in der wäßrigen Phase verblieben, doch zeigte auch der Cystin-diäthylester Aktivität in der wäßrigen Phase nach Ausschütteln mit Chloroform. Aus der Voruntersuchung ist zu folgern, daß das chloroformunlösliche zyklische Disulfid mit dem Cystin-diäthylester durch peptidische Verknüpfung reagierte und daß ferner der Cystin-diäthylester der Selbstkondensation zu Poly-
cystinen unterlag.


Kolloide und natürliche Makromoleküle

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On the Hole Theory of Viscosity, Compressibility, and Expansivity of Liquids

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With 1 figure in 2 details and 2 tables

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1. Introduction

An approach to a theoretical treatment of viscosity which has been rather successful is based on the assumption that a liquid has a quasi-crystalline structure.

In this model of liquid matter, the molecules oscillate about equilibrium positions; they can move from one equilibrium position to a neighboring one when their energy momentarily is equal to or larger than the height of the potential barrier between the equilibrium positions and when the next equilibrium position is empty. The probability that the latter is the case is called the transition probability $\kappa$. One can increase the frequency of transitions in a certain direction by applying an outer shear stress. This results in a shear motion on a macroscopic scale.

Eyring's name is most prominently connected with this approach for his application of the reaction rate theory to this model. According to his theory the viscosity $\eta$ can be expressed by

$$\eta = \frac{2 k T}{A E_{\text{vap}}} \left( \frac{2 \pi m k T \kappa^{1/2}}{v^{3/2}} \right) \exp \left( \frac{\epsilon_0}{k T} \right),$$  \[1\]

where $E_{\text{vap}}$ = molar energy of vaporization, $\epsilon_0$ = height of the potential barrier between equilibrium positions, $m$ = mass of molecule, $\kappa$ = transition probability. $v^{3/2}$ is equal to $\lambda_2 \lambda_\oplus / \lambda$, with $\lambda = $ distance between neighboring equilibrium positions, $\lambda_2$ = distance between two gliding planes, and $\lambda_2 \lambda_\oplus$ = area of the molecule on which the shear force acts. This means that $v$ is about equal to the volume of one molecule.

Starting from the same model of liquid structure, the present author gave a theoretical treatment of the mechanism of viscosity (2) which employed mechanical and statistical concepts only and did not make use of the reaction rate theory. From this theory the viscosity results as

$$\eta = \left( \frac{k T}{\epsilon_0} \right)^{1/2} \frac{2 m k T \kappa^{1/2}}{v^{3/2}} \exp \left( \frac{\epsilon_0}{k T} \right).$$  \[2\]

The two results do not differ markedly as $k T/\epsilon_0$ and $2 RT/A E_{\text{vap}}$ are both of the order of unity.

It should be pointed out that equations[1] and [2] are derived under simplifying assumptions. Firstly, it is assumed that the direction of the shear stress lies in the gliding plane. As the thermal motion of the molecules perpendicular to the direction of flow gives no macroscopic mass flow, one assumes further that it is sufficient to study a linear model in which essentially one row of molecules moves through the potential field of a second row of molecules. The discussion of the transition probability given here is based on the same model of liquid structure.

The transition probability $\kappa$ depends on the relative number and the arrangement of the holes in the liquid. Although some attempts have been made to correlate $\kappa$ and the number of holes (1, 2) no thorough analysis has been made as yet. The present paper will be concerned mostly with the dependence of $\kappa$ on the number and the arrangement of the holes in the liquid and its influence on the viscosity. In addition one can derive very
easily the equation of state, the compressibility, and the thermal expansivity on the basis of the same ideas. This allows a welcome check of the soundness of the theory.

