Physics. — A calculation of the viscosity and the sedimentation velocity for solutions of large chain molecules taking into account the hampered flow of the solvent through each chain molecule. By H. C. Brinkman. (Laboratory N.V. De Bataafsche Petroleum Maatschappij.) (Communicated by Prof. J. M. Burgers.)

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Summary.

In a solution of long chain molecules each polymer molecule forms a molecular cluster according to Kuhn. Hermans and Kramers have calculated the viscosity of such solutions on the assumption that the solvent can move freely through each molecular cluster. On the other hand Hermans has calculated the sedimentation velocity under the assumption that the flow through each cluster is hampered. In this paper expressions are derived for the viscosity and sedimentation velocity based on a single model. According to this model each molecular cluster is represented by a porous sphere which has a certain permeability for the solvent. The specific viscosity is found to be proportional to $P_1 P_2$, where $P$ is the degree of polymerization. This is somewhat different from Staudinger's law which gives proportionality with $P^2$ and which follows from Hermans' and Kramers' theories of unhampered flow. Our results for the viscosity and the sedimentation velocity show excellent agreement with the experiments for various polymers.

§ 1. Introduction.

Kuhn 1) has pointed out that in a solution of longchain molecules each polymer molecule forms a molecular cluster. A calculation of the viscosity of such solutions has been given by Hermans 2) and by Kramers 3) on the assumption that the solvent can flow freely through the molecular clusters. Both authors are led to Staudinger's viscosity law which is verified approximately by experiments. On the other hand Hermans 4) has given a calculation of the sedimentation velocity on the assumption that the flow of the solvent through the molecular clusters is hampered. This calculation likewise gives results in accordance with the experiments. Hermans 4) pointed out that evidently the flow through the molecular clusters is hampered, but that this hindrance has a large effect on the sedimentation velocity only and a small effect on the viscosity.

In this paper a calculation is given of the hampered flow through a molecular cluster. As a result formulae for the viscosity and the sedimentation velocity are found which support the above mentioned assumption of Hermans and which are in excellent agreement with experiments. Debye 5) recently has given a summary of a theoretical treatment of the hampered flow through a molecular cluster. He introduces a depth of penetration of the fluid flow into the cluster. For large values of this depth his results for the viscosity approximate those of Hermans and Kramers. The sedimentation constant is not mentioned by Debye. Apparently Debye's way of treatment is quite different from ours as described below. His results moreover seem to differ in some ways from ours. Unfortunately Debye's very short description of his theory has until now made a detailed comparison impossible.

§ 2. A model for the hampered flow through a molecular cluster.

In a previous paper 6) a theory was developed describing the viscous flow of a fluid through a dense swarm of particles. In this theory the swarm of particles is represented by a porous mass. An equation describing the fluid flow through a porous mass was already proposed by Darcy in 1856 7):

$$v = - \frac{k}{\eta} \nabla p$$

where $v$ is the rate of flow through a section of unit area in the porous mass;

$k$ is the permeability of the porous mass (i.e. a phenomenological constant determining the rate of flow);

$\eta$ is the fluid viscosity;

$\nabla p$ is the pressure-gradient.

It appeared, however, that (1) is an approximation. It is valid for low permeabilities as occurring in subterranean flow problems. For high values of the permeability the true equation should tend to the Navier-Stokes equation for unhampered flow. This last equation has the following form for stationary viscous flow:

$$\nabla p = \eta \Delta v$$

where:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

1) W. Kuhn, Koloid Z. 68, 2 (1934); 76, 258 (1936).
2) J. J. Hermans, Koloid Z. 106, 22 (1944); Physica 10, 777 (1943).
We suggested to modify (1) into (6):

\[ \text{grad} \rho = - (\eta / k) \mathbf{v} + \eta \Delta \mathbf{v} \quad . \quad . \quad . \quad (3) \]

Equation (3) gives an approximate description of an equilibrium between the pressure gradient (\text{grad} \rho), a damping force caused by the porous mass (\eta \mathbf{v} / k) and viscous shearing stresses (\eta \Delta \mathbf{v}). For low permeabilities it tends to (1) and for high permeabilities to (2).

