

solution of potassium cyanosilverate, each piece reacts slowly to be replaced by a clump of black pyrophoric silver. Only a trace of hydrogen gas is given off before the solution becomes blue with excess potassium after reaction of all the complex cyanide. Thereafter hydrogen is very, very slowly given off until the blue color of the dissolved potassium disappears. Thus the clumps of silver are very poor catalysts for the formation of potassium amide and hydrogen. The silver was not reactive with water.

**Potassium Cyanozincate,  $K_2Zn(CN)_4$ , and Sodium.**—Sodium reacts rapidly with a liquid ammonia solution of potassium cyanozincate to give a finely divided precipitate of metallic zinc. This precipitate is not reactive with water nor is it pyrophoric. No hydrogen gas is given off during its formation nor after the solution has become blue with excess sodium. Thus the precipitate is not a catalyst for the amide formation. At the instant the solution becomes blue with excess sodium, a beautiful silvery mirror is formed on the walls of the reaction tube exposed to the solution. This mirror was not reactive with water.

The formation of zinc instead of  $NaZn_4$  is comparable to the case wherein Burgess and Rose<sup>4</sup> observed the formation

(4) Burgess and Rose, *THIS JOURNAL*, **51**, 2127 (1929).

of metallic zinc by reaction of sodium with a 20% excess of zinc cyanide.

**Potassium Cyanonickelate,  $K_2Ni(CN)_4$ , and Calcium.**—Calcium, when added to a solution of potassium cyanonickelate in liquid ammonia, gives the same type of reaction as does sodium and potassium,<sup>2</sup> but with the difference that hydrogen gas is given off throughout the course of the reaction. The insoluble reaction products are soluble in water to give the characteristic red solutions.

### Summary

Unlike that of nickel, the complex cyanides of cadmium, copper, silver and zinc are reduced to the free metal by alkali metals in liquid ammonia solutions. Under the conditions used all of the precipitated metals but zinc were pyrophoric.

Calcium, in liquid ammonia solution, reduces alkali metal cyanonickelates to give the same type of products as obtained by reduction with alkali metals

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## The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration<sup>1</sup>

BY MAURICE L. HUGGINS

In the first<sup>2</sup> and second<sup>3</sup> papers of this series an equation was derived for the specific viscosity ( $\eta_{sp}$ ) of dilute solutions of randomly-kinked chain compounds. At the limit of infinite dilution this equation reduces to

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = \frac{\eta - \eta_0}{\eta_0} = K_0 + K_n n = K_0 + K_M M \quad (1)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and of the pure solvent,  $c$  is the concentration in submoles per liter (or any units proportional to these),  $n$  is the number of submolecules per molecule,  $M$  is the molecular weight, and  $K_0$ ,  $K_n$  and  $K_M$  are constants.

In deriving this expression, Stokes' law

$$\text{Force} = 6\pi\eta au \quad (2)$$

was assumed in computing the frictional force acting on each submolecule as a result of its velocity ( $u$ ) relative to the liquid immediately sur-

rounding it. The insertion of  $\eta_0$  for  $\eta$  in (2) leads to the limiting Equation (1) just given. If, instead, one inserts into (2) the value of the viscosity of the solution

$$\eta = \eta_0(1 + \eta_{sp}) \quad (3)$$

the expression

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} (1 + \eta_{sp}) \quad (4)$$

is obtained.<sup>4</sup>

For small concentrations, (4) is equivalent to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + \left(\frac{\eta_{sp}}{c}\right)_{c=0}^2 c \quad (5)$$

At first sight, it might seem that this should give the initial variation of  $\eta_{sp}/c$  with concentration. The application of Equation (2) to the solutions under discussion is, however, very questionable. Strictly speaking, this equation would be applicable only if each submolecule were isolated from all others, so that the liquid streaming past one

(4) This is equivalent to Eq. (25) of ref. 2 and, except for the Einstein term in the numerator, to Eqs. (123) and (126) of ref. 3. If Einstein's derivation (which also depends on (2)) is similarly modified, to make it applicable to solutions of finite concentration, by the use of  $\eta$  instead of  $\eta_0$  for the frictional coefficient in Stokes' law, Eqs. (123) and (126) of ref. 3 also become equivalent (as regards the concentration dependence) to (4) above.

(1) Presented before the Division of Colloid Chemistry at the Buffalo Meeting of the American Chemical Society, Sept. 9, 1942. Some of the material contained herein was previously presented at the Symposium on "Viscosity, Molecular Size and Molecular Shape," held under the sponsorship of the Society of Rheology at the Polytechnic Institute of Brooklyn on Feb. 20, 1942.

(2) M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938).

(3) M. L. Huggins, *ibid.*, **43**, 439 (1939).

would not be affected by the disturbances of the streaming around other submolecules. Moreover, the use of this equation involves the assumptions that the submolecules are spherical and are large relative to the solvent molecules, also that there is no sliding friction, as the solvent molecules move around the submolecules. It certainly does not seem proper, in calculating the dissipation of energy when a *solute* submolecule interacts with the surrounding (chiefly *solvent*) molecules, to use a value of  $\eta$  which is related primarily to the mutual interaction between *solvent* molecules.

