$

Since  $b = a - 1$ ,

$$2a(a - 1)\varphi_1\varphi_2 + a(1 - a)(\varphi_1^2 + \varphi_2^2) \begin{matrix} > \\ < \end{matrix} 0.$$



Discarding the known roots,  $a = 0$  and  $a = 1$ , we obtain

$$\varphi_1^2 - 2\varphi_1\varphi_2 + \varphi_2^2 \begin{matrix} > \\ = \\ < \end{matrix} 0,$$

which is a perfect square and therefore must be positive, hence  $\Phi'$  must always be greater than  $\Phi$ . *Thus in every emulsion, the fluidity must be less than would be the case if the components formed a perfectly homogeneous solution.*

### Historical.

When the literature of the subject was investigated, much evidence was found to support the above conclusion, but it was also found that several independent theories had been proposed to account for the facts.

Ostwald and Stebutt<sup>1</sup> observed an abnormally large viscosity in mixtures of isobutyric acid and water in the neighborhood of the critical-solution temperature. This was attributed to the fact that at the critical-solution temperature the surface energy becomes zero.

Friedländer<sup>2</sup> undertook to investigate the phenomena around the critical-solution temperature in an intensive manner. He found a very marked increase in the viscosity as the solution was cooled to temperatures where the opalescence became evident and the critical-solution temperature approached. He observed the opalescence with great care. His investigation was extended to include phenol and water, and the ternary mixture of benzene, acetic acid, and water. Similar relations were found in all proving that the phenomena are quite general. He concluded that the temperature coefficient of viscosity was greatest at the temperature where the opalescence and the tendency to foam were greatest. He says: "Der Trübungsgrad und temperaturkoeffizient der inneren Reibung zeigen eine sehr starke Zunahme in kritischen Gebiete und stehen mit einander in eineminnigen Zusammenhange." Friedländer also observed that the expansion coefficient and the coefficient of electrical conductivity and the refractive index remained normal. He believed that it was necessary to go farther than had Ostwald and that a definite radius of curvature of the separating surfaces must belong to each temperature, otherwise the degree of opalescence could not be definitely determined. He therefore attributed the increase in viscosity to the formation of drops, but he was puzzled by the fact that when a solution of rosin in alcohol is poured into a large quantity of water, a highly opalescent liquid is obtained which has, nevertheless, practically the same viscosity as pure water. This theory of Friedländer is apparently an outgrowth of the theory of "halbbegrenzte Tropfen" of Lehmann.<sup>3</sup> Friedländer discussed the electrical theory of Hardy<sup>4</sup> that an increase of work

<sup>1</sup> *Lehrb. der. allgem. Chem.*, 2 Aufl. 2<sup>2</sup>, 684, etc.

<sup>2</sup> *Z. physik. Chem.*, **38**, 385 (1901).

<sup>3</sup> *Molecularphysik.*, p. 270 (1888).

<sup>4</sup> *Z. physik. Chem.*, **33**, 398 (1900).



would be required to move the particles of a liquid among charged particles, so that if the "drops" were charged an increase in viscosity might result. He found by experiment that an electrical field was without noticeable effect upon an opalescent liquid. The values of viscosity given by Friedländer are not in absolute units.

Scarpa<sup>1</sup> made a study of the viscosity of solutions of phenol and water. His results are expressed in absolute units. For a given temperature he plotted the viscosities for different concentrations. The curves showed a point of inflection which was most marked at the critical-solution temperature. He tried to explain the irregularities on the assumption that hydrates were formed. He does not refer to the work of Friedländer.