A calculation of the viscous force exerted on a sphere embedded in a porous mass on the basis of this equation combined with certain auxiliary assumptions regarding boundary conditions, was given in the paper mentioned in (6). It could be used to deduce an expression for the permeability:

\[ k = \frac{\sigma^2}{18} \left[ 3 + \frac{4}{\varphi} - 3 \left( \frac{8}{\varphi} - 3 \right)^{1/3} \right] \quad . \quad . \quad . \quad (4) \]

where \( \varphi \) is the volume-fraction of solid matter in the porous mass (\( 1 - \varphi \) is the porosity) and \( \sigma \) is the radius of a sphere defined in the following way: we consider a unit of volume of the porous mass built up of \( n \) spheres each of radius \( \sigma \), so that:

\[ \varphi = \frac{1}{2} \pi \sigma^3 \quad n \quad . \quad . \quad . \quad . \quad (5) \]

Now the area \( a \) of the porous mass per unit of volume is:

\[ a = 4 \pi \sigma^2 \quad n \quad . \quad . \quad . \quad . \quad (6) \]

We then put:

\[ \vartheta = \frac{1}{2} \pi \sigma^3 \quad a \quad . \quad . \quad . \quad . \quad (7) \]

and take this as the definition of \( \vartheta \).

According to KÜHN \(^1\) a long chain molecule is built up from \( N \) statistical elements in such a way that the orientation of each element is approximately independent of all others. Each element contains \( v \) monomeric units of length \( l_e \). Therefore the degree of polymerization \( P \) is:

\[ P = v N \quad . \quad . \quad . \quad . \quad (8) \]

The length of a statistical element \( A \) is given by

\[ A = s l_e \quad . \quad . \quad . \quad . \quad (9) \]

where \( s \) is approximately equal to \( \frac{1}{2} v \) \(^4\).

The centres of the chain elements are distributed statistically with a probability proportional to

\[ \psi (r) = r^2 e^{-r^2} \quad . \quad . \quad . \quad . \quad (10) \]

where \( \mu^2 = 3 / (2 N A^2) \).

In our theory we will represent this molecular cluster by a porous sphere of radius \( R \). For \( R \) the mean radius of the cluster following from (10) will be substituted:

\[ R = \frac{2}{\mu} \left[ \frac{2}{3} \pi \right] = A \sqrt{\frac{8 N}{3 \pi}} \quad . \quad . \quad . \quad . \quad (11) \]

Then the permeability of the porous sphere will be derived from (4) with \( \vartheta = A / 2 \).

It should be pointed out that in consequence of (10) the porosity of the cluster is in fact variable with \( r \). A more subtle approximation might be obtained by introducing a model with an infinite radius and a varying permeability in accordance with (10), again to be combined with (4). Instead of this more subtle model we introduced the mean values for \( R \) and for the permeability \( k \). We are confident, however, that the results obtained will be satisfactory for both models.

\section*{§ 3. Solution of the equations of flow.}

The mathematical problem to be solved may be stated in the following way: The equations of flow must be solved for a fluid surrounding and penetrating a porous sphere of radius \( R \). Inside of the sphere these equations are (3) and the condition of incompressibility

\[ \text{div} \mathbf{v} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12) \]

Outside of the sphere we have (2) and (12).

The boundary conditions at the surface of the sphere are the following:

a. For the calculation of the sedimentation the velocity of flow must represent a parallel flow, e.g. in the direction of the \( z \)-axis.

b. For the calculation of the viscosity some type of flow containing velocity gradients must be introduced. We choose:

\[ v_x = - \frac{v_0}{2} x; \quad v_y = - \frac{v_0}{2} y; \quad v_z = v_0 \quad z. \]

Introducing polar coordinates \( r \) and \( \theta \) symmetrically round the \( z \)-axis the solution of the equations is found to be:

