repeated until crystallization no longer occurred. The total yield of slightly impure acid obtained in this fashion was 20.0 g. (26%). The acid was purified by four recrystallizations from absolute alcohol.

N,N'-Dibutylethylenediaminediacetic Acid.—The procedure employed was the same as that given for the N,N'-dicyclohexylethylenediaminediacetic acid: 25.0 g. of N,N' dibutylethylenediamine in 150 ml. of water reacted with 35.0 g. of sodium chloroacetate to give 6.0 g. (15%) of N,N'-dibutylethylenediaminediacetic acid. Five recrystallizations from absolute alcohol gave fine colorless crystals of pure material.

N,N'-Dibenzylethylenediaminediacetic Acid.—By the same procedure, 24.03 g. (0.1 mole) of N,N'-dibenzylethylenediamine in 100 ml. of alcohol reacted with 23.3 g. (0.2 mole) of sodium chloroacetate to give 4.25 g. (12%) of N,N'-dibenzylethylenediaminediacetic acid.

N,N'-Didodecylethylenediaminediacetic Acid.—To 26.54 g. of the sodium salt of N-dodecylglycine in 200 ml. of water, 4.94 g. (0.05 mole) of ethylene dichloride was added dropwise over a period of one hour. The mixture was then refluxed for one and one-half hours after which 4.94 g. more of ethylene dichloride was added and the mixture refluxed for thirty-two more hours. To minimize foaming of the mixture, a current of air was passed over the surface throughout the entire reaction. Evaporation of the mixture to dryness *in vacuo* produced a slightly yellow residue which was ground to a fine powder and extracted with absolute alcohol. The solution was evaporated to dryness under reduced pressure. This resulted in the isolation of a viscous residue which was obtained in crystalline form by the addition of acetone; 10.30 g. (20%) of impure material was thus obtained. The impure N,N'-didodecylethylenediaminediacetic acid was purified by two recrystallizations from a 70% acetone–30% water solution.

Potentiometric Method.—One hundred milligrams of the N,N'-dialkylethylenediaminediacetic acid was dissolved in 100 ml. of water and titrated with standard sodium hydroxide (approximately 0.0100 N). The *p*H was determined with the aid of a Beckmann model G *p*H meter. To test for complex formation with copper, stoichiometric amounts of cupric sulfate were added to the solution of the N,N'-dialkylethylenediaminediacetic acid and the resulting solution titrated as outlined. Complex formation with calcium was determined in the same fashion; the ratio of calcium chloride to N,N'-dialkylethylenediaminediacetic acid used was 15 to 1. In cases where the acid was only slightly soluble in water, the titrations were carried out on a vigorously stirred suspension of the acid.

Spectrophotometric Method.—The absorption spectra were determined by means of a Beckmann model DU photoelectric quartz spectrophotometer. All measurements were made in the ultraviolet region (220–350 mμ) with quartz cells having a light path of 1 cm.

TABLE II

ABSORPTION DATA

COPPER CHELATES OF N,N'-DIALKYLETHYLENEDIAMINEDIACETIC ACIDS

Alkyl	Obs. max. in mμ	$E \times 10^3$	Solvent
Butyl	260	3.78	Water
Cyclohexyl	260	1.50	Water
Octyl	245	3.40	Ethanol
Dodecyl	250	7.14	Ethanol
Benzyl	255	2.70[a]	Water

[a] The extinction varied somewhat with concentration in this case. Otherwise Beer's law seemed to hold.

Acknowledgment.—The authors express their appreciation to F. C. Bersworth of Framingham, Massachusetts, for financial support for this research. The choice of the topic was made with his full coöperation, and the work was greatly aided by his continued interest and advice.

Summary

The preparation of N,N'-dialkylethylenediaminediacetic acids from dibutyl-, dioctyl-, didodecyl-, dicyclohexyl- and dibenzylethylenediamine is described. Titration and absorption spectra studies indicated that all the amino acids with the exception of the dicyclohexyl derivative formed strong chelates with copper ions, while titration data indicated only weak chelate-formation with calcium ions.

BERKELEY, CALIF. RECEIVED NOVEMBER 25, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Mechanical Properties of Substances of High Molecular Weight. VI. Dispersion in Concentrated Polymer Solutions and its Dependence on Temperature and Concentration

BY JOHN D. FERRY

In previous studies of the rigidities of concentrated polystyrene[1] and polyisobutylene[2] solutions, derived from measurements of transverse wave propagation, the dependence on frequency appeared to be small over a limited frequency range; it was ignored except in the more dilute polystyrene solutions, where an effort was made to extrapolate to a limiting high frequency value based on the assumption of a Maxwell model. On this basis, it was found that the rigidity was an exponential function of the reciprocal absolute temperature and was proportional to the third power of the volume concentration.

Subsequent measurements on solutions of polyvinyl acetate in various solvents,[3] of polystyrene in decalin,[4] and of a styrene–maleic anhydride copolymer in dioxane–water mixtures[5] have shown a dispersion which cannot be ignored; the wave rigidity,[2] $\tilde{G}$, increases monotonically with frequency. Also, solutions of polystyrene in xylene have been re-examined in larger cells than used previously[1]

---

(1) J. D. Ferry, THIS JOURNAL, **64**, 1323, 1330 (1942).

