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Electron Radiation of Aqueous Methyl
Cellulose Solutions

W. Jack Hillend

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ELECTRON RADIATION OF AQUEOUS METHYL CELLULOSE SOLUTIONS

A thesis submitted by

W. Jack Hillend

B.Ch.E. 1958, Oregon State University
M.S. 1960, Lawrence College

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Appleton, Wisconsin

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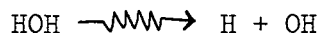
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EFFECT OF RADIATION ON SIMPLE MOLECULES

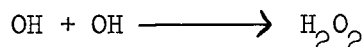
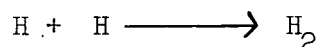
Researchers have found that radiation can alter the chemical properties of many organic molecules (1). Of particular interest to the radiation of the methyl cellulose-water system are the radiation effects on water, alcohols, and ethers.

RADIATION OF WATER

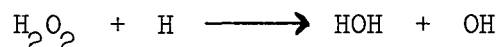
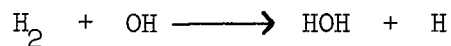
When water is radiated with electrons, hydrogen radicals and hydroxyl radicals are formed (2-6, 56):



It is generally accepted that these radicals are formed along the track of the electrons passing through the water. In the absence of any solute molecules with which they can react, these radicals will disappear by reaction with one another (2-6, 56):



The hydrogen peroxide and hydrogen gas, in so far as they stay dissolved in the water, will be able to react with the hydrogen radicals and hydroxyl radicals formed by the decomposition of further water molecules (2-6, 56):

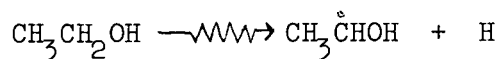


A steady-state concentration of hydrogen gas and hydrogen peroxide is reached at high doses during radiation. Higher dose rates have been found to give higher steady-state concentration of hydrogen and hydrogen peroxide (2-4). It has been suggested that a high activation energy is required to join two hydroxyl radicals

because of the dipole repulsion between the radicals when they approach in the proper configuration to combine (7). The combination of H with H or with OH would not be expected to require an activation energy. If the combination of OH's is slow while that of the H's is fast, the OH radicals will immediately assume a much higher concentration than the H, and nearly all the H formed will, consequently, combine with OH rather than with another H. In the zones of high radical concentration formed at high dose rates, local hot spots of high temperature could be formed. The energy for the temperature rise would come, of course, from the kinetic energy loss of the electrons during collision with water molecules. The high local temperature could cause the reaction rates of OH with H or with another OH to become more nearly the same. The yield of peroxide and hydrogen would then be high in these hot spots produced at high dose rates (2).

RADIATION OF ALCOHOLS

The effect of radiation on alcohols is believed to follow a free-radical process whether the alcohol is radiated in the absence (8-10) or presence (11) of oxygen. Burr (8) found that the primary effect of radiation on pure ethanol in the absence of oxygen was dehydrogenation at the α -carbon atom:

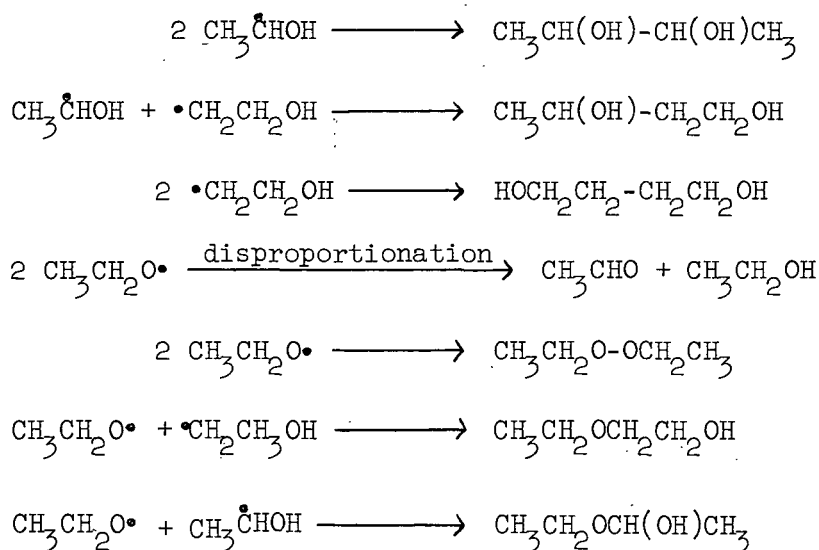


This primary reaction was believed to be followed by two secondary reactions involving the dehydrogenation of ethanol by attack of the hydrogen atom (8):

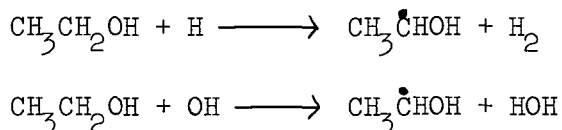


These primary radicals could then combine and react to account for the products butane-2,3-diol, butane-1,3-diol, butane-1,4-diol, acetaldehyde, diethyl peroxide,

1-hydroxyethyl ethyl ether, and 2-hydroxyethyl ethyl ether (8):

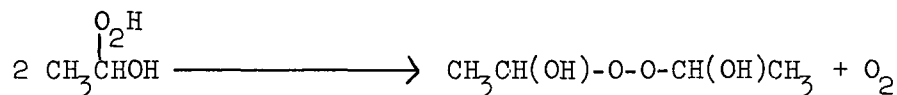
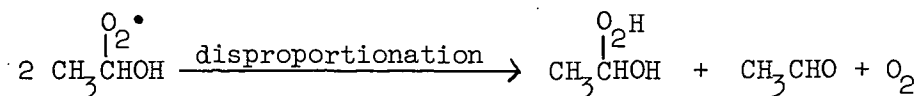
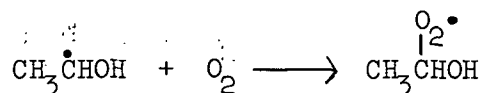


The radiation of aqueous solutions of alcohols in the absence of oxygen has been studied by Allen, et al. (9) and McDonnell and Gordon (10). As previously discussed, radiation decomposes water into hydrogen atoms and hydroxyl radicals: $\text{HOH} \xrightarrow{\gamma} \text{H} + \text{OH}$. The effects of these radicals with ethanol in aqueous solution are assumed to result in dehydrogenation at the α -carbon atom (9):



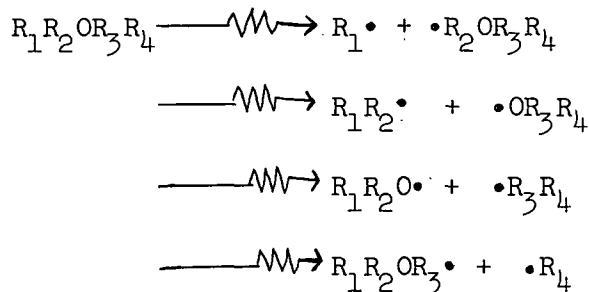
The observed products, butane-2,3-diol and acetaldehyde, can be accounted for by the equations previously advanced by Burr (8). Allen, et al. (9) found that an increase in concentration of ethanol from 0.1 to 15M increased the yields of acetaldehyde from 1.95 to 21.6 molecules per 100 electron volts of energy absorbed by the solution. Similarly, McDonnell and Gordon (10) observed that the yields of the products ethylene glycol and formaldehyde increased with higher concentrations of methanol in aqueous solution.

Jayson, et al. (11) have studied the effect of radiation on aqueous solutions of ethanol in the presence of oxygen. Unlike radiations of alcohols in the absence of oxygen (9, 10), no glycols and no new carbon-carbon bonds were formed. The following reactions were proposed to account for the products formed during radiation of ethanol in the presence of oxygen (11):



RADIATION OF ETHERS

Newton (12) has studied the effect of radiation on pure ethyl, propyl, and butyl ethers in the absence of oxygen. From the extensive analysis of products, Newton deduced that the following general radicals were formed during radiation:

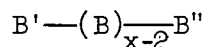


The compounds that were formed during radiation could be explained by the various coupling reactions between the above radicals. Newton also found that radiation of ethers gave small yields of nonvolatile "polymer."

Radiation is known to change the properties of polymers and alter their properties in solution. Before dealing with the effect of radiation on polymers, however, the general nature of polymers in solution will first be presented.

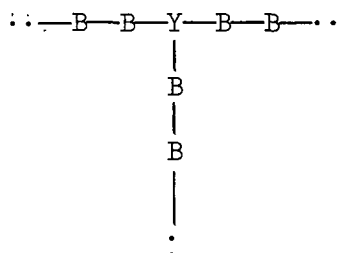
NATURE OF POLYMER MOLECULES IN SOLUTION (13, 14)

The elementary units of a polymer may be interconnected in any conceivable pattern by covalent bonds (13). A linear polymer possesses structural units which are connected one to another in linear sequence. Such a polymer may be represented by the formula

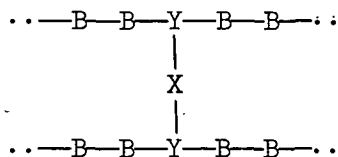


where B is the principal structural unit and x is the degree of polymerization, or the number of structural units in the molecule. The principal structural unit of a linear polymer is bifunctional (attached to two other units) whereas the terminal units B' and B'' are monofunctional. The group B' may or may not be identical with B''.

Nonlinear polymers--branched and crosslinked polymers--possess structural units some of which are polyfunctional. A typical branched polymer containing the trifunctional unit $\begin{smallmatrix} -Y- \\ | \end{smallmatrix}$ may be illustrated as follows:



A typical crosslinked polymer possessing the tetrafunctional group $\begin{smallmatrix} | & & | \\ Y-X-Y \\ | & & | \end{smallmatrix}$ is represented below:



For the sake of simplifying ensuing discussions, the term branching will be used to include also the specialized case of crosslinking.

DETERMINATION OF THE MOLECULAR WEIGHT OF POLYMERS

For determination of the absolute molecular weight of polymer molecules, the four physical methods that are in present use are: osmometry, sedimentation equilibrium, sedimentation velocity, and light scattering. Each of these methods require extrapolation of the data to infinite dilution to be theoretically valid (13). Only the last two of these methods will be discussed here.

SEDIMENTATION VELOCITY MEASUREMENTS (13-15)

In centrifugation the cell containing the polymer solution is rotated at an angular velocity of ω about some distant point. At a position in the cell a distance x from the center of rotation, the force acting on a molecule of molecular weight M and specific volume v is $M(1-\rho v)x\omega^2/N$ where ρ is the density of the solution and N is Avogadro's number. This centrifugal force on the molecule is opposed by the frictional force $f(dx/dt)$, where f is the frictional coefficient of the molecule and (dx/dt) is its velocity of sedimentation. Equating the centrifugal force to the frictional force gives

$$M(1-\rho v)x\omega^2/N = f(dx/dt).$$

This equation can be arranged to define the sedimentation coefficient s :

$$s = \frac{dx/dt}{\omega^2 x} = \frac{d(\ln x)/dt}{\omega^2} = \frac{M(1-\rho v)}{Nf} \quad (1)$$

According to Stokes' law, the frictional coefficient of a molecule is related to the viscosity of the solution η by the equation (13)

$$f = 6\pi\eta R_e \quad (2)$$

where R_e is the radius of the sphere that is hydrodynamically equivalent to the molecule.

The sedimentation coefficient also decreases with increasing concentration according to the empirical equation (14, 15)

$$1/s = 1/s_0 + kc$$

where s_0 is the sedimentation coefficient at the limit of zero concentration, c is the concentration in grams per unit volume, and k is a constant having a positive value.

If a solution contains a dilute mixture of polymer molecules covering a range of molecular weights, each molecule would sediment with its own velocity. In this case, a broad boundary of sedimenting molecules would occur which would be indicative of the distribution of molecular weights. Because of the previously mentioned dependence of the sedimentation coefficient on concentration, however, a single sedimentation velocity experiment cannot be taken as an infallible guide to the composition of a polymer mixture (16). More specifically, Johnson and Ogston (17) studied the sedimentation velocity of mixtures of two components one of which sedimented much faster than the other. At high concentrations, the two components tended to sediment together as one peak. Only at relatively dilute concentrations did the two components sediment independently of each other to give two resolved peaks.

LIGHT-SCATTERING MEASUREMENTS (13, 14, 18)

The intensity of light scattered by a suspension of colloidal particles is dependent on the size of the particles, their concentration, and the difference in

refractive indices of the particle and the surrounding medium. It can be shown for dilute solutions that the intensity of scattered light is equal to the sum of the contributions of the individual particles leading to the relationship

$$(Hc/\tau) = 1/M + 2Ac \quad (3)$$

where c is the polymer concentration in grams per milliliter; M is the weight-average molecular weight; H is a constant which depends on the wavelength of the light source, the refractive index of the solvent, and the change in the refractive index of the solution with the concentration of the polymer; τ is the turbidity which involves the ratio of the intensity of light scattered by the solution to the intensity of the incident light; and A is the second virial coefficient which depends both on the volume of the molecule and the nature of the solvent-polymer interaction.

Small particles will behave as point sources of scattered radiation with the scattering being symmetrical about 90° from the direction of the incident light. When the dimensions of a scattering particle become more than about one-twentieth of the wavelength of light, however, destructive interferences occur due to phase differences between rays scattered by the different elements within the same molecule. Due to these interferences, the scattering intensity will not be symmetrical about 90° and will be less in the direction for which $\theta = 90^\circ + \beta$ than for $\theta = 90^\circ - \beta$. The observed ratio of the intensities at these angles is conveniently defined as the dissymmetry coefficient Z_β .

$$Z_\beta = i_{90^\circ - \beta} / i_{90^\circ + \beta} = [i_{45^\circ} / i_{135^\circ}]_{\beta=45^\circ} \quad (4)$$

where i is the intensity of scattered light. The most commonly used value for β is 45° giving the dissymmetry coefficient Z_{45° .

The dissymmetry coefficient will increase with increasing particle size according to the relationships summarized by Doty and Steiner (19) for particles having rod, coiled, or spherical shapes. When molecular weights are calculated by Equation (3) using scattering measurements at 90° , the observed molecular weight will be low by the factor $1/P(90)$, where $P(90)$ is the particle scattering factor expressing the reduction in scattered intensity at 90° due to interference of light within the particle. Convenient tables summarizing the interdependence of Z_{45° , $P(90)$, and the particle size for particles of various shapes have been prepared by Doty and Steiner (19).

MOLECULAR DIMENSIONS OF RANDOMLY COILED POLYMERS (13, 14)

The hydrodynamic volume of polymer molecules in solution can be given by the product of the number of molecules per unit volume ($\underline{n}_2/\underline{V}$) and equivalent volume of a single molecule $\underline{V}_e = (4\pi/3)\underline{R}_e^3$, where \underline{R}_e is the equivalent hydrodynamic radius of a polymer molecule. According to the Einstein viscosity relation, the viscosity of a solution varies directly with the hydrodynamic volume of molecules in solution by the relation

$$(\eta - \eta_o)/\eta_o = 2.5 (\underline{n}_2/\underline{V})\underline{V}_e \quad (5)$$

where η and η_o are the viscosities of the solution and solvent, respectively. The number of molecules per unit volume ($\underline{n}_2/\underline{V}$) can be replaced in Equation (5) by ($\underline{cN}/100\underline{M}$) to give

$$(\eta - \eta_o)/\underline{c}\eta_o = 0.025 \underline{N}\underline{V}_e/\underline{M}$$

where \underline{N} is Avogadro's number and \underline{c} the concentration in grams of polymer per 100 ml. It is then convenient to define an intrinsic viscosity $[\eta]$ such that

$$[\eta] = [(\eta - \eta_o)/\underline{c}\eta_o]_{\underline{c} \rightarrow 0} = 0.025 \underline{N}\underline{V}_e/\underline{M} = 0.105 \underline{N}\underline{R}_e^3/\underline{M} \quad (6)$$

One can thus see that the intrinsic viscosity is simply a measure of the hydrodynamic volume occupied by a molecule per unit molecular weight.

Intuitively, it has been suggested by various investigators that \underline{R}_e should increase as the root-mean-square end-to-end distance $(\underline{r}^2)^{1/2}$ of a linear polymer chain or as the root-mean-square radius of gyration $(\underline{s}^2)^{1/2}$ of the units of a polymer chain from the center of a linear or nonlinear molecule. Based on theory by Kirkwood and Riseman (20), Flory (13) has developed the following relationships:

$$[\eta] = \Phi (\underline{r}^2)^{3/2}/M \quad (7)$$

$$[\eta] = \Phi' (\underline{s}^2)^{3/2}/M \quad (8)$$

$$(\underline{r}^2)^{1/2} = f/\eta P \quad (9)$$

$$(\underline{s}^2)^{1/2} = f/\eta P' \quad (10)$$

where Φ , Φ' , \underline{P} , and \underline{P}' are constants for randomly coiled chain molecules. These constants are theoretically independent of the molecule and the solvent. A widely used value for Φ is $2.1 (+0.2) \times 10^{21}$, where $(\underline{r}^2)^{1/2}$ is expressed in centimeters and $[\eta]$ in deciliters per gram (13). This makes the value of Φ' become $3.09 (+0.3) \times 10^{22}$ since for a randomly coiled linear chain $(\underline{s}^2) = (\underline{r}^2)/6$. The value of \underline{P} is theoretically predicted to be 5.1 (20).

As has been pointed out previously, the intrinsic viscosity is proportional to the ratio of the effective volume of a molecule in solution divided by its molecular weight. In particular, Equations (7) and (8) show that the effective volume is proportional to the cube of a linear dimension of the polymer chain. To get at the factors influencing the intrinsic viscosity it is convenient to separate the quantity $(\underline{s}^2)^{1/2}$ of Equation (8) into its component factors $(\underline{s}_0^2)^{1/2}$ and α to give (13)

$$[\eta] = \Phi' [(\bar{s}_0^2)^{1/2} \alpha]^3 / M \quad (11)$$

where $(\bar{s}_0^2)^{1/2}$ is the root-mean-square radius of gyration of a polymer in an ideal solvent and α is a molecular expansion factor due to solvent-polymer interaction. The value of α is unity for a polymer in an ideal solvent.

The sedimentation coefficient varies inversely with the frictional coefficient as previously presented in Equation (1). From the relationship between \underline{f} and $(\bar{s}^2)^{1/2}$ in Equation (10) and the substitution of $(\bar{s}_0^2)^{1/2} \alpha$ for $(\bar{s}^2)^{1/2}$, the frictional coefficient can be rewritten as

$$f = (\bar{s}_0^2)^{1/2} \alpha P' \quad (12)$$

The substitution for \underline{f} in Equation (1) gives

$$s = \frac{M(1-\rho v)}{N(\bar{s}_0^2)^{1/2} \alpha \eta P'} = \frac{K' M(1-\rho v)}{(\bar{s}_0^2)^{1/2} \alpha \eta} \quad (13)$$

where K' is a constant and η is the viscosity of the solution. This equation predicts that as greater solvent-solute interaction expands the molecule (increases α) from its normal size in ideal solvents, the sedimentation coefficient will decrease. Equation (13) also predicts that the sedimentation coefficient would decrease with increases in the density and viscosity of the solution. The density and viscosity of the solution could be increased, for example, by adding an inorganic salt to an aqueous solution of a polymer.

