

Immobilization of Solvent in Randomly Coiled Chain Molecules

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(b) Within four percent, the ionization cross sections (for 50 volt electrons) of H_2^+ and D_2^+ , and probably HD^+ , are the same, as should be expected from theoretical considerations.

(c) The theoretical analysis mentioned above appears to be corroborated by experiment. Ion currents are proportional to partial pressure in the reservoir, but not to flow rate, and no mass corrections should be made.

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The Superconductivity of Lanthanum and Cerium¹

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June 10, 1948

MEASUREMENTS have been made of the variation with temperature of the magnetic permeability of lanthanum and cerium, using an apparatus and method similar to that described by Horn and Ziegler.² Lanthanum was found to be a superconductor, while cerium did not become superconducting down to 2°K, the lowest temperature at which these metals were studied.

Two different samples of lanthanum were studied. Sample 1,³ reported to contain 0.8 percent iron, exhibited a magnetic transition into superconductivity at $4.85 \pm 0.15^\circ K$. Sample 2 (Hilger, Lab. No. 7259), reported to contain between 0.5 and 1 percent aluminum, silicon, and tungsten, showed a similar transition at $4.45 \pm 0.10^\circ K$. In each instance the transition occurred over a range of less than 0.1° .

The sample of cerium² used was reported to contain 2.5 percent iron. No evidence for superconductivity in the material was observed down to 2°K, the lowest temperature reached. It is estimated that a transition of 10 percent of the material from the normal to a superconducting state could have been detected.

Lanthanum metal has previously been studied by Mendelssohn and Daunt,⁴ using a magnetic method. These investigators reported a transition temperature of $4.71^\circ K$ for a sample containing about 1 percent iron. Shoenberg,⁵ also using a magnetic method, has reported that a lanthanum sample (Hilger, Lab. No. 7259), presumably identical with our Sample 2, was superconducting at $4.2^\circ K$. On the other hand, McLennan, Allen, and Wilhelm⁶ have measured the electrical conductivity of "pure" samples of lanthanum and cerium from 300 to $1.9^\circ K$ and reported that neither substance became superconducting.

Further work on these and other rare earth metals is underway and will be reported in the near future.

¹ This work was carried out with the assistance of the Office of Naval Research under Contract No. N6-ori-192, Task Order 1.

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Immobilization of Solvent in Randomly Coiled Chain Molecules

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June 7, 1948

IT has been generally accepted that chain molecules, dissolved in a proper medium, assume the shape of a statistical coil.¹

The hydrodynamic behavior of a coil in a liquid has been studied first by W. Kuhn.¹ He has treated the limiting case in which the liquid inside the coil is completely immobilized if a translational motion of the coil is carried out or if the coil is suspended in a liquid with flow gradient. He has found that the intrinsic viscosity in this case is proportional to the square root of the degree of polymerization Z , and that the sedimentation constant s and the diffusion constant D are proportional to $Z^{1/2}$ and $Z^{-1/2}$, respectively.

$$\left. \begin{array}{l} \eta_{sp} \sim Z^{0.5} \\ s \sim Z^{0.5} \\ D \sim Z^{-0.5} \end{array} \right\} \text{ (complete immobilization). } \quad (1)$$

M. L. Huggins² assumed a few years later free draining of the solvent through the coil, using Kuhn's result concerning the shape of the coil and his treatment of the hydrodynamic behavior of a completely drained rod or filament (Perlenkettenmodell).³ In this case, the intrinsic viscosity turns out to be proportional to Z ,² the sedimentation constant independent on Z ⁴ and the diffusion constant proportional to Z^{-1} .⁴

$$\left. \begin{array}{l} \eta_{sp} \sim Z \\ s \sim Z^0 \\ D \sim Z^{-1} \end{array} \right\} \text{ (free draining). } \quad (2)$$

It has been pointed out⁴ in 1943 that the cases (1) and (2) are two limiting cases. The low members in a homologous series of polymers approach the limit (2) (free draining), the highest members the limit (1) (complete immobilization). The correctness of this statement was proved by empirical data concerning diffusion,* sedimentation,** viscosity,*** and birefringence of flow.† These considerations have been confirmed and extended on the basis of experiments on macroscopic models, using a hydrodynamic similarity principle.^{5,6}

In order to account for the hydrodynamic influence of partial immobilization upon the translational resistance of a statistical coil, the force K necessary to transport the coil through the liquid with a uniform velocity, u , was set up as

$$K = \lambda_{trans} \eta_0 L u, \quad (3)$$

η_0 is the viscosity of the solvent, and L the hydrodynamic length (end-to-end distance in the maximum extended chain). λ_{trans} is a numerical factor depending on the shape of the coil. On the basis of experiments on macroscopic models, λ_{trans} was found to be equal to

$$\lambda_{trans} = 1 / \left(0.02 + 0.16 \log^{10} \frac{A_m}{d_h} + 0.1 \left(\frac{L}{A_m} \right)^4 \right), \quad (3a)$$

d_h is the hydrodynamic thickness of the chain, and A_m the so-called length of the preferential statistical element (the

latter parameter is a constant for each homologous series and is equal to $A_m = \bar{h}^2/L$, \bar{h}^2 being the mean square distance between the ends of the chain).

Equations (3), (3a) include the two aforementioned limiting cases. For instance, in the case of large values of Z , it transforms to

$$\mathbf{K} = \eta_0 L u / \left(0.1 \left(\frac{L}{A_m} \right)^{\frac{1}{2}} \right) = 10 \eta_0 (L A_m)^{\frac{1}{2}} = 10 \eta_0 (\bar{h}^2)^{\frac{1}{2}} u,$$

which is approximately equal to the resistance $\mathbf{K} = 3\pi\eta_0(\bar{h}^2)^{\frac{1}{2}}u$ of a compact sphere of diameter equal to the average diameter of the coil (complete immobilization).