Rothmund<sup>2</sup> started from Friedländer's work to make a study of the opalescence at the critical temperature. He measured the viscosities of butyric and isobutyric acid solutions in water, noting particularly the effect of the addition of various substances, both electrolytes and non-electrolytes, upon the opalescence. Rothmund objected to the hypothesis of Friedländer in that, according to the well known formula of Lord Kelvin, small drops are less stable than large ones, so that the small ones must disappear. Furthermore, he remarked upon the entirely analogous opalescence which is observed with a single substance at its critical temperature. Rothmund therefore called to his aid Donnan's hypothesis that when drops are very small their surface tension is very different from that of the liquid in bulk and is a function of the radius of curvature. Since at the critical temperature the surface tension is normally zero, it was thought that the small drops might thus exist in a state of stable equilibrium in the neighborhood of the critical-solution temperature. As the temperature was raised the opalescence would become less and less, due to the solution of the drops. Rothmund found that the addition of naphthalene to his solutions greatly increased the opalescence, while the addition of grape sugar decreased it very greatly, although the effect of these additions upon the viscosity was negligible. Rothmund reasoned that the refractive index of butyric acid is greater than that of water and sugar and electrolytes raise the refractive index of water, hence they make the presence of small drops less evident. Naphthalene does not dissolve in water but does dissolve in the butyric acid, raising its refractive index, and therefore makes the opalescence more apparent.

Von Smoluchowski<sup>3</sup> regards Rothmund's hypothesis as superfluous, believing that the kinetic theory is sufficient to explain the opalescence. According to him, differences in molecular motion, local differences in

<sup>1</sup> *Cimento* [5] 5, 117 (1903) and *J. chim. phys.*, 2, 447 (1904).

<sup>2</sup> *Z. physik. Chem.*, 63, 54 (1908).

<sup>3</sup> *Drude's Ann.*, 25, 205 (1903).



density, and therefore differences in surface tension cause the critical temperature to be not entirely definit, resulting in a rough surface which must remain of smaller thickness than a wave length of light, since greater thicknesses would not reflect light. The inequalities in the density become a maximum at the critical temperature.

Bose and his co-workers<sup>1</sup> have also verified the earlier observations that abnormally large viscosities are obtained at the critical-solution temperature. Bose regards this as being due to the rolling of drops of liquid along the capillary. They did a considerable amount of work to prove that "crystallin" or "anisotropic" liquids are similar to the emulsions here discussed. Bose proved that these liquids have abnormal viscosities near the clarifying point and they also possess marked opalescence. They started from the work of Vorländer and Gähren,<sup>2</sup> who found that a crystallin liquid might result from the mixing of two liquids neither of which was itself "crystallin" in the pure condition. The mixture therefore resembles an emulsion. Bose regards all "crystallin" liquids as emulsions of very long life, *i. e.*, they settle out with extreme slowness; and he proposes an extension of the kinetic theory to account for them. According to van der Waals, the molecules are to be regarded as spheres. However, the molecules of the substances known to form "crystallin" liquids do not approximate to a spherical form but consist of two or more benzene rings united in such a way as to make a rather elongated compound. Hence Bose thinks that they might be better represented by ellipsoids of revolution. As the temperature is lowered, these molecules naturally arrange themselves with their long axes in parallel planes. As the molecules thus unite to form "swarms," the viscosity is increased. This ordered arrangement also causes the liquids to show double refraction.

It was shown that quite often the viscosity *increases* rapidly as the temperature is raised at the clarifying point, but there is also then an increase in density.

It occurred to Bose, Willers, and Rauert<sup>3</sup> that the orderly "swarm" arrangement might be destroyed by measuring the viscosity under conditions for turbulent flow. It was shown by them, in fact, that the abnormalities at the critical-solution temperature do decrease as the transpiration velocity is increased. But these results are not very conclusive, since the conditions of turbulent flow are themselves not very thoroughly understood. Pure liquids were studied under conditions of turbulent flow and it was found that there is not a complete parallelism be-

<sup>1</sup> *Physik. Ztschr.*, 8, 313 (1907); 8, 347 (1907); 9, 769 (1908); 9, 707 (1908); 10, 32 (1909); 10, 230 (1909); 10, 406 (1909). *Z. Elektrochem.*, 8, 449 (1907).

<sup>2</sup> *Ber.*, 40, 1966 (1907).

<sup>3</sup> *Physik. Z.*, 10, 406 (1909).



tween the viscosities measured by the two methods. In fact, there are several cases where one substance has a higher viscosity than another substance under the conditions for linear flow, but a lower viscosity under the conditions for turbulent flow. For this no explanation has been given. Schenck, Eichwald, Bühne, and Dunkenscheid have worked in this field, but we have not had access to their work.