\section*{a. For the sedimentation problem:}

outside of the sphere:

\[ \mathbf{v} = \text{grad} \left\{ v_0 \left[ r - \frac{e}{r} \right] \cos \theta \right\} + \frac{e}{r} \quad i \quad . \quad . \quad . \quad . \quad (13) \]
inside of the sphere:
\[ \mathbf{v} = \nabla \left[ \left\{ -\frac{g}{x^2} \frac{\partial}{\partial r} \sinh \frac{\lambda r}{x} - hr \right\} \cos \theta \right] + \frac{g}{x^2} \sinh \frac{\lambda r}{x} - 1 \]  \hspace{1cm} (14)

b. For the viscosity problem:
outside of the sphere:
\[ \mathbf{v} = \nabla \left\{ \frac{v_0 \rho^2}{4} \frac{e}{r^3} P_2(\cos \theta) - \frac{\partial}{\partial r} (1 - \cos^2 \theta) \right\} \sinh \frac{\lambda r}{x} - 1 \]  \hspace{1cm} (15)

inside of the sphere:
\[ \mathbf{v} = \nabla \left\{ br^2 P_2(\cos \theta) - \frac{a}{x^2} \frac{\partial^2 \sinh \frac{\lambda r}{x}}{\partial z^2} + \frac{a}{x^2} \sinh \frac{\lambda r}{x} - 1 \right\} \hspace{1cm} (16)

where \( \lambda = 1/k \); \( i \) is the unit-vector in the direction of the \( z \)-axis; \( a, b, c, d, e, f, g \) and \( h \) are constants to be determined from the boundary conditions.

We will not give the expressions for these constants which would fill some pages, but will indicate in which way the final results are to be obtained from them: For the sedimentation the viscous force acting on the porous sphere should be calculated by integration of the viscous stresses over the surface of the sphere. This force should be in equilibrium with the gravitational force. For the viscosity the energy dissipation should be calculated in the same way as in Einstein's well known paper 8).

It should be pointed out that (15) and (16) are valid for a sphere which is at rest relative to the mean flow velocity of the liquid. If this is not the case the term \( \eta \mathbf{v}/k \) (i.e. the damping force inside the sphere) will modify the results. Mostly, however, the experimental conditions will approximately fulfill our assumption.

The following expressions for the viscous force \( K \) on the sphere and for the viscosity \( \eta' \) of the suspension are found:
\[ K = 6 \pi \eta v_0 R f_1(\lambda R) \]  \hspace{1cm} (17)
\[ \eta' = \eta \left\{ 1 + 2.5 \frac{\rho v}{\rho V} f_1(\lambda R) \right\} \]  \hspace{1cm} (18)

where: \( \eta \) is the viscosity of the solvent; \( v_0 = \frac{1}{6} R^3 G V \); \( G \) is the number of spheres per unit of volume of the fluid; \( V \) is the total volume of the fluid:
\[ f_1(\lambda R) = \frac{1 - \frac{11 T}{3 R^2} + \frac{8 T}{2 R^2} - \frac{8 T}{R^2} + \frac{1}{2 R^2} + \frac{2 T}{R^2} - \frac{8 T}{2 R^2} + \frac{36 T}{3 R^2} + \frac{36 T}{R^2} - \frac{36 T}{2 R^2}}{1 + \frac{10}{2 R^2} + \frac{90 C}{2 R^2} + \frac{72 C}{R^2} + \frac{360 C}{3 R^2} - \frac{360 C}{R^2}} \]  \hspace{1cm} (17a)

\[ \mu \]

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8) A. Einstein, Ann. Phys. 19, 289 (1906); 34, 591 (1911).

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In order to be able to compare (17) and (18) with experiments the various quantities occurring in these formulae should be expressed in experimentally known quantities with the help of Kuhn's statistics (cf. § 2). With the help of (4), (5), (7), (8), (9) and (11) we find:
\[ \frac{iR}{\sqrt{k}} = \sqrt{\frac{8N}{3\pi}} \cdot \frac{9 + 3}{2} \sqrt{\frac{8}{\eta} - 3} \]  \hspace{1cm} (19)
\[ \varphi = \frac{1}{8} \frac{3 \pi}{8} \]  \hspace{1cm} (20)
\[ V_0 = \frac{4 \pi}{3} A \left( \frac{8 N}{\pi} \right)^{3/2} \]  \hspace{1cm} (21)

Applying these expressions we find from (18):
\[ \eta = \sqrt{\frac{c}{9}} \]  \hspace{1cm} (22)

The sedimentation constant (i.e. the sedimentation velocity in a gravitational field giving unit-acceleration) is found by equating (17) to the gravitational force \( M - V_0 \varphi \), \( M \) is the molecular mass of the polymer and \( \varphi \) the density of the solvent. We find:
\[ a = \frac{M - V_0 \varphi}{6.1 \times 10^3 \sqrt{\pi}} \cdot \frac{1}{4} \sqrt{\frac{N}{\phi}} \]  \hspace{1cm} (23)

In fig. 1 we have plotted \( \sqrt{\phi} \left( f_1(N) \right) \) and \( \sqrt{\phi} f_2(N) \) as functions of \( N \) with help of (17a), (18a), (19) and (20).