MOLECULAR DIMENSIONS OF BRANCHED POLYMERS

For the same molecular weight, the effect of branching is to reduce the viscosity since the size of the molecular coil is reduced (21-24). In the analysis of systems involving branching, investigators have found that the intrinsic viscosity

decreased even with increases in molecular weight (25-27). It is convenient to write the ratio g for a nonlinear polymer

$$g = (\bar{s}^2)_{\text{nonlinear}} / (\bar{s}^2)_{\text{linear}}$$

where g is less than unity. Combination with Equation (8) yields

$$g = \left\{ [\eta]_{\text{nonlinear}} / [\eta]_{\text{linear}} \right\}_{\underline{M}=\text{constant}}^{2/3} \quad (14)$$

Zimm (28) has derived an approximation for the number of branches per molecule. The weight-average number of trifunctional branches per molecule was given by

$$n_w = 3(1-g)/g \quad (15)$$

Qualitative evidence for branching is indicated by a decrease in the ratio of a linear dimension of the polymer chain to r_{max} , the maximum length of the molecule if unbranched and fully extended. The concept of an end-to-end distance is clearly ambiguous and inapplicable to branched polymers. Thus, the presence of branching can be indicated by a decrease in the ratio of the root-mean-square radius of gyration $(\bar{s}^2)^{1/2}$ to r_{max} . The quantity r_{max} is given by the product $\ell M / \underline{m}$, where ℓ is the length of a monomer unit in centimeters and \underline{m} is the weight of a monomer unit. Substitution of the value of $(\bar{s}^2)^{1/2}$ from Equation (8) gives

$$(\bar{s}^2)^{1/2} / r_{\text{max}} = ([\eta] M / \Phi')^{1/3} / (\ell M / \underline{m}) \quad (16)$$

where Φ' has the value of 3.09×10^{-22} .

Branching would also be expected to alter light-scattering measurements. The decrease in molecular volume by branching not only should decrease the second virial coefficient A in Equation (3) but also should decrease the dissymmetry coefficient Z_{45° in Equation (4).

In addition to the reduction in intrinsic viscosity by branching, it would be expected that the sedimentation coefficient would also be altered. The branching of dextrans has been studied by Granath (29). For the same light-scattering molecular weight, Granath found, as expected, that branching gave lower values of intrinsic viscosity and therefore lower apparent values of $(\bar{s}^2)^{1/2}$ in Equation (11). The frictional factor \bar{f} in Equation (12) would then be expected to decrease accordingly to give an increase in sedimentation coefficient in Equations (1) and (13). However, Granath found that branched molecules had lower sedimentation coefficients and higher frictional coefficients than linear molecules of the same molecular weight. The only explanation is that branching increased \bar{P}' in Equation (12) or decreased $\bar{\Phi}'$ in Equation (11), or both. In any event, the work by Granath and the lack of other similar investigations indicate that the effect of branching on the sedimentation of polymers is not fully understood.

THE NATURE OF POLYELECTROLYTES IN SOLUTION (13, 14)

If one or more of the structural units of a polymer contains an ionic group, the polymer is known as a polyelectrolyte. Due to the repulsion between ionized groups on the polymer chain, polyelectrolyte molecules in dilute solution may be highly expanded and have very large values of intrinsic viscosity. This increase in intrinsic viscosity is due to a molecule occupying a larger domain and can be accounted for by an increase in the solvent-solute interaction term α in Equation (11).

The presence of charged groups along the polymer chain can complicate viscometry and sedimentation measurements. The presence of charges on the chain makes difficult the extrapolation of viscosity data to infinite dilution. Polyelectrolytes will also tend to sediment slower in a centrifugal field for two

reasons: First, the frictional coefficient is increased as seen in Equations (12) and (13), due to increases in η and large increases in α . Secondly, an electrostatic field is set up when a charged macroion sediments away from its counteracting ions. This field can oppose the centrifugal field and Pederson (30) reports that this may decrease the sedimentation velocity by 50%.

The presence of charged groups on the polymer chain would also be expected to cause changes in light-scattering measurements (31, 32). The dissymmetry coefficient in Equation (4), which is a measure of the particle size, should be increased as the molecule occupies a larger domain. Furthermore, the second virial coefficient A in Equation (3), which depends on the molecular volume, would be expected to be increased by the presence of charged groups. Schneider and Doty (31) found this to be the case for sodium carboxymethyl cellulose at increasing degree of dissociation.

It is usually desirable to carry out viscometry, sedimentation, and light scattering of polyelectrolytes in aqueous solutions containing an inorganic salt. The small ions of the salt tend to eliminate not only the attraction between macroions and their counteracting ions during sedimentation but also the repulsion between macroions to give electrically neutral solutions. Polyelectrolyte molecules in the presence of salt have been found to decrease in size and behave as uncharged polymers during viscometry (32-34), sedimentation (30), and light scattering (31).

PROPERTIES OF BRANCHED POLYELECTROLYTES IN SOLUTION

The individual effects of branching and charged groups on viscosity, sedimentation, and light scattering have been discussed previously. The presence of both branches and charged groups within a polymer would pose a more complex system. For sake of discussion, two equations are again presented relating the intrinsic viscosity

and sedimentation coefficient to the effective radius of the polymer molecule

$$(\underline{s})^{1/2} = (\underline{s}_0)^{1/2} \alpha:$$

$$[\eta] = \Phi' [(\underline{s}_0)^{1/2} \alpha]^3 / M \quad (8)$$

$$s = \frac{M(1-\rho v)}{N [(\underline{s}_0)^{1/2} \alpha] \eta P'} \quad (13)$$

Provided that \underline{M} , Φ' , and \underline{P}' remain constant, these equations predict that $[\eta]$ varies directly and \underline{s} inversely with the quantity $[(\underline{s}_0)^{1/2} \alpha]$. It is recalled that also varying directly with $(\underline{s}_0)^{1/2} \alpha$ are the second virial coefficient and the dissymmetry coefficient from light scattering.

Branching would decrease $(\underline{s}_0)^{1/2}$ and the presence of charged groups would increase α . The effective radius of the molecule $(\underline{s})^{1/2} = (\underline{s}_0)^{1/2} \alpha$ could either increase or decrease depending on the extent of branching and the number of ionized groups on the polymer chain. Thus, the presence of both branches and charged groups could either increase $[\eta]$, \underline{A} , and \underline{Z}_{45° and decrease \underline{s} , or the reverse could be true.

Viscometry, sedimentation, and light-scattering measurements could be done in the presence of inorganic salts to depress the polyelectrolyte effects and decrease α to that of an uncharged polymer. In this event, the measurements would more nearly be those for an uncharged branched polymer. If, however, salt was not added to shield the charge effects and decrease α , the values of $[\eta]$, \underline{A} , and \underline{Z}_{45° would be higher and of \underline{s} lower than respective values taken in the presence of added salt.

NATURE OF GELS FORMED FROM POLYMER SOLUTIONS (13,14,35)

Gelation involves the transformation of a viscous sol into an elastic gel. The onset of gelation marks the division of the mixture into two parts: the gel, which is insoluble in all nondegrading solvents, and the sol, which remains soluble

and can be extracted from the gel. Beyond the gel point, the amount of gel increases at the expense of the sol and the mixture transforms from a viscous liquid to an elastic material of infinite viscosity.

Gels are characterized by a three-dimensional network (infinite network) composed of linear polymer chains interconnected by polyfunctional units--branches and cross links. These polyfunctional units in a gel could conceivably be linked to other units by any combination of secondary bonds (weak forces of intermolecular attraction) and primary bonds.

Gels contain aggregates and microgel particles which are arranged in some ordered manner. This arrangement, however, sometimes can be disrupted by shaking to cause temporary or even permanent liquefaction of the gel to a sol. The presence of these aggregates and microgel particles often can be detected by light-scattering and sedimentation measurements. It has been shown theoretically (14) and experimentally (36) that the presence of aggregates and microgel particles can lead to a negative second virial coefficient in the light-scattering Equation (3). Dispersions containing aggregates have also been observed to give a fraction of rapidly sedimenting material during ultracentrifugation (37).

RADIATION OF POLYMERS

Gamma and electron radiation can alter the physical and chemical properties of polymers (38, 39). The absorption of radiation by polymers, resulting in the excitation and ionization of molecules, produces two conflicting effects. Radiation can induce branching and cross linking and simultaneously can cause chain scission and oxidation of the polymer chains. Predominant branching and cross linking can improve the physical properties of some polymers. The strength, molecular weight, and resistance to solvents have been found to increase during radiation of polyethylene, natural rubber, and nylon (38, 39). Certain other polymers, however, are degraded by radiation. The strength, molecular weight, and viscosity were shown to decrease during radiation of polyisobutylene, polymethylmethacrylate, butyl rubber, and polytetrafluoroethane (teflon).

The presence of oxygen generally promotes the degradation of polymers. Solutions of polyethylene (40, 41), polystyrene (41, 42), and polyvinyl alcohol (43) will gel during radiation only in the absence of oxygen. Furthermore, Alexander and Fox (44) found that although radiation of polymethacrylic acid in the absence of oxygen caused no decrease in viscosity, 10^{-6} and 10^{-3} M dissolved oxygen during radiation decreased the viscosity by 15 and 60%, respectively.

The rate of formation of polymer radicals would be expected to increase with dose rate (38). If the diffusion of oxygen into a polymer or polymer solution is slow compared to the rate of formation of polymer radicals, the oxygen initially dissolved will be consumed quickly. The reaction could then proceed as though the oxygen were absent (45, 46). Dole, *et al.* (46) found, with thick blocks of polymer, that the effects of oxidation were confined to the surface. With thin blocks, however, the effects were observed throughout the samples, particularly at low dose rates.

The concentration of polymer to be radiated has been found to be an important factor. Alexander and Charlesby (43) found with polyvinyl alcohol in water that gelation occurred only at concentrations above 0.3%. This was explained by the expectation that scission of polymer chains would occur about equally at all concentrations, but that intermolecular cross-linking would tend to be discouraged when the polymer chains are widely separated.

RADIATION OF SIMPLE SUGARS AND POLYSACCHARIDES (47)

A number of workers have reported evidence for degradation of carbohydrates during radiation. Degradation of cellulose was indicated by increased reducing value (increased carbonyl content), carboxyl content, rate of acid hydrolysis, solubility in water and alkali, and decreased tensile strength, modulus of elasticity, and intrinsic viscosity (48-55). The extent of degradation was slightly less when radiations were made under nitrogen rather than under oxygen (51). Radiation in the solid state decreased the intrinsic viscosity of pectin (57). In addition, the viscosity and molecular weight were both decreased during radiation of solid dextran (58) and starch solutions (59). Radiation of dry glucose (50, 60) and glucose solutions (61, 62) resulted in oxidation and caused the formation of fragments of low molecular weight.

Along with this evidence for degradation of carbohydrates by radiation, evidence has been obtained also for the branching of carbohydrate molecules. The formation of 25-45% yields of nondialyzable materials during gamma radiation of oxygen-free water solutions of hexoses (63) and hexitols (64) indicated that end-linking or branching had occurred. No nondialyzable materials were formed during radiation under an oxygen atmosphere, however.

Radiation also appears to induce branching in polymeric carbohydrates. Samec (65) found that gamma radiation of an aqueous starch solution increased the molecular weight from 164,000 to 264,000 while the relative viscosity decreased from 1.16 to 1.07. Granath and Kinell (66) presented evidence that gamma radiation of solid dextran caused branching even though the molecular weight was continuously decreased.

RADIATIONS OF METHYL CELLULOSE

PREVIOUS RESEARCH ON RADIATED METHYL CELLULOSE

Investigators have obtained evidence that radiation causes both degradation and branching of methyl cellulose. Arthur, et al. (67) observed that gamma radiation degraded dry methyl cellulose. The treatment decreased the intrinsic viscosity and methoxyl content and caused the formation of carbonyl, carboxyl, and peroxy groups. Miller (68) found that electron radiation of dry methyl cellulose caused decreases in bulk viscosity.

Miller (68) and Leavitt (69) showed that electron radiation could promote gelation of methyl cellulose in aqueous solution. Gel formation also occurred during radiation of aqueous solutions of hydroxyethyl, methylhydroxypropyl, and hydroxybutyl ethers of cellulose. Miller interpreted this gelation phenomenon as evidence of cross linking since large quantities of water would not dissolve the gels. Leavitt hypothesized that bimolecular coupling reactions between polymer chains caused the gelation.

Miller (68) and Leavitt (69) observed that four radiation conditions affected the gelation of aqueous methyl cellulose: (1) Gelation occurred only with radiation at high dose rates. Radiation at dose rates greater than about five megarads per minute induced gelation. (One megarad involves the absorption of 100,000,000 ergs

of radiation energy by one gram of matter.) (2) A minimum polymer concentration of about 0.5% was necessary for gelation. Above this concentration the amount of radiation energy required for gelation increased with polymer concentration. (3) The presence of oxygen decreased the extent of gelation. The solution viscosities were at least 20-30% higher when solutions were radiated under nitrogen instead of under air. (4) The presence of organic molecules during radiation (methanol, butanol, or acrylonitrile) decreased or prevented gelation.

In addition, Leavitt (69) reported that gelation occurred in methyl cellulose solutions at pH values of 2.5 and 11.5. These pH values were obtained by the addition of mineral acid or sodium hydroxide. But, Leavitt observed that alkali rapidly dispersed the gels. Neither weak acid nor mechanical agitation dispersed the gels, however.

POSSIBLE MECHANISMS DURING RADIATION OF METHYL CELLULOSE

Branching Mechanisms

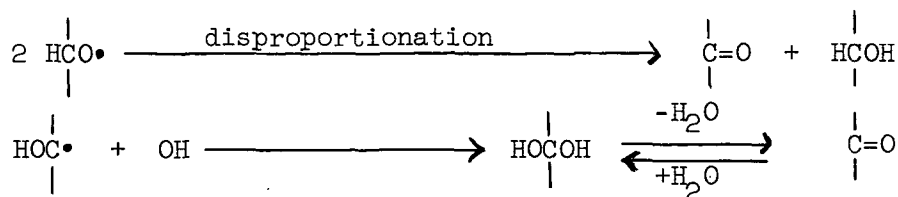
As presented on page 1, the electron radiation of water involves the formation of clusters of H and OH radicals along the track of electrons passing through the water (2-6, 56): $\text{HOH} \xrightarrow{\text{radiation}} \text{H} + \text{OH}$. With the radiation of aqueous methyl cellulose, these radicals could abstract H or OH radicals from the alcohol groups in methyl cellulose to give the following polymer radicals: HC^\bullet , HOC^\bullet , and HCO^\bullet . Radiation could also attack the methyl ether groups and glycosidic linkages to give these radicals: ROCH_2^\bullet , RO^\bullet , and R^\bullet . These radicals are noted to be similar to those formed during radiation of alcohols (8-11) and ethers (12) as shown on pages 2 and 4.

Combination reactions between the above polymer radicals would yield six types of branches between methyl cellulose molecules: carbon-carbon, ether, acetal,

glycosidic, hemiacetal, and peroxy. Peroxy branches would likely be labile to heat and alkali--primary and secondary alkyl peroxides are often decomposed by alkali and heat (70). Hemiacetal branches would probably be labile to alkaline borohydride at pH 9.5 (71). Carbon-carbon, ether, acetal, and glycosidic branches would likely be stable in alkaline borohydride and hot alkali below pH 11.

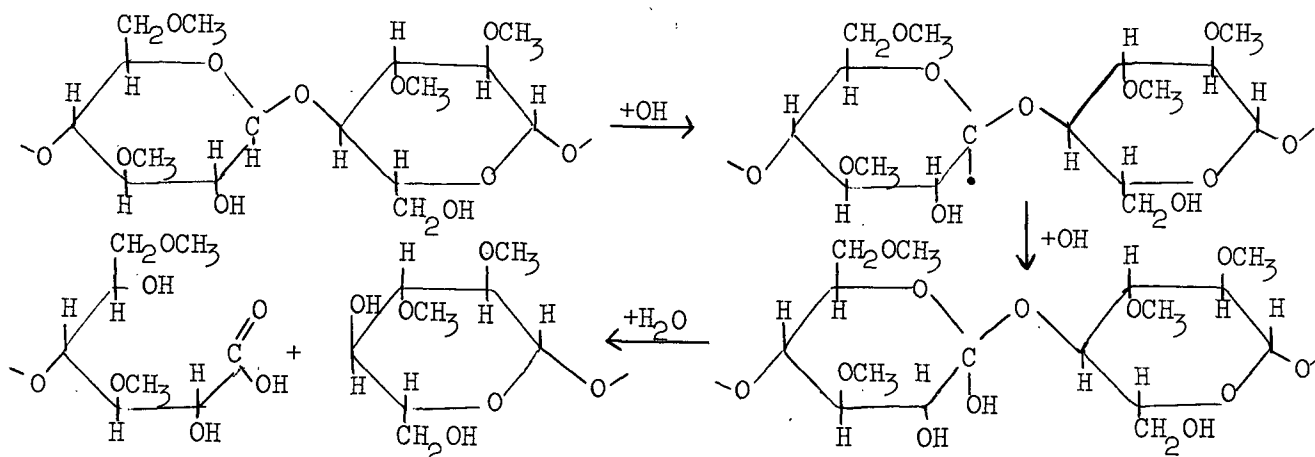
Mechanisms of Oxidation and Chain Scission

Oxidation could occur when aldehyde and ketone groups are formed through disproportionation or through reaction of polymer radicals with the OH radicals from water:



It is noted that these reactions are similar to those believed to occur during radiation of alcohols (8-11) as shown on page 2.

The above reactions could compete with the coupling of polymer radicals. Further attack on the carbonyl groups by OH radicals could yield carboxyl groups. The attack on polymer radicals by OH radicals might result in chain scission as well as the formation of carboxyl groups:



Gelation Mechanisms

It is known that radiation can cause gelation of aqueous solutions of methyl cellulose. In addition to the possibility that branching caused gelation of methyl cellulose during radiation, aggregation of molecules might also have contributed to gelation. Four plausible causes of aggregation are as follows: (1) Loss of methoxyl groups from methyl cellulose could yield a water-insoluble product. Methyl cellulose is normally soluble in water above a methoxyl content of 22% (72). Leavitt (69), however, found that gelation could occur when the methoxyl content dropped only from 30.3 to 29.7%. This suggests that loss in methoxyl groups is not the cause of gelation. (2) The carboxyl groups that are introduced in methyl cellulose during radiation might cause insolubility of the polymer in water. The free-acid forms of other carboxylated carbohydrates, such as carboxymethyl cellulose (73), alginic acid, and pectic acid (74), are soluble in dilute alkali but are not soluble in distilled water or dilute acid. (3) Solutions of radiated methyl cellulose could have high viscosities due to repulsion between ionized carboxyl groups along the polymer chain. As previously discussed, polyelectrolytes often have high viscosities due to repulsion of charged groups (13). (4) High electric fields are known to orient molecules in line with the field (75). Gelation of methyl cellulose might then be due to preferential alignment of polymer chains in such a way that extensive hydrogen bonding could occur between hydroxyl groups of neighboring chains.

RESEARCH OBJECTIVE

Previous research has not adequately defined the effect of electron radiation on aqueous solutions of methyl cellulose. Thus, this system was selected for further investigation. The primary objective was to observe the importance of radiation dose, dose rate, and the presence of oxygen to branching, scission, and oxidation of the polymer chain. The secondary objective was to investigate the general nature of branching and to examine other possible causes of gelation.