Bose measured the viscosities of suspensions of finely divided quartz particles in bromoform and water and found, as did Friedländer, that the suspended substance affected the viscosity of the solvent but little. There is a paucity of literature on this subject.

Several investigators have worked on the viscosity of colloidal solutions. Now if the "foam-cell" or some similar theory of colloidal solutions is correct, that the solidification of the solution is accompanied by the separation into two phases, then the peculiarities in the viscosities of colloidal solutions may possibly be explained by the considerations which are the object of study in this paper.

Griffiths<sup>1</sup> studied the viscosity and electrical resistance of gelatin solutions. He found that one part of gelatin and five parts of sodium chloride dissolved in ten parts of water at 20° gave an electrical resistance which was always *less* than that of a solution free from gelatin. On the other hand the viscosity continually increased. So far as his experiments went, they indicated no connection at all between the viscosity of the mixture and the internal friction opposing the movements of the ions.

Levites<sup>2</sup> studied the rates of gelatinization when various substances were added to the solution of gelatin and other colloids. He found that the salts of monobasic acids lessen the velocity of gelatinization, while salts of the di- and tribasic acids increase this velocity. He tried to relate this to viscosity, but he found that at the higher temperatures the viscosity is independent of the amount of colloid and is dependent upon the amount of dissolved substance only.

Garrett<sup>3</sup> made an interesting study of several colloidal solutions and measured their viscosities by both the transpiration method and the method of an oscillating disk. In a homogeneous liquid the logarithmic decrements of the amplitude of vibration of an oscillating disk are constant, but in solutions of gelatin, silicic acid, and albumen they increase. Garrett explains this on the assumption that the "cells" of the highly viscous phase become attached to the disk. It is in harmony with this explanation that when the disk is thoroughly cleansed and reintroduced

<sup>1</sup> *Proc. Manchester Lit. and Phil. Soc.*, **41**, 9 (1896).

<sup>2</sup> *J. Russ. Phys. Chem.*, **35**, (1903).

<sup>3</sup> *Phil. Mag.*, [6] **6**, 374 (1903).



into the liquid, the original value of the logarithmic decrement is restored. Moreover, an exceptionally large vibration dislodges some of the cells, thereby causing an increased logarithmic decrement for the succeeding vibrations.

Below a certain temperature a richly colloidal solution separates out slowly as a "liquid precipitate" with a constantly increasing viscosity in whatever way the viscosity may be measured. On continued boiling, the "cell-walls" are destroyed and a gelatin solution then resembles a homogeneous liquid. Other interesting and suggestive relations may be found in the original paper.

Müller<sup>1</sup> compared the "gold numbers" of various colloidal solutions with their fluidities and showed that there is a relation between them as shown by the following table:

Substance.	Fluidity as compared with water at 15°.	Gold number.
Gelatin.....	0.693	0.005-0.01
Casein.....	0.824	0.01
Glue.....	0.924	0.15-0.4
Tragacanth.....	0.933	About 2
Dextrin.....	0.973	6-20
Potato starch.....	0.980	25
Cane sugar.....	0.998	∞

The gold number is defined "as the number of milligrams of colloid which are just sufficient to prevent the change to violet of ten cubic centimeters of bright red colloidal gold solution by the addition of one cubic centimeter of a ten per cent. solution of sodium chloride."

The ions of the sodium chloride serve as nucleating centers. It now becomes clear why an excessively large addition of cane sugar is required to delay the nucleation appreciably, since the fluidity of the solution differs so little from that of water. On the other hand, the gelatin solution has a much lower fluidity than water, hence the nucleation is considerably retarded by a small addition.

Von Schroeder<sup>2</sup> used the viscosity method for studying the behavior of solutions of gelatin. He found that the viscosity of a given solution at a given temperature was not a constant but depended largely upon the past history of the solution. He differentiated two sets of phenomena, as follows: 1. An irreversible saponification, which is greatly increased as the temperature is raised, and is a logarithmic function of the time. 2. A reversible "gel-sol" transformation. The gelatinization takes place at low temperatures, causing the increase in viscosity, but an indefinite time is required for equilibrium to be established at a given temperature.