Discussion of the viscosity relation.
It should be observed that in the region \( N > 30 \) the function \( \sqrt{\phi} f_2(N) \) may be approximated by a linear relation \( a + b N \). Such a linear relation is also proposed by Baker, Fuller and Heiss on experimental evidence 9).

A better comparison with experiment is obtained by comparing (22) to the modified Staudinger law:
\[ \eta = K c P^a \]  \hspace{1cm} (24)

where \( K \) is a constant; \( c \) the concentration in gram/liter; \( P \) the degree of

polymerization, and \( \alpha \) is an exponent which is equal to 1 for the original Staudinger law. It should be remembered that Hermans \(^2\) and Kramers \(^3\) find \( \alpha = 1 \) from their theories. As the factor \( c \) in (24) is proportional to \( P \) this means that \( \eta \cdot P \) is proportional to \( N^2 \).

In fig. 2 we have plotted the logarithm of \( f_2 \sqrt{N} \) against \( \log N \). The resulting curve is very nearly a straight line for \( N > 3 \). This means that relation (22) may be written in the form (24). The exponent is found to be:

\[
\alpha = 0.81.
\]

This agrees very well with many experimental results. We give some experimental values \(^10\):

- polyvinylacetate \( \alpha = 0.79 \)
- polyvinylchloride \( \alpha = 0.76 \)
- polymethylmethacrylate \( \alpha = 0.82 \) (solvent benzene)
- \( \alpha = 0.76 \) (solvent chloroform)

**Discussion of the sedimentation-constant.**

For the sedimentation constant we have compared our results to those discussed by Hermans \(^4\). The values for the various constants are found in his paper.

**Nitrocellulose (\( A = 62, s = 12, I_g = 5.2 \))**

<table>
<thead>
<tr>
<th>( N )</th>
<th>1.3</th>
<th>6.3</th>
<th>17</th>
<th>42</th>
<th>129</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^3 \sigma_{\text{theor.}} )</td>
<td>4.5</td>
<td>8.6</td>
<td>12.7</td>
<td>18.3</td>
<td>28.4</td>
</tr>
<tr>
<td>( 10^3 \sigma_{\text{exp.}} )</td>
<td>5.2</td>
<td>8.7</td>
<td>12.0</td>
<td>18</td>
<td>30</td>
</tr>
</tbody>
</table>

**Cellulose-acetate (\( A = 73, s = 15, I_g = 5.2 \))**

<table>
<thead>
<tr>
<th>( N )</th>
<th>14</th>
<th>20</th>
<th>22</th>
<th>25</th>
<th>43</th>
<th>56</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^5 \sigma_{\text{theor.}} )</td>
<td>2.7</td>
<td>3.1</td>
<td>3.3</td>
<td>3.5</td>
<td>4.3</td>
<td>4.8</td>
</tr>
<tr>
<td>( 10^5 \sigma_{\text{exp.}} )</td>
<td>2.9</td>
<td>3.2</td>
<td>3.4</td>
<td>3.5</td>
<td>4.3</td>
<td>4.8</td>
</tr>
</tbody>
</table>

For nitrocellulose Hermans' value of \( s \) was taken. For cellulose-acetate, where the various experimental quantities necessary for a comparison are known less accurately, \( s = 15 \) was taken instead of Hermans' value \( s = 10 \). The variation of \( \sigma \) with \( N \) is represented excellently by our formula, while the magnitude of \( \sigma \) also agrees with the experimental results.

It may be concluded therefore that our substitution of a porous sphere for a molecular cluster leads to expressions for the viscosity and for the sedimentation constant which agree well with experiment.

The author is indebted to Prof. J. J. Hermans for a discussion of the experimental material.