2. The Transition Probability

The transition probability was defined in the previous section as the probability that a molecule which has enough energy to overcome the potential barrier to the next equilibrium position finds this position actually empty. The transition probability depends, therefore, on the number and the arrangement of the holes. In this context all holes shall have the same volume \( v_h \). The energy to create one hole against the intermolecular forces will be called \( \varepsilon_h \). If two or more holes conglomerate the sum of these holes will be called a cavity or an aggregate of holes. The volume of such a cavity is assumed to be an integral multiple of the volume of one hole and the total energy is assumed to be an integral multiple of \( \varepsilon_h \).

In reality both \( v_h \) and \( \varepsilon_h \) will change as holes conglomerate. It will be seen later in this paper, however, that the present assumptions lead to a very useful first approximation.

It shall be assumed that the specific volume (volume per gram) contains \( n_m \) molecules and \( n_h \) holes. In a linear array, the probability of finding a hole next to a given molecule at a given point follows from elementary theory as

\[
\kappa = \frac{n_h}{n_h + n_m}.
\]

This is true, however, only when the holes and molecules are distributed at random. If one assumes that two holes are always separated by at least one molecule, the transition probability becomes

\[
\kappa = \frac{n_h}{n_m},
\]

which is derived in the appendix. The two assumptions about the distribution of the holes in the liquid represent two extremes. The actual distribution will be between these extremes and will depend on the state of motion of the liquid. For a liquid at rest one can assume that the distribution of the holes is random, with the condition that very large cavities are unstable and do not occur for any length of time. The distribution for the liquid at rest is thus very close to the random distribution (R-distribution). Shearing motion in a liquid, on the other hand, will tend to break up aggregates of holes and thus establish a distribution in which holes are singly and more evenly spaced (S-distribution). How close to the S-distribution the actual distribution of holes in a liquid comes is difficult to estimate. It shall be assumed that in a first approximation the arrangement of holes in a liquid at rest is given by the R-distribution and in a liquid in shear motion by the S-distribution. Hence, \( \kappa \) has to be computed according to equation [4].

The relative number of holes \( n_h/n_m \), which appears in equation [4], can be calculated for a given pressure and temperature from the condition that the derivative of the Gibbs potential \( G \) with respect to the variable \( n_h \) must be zero. If \( U = \) internal energy, \( p = \) pressure, \( V = \) specific volume, \( T = \) absolute temperature, and \( S = \) entropy, we have

\[
\frac{dG}{dn_h} = \frac{dU}{dn_h} + p \frac{dV}{dn_h} - T \frac{dS}{dn_h} = 0 ; \quad [5]
\]

where \( \varepsilon_h = dU/dn_h \) is the energy necessary to create one hole against the intermolecular forces and \( v_h = dV/dn_h \), the volume of a hole, is the increase in liquid volume when one new hole is introduced.

One can express \( S \) by

\[
S = k \ln P, \quad [6]
\]

where, according to Frenkel (3), \( P \) is the number of combinations which one can arrange from \( n_h \) holes and \( n_m \) molecules. \( P \) like \( \kappa \) depends on the form of the distribution of the holes (see Appendix). It is reasonable to assume that the number of holes does not change when a liquid at rest is subjected to a shear motion, as long as pressure and temperature remain constant. This is equivalent to the assumption that the volume of a liquid does not depend on its state of shear motion. In this case \( P \) has to be computed from the R-distribution and is found to be

\[
P = \frac{(n_h + n_m)!}{n_h! n_m!}. \quad [7]
\]

After introducing equations [6] and [7] into equation [5], one arrives at

\[
\frac{n_h}{n_h + n_m} = \exp \left( -\frac{\varepsilon_h + p v_h}{k T} \right) \quad [8]
\]

or

\[
\frac{n_h}{n_m} = 1 \left[ \exp \left( \frac{\varepsilon_h + p v_h}{k T} \right) - 1 \right]. \quad [9]
\]

The transition probability is then obtained by substituting equation [9] into equation [4] which results in

\[
\kappa = 1 \left[ \exp \left( \frac{\varepsilon_h + p v_h}{k T} \right) - 1 \right]. \quad [10]
\]