From Eqs. (3), (3a) can easily be obtained the following expressions for the sedimentation constant s and for the diffusion constant D ^{6,††}

$$s = a_1 + b_1(Z)^{\frac{1}{2}}, \quad (4)$$

$$D = (a_2 + b_2(Z)^{\frac{1}{2}}) \frac{1}{Z}, \quad (5)$$

where the constants

$$a_1 = \frac{M_g}{N_L b} \frac{1 - v_{\text{part}} \rho_0}{\eta_0} \left(0.02 + 0.16 \log^{10} \frac{A_m}{d_h} \right), \quad (4a)$$

$$b_1 = \frac{M_g}{N_L b} \frac{1 - v_{\text{part}} \rho_0}{\eta_0} 0.1 \left(\frac{b}{A_m} \right)^{\frac{1}{2}}, \quad (4b)$$

$$a_2 = \frac{kT}{\eta_0 b} \left(0.02 + 0.16 \log^{10} \frac{A_m}{d_h} \right), \quad (5a)$$

$$b_2 = \frac{kT}{\eta_0 b} 0.1 \left(\frac{b}{A_m} \right)^{\frac{1}{2}} \quad (5b)$$

are independent upon the degree of polymerization Z . N_L is Loschmidt's number, M_g the molecular weight of the monomer unit, v_{part} the partial specific volume of the solute, ρ_0 the density of the solvent, k Boltzmann's constant, T the absolute temperature, and b the hydrodynamic length of the monomer unit (b is related to the hydrodynamic length L of the chain by the expression $L = b \cdot Z$). Equations (4) and (5) are found to be verified by the empirical data.

The partial immobilization is as important for rotational as for translational motions of the coil. Rotational experiments on models have shown that the rotational resistance and thus the rotational diffusion constant of random coils are given by simple expressions [analogous to (3), (3a)] as functions of A_m , d_h , and L .⁵

The motion of a particle suspended in a liquid with flow gradient is a translation superimposed by a rotation of the particle; therefore the rotational diffusion constant determines to a large extent the birefringence of flow and the viscosity of the solution.^{3,7}

By introducing the result of our rotational experiments on models into our earlier equation,⁴ we obtain for the intrinsic viscosity^{6,8}

$$\frac{\eta_{sp}}{c} = \frac{A_m b^2}{48} \frac{N_L}{10^3} \frac{Z}{-0.05 + 0.12 \log^{10} \frac{A_m}{d_h} + 0.037 \left(\frac{bZ}{A_m} \right)^{\frac{1}{2}}} \quad \dagger, \ddagger \quad (6)$$

(c concentration in base moles per liter).

The orientation and the value of the birefringence of flow can equally be described by expressions that take into account the partial immobilization of liquid inside the coil.⁶

P. Debye¹¹ and H. C. Brinkman¹² have recently also recognized the importance of partial immobilization on the viscosity, apparently without knowledge of our investigations in this field. The considerations of these authors are, as far as they have come to our knowledge, very similar to our own and represent to a considerable extent another expression of the same results. Thus the introduction of a "shielding ratio" by Debye corresponds entirely to our partial immobilization, and the cases (1) and (2) discussed in 1943 have again been found by Debye. Our expressions have the advantage of containing parameters that are determined by experiments on models, while the corresponding parameters of these authors refer to a non-realized spherical shape of the coils considered.

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³ W. Kuhn, *Zeits. f. physik. Chemie A* **161**, 1 (1932); *Kolloid Zeits.* **62**, 269 (1932).

⁴ W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **26**, 1324 (1943).

* Reference 4, p. 1398.

** Reference 4, p. 1397.

*** Reference 4, p. 1443-44.

† Reference 4, p. 1420-21.

†† The linear relationship between the sedimentation constant and the square root of the degree of polymerization has already been recognized in our 1943 paper (reference 4, p. 1398).

‡ Equation (6) has been used already in reference 9, p. 85 and 92, reference 10, pp. 1573 and 1577.

‡‡ Reference 8 contains equally the corresponding quantitative expressions for branched chain molecules.

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"Volume Effect" and Random Flights

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June 14, 1948

THE so-called "volume effect" in flexible high polymer molecules has been a troublesome feature of high polymer theory since 1934.¹⁻³

This note is to point out that the effect may be computed by elementary methods. In the random flight notation of Chandrasekhar⁴ the probability of a flight of N randomly directed unit vectors from (x_1, y_1, z_1) to (x_2, y_2, z_2) (vector r_{12}) is

$$W_N(r_{12}) dx_2 dy_2 dz_2 = (2\pi^2 |r_{12}|)^{-1} \int_0^\infty \sin(|\lambda| |r_{12}|) \times (\sin |\lambda| / |\lambda|)^N |\lambda| d|\lambda| dx_2 dy_2 dz_2.$$

We write this in terms of the coordinates and abbreviate somewhat to

$$W_N(r_{12}) dx_2 dy_2 dz_2 = W_N(x_1, x_2) dx_2.$$

A path from point 1 to point 2 in N steps is denoted $1N2$.

Now the probability of a path of $S = L + M + N$ steps, $0L1M2N3$, is

$$W_L(0, x_1) W_M(x_1, x_2) W_N(x_2, x_3) dx_1 dx_2 dx_3.$$