(2) J. N. Ashworth and J. D. Ferry, *ibid.*, **71**, 622 (1949).

(3) W. M. Sawyer and J. D. Ferry, unpublished.

(4) L. D. Grandine, Jr., and J. D. Ferry, unpublished work.

(5) D. C. Udy and J. D. Ferry, unpublished work.

to permit observation of longer wave lengths and consequently extension of the frequency range originally covered. The results show a definite increase in rigidity with frequency (Fig. 1), even though they are consistent with the values originally reported within the frequency range then available.

When dispersion exists, the dependence of rigidity on temperature and concentration can be recorded at constant frequency, but this is of doubtful significance because marked shifts of the dispersion spectrum with temperature and concentration can be anticipated.[6,7]

On the basis of some simple assumptions regarding stress relaxations in these solutions, however, the simultaneous variation of rigidity with frequency, temperature, and composition can be expressed by a single empirical function for each polymer–solvent system, as shown below. This treatment indicates that the relationships previously described were fortuitous, and it leads to a somewhat different, and simpler, molecular interpretation.

Theory

It is assumed that the behavior of a linear polymer in small shear deformations, whether undiluted (as long as the temperature is above the brittle point) or in concentrated solution, corresponds to an (unspecified) array of springs coupled by viscous elements. Any such array can be represented[8] by a group of Maxwell elements in parallel, forming the Maxwell model used by Kuhn,[9] Alfrey and Doty,[10] and others in which each spring[11] G_i is relaxed by a dashpot $\tau_i G_i$. The real part of the dynamic rigidity,[12] G', real part of the dynamic viscosity,[12] η', and steady flow viscosity, η, are given[9,10] by

$$G'(\omega) = \sum_i G_i\omega^2\tau_i^2/(1 + \omega^2\tau_i^2) \qquad (1)$$

$$\eta'(\omega) = \sum_i \tau_i G_i/(1 + \omega^2\tau_i^2) \qquad (2)$$

$$\eta = \sum_i \tau_i G_i \qquad (3)$$

where ω is the circular frequency.

Dependence on Temperature.—It is assumed that all relaxation mechanisms—at least those contributing significantly to G', η', and η under the experimental conditions—have the same temperature dependence, so that when the temperature is changed from a standard value T_0 (*e. g.*, 298°K.) to T each τ_i is multiplied by the same factor a_T. If the springs are rubberlike elasticity mechanisms, each G_i is proportional to T; $G_i = (T/T_0)G_{i_0}$ where G_{i_0} is the contribution of the mechanism at the standard temperature T_0. Eqs. 1–3 become

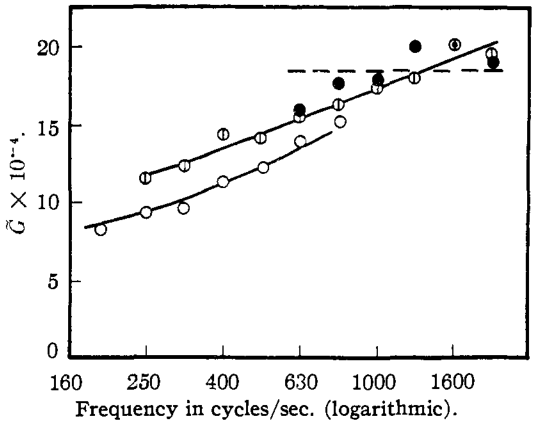


Fig. 1.—Wave rigidities of solutions of polystyrene in xylene: ○, $\bar{M}_n$ = 187,000, 41.5%; ⦶, $\bar{M}_n \cong$ 150,000, 39.5%; ●, earlier measurements,[1] $\bar{M}_n$ = 153,000, 42.2%. The dashed line indicates the average value reported previously on the assumption of independence of frequency.

$$G'(\omega) = (T/T_0) \sum_i G_{i0}\omega^2 a_T^2\tau_i^2/(1 + \omega^2 a_T^2\tau_i^2) = (T/T_0)G_0'(\omega a_T) \qquad (4)$$

$$\eta'(\omega) = (a_T T/T_0) \sum_i \tau_i G_{i0}/(1 + \omega^2 a_T^2\tau_i^2) = (a_T T/T_0)\eta_0'(\omega a_T) \qquad (5)$$

$$\eta = (a_T T/T_0) \sum_i \tau_i G_{i0} = (a_T T/T_0)\eta_0 \qquad (6)$$

where G_0', η_0', and η_0 are the values of the respective quantities at T_0. It is clear that, by plotting $(T_0/T)G'$ and $(T_0/a_T T)\eta'$ against ωa_T, data at different temperatures should superpose to give two universal dispersion functions. Moreover, the value of a_T for this transformation can be obtained simply from the ratio of the steady flow viscosities at the two temperatures (Eq. 6). This type of superposition has already been shown to be successful for the dynamic mechanical properties of undiluted polyisobutylene.[13]

Strictly, there should be a small correction for thermal expansion, because the mechanical quantities refer to a unit cube of material and with decreasing density this cube contains fewer elastic and viscous elements. This can be taken into account together with the effect of dilution, as follows.

