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

Mechanical Properties of Substances of High Molecular Weight. VII. Rigidities of Polyvinyl Acetate Solutions in Various Solvents[1]

BY W. M. SAWYER[2] AND JOHN D. FERRY

From measurements of the propagation of transverse waves, the rigidities of concentrated solutions of polystyrene[3] and polyisobutylene[4] have been determined, and their dependence on frequency, temperature and concentration has been described.[5] For comparison with these non-polar polymers, which are soluble only in solvents of low cohesive energy density, we have now investigated polyvinyl acetate, in whose solutions stronger intermolecular forces may be expected. Rigidities have been measured in several polar solvents; and, in one solvent, for several polymer fractions of different molecular weights.

At constant frequency and concentration, the dependence of rigidity on temperature is greater than for the non-polar polymers, and its dependence on the nature of the solvent is considerable. When the reduced wave rigidity is plotted against the reduced frequency, however, following a treatment developed elsewhere,[5] the temperature dependence disappears and the solvent dependence becomes rather slight.

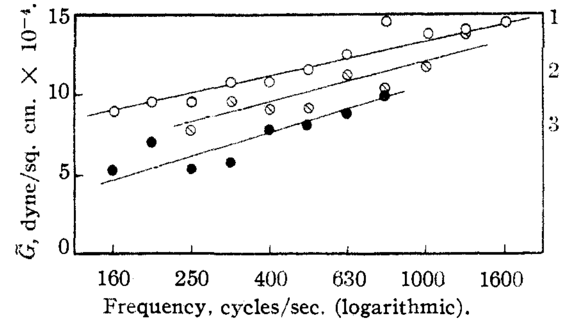

Fig. 1.—Dispersion of rigidity in trichloropropane, 17% at −4.7 ± 0.4°: 1, Fraction I; 2, Fraction II; 3, unfractionated (interpolated).

Materials and Methods

The polyvinyl acetate (AYAX, lot 1232) was kindly furnished us by Mr. A. K. Doolittle, of the Carbide and Carbon Chemicals Corporation. Its number-average molecular weight,[6] $\overline{M}_n$, was 140,000. While most of the experiments were made with unfractionated polymer, a few were carried out on rough fractions[6] with the following values of $\overline{M}_n$: I, 840,000; II, 280,000; III, 62,000. In handling the fractions care was taken to exclude dust and lint which would interfere with optical measurements.[4]

Methyl ethyl ketone, cyclohexanone and 1,2,3-trichloropropane were distilled through a 30-plate Oldershaw column. Methyl isobutyl ketone and diisopropyl ketone (Carbide and Carbon Chemicals Corp.) were dried over anhydrous sodium sulfate and used without further purification.

The preparation and analysis of solutions, measurements of wave length, and calculation of the wave rigidity $\tilde{G}$ were carried out following procedures previously described.[4] Measurements of wave damping, which were made in some cases, will be reported subsequently.[7] Densities were calculated on the assumption that the volumes of polymer and solvent were additive, using the value of 1.19 for the density of the polymer. In the case of methyl ethyl ketone and 1,2,3-trichloropropane, this has been shown to be a close approximation.[6] In some cases Eastman Kodak Co. Tri-X cut film was used for photographing the wave patterns, but the best results were obtained with Contrast Process Panchromatic film, which afforded much higher contrast between light and dark Babinet bands.

Three combinations of different sizes of cells and vibrator plates were used, described as a, c and d in Paper V of this series.[4] Since both theoretical analysis[8] and experimental comparison[4,8] have shown that within experimental error the measured wave parameters of these polymer-solvent systems are not influenced by cell and plate dimensions, the different combinations are not distinguished here.[9]