PRELIMINARY RADIATION EXPERIMENTS IN AIR

RADIATION AND ANALYSIS OF SAMPLES

RADIATION OF SOLUTIONS

A stock solution was prepared which contained 0.9% methyl cellulose [Dow "Methocel," 100 centipoise (cp.) grade] in deionized water. Dow Chemical Company listed the following properties of this methyl cellulose: U.S.P. grade; $29 \pm 2.0\%$ methoxyl; and viscosity of 100 ± 20 cp. for a 2% (wt.) solution at 20°C. The weight-average molecular weight of this sample was found to be 231,000 (see page 32) which is in agreement with the data of Neely (76).

For each sample to be radiated, 60 ml. of the stock solution was placed in an aluminum pan 6.63 by 2.88 by 2 inches high giving a liquid depth of 0.21 inch. The trays were then covered with a 0.001 in. film of polyethylene and radiated at $23 \pm 2^\circ\text{C}$. with electrons at a potential of two-million electron volts (2 M.e.V.). The electron source was a 2 M.e.V.-2 milliamperes resonant transformer located in the Application Laboratory at the X-Ray Department, General Electric Company in Milwaukee, Wisconsin. This transformer delivered a beam with a diameter of approximately 1.5 inches. This beam was scanned 180 times per second along the length of the sample and swept 56 times per second across the width of the sample. The beam current was pulsed 180 times per second with the square wave form shown in Fig. 1. The relative dose rate in the solutions was constant along the length of the sample, but the dose rate varied along the width and depth of the solutions as shown in Fig. 2. This figure is based on calibrations by General Electric Company. The distance from the beam window to the sample was 7.5 inches. The average dose rate received by each sample was 10.5 Mrad./min. using a beam current of 0.33 milliamperes. Radiation doses of 0.4 to 40 Mrad. were obtained by controlling the exposure time.

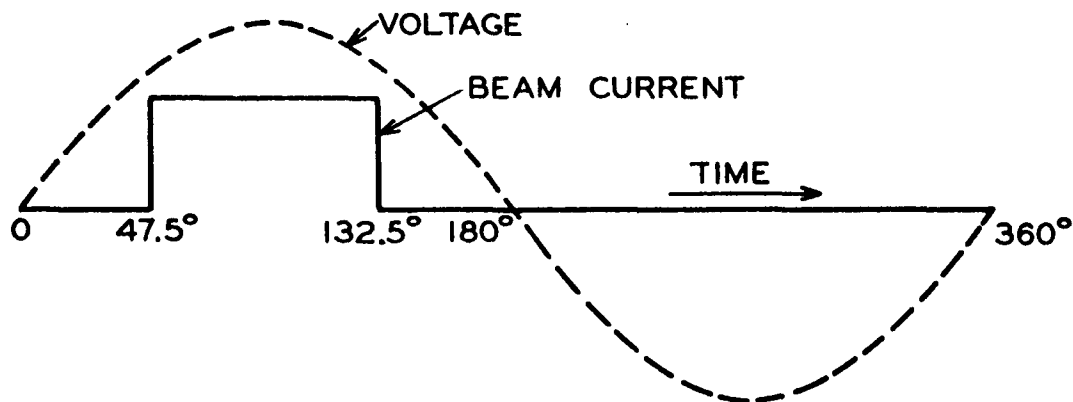


Figure 1. Accelerating Voltage and Beam Current
Wave Forms of Radiation Source

METHODS OF ANALYSIS

Viscosity of Undiluted Solutions

The apparent viscosities of the 0.9% solutions were measured at $21 \pm 1^\circ\text{C}$. on a Hercules Hi-Shear Viscometer having a cup diameter of 4.000 cm. and a rotating bob diameter of 3.898 cm. This instrument plotted the torque developed upon shearing an annulus of fluid (between the rotating bob and its concentric cup) at various speeds of revolution of the bob. The apparent viscosity is proportional to the torque divided by the bob speed; the rate of shear strain varies directly with the bob speed. The Hercules viscometer employs a Graham transmission in such a way that the bob speed is regularly increased from zero to 1150 r.p.m. in thirty seconds. The bob speed of 1150 r.p.m. corresponded to a rate of shear strain of 4680 sec.^{-1} . A complete shear cycle took one minute to complete.

Intrinsic Viscosity Measurements

Prior to the determinations of intrinsic viscosity, molecular weight, and sedimentation coefficient, all solutions were passed through a fine fritted-glass

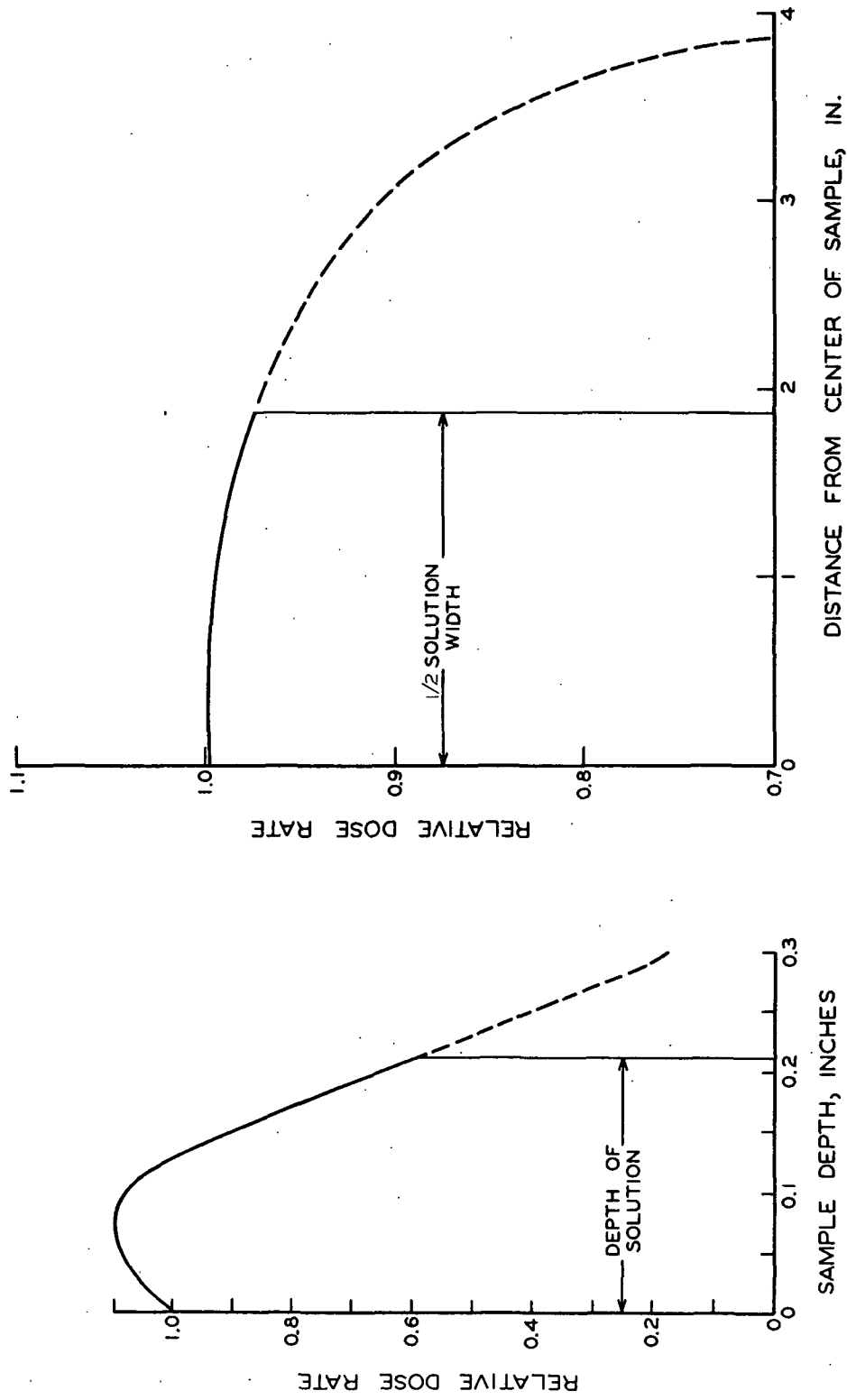


Figure 2. Variation of Dose Rate with Width and Depth of Solutions

filter. Viscosities were determined using a modified Ubbelohde dilution viscometer (77) at shear rates (78) of 1070 sec.^{-1} for water at $25 \pm 0.02^\circ\text{C}$. For the molecular weights involved in the present study, data by Immergut, et al. (79) indicate that the intrinsic viscosities would be low by less than 2% at a shear rate of 1000 sec.^{-1} .

Intrinsic viscosity $[\eta]$ was calculated using the equation

$$\log(\eta_{\text{sp}}/c) = \log\left\{[(\eta/\eta_0) - 1]/c\right\} = \log[\eta] + K[\eta]c \quad (16)$$

where η and η_0 are the viscosities of the solution and solvent, respectively, c the concentration of the polymer, and K the Martin constant (80). Data were taken 3 weeks after radiation.

Molecular Weight

Weight-average molecular weight was measured by light scattering at a wavelength of 4358 Å. using a Brice-Phoenix Photometer Series 1937 (81). Earlier calibration of this instrument was confirmed by measurements on Cornell standard polyethylene in benzene (82). Scattering intensities were measured at $21 \pm 1^\circ\text{C}$. for angles of 45, 90, and 135° . Rayleigh interferometer measurements gave the refractive index increment, $dn/dc = 0.145 \pm 0.002 \text{ ml./g.}$ at a wavelength of 5460 Å.; electron radiation did not change dn/dc . Molecular weights were calculated by Debye's method (83, 84) employing the previously presented equation.

$$(Hc/\tau) = 1/M + 2Ac \quad (3)$$

where M is the weight-average molecular weight, τ is the excess turbidity due to dissolved polymer, c the concentration of polymer, A the second virial coefficient, and H is a constant. The data, taken 5 weeks after radiation, were fitted by least

squares to find the intercept. The depolarization corrections were less than 6%, and no molecular weight corrections were made. No fluorescence of the solutions was detected. Dissymmetry ratios were found to be 1.52 and 1.78, respectively, for methyl cellulose before and after radiation. Since these ratios would result in corrections to the molecular weight which would be too high by 20 to 40%, no dissymmetry corrections were made. The degree of error introduced by not making the corrections was estimated using calculations of molecular size from Equation (7). This allowed estimation of the particle scattering factor (see page 10) which indicated that the molecular weight values of 100 cp. grade methyl cellulose could be low by 18%.

Sedimentation Coefficient

A Beckman Model E ultracentrifuge, with Analytical-D rotor, was used for sedimentation velocity experiments. All runs were made at 42,040 r.p.m., at $20.2 \pm 0.1^\circ\text{C}$., and at a polymer concentration of 0.235 ± 0.005 g./100 ml. A double sector cell was used with radiated methyl cellulose in one sector and an equal volume of nonradiated methyl cellulose in the other. Schlieren patterns were recorded photographically at known times, t . The distance, x , of the peak of the boundary curve from the center of rotation was measured with a microcomparator. Sedimentation coefficient s was obtained by finding the slope (by least-squares) of the $\ln x$ vs. t plot according to the equation

$$s = (1/\omega^2)(d \ln x/dt) \quad (1)$$

where ω is the angular velocity in radians per second. Data were taken 6 weeks after radiation.

EFFECT OF RADIATION ON BULK VISCOSITY
OF 100 CP. GRADE METHYL CELLULOSE

Aqueous solutions of 0.9% methyl cellulose were radiated under air at a dose rate of 10.5 Mrad./min. Figure 3 and Table I show the effect of radiation dose on the Hercules bulk viscosity at zero rate of shear strain. A low dose of 0.4 Mrad. decreased the viscosity from 7.9 to 3.4 cp. Additional radiation to a dose of 1.7 Mrad., however, increased the viscosity to that of a gel of 1000 cp. Above this dose the viscosity was rapidly decreased and severe degradation was evidenced by the dark yellow color that developed at high doses of 15 to 40 Mrad.

Figure 3 illustrates also the Hercules bulk viscosities after application of one shear cycle. The gels are shown to be rapidly and easily broken down by shear forces. The one minute shear cycle decreased the viscosity of the most rigid gel from 1000 to 440 cp. To verify the assumption that this shear action was not breaking the primary bonds originally present in the nonradiated methyl cellulose, a 4% solution of 100 cp. grade methyl cellulose was sheared for 20 minutes at an average rate of shear of 4680 sec.^{-1} . No decrease in the apparent viscosity of 1200 cp. was observed, however. Thus, the primary bonds of the type found in nonradiated methyl cellulose were apparently not cleaved by the shear forces encountered in the Hercules viscometer. This does not, however, eliminate the possibility that branches and cross links would be cleaved under these high rates of shear.

The destruction of gel viscosity by shear forces indicates that, unlike non-radiated samples, gels of radiated methyl cellulose contain bonds and bond arrangements which were labile to mechanical action.

OXIDATION EFFECTS FROM RADIATION

To obtain a measure of the extent of oxidation, carboxyl contents and pH values were also taken on radiated methyl cellulose. Carboxyl contents were determined

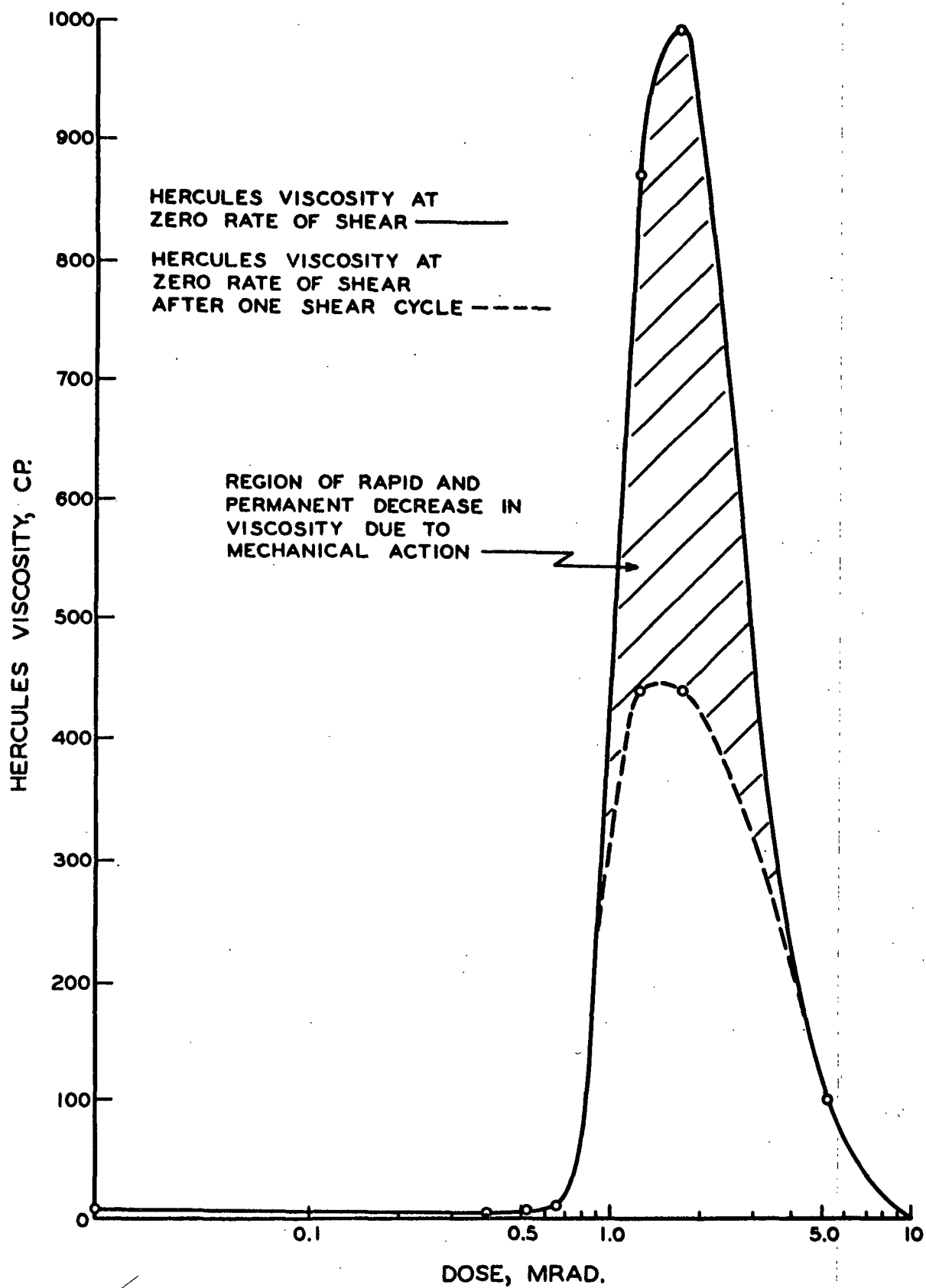


Figure 3. Effect of Electron Radiation on Bulk Viscosity of 0.9% Solutions of 100 cp. Grade Methyl Cellulose

TABLE I
EFFECT OF RADIATION ON 0.91% SOLUTIONS OF
100 CP. GRADE METHYL CELLULOSE^a

Sample	Dose, Mrad.	pH	Carboxyl, %	Bulk Visc., ^b		$[\eta]^c$	\bar{M}^d	S^e	
				η_H	η'_H			Water	0.8M NaCl
Non-radiated	--	7.12	0.00	7.9	7.9	2.81	231,000	0.835	0.788
1	0.4	7.10	--	3.4	3.4	--	--	--	--
21	0.5	6.91	--	4.8	4.8	--	--	--	--
3	0.7	6.75	0.06	9.5	9.5	1.41	--	--	--
9	1.25	5.80	--	875	440	--	--	--	--
7	1.7	5.35	0.31	1000	440	--	--	--	--
6	10.5	3.57	1.06	10.4	10.4	0.97	710,000	1.01	0.991
11	15	3.36	--	6.2	6.2	--	--	--	--
22	25	3.12	2.95	3.1	3.1	--	--	--	--
19	40	3.08	--	1.6	1.6	--	--	--	--

^aRadiated under air at dose rate of 10.5 Mrad./min.

^b η_H = Hercules bulk viscosity at zero rate of shear strain, cp.

η'_H = Hercules bulk viscosity at zero rate of shear strain after one shear cycle, cp.

^cIntrinsic viscosity in 0.8M NaCl, dl./g.

^dLight-scattering molecular weight in water.

^eSedimentation coefficient at concentration of 0.235 g./dl. in water or 0.8M NaCl, svedbergs.

under an atmosphere of nitrogen by potentiometric titration with 0.01N sodium hydroxide in the presence of 0.1N sodium chloride (85, 86). Table I shows that radiation caused oxidation of methyl cellulose as indicated by the formation of carboxyl groups. The increase in carboxyl content is seen to correlate with decreases in pH of the system. Thus, decreases in pH value gave an indication of the relative amount of oxidation caused by radiation.

INTRINSIC VISCOSITY OF SAMPLES AND THE POLYELECTROLYTE EFFECT

The reduced viscosity-concentration relationships for 100 cp. methyl cellulose before and after two levels of treatment are shown in Fig. 4. The relationship for the nonradiated sample was linear, but those for the radiated samples were curved upward at the origin. These curved viscosity plots were very likely due to a polyelectrolyte effect since it has already been shown that radiation introduced carboxyl groups in methyl cellulose.