<sup>1</sup> *Ber.*, 37, 11 (1904).

<sup>2</sup> *Z. physik. Chem.*, 45, 75 (1903).



The effects of different acids, bases, and salts were investigated and found to be quite diversified.

Woudstra<sup>1</sup> worked with colloidal silver solutions and showed that the viscosity decreases with the time and on the addition of electrolytes, but increases with the concentration of the colloid. Both of the first effects are due to coagulation. Woudstra believes that this is due to the lack of that coherence in the surfaces which come into contact, which is present in the gelatin solutions.

### Experimental.

Thorpe and Rodger<sup>2</sup> and others have already shown that the horizontal tube method of Poiseuille may be used for measuring viscosities with exceedingly satisfactory results. This is not altogether true of the Ostwald viscosimeter, which is the form that is perhaps most commonly used. On the other hand, the latter type is exceedingly simple to set up and use, while the former type requires a large amount of preliminary work, and the measurements themselves are much more complicated. It therefore seemed worth while to spend some effort in the attempt to increase the accuracy of the one method, so that the present great disparity between the two methods might be eliminated, or to so simplify the other method that it might be adapted for general use.

Our object at the time was to study intensively some solutions of non-electrolytes in water, which have been shown in a previous paper<sup>3</sup> to be abnormal in that they do not give linear fluidity curves. This so-called "abnormality" is doubtless due to the formation of hydrates; and since in the study of viscosity and fluidity, it has already been shown<sup>4</sup> by one of us that the molecular condition within a liquid may be learned by means of fluidity data, it was hoped that some light might be thus thrown upon the question of hydrates in solution. However, before this problem was finished, the problem arose which is the subject of discussion in this paper. We have therefore used our apparatus for its solution, but we will delay giving the details in regard to our apparatus until a succeeding paper. Suffice it for the present to say that the apparatus consisted of a horizontal capillary of known length and cross section, which was connected to two vertical arms by means of carefully ground glass joints. The vertical arms were so arranged as to allow a perfectly definite amount of liquid to flow through the capillary under conditions which practically eliminated the effect of hydrostatic pressure. The vertical arms were connected to an air reservoir under pressure, the pressure being measured

<sup>2</sup> *Z. physik. Chem.*, 63, 619 (1908).

<sup>3</sup> *Phil. Trans.*, 185A, 397 (1894).

<sup>1</sup> *Amer. Chem. J.*, 35, 195 (1906).

<sup>2</sup> *Z. physik. Chem.*, 66, 1 (1909).



by a water manometer. The apparatus was carefully tested and found to give absolute viscosities which agree very well with the values of Poiseuille, Slotte, Thorpe and Rodger, and others.

For the study of emulsions, the apparatus proved rather tedious to manipulate on account of the difficulty of getting satisfactory mixture of the solutions after they had once separated out. This was best accomplished by blowing air through the solutions, the precaution being taken to have the aqueous pressure such that the evaporation from the emulsion would be negligible. That the results were satisfactory was indicated by the duplication of results.

In the choice of mixtures one is restricted. Isobutyric acid and phenol both give critical solutions with water which are readily reached. Consequently these mixtures have already been studied repeatedly. Only once have the absolute viscosities of such mixtures been obtained. Moreover, it is especially desirable that the same pairs of substances should be studied, using capillaries of different dimensions, or even using different methods. Consequently phenol and water were chosen for study. The water was redistilled from chromic acid and barium hydroxide with particular care to eliminate all dust. The phenol was fractionated by distillation and crystallization. It boiled at  $182.4^{\circ}$  under 763 mm. pressure. At the close of the investigation it melted at  $38^{\circ}$ , indicating the presence of a small amount of impurity, but a trace of water could not affect the viscosity of our emulsions.

It seemed more likely that any relation would be apparent when the solutions were made up on the basis of molecular per cent. Thus a ten per cent. phenol solution is a solution containing  $10 \times 94.05$  grams of phenol and  $90 \times 18.02$  grams of water. The specific gravities were determined by means of an Ostwald pycnometer.

The following tables show the results obtained:

TABLE I.—THE FLUIDITY OF PURE PHENOL.