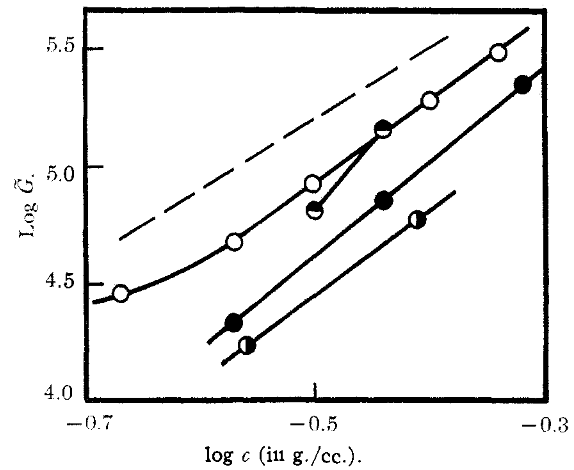

Fig. 2.—Log $\tilde{G}$ plotted against log c (concentration in g./cc.) at 500 cycles/sec. and 25°, for solutions of unfractionated polymer in: 1,2,3-trichloropropane (○); methyl isobutyl ketone (●); methyl ethyl ketone (◑); and cyclohexanone (◓). Dashed line is drawn with slope of 3.

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[2] Shell Development Company, Emeryville, California.

[3] J. D. Ferry, THIS JOURNAL, **64**, 1323 (1942).

[4] J. N. Ashworth and J. D. Ferry, *ibid.*, **71**, 622 (1949).

[5] J. D. Ferry, *ibid.*, **72**, 3746 (1950).

[6] G. V. Browning and J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).

[7] J. D. Ferry, W. M. Sawyer, G. V. Browning and A. H. Groth, Jr., *J. Applied Phys.*, **21**, 513 (1950).

[8] F. T. Adler, W. M. Sawyer and J. D. Ferry, *ibid.*, **20**, 1036 (1949).

[9] The complete data exclusive of those for the fractions are recorded in the Ph.D. Thesis of W. M. Sawyer, University of Wisconsin, 1948.

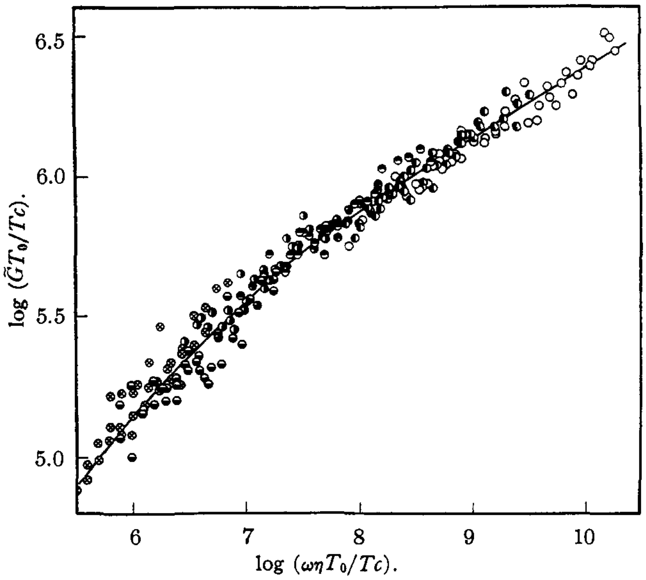

Fig. 3.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency, for solutions of unfractionated polymer in trichloropropane at concentrations (weight per cent.) of: 15.8% (⊗); 20.0% (◒); 23.8% (◑); 30.4% (◓); 35.1% (◐); and 40.3% (○). Temperatures range from −3 to 41°.

Results and Discussion

In every solution, the wave rigidity increased monotonically with frequency. The magnitude of the dispersion diminished with increasing molecular weight (Fig. 1). At constant frequency and weight concentration, over the temperature range from −5 to 40°, plots of the logarithm of the rigidity against the reciprocal absolute temperature, following the original method used[3] to describe temperature dependence, could be fitted by straight lines within experimental scatter. The slopes of these lines gave values of $Q_{\tilde{G}}$ ($= R(\mathrm{d}\ln\tilde{G}/\mathrm{d}(1/T))$) of about 2500 cal. for Fractions I and II in 1,2,3-trichloropropane and 3800 cal. for the unfractionated polymer in all solvents, as compared with 500 cal. for polyisobutylene[4] and 1500 cal. for polystyrene.[3]

At constant frequency and temperature, the rigidity was roughly proportional to the third power of concentration (expressed as g./cc.), as found previously for other polymer–solvent systems.[4] This relationship is shown in Fig. 2 for solutions of the unfractionated polyvinyl acetate in 1,2,3-trichloropropane, methyl isobutyl ketone and methyl ethyl ketone. The concentration range covered is from about 0.2 to 0.5 g./cc.