Dependence on Concentration.—The superposition scheme may now be extended by supposing that all relaxation mechanisms have the same concentration dependence; *i. e.*, the addition of diluent to reduce the polymer concentration from ρ (density of pure polymer) to c (g. polymer per cc. solution) multiplies each τ_i by the same factor a_c. The effect of dilution on the

---

(6) A. P. Alexandrov and J. S. Lazurkin, *Acta Physiochim. U. R. S. S.*, **12**, 647 (1940).

(7) A. W. Nolle, *J. Polymer Sci.*, **5**, 1 (1950).

(8) W. Kuhn, *Helv. Chim. Acta*, **30**, 487 (1947).

(9) W. Kuhn, O. Künzle and A. Preissmann, *ibid.*, **30**, 307 (1947).

(10) T. Alfrey and P. Doty, *J. Appl. Physics*, **16**, 700 (1945).

(11) A continuous distribution of elements may of course be employed, but this leads to normalization complications in the present discussion.

(12) J. D. Ferry, W. M. Sawyer and J. N. Ashworth, *J. Polymer Sci.*, **2**, 593 (1947); *cf.* H. Leaderman, *J. Colloid Sci.*, **4**, 193 (1949).

(13) R. S. Marvin, E. R. Fitzgerald and J. D. Ferry, *J. Appl. Physics*, **21**, 197 (1950).

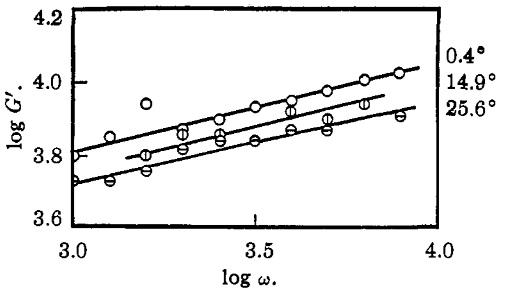


Fig. 2.—Dispersion of dynamic rigidity for polyvinyl acetate (M_n = 840,000) in 1,2,3-trichloropropane, concentration 17.0%, at three temperatures indicated by figures in margin.

contribution of each spring to the rigidity is not obvious *a priori*. However, the experimental data can be fitted only by postulating that each G_i is directly proportional to c; each type of mechanism contributes in proportion to the mass of polymer per unit volume. Then, at constant temperature, Eqs. 1–3 become

$$G'(\omega) = (c/\rho)\sum_i G_{i0}\omega^2 a_c^2\tau_i^2/(1 + \omega^2 a_c^2\tau_i^2) = (c/\rho)G_0'(\omega a_c) \quad (7)$$

$$\eta'(\omega) = (a_c c/\rho)\sum \tau_i G_{i0}/(1 + \omega^2 a_c^2\tau_i^2) = (a_c c/\rho)\eta_0'(\omega a_c) \quad (8)$$

$$\eta = (a_c c/\rho)\sum_i \tau_i G_{i0} = (a_c c/\rho)\eta_0 \quad (9)$$

where the subscript 0 here refers to the pure polymer. It follows that when $(\rho/c)G'$ and $(\rho/a_c c)\eta'$ are plotted against ωa_c, data at different concentrations should superpose, and the values of a_c for this transformation are again obtainable from the steady flow viscosities of solution and pure polymer.

Dependence on Temperature and Composition.—The effects of both temperature and composition on the dispersion functions can be combined by multiplying the coefficients of the summations, and using the product $a_T a_c$ as the coefficient of ω. Since $\eta = (a_T a_c cT/T_0\rho)\ \eta_0$, $a_T a_c$ may be replaced by $(\eta/\eta_0)(\rho T_0/Tc)$, giving

$$G'(\omega) = (cT/T_0\rho)G_0'(\omega\eta T_0\rho/\eta_0 Tc) \quad (10)$$

$$\eta'(\omega) = (\eta/\eta_0)\eta_0'(\omega\eta T_0\rho/\eta_0 Tc) \quad (11)$$

where now the subscript 0 refers to pure polymer at T_0. (If the brittle point temperature is above T_0, this is a hypothetical state.)

In practice, since for a given polymer ρ and η_0 are constant, we plot log $(G'T_0/Tc)$ (reduced dynamic rigidity) and log (η'/η) (reduced dynamic viscosity) against log $(\omega\eta T_0/Tc)$ (reduced frequency), and expect to find superposition at all temperatures and concentrations to give two universal dispersion curves. Such curves refer to a hypothetical rheological standard state of unit density and unit steady flow viscosity. Even though this standard state is non-existent, it affords the most convenient method for correlating data at different temperatures and concentrations; there is, of course, a good precedent from thermodynamics for the use of a hypothetical reference state. Logarithmic plots are chosen because the relative, rather than the absolute, precision of the data is roughly constant over the ranges covered.