Temp.	Fluidity.		Temp.	Fluidity.	
	Left limb.	Right limb.		Left limb.	Right limb.
33.96°	16.64	...	60.00°	39.02	39.01
35.98	...	17.93	65.00	44.44	44.45
36.60	18.36	...	70.00	50.14	50.04
40.00	...	20.82	75.00	56.25	56.16
45.00	25.02	...	79.97	62.52	62.65
50.00	29.23	29.24	85.03	69.41	69.64
55.00	34.01	34.05	90.15	...	76.70

The values of the fluidity of pure phenol were plotted to a large scale, and the values for every five degrees were read off. These are given in Table II:



TABLE II.—THE FLUIDITY OF PURE PHENOL FOR EVERY 5°.

Temp.	Fluidity.	Temp.	Fluidity.
35.00°	16.60	65.00°	44.46
40.00	20.82	70.00	50.06
45.00	25.00	75.00	56.18
50.00	29.24	80.00	62.64
55.00	34.03	85.00	69.48
60.00	39.03	90.00	76.56

TABLE III.—THE FLUIDITY OF 20 PER CENT. PHENOL IN WATER.

Temp.	Fluidity.		
	Left limb.	Right limb.	
59.00°	76.31	...	
64.00	82.94	81.78	
65.00	85.32	84.43	Cooled quickly from above critical-sol. temp.
66.00	87.35	86.36	Critical-solution temperature.
67.00	89.53	88.91	Slight opalescence.
68.00	91.34	89.99	
70.00	95.40	95.60	
73.20	102.3	101.8	
75.00	104.7	104.7	
79.90	115.1	115.3	
85.00	126.6	126.1	
90.00	136.8	136.2	
95.00	147.3	146.8	

TABLE IV.—THE FLUIDITY OF 10 PER CENT. PHENOL IN WATER.

Temp.	Fluidity.		
	Left limb.	Right limb.	
26.00°	32.04	...	
70.00	98.91	98.87	
73.00	103.9	103.2	
73.20	106.6	106.5	Critical-solution temperature.
75.00	118.0	118.3	Opalescence. Appearance as indicated in Fig. 6.
80.00	136.5	135.6	
85.00	...	150.7	
90.00	164.8	165.0	
95.00	179.3	179.3	

TABLE V.—THE FLUIDITY OF 5 PER CENT. PHENOL IN WATER.

Temp.	Fluidity.		
	Left limb.	Right limb.	
71.50°	164.4	160.5	
72.50	165.6	165.1	Critical-solution temperature.
73.00	167.5	167.6	Liquid perfectly clear with no opalescence.
75.00	174.5	174.6	
80.00	190.1	191.7	
85.00	204.5	206.4	
90.00	221.6	222.7	
95.00	238.7	238.5	



In all of the mixtures it is to be observed that the fluidity increases with the temperature very rapidly in the neighborhood of the critical-solution temperature. This is shown graphically in Fig. 5.