The above relationships are probably less significant, however, than those revealed by plotting the reduced wave rigidity,[5] $\tilde{G}T_0/Tc$, against the reduced frequency, $\omega\eta T_0/Tc$, a procedure which affords an economical presentation of large numbers of data. Here T is the absolute temperature, c the concentration in g. polymer per cc. solution, T_0 = 298°K., and η is the steady flow viscosity, interpolated from measurements on these same solutions which are reported elsewhere.[10] 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, it can be shown[5] that a plot of reduced rigidity against reduced frequency as defined above should yield a single curve for data at different temperatures and concentrations.

The reduced rigidity is plotted logarithmically against reduced frequency in Figs. 3–5 for solutions of the unfractionated polymer in 1,2,3-trichloropropane, methyl isobutyl ketone and methyl ethyl ketone; the ranges of temperature and concentration covered are given in the legends of the figures.[11] Some fragmentary data in cyclohexanone and diisopropyl ketone are given in Fig. 6. The superposition at all concentrations and temperatures is satisfactory within experimental error, and indicates that the dependence of rigidity on these variables is primarily due to shifts of the relaxation spectrum along the logarithmic frequency scale[5]; the con-

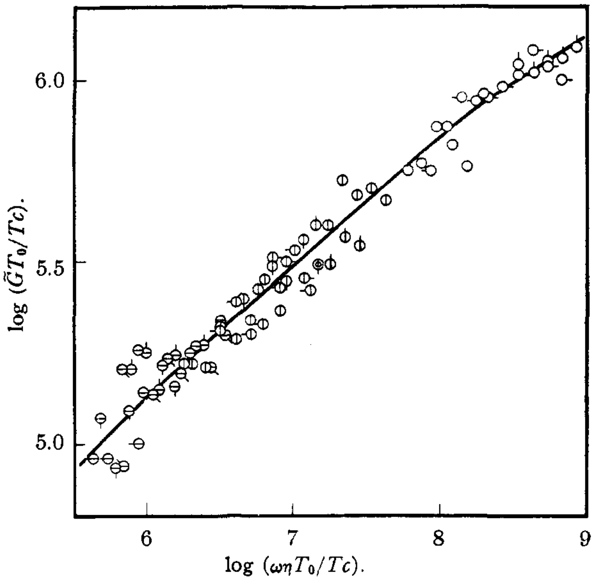

Fig. 4.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency, for solutions of unfractionated polymer in methyl isobutyl ketone at concentrations (weight per cent.) of: 30.5% (⊖); 40.9% (⦶); and 50.2% (○). Different temperatures, ranging from −8 to 21°, are distinguished by tags.

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[10] J. D. Ferry, E. L. Foster, W. M. Sawyer and G. V. Browning, *J. Phys. Coll. Chem.*, to be submitted.

[11] We are much indebted to Mr. W. Van Valkenburg for assistance in preparing these plots.