Repulsions between charged groups in polyelectrolytes are known to cause expansion of the polymer chain leading to high viscosity. Addition of simple electrolytes to shield the repulsion between charged groups within the polymer is used to prevent expansion of the polymer chain so that linear viscosity curves are obtained (28). As shown in Fig. 4, the addition of sodium chloride to radiated samples resulted in linear viscosity-concentration relationships which were decreased in level. The added electrolyte decreased the intrinsic viscosity of the unirradiated methyl cellulose only from 2.85 to 2.81 dl./g., however. Figure 4 and Table I show that radiation doses of 0.7 and 10.5 Mrad. decreased the intrinsic viscosity from the original value of 2.81 to 1.41 and 0.97 dl./g., respectively, when charge effects were suppressed by addition of sodium chloride.

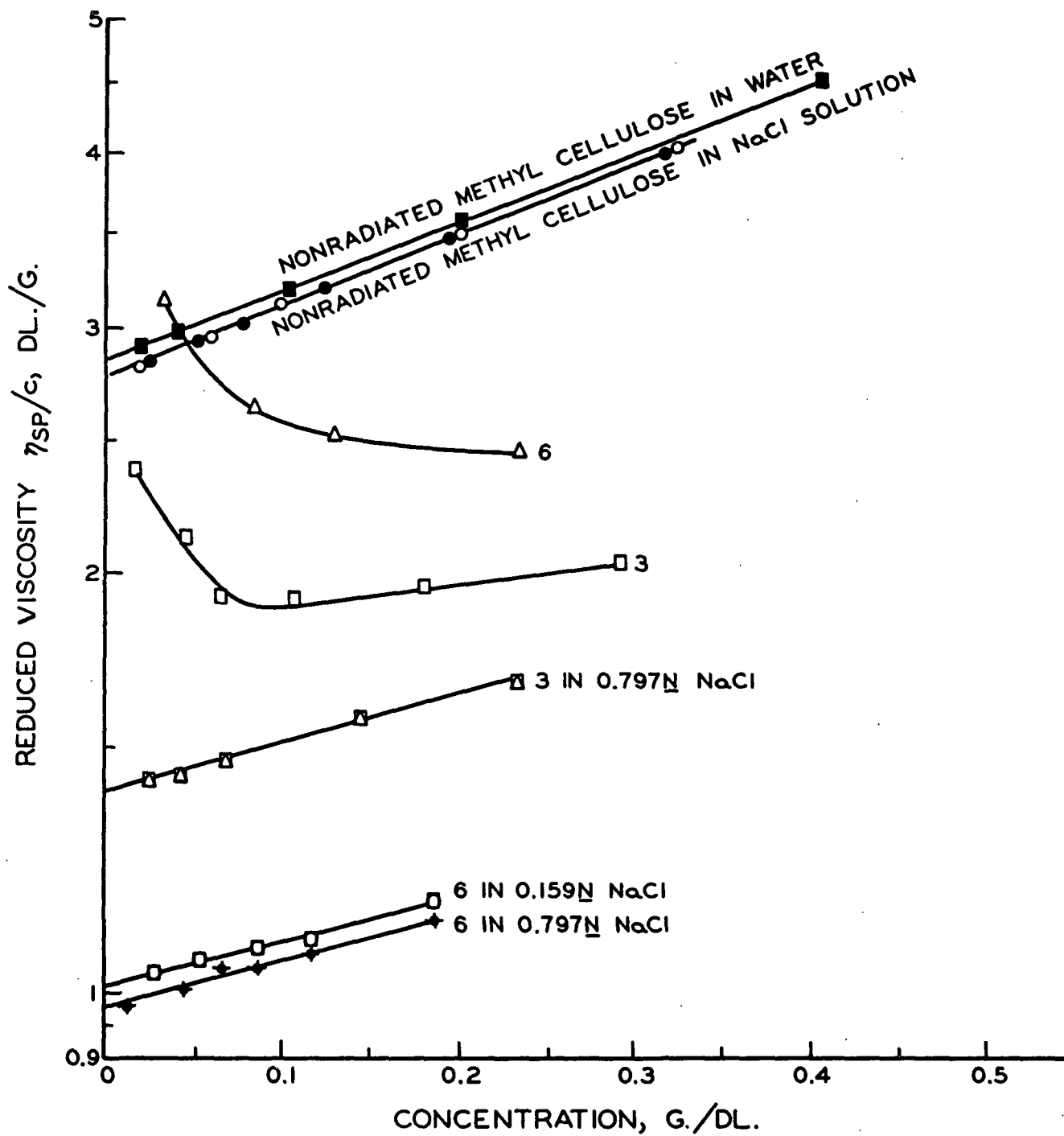


Figure 4. Dilution Viscometry of 100 cp. Grade Methyl Cellulose Radiated Under Air

MOLECULAR WEIGHT AND SEDIMENTATION
OF RADIATED METHYL CELLULOSE

Determinations of molecular weight were made in water on 100 cp. grade methyl cellulose before and after radiation in air. Table I shows that radiation increased the molecular weight of Sample 6 from 231,000 to 710,000. This increase in molecular weight, however, occurred with a decrease in intrinsic viscosity from 2.81 to 0.91 dl./g. This increase in molecular weight along with the large decrease in intrinsic viscosity implies that radiation induced a marked branching effect in methyl cellulose.

It is recalled that the sedimentation coefficient theoretically should increase both when the molecular weight is increased and when branching decreases the molecular volume (decreases the frictional coefficient) at constant molecular weight. As previously mentioned, however, polyelectrolytes (such as radiated methyl cellulose has been shown to be) would tend to sediment slower not only because of the attractions between the macroions and their counteracting ions but also due to the larger frictional coefficients involved with the expanded molecular volume. Sedimentation coefficients were thus determined for methyl cellulose using 0.8M sodium chloride as the solvent. Since the density of this salt solution is 3% higher than that for water, the $(1-\rho v)$ term in Equation (1) would become lower by 7%. The sedimentation coefficient, which is proportional to this term, would thus be expected to be low by 7%. This calculation assumed that the specific volume v remained constant at 0.71 ml./g. Actually, the specific volume, taken in triplicate with a pycnometer (87), decreased slightly during radiation from 0.710 ± 0.008 to 0.702 ± 0.008 ml./g. for Sample 6.

Table I shows that radiation increased the sedimentation coefficient of Sample 6 from 0.788 to 0.991 svedbergs when measurements were made in 0.8M sodium chloride.

This increase in sedimentation coefficient is consistent with the previously observed increase in molecular weight and provides additional evidence that radiation caused branching in methyl cellulose.

Comparison of the sedimentation coefficient in the presence and absence of added salt should indicate the magnitude of a polyelectrolyte effect. Hence, sedimentation coefficients were also determined for methyl cellulose with pure water as the solvent. As shown in Table I, radiation increased the sedimentation coefficient of Sample 6 from 0.835 to 1.01 svedbergs. Comparison of the sedimentation coefficients of Sample 6 with the control sample in the presence and absence of added salt reveals two points: First, radiation gave a relative increase in sedimentation coefficient of 1.21 for measurements in water compared to 1.26 for measurements taken in salt. The lower relative increase in water would then appear to be due to a small polyelectrolyte effect. Second, the same sample is seen to have a 2-6% lower sedimentation coefficient in the presence of salt. This can be expected, as previously discussed, since the higher salt density made the $(1-\rho v)$ term in Equation (1) lower by 7% and thus the sedimentation coefficient should be lower by 7%.

RADIATION EXPERIMENTS UNDER NITROGEN

PREPARATION AND RADIATION OF SOLUTIONS

Stock solutions of methyl cellulose were prepared from Dow "Methocel" (15 cp. technical grade) and deionized water. The methoxyl content of this methyl cellulose was $29.4 \pm 0.1\%$ as determined by the Zeisel method on methyl cellulose (88). The ash content was $0.60 \pm 0.01\%$ determined as the amount of material remaining after heating the samples for 6 hr. at 900°C . The weight-average molecular weight of this sample was found to be 85,000 (see page 44) which is in agreement with the data of Neely (76). The solutions were evacuated and replaced with nitrogen three times at room temperature and finally stored under a 0.5 p.s.i.g. pressure of nitrogen. To hold to a minimum possibilities of hydrolytic depolymerization and degradation by micro-organisms, methyl cellulose solutions were stored at 1°C . until ready for use. One-hundred milliliter volumes of the nitrogen-saturated solution were sealed under nitrogen in Dow-Corning No. 213D 1-1/2 qt. glass loaf-pans which had base dimensions of 3.75 by 7.60 inches. This gave a solution depth of 0.21 ± 0.01 inch.

The solutions were sealed in loaf pans by two methods: (1) One solution was delivered to a pan in a nitrogen atmosphere containing less than 0.3% oxygen by volume. The oxygen content was determined by Orsat analysis. The pan with solution was then heat-sealed in a polyethylene bag while still under nitrogen. (2) The pans for the rest of the solutions were inserted in polyethylene bags. The bags were closed by sealing with heat. Nitrogen gas was then flushed for 60-90 sec. through a small hole in the bags. The methyl cellulose solutions were delivered through the small holes in the bags and the holes were closed by heat sealing.

From an average of five determinations, this procedure was found to give atmospheres in the bags of $3.7 \pm 0.5\%$ oxygen (by volume) in nitrogen.

All solutions were radiated at $23 \pm 2^\circ\text{C}$. with 2 M.e.V. electrons using the same electron source as previously described. Average dose rates were varied from 0.15 to 10 Mrad./min. using beam currents of 0.0050 to 0.333 milliampere. Radiation doses of 0.45 to 2.1 Mrad. were obtained by controlling the exposure time.

METHODS OF ANALYSIS OF SAMPLES

VISCOSITY OF UNDILUTED SOLUTIONS

Bulk viscosities, or the viscosities of the undiluted solutions, were measured at $21 \pm 1^\circ\text{C}$. with a Brookfield Model LVF rotational viscometer. The bulk viscosities for systems having viscosities below 1000 cp. were taken with the Brookfield spindle No. 2 at 30 r.p.m. Spindle No. 3 at 12 r.p.m. was used in systems having bulk viscosities between 1000 and 10,000 cp. Spindle No. 4 at 6 r.p.m. was used in systems having bulk viscosities above 10,000 cp. Data were taken within four days after radiation.

An increase in the rate of shear strain will decrease the observed values of viscosity (14). The rate of shear strain for the Brookfield viscometer increases with higher speeds of rotation and with larger spindle diameters (lower spindle numbers). Thus, differences in bulk viscosities of samples are only approximate for data taken at different speeds and with different Brookfield spindles. Furthermore, viscosity measurements taken on gelled systems do not have precise meaning. The high viscosity of these systems could arise through any combination of friction between gel particles and friction causing the gel particles to break down to a sol.

Radiated systems having bulk viscosities of more than 500 cp. were dispersed before taking light-scattering, sedimentation, and intrinsic viscosity measurements. Dispersion of these systems was attained by diluting to about 0.8% followed by agitation for 15 minutes in a Waring Blendor at 1000 r.p.m. This same treatment with nonradiated methyl cellulose did not decrease the intrinsic viscosity or molecular weight. But not to be discounted is the possibility that this treatment could cleave branches and cross links in the radiated samples.

A Beckman Model E ultracentrifuge was used to clarify solutions and dispersions prior to light-scattering, sedimentation, and intrinsic viscosity measurements. The samples, at a concentration of 1 to 1.5%, were sealed in 0.5 x 3 in. centrifuge tubes and placed in a Beckman K-rotor maintained at $20 \pm 2^\circ\text{C}$. Clarification was achieved by centrifuging for 0.5 hour at a centrifugal field of 100,000-times that of gravity. A syringe was carefully inserted through the top of the centrifuge tube and the middle two-thirds of the contents of the tube was slowly removed and stored at 1°C . The centrifugal clarification was necessary for removing dust prior to light-scattering measurements. The intrinsic viscosity was not changed by this clarification procedure.

The reason for storing the solutions at 1°C . prior to taking physical measurements was to assure complete solution of the methyl cellulose. It has been found that molecular aggregation occurs in aqueous solutions of methyl cellulose at temperatures above $30\text{-}35^\circ\text{C}$. (89, 90). The aggregates could be dispersed by cooling to 1°C . but could slowly reform when the solutions were warmed to $20\text{-}25^\circ\text{C}$. (89, 90). This writer found, however, after cooling the solutions to 1°C . and then warming them back to 21°C . for light-scattering measurements, that the apparent molecular weight did not increase in 12 weeks above the initial value.

MOLECULAR WEIGHT

Weight-average molecular weight was measured by light-scattering using the methods previously described on page 28. Before taking measurements, however, the centrifuged solutions were passed through 4500 A. Millipore filters (Millipore Filter Corp., Bedford, Mass.) directly into the light-scattering cell. The depolarization measurements were less than 3%, and no corrections to the observed molecular weight were made. No fluorescence of the solutions was detected. Dissymmetry ratios were found to range from 1.3 to 1.8 for the samples. Since these ratios would result in corrections to the molecular weight which would be too high by 15 to 50%, no dissymmetry corrections were made. The error introduced by not making the corrections was estimated as before using calculations of molecular size from Equation (7). This allowed estimation of the particle scattering factor which indicated that the molecular weight values of .15 cp. grade methyl cellulose could be low by 6-15%. Because five replicate determinations of molecular weight for nonradiated methyl cellulose were between 80,900 and 90,600, molecular weight values were judged to be precise to $\pm 6\%$. Data were taken in a two-week period seven weeks after radiation.

SEDIMENTATION VELOCITY

Sedimentation velocities were measured on the clarified samples by the methods previously presented on page 31. However, all runs were made at a polymer concentration of 0.82 ± 0.01 g./100 ml. Data were taken nine weeks after radiation.

INTRINSIC VISCOSITY

Intrinsic viscosities were measured on the clarified samples by the methods previously presented on page 28. Data were taken nine weeks after radiation.

EFFECT OF RADIATION ON BULK VISCOSITY AND pH

Under an atmosphere of 3.7% oxygen, 4% solutions of methyl cellulose were radiated at dose rates from 0.15 to 10 Mrad./min. As shown in Fig. 5, the bulk viscosity after radiation was highly dependent on dose rate. With a dose rate of 0.15 Mrad./min., a 2.1 Mrad. dose decreased the bulk viscosity from 96 to 31 cp. But with a sixty-seven times higher dose rate of 10 Mrad./min., a 2.1 Mrad. dose increased the bulk viscosity from 96 to 58,000 cp. resulting in gel formation. This gelation could have occurred through new bonds being formed between molecules (cross linking and branching) or through formation of secondary valence bonds between molecules (such as hydrogen bonds).

Data presented in Fig. 6 show that radiation decreased the pH of the samples, but this decrease was less extensive at higher dose rates. For a 2.1 Mrad. dose, the pH was decreased from 5.82 to 3.92 and 4.26 with dose rates of 0.15 and 10 Mrad./min., respectively. These data suggest that high dose rates caused less oxidative degradation.

A 4% methyl cellulose solution was radiated at 4.5 Mrad./min. to a dose of 2.1 Mrad. under an atmosphere of less than 0.3% oxygen in nitrogen. Comparison of this Sample 62b with Sample 62 of Table IV, which was radiated under 3.7% oxygen, shows that lower oxygen contents during radiation resulted in higher bulk viscosity and pH. The data thus indicate that higher oxygen contents increased oxidative degradation and interfered with gelation.

MOLECULAR WEIGHT OF RADIATED SAMPLES

Prior to determinations of molecular weight, sedimentation coefficient, and intrinsic viscosity, all solutions were clarified by the centrifuge method previously

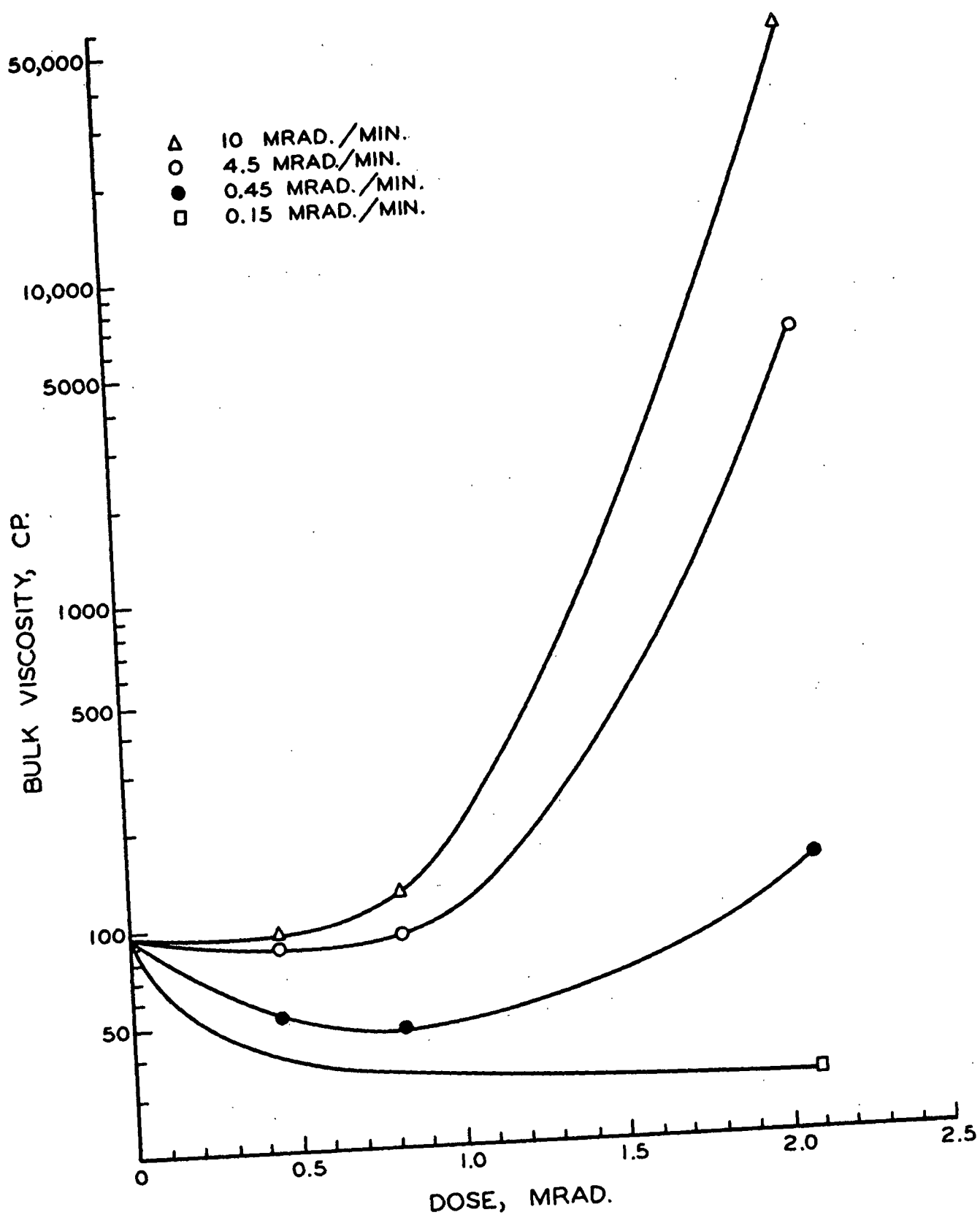


Figure 5. Effect of Dose and Dose Rate on Bulk Viscosity of 4% Solutions of 15 cp. Grade Methyl Cellulose Under Nitrogen