It seems reasonable to assume that these objections to the use of Equation (2) can all be met, approximately, by the introduction in it of another factor,  $k'$ , having a magnitude characteristic of the system under consideration—depending on the sizes, shapes and cohesive properties of both solvent molecules and solute submolecules, but not on the number of submolecules (*i. e.*, the length) of the solute molecule chain. In place of (2), we thus put

$$\text{Force} = 6\pi k' \eta a u \quad (6)$$

This leads to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} (1 + k' \eta_{sp}) \quad (7)$$

which is identical with an empirical equation recently published by Schulz and Blaschke<sup>5</sup> and tested by them on solutions in chloroform of methyl methacrylate polymers. The same value of  $k'$  (0.30) was found satisfactory for unfractionated polymers of various average sizes and for their fractions (see Fig. 1).

Equation (7) can readily be put into the form

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + k' \left(\frac{\eta_{sp}}{c}\right)_{c=0}^2 c + \text{terms in higher powers of } c \quad (8)$$

the higher terms being negligible for dilute solutions. This form is especially well suited for comparison with the many other equations which have been proposed to represent the variation with concentration of the viscosity of solutions. Nearly all of them can be expanded into an expression of this sort; they differ only with respect to the value and interpretation of  $k'$  and with respect to the higher terms. Although we shall not here enter into an exhaustive comparison of these various equations, a few will be mentioned.

Martin,<sup>6</sup> considering data for solutions of a

(5) G. W. Schulz and F. Blaschke, *J. prakt. Chem.*, **158**, 130 (1941).

(6) A. F. Martin, paper presented at the Memphis Meeting of the American Chemical Society, April, 1942.

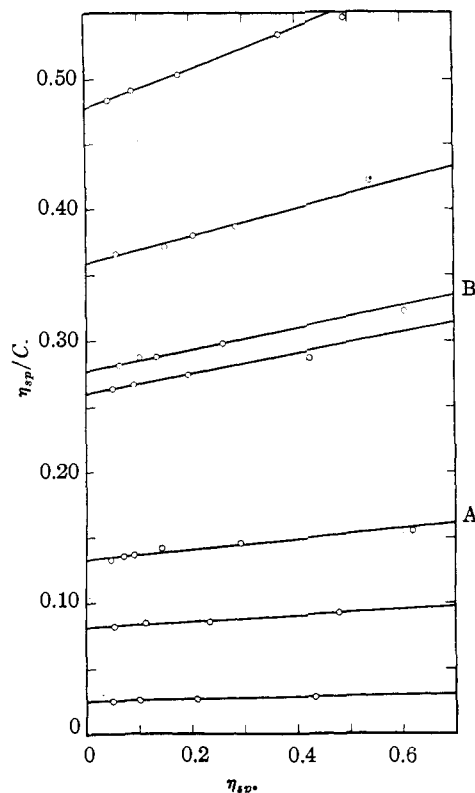


Fig. 1.—Illustrating the agreement with Eq. (4) for solutions in chloroform of methyl methacrylate polymers: concentrations in g./l.; data by Schulz and Blaschke.<sup>5</sup> The samples giving the curves labelled A and B were obtained by fractionation; the other samples were unfractionated.

variety of high-molecular weight solutes in various solvents, has concluded that the relation

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} \exp \left[ k_M \left(\frac{\eta_{sp}}{c}\right)_{c=0} c \right] \quad (9)$$

accurately represents the viscosity-concentration relationships up to concentrations of 5%, the constant  $k_M$  varying with solvent and with solute, but being constant for members of a given polyhomologous series dissolved in a given solvent. Neglecting the higher terms in the expansion of the exponential, this equation reduces to Equation (8), with  $k'$  equal to  $2.3 k_M$ , thus confirming the theoretical argument just outlined.

The equations

$$\frac{\eta}{\eta_0} = (1 + k_B c)^{k'_B} \quad (10)$$

$$\eta_{sp} = \frac{k_F k' c}{1 - k' c} \quad (11)$$

and

$$\eta_{sp} = k_J c e^{k'_J c} \quad (12)$$

have been proposed by Baker,<sup>7</sup> by Fikentscher

(7) F. Baker, *J. Chem. Soc.*, **103**, 1653 (1913).

and Mark,<sup>8</sup> and by de Jong, Kruyt and Lens,<sup>9</sup> respectively. Here  $k_B$ ,  $k_B'$ ,  $k_F$ , etc., are empirically determined constants. These equations all reduce to Equation (8), with  $k'$  equal to  $1/2 - 1/2k_B'$ ,  $1/k_F$ , and  $k'_J/k_J$ , respectively.