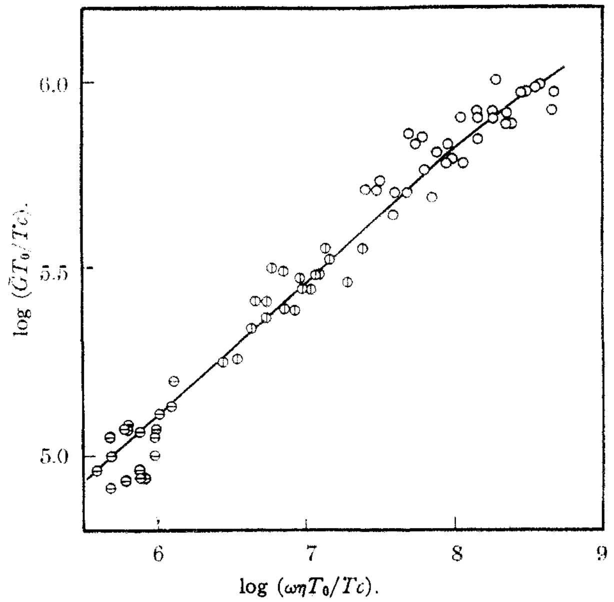

Fig. 5.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency, for solutions of unfractionated polymer in methyl ethyl ketone at concentrations (weight per cent.) of: 31.1% (⊖); 42.4% (⦶); and 50.4% (○). Temperatures range from −8 to 16°.

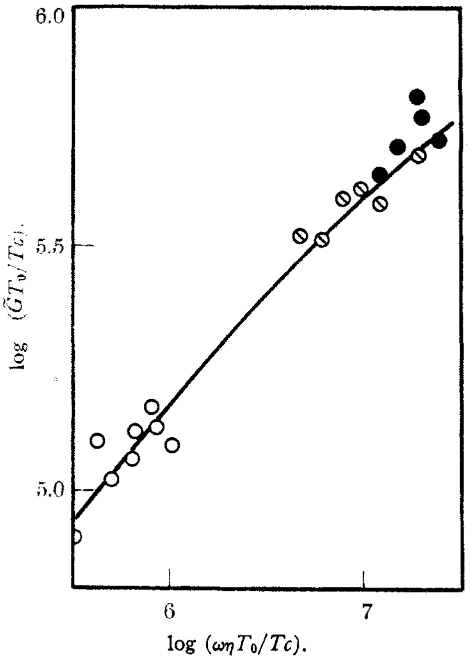

Fig. 6.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency, for solutions of unfractionated polymer in cyclohexanone at 20.2% (○) and 35.5% (⊖); and in diisopropyl ketone at 43.8% (●).

tribution of each elasticity mechanism is evidently proportional to the volume concentration and to the absolute temperature.

Effect of Solvent.—If the rigidities are compared at constant frequency, temperature and concentration, the effect of solvent appears rather large, as Fig. 2 shows; the rigidity in trichloropropane is greater than that in methyl ethyl ketone by over a factor of three. If, however, the reduced rigidity is expressed as a function of reduced frequency, the curves for different solvents fall very close together, as shown by the superposition of Figs. 3–6 in Fig. 7. As a first approximation, therefore, the nature of the solvent is without effect except as it shifts the relaxation spectrum. Comparison of steady flow viscosities (which reflect the same shift, since they depend on summations over all relaxation mechanisms[5]) relative to solvent viscosities shows[10] that this effect is primarily due to the viscosity of the solvent itself. The case of diisopropyl ketone is of interest because it is only partially miscible with the polymer; unless the concentration of polymer exceeds about 40%, a two-phase system is formed. In spite of the considerable mismatch of cohesive energy density indicated by this behavior, the reduced rigidity fits in rather closely with the values for the other solvents, all of which mix with the polymer in all proportions.

The small differences which remain apparent in Fig. 7 show a decrease in the reduced rigidity in the order cyclohexanone > 1,2,3-trichloropropane > methyl isobutyl ketone > methyl ethyl ketone; their significance is uncertain. The order is almost the same as that for the small differences in steady flow viscosity data when relative viscosities are compared at constant volume concentration,[10] between 0.15 and 0.30 g./cc.: trichloropropane > cyclohexane > methyl