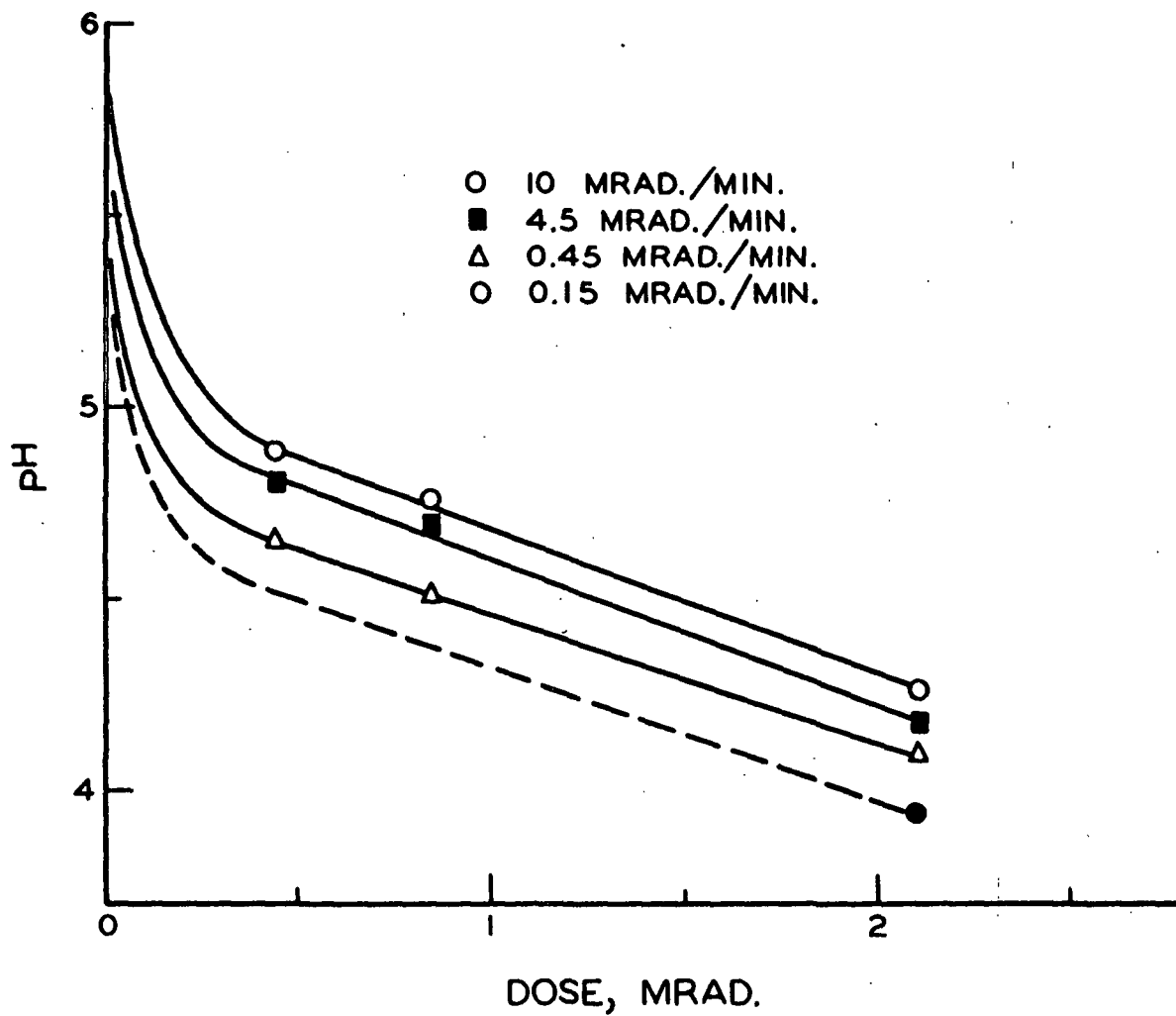


Figure 6. Effect of Radiation on pH of 4% Solutions of 15 cp. Grade Methyl Cellulose Under Nitrogen

TABLE IV
EFFECT OF RADIATION ON 4% SOLUTIONS
OF 15 CP. GRADE METHYL CELLULOSE

Sample	Dose, Mrad.	Dose Rate, Mrad./min.	Atmos., % O ₂	<u>M</u> ^a	<u>s</u> ^b	[η] ^c	η ^d	pH
00	--	--	--	85,000	0.666	1.62	96	5.82
70	0.45	0.45	3.7	--	--	1.40	51	4.68
60	0.45	4.5	3.7	167,000	0.740	1.50	86	4.80
63	0.45	10	3.7	--	--	--	94	4.86
71	0.84	0.45	3.7	185,000	0.740	1.33	47	4.50
61	0.84	4.5	3.7	204,000	0.758	1.47	92	4.70
65	0.84	10	3.7	--	--	--	122	4.73
66	2.10	0.15	3.7	--	--	0.86	32	3.92
72	2.10	0.45	3.7	207,000	0.792	1.36	148	4.10
62	2.10	4.5	3.7	215,000	0.801	1.61	6200	4.18
68	2.10	10	3.7	--	--	--	58,000	4.26
62b	2.10	4.5	<0.3	270,000	0.992	2.32	>100,000	4.37
82 ^e	2.10	4.5	3.7	183,000	--	--	--	--

^aLight-scattering molecular weight.

^bSedimentation coefficient in water at 0.82% methyl cellulose svedbergs.

^cIntrinsic viscosity in water, dl./g.

^dBulk viscosity with Brookfield viscometer, cp.

^eThis sample was radiated at 0.4% methyl cellulose.

discussed. Two of the radiated samples in Table IV were gels (62 and 62b) and were dispersed in the Waring Blendor before clarification. Clarification of these two dispersions decreased the methyl cellulose concentrations by 3.4 and 5.3%, respectively, of the original gel concentrations of Samples 62 and 62b. Clarification of the other samples for analyses removed less than 0.5% of the original solids.

EFFECT OF DOSE, DOSE RATE, AND OXYGEN ON MOLECULAR WEIGHT

The extrapolation of light-scattering data to zero concentration and sedimentation data to zero time are shown in Fig. 7-10 for radiated and nonradiated methyl cellulose. As shown in Fig. 11 and Table IV, radiation of 4% solutions under nitrogen increased both the molecular weight from light scattering and the sedimentation coefficient. At the lower dose rate of 0.45 Mrad./min., a radiation dose of 2.10 Mrad. increased the molecular weight from 85,000 to 207,000 and increased the sedimentation coefficient from 0.666 to 0.792 svedbergs. At the same dose of 2.10 Mrad., Fig. 11 shows that a tenfold increase in dose rate from 0.45 to 4.5 Mrad./min. gave rise to an additional increase in molecular weight from 207,000 to 215,000 and sedimentation coefficient from 0.792 to 0.801 svedbergs. At the same dose and dose rate, comparison of Samples 62 and 62b in Table IV shows that a decrease in the oxygen above the solutions from 3.7% to less than 0.3% caused the molecular weight to increase from 215,000 to 270,000 and the sedimentation coefficient to increase from 0.801 to 0.992 svedbergs.

EFFECT OF TIME AFTER RADIATION ON MOLECULAR WEIGHT

In addition to the molecular weight determinations in Table IV which were taken eight weeks after radiation, determinations were also made on nonradiated methyl cellulose and Samples 62 and 62b two weeks after radiation. Whereas the molecular weight of the nonradiated sample remained constant over the six-week