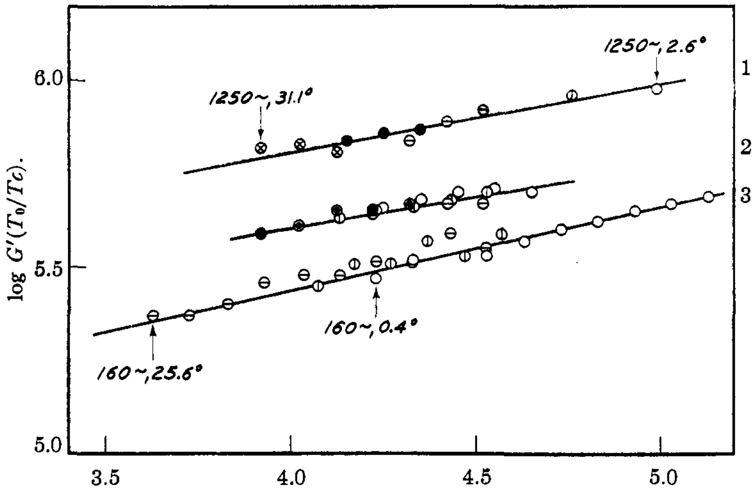


Fig. 3.—Superposition of reduced dynamic rigidity *vs.* reduced frequency at different temperatures: Curve 1, polystyrene in xylene, concentration 52.3%; O, 2.6°; ⦶, 8.0°; ⊖, 16.5°; ●, 22.9°; ⊗, 31.1°. Curve 2, polyisobutylene in xylene, concentration 25.1%; O, 1.8°; ⦶, 10.8°; ⊖, 20.0°; ●, 28.0°. Curve 3, polyvinyl acetate in 1,2,3-trichloropropane (data and key same as in Fig. 2). The logarithm of the viscosity at 25° has been subtracted from the logarithm of the reduced frequency in each case to bring the three curves in the same range of abscissas.

Experimental Tests

Superposition at Different Temperatures.—An example of dispersion of G' at three different temperatures for a solution of polyvinyl acetate in 1,2,3-trichloropropane[3,14] is shown in Fig. 2. When the reduced rigidity is plotted logarithmically against the reduced frequency (which has been calculated using steady flow viscosity measurements reported elsewhere[15]), these three curves superpose within experimental scatter, forming curve 3 of Fig. 3. Here the weight concentration of polymer is constant, and c varies only slightly because of thermal expansion with changing T. Figure 3 shows also superposition of the reduced dynamic rigidity at different temperatures for solutions of polystyrene in xylene[1,16] and polyisobutylene in xylene.[2,17] (To condense the figure, the

---

(14) F. T. Adler, W. M. Sawyer and J. D. Ferry, *J. Appl. Physics*, **20**, 1036 (1949).

(15) J. D. Ferry, E. L. Foster, W. M. Sawyer and G. V. Browning, *J. Phys. Coll. Chem.* (to be submitted).

(16) The viscosity values used for polystyrene solutions were extrapolated to zero shearing stress from the original data[1] by a hyperbolic sine function, and differ slightly from the values reported earlier based on a linear extrapolation.

(17) Viscosity measurements on polyisobutylene solutions have been made by Drs. T. L. Smith and M. F. Johnson and Mr. L. D. Grandine, Jr.

logarithm of the viscosity at 25° has been subtracted from the logarithm of the reduced frequency in each case.)

The calculation of the dynamic rigidity G' requires measurement of not only the wave length of transverse waves (λ) but also the damping index (λ/x_0), which often cannot be determined with sufficient accuracy. Data are usually presented in the form of the wave rigidity $\tilde{G}$, which is calculated from the wave length alone and is greater than G' by the factor $[4\pi^2 + (\lambda/x_0)^2]^2/4\pi^2[4\pi^2 - (\lambda/x_0)^2]$. In practice, λ/x_0 varies within the extreme limits of 0.6 to 2.0, and is most often about 1.2; the ratio $\tilde{G}/G'$ varies from 1.07 to 1.33, and is most often about 1.1. To the extent that this ratio is constant, the reduced wave rigidity $\tilde{G}T_0/Tc$ should also give superposition when plotted against reduced frequency. This is illustrated in Fig. 4 for three polystyrene solutions, each at several different temperatures.

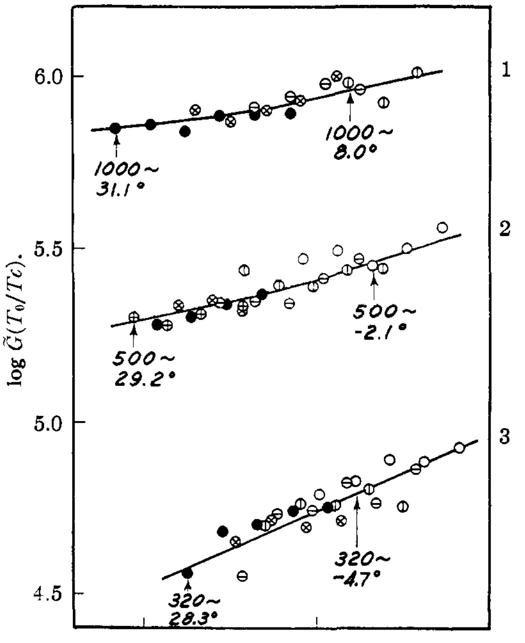


Fig. 4.—Superposition of reduced wave rigidity *vs.* reduced frequency at different temperatures, for polystyrene in xylene.[1] Curve 1, 52.3%; ⦶, 8.0°; ⊖, 16.5°; ⊗, 22.9°; ●, 31.1°. Curve 2, 31.8%; O, −2.1°; ⦶, 8.3°; ⊖, 12.5°; ⊗, 20.1°; ⊕, 24.7°; ●, 29.2°. Curve 3, 15.3%; O, −4.7°; ⦶, 8.6°; ⊖, 14.0°; ⊗, 25.4°; ●, 28.3°. The logarithm of the viscosity at 25° has been subtracted from the logarithm of the reduced frequency in each case to bring the three curves in the same range of abscissas.