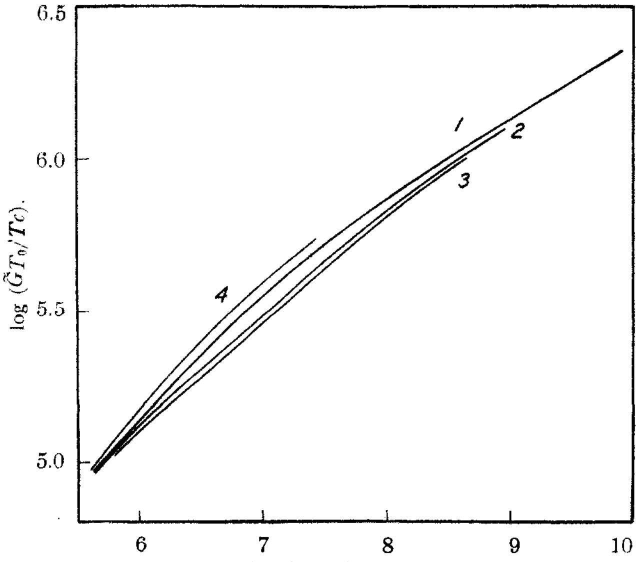

Fig. 7.—Superposition of curves from Figs. 3–6: 1, trichloropropane; 2, methyl isobutyl ketone; 3, methyl ethyl ketone; 4, cyclohexanone.

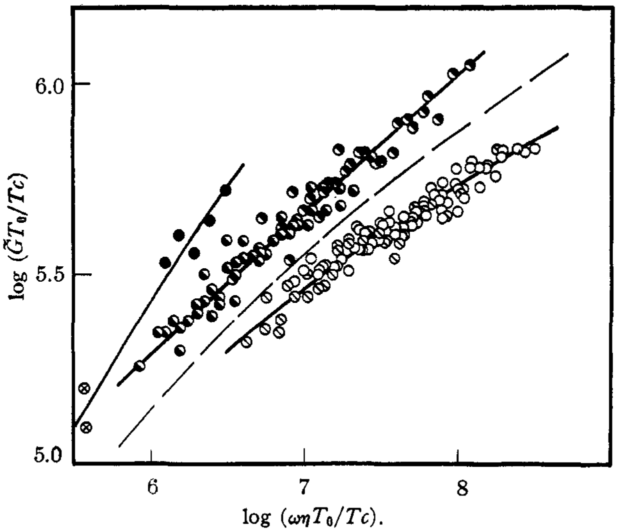

Fig. 8.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency, for solutions of samples of different molecular weight in 1,2,3-trichloropropane. Fraction I: ⊖, 14.3%; O, 17.0%. Fraction II: ◐, 17.3%; ◑, 22.6%. Fraction III: 26.1%;' ●, 0.1°; ⊗, 25.0°. Unfractionated: dashed line. Temperatures for Fractions I and II range from −4 to 25°. Concentrations are given in weight per cent.

isobutyl ketone > methyl ethyl ketone. All these four liquids are excellent solvents; both the trichloropropane and methyl ethyl ketone have negative partial molal heats of dilution.[6] However, the trichloropropane interacts more strongly than the ketone, since its heat of dilution is numerically much larger, as is also its partial molal entropy of dilution. Differences in local molecular interaction are probably responsible for the differences in mechanical properties.

Effect of Molecular Weight.—The reduced rigidities of the three fractions in trichloropropane are plotted logarithmically against the reduced frequency in Fig. 8, where the curve for the unfractionated polymer is also reproduced from Fig. 3. At constant reduced frequency, the rigidity decreases with increasing molecular weight. However, this is equivalent to comparing the different samples in hypothetical standard states of unit viscosity at 25°. It would be more significant to compare them referred each to the standard state of the pure polymer above its brittle point; or, since this is impractical for polyvinyl acetate, whose brittle point is above room temperature, the standard states may be chosen as solutions of identical concentration. This is achieved for $c = 0.25$ g./cc. by subtracting the logarithm of the viscosity at this concentration from the logarithm of the reduced frequency, with the result shown in Fig. 9. The rigidity increases with molecular weight as expected, and the curves tend to converge at high frequencies, where it would be expected that the mechanical properties, being determined by smaller and smaller chain segments, would become independent of molecular weight.