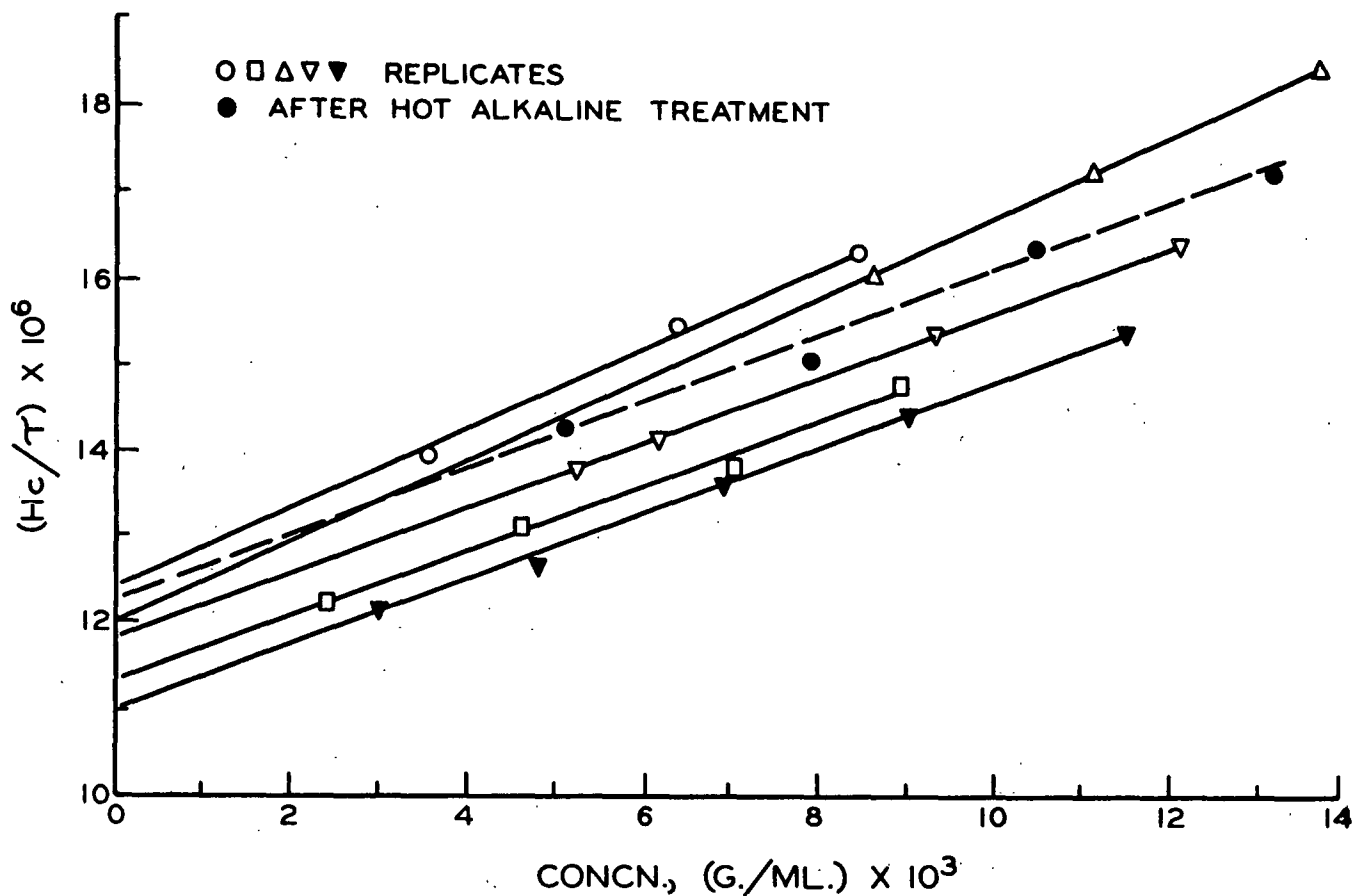


Figure 7. Light Scattering at 90° for Unradiated 15 cp. Grade Methyl Cellulose

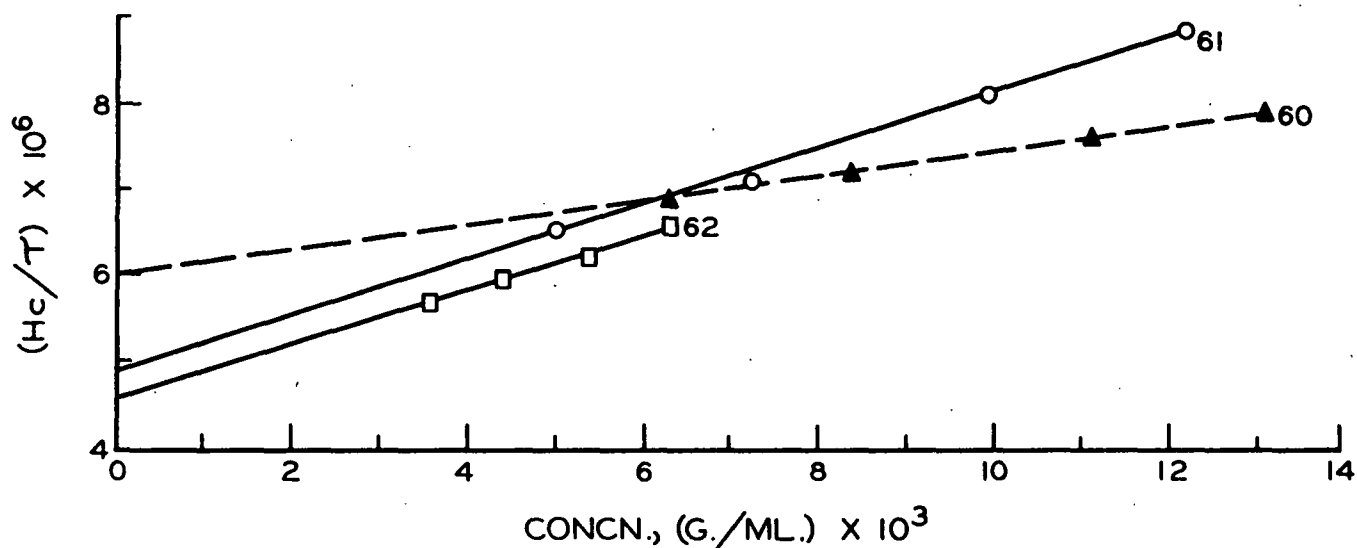


Figure 8. Light Scattering at 90° for Radiated 15 cp. Grade Methyl Cellulose

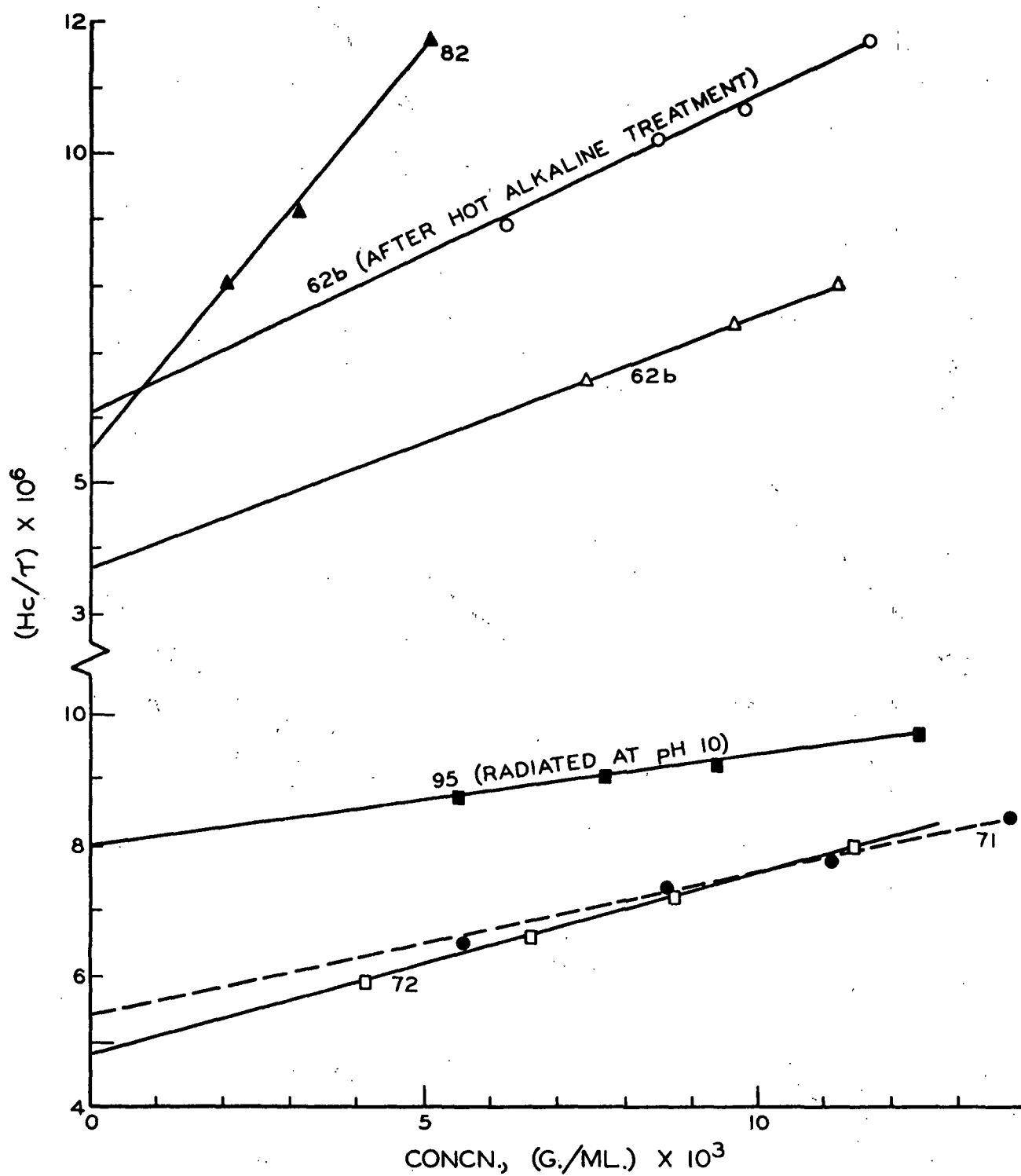


Figure 9. Light Scattering at 90° for Radiated 15 cp. Grade Methyl Cellulose

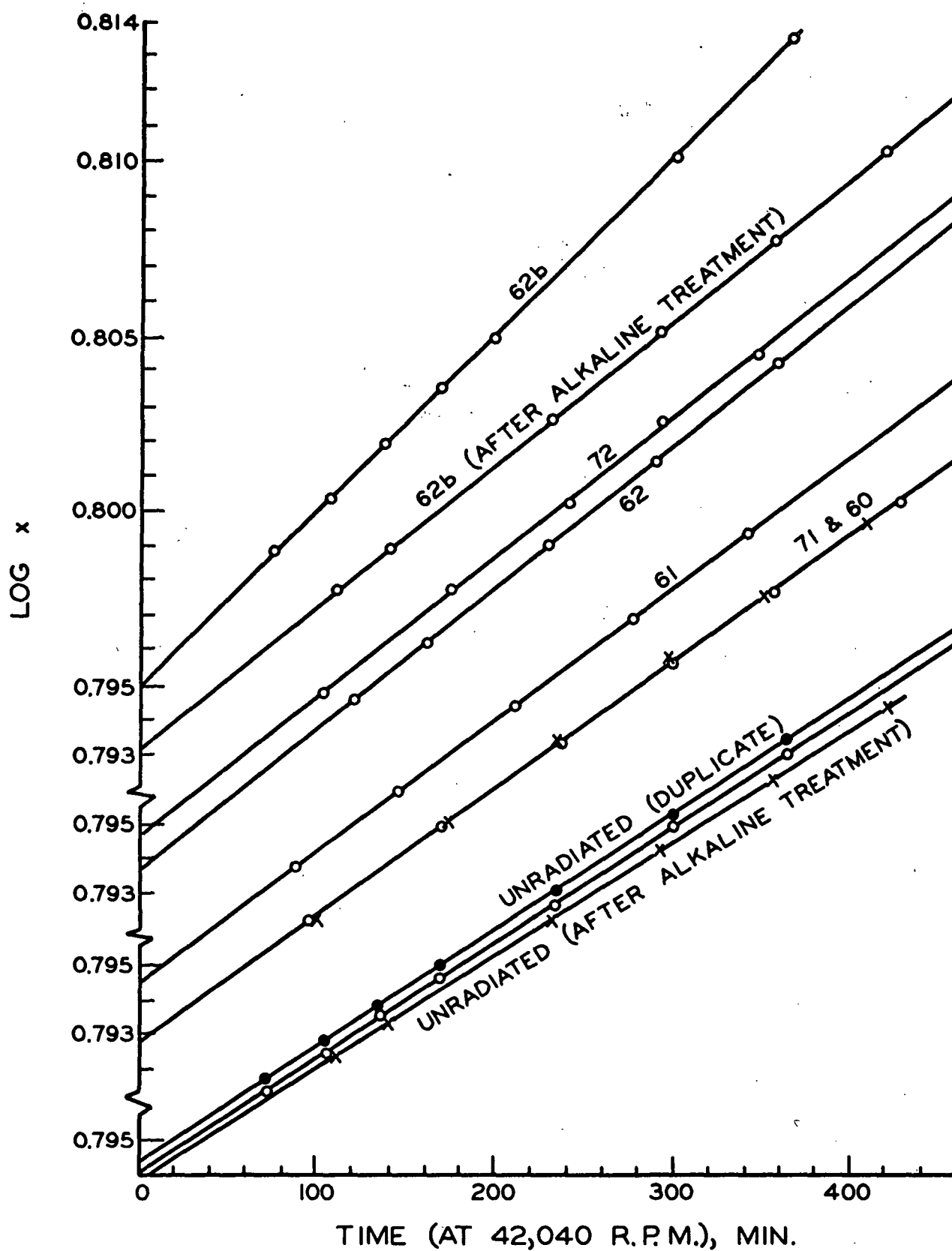


Figure 10. Sedimentation-Velocity Data for 15 cp.
Grade Methyl Cellulose

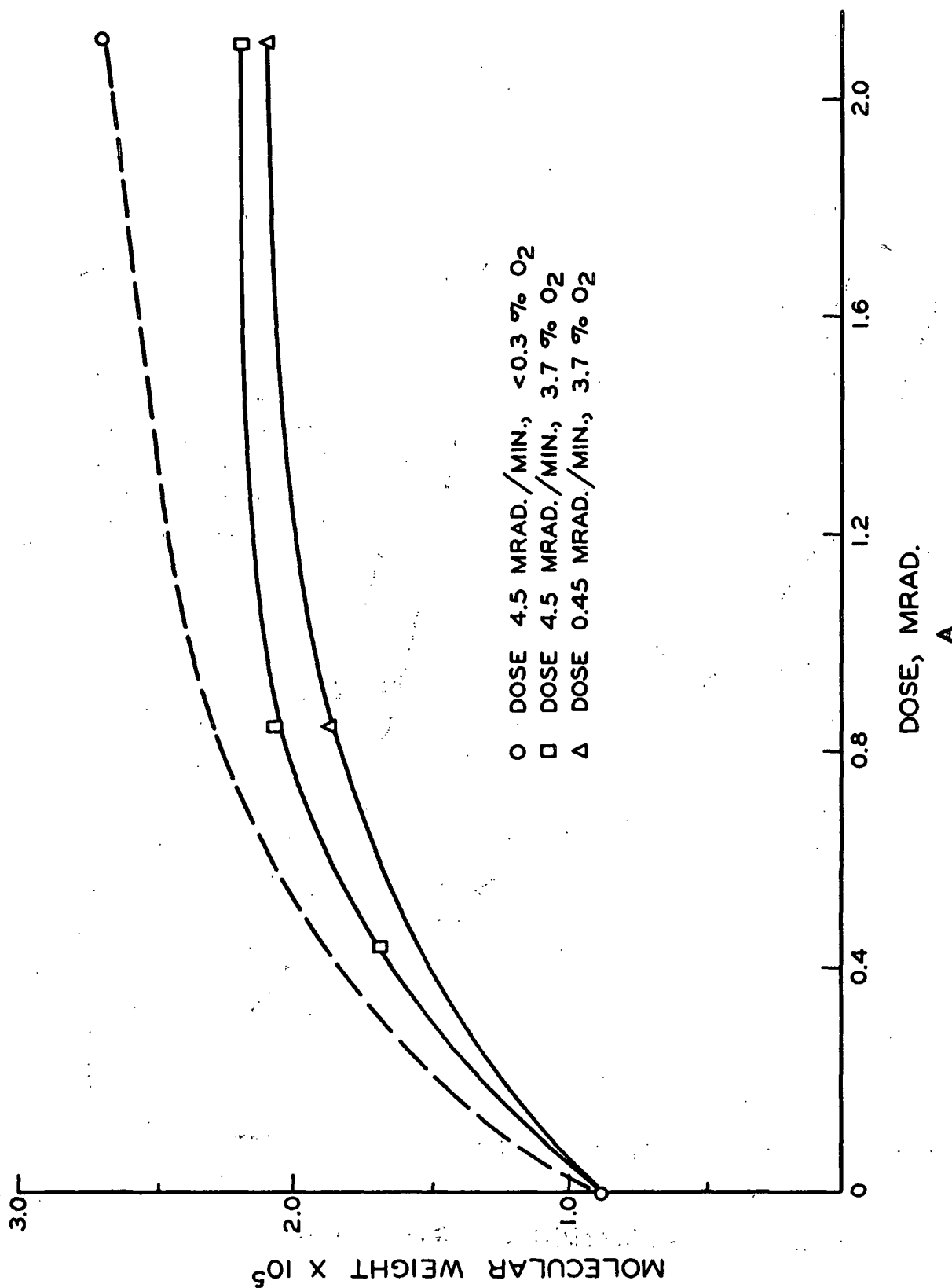


Figure 11a. Effect of Dose, Dose Rate, and Atmosphere on Molecular Weight of 15 cp. Grade Methyl Cellulose

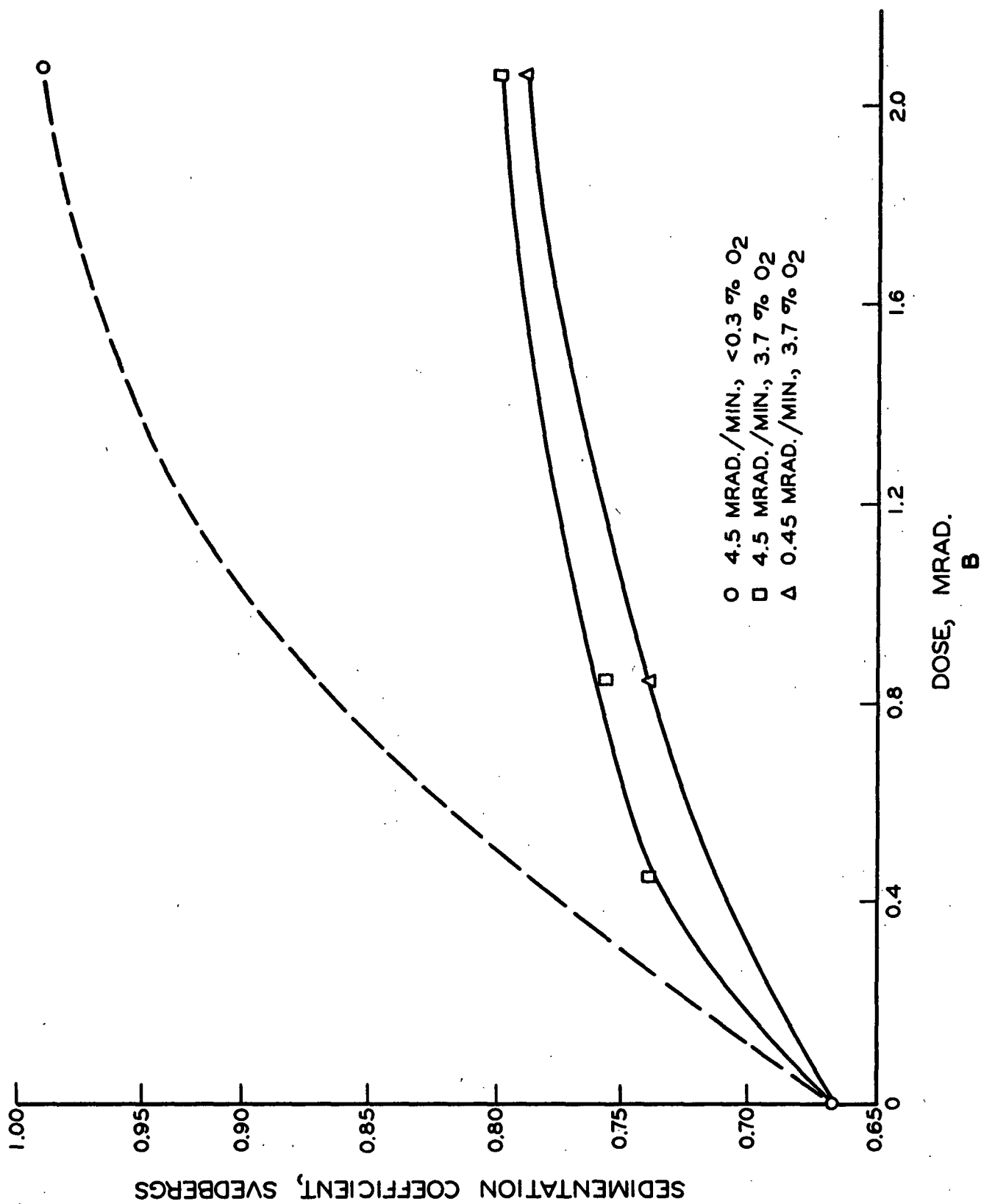


Figure 11b. Effect of Dose, Dose Rate, and Atmosphere on Sedimentation Coefficient of 15 cp. Grade Methyl Cellulose

period, the molecular weight dropped from 241,000 to 215,000 for Sample 62 and from 308,000 to 270,000 for Sample 62b. These decreases in the molecular weight of radiated methyl cellulose amounted to 2% per week. Thus, analyses would appear to be comparable only when data are taken within a short period of time.

EFFECT OF METHYL CELLULOSE CONCENTRATION ON MOLECULAR WEIGHT

The effect of methyl cellulose concentration is also shown in Table IV. A 0.4% solution of methyl cellulose was radiated. As shown for Sample 82 in Table IV, the treatment increased the molecular weight from 85,000 to 183,000. A similar radiation of a 4% solution increased the molecular weight to 215,000. A tenfold increase in methyl cellulose concentration from 0.4 to 4% thus resulted in only a 30% additional increase in the molecular weight after radiation.

ABSENCE OF AGGREGATES IN CLARIFIED SOLUTIONS

Both sedimentation and light scattering indicated that radiation increased the molecular weight of methyl cellulose. Had a small fraction of aggregates of larger mass caused this increase in the observed molecular weight, a fraction of rapidly sedimenting material would be expected during ultracentrifugation (37, 82). No rapidly sedimenting fraction was observed with any of the centrifuge runs, however. Furthermore, as previously discussed, had the increase in molecular weight been due to aggregation, the second virial coefficient would be expected to be negative (14, 36). No negative second virial coefficients were observed for any of the radiated samples; however.

Figure 12 is a traced enlargement of the schlieren pattern that was photographically recorded during simultaneous sedimentation of nonradiated methyl cellulose and radiated methyl cellulose Sample 62b. The photograph was taken 170

minutes after attaining a constant speed of 42,040 r.p.m. This figure indicates a unimodal distribution of sedimenting masses which suggests that the observed increases in molecular weight were not due to a small fraction of large aggregates. The absence of rapidly sedimenting material cannot be considered as conclusive since polymodal distributions have been known to appear as unimodal at high concentrations of sedimenting material (17).

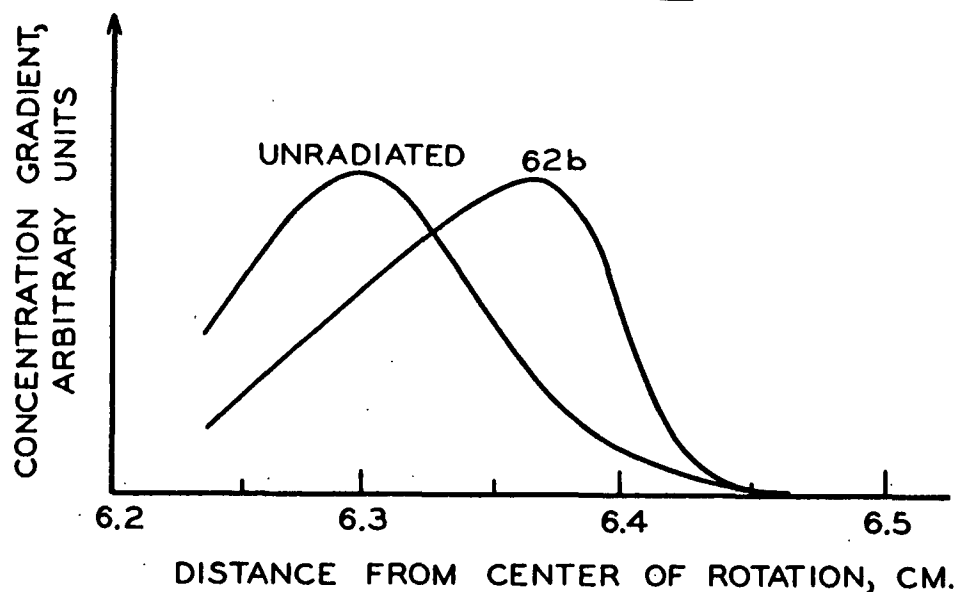


Figure 12. Schlieren Pattern of Radiated and Nonradiated 15 cp. Grade Methyl Cellulose

EFFECT OF RADIATION ON INTRINSIC VISCOSITY

The extrapolations of viscosity to zero concentration are shown in Fig. 13. As presented in Fig. 14c and Table IV, radiation of 4% solutions of methyl cellulose under 3.7% oxygen involved no increase in intrinsic viscosity above the original of 1.62 dl./g. At the same radiation dose, however, Fig. 14c illustrates that higher dose rates gave higher values of intrinsic viscosity. Higher intrinsic viscosities also resulted when the oxygen content was decreased from 3.7 to 0.3% as shown in Table IV. In this case the intrinsic viscosity was higher than that before radiation.