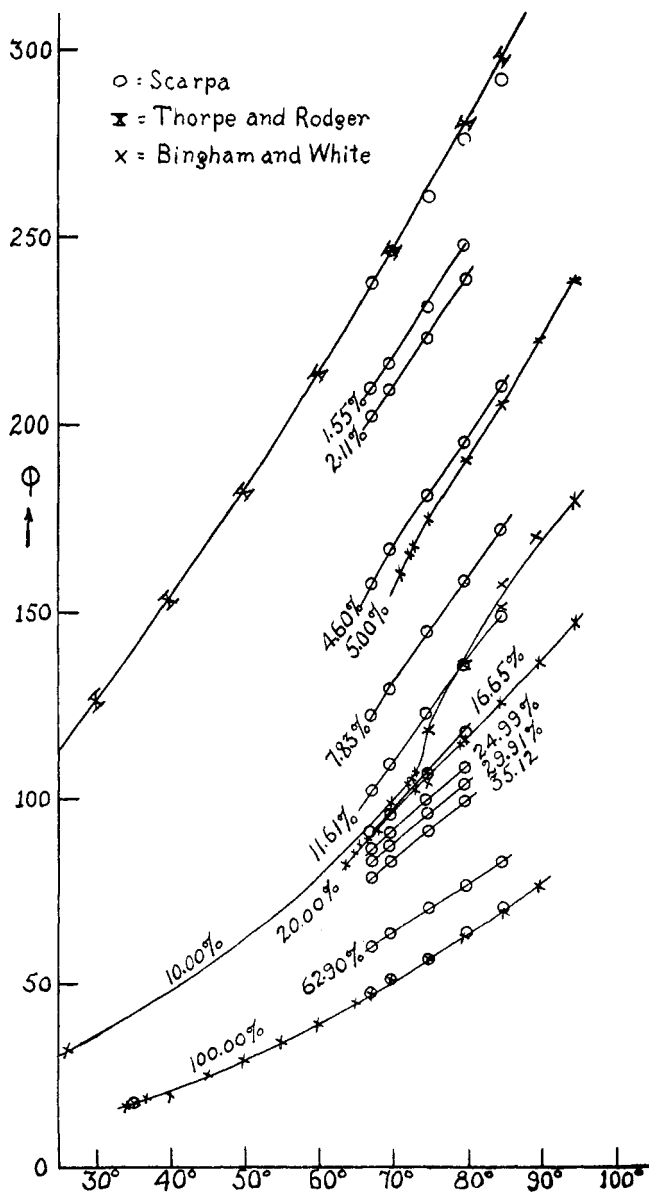


Fig. 5.—The fluidities of phenol and water mixtures.



TABLE VI.—THE FLUIDITIES OF PHENOL AND WATER MIXTURES AS CALCULATED FROM THE DATA OF SCARPA.

Concentrations in molecular per cent.	Temperatures.				
	67.5°.	70.0°.	75.0°.	80.0°.	85.0°.
0.00	238.1	246.9	261.1	276.24	292.4
1.55	209.6	216.4	232.0	248.1	...
2.11	202.0	209.2	223.2	239.2	...
4.60	157.2	166.1	181.1	195.32	210.1
7.83	122.0	129.4	144.9	158.7	171.8
11.61	101.8	108.9	123.0	135.9	148.8
16.65	90.91	96.16	106.38	117.92	...
24.99	86.21	90.66	99.01	107.99	...
29.91	83.20	87.26	96.16	103.73	112.11
35.12	78.74	83.12	90.74	99.50	...
62.90	60.10	63.37	70.92	76.92	83.89
100.00	47.39	50.35	56.43	63.65	70.62

### Discussion of Results.

It is to be noticed that our data for pure phenol agree satisfactorily with that of Scarpa at the low temperatures. At high temperatures the deviation is far too great, being nearly two per cent. at 85°. Scarpa's data for pure water also differs from the values of other observers at high temperatures, the value at 85° being 2 per cent. lower than the value given by Thorpe and Rodger. When we consider the much greater difficulties in introducing the mixtures into the viscosimeter and keeping the liquids mixed, it is not surprising that the agreement for them is even less satisfactory. We have studied a few mixtures at many temperatures. Scarpa studied many mixtures at a few temperatures. Both investigations agree in showing that there is at least a tendency for the fluidity to fall off abnormally as the temperature is lowered to the critical-solution temperature. Not all of the mixtures show this falling off to the same extent nor does the same mixture appear to give the same curve when measured in different forms of apparatus. Thus our 10 per cent. mixture and Scarpa's 11.61 per cent. mixture give entirely different curves. Furthermore, our own data show that, although our measurements were made with great care, the values of the fluidity near the critical-solution temperature do not always agree with each other. We believe that the explanation of these distressing differences is partly that, in an emulsion, the fluidity is dependent upon the size of the drops and the dimensions of the apparatus, the viscosity being greatest when the drops are large in comparison with the cross-section of the capillary. That the fall in fluidity at the critical-solution temperature cannot be due to lack of complete mixing can be proved in the case of our own measurements by the fact that the heavier liquid was also the more viscous. If this settled out, it would be driven through the capillary before the measurement began. The remaining liquid which would be



used for the measurement would therefore possess too great a fluidity. Hence the drop in the fluidity at the critical-solution temperature must be a real effect. Furthermore, we may point out that the same irregularity of the results is shown by the work of Friedländer, for some of his curves cross each other. To test still further the effects of better mixing than we were able to get, we measured the viscosity of our 5 per cent. emulsion from 25° to 75° in a modified Ostwald viscosimeter. The drop in fluidity at the critical-solution temperature was quite apparent.