The dependence of slope on molecular weight in Fig. 9 may be interpreted similarly. It would be expected that with decreasing frequency the slope would become steeper, as the rigidity is determined more and more by long segments and the limitation imposed by the finite length of the polymer molecules becomes increasingly serious. The smaller the molecular weight, the higher the frequency range to which the effect of finite length extends. Thus, in a plot such as Fig. 9, at a given frequency the slope increases with decreasing molecular weight.

Conclusions.—The rigidity behavior of a given sample of polyvinyl acetate in concentrated solutions in several different solvents can be described to a fair approximation by a single dispersion curve giving the dependence of reduced rigidity on reduced frequency. In spite of the polar nature of polyvinyl acetate compared with polyisobutylene or polystyrene, and the higher cohesive energy densities of the solvents used in this study compared with the hydrocarbons used to dissolve the latter polymers, the dispersion curve represented by Fig. 7 is very similar in shape to those obtained for the non-polar polymers.[5] A quantitative comparison

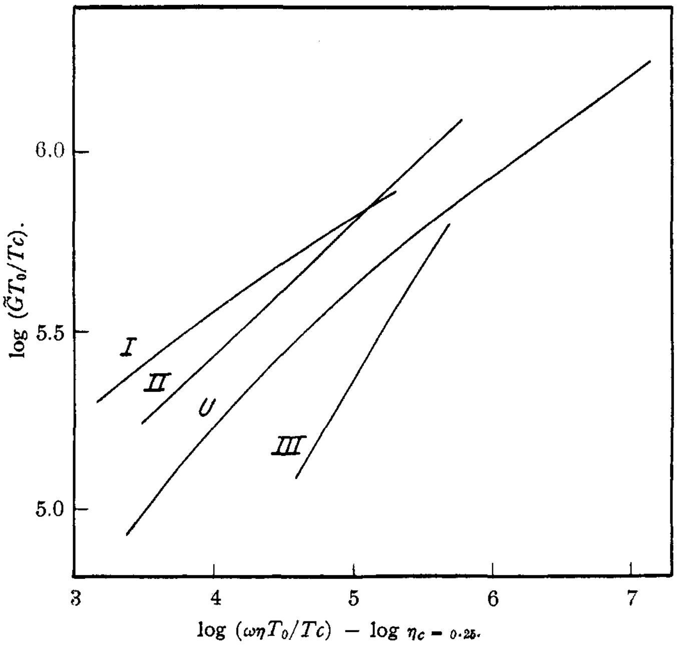

Fig. 9.—Logarithm of reduced rigidity plotted against logarithm of reduced frequency minus logarithm of viscosity at $c = 0.25$ g./cc., for solutions of different samples in trichloropropane. U = unfractionated; numerals denote fractions.

must await a more complete study of the effect of molecular weight and molecular weight distribution on these curves. It appears, in any case, that all amorphous polymers of similar molecular weights in reasonably good solvents will show very similar behavior, and that the shape of the dispersion curve is characteristic of a loose entanglement of flexible molecules.

Summary

1. The propagation of transverse waves in solutions of an unfractionated polyvinyl acetate ($\bar{M}_n = 140{,}000$) in 1,2,3-trichloropropane, methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone and diisopropyl ketone, and of three fractions of different molecular weights in trichloropropane, has been studied as a function of temperature, concentration and frequency.
2. The wave rigidity, $\tilde{G}$, increases with frequency, decreases with increasing temperature, and increases with concentration.
3. In each solvent, the reduced wave rigidity, $\tilde{G}T_0/Tc$, plotted against the reduced frequency, $\omega\eta T_0/Tc$ (where ω is the circular frequency, η the steady flow viscosity, c the concentration in g./cc., T the absolute temperature, and $T_0 = 298°$ K.) gives a single dispersion curve on which data for all concentrations and temperatures superpose.
4. The dispersion curves for the unfractionated polymer in different solvents lie very close together and resemble in shape the corresponding curves obtained previously for polystyrene and polyisobutylene.
5. When the dispersion curves for samples of different molecular weight are reduced to comparison at $c = 0.25$, they appear to converge at high frequencies, while with decreasing frequency they diverge, the rigidity falling off more rapidly the lower the molecular weight.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. VII. Further Studies on the Argentation of Substituted Benzenes