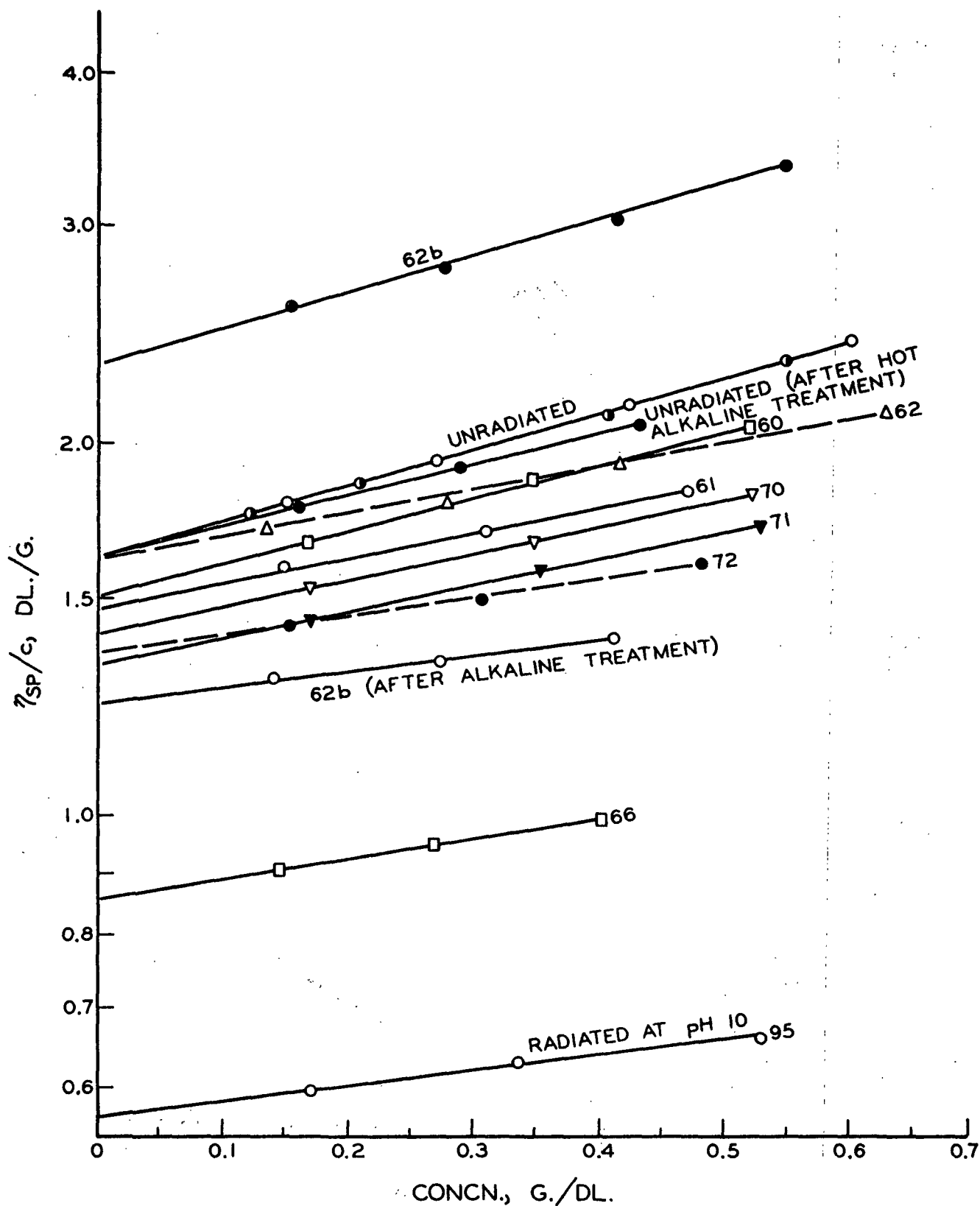


Figure 13. Viscometry of 15 cp. Grade Methyl Cellulose

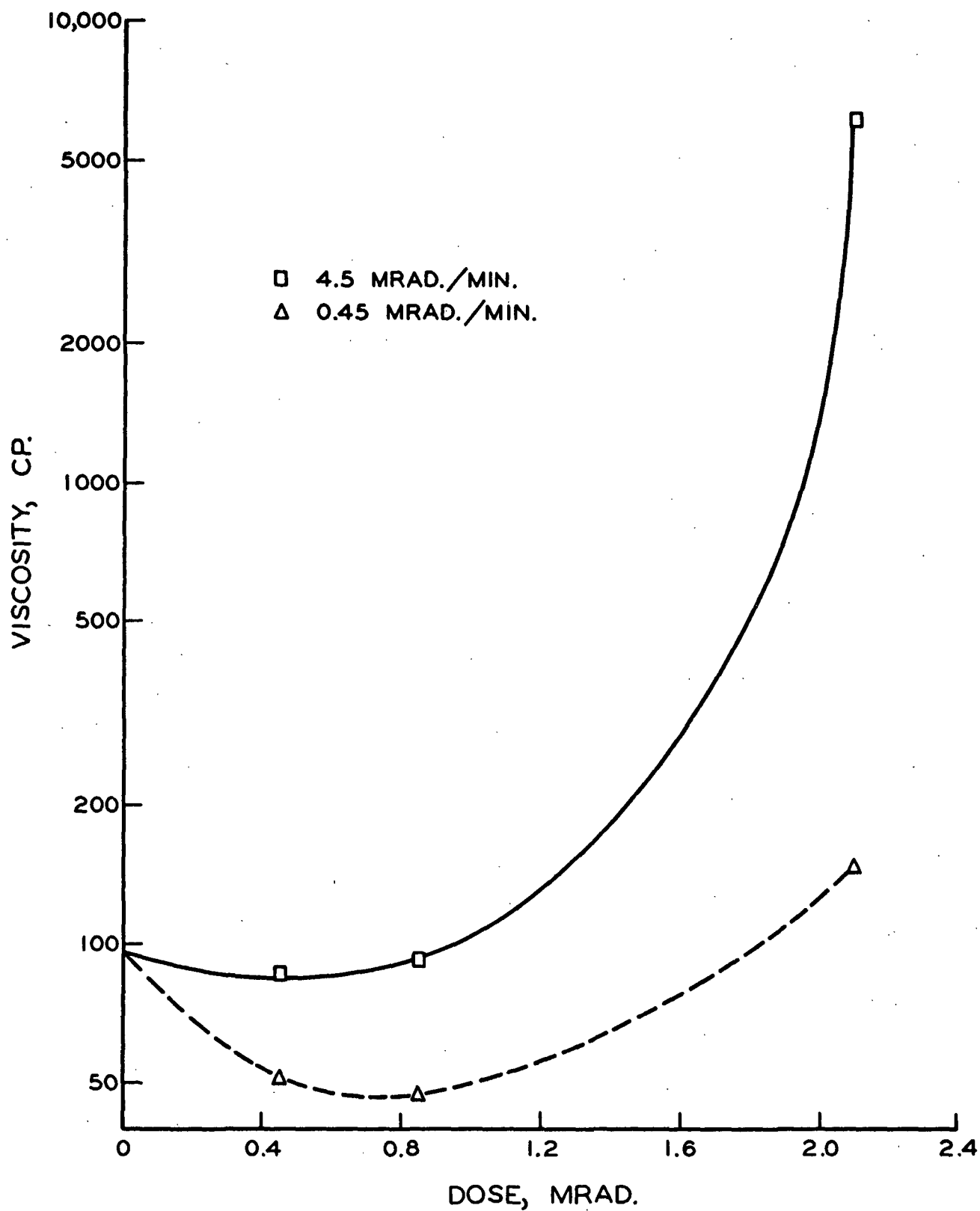


Figure 14a. Effect of Radiation on Viscosity of 15 cp.
Grade Methyl Cellulose Under Nitrogen

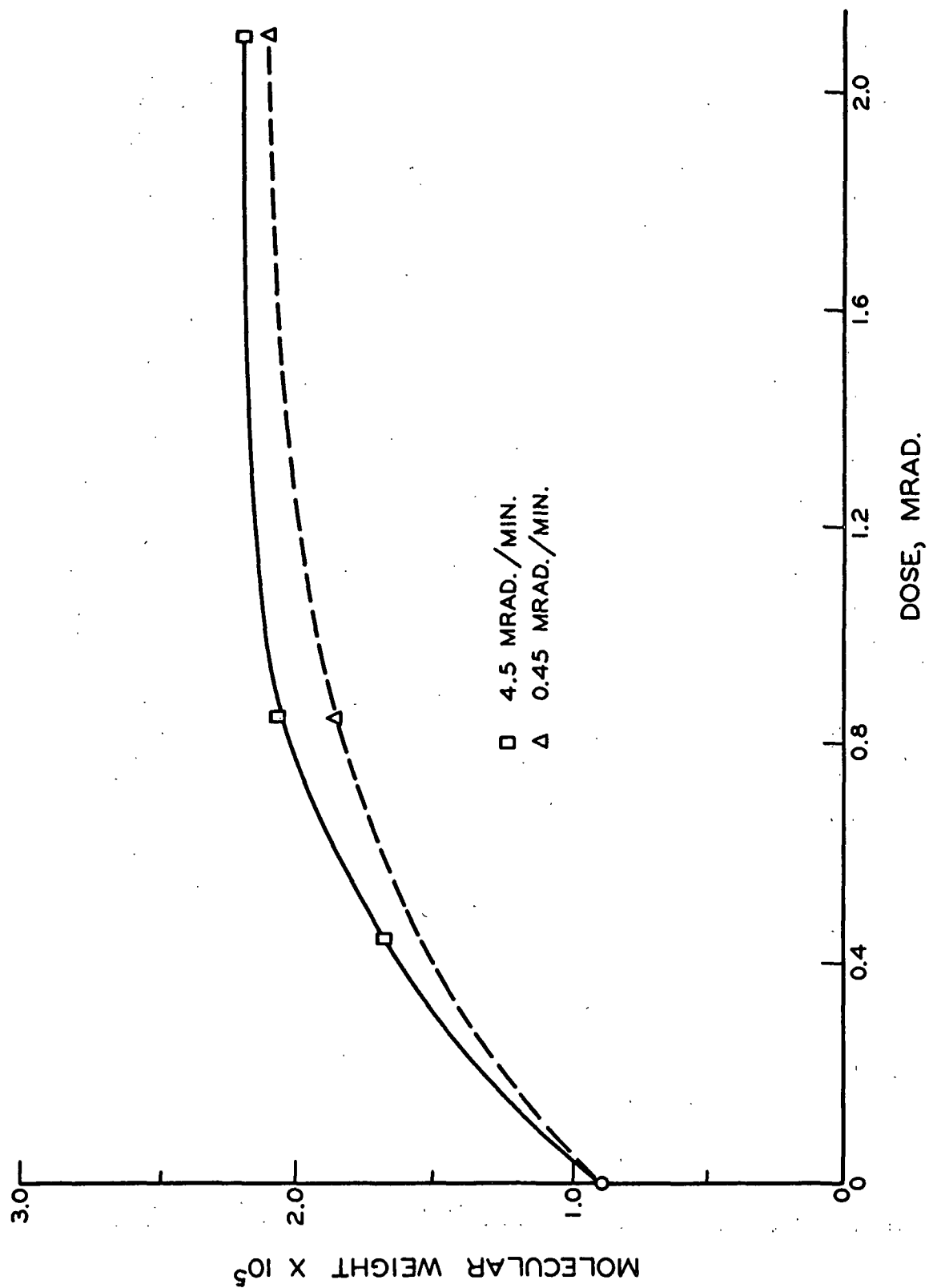


Figure 14b. Effect of Radiation on Molecular Weight of
15 cp. Grade Methyl Cellulose Under Nitrogen

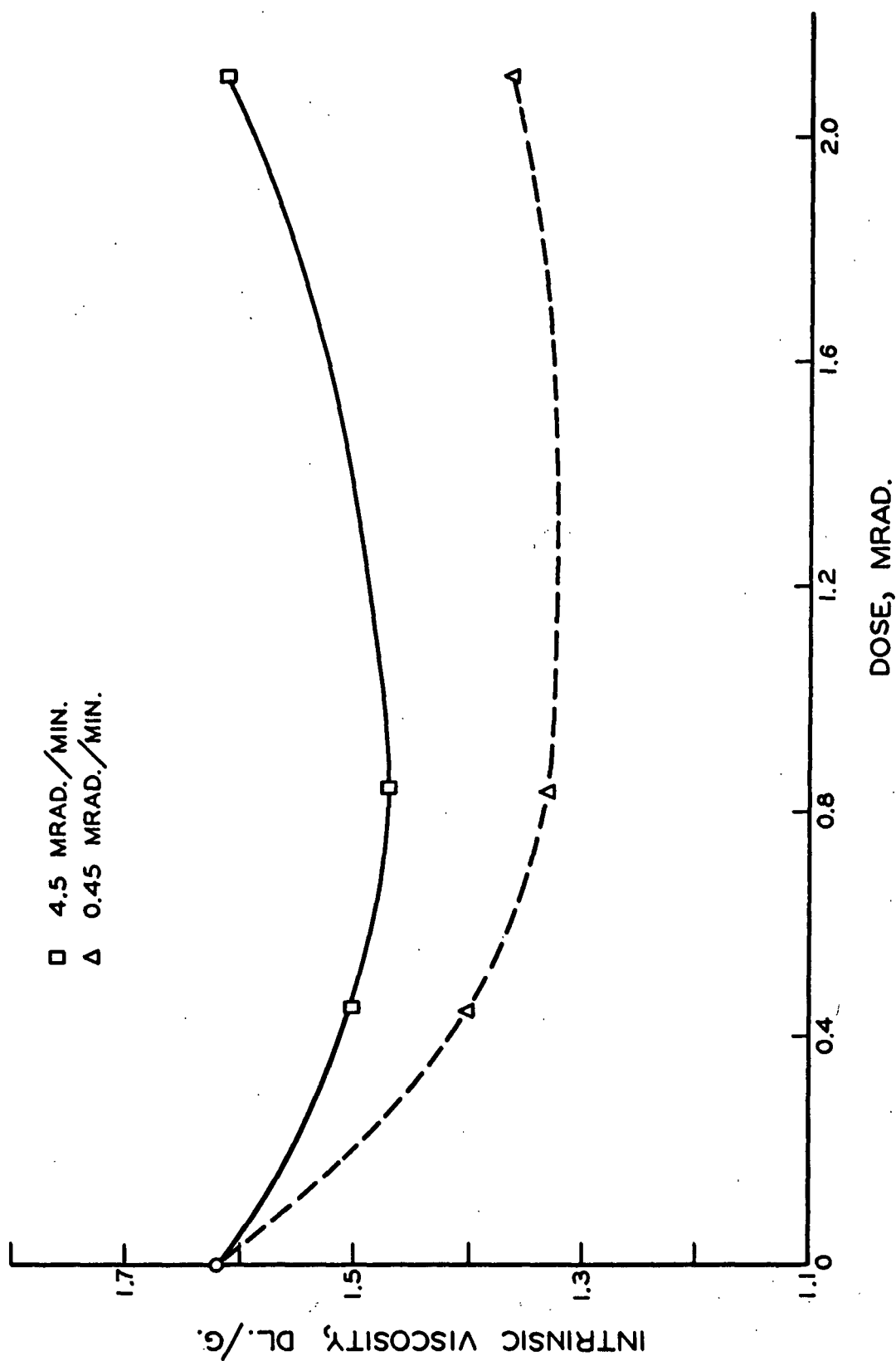


Figure 14c. Effect of Radiation on Viscosity of 15 cp.
Grade Methyl Cellulose Under Nitrogen

EVIDENCE FOR BRANCHING

As previously presented in Equation (15), evidence for branching is indicated by a decrease in the ratio $(\bar{s}^2)^{1/2}/r_{\max}$, where $(\bar{s}^2)^{1/2}$ is the root-mean-square radius of gyration and r_{\max} is the hypothetical maximum extended length of the polymer chain. Table V shows the ratio $(\bar{s}^2)^{1/2}/r_{\max}$ of methyl cellulose before and after radiation. For this table, the monomer weight was taken as 195 and the length of the monomer unit as 5.15×10^{-8} cm. The decrease in the ratio $(\bar{s}^2)^{1/2}/r_{\max}$ from 0.074 to approximately 0.040 after radiation indicates that radiation caused branching in methyl cellulose.

TABLE V

BRANCHING AND CHANGE IN RELATIVE
MOLECULAR EXTENSION DURING RADIATION
OF 4% SOLUTIONS OF 15 CP. GRADE METHYL CELLULOSE

Sample	Dose, Mrad.	Dose Rate, Mrad./min.	Atmos., % O ₂	\bar{M}^a	$[\eta]^b$	$(\bar{s}^2)^{1/2}/r_{\max}$	$\frac{\text{Branches}}{\text{Molecule}}$
00	--	--	--	85,000	1.62	0.074	0.00
60	0.45	4.5	3.7	167,000	1.50	0.046	1.05
61	0.84	4.5	3.7	204,000	1.47	0.040	1.40
62	2.10	4.5	3.7	215,000	1.61	0.040	1.23
62b	2.10	4.5	<0.3	270,000	2.32	0.039	0.62
62b-NaCl ^c	--	--	--	(270,000)	1.41	0.033	1.55
71	0.84	0.45	3.7	185,000	1.33	0.041	1.56
72	2.10	0.45	3.7	207,000	1.36	0.038	1.66

^aLight-scattering molecular weight.

^bIntrinsic viscosity in water, dl./g.

^cSample 62b for which the intrinsic viscosity was determined with 0.2M NaCl as the solvent.

The number of branches per molecule was calculated by Equation (13). To obtain an estimate of the value of $[\eta]_{\text{linear}}$ for a particular value of molecular weight, the relation by Neely (76) was used: $[\eta]_{\text{linear}} \propto \bar{M}^{0.55}$. Table V indicates that as many as 1.5 to 1.7 branches per molecule were formed during radiation.

Addition of salt to suppress polyelectrolyte effects is shown in Table V for Sample 62b. The use of 0.2N sodium chloride for the solvent in viscometry decreased the intrinsic viscosity of this sample from 2.32 to 1.41 dl./g. The addition of salt did not change the intrinsic viscosity of nonradiated methyl cellulose, though. This decrease in the intrinsic viscosity of 62b decreased $(\bar{s}^2)^{1/2}/r_{\text{max}}$ from 0.039 to 0.033 and increased the estimation of the number of branches per molecule from 0.62 to 1.55. Viscometry of the other samples of Table V was not done in the presence of salt. Hence, the intrinsic viscosities of these samples may be too high and would make $(\bar{s}^2)^{1/2}/r_{\text{max}}$ too large and the estimation of the number of branches per molecule too low.

MECHANISMS BY WHICH BRANCHING AND SCISSION ARE AFFECTED BY DOSE RATE AND OXYGEN

The amount of oxygen present and the radiation dose have been shown to be important factors in the radiation of aqueous solutions of methyl cellulose. As summarized from Table IV, Table VI shows that lower oxygen content and higher dose rate favored higher light-scattering molecular weight, sedimentation coefficient, intrinsic viscosity, and bulk viscosity and gave less decrease in pH. These data indicate that high dose rates and lower oxygen content promoted branching and caused less oxidation. The following discussion, which is similar to discussions by other workers (4,11,38,45,46,56), would be consistent with these data.

TABLE VI

IMPORTANCE OF DOSE RATE AND OXYGEN DURING RADIATION
OF 4% SOLUTIONS OF 15 CP. GRADE METHYL CELLULOSE

Radiation Conditions and Properties	Sample			
	00	72	62	62b
Dose, Mrad.	--	2.10	2.10	2.10
Dose rate, Mrad./min.	--	0.45	4.5	4.5
Oxygen above solution, mole %	--	3.7	3.7	<0.3
Bulk viscosity, cp.	96	148	6200	>100,000
Molecular weight (light-scattering)	85,000	207,000	215,000	270,000
Sedimentation coefficient, svedbergs	0.666	0.792	0.801	0.992
pH	5.82	4.10	4.18	4.37
Intrinsic viscosity, dl./g.	1.62	1.36	1.61	2.32

With radiation of aqueous solutions of methyl cellulose, H and OH radicals from water could abstract H or OH radicals from the polymer molecules to form polymer radicals. At high oxygen contents, the polymer radicals could react with the oxygen. This would prevent the coupling reaction between polymer radicals. The new radicals formed from the reaction between oxygen and the polymer radicals could rearrange to give a net effect of oxidation and scission. The radical-oxygen species would likely be more susceptible to further oxidative attack.

At low dose rates, the distance between electron tracks in the solution would be large. In this case, the polymer radicals formed in any one track would then further react with H and OH radicals from the water. This intratrack reaction would occur before the polymer radicals in one track could diffuse to and combine with the polymer radicals in a neighboring track. This preferential reaction between polymer radicals and the radicals from water would lead to oxidation and degradation.

At higher dose rates, however, electron tracks in the solution would be close together. Regions with high concentrations of polymer radicals would overlap (regions along electron tracks). In this case the intertrack reactions between polymer radicals would yield branching at the expense of intratrack oxidation and degradation reactions.

In addition, at high dose rates the diffusion of oxygen into the solution could be slow compared to the rate of formation of polymer radicals. The reaction could then proceed as though the oxygen were absent.

THE GELATION PHENOMENON

COMPARISON OF BULK VISCOSITY AND MOLECULAR WEIGHT

An increase in molecular weight was found to occur even when the bulk viscosity was decreased by radiation. Figure 14 shows that radiation caused an increase in the molecular weight from 85,000 to 135,000 at a dose of 0.84 Mrad. and a dose rate of 0.45 Mrad./min. The bulk viscosity, however, decreased from 96 to 47 cp. under this treatment. The formation of more compact molecules through branching is the probable reason for the bulk viscosity to decrease as the molecular weight increased. The decrease in the bulk viscosity did not in any way indicate a decrease in molecular weight through degradation.

Figure 14a also illustrates that at 2.1 Mrad. a tenfold increase in dose rate, however, increased the bulk viscosity from 148 to a gel of 6200 cp. This gelation occurred as the molecular weight increased only from 207,000 to 215,000. The latter molecular weight was taken on 96.6% of the polymer which was recovered after dispersion and clarification. This reported molecular weight value of 215,000 may be low, therefore.

ALKALI AND HEAT STABILITY OF RADIATED METHYL CELLULOSE

Addition of Salts to Radiated Methyl Cellulose

In order to determine the stability of gels with changes in pH, neutral and alkaline salts were added in pulverized form to gels and the bulk viscosities were measured. A 4% gel (Sample 62 in Table IV) was equally divided into four bottles. Sufficient salts were added to give the following four systems of 4% methyl cellulose: no additive, 0.4M sodium chloride, 0.33M boric acid and 0.10M sodium metaborate, and 0.018M boric acid and 0.18M sodium metaborate. The four systems were mixed by continuously shaking them for 3 days. Table VII shows the bulk viscosities of the systems after mixing.

TABLE VII

EFFECT OF ADDED SALT ON THE BULK
VISCOSITY OF 4% GELS

Sample	Concentration of Added Salts	pH	Bulk Viscosity, cp.
Unradiated	--	6.1	96
62 (Table IV)	no additive	4.2	4400
62-1	0.4M NaCl	3.9	4120
62-2	0.33M H_3BO_3
	0.10M $NaBO_2$	7.9	140
62-3	0.018M H_3BO_3		
	0.18M $NaBO_2$	10.1	37

The mixing operation decreased the bulk viscosity of the control from 6200 to 4200 cp. The presence of neutral salt did not significantly change the bulk viscosity from that of the control. However, alkaline salts at pH values of 8 and 10 drastically decreased the bulk viscosity and dispersed the gel. This shows that alkali-labile bonds were important to gel stability.