Superposition at Different Concentrations.—The best single test of the superposition method is provided by the very precise data of Philippoff[18] on the dynamic viscosity of cellulose acetate in dioxane. At 25°, over the concentration range from 8 to 18%, the steady flow viscosity varies from 28 to 2500 poises and the dynamic viscosity from 6 to 110 poises within the frequency range from 52 to 630 cycles/sec.[19] When the reduced dynamic viscosity is plotted logarithmically against the reduced frequency, excellent superposition is obtained (Fig. 5) except for the lowest concentration, which represents the least precision.

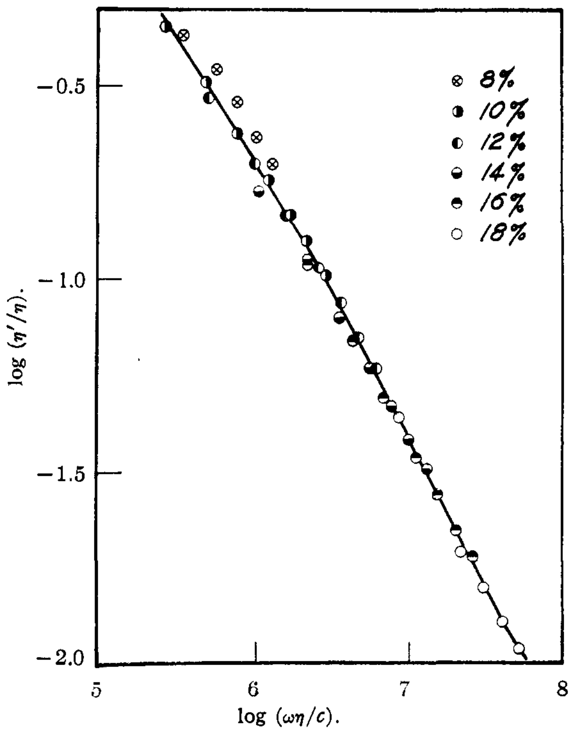


Fig. 5.—Superposition of reduced dynamic viscosity *vs.* reduced frequency at different concentrations, for cellulose acetate in dioxane at 25° (data of Philippoff). The figures denote concentrations in weight per cent. Since $T = T_0$, the factor T_0/T is omitted from the reduced frequency.

A similar plot of fragmentary data from this Laboratory on dynamic viscosities of polyvinyl acetate in 1,2,3-trichloropropane[21] and polyisobutylene in xylene,[22] obtained from transducer measurements,[23] is shown in Fig. 6. While the different concentrations do not overlap, they are fitted by a single smooth curve in each case.

Superposition at Different Concentrations and Temperatures.—Superposition of reduced dynamic rigidity when both concentration and temperature are varied is illustrated for polyisobutylene in xylene in Fig. 7. The data are calculated from the measurements of Ashworth[24] and unpublished viscosity studies,[17] and they fall on a single smooth curve.

Further tests at different concentrations and temperatures are at present limited to the wave rigidity, $\tilde{G}$. A composite plot[25] of reduced wave rigidity for polyisobutylene in xylene[24,17] is given in Fig. 8, and one for polystyrene in xylene[1,16] in Fig. 9. The different concentrations are identified; each concentration covers several different temperatures ranging from about −5 to 40°. These plots show more scatter, but the fit by a single curve in each case is probably within experimental error. The polystyrene data antedate experimental refinements currently in use and are the least accurate of those discussed here.

---

(18) W. Philippoff, *Physik. Z.*, **35**, 900 (1934).

(19) Plots of some of Philippoff's data have been reproduced in References 12 and 20. It was shown[11] that curves of η'/η against the logarithm of the frequency could be made to superpose by arbitrary shifts along the latter axis, but the relation of these shifts to η and c was not then recognized.

(20) J. D. Ferry, *J. Res. Nat. Bur. Standards*, **41**, 53 (1948).

(21) G. V. Browning, Ph.D. Thesis, University of Wisconsin, 1948.

(22) T. L. Smith, Ph.D. Thesis, University of Wisconsin, 1948.

(23) T. L. Smith, J. D. Ferry and F. W. Schremp, *J. Appl. Physics*, **20**, 144 (1949).

(24) J. N. Ashworth, Ph.D. Thesis, University of Wisconsin, 1948.

(25) We are indebted to Mr. W. Van Valkenburg for assistance in preparing these figures.