BY L. J. ANDREWS AND R. M. KEEFER

In previous communications[1,2] the solubilities of certain aromatic hydrocarbons and substituted benzenes in aqueous silver nitrate have been reported. These data have been used to calculate equilibrium constants for the formation of the water soluble complexes, $AgAr^+$ and Ag_2Ar^{++}. It has been postulated[1,3] that the aromatic nucleus donates electrons to silver ion in forming such complexes and that the magnitude of the equilibrium constant for the formation of $AgAr^+$ may be considered a measure of the basicity of the aromatic ring in question.[4] Supporting these postulates is the observation that the magnitudes of the argentation constants for the formation of $AgAr^+$ using a variety of monosubstituted benzenes increase with increasing capacity of the substituents to furnish electrons to the ring.[2] In this regard it is of interest to note that the logarithms of these argentation constants yield a straight line when plotted against the Hammett[5] σ_{meta} values for the various ring substituents.

With these facts in mind the argentation studies have been extended, as described in this report, to include a number of other aromatic substances. In particular the solubilities in aqueous silver nitrate of mesitylene, several monoalkylbenzenes, styrene and a few of its derivatives have been investigated.

Experimental

Materials.—The following Eastman Kodak Co. white label materials were fractionated for use in the solubility measurements: mesitylene, b. p. 165.0°; ethylbenzene, b. p. 136.0°; isopropylbenzene, b. p. 151.5–152.0; *n*-propylbenzene, b. p. 157.8–158.1°; *t*-butylbenzene, b. p. 167.8–168.0°; *n*-butylbenzene, b. p. 182.0–183.0°; *s*-butylbenzene, b. p. 175.0–175.8°; *t*-amylbenzene, b. p. 188.0–189.0°. Eastman Kodak Co. white label styrene was distilled shortly before it was used. A sample (11.9 g.) of the distillate, b. p. 76° at 78 mm., was treated with 0.1 g. hydroquinone to stabilize it. In terms of the available absorption spectrum of hydroquinone[6] this quantity of the antioxidant should not be expected to introduce appreciable error into the spectrum measurements used in investigating the solubility of the styrene sample. Even though a sample of styrene so prepared was exposed to aqueous silver nitrate for twenty hours in the solubility measurements, no visible evidence of polymerization was observed. Eastman Kodak Co. white label bibenzyl, m. p. 51–52°, was used without further purification. Ethyl cinnamate, b. p. 131–132° at 7 mm., and ethyl hydrocinnamate, b. p. 121.9° at 11 mm., were prepared from the corresponding acids by the method of Fischer and Speier.[7] Samples of *trans*-stilbene, m. p. 120–121° and of 1,1-diphenylethylene, b. p. 125–127° at 6 mm.,

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[1] Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949).

[2] Andrews and Keefer, *ibid.*, **72**, 3113 (1950).

[3] Winstein and Lucas, *ibid.*, **60**, 836 (1939).

[4] Several other methods recently have been suggested as being useful in the measurement of relative base strengths of aromatic substances; *cf.* Benesi and Hildebrand, *ibid.*, **70**, 3978 (1948); **71**, 2702 (1949); Brown and Brady, *ibid.*, **71**, 3573 (1949); McCaulay and Lien, Abstracts of Papers Presented to the Division of Physical and Inorganic Chemistry, Detroit, Mich., April, 1950.

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 198.

[6] "International Critical Tables," Volume V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 361.

[7] Fischer and Speier, *Ber.*, **28**, 3252 (1895).