As discussed earlier, hot alkaline-borohydride would be expected to cleave peroxy and hemiacetal branches that might occur in radiated methyl cellulose (70, 71). An experiment was done with 0.82% solutions of nonradiated methyl cellulose and the 94.7% sol fraction from a dispersed gel (62b in Table IV). Salts were added to attain solutions of sodium borohydride buffered at pH 10. These solutions had the combined concentrations of 0.05M sodium borohydride, 0.014M boric acid, and 0.136M sodium metaborate. The solutions containing the polymer and the alkaline-borohydride were heated at 100°C. for one hour. Table VIII shows that this treatment of nonradiated methyl cellulose caused only a small reduction in the molecular weight, sedimentation coefficient, and intrinsic viscosity. The alkaline-borohydride treatment of radiated methyl cellulose, however, did decrease the molecular weight, sedimentation coefficient, and intrinsic viscosity. Since both the molecular weight and sedimentation coefficient of the radiated methyl cellulose after alkaline-borohydride treatment were higher than those values for nonradiated methyl cellulose, the indication is that radiation of methyl cellulose caused the formation of bonds both labile and stable to alkaline-borohydride. Carbon-carbon, ether, acetal, and glycosidic bonds would likely be stable to this treatment whereas hemiacetal and peroxy bonds would probably be labile.

TABLE VIII

STABILITY OF 15 CP. GRADE METHYL CELLULOSE TO HOT ALKALI

Sample	Molecular Weight		Sedimentation Coeff. ^a		Intrinsic Viscosity	
	Before ^b	After ^c	Before ^b	After ^c	Before ^b	After ^c
Nonradiated	85,000	81,000	0.666	0.658	1.62 dl./g.	1.62 dl./g.
62b	270,000	165,000	0.972	0.820	2.32	1.23

^aSvedberg units.

^bBefore treatment with hot alkaline-borohydride.

^cAfter treatment with hot alkaline-borohydride.

Radiation of Samples in Presence of Salts

Solutions having two grams of 15 cp. grade methyl cellulose per deciliter were prepared in the presence of neutral and alkaline salts. The values of bulk viscosity and pH of these solutions are shown in Table IX. The solutions were then evacuated and replaced with nitrogen. This resulted in an atmosphere above the solutions which contained 3.7% oxygen. The solutions were radiated to a dose of 2.10 Mrad. at a dose rate of 4.5 Mrad./min. Table IX shows that radiation caused gelation both in water and in the presence of sodium chloride, but gelation was prevented by the presence of alkali at pH 8 and 10. This is contrary to the observation by Leavitt (69) that radiation caused gelation of methyl cellulose solutions in the presence of sodium hydroxide at pH 11.5. In Leavitt's system, however, the pH could rapidly have become acidic by neutralization of sodium hydroxide by the carboxyl groups formed on methyl cellulose during radiation. The inhibition of gelation by alkali at pH 8 and 10 is further indication that alkali-labile bonds were important to gelation.

The light-scattering molecular weight was measured for Sample 95 of Table IX. Using the buffer solution as the solvent, the molecular weight was found to increase from 85,000 to 125,000 with radiation at pH 10. Stable bonds can thus be formed during radiation in alkaline-borohydride at pH 10.

Effect of Heat on Radiated Sample

Four per cent systems of Sample 62 and nonradiated methyl cellulose were heated for 4 hours at 100°C. and then cooled to room temperature. This heat treatment was found to decrease the bulk viscosity of nonradiated methyl cellulose only from 96 to 91 cp. However, the bulk viscosity of Sample 62 was decreased from 6200 to 460 cp. by the heat treatment. Since the gel had a pH of 4.2, an acid hydrolysis

might have caused a portion of this decrease in bulk viscosity. The data would seem to indicate, though, that methyl cellulose gels involved bonds which, unlike nonradiated methyl cellulose, were labile to heat.

TABLE IX

BULK VISCOSITY BEFORE AND AFTER RADIATION OF 15 CP.
GRADE METHYL CELLULOSE SOLUTIONS IN PRESENCE OF SALT

Sample	Solvent	pH		Bulk Viscosity, cp. ^c	
		Initial ^a	Final ^b	Initial ^a	Final ^b
90	Pure water	6.1	3.7	17	1190
91	0.4M NaCl	6.6	4.0	20	640
92	0.01M NaH ₂ PO ₄	8.0	7.9	32	14
	0.191M Na ₂ HPO ₄				
93	0.33M H ₃ BO ₃	7.8	7.6	19	10
	0.067M NaBO ₂				
94	0.018M H ₃ BO ₃	10.0	9.9	19	10
	0.182M NaBO ₂				
95	0.013M H ₃ BO ₃	10.2	10.0	20	8
	0.14M NaBO ₂				
	0.05M NaBH ₄				

^aBefore radiation.

^bAfter radiation under 3.7% O₂ at dose rate of 4.5 Mrad./min. and dose of 2.10 Mrad.

^cFor 2% solutions.

EFFECT OF pH AND METHYL CELLULOSE CONCENTRATION ON GELATION

Previous data have established that radiated methyl cellulose contains carboxyl groups. As presented earlier, carbohydrates having carboxyl groups are often insoluble in water solutions although they are soluble in alkali (73, 74). The

insolubility of radiated methyl cellulose in neutral or acidic media could be a cause of gelation. Three experiments were made to investigate this.

One-half milliliter of 1N sodium hydroxide was added to 92 g. of Sample 68. This treatment increased the pH from 4.3 to 11.4 and decreased the bulk viscosity from 58,000 to 160 cp. Six-tenths milliliter of 1N hydrochloric acid was then added. This caused the pH to decrease from 11.4 to 3.6, but the bulk viscosity did not increase above 160 cp. Thus, the mere presence of carboxyl groups in the free-acid form would not appear to cause gelation of radiated methyl cellulose.

The second experiment involved Sample 82 of Table IV which had been radiated at a dilute concentration of 0.4%. The 0.4% solution was concentrated to 4% by placing it under a vacuum at room temperature to remove the water. The bulk viscosity was increased from 2.2 to 11 cp. by this tenfold increase in the methyl cellulose concentration. This viscosity of 11 cp. was much lower than that of 96 cp. for a 4% solution of nonradiated methyl cellulose. Thus, a high concentration of radiated methyl cellulose alone did not give a gel.

The last experiment involved Sample 62. This 4% gel with viscosity of 6200 cp. was diluted to about 0.8%. This 0.8% system was dispersed by agitating for 15 min. in a Waring Blendor at 1000 r.p.m. With use of vacuum at room temperature, the concentration of this 0.8% dispersion was increased to 4%. This did not give a gel but only a dispersion with a bulk viscosity of only 140 cp. Again a high concentration of radiated methyl cellulose did not give a gel.

STRENGTH OF FILMS FORMED FROM RADIATED METHYL CELLULOSE

An Instron tester (Instron Eng. Corp., Quincy, Mass.) was used to get stress-strain curves of films. Films were formed by evaporation of 0.8% solutions of

Sample 62 and nonradiated methyl cellulose. Prior to testing, films were conditioned at 72°F. and 50% relative humidity for 48 hr. Films of 0.0025 ± 0.0005 in. thickness, 0.15 in. length and 15 mm. width were strained at a uniform rate of 0.02 in./min. Data, taken in triplicate, indicated that radiation caused little change in the modulus of elasticity from $244,000 \pm 12,000$ to $231,000 \pm 15,000$ p.s.i. Radiation did decrease the ultimate breaking stress from $10,100 \pm 1700$ to 8400 ± 1200 p.s.i., however.

SUMMARY AND CONCLUSIONS

Previous research by other workers showed that high-energy radiation could cause oxidation and gelation of methyl cellulose in aqueous solution. As a continuation of these investigations, the present study was undertaken to examine possible causes of gelation and to observe the importance of radiation dose, dose rate, and the presence of oxygen to branching and oxidation of the polymer. Aqueous solutions of methyl cellulose were radiated with 2 M.e.V. electrons and measurements of pH, bulk viscosity, light-scattering molecular weight, sedimentation coefficient, and intrinsic viscosity were made. The latter three determinations were taken on solutions and dispersed gels which had previously been clarified by centrifugation.

Both molecular weight determinations by light scattering and sedimentation analyses by ultracentrifugation indicated that radiation increased the molecular weight of methyl cellulose. These observed increases did not appear to be due to the presence of aggregates since fast moving components were not observed during sedimentation and negative second virial coefficients were not found during light-scattering measurements. The increases in molecular weight were accompanied by decreases in intrinsic viscosity. These decreases reflect reductions in molecular volume per unit weight and are characteristic of a more compact molecule per unit mass. The increase in molecular weight through the formation of these more compact molecules indicates that molecular growth occurred through branching along the polymer chain.

The stability of radiated solutions to alkali was observed to gain insight into the nature of branches formed during radiation. The presence of alkali during radiation did not completely inhibit molecular growth through branching. Also,

addition of alkali to a sample previously radiated in water removed one-half of the original increase in molecular weight. This partial stability of these samples indicates that radiation increased the molecular weight through the formation of two general types of bonds: (1) those stable to alkali which could include carbon-carbon, ether, acetal, and glycosidic branches, and (2) bonds labile to alkali which could include hemiacetal and peroxy branches.

Oxidation of the samples by radiation produced carboxyl groups with an accompanying decrease in pH. The presence of carboxyl groups was further shown by the curved viscosity plots typical of polyelectrolyte molecules expanded in solution.

A competition was found to exist between oxidation and branching. High dose rates and low amounts of oxygen present in the solutions favored higher molecular weights and less oxidation of the polymer. These data indicate that the competition between branching and oxidation is controlled by the instantaneous concentrations of radicals from water, polymer radicals, and oxygen.

The stability of gels was observed to gain insight into the causes of gelation. The bulk viscosity of gels formed during radiation could be decreased by methods which had little or no effect on the bulk viscosity before radiation. Gels could be dispersed by heat, mechanical agitation, and the addition of alkali at pH 8 and 10. Thus, gelation would appear to involve the formation of bonds between molecules which were much weaker than bonds present in nonradiated methyl cellulose. Gels which were dispersed by alkali were not reformed upon neutralization with acid. Furthermore, gels which were dispersed by dilution and mechanical agitation could not be reconstituted by increasing the concentration back to the original value. Hence, gelation would not seem to be caused by an insolubility of radiated methyl cellulose in neutral or acidic media.

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LITERATURE CITED

1. Swallow, A. J. Radiation chemistry of organic compounds. New York, Pergamon Press, 1960.
2. Allen, A. L., J. Phys. & Colloid Chem. 52:479(1948).
3. Dewhurst, H. A., Samuel, A. H., and Magee, J. L., Radiation Research 1:62 (1954).
4. Anderson, A. R., and Hart, E. J., J. Phys. Chem. 66:70(1962).
5. Brasch, A., and Huber, W., Science 105:112(1947).
6. Rotblat, J., and Sutton, H. C., Proc. Roy. Soc. A255:490(1960).
7. Weiss, J., Trans. Faraday Soc. 36:856(1940).
8. Burr, J. G., J. Phys. Chem. 61:1477(1957).
9. Allen, J. T., Hayon, E. M., and Weiss, J., J. Chem. Soc. 1959:3913.
10. McDonnell, W., and Gordon, S., J. Chem. Phys. 23:208(1955).
11. Jayson, G. G., Scholes, G., and Weiss, J., J. Chem. Soc. 1957:1358.
12. Newton, A. S., J. Phys. Chem. 61:1485, 1490(1957).
13. Flory, P. J. Principles of polymer chemistry. Chap. 2, 7, and 14. Ithaca, New York, Cornell Univ. Press, 1957.
14. Tanford, C. Physical chemistry of macromolecules. Chap. 4-7. New York, John Wiley & Sons, Inc., 1961.
15. Schachman, H. K. Ultracentrifugation in biochemistry. New York, Academic Press, 1959.
16. Williams, J. W., van Holde, K. E., Baldwin, R. L., and Fujita, H., Chem. Revs. 58:715(1958).
17. Johnson, J. P., and Ogston, A. G., Trans. Faraday Soc. 42:789(1946).
18. Stacey, K. A. Light scattering in physical chemistry. New York, Academic Press, 1956.
19. Doty, P., and Steiner, R., J. Chem. Phys. 8:1211(1950).
20. Kirkwood, J. G., and Riseman, J., J. Chem. Phys. 16:565(1948).
21. Zimm, B. H., and Kilb, R. W., J. Polymer Sci. 37:19(1959).
22. Thurmond, C. D., and Zimm, B. H., J. Polymer Sci. 8:477(1952).

23. Charlesby, A., J. Polymer Sci. 17:379(1955).
24. Schaefgen, J. R., and Flory, P. J., J. Am. Chem. Soc. 70:2709(1948).
25. Kilb, R. W., J. Phys. Chem. 63:1838(1959).
26. Kotliar, A. M., and Podgor, S., J. Polymer Sci. 55:423(1961).
27. Schultz, A. R., Roth, P. I., and Rathmann, G. B., J. Polymer Sci. 22:495(1956).
28. Zimm, B. H., and Stockmayer, W. H., J. Chem. Phys. 17:1301(1949).
29. Granath, K., J. Colloid Sci. 13:308(1958).
30. Pederson, K. O., J. Phys. Chem. 62:1282(1958).
31. Schneider, N. S., and Doty, P., J. Phys. Chem. 58:762(1954).
32. Oth, A., and Doty, P., J. Phys. Chem. 56:43(1952).
33. Fousa, R. M., and Strauss, U. P., J. Polymer Sci. 3:246, 602(1948).
34. Pals, D. T. F., and Hermans, J. J., Rec. trav. chim. 71:433(1952).
35. Billmeyer, F. W. Textbook of polymer chemistry. New York, Interscience, 1957.
36. Doty, P., and Myers, G. E., Disc. Faraday Soc. 1953:51.
37. Doty, P., Wagner, H., and Singer, S., J. Phys. & Colloid Chem. 51:32(1947).
38. Bovey, F. A. The effects of ionizing radiation on natural and synthetic high polymers. New York, Interscience, 1960.
39. Charlesby, A. Atomic radiation and polymers. New York, Pergamon Press, 1960.
40. Alexander, P., and Toms, D., J. Polymer Sci. 22:343(1956).
41. Chapiro, A., J. chim. phys. 52:246(1955).
42. Feng, P. Y., and Kennedy, J. W., J. Am. Chem. Soc. 77:847(1955).
43. Alexander, P., and Charlesby, A., J. chim. phys. 52:694(1955).
44. Alexander, P., and Fox, M., Trans. Faraday Soc. 50:605(1953).
45. Charlesby, A., Proc. Roy. Soc. A215:187(1952).
46. Dole, M., Keeling, C. D., and Rose, D. G., J. Am. Chem. Soc. 76:4304(1954).
47. Phillips, G. O. In Wolfrom's Advances in carbohydrate chemistry. p. 13-58. New York, Academic Press, 1961.

48. Teszler, O., Kiser, L. H., Campbell, P. W., and Rutherford, H. A., Textile Research J. 28:456(1958).
49. Glegg, R. E., and Kertesz, Z. I., J. Polymer Sci. 26:289(1957).
50. Saeman, J. F., Millett, M. A., and Lawton, E. J., Ind. Eng. Chem. (Anal. Ed.) 44:2848(1952).
51. Arthur, J. C., Blouin, F. A., and Demint, R. J., Am. Dyestuff Reprtr. 49:383 (1960).
52. Pan, H., Proctor, B. E., Goldblith, S. A., Morgan, H. M., and Naar, R. Z., Textile Research J. 49:415(1959).
53. Arthur, J. C., and Demint, R. J., Textile Research J. 32:108(1962).
54. Glegg, R. E., and Kertesz, Z. F., J. Polymer Sci. 26:289(1957).
55. Harmon, D. J., Textile Research J. 27:318(1957).
56. Allen, A. L. Radiation chemistry of water and aqueous solutions. New York, Van Nostrand, 1961.
57. Skinner, R. E., and Kertesz, Z. I., J. Polymer Sci. 47:99(1960).
58. Price, F. P., Bellamy, W. D., and Lawton, E. J., J. Phys. Chem. 58:821(1954).
59. Samec, M., Stärke 10:76(1958).
60. Moody, G. J., and Phillips, G. O., Chem. & Ind. 1959:1247.
61. Barker, S. A., Grant, P. M., Stacey, M., and Ward, R. B., J. Chem. Soc. 1959: 2871.
62. Phillips, G. O., Moody, G. J., and Mattok, G. L., J. Chem. Soc. 1958:3522.
63. Barker, S. A., Stacey, F. R. S., Grant, P. M., and Ward, R. B., J. Chem. Soc. 1959:2648.
64. Phillips, G. O., and Criddle, W. J., J. Chem. Soc. 1961:3756.
65. Samec, M., J. Appl. Polymer Sci. 3:224(1960).
66. Granath, K. A., and Kinell, P., Acta Chem. Scand. 15:141(1961).
67. Blouin, F. A., Ott, V. J., and Arthur, J. C., Jr., Presented at SW-SE-ACS Meeting in New Orleans Dec. 7, 1961.
68. Miller, A. A., U. S. patent 2,895,891(July 21, 1959).
69. Leavitt, F. C., J. Polymer Sci. 51:349(1961).
70. Tobolsky, A. V., and Mesrobian, R. B. Organic peroxides. New York, Interscience, 1954.

71. Head, F. S. H., J. Textile Inst. 49:T345(1958).
72. Gloor, W. E., and Klug, E. D. Cellulose data. p. 40. New York, Interscience, 1955.
73. Savage, A. B., Young, A. E., and Massberg, A. T. In Ott, Spurlin, and Grafflin's Cellulose and cellulose derivatives. Part II, IX.E. p. 905. New York, Interscience, 1954.
74. Roff, W. J. Fibres, plastics, and rubbers. p. 39-44. New York, Academic Press, 1956.
75. Le Fevere, C. G., and Le Fevere, R. I. W. The Kerr effect. In Weissberger's Physical methods of organic chemistry. Vol. I, Part III. Chap. 26. New York, Interscience, 1960.
76. Neely, W. B. A study of the solution properties of methyl cellulose using light scattering data. Presented at ACS Division of Cellulose, Wood, and Fiber Chemistry, Chicago, Ill., Sept. 3-8, 1961.
77. Craig, A. W., and Henderson, D. A., J. Polymer Sci. 19:215(1956).
78. Schurtz, J., and Immergut, E. H., J. Polymer Sci. 9:279(1952).
79. Immergut, E. H., Rånby, B. G., and Mark, H. F., Ind. Eng. Chem. 45:2483(1953).
80. Martin, A. F., Tappi 34:363(1951).
81. Brice, B. A., Halwer, M., and Speiser, E., J. Opt. Soc. Am. 40:768(1950).
82. Swenson, H. A., Morak, A. J., and Kurath, S., J. Polymer Sci. 51:231(1960).
83. Debye, P., J. Appl. Phys. 15:338(1944).
84. Doty, P., Zimm, B. H., and Mark, H., J. Chem. Phys. 12:144(1944).
85. Neale, S. M., and Stringfellow, W. A., Trans. Faraday Soc. 33:881(1937).
86. Fortuin, J. M. H., Anal. Chem. Acta 24:175(1961).
87. Bauer, N., and Lewin, S. Z. Determination of density. In Weissberger's Physical methods of organic chemistry. Vol. I, Part I, p. 131. New York, Interscience, 1960.
88. Samsel, E. P., and McHard, J. H., Ind. Eng. Chem., Anal. Ed. 14:750(1942).
89. Kuhn, W., and Moser, P., Makromol. Chem. 44:71(1961).
90. Neely, W. B. Private communication, 1962.