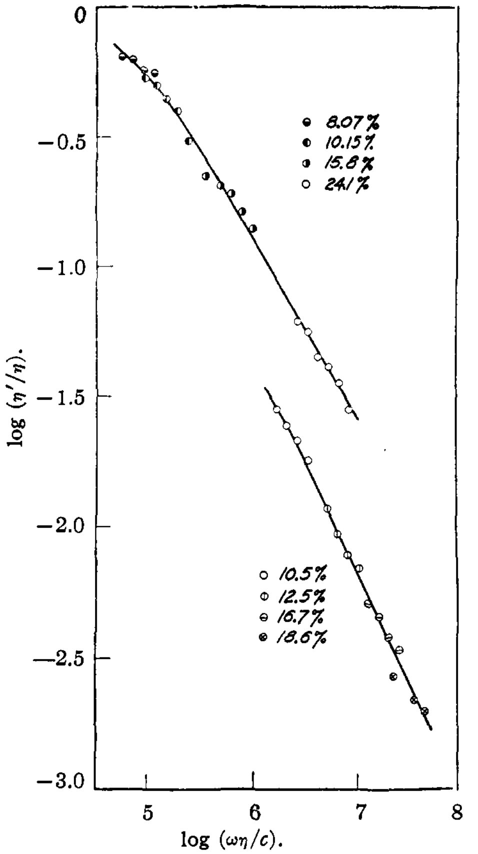


Fig. 6.—Superposition of reduced dynamic viscosity *vs.* reduced frequency at different concentrations at 25°: upper curve, polyvinyl acetate in 1,2,3-trichloropropane; lower curve, polyisobutylene in xylene. The figures denote concentrations in weight per cent.

A subsequent paper[3] will give further examples of superposition tests for solutions of polyvinyl acetate in different solvents. The reduced wave rigidity shows good superposition in each solvent, and the composite curves for the different solvents fall quite close to each other. Other applications of the method will be reported later.[4,5]

Discussion

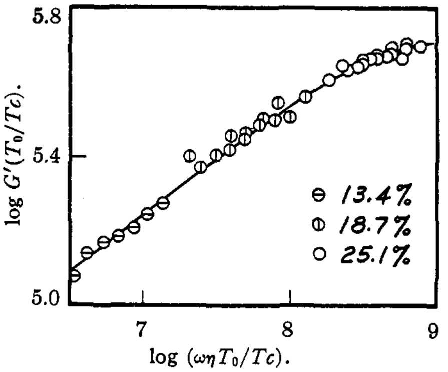


Fig. 7.—Superposition of reduced dynamic rigidity *vs.* reduced frequency, for polyisobutylene in xylene at different concentrations and temperatures. The figures denote concentrations in weight per cent.; temperatures range from −5 to 25°.

The above tests show that a single function can represent the simultaneous dependence of dynamic rigidity or viscosity on frequency, temperature, and concentration well enough to make the method useful for economical presentation of large numbers of data. A more critical test can be provided by measurements of very concentrated solutions at very low frequencies or dilute solutions at very high frequencies, which will be attempted subsequently. It is doubtful whether the single function can be employed either for extremely dilute solutions where polymer coils no longer overlap (and the solvent viscosity no doubt enters explicitly), or for extremely high concentrations (where associations between polymer segments, especially if the brittle point of the pure polymer lies above the experimental temperature, or the solvent cohesive energy density is not well matched, may affect long relaxations more than short relaxations).

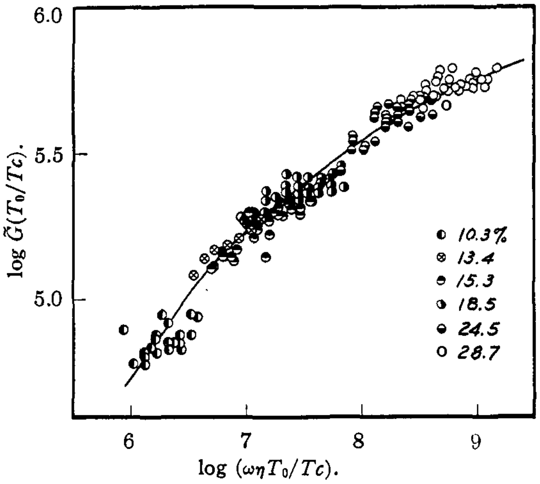


Fig. 8.—Superposition of reduced wave rigidity *vs.* reduced frequency, for polyisobutylene in xylene at different concentrations and temperatures. The figures denote concentrations in weight per cent.; temperatures range from −5 to 36°.

Within the ranges investigated, however, the success of this treatment supports the postulates on which it is based. The postulate that the temperature dependence of all relaxation mechanisms is the same has been previously made, though with reservations concerning its range of applicability.[26] Since the steady flow viscosity involves a summation (Eq. 3) over mechanisms that increase in number and variety with increasing molecular weight of the polymer, it is a corollary that the ratio of two steady flow viscosities at different temperatures (and the same concentration) should be independent of the polymer molecular weight.

[26] H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," The Textile Foundation, 1943, p. 76; T. Alfrey, "Mechanical Behavior of High Polymers," Interscience Publishers, New York, N. Y., 1948, p. 132.