Lastly, we again made up a 20 per cent. solution of phenol, which we had found to give results not agreeing with those of Scarpa and measured its fluidity to see whether an error had crept into our work at some step. The mixture contained 8.221 g. of phenol and 6.302 g. of water. The fluidities measured at 80° and 85° were as follows:

Temp.	Fluidity.	
	Left limb.	Right limb.
80.00°	115.56	115.53
85.00	125.70	125.69

Our earlier measurements for the same temperatures were:

80.00°	114.62	115.55
85.00	126.62	126.09

The agreement is sufficiently satisfactory, hence no further measurements were made with this mixture.

Let us now recapitulate the explanations which have been offered to explain this drop in fluidity, as follows:

1. The electrical theory of Hardy.
2. The surface energy theory proposed by Ostwald and modified by Friedländer and Rothmund.
3. The theory of hydrates of Scarpa.
4. The rolling drops of Bose.
5. With the above should be grouped the attempted explanation by von Smoluchowski of the opalescence of liquids, as due to differences in density, for the opalescence of liquids and the decrease in fluidity seem to be intimately associated.
6. To these we add our own explanation on the basis of the theory of viscosity.

In regard to the first two, sufficient remark was made in the historical part of this paper. Scarpa's explanation by the assumption of hydrates seems unnatural, because it would be reasonable to suppose that the hydrates would be formed, if at all, as the phenol and water dissolved in each other and that this hydration would be connected with an increase of viscosity. On the contrary, we find the increased viscosity as the mixture separates out into two phases.



Bose would explain the phenomenon on the basis of the transverse motions discussed in the first part of this paper. This loss of energy by transverse motions will decrease as the drops become larger and become zero as the liquids become completely separated out. Hence this is inadequate as a complete explanation although it may explain some of the irregularities in the measurements at the critical-solution temperature.

The difficulty with our own explanation seems to be to explain why the drop in fluidity begins before the critical-solution temperature is actually reached, *viz.*, in the opalescent condition of the liquid. It does not seem reasonable that discreet "drops" can exist several degrees above the critical-solution temperature, therefore the explanation of Rothmund for the fall in fluidity lacks probability. But all that is necessary is that there should be incomplete mixing in the liquid, and this is the basis also of the explanation of opalescence by von Smoluchowski. Near the critical temperature any slight changes in temperature have a maximum effect and while no drops may be formed nor the critical temperature reached in any part of the liquid, since the temperature of the liquid may be maintained at a temperature several degrees above the critical temperature, nevertheless the liquid may become poorly mixed. This conception may be made more definite as follows: At the critical-solution temperature the affinity of molecules of phenol for other molecules of phenol and of molecules of water for other molecules of water becomes equal to the affinity between the phenol and water. At temperatures even considerably above the critical-solution temperature, some of the phenol molecules and some of the water molecules must have velocities below the critical value. The result will be that the molecules of phenol will group themselves together, and if they reach sufficient size before being redissolved, the action of gravity will be appreciable in causing a separation of the liquids. The particles may be ultramicroscopic and not properly regarded as "drops," though perhaps not very different from the "halbbegrenzte Tropfen" of Lehmann. We do not think that it is necessary to go so far as von Smoluchowski in assuming that the critical-solution temperature is not entirely definite.

The simple way of regarding the phenomenon outlined above is borne out by the optical appearance of the liquid in the opalescent condition. We have observed that whenever the liquid was opalescent, if the liquid was observed by direct light, unequal refraction could be seen as suggested by Fig. 6. The partial separation of the liquid into parts of different densities explains at the same time both the opalescence and the increase in viscosity. It is only necessary for



Fig. 6.



a liquid of a given density to fill the cross-section of the capillary at any time in order to make the viscosities additive and, as we have shown, the viscosity must then be greater than in a thoroughly mixed solution.