Arrhenius,<sup>10</sup> Hess and Philippoff<sup>11</sup> and Bredée and de Booy<sup>12</sup> have proposed the following equations, respectively

$$\ln\left(\frac{\eta}{\eta_0}\right) = k_{AC}c \quad (13)$$

$$\frac{\eta}{\eta_0} = \left(1 + \frac{k_{HC}c}{8}\right)^8 \quad (14)$$

$$\frac{\eta}{\eta_0} = \left(1 + \frac{5k_{BBC}c}{12}\right)^6 \quad (15)$$

The last two are special cases of Baker's equation, (10). All three reduce to Equation (8), with  $k'$  equal to  $1/2$ ,  $7/16$  and  $5/12$ , respectively,—constants independent of the solvent-solute system. As would be expected, these inflexible equations do not give as good general agreement as do (7) and (9)–(12), which contain an additional adjustable constant.

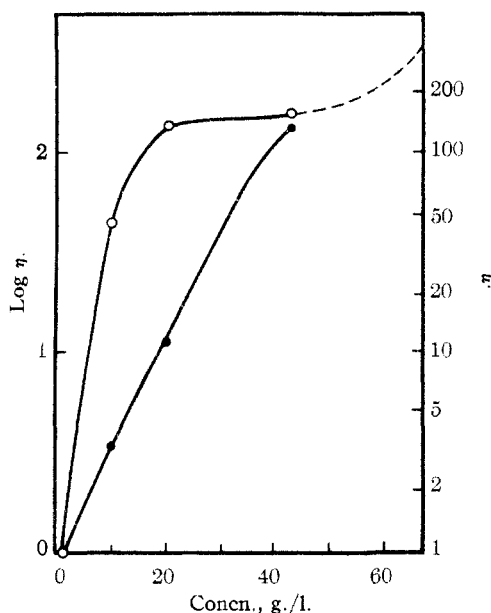


Fig. 2.—Dependence of viscosity on concentration, for polyisobutylene (polybutene) solutions in *n*-butyl ether: O, 20°; ●, 37.78°; data by Evans and Young.<sup>14</sup>

It should be noted that our comparison of these various equations for the concentration dependence of viscosity has concerned only the initial slope of the  $\eta_{sp}/c$  vs.  $c$  curve and so applies only

(8) H. Fikentscher and H. Mark, *Kolloid-Z.*, **49**, 135 (1930).

(9) H. G. de Jong, H. R. Kruyt and W. Lens, *Kolloid-Beihfte*, **36**, 429 (1932).

(10) S. Arrhenius, *Medd. Vetenskapskad., Nobel-inst.*, **4**, 13 (1916).

(11) K. Hess and W. Philippoff, *Ber.*, **70B**, 639 (1937).

(12) H. L. Bredée and J. de Booy, *Kolloid-Z.*, **79**, 31 (1937).

to quite dilute solutions. We shall not here enter into a discussion of the theoretical or empirical treatment of this dependence at higher concentrations, except to make one remark:

If the attractions between *like* molecules in the solution are considerably more potent than those between *unlike* molecules—as indicated<sup>13</sup> by a large value of  $\mu_1$  and by a separation into two phases at sufficiently high concentrations—the solute molecules tend to form aggregates at concentrations somewhat below that at which the second phase becomes evident. This results in a viscosity-concentration curve with a slope which decreases (or even becomes negative) at the higher concentrations. Solutions of polyisobutylene in *n*-butyl ether at 20°, for example, show this effect<sup>14</sup> (see Fig. 2). As would be expected, the anomalous behavior disappears as the temperature is raised;  $\mu_1$  is decreased and the aggregates are dissociated. The viscosity behavior of solutions of polyisobutylene in benzene is likewise anomalous,<sup>15</sup> apparently for the same reason.

### Summary

1. It has been shown that a simple, reasonable modification of the author's previous theoretical treatment of the viscosity of dilute solutions of long-chain molecules leads to the equation

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} (1 + k'\eta_{sp})$$

for the initial concentration dependence of the viscosity. This is identical with an equation arrived at empirically by Schulz and Blaschke.

2. The constant  $k'$  is characteristic of a given solute-solvent system; it is the same for solutions, in a given solvent, of different members of a polymer-homologous series, however.

3. At low concentrations (such as assumed in the theoretical derivation), this relationship is equivalent to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + k' \left(\frac{\eta_{sp}}{c}\right)_{c=0}^2 c$$

Equations proposed by Baker, by Fikentscher and Mark, by de Jong, Kruyt and Lens, and by Martin all reduce to this same limiting equation, with  $k'$  different for different systems. Equations proposed by Arrhenius, by Hess and Philippoff, and by Bredée and de Booy likewise reduce to this form, but with  $k'$  having the same value for all systems.

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(13) M. L. Huggins, *THIS JOURNAL*, **64**, 1712 (1942).

(14) H. C. Evans and D. W. Young, *Ind. Eng. Chem.*, **34**, 461 (1942).

(15) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1192 (1942).