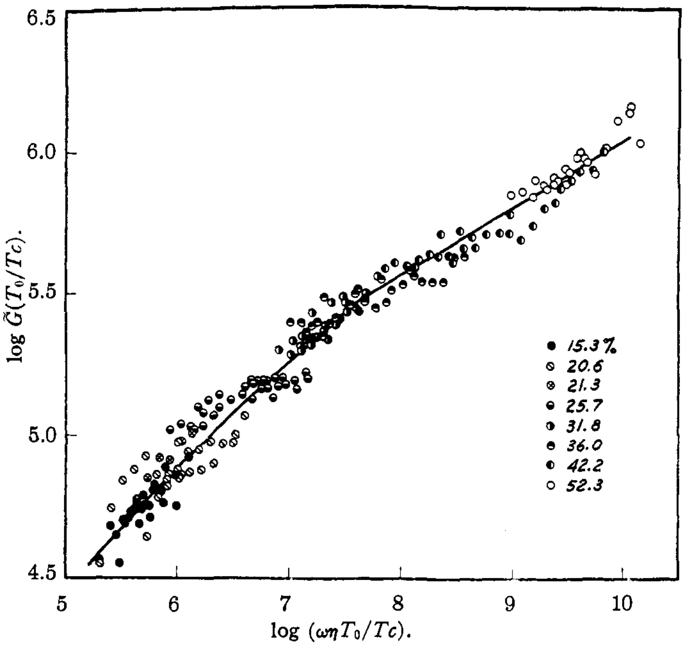


Fig. 9.—Superposition of reduced wave rigidity *vs.* reduced frequency for polystyrene in xylene at different concentrations and temperatures. The figures denote concentrations in weight per cent.; temperatures range from −6 to 43°.

This is true for undiluted polyisobutylene and for polystyrene (above the brittle point) provided the molecular weight is not too small[27]; and it is approximately true for concentrated solutions of polystyrene,[28] polyisobutylene,[17] and polyvinyl acetate,[15] although in the latter case a slight increase in temperature dependence with molecular weight is observed.

The postulate that the concentration dependence of all relaxation mechanisms is the same is less familiar, but it is reasonable that the rate of rearrangement of any chain segment should depend in the same manner on the concentration of foreign molecules interlaced through it. It is a corollary of this postulate that the ratio of two steady flow viscosities at different concentrations should be independent of the polymer molecular weight. This is approximately true for polystyrene,[28] polyisobutylene[17] and polyvinyl acetate[15]; the concentration dependence increases slightly with molecular weight, but except for quite low molecular weights the effect is small.

The present treatment shows that, although at constant frequency the rigidity has been found to be proportional to the third power of concentration, at constant *reduced* frequency it is proportional to the first power. The number of elasticity mechanisms of each type is apparently proportional to the amount of polymer present, and the distribution of types is unaffected by dilution. This behavior cannot be described by the oversimplified concept, used previously,[2,20] of distinct entanglement points whose number depends on concentration. The concept of energy storage by twist against the hindering potential opposing free rotation,[2,20] previously introduced to explain the dependence of rigidity on concentration, and of dubious plausibility at low audio frequencies, is no longer necessary. Instead, the energy storage may be attributed to rubberlike elasticity mechanisms.

It is of interest to show *a posteriori* that the damping index, λ/x_0, is approximately independent of frequency within the ranges considered here, so that a logarithmic plot of reduced wave rigidity ($\tilde{G}$) should have approximately the same shape as one of reduced dynamic rigidity (G'). The slopes of logarithmic reduced viscosity plots (Figs. 5 and 6) are about -0.7; those of logarithmic reduced rigidity plots (Figs. 3, 4, 7, 8 and 9) range from 0.25 to 0.45. Thus, roughly, $\eta'/\eta \propto (\omega\eta T_0/cT)^{-0.7}$ and $G'(T_0/Tc) \propto (\omega\eta T_0/cT)^{0.35}$. The ratio $\eta' Tc/\eta G' T_0 \propto (\omega\eta T_0/cT)^{-1.05}$. If the damping is not large,[12] $\lambda/x_0 \cong \pi\omega\eta'/G'$, which is then proportional to $(\omega\eta T_0/cT)(\omega\eta T_0/cT)^{-1.05} = (\omega\eta T_0/cT)^{-0.05}$. Within the ranges covered in these studies, therefore, the damping index changes only slightly with reduced frequency. This conclusion is supported by experience,[29] although in other ranges of the reduced frequency, inaccessible by wave propagation measurements but studied by transducers,[13,23] the ratio $\omega\eta'/G'$ does vary considerably.

Measurements at different temperatures and concentrations can thus be combined to give an approximate picture of the dispersion functions of dynamic viscosity and rigidity over an extended frequency range. The relations of these empirical functions to each other, to similar functions derived from measurements on undiluted polymers, and to molecular behavior, will be considered subsequently.

This work was supported in part by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation, and in part by a grant from Research Corporation.

Summary

1. The dynamic mechanical properties of concentrated polymer solutions may be described by the reduced dynamic rigidity, $G'T_0/Tc$, and reduced dynamic viscosity, η'/η, where G' and η' are the real parts of the complex dynamic rigidity and viscosity, respectively, η is the steady flow viscosity, T the absolute temperature, c the concentra-

---

(27) T. G. Fox and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948).