It is evident that this explanation is at once applicable to the increase in viscosity in crystalline or "anisotropic" liquids. It is only necessary that the "swarms" be of sufficient size in order that the viscosities of the components of the liquid shall be additive.

In colloidal solutions, the "foam-cell" theory is already based upon the assumptions which make the above explanation immediately applicable. As a gelatin solution sets, a "liquid precipitate" is formed which has a very high viscosity. The liquid filling the cells of this precipitate has a viscosity not very different from water. Since the viscosities are here additive, the viscosity of the mass is very high even though the electrical resistance is low. The ions evidently wander through the medium of low viscosity, in the interstices of the jelly.

It becomes evident why very opalescent suspensions, such as that tested by Friedländer, of rosin suspended in water, give viscosities which are not different from the viscosity of pure water. The particles in this case are so very small that they are incomparably smaller than the cross-section of the capillary, hence the fluidities are additive. The fluidity of rosin is certainly nearly zero, so that when it is present in small amounts it does not affect the fluidity of water appreciably. That the particles are indeed small is shown by the fact that such a suspension of rosin will not settle if left for many weeks. On the other hand, a little water added to a solution of rosin in alcohol will give an emulsion containing two liquid phases which behaves exactly like the emulsion of phenol and water. We believe that no explanation has been given for these phenomena heretofore.

The decrease in the viscosity of colloidal silver solutions on standing is explained by the gradual deposition of the silver as a very fine solid suspension which does not affect the viscosity appreciably, as in the case of small amounts of rosin in water, when the particles are small, the *fluidities* are additive, hence the solid silver particles do not exert much influence upon the viscosity until the particles become aggregated together.

In another paper, the fluidities of solid suspensions will be considered in detail. It will be shown that simple laws govern the relation of fluidity to concentration, which are in harmony with the above considerations. Moreover, when a suspension is coagulated by any means, as by the addition of a trace of electrolyte, there is a marked decrease in the fluidity.

We therefore conclude that when liquids are thoroughly mixed, their fluidities will be additive; but if the liquids form an emulsion, a crystalline liquid, a colloidal solution, or if the mixture is for any other reason



incomplete, the fluidity of the mixture will be less than would be the case in a homogeneous solution. This conclusion can be deduced mathematically and it is verified experimentally. These experimental facts have been known for a long time and several theories have been proposed to account for them. We have indicated that some of these are not inconsistent with our explanation, though others are unnecessary if not untenable.

We wish to acknowledge indebtedness to Dr. R. E. Loving for suggestions in the preparation of this paper.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY,  
No. 197.]

**THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. IX.  
THE DROP WEIGHTS OF THE ASSOCIATED LIQUIDS, WATER,  
ETHYL ALCOHOL, METHYL ALCOHOL AND ACETIC ACID;  
AND THE SURFACE TENSIONS AND CAPILLARY CON-  
STANTS CALCULATED FROM THEM.**

BY J. LIVINGSTON R. MORGAN AND A. MCD. MCAFEE.

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In the previous papers of this series the modified definition of normal molecular weight in the liquid state,<sup>1</sup> *viz.*, the finding of a calculated value of  $t_c$  in the relationship

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B (t_c - t - 6),$$

where  $k_B$  is found by a similar equation for benzene, using for  $t_c$  its observed critical temperature,  $288.5^\circ$ , has been applied to the drop weight results, on the Morgan drop weight apparatus, of forty-five (45) different liquids, with the result that all, with but four (4) exceptions, dimethylaniline, and the methyl, ethyl, and propyl formates, are found to be perfectly normal and non-associated, the value of  $t_c$  remaining constant, within reasonable limits, at the various temperatures of observation. Slight differences are to be expected here, of course, due to variations in the densities, unless these are also determined on the sample of liquid used.

In the cases of the four exceptions, as has already been pointed out, the dimethylaniline probably undergoes a rapid and permanent decomposition, which affected, in this work, the result at the higher temperature of observation, but not that at the lower; while there are indications that the formates undergo, with increased temperature, a decomposition, or change of some sort, which persists for several days after the liquid cools slowly to a lower temperature, but not when it cools rapidly. For the

<sup>1</sup> Morgan, THIS JOURNAL, 33, 648-649 (1911).