(28) R. S. Spencer and J. L. Williams, *J. Colloid Sci.*, **2**, 117 (1947).

(29) The retarded Maxwell model, used previously to fit data within a limited frequency range,[2] predicts a rapid increase of λ/x_0 at both high and low frequencies which cannot be reconciled with this treatment.

tion (mass polymer per unit volume), and T_0 a standard absolute temperature. These are plotted against a reduced frequency, $\omega\eta T_0/Tc$, where ω is the circular frequency. For a given polymer–solvent system, all data at different temperatures and concentrations superpose to give two universal dispersion functions for the reduced dynamic rigidity and viscosity. A single function is also obtained, approximately, if $\tilde{G}$, the wave rigidity, is substituted for G'.

2. These relations can be derived by postulating a set of elasticity mechanisms, each of which contributes to the rigidity in proportion to the total mass of polymer per unit volume and to the absolute temperature, and is relaxed by a viscous mechanism such that all relaxation times depend identically on temperature and concentration.

MADISON, WISCONSIN RECEIVED JANUARY 16, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

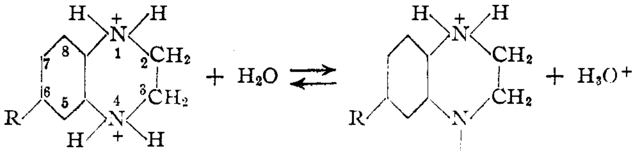
1,2-Diamines. II.[1] Thermodynamic Acidity Constants of 1,2,3,4-Tetrahydroquinoxaline and its 6-Methyl and 6-Methoxy Derivatives[2]

BY J. C. CAVAGNOL AND GORDON WILSON, JR.

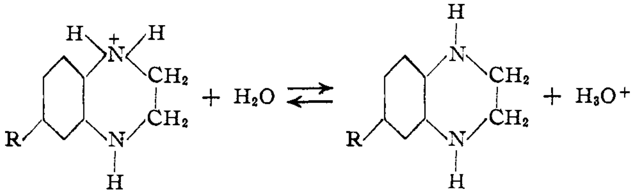
Introduction.—Compelling experimental evidence has been presented by Hammett[3,4] for the existence of a quantitative relationship between the type and position of a nuclear substituent and the effect of the concomitant internal electronic displacement on side-chain reactions. His substituent constant σ is defined as

$$\sigma = \log K_i - \log K_i^0 = pK_i^0 - pK_i \qquad (1)$$

where K_i^0 and K_i are the thermodynamic acidity constants of unsubstituted, and the corresponding meta- or para-substituted, acids. This constant is characteristic of the substituent only and is practically independent of the type of equilibrium involved. Since a series of these constants were derived from studies involving side-chain reactions of simple benzene derivatives, the possibility existed that a new variation in the structure of the reactive moiety might produce molecules that were capable of yielding similar correlations. One interesting aspect of this theory is a consideration of the effect of structural modifications upon the reactivity of bifunctional heterocyclic systems. The present paper is concerned with the feasibility of extending Hammett's equation to equilibria involving diprotic 1,2,3,4-tetrahydro-6-substituted quinoxalines (I), where the 6-position is "meta" to N^4 and "para" to N^1, as shown.



I (2)



(3)

A number of methods have been developed for calculating acidity constants of dibasic acids from pH measurements of solutions containing the acid and various amounts of inorganic base. Britton[5] and Gane and Ingold[6] determined the first and second acidity constants of several aliphatic dicarboxylic acids in the concentration range of 0.00125–0.05 M, but made no corrections for activity coefficients. Speakman,[7] in a similar study, limited the concentration of acid to below 10^{-3} M and was able to closely approximate the ionic strength from simple solution constants. Activity coefficients were calculated by using the Debye–Hückel limiting law.[8] German, *et al.*,[9] used Britton's method for computing the classical acidity constants of several series of dicarboxylic acids, then converted these values to thermodynamic acidity constants by utilizing the Debye–Hückel limiting law. These workers determined ionic strengths accurately with an equation derived by considering the degree of dissociation of the weak acid and acid anion.

The thermodynamic acidity constants of 1,2,3,4-tetrahydroquinoxaline dihydrochloride were determined previously[1] after evaluating activity coefficients by means of Bjerrum's[10] equation.

---

[1] This paper is an extension of the work described in the article entitled, "1-Alkyl-1,2,3,4-tetrahydroquinoxalines," by Cavagnol and Wiselogle, THIS JOURNAL, **69**, 795 (1947).

[2] Abstracted from a thesis submitted to the Graduate School by Gordon Wilson, Jr., in partial fulfillment of the requirements for the degree of Master of Science.

[3] Hammett, THIS JOURNAL, **59**, 96 (1937).

[4] See also "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940. Chapter VII.

[5] Britton, *J. Chem. Soc.*, **127**, 1896 (1925).

[6] Gane and Ingold, *ibid.*, 2153 (1931).

[7] Speakman, *ibid.*, 855 (1940).

[8] Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, Chapter V.

[9] German, Jeffery and Vogel, *J. Chem. Soc.*, 1624 (1935); German and Vogel, THIS JOURNAL, **58**, 1546 (1936